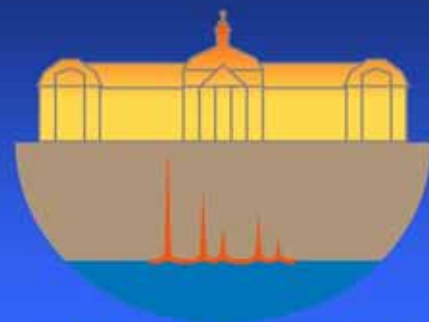Group of Prof. Jan Andersson - University of Münster

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Abstracts

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Abstracts

* presenting author

Synthesis

Oral

Plenary Lecture 1

Giant Polycyclic Aromatic Hydrocarbons as Graphene Materials

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Research into electronic devices and energy technologies is strongly governed by the available materials. More recently, carbon allotropes and carbon-rich molecules play an increasingly important role as electronic conductors, semiconductors and catalysts which strongly suggests a comparison with, for example, metal and metal oxides. Of particular importance are polycyclic aromatic hydrocarbons (PAHs) as graphene molecules. In both cases creative and structurally perfect synthesis is crucial.

We introduce a synthetic route to PAHs which is based upon the cyclodehydrogenation ("graphitization") of well-defined dendritic (3D) polyphenylene precursors. This approach makes giant PAHs accessible and is superior to physical methods of graphene formation such as chemical vapour deposition or exfoliation in terms of its (i) size and shape control, (ii) structural perfection, and (iii) processability (solution, melt, and even gas phase). Formation of discotic mesophases is another exciting aspect of PAHs. Columnar superstructures thus assembled serve as charge transport channels in electronic devices. Field-effect transistors (FETs), solar cells, and sensors are described as examples and their exemplary performance is discussed in terms of supramolecular order and interfacing. Exciting applications are also shown for batteries, supercapacitors and fuel cells.

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SYNT 1

Functionalized Acenes: Synthesis and Performance

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Over the past decade or so, there have been significant advances in the development of acene derivatives for semiconductor applications. Studies of these new materials demonstrate remarkable potential for their use in, for example, field effect transistors and photovoltaics. The ability to control the function of acene materials often depends on synthesis, where substitution can be used to dictate electronic and solid-state structure.
We have recently developed synthetic methods that allow for the stepwise formation of unsymmetrical pentacene and anthradithiophene molecules with a variety of substitution patterns and geometries. These synthetic efforts afford, for example, pentacenes with donor-acceptor units, pentacene oligomers, and new types of acene chromophores. The electronic properties of these new materials have been evaluated via a variety of methods, and this talk will highlight both our recent synthetic achievements as well as some of the semiconducting properties these molecules.

SYNT 2

Aryne-Mediated Syntheses of Large Polycyclic Aromatic Compounds

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The recent entry onto the scientific scene of graphene[1], a material with a close structural similarity to nanosized polycyclic aromatic hydrocarbons, has led to a remarkable renaissance in the development of methods for the preparation of large polycyclic aromatic compounds (PACs) [2]. Aryne-based reactions have been extensively used for this purpose [3]. In particular, the use of polycyclic arynes has allowed the synthesis of a variety of structurally fascinating PACs.
In this contribution we present our efforts to prepare large PACs through cycloaddition reactions of arynes, in particular using metal-catalyzed [2+2+2] cycloadditions and domino Diels-Alder processes [4].

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SYNT 3

Recent Progress in the Syntheses of pi-Extended Thienoacenes

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Recent progresses in the syntheses of pi-extended thienoacenes, such as dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophenes (DNTTs) [1], dianthra[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DATT) [2], and four isomeric naphtodithiophenes (NDTs) including naphtho[2,3-*b*:6,7-*b'*]dithiophene, naphtho[2,3-*b*:7,6-*b'*]dithiophenes, naphtho[1,2-*b*:5,6-*b'*]dithiophene, and naphtho[2,1-*b*:6,5-*b'*]dithiophene [3], are presented. The syntheses features several important reactions; regio-selective functionalization of naphthalene/anthracene cores and facile ring closing reaction of thiophene [4] or thieno[3,2-*b*]thiophene substructure [5].
In addition to the new synthetic chemistry of these thienoacenes, we also report on their properties and utilities as organic semiconductors; in fact they act as superior organic semiconducting materials applicable to organic field-effect transistors (OFETs) [6] and organic photovoltaics (OPVs) [7]. In particular, very high-performance OFETs with high carrier mobilities of up to 8 cm^2/Vs [6] can be readily fabricated by using these thienoacenes.

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SYNT 4

Pyrene- and Phenanthroline-Fused Azaacenes: Synthesis and Self-Assembly

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The synthesis and self-assembly of a series of pyrene- and phenanthroline-fused azaacenes will be discussed in detail. First, the synthetic routes for the preparation of key building blocks for the synthesis of soluble pyrene-fused oligo- and polyazaacenes will be described. In addition, a novel and simple methodology to arrange Au nanoparticles (NPs) along self-assembled phenanthroline nanowires (NWs) of different dimensions will be also presented. The different sizes of the supramolecular phenanthroline scaffold influence the NP surface plasmon band coupling as an effect of the different arrangements of the NPs on the NWs surface [1-4].

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SYNT 5

A General Chiral Building-Block for the Asymmetric Synthesis of PAC Metabolites

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As environmental pollutants, polycyclic aromatic compounds (PAC) are well known to form metabolites which can react with DNA and proteins to form mutagenesis and create cancer. For chrysene, (1R,2R)-dihydrodiolchrysene **1** (scheme) has been found to be the most carcinogenic, and in the attempt to understand more about the metabolism of PACs and the absolute stereochemistry for PAC metabolites formed *in vivo*, we would like to synthesize the pure enantiomers of *trans*-1,2-dihydrodiolchrysene, to be available for further research. The synthetic strategy in the synthesis of **1** is the formation of compound **2** (R = protection group) which can be incorporated as a building-block to form chrysene, and other PACs. The key step is the formation of the chiral centers from the Shi-epoxidation of a protected enol formed from tetralone **5**. In the presentation our results on the synthesis towards **1** will be shown.
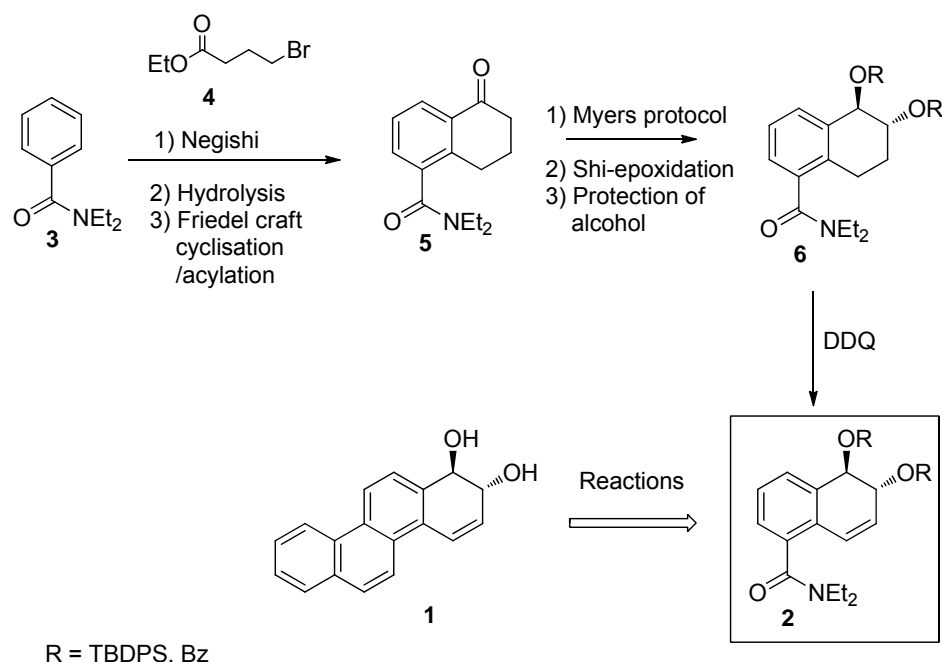
Scheme: Synthetic strategy toward the synthesis of *trans*-1,2-dihydrodiol **1**

SYNT 6

Synthesis of a New Lariat Ether Compound as Molecular and Cationic Acceptors

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A nanomachine is an assembly of a discrete number of supramolecular components designed to perform mechanical - like movements as a consequence of appropriate external stimuli.
Our purpose is the preparation of a part of nanomachines that are based on interlocked macrocycle named rotaxanes and catenanes.
The dibenzisulfide (1) was synthesized by p-cresol and sulfur dichloride in 50% yield. Treatment of (1) with methyl choloroacetat gave dimethyl ester (2) in 98% yield. Macrocycle (3) in 75% yield was synthesized from reaction of diamidation diester and diethylentriamine. Reaction of compound (3) with sebacoyl dicholoride gave bis azacrown (4).

A nanomachine can be defined as an assembly of a distinct number of molecular components that are designed to perform mechanical movements as a result of an appropriate external stimulation. Although there are many chemical compounds whose structure and shape can be modified by an external stimulus (e.g. photoisomerizabe species), the term nanomachine is used only for systems showing large amplitude movements of the molecular components [1].
Like macroscopic machines, nanomachines are characterized by (i) the kind of energy input supplied to make them work, (ii) the kind of movement performed by their components, (iii) the way in which their operation can be controlled and manitored, (iv) the possibility to repeat the operation at will and establish a cyclic process, (v) the time scale needed to complete a cycle of operation, and (vi) the function performed. Chemical, photochemical or electro chemical stimuli can be used to feed nanomachines [2] .
Our purpose is preparation of a part of nanomachines that would constitute any passive or active structure capable of actuation, mesoscale molecular electronic devices, sensing, signaling, information processing, intelligence, swarm behavior at the nano scale [3].
A nanomachine is essentially a controllable machine at the nano meter or molecular scale that is composed of nano scale component. Designed artifical nanomachines and motors are based on interlocked macrocycles named rotaxanes, knots and catenanes which can be made of macrocycles such as azacrown compounds. Rotaxanes consist of a dumbbell - shaped component which incorporates one or more recognition sites in its rod section and is terminated by macrocyclic compound encircled by one or more ring components. Catenanes can be defined as interlocked molecular compounds in which two or more rings are joined together by a mechanical bond [4].
 To understand the dynamic behavior of these nanomachines in solution, degenerate molecular shuttles, in which a macrocyclic unit oscillates between identical recognition sites, are commonly used as probe substrates because rate data can be obtained readily using dynamic 1H NMR spectroscopy. In some instances, the placing of two identical recognition sites in the thread - like component involves a more lengthy synthetic process. For example, if one of the recognition sites must be protected to prevent the formation of a fully occupied rotaxene [5].

In this research work, we explain synthesis of a new constructive compound of rotaxanes and catenans. Several preparation methods have been developed for the preparatone of macrocycle diamides. Among these methods we used the diester technique with good yields.

The *bis* azacrown macrocycle (4) is a ditopic system in which two azacrown ring *bis* macrocycle can move in long of linear molecules, like shuttling (shown under figure). Macrocyclic diamide aza, oxa, thia 16-crown-6 also can interlock with the same macrocycle and form a catenane. Therefore, this molecule can be used on structure of rotaxanes and catenanes in nanomachines and nanomotors. The design, synthesis and investigation of chemical systems able to function as molecular machines and motors are of interest not only for basic research, but also for the growth of nanoscience and the subsequent development of nanotechnology.

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Poster

SYNT 10

Exploration of Tandem Cycloisomerization Leading to Tetrahydro[8]helicene

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Recently, we have developed modular approach to racemic [6]helicenes and 2-aza[6]helicenes based on double cycloisomerization of biarylnaphthalenes bearing two alkynyl chains.[1] In pursuit of our previous investigations in this field, we describe an alternative approach to tetrahydro[8]helicene based on a $PtCl_x$ and Hg^{2+} catalyzed tandem cycloisomerization reaction of naphthalene tetraynes. Exploration of their cycloisomerization reaction and finding its scopes will be discussed herein.

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SYNT 11

Non-Covalent Donor-Acceptor Assembled Systems Vased on Porphyrin Molecular Gels for Unusually High Efficiencies in Electron Transfers

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In natural photosynthetic systems, various low molecular compounds such as chlorophylls and carotenoids construct a light-harvesting antenna complex (LH1) through non-covalent interactions such as hydrogen bonding, van der Waals interaction, and coordination bonding. LH1 is a supramolecular system that can capture sunlight energy and transfer the gained energy to the photosynthetic reaction center (RC). Further, many types of complex donor-acceptor (D-A) models have been proposed in order to mimic electron-transfer systems in photosynthetic systems. In particular, porphyrin-fullerene complexes have attracted considerable attention as a promising candidate as D-A models.

In this paper, we demonstrate a new approach for fabricating donor-acceptor assembled systems. Our strategy is based on the J-type ordered aggregation of a low molecular zinc porphyrin derivative (g-TPP/Zn) and the subsequent integration of a pyridylated fullerene derivative (py-C60) with coordination and orientation onto the porphyrin aggregates. Our system achieves unusually high efficiencies in the case of fluorescence quenching during one-to-one mixing of the donor and acceptor. When g-TPP/Zn was mixed with the pyridylated fullerene py-C60 in a cyclohexane solution (20 °C). The quenching efficiencies reached 95 and 99% solely due to the addition of 0.5 and 1.0 equivalents, respectively, of py-C60 to g-TPP/Zn. To the best of our knowledge, such a high quenching efficiency has been reported only in a few covalent intra-linked donor-acceptor systems. Moreover, the Stern-Volmer constant (KSV) and association constant (K) of this system are 2,520 and 56 times higher, respectively, than those of the corresponding non-assembled system. We have also demonstrated that the quenching efficiency is thermotropically switchable since order-to-disordered transitions are essential characteristics of non-covalent low molecular assemblies. The detailed mechanism of efficient fluorescence quenching and assembling formation will be discussed in this presentation.

SYNT 12

Fullerene-Driven Molecular Machines

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Molecular machines are molecular-scale devices that carry out predetermined tasks derived from molecular motion. A versatile prototype of such nanomachines displays an analogous structure to that of an abacus, in which the ring component can be placed in different positions under controlled conditions. These systems have been named molecular shuttles and are basic components in molecular machinery. The preparation and behaviour of molecular shuttles stoppered with fullerenes will be discussed in detail, focusing on how fullerenes can be applied to monitor and to induce molecular motion [1]. Also, it will be illustrated how such motion can be employed to modulate the physicochemical properties of molecules such as light-driven electron transfer events [2, 3], non-linear optical properties [4], fluorescence [2, 5], electrochemical potential [5, 6] and chemical stability [7].

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SYNT 13

Control of Chiroptical Property of Porphyrin Assembly-Doped Solid Polymer Film

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In the last two decades, a considerable number of molecular organogels have been reported. Molecular organogels are a candidate for the chiroptical materials because they often show enhanced secondary chirality based on the chirally-oriented structure. We have reported that the dialkylated L-glutamide-derived lipids form self-assemblies with unique fibrous morphologies such as tubes, fibers and helices in aqueous and organic media and show large circular dichroism (CD) signals around the chromophore group. Such an enhanced secondary chirality is much attractive properties because the chiral orientation is very sensitive to environmental conditions such as temperature, pH and additives. For example, the zinc-tetraphenylporphyrin-attached L-glutamide lipids (gTP/Zn) formed highly-oriented structures in organic solvents such as cyclohexane and showed drastic color changes from dark green to purple via the formation of chirally-stacked structures through selective axial coordination on zinc with pyridine derivatives.

In this report, we describe that the preparation of polymer composite materials containing gTP/Zn assemblies with controllable chiroptical property using guest ligands. gTP/Zn was synthesized according to the previously reported method [1] and dissolved in a polystyrene-containing benzene solution. The mixed solution showed absorptions at 424, 551 and 593 nm, which correspond to the Soret, β and α bands of zinc-tetraphenylporphyrin. The transparent red-purple colored polymer film was prepared by casting and evaporating the mixed solution on a quartz plate. The λ_{max}s of gTP/Zn were shifted to 434, 560 and 600 nm in the polymer composite film, and the enhanced CD signals appeared around the Soret band of gTP/Zn. It is considered that the orientation state of the gTP/Zn changed in the preparation process of the polymer composite film. On the other hand, the pyridine-doped gTP/Zn film showed no significant λ_{max} shift but CD spectrum remarkably changed. These results indicate that the complex formation of zinc-tetraphenylporphyrin with pyridine induces change of chirally-oriented structure of gTP/Zn. In this report we demonstrate the control of chiroptical property of the gTP/Zn-containing polymer composite film by axial coordination with various guest ligands on Zn.

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SYNT 14

Formation of Lipid Bilayer-Based Nanotubular Aggregates Containing Zinc Porphyrin

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Recently, we have reported that the zinc porphyrin-functionalized L-glutamide derived-lipid (gTP/Zn) form nanofibrillar assemblies and show unique chiroptical properties based chirally-oriented structures in organic solvents such as cyclohexane. The oriented structure is very sensitive to external environments such as temperature, pH and additives. For example, addition of pyridine derivatives triggered drastic spectral changes in both the visible and CD spectra in the Soret band of the gTP/Zn, accompanying by changes of intensity, shift and splitting.

In this paper, we demonstrate to incorporate of gTP/Zn into the aqueous nanotubes based-on bilayer membrane structures, which are formed from L-glutamide derived-lipid with a hydrophilic pyridinium head group (gPy). Typical preparation procedure for gTP/Zn containing aqueous nanotube is as follows: [1] gPy was dissolved in water at 60 °C by ultra-sonication for 5 min and the obtained clear solution was kept at room temperature for 30 min. [2] A given amount of the gTP/Zn THF solution was added to the gPy aqueous solution. The mixture was ultra-sonicated in an ice bath for 5 min. Finally, the obtained solutions were diluted with water and aged at 10 °C for an hour. The final concentration of gPy was 0.5 mM and the molar ratios of gTP/Zn and gPy were adjusted as 2 : 100, 10 : 100 and 20 : 100. The mixed solution was casted on a capper grid and dried over to observe the aggregation morphology by transmission electron microscope (TEM). When an uranyl acetate aqueous solution was used to stain the gPy assemblies, the TEM image indicated that nano-tubular aggregates were produced, but no aggregate was observed without staining. On the contrary, nanofiber-like aggregates were observed in the mixture of gPy and gTP/Zn even without staining. These observations indicate that gTP/Zn is incorporated homogenously into the gPy aggregates. By staining the fiber-like aggregates with uranyl acetate, the inner-wall can be visualized on the TEM image, indicating that the mixture actually formed tubular aggregates. It is clearly observed that the inner diameter of the tubular aggregates was increased with increase the amount of gTP/Zn. This is probably due to the bulkiness of gTP/Zn. Detailed investigations of the oriented structure of gTP/Zn among the tubular aggregates from gPy will be discussed with spectroscopic measurements and thermal analysis.

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SYNT 15

Photochemical Synthesis of 3-Nitrophenanthrene

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A common way to synthesize phenanthrenes is the photochemical oxidative cyclisation of stilbenes in the Mallory-reaction. The Mallory-reaction is compatible to a number of substituents, but not nitro-, acetyl- and dimethylamino substituents [1]. Some years ago Katz introduced new conditions [2] with stoichiometric amounts of iodine and an epoxide as iodide-scavenger, which often give improved yields in these reactions.
We investigated the use of Katz´s conditions on various substituted stilbenes to explore compatibility of substituents to these new conditions. It turns out that the increased concentration of iodide did not cause any problems. As an example of a group that should not react we used the nitro-group. To our surprise nitro-substituted stilbene (1) also formed some 3-nitrophenanthrene (2). The corresponding orto-substituted stilbene did not work at all in the reaction. By variation of the conditions we can reach 22% yield from a mixture of 3:2 Z/E-stilbene. The product appears to be formed exclusively from the cis-isomer (1a), as all remaining starting-material after the reaction is trans-stilbene (1b). Usually the photochemical conditions allow *cis/trans*-isomerisation during the reaction, forming high yields, but apparently the nitro-group block the isomerisation back to *cis*-stilbene which is needed to form phenanthrene.

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Microbial Availability and Transformation of PAC

Oral

MICR 1

How Well Can Measurements of PAH Bioavailability Predict PAH Biodegradation?

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Various methods have been proposed to measure the potential bioavailability of PAHs in contaminated soil or sediment. These measurements are often accompanied by simultaneous measurements of PAH biodegradation or effects on test organisms in bioassays. However, all of these measurements are usually made over relatively short time scales that are not representative of time scales over which the phenomena of interest (biodegradation, bioaccumulation, or chronic toxic effects) might be manifested in contaminated environmental systems. We used the infinite-sink method (desorption of PAHs to Tenax resin) to assess PAH bioavailability in treated soil from two laboratory systems designed to simulate bioremediation of contaminated soil from a former manufactured-gas plant site under field conditions. One system simulated treatment in a slurry-phase bioreactor followed by addition of a nonionic surfactant to enhance the bioavailability of residual PAHs. The second system simulated in situ biostimulation in the subsurface. In both cases, the desorption assay under-predicted observed biodegradation, particularly in the system that simulated *in situ* biostimulation. Our observations are consistent with recent observations by others that re-partitioning of PAHs in the solid phase (e.g., soil) occurs over time scales that would not be captured in the typical desorption assay. Such longer-term phenomena should be taken into account when assessing the fate of PAHs and other hydrophobic contaminants in the environment.

MICR 3

Interactions Between The Bacterial Community Diversity and Polycyclic Aromatic Hydrocarbon (PAH) Contaminations in Agricultural Soils

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Atmospheric inputs are the main source of diffuse PAH contamination in agricultural soil. They contribute to chronic and diffuse contaminations, characterized by large area extents, relatively low contaminant concentrations and unidentified point sources. Several bacterial populations are able to degrade PAHs in soil and use them as a source of carbon and energy for their growth. These PAH-degrading populations belong to several genus among which *Pseudomonas* is well represented. Several *Pseudomonas* isolates have been described for their ability to degrade PAHs in different compartments of the environment [1]. Moreover, because the culturable and not culturable diversities of *Pseudomonas* are similar, comparison between molecular and Pasteurian studies should be facilitated [e.g. 2, 3]. In this context, the objective of our study is to assess the impact of diffuse PAH contaminations on the microbial diversity in agricultural soils with a special focus on the *Pseudomonas* genus. Microcosms of agricultural soils (Yvetot, France) not exposed (controls) or exposed to 300 mgkg^{-1} of PAHs [(i) phenantrene, (ii) pyrene or (iii) a mixture of 8 PAHs (phenanthrene, pyrene and the six PAHs listed by the World Health Organisation)] were established (n = 3, per treatment). Microcosms were analysed after 8, 30, 60 and 90 days of incubation. Global bacterial diversity was studied with both molecular and culturable methods. This approach was completed by a specific study on the *Pseudomonas* bacterial genus as well as by a study on some genes encoding enzymes implied in the PAH-degradation pathway (the PAH-RHDα genes). PAHs fate was monitored by gas chromatography-mass spectrophotometry (GC-MS) and by CO_2 production monitoring. The bacterial community diversity was characterized by culturable method, molecular fingerprint (ARISA) and quantitative PCR (qPCR) targeted on the 16S rRNA gene allowing the quantification of the whole bacterial abundance and of the relative abundances of 11 bacterial taxa. Minor modifications of bacterial community structure were observed on ARISA fingerprints of soil microcosms exposed to PAHs. However, the relative abundances of the 11 bacterial taxa were not affected by PAHs exposure as compared to control. The impact of PAHs contamination on the abundance of culturable *Pseudomonas* and of the total *Pseudomonas* population estimated by qPCR targeting the oprF gene was estimated. Preliminary results show a transient increase of the culturable *Pseudomonas* population (P <0,05; Mann-Whitney) in accordance with the PAHs dissipation kinetics. At this stage, *Pseudomonas* population seems to be a marker of PAH dissipation. The preliminary results obtained from the culturable methods should be confirmed on the molecular level. Finally, the PAH degradation potential will be also determined by quantifying the PAH-RHDα genes and by further characterizing the phenanthrene-degrading bacterial isolates from soil microcosms.

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MICR 4

Organic Micropollutants Degradation Under Anaerobic Mesophilic Conditions with Respect to the Inoculum Origin

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Due to anthropogenic practices, the sludge of urban origin is contaminated by organic pollutants such as polycyclic aromatic hydrocarbons (PAH) and nonylphenols (NP). Efficient anaerobic biodegradation under methanogenic conditions was reported for PAH and NP [1 – 3]. However, the potential of degradation relied on the type of the sludge. Indeed, the sludge impacts either the compounds availability depending on its organo-mineral composition, or the metabolic versatility of microbial populations. In order to understand the respective role of these two hypothetic influences, this study first aimed to physically separate on the one hand the matrix (all the sludge compounds devoided of microorganisms) and on the second hand the alive microorganisms. Secondly, using a well-described, stable and sterilized matrix, we investigated the ability of environmental microbial communities coming from three different origins with contrasting pollution history (two contaminated soils and an anaerobic sludge) to degrade PAH and NP.

The microorganisms were extracted with an original combination of enzymatic pre-treatments followed by a cell flotation step [4, 5]. Each of the three microbial communities served as inoculum for three replicated mesophilic anaerobic reactors fed continuously with the sterilized sludge and with a hydraulic retention time of 20 days. This sludge was spiked with 13 PAH (5 mg kg-1 DM) and NP (100 mg kg-1 DM). The biogas production rate, the biogas composition, the micropollutants concentration, the bacterial/archaeal abundances and the bacterial/archaeal community structures were monitored during 100 days.

The amount and composition of biogas were different for the three inoculates communities, whereas the dry matter reduction was similar. This was attributed to differences in the metabolic pathways. Apart the fact that H_2 was initially found in the first two conditions (inoculated with contaminated soil communities), the mean proportions of CO_2/CH_4 at the end of experiment were 60/40, 40/60 and 20/80, respectively. As expected, the microbial communities were selected over time to produce CO_2 and CH_4. The pollutants degradation capacities were different at initial stage. In particular, the degradation rate for high molecular weight PAHs was very different according to the inoculated communities. For all the compounds, the degradation capacities of all inocula converge over time to the same value. The bacterial/archaeal community structures for the two inocula originating from contaminated soils converged toward a simpler and lower diversity. In contrast, more diverse community structures and diversities were found in the reactors inoculated with the anaerobic sludge.

To summarize, regardless of the inoculated microbial community or the metabolic routes involved, the degradation of PAH and NP was similar. Taken together, these results indicated that the micropollutant type and/or the bioavailability are the driving factors for their degradation under anaerobic conditions.

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MICR 5

Transformation Pathways of Benzo[*a*]pyrene by Ligninolytic Enzymes of *Polyporus sp.* S133

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Polyporus sp. S133, a ligninolytic basidiomycete that cause white rot of wood, can also degrade a wide variety of compounds that are significant environmental pollutants, including certain polycyclic aromatic hydrocarbons (PAHs). The breakdown of most organopollutants by ligninolytic fungi is closely linked with ligninolytic metabolism, in the process is stimulated by nutrient limitation, and it is generally thought that enzymes whose normal function is lignin degradation also catalyze the highly nonspecific xenobiotic oxidations that are characteristic of these organisms. Presently, biodegradation has been shown to be effective in remediating environment contaminated with low molecular weight of PAHs; however the high molecular weight PAHs are generally recalcitrant to microbial attack. Benzo[*a*]pyrene (BaP), a representative high molecular weight (HMW) polycyclic aromatic hydrocarbon and persistent organic pollutant, is of environmental concern due to its known carcinogenicity and bioaccumulation potential. Limited success of physical, chemical, and biological treatment of contaminated soils and sediments is often attributed to contaminant physical properties. Some accumulated metabolites of BaP may be even more toxic than their parent PAHs. Further degradation of these toxic metabolites is essential for the continuous degradation of BaP. For biodegradation only, their degradation is known to involve co-metabolic process. Co-metabolic substances could induce microorganisms to produce some enzymes that can degrade BaP and have the potential to degrade other similar (poly)aromatic. This study is focused on investigation ligninolytic fungal strain for their ability to oxidize ubiquitous BaP and to identify their oxidation product.

MICR 06

Evidence of Aerobic Polycyclic Aromatic Hydrocarbon (PAH) Biodegradation in a Contaminated Aquifer Using In-Situ Microcosms (BACTRAP®s) and Laboratory Microcosms

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Polycyclic aromatic hydrocarbons (PAH) are among the most abundant groundwater contaminants and their removal from contaminated field sites requires cost-effective clean up technologies. Biodegradation of PAHs has been demonstrated under oxic and anoxic conditions, thus showing great promise for the natural removal of the contaminants. Nevertheless, the degradation is highly hampered due to the high activation energy needed to attack aromatic ring, the tendency to sorb on hydrophobic surfaces and furthermore the high toxicity to many organisms. One prerequisite to employ bioremedial strategies as a clean up technology at contaminated field sites is to provide evidence that in situ biodegradation is taking place at the field site.

In this study, biodegradation of four polycyclic aromatic hydrocarbons (acenaphthene, fluorene, naphthalene, phenanthrene) was demonstrated at a PAH-contaminated aquifer in South Germany using an integrative approach. In situ microcosms (BACTRAP®s) consisting of activated carbon pellets were loaded with $[^{13}C_6]$-naphthalene and incubated in PAH contaminated site monitoring wells to collect indigenous groundwater communities. After 99 days of in situ incubation, the ^{13}C-incorporation into microbial amino acids was analyzed. ^{13}C-incorporation of up to 30.4 atom% compared to the natural abundance of 1.1 atom% clearly demonstrated a highly active naphthalene-degrading community at the field site. To further assess the biodegradation potential for the PAHs, laboratory microcosms were set up with $[^{13}C_6]$-naphthalene, $[^{13}C_5/^{13}C_6]$-fluorene (50:50), $[^{13}C_1]$-acenaphthene or $[^{13}C_1]$-phenanthrene. In situ microcosms exposed over a period of 99 days in field monitoring wells and groundwater samples served as inoculum for the laboratory microcosms. Analysis of ^{13}C-incorporation into the mineralization product CO_2 using gas chromatography coupled to isotope ratio mass spectrometry (GC-IRMS) revealed a high degradation potential for all tested PAHs. When the biodegradation potential for continuously and intermittently contaminated wells was compared, in situ microcosms and laboratory microcosms revealed different tendency. While a higher degradation potential at continuously contaminated wells compared to intermittently contaminated wells was found using in situ microcosms, no significant difference was observed in the laboratory microcosms. This may confirm the usefulness of combining different methods for a robust and reliable characterization of in situ biodegradation processes. The approach suggested here can be a powerful tool for evaluating PAH biodegradation at subsurface impacted sites. The BACTRAP® system turned out to be suitable to study the degradation activity directly at the field site but also to enrich PAH-degrading communities for further laboratory cultivation experiments.

Poster

MICR 10

Polycyclic Aromatic Hydrocarbons from Coal-rich Soils Were not Biodegraded in Aerobic Microbial Laboratory Experiments

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Polycyclic aromatic hydrocarbons (PAH) are detectable in soils, sediments and groundwater. Because of their known toxic, teratogenic, mutagenic, or carcinogenic effects, several PAH compounds have been classified as priority pollutants (16 EPA PAH). A major task in environmental sciences is the evaluation of actual or potential risks that arise from PAH-polluted environments. For the purpose of risk assessment, several analytical techniques are used that consider only abiotic (i.e. structural, physical, chemical) sample parameters. Microbiological parameters are not considered routinely, although microbial communities may influence pollutant mobility and bioavailability by degradation or transformation processes. In previous studies an extensive PAH contamination of two distinct floodplain soils (near Konzerbrück and Temmels) along the Mosel River was observed [1]. It was caused by coal and coal-derived particles from the long history of coal mining, coal industry and coal shipping activities in this area. Furthermore, supercritical fluid extraction experiments showed that desorption rates of soil PAH compounds were very slow, suggesting a reduced environmental concern of PAH contamination in these floodplain soils [2]. In the present study [3], we elucidated whether laboratory soil slurry experiments would support these predictions that were based solely on abiotic parameters. For two series of degradation experiments, soil slurries were prepared with fresh soil samples (Konzerbrück, Temmels) and buffered mineral medium to supply indigenous soil microorganisms with macro and micro nutrients. As microbial PAH degradation proceeds most efficiently under oxic conditions, soil slurries were incubated on a rotary shaker to prevent oxygen depletion. The experimental conditions applied, stimulated the degradative activity of indigenous soil microorganisms in slurry experiments of both soils: ~10 mgkg^{-1} to silica gel spiked deuterated phenanthrene was degraded within two (Temmels) or four (Konzerbrück) weeks. After incubating the soil slurries for 29 weeks (203 days) at constant temperature and constant moisture content, however, no significant decrease of soil or coal bound PAH was observed. This suggests that coals and coal-derived particles of the two soils acted as very strong sorbents and reduce or hinder bioavailability. They controlled the mass transfer of PAH compounds from soil or coal particles to the liquid phase, thereby preventing microbial PAH degradation. The long history of PAH exposure and the degree of coal contamination apparently had no influence on the capability of the microbial soil community to overcome constraints of PAH availability: neither aged soil PAH compounds nor PAH compounds from coal particles that had previously not been exposed to soils were degraded. Hence, the present study supports the previous risk evaluation. However, the results of the present study are intimately connected to the experimental conditions chosen.

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MICR 12

Community Structure and Function Analyses of a HMW PAH-Degrading Soil Microbial Consortium

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The high molecular weight (HMW) PAH-degrading microbial populations present in a creosote-contaminated soil were enriched using biphasic cultures (sand and mineral medium). As a carbon source we used a mixture of creosote HMW PAHs obtained from commercial creosote from which 2- and 3-ring compounds had been removed by biodegradation with a versatile fluorene-degrading bacterial strain. This HMW PAH mixture was supplied to the cultures adsorbed to the sand to increase substrate bioavailability. After four monthly transfers, the cultures showed a significant degradation of all the four ring compounds (i.e. fluoranthene, pyrene, benzo[a]anthracene, and chrysene).

PCR-DGGE fingerprints obtained throughout the enrichment procedure demonstrated the stability of this microbial consortium. Clone library was used for the study of the microbial diversity. Most of the analyzed clones corresponded to Gammaproteobacteria (45%) such as *Pseudoxanthomonas*, recently described as a pyrene degrading bacteria, and *Pseudomonas*, largely reported as a PAH degrading genera. Alphaproteobacteria (30%) also constituted an important group, with representatives of *Sphingobium* (described as both pyrene- and fluoranthene- degrading bacteria), *Azospirillum* (previously found during the bioremediation of a creosote-contaminated soil) and *Bradyrhizobium* (previously isolated from a PAH contaminated soil). The rest of the clones belonged to CFB (19%) and Betaproteobacteria (6.5%), such as Achromobacter.

In order to identify the detected populations and associate them with the necessary functions to degrade the HMW PAH mixture, two approaches were taken. First, different most probable number plates containing a variety of hydrocarbons (hexadecane, C_{28}, phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene) were inoculated with the enriched consortium and, after total DNA extraction, the populations grown in positive wells were analyzed by PCR-DGGE. Second, several solid culture media we assayed in order to recover the detected populations in pure cultures: soil extract medium, mineral medium with different PAHs (fluoranthene, pyrene, benzo[a]anthracene, chrysene and the degraded creosote-PAH mixture), and LB1/100. Here we report the obtained results.

MICR 13

Microbial Community Structure of a Pyrene-degrading Marine Consortium

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It is estimated that each year about 0.1% of the total oil production ends up in marine systems [1]. A recent example is the heavy fuel oil spill from the tanker Prestige in 2002. After the spill a bioremedation study was performed in which, a marine microbial consortium was established [2]. This consortium (UBF) was obtained by enrichment culture of natural populations from a polluted sand sample. Further studies [3] revealed that this consortium causes an extensive degradation of the aliphatic and aromatic fractions of the fuel, and of the four-ring PAHs fluoranthene and benzo[*a*]anthracene compounds. Pyrene, chrysene and benzo[*a*]pyrene were attacked to a lesser extent (75%, 73% and 30% respectively).

Our research focuses on the microbial processes involved in the degradation of high molecular weight (HMW) PAHs in the environment, using pyrene as a model compound. Enrichment procedures for pyrene degrading strains from contaminated soils often leads to the isolation of actinobacteria, belonging to the genus *Mycobacterium*. However, little is known about the microbial populations involved in HMW-PAHs in marine environments.

The microbial consortium UBF-Py was established from a subenrichment from the UBF fuel consortium in nutrient-supplemented artificial sea water using pyrene as sole carbon source. This consortium has been monthly transferred for four years. After 30 days of incubation, the consortium UBF-Py produced a 34% depletion of this hydrocarbon respect to abiotic controls. For a better characterization, mineralization experiments were carried out both in ^{14}C-pyrene and ^{14}C-phenanthrene. The cumulative mineralization curves in ^{14}C-pyrene and ^{14}C-phenanhrene showed that UBF-Py is able to mineralize 24.7% and 31.7%, respectively. Since UBF-Py is maintained by monthly transfers, a 30 day time course experiment was set up to analyze the changes in the DGGE fingerprints of the eubacterial microbial community in parallel with biodegradation experiments. The DGGE fingerprints obtained from duplicate cultures and throughout the incubation time showed a highly similar profiles indicating a high stability of the microbial community. Analysis from clone libraries revealed the presence of 5 distinct OTUs belonging to the genera *Breoghania, Thalassospira, Gordonia, Martelella* and *Paracoccus.* In an attempt to identify the microbial populations associated with the utilization of pyrene, 42 isolates were obtained using different culture media corresponding to 7 different bacterial strains. Three of them presented 16S rRNA gene sequences previously found in clone libraries. Interestingly, four of the isolates obtained from UBF-Py were not observed during the molecular analysis. According to their partial 16S rRNA gene sequences the new strains were identified as members of the *Alcanivorax, Microccus*, *Aurantimonas* and *Novosphingobium* genera. The catabolic capabilites of these isolates are now being studied in an attempt to link the different isolates with specific degradative functions in pyrene degradation.

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Monitoring Human Exposure to PACs

Oral

Plenary Lecture 2

Epidemiological Evidence of the Carcinogenicity of PAC

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There is a long history in the identification of PAHs as human carcinogens starting with the observation by Sir Percivall Pott in 1775 of increased risk for scrotal cancer in chimney sweeps exposed to soot. Several occupations may have very high exposure to PAHs and epidemiological studies have shown that those workers have higher risk for lung, bladder and skin cancer.

Recent research in humans non-occupationally exposed to PAHs examines various health outcomes including immunologic responses and reproductive outcomes such as birth weight. Among the major problems in epidemiological research has been the difficulty in exposure assessment and the evaluation of exposure to mixtures rather than to specific PAHs. Benzo[*a*]pyrene has been frequently evaluated as a marker compound although other congeners not evaluated in humans have been shown to be more toxic in experimental studies. In recent years, the use of molecular techniques and of genetics has allowed a more comprehensive evaluation of health risks of PAHs. In my talk I will refer initially to existing knowledge and the evaluations by the IARC/WHO and will then discuss recent findings of studies examining PAHs using biomarkers including studies on cancer and birth outcomes, and also studies examining genetic susceptibility in the response to exposure to PAHs.

HUMA 1

Urinary Carcinogenic 4-6 ring Polycyclic Aromatic Hydrocarbons in Coke Oven Workers and in Subjects Belonging to General Population: Role of Occupational and Environmental Exposure

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Aim
Polycyclic aromatic hydrocarbons (PAHs) are organic compounds formed by two or more condensed aromatic rings. They are present as common environmental pollutants in both living and working environments and some of them have been classified as carcinogen for humans by the International Agency for Research on Cancer. Aim of this study was the assessment of exposure of coke oven workers to carcinogenic PAHs by determination of urinary unmethabolized 3-6 ring PAHs (U-PAHs).

Methods
104 coke oven workers from Poland (recruited in two different years CW1 n= 55; CW2 n= 49) and 45 controls subjects from the same area were investigated by measurement of 10 U-PAHs (from phenanthrene to benzo[*g,h,i*]perylene) in urine spot samples by a solid phase microextraction gas chromatography-isotope dilution mass spectrometry method newly developed. Data regarding personal characteristics, habits, and job variables were collected by a questionnaire. A regression model was applied to evaluate the role of several occupational and environmental variables on U-PAHs levels.

Results
Urinary PAHs were above or equal to LOQ, depending on different compounds, in 67- 100% (min - max), 26 - 100% and 6-100% of samples from CW1, CW2 and control, respectively. Phenanthrene was the most abundant compound (median levels 634.0, 219.7 e 20.6 ng/L in CW1, CW2 e controls). Chrysene and benz[*a*]anthracene were the most abundant carcinogenic PAHs with median levels of 43.4, 13.4 and 2.3 ng/L and 45.9, 14.9 and 0.7 ng/L in CW1, CW2 and controls, respectively, while benzo[*a*]pyrene levels were 6.5, 0.7 and <0.5 ng/L. The multiple linear regression model showed that major determinants of exposure were job title and cigarette smoke, relevant influence was exerted also by using wood and/or coke for house heating, grilled food consumption and dermal contamination at work.

Conclusions
Urinary benzo[*a*]pyrene and other carcinogenic PAHs were quantified in urine samples from both occupationally and environmentally exposed subjects. These results show that U-PAHs can discriminate PAHs exposure at different levels. Moreover, the simultaneous determination of several U-PAHs gives the possibility to obtain excretion profiles and to assess exposure to specific compounds.

HUMA 2

Representativeness of Urinary Hydroxylated Polycyclic Aromatic Hydrocarbons (OH-PAHs) as Biomarkers for PAH Exposure

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Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental pollutants formed during incomplete combustion of organic materials such as wood, fossil fuels, meat, and tobacco. PAHs are found in automobile exhaust, wood smoke, cigarette smoke, and also found at high concentrations in certain food such as barbequed food. PAHs have generated considerable interest, not only because of their wide distribution in the environment, but also because of their carcinogenic and mutagenic potential.

Humans are exposed to PAHs through inhalation of ambient air or cigarette smoke and ingestion of food containing PAHs, as well as dermal absorption from soil or material that contains PAHs. For the general population, ingestion and inhalation are the two major routes of exposure, with the former as the main route of PAH exposure. After entering the human body, PAHs undergo rapid initial distribution to fatty tissues. The liver is often regarded as a primary site for biotransformation of PAHs regardless of the route of entry, because this organ contains many of the enzymes needed in the biotransformation of the parent compounds. PAHs are metabolized to form hydroxylated metabolites that are subsequently conjugated with glucuronic acid and/or sulfate to facilitate elimination through urine and/or feces. Generally, metabolites of PAHs with two to three rings are excreted preferentially in the urine, whereas PAHs with higher molecular weight are excreted primarily in feces.

This presentation will provide an overview on the representativeness of urinary hydroxylated PAHs (OH-PAHs) as a marker of exposure when conducting studies aimed at determining the exposure in the general population and/or occupational exposures exceeding the general population´s exposures. Urinary biomonitoring typically provides information on recent exposure. The biological half-life of PAHs are less than 24 hours, hence, urinary biomonitoring is limited to provide information on exposures occurring within this exposure window. Due to this, it was decided in the laboratory to conduct a series of studies to assess the variability and representativeness of a urine sample and to provide a solid foundation for future exposure assessment studies. The first step was to investigate the variability of urinary metabolites in a group of non-occupationally exposed individuals and to use this dataset to calculate sample size required to reach a certain statistical power. We also compared different methods of standardizing urinary collection including first morning and 24 hour void sampling. In subsequent investigations the biological half-life of the metabolites monitored was determined to range between 5 and 7 hours, and the sources of exposure (inhalation and ingestion) was studied in a group of non-occupationally exposed volunteers to provide a solid understanding on background exposure from which future exposure assessment studies may be designed.

HUMA 3

Biomarkers and Pharmacogenetics of Maternal and Fetal Tobacco Exposure: Effect of Maternal Smoking on Fetal Growth and Delivery

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Smoking during pregnancy has been linked to a variety of adverse pregnancy outcomes, including low birthweight, spontaneous abortion, and infant death. In addition, premature delivery (<36 weeks gestational age) has been linked to maternal smoking during pregnancy. Some biological mechanisms which have been clinically confirmed link cigarette smoke to fetal health and include an association between nicotine and decreased placental blood flow and an increase in fetal heart rate. Of the fetal outcomes documented, low birthweight shows the clearest and most consistent association with maternal smoking. Evidence suggests that a dose response relationship exists between cigarette consumption, especially during the third trimester and birth weight. The prevalence of smoking during pregnancy has been estimated at between 15 and 30 % of all pregnant women with the percentages varying slightly dependent on the source of the data used and with State - to - State variations (Kentucky generally ranks among the highest States in % of women smokers). Recently the Centers for Disease Control (CDC) reported that the incidence of State-specific smoking prevalence among U.S. adults varied widely ranging from a low of 14.2 percent in Utah to a high of 30.8 percent in Kentucky. In addition, women with mistimed or unwanted pregnancies are more likely to smoke throughout pregnancy as are women that are single and of teenage years. Smoking cigarettes during pregnancy has been shown to increase the risk of numerous adverse pregnancy outcomes, including low birthweight, preterm delivery, miscarriage, ectopic (tubal) pregnancy, infant death, low Apgar scores, and early childhood illness (respiratory illness, asthma).
In this presentation, we will discuss biological markers for assessing both maternal and fetal exposures to various tobacco smoke carcinogens and determine populations at greatest risk by assessing various genotypes in both maternal and fetal blood. We will examine the effects of genotype on the formation of biomarkers and will assess ethnic differences in pharmacogenetics to genotype to glutathione S-transferases (GST) and N-acetyltransferases (NAT). These genotypes will be examined to determine their effects on both maternal and fetal tobacco biomarkers. Specifically, we intend to examine the formation of hemoglobin tobacco smoke carcinogen adducts in smoking and non-smoking exposed pregnant women and correlate these tobacco smoke carcinogen biomarkers with DNA adducts and genotype. In addition, we will investigate the relationship between intrauterine growth retardation, as expressed by fetal birth weight, and gestational age as a consequence of both maternal smoking histories during pregnancy, biological markers of tobacco related carcinogens, and pharmacogenetics.

HUMA 4

Amniotic Fluid Polycyclic Aromatic Hydrocarbons: A Potential Biomarker of First Trimester Exposure to PACs

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Exposure to carcinogenic PAH at early stages of pregnancy and fetal development has a much greater impact than late term exposures. Women that smoke during pregnancy tend to have higher risks of developing problems during their pregnancy, including premature labor and deliver, low birthweight infants, intrauterine growth retardation, and potential for birth defects. Biological markers of exposure assessment to environmental carcinogens in the developing fetus have been limited previously to studies that have examined either placental exposure to carcinogens after delivery or the obtaining of biological specimens from the neonate.

One of the biological fluids that offers promise in the early term pregnancy exposure assessments to carcinogens is the application of amniotic fluid as a biomarker of exposure assessment. Amniotic fluid is an integral part of pregnancy and fetal development. This watery fluid is found inside a casing called the amniotic membrane (or sac) and the fluid surrounds the fetus throughout the duration of pregnancy. In average pregnancies, approximately 500 - 800 ml of amniotic fluid surrounds the fetus. Amniotic fluid helps protect and cushion the fetus and plays an important role in the development of many of the fetal organs including the lungs, kidneys, as well as gastrointestinal tract. Amniotic fluid is produced by the fetal lungs and kidneys, with the largest component being that of urine produced by the fetal kidneys. Amniotic fluid problems occur in approximately 7% of all pregnancies with production of excessive or inadequate amounts of amniotic fluid being associated with abnormalities in fetal development and pregnancy complications. During pregnancy, the amniotic fluid increases in volume as the fetus grows. Amniotic fluid volume is greatest at approximately 34 weeks of gestation, when it averages 800 ml, with approximately 600 ml of amniotic fluid surrounding the fetus at full term (40 weeks gestation). This fluid is constantly circulated by the fetus in swallowing and "inhaling" existing fluid and replacing it through "exhalation" and urination.

In this study, we determined the presence of selected PAHs in first trimester amniotic fluid obtained from both smokers as well as nonsmokers. These results will help elucidate the potentially harmful effects of smoking during pregnancy and will potentially lead to the identification of specific compounds found in tobacco that may cause harm to the fetus during this critical period of development. These results demonstrate that detectable levels of potentially carcinogenic compounds occurs in early pregnancy in the fetus and that amniotic fluid samples can serve a reliable biomarker of exposure to harmful substances during pregnancy. Identification of potentially harmful compounds detected at an early stage of pregnancy may prevent subsequent exposures to the fetus and as a result decrease the risk of potential genotoxic as well as teratogenic events.

HUMA 5

Identification and Quantitation of 3-Hydroxybenzo[*a*]pyrene and 1-Hydroxypyrene as Polycyclic Aromatic Hydrocarbons Exposure Biomarkers in a Population of Traffic Police Officers

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In Megacities like Bogotà, Colombia, with the increasing industrial and development levels, different population sectors are environmentally exposing to vehicular total particulate matter emissions (TPME) and as part of them, workers are exposing to polycyclic aromatic hydrocarbons (PAHs) through inhalation, dermal and oral way. Some of these groups are the traffic police officers, buses drivers and other street workers.

Urinary metabolite monitoring is a significant part of industrial hygiene control and it is complementary to air sampling. This investigation is part of a larger project that investigates the level of exposure of traffic police officers in Bogotà, Colombia, SA. As main goal, the exposure levels are evaluating through the identification and quantitation of the polycyclic aromatic hydrocarbons hydroxylated metabolites (OH-PAHs), as selected exposure biomarkers.

A cross-sectional observational descriptive study with an analytical component was conducting to compare traffic police officers with a control group of police officers that works at administrative jobs. This analysis can offer an estimate of internal dose by total exposure. Levels of two urine derivatives, 1-hydroxypyrene and 3-hydroxybenzo-[*a*]-pyrene were measured in urine samples, that were collected pre and post- work transfers for three days. To enable extraction of OH-PAHs from urine, the conjugate metabolites were recovering by enzymatic hydrolysis with β-glucuronidase and β-aryl-sulfatase.. After overnight deconjugation, samples were extracted by solid-phase extraction (SPE) and finally analyzing by gas chromatography - mass spectrometry. An analytical technique based on (HRGC-MS), is used to quantify the exposure biomarkers in urine, founded on a significant Limit of Detection (LOD).

The study found the biomarkers presence in the population environmentally exposed. Results of the analysis of prevalence ratio -Odds Ratio- show, that among the possible sources of PAHs, the environmental exposure to vehicular emissions has the strongest association with the outcome, that is, the presence of biomarkers in urine (values in traffic police officers are >15 times higher than control group). This factor is following by smoking. The presence of the biomarker 3-OH-benzo-[*a*]-pyrene, was found in one third part of the population exposed, allowing the use of this method as a tool for the early diagnosis of exposure to carcinogens. Although these results do not reveal a genotoxic effect yet, they could be considered as a warning for the exposed population, to take protective measures to reduce or avoid exposure to such substances.

HUMA 6

Measurement of Mono- and Dihydroxylated Metabolites of PAHs in Urine through Automated Liquid-Liquid Extraction and Gas Chromatography/Isotope Dilution Tandem Mass Spectrometry

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Polycyclic aromatic hydrocarbons (PAHs) are a class of pollutants that exist ubiquitously in the environment and are formed during incomplete combustion of organic materials, such as coal, gasoline, oil, wood, and cigarettes. Studies have shown that exposure to PAHs is potentially carcinogenic to humans, as exemplified by elevated incidence of cancer in certain occupations such as coke-oven workers. Hence it is of importance to monitor exposure of these compounds in the general population and identify specific populations that may be at an increased risk of exposure.

Two groups of urinary metabolites have been identified as biomarkers to assess human exposure to PAH, i.e. mono-hydroxylated PAHs (OH-PAH) and dihydrodiol PAHs (PAH diols). Our lab at the Centers for Disease Control and Prevention has been measuring OH-PAHs for several years. Here, we are reporting an improved method measuring 10 OH-PAHs, metabolites of naphthalene, fluorene, phenanthrene and pyrene. We also modified and expanded this method to measure 2 PAH diols, i.e. trans-1,2-dihydrodiolnaphthalene and trans-9,10-dihydrodiolphenanthrene. The sample preparation method includes enzymatic deconjugation, automated liquid-liquid extraction to isolate OH-PAHs, silver nitrate cleanup, a second liquid-liquid extraction to isolate the diols, evaporation and derivatization. Samples are analyzed by gas chromatography coupled with isotope-dilution triple quadrupole tandem mass spectrometry (GC-ID-MS/MS).

The improved method provides cleaner extracts which leads to more accurate and precise measurements of OH-PAHs. The use of tandem mass spectrometry allows for higher selectivity and sensitivity, while reducing analysis cost compared to the previous method using high resolution mass spectrometry. In addition, the ability to isolate and determine another major group of PAH metabolites, PAH diols, from the same samples will greatly improve the versatility and capacity of this method, provide unique information on PAH metabolic pathways, and improve the understanding of PAH metabolism and exposure assessment.

HUMA 7

Measuring Polycyclic Aromatic Hydrocarbons (PAHs) in Urine from Xuanwei, China as Biomarkers of Exposure to Fuel Smoke

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Xuanwei County has the highest lung cancer rate in China, with up to 20 times the lung cancer mortality in women compared to the rest of China [1]. Epidemiologic studies have associated indoor combustion of smoky (bituminous) coal with lung cancer risk in Xuanwei [1,2]. Air samples from Xuanwei homes revealed that smoky coal emissions contain very high concentrations of carcinogenic PAHs that approach the exposure levels of coke oven workers [1].
The International Agency for Research on Cancer (IARC) classifies certain PAHs and occupational exposures to concentrated sources of PAHs, such as coke production, as Group 1 (carcinogenic to humans) [3]. IARC also classifies indoor emissions from the household combustion of coal as carcinogenic to humans [4]. PAH exposure has been suggested to contribute to the etiology of the extraordinary lung cancer rate in Xuanwei [5], although a causative relationship has not been established. Our goal is to measure urinary levels of PAH among Xuanwei women as part of an extensive research effort to characterize exposure to various components of coal smoke and study their relationships with lung cancer risk. The sources of PAH exposure include inhalation, ingestion and dermal contact. Since <1% of Xuanwei women smoke, fuel smoke is presumably the main source of PAH exposure by inhalation. Therefore, PAH biomarkers can be surrogates of PAH exposure from solid fuels in these women without confounding by cigarette smoking.
Human spot urine sampling is personal, non-invasive and can be repeated throughout the day. Unmetabolized PAHs in urine directly reflect the exposure levels of PAHs at the time of urination. The levels of unmetabolized PAHs in urine are low, and few studies have reported urinary PAH levels from Xuanwei residents.
We updated a rapid, precise, sensitive and specific method [6] to simultaneously measure 12 two-ring to four-ring PAHs in urine. Several of these compounds are EPA priority PAHs and also belong to IARC Group 2B (possibly carcinogenic to humans). Our method employs automated headspace solid phase microextraction (HS-SPME) coupled with gas chromatography mass spectrometry (GC-MS) using only 0.7 mL of urine per sample. It can detect PAH levels at ng/l concentrations in urine with sufficiently-large linear ranges for accurate quantitation. A pilot study showed that Xuanwei women in the a priori high-exposure group had significantly higher levels of urinary PAHs than women in the low-exposure group, for 10 out of the 12 PAHs. This suggests that urinary PAHs can serve as biomarkers of PAH exposure. Here, we will report urinary PAH levels among more than 200 samples from Xuanwei women exposed to a wide range air PAH concentrations. Our results will allude to the feasibility of using this method to monitor PAH exposure in epidemiologic studies such as those in Xuanwei.

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HUMA 8

Monitoring Polycyclic Aromatic Compounds and Their Metabolites in the Urine of Hot-Mix Asphalt Paving Workers Using the Ames Mutagenicity Assay of Their Nitrated Derivatives

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This study was part of an industrial hygiene assessment of the asphalt paving industry in the U.S., one of the goals of which was to determine the relative contributions of the dermal and inhalation routes of exposure to the levels of PAC metabolites in the urine of exposed workers. Three biomonitoring methods were used: gas chromatography-high-resolution mass spectrometry, the enzyme-linked immunosorbent assay (ELISA), and a variation of the Ames Test biomonitoring method termed The Nitration Assay. This report will deal with the results obtained using the latter method, which takes advantage of the 10-to-10^5-fold amplification of Ames Test mutagenicity that chemical nitration of PACs and their metabolites produces. Urine samples were collected pre-shift, post-shift, and at bedtime from each of twelve workers in three paving crews three days a week for four weeks. During the first week, standard work practices were followed. In the second week, biodiesel was substituted for diesel fuel for cleaning tools and equipment. In the third week, workers wore protective clothing to minimize dermal exposures, and during the fourth week, they wore powered air-purifying respirators to minimize inhalation exposures. The data analysis focused on the post-shift samples, which in general had the highest metabolite levels. The twelve Nitration Assay endpoints (Nitration Mutagenicity Indices or NMIs) for a given worker were correlated against corresponding ELISA values as a means of assessing the consistency of his exposures over the four week period. It was assumed, given the two assays' differing specific activities for individual PACs, the correlations between the two aggregate endpoints would be strongest in cases where exposures were qualitatively most similar over time, and that poorer correlations would result from occasional exposures to sources of PACs other than bitumen fume - the most important one being the sporadic use of diesel fuel or biodiesel for tool and equipment cleaning, a practice which produces PAC-containing aerosols subject to inhalation (diesel fuel only) and solutions of PACs subject to dermal absorption (both agents). When the divergence of the two endpoints caused by these mixed exposures was corrected for by the application of appropriate normalization factors, the data sets correlated well for nearly all the workers, and the effects of the protective measures, largely obscured in the unnormalized data sets, were revealed. The principal findings were: The use of biodiesel rather than diesel fuel for tool and equipment cleaning appeared to promote greater dermal penetration of PACs and lead to higher metabolite levels. For fume and aerosol exposures, the dermal and inhalation routes contributed equally to the levels of urinary PACs and their metabolites. More than 90% of the dermal contribution to metabolites was a result of hand contamination with bitumen dissolved in biodiesel or diesel fuel. Ancillary findings were: Absorbance at 405 nm provided a better urine-concentration normalization than the standard creatinine correction. Each of the speciation biomarkers measured by GC-HRMS showed strong pairwise correlations with the others once they were adequately normalized, indicating that any one of them would have been a sufficient index of exposure.

HUMA 9

Contribution of PAH Emission to Lung Cancer Rates around the World

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Polycyclic aromatic hydrocarbons (PAH) are products of incomplete fuel combustion. Some of them (e.g. benzo[a]pyrene) have carcinogenic properties. Because of this, it is important to be able to measure and estimate human exposure to PAHs. Although other factors, such as cigarette smoking, can lead to lung cancer, PAH emissions may also contribute to lung cancer rates. A multiple linear regression model was developed to investigate the potential contribution of gross domestic product (GDP), smoking rates, cigarette price, population and PAH emissions on the number of lung cancer deaths (NLCD) around the world. These data were collected from the World Health Organization, the International Agency for Research on Cancer, and other sources. Diagnostic procedures suggested logarithmic transformation of the data, followed by use of a Poisson distribution. The indicator variables were used to investigate the contribution of PAH emissions on NLCD for seven major parts of the world.

After accounting for smoking rates, GDP, cigarette price and geography, we found that PAH emissions contribute significantly to the number of lung cancer deaths and that this contribution varies for different parts of the world. In North America and Europe, a 10% increase in PAH emission was associated with a 5.6% and 2.9% increase in median NLCD, respectively. On average worldwide, a 10% increase in smoking rates was associated with a 5.7% increase in median NLCD. While a 10% increase in cigarette price was associated with 4.7% decrease in median NLCD [1-4].

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HUMA 10

Biomarkers of Environmental Pollution in Egypt

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Air pollution can come from a variety of sources, including automobile and diesel exhaust, as well as various industrial emissions. Chemicals that comprise air pollution are some of the most toxic chemicals known to man, and they have clearly been shown to lead to incidents of respiratory problems and even asked you increases in death in populations exposed to excessive amounts. Specific chemicals involved in air pollution include the volatile organic compounds, as well as the class of chemicals known as polycyclic aromatic hydrocarbons. While considerable work has been done at recognizing the hazards of air pollution and minimizing its extent in many of the world's cities, the major metropolitan areas of Egypt still suffer from excessive air pollution. The cities of Cairo, Ismailia, and Alexandria comprise some of the largest cities of Egypt, and these cities are some of the most highly polluted. Specifically Cairo, with its population in excess of 15 million people, air pollution from automobile and diesel exhaust, as well as industrial emissions is becoming a major factor in the deteriorating air quality. While studies have been carried out to measure a few organic pollutants, most notably carbon dioxide levels, sulfur dioxide levels, and other greenhouse gases, there have not been to date studies that have systematically characterized specific organic pollutants in the Egyptian air. More specifically, there has not been any study that is correlated the ambient levels of exposure with human biological markers of exposure assessment. In this study, we will undertake a systematic evaluation of the air quality in the Egyptian cities of Cairo, Ismailia, and Alexandria and we will characterize specific chemicals known as volatile organic compounds as well as polycyclic aromatic hydrocarbons. In order to link pollution with human exposure, we will recruit volunteers at major hospitals in each of the cities and obtain both blood and urine samples for the characterization of hemoglobin adducts to specific environmental chemicals, and urinary degradation products of the selected chemicals. Personal monitoring will be carried out to more closely establish the relationship between environmental levels and human biomarker levels. These studies will be the first to be conducted in Egypt that will link specific levels of environmental air pollution with human biological markers of exposure assessment. These will be the first steps at continuing studies to investigate air quality in Egypt and relate the environment with human exposure and disease.

HUMA 11

Assessment of Exposure to Polycyclic Aromatic Hydrocarbons in Asphalt Workers by Measurement of Urinary 1-Hydroxypyrene

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Aim
Asphalt workers are potentially exposed to polycyclic aromatic hydrocarbons (PAHs). As some PAHs are classified as carcinogenic, the assessment of occupational exposure to these agents is required under the Italian regulations. Aim of this study was to assess the exposure to PAHs by urinary 1-hydroxypyrene (1-OHPyr).

Methods
We studied 22 asphalt (14 smokers) and 5 control subjects (1 smoker). Multiple samples of urine (up to 4 per subject) were collected at the end of the shift for the determination of 1-OHPyr by LC-MS/MS. Univariate and multivariate linear models for repeated measures were used to evaluate the differences between groups and to identify the determinants of exposure.

Results
The median excretion of 1-OHPyr in asphalt workers was low, but higher than that of control subjects (184 vs. <20 ng/L, or 106 vs. 20 ng/g creatinine, $p < 0.001$); cigarette smoking marginally increased 1-OHPyr in smoking asphalt workers in comparison to non-smokers (129 vs. 208 ng/L or 94 vs. 121 ng/g creatinine, $p = 0.06$). The number of consecutive days at work significantly influenced the excretion of 1-OHPyr [+59% every day, CI: (2, 147), $p = 0.04$]. Subjects using the paving machine had the highest exposure. A strong association between 1-OHPyr and urinary creatinine was observed.

Conclusions
1-OHPyr is a useful indicator of occupational exposure to low levels of PAHs, such as those found in the investigated subjects; for the use of this biomarker it is recommended collecting urine sample at the end of the work week and expressing levels of the biomarker corrected for urinary creatinine.

Poster

HUMA 13

Quantification and Characterization of Vehicle - Based Polycyclic Aromatic Hydrocarbons (PAHs) from the Tamale Metropolis, Ghana

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Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in street dust in the Tamale Metropolis, Ghana have been measured in this study. The concentrations of the various types of PAHs identified in street dust samples from high vehicular traffic density in the metropolis are as follows: naphthalene - 10,000 µg/kg, acenaphthylene - 13,000 µg/kg, acenaphthene - 76,000 µg/kg, fluorene - 18,900 µg/kg, phenanthrene - 40,000 µg/kg, anthracene - 21,000 µg/kg, fluoranthene - 35,200 µg/kg, pyrene - 119,000 µg/kg, benzo[*a*]anthracene - 17,700 µg/kg, chrysene - 10,600 µg/kg, benzo[*k*]fluoranthene - 18,700 µg/kg, benzo[*a*]pyrene - 10,900 µg/kg, and benzo[*ghi*]perylene - 21,000 µg/kg. Calculation of the phenanthrene/anthracene ratio indicated that the PAHs identified in this study were from vehicular fallout as the ratio was less than 10. It is clear from the results of the study that road users in the Tamale metropolis especially hawkers are exposed to the harmful effects of PAHs; and this suggests the need for the establishment of mitigation measures by the regulatory agencies.

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HUMA 14

Rapid Determination of PAHs in Zebrafish Larvae as a Model for the Evaluation of PAHs Bioconcentration

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A simply and rapid approach for two polycyclic aromatic hydrocarbons (PAHs) determination in zebrafish larvae as a part of the new protocol for evaluation of bioconcentration factors and toxicology rate constants by utilizing zebrafish larvae is presented. European Union (EU) strives to protect human health and the environment throughout REACH Regulation [1] by accurately identification of toxicity, persistency and bioaccumulation of all substances that are produced and consumed. Bioaccumulation of a chemical in an organism is one of the most important properties to determine its potential danger to the environment. OECD bioconcentration Test 305 [2] is the most commonly used to establish bioconcentration data (also recommended by REACH´s Test Methods Regulation). Briefly, this test evaluates the accumulation of a dissolved chemical in adult fish by measuring its final concentration in both, the fish and the surrounding media after an equilibration time is reached. REACH European legislation proposes also to replace animal testing wherever possible and to use another animal free approaches (Quantitative Structure Activity Relationship (QSAR), cell-based assays using liver slices, hepatocytes, cell lines, S9 fractions, microsomes, recombinat enzymes, nuclear receptors,…). The use of zebrafish larvae, instead of adult fishes to perform bioaccumulations assays is not straightforward and requires an adaptation of the protocol.
Therefore, OCDE 305 protocol has been adapted and larvae were exposed to concentrations of 1 and 0.1% of their LC50 (OECD guideline 305) on a cycle of bioaccumulation and depuration experiments during 72 hours. Different samples of larvae and media were taken and analyzed along the experiment cycle. PAHs concentration in zebrafish larvae was determined after ultrasonication using acetonitrile as extractant and a simple step of filtration (0.22 µm filters) previous to separation and quantification using liquid chromatography coupled to a molecular fluorescence detector (HPLC-FL). The developed method provided efficient recoveries and adequate limits of detection (LODs) for PAHs determination in the very small and with a high lipidic content samples of zebrafish larvae. PAHs concentrations in the exposure medium were determined using similar methodology but just mixing with acetonitrile, filtration and HPLC-FL determination.
An almost steady-state conditions during the bioconcentration phase were reached after 12 and 22 hours of exposure for fluorene and anthracene, respectively The rate constants and the BCF were obtained from the concentration-time profile with the use of a least-square fit to a non-linear model. Two different methods to estimate toxicokinetic rate constants of PAHs were used. Uptake and depuration rate constants obtained were similar for the low and high exposure levels, so toxicokinetic rate constants appeared to be independent upon the level of exposure. These results of BCFs are in good agreement with those reported in the literature (METI-NITE Japan database [3]). Results obtained show the feasibility of the method assayed for estimation of toxicokinetic parameters and bioconcentration factors using zebrafish larvae instead of adult fishes. This protocol, supported with similar results using other chemicals, can be proposed as an alternative to OCDE 305 methodology reducing considerable animal testing, as suggested by REACH legislation.

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HUMA 15

Kinetics of Formation of Epoxide Adducts of Polycyclic Aromatic Hydrocarbons in Vitro and in Vivo with Hemoglobin

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We investigated the binding of selected PAH epoxides (benzo[a]pyrene, benzo[b]fluoranthene, dibenz[a,h]anthracene, fluoranthene, benzo[ghi]perylene, and benz[a]anthracene) to Hb in order to determine the overall extent of binding kinetics of the PAH to Hb. The following experiments were carried out using mouse (C57BL/6 male) and human Hb in vitro. Packed red cells were resuspended in isotonic saline (2 mls) and 100 l aliquots were used in reactions. PAH epoxide stock solutions were dissolved in tetrahydrofuran (1 mg/ml) and 10 l PAH stock was added to reactions which were carried out at 370 for various times. Reactions were stopped by addition of ice cold water and globin precipitated by addition of Hb to acidified acetone. PAH epoxides were released by incubation with pronase and PAH tetrols extracted using of liquid and solid phase extraction and analyzed spectrophotometrically by HPLC. Similar kinetics were found in both mouse and human suggesting that similar nucleophilic sites of attack of the epoxide are present in both species. In addition, these results point out that the mouse model is appropriate for carrying out investigational studies using carcinogens which potentially can be applied to human biomarker studies. The results demonstrated that that those carcinogens that are weakly active had only a slight degree of binding to hemoglobin, while those that are stronger, such as BPDE, had a larger degree of protein binding. All of the epoxide metabolites yielded detectable levels of Hb adducts that were in proportion to the known carcinogenicity of the parent PAH. These results suggest that the formation of hemoglobin adducts to PAH carcinogens may serve as reliable biomarkers of exposure as well as carcinogenicity.

HUMA 16

Measuring Prenatal Tobacco Exposure in Newborn Blood Spots via Assessment of Polycyclic Aromatic Hydrocarbons

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Research on the health effects of active and secondhand smoking (SHS) during pregnancy is hampered by the inability to accurately measure tobacco exposure. The lack of an objective and accurate measure of prenatal exposure to maternal active smoking and secondhand smoke has especially hindered retrospective case-control investigations that take place years after the pregnancy and require very large populations because of rare outcomes, such as childhood cancers, which affect approximately 1 in every 500 children before the age of 14. The availability of a frozen repository of newborn blood spots on filter paper specimens in California, comprising over 12 million babies and dating back to 1982, offers researchers with a potential new medium to measure tobacco exposure during pregnancy.

In this investigation, we will evaluate two groups of compounds, cotinine and tobacco-derived hemoglobin adducts in newborn dried blood spots, as biomarkers of active and secondhand smoking in pregnancy. We will measure cotinine and N-nitrosamines, 4-aminobiphenyl, and benzo[a]pyrene hemoglobin adducts in stored newborn blood spots using the most sensitive laboratory methods currently available. We will determine the level of correlation between concentrations of these compounds in newborn blood spots and serum/plasma cotinine measured in mid-pregnancy and at birth. We will seek to find a cutoff value that can distinguish prenatal exposure to active smoking from SHS. We will investigate whether changes in smoking behavior during pregnancy can be determined by looking at patterns of compounds in newborn blood spots. We will also look for possible effects on cotinine concentrations of blood spot storage conditions, including time in freezer storage, age at specimen collection, and potential cross contamination of filter paper cards.

HUMA 17

Effect of Temperature on the Polycyclic Aromatic Compound (PAC) Content of Bitumen Fumes: Assessment Using a Laboratory Fuming Protocol in Combination with a Sensitive Method for Determining Relative Aggregate Levels of PACs in Complex Mixtures

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A micro-scale laboratory fuming procedure was used in combination with a sensitive method for determination of relative aggregate levels of PACs in complex mixtures to investigate the relationship between temperature and the PAC content of fumes for six paving grade bitumens with varying performance specifications. Fumes were generated from 0.5 g of bitumen held at temperatures of 110, 135, 150 and 160 ºC for one-half hour, and were collected on a condenser, the tip of which was placed in an enclosed chamber 1 cm above the bitumen surface. The fumes thus produced were washed from the condenser with dichloromethane (DCM), the DCM removed, and the fume residue chemically nitrated by treatment with 50 µl 16N nitric acid at 80 ºC for one-half hour. This process has been show to efficiently convert PACs and their metabolites to mono- and in some cases, di-, tri- or tetra-substituted derivatives. The resulting nitrated residues were then dissolved in dimethyl sulfoxide (DMSO) and tested in the non-activated Ames Mutagenicity Assay. This procedure, termed the Nitration Assay, takes advantage of the 10-to-105-fold amplification of mutagenicity in the Ames Test following conversion of PACs to their nitro-derivatives. The slopes of the dose-response curves for mutagenicity from the test (Nitration Mutagenicity Indices or NMIs) were plotted against temperature of collection to generate temperature profiles for the bitumens. The resulting curves were well fit by exponential regression. They showed that the NMIs of the six bitumens were similar and quite low at 110ºC, but exponentially increased with increasing temperatures by factors ranging from 2.8-fold at 135 ºC to 38-fold at 160 ºC, with the softer bitumens showing the largest fold-increases. The fume samples were analytically characterized according to the molecular weight ranges of their PAC constituents using HPLC as well as a fluorescence method that distinguishes between the low- and higher-ring number PAC categories. The results suggest that even relatively small reductions in paving temperature could result in significant declines in workplace PAC exposures, and that the benefits of such reductions might be effective for bitumens of all grades and types. These findings are seen as having significant implications for future industrial hygiene improvements in the paving industry, especially given the recent introduction of so-called "warm-mix" technology in the U.S. and Europe, which typically employs paving temperatures in the 110 to 120 ºC range - well below the minimum hot-mix paving temperature of approximately 135 ºC.

HUMA 18

Structure-Mutagenicity Correlation of Nitrated Pyrenes by Molecular Orbital Calculations

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Nitrated pyrenes (NPs) included in diesel exhaust particles are potent mutagens in the environment. Their mutagenic strength, M, depends largely on the number and the position of the nitro group as 1,8-DNP > 1,6-DNP > 1,3-DNP > 2-NP > 4-NP> 1-NP > 1,2-DNP in order; DNP denotes dinitropyrene. Previously Maynard *et al.* reported that the logarithms of the M values for twenty nitrated aromatic compounds including five NPs correlate with the lowest unoccupied molecular orbital (LUMO) energy with a correlation coefficient, R, of 0.787. However, the R value reduces to 0.691 when objective molecules are restricted to NPs. In particular 1,2-DNP largely deviates from a linear correlation; its LUMO energy is fairly low, predicting strong mutagenicity, but this is not the case. This suggests that the two neighboring nitro-groups give rise to a steric hindrance, resulting in a rate-limiting step in the metabolic transformation.

To improve the structure-mutagenicity correlation for NPs, we noticed the stability of mutagen-DNA adducts which are finally produced in the metabolic transformation and investigated correlation between the heat of formation and mutagenicity. A double helix molecule having a base sequence of guanine-thymine-guanine-guanine-guanine, was created and a NP molecule was bonded to the C8 position of the middle guanine. A NP-DNA adduct thus generated was optimized by the MM2 molecular mechanics method and then by the PM3 semi-empirical molecular orbital method.

A plot of the heats of formation of NP-DNA adducts against log M showed a good linearly. The correlation coefficient (R) was increased to 0.817. This improvement in the structure-mutagenicity correlation for NPs is ascribed to a large heat-of-formation, -8480 kJ/mol, of the DNA adduct with 1,2-DNP. The adducts with 1,3-, 1,6-, 1,8-DNP provided heats-of-formation in a range from -8530 to -8510 kJ/mol, lower by 30 -50 kJ/mol than the adduct with 1,2-DNP. Since the former three adducts are more stable than the latter, the mutagenicity of 1,3-, 1,6-, and 1,8-DNP becomes larger than that of 1,2-DNP. On the other hand, the heats-of-formation of the adducts with mononitropyrenes are in a range from -8530 to -8470 kJ/mol, being middle of those of the adduct with 1,2-DNP and adducts with other DNPs. Thus the mononitropyrenes exhibit moderate mutagenicity.

The present study shows that calculations for mutagen-DNA adducts are useful for improvement in structure-mutagenicity correlation. In particular, when bulky molecules are investigated and steric effects are expected, such calculations are necessary.

HUMA 19

Identification and Quantification of the Urinary Metabolites of 9, 10-Phenanthrenequinone Associated with Producing Reactive Oxygen Species

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Airborne particulate matter (PM) is an important pollutant in urban atmospheres. PM has been suspected to be a causative factor in several diseases, such as pulmonary and cardiovascular diseases which have been reported to be oxidative stress-related disorders. Polycyclic aromatic hydrocarbon quinones (PAHQs) have been identified as a PM component, and generate reactive oxygen species (ROS) in a redox cycling process. Human exposure to this new type hazardous chemical is not assessed at all, therefore, a biomarker for PAHQ exposure is required in addition to the investigation of PAHQ concentration in PM. One of PAHQs, 9,10-phenanthrenequinone (PQ) has been identified in diesel exhaust particulates and PM and causes massive overproduction of ROS compared to other PAHQs. In this study, a highly specific and sensitive analytical method using liquid chromatography with tandem mass spectrometry (LC-MS/MS) was developed to determine urinary metabolites of PQ. An in vitro study demonstrated that PQ is reduced enzymatically by two electrons to 9,10-dihydroxyphenanthrene (PQH2) and the monoglucuronide of PQH2 (PQHG) is transported into extracellular space 1). Therefore, we tried to identify urinary PQHG and also determine PQ produced by the autoxidation of PQH2, resulting from the enzymatic hydrolysis of PQHG. To determine PQHG, the urine was treated with a mixed-mode anion-exchange and reversed-phase solid-phase extraction cartridge (Oasis MAX, waters). On the other hand, after enzymatic hydrolysis, the hydrolyzed urine was purified on a reversed-phase solid-phase extraction (Oasis HLB) to determine PQ. Each of the analytes was separated on C18 reversed-phase columns with gradient elution, followed by tandem mass spectrometry (MS/MS). PQHG and PQ were detected by the MS/MS with ESI in negative ion mode and with APCI in positive mode, respectively. We successfully identified PQHG as a major metabolite of PQ in human urine and PQ (hydrolyzed PQHG) in the urine after enzymatic hydrolysis of the conjugated metabolites. Free (unconjugated) PQ in the unhydrolyzed urine was hardly quantitated. The concentrations of PQHG in urine samples from healthy non-occupationally exposed subjects were 12.6 - 46.5 ng/L. This study is the first to demonstrate the presence of PQHG in human urine. The determination of the urinary PQ metabolite should be useful for the surveillance of the health effects of ROS through PQ exposure.

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HUMA 20

Analysis of Additional Non-Occupational Exposure to Polycyclic Aromatic Hydrocarbons ot the Traffic Police Officers in Columbia

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Polycyclic aromatic hydrocarbons (PAHs) formed during incomplete combustion of motor emissions as constitutive components of total particulate materials (TPM), are widely spread environmental contaminants. Assessment of urinary mono-hydroxylated derivatives from PAHs (OH-PAHs), are often used as biomarkers for human exposure to PAHs according to the Institute of Environmental Studies (IDEAM) in Colombia, and other regulatory entities.

Besides the work atmospheric exposure, there are other sources of non-occupational exposure to polycyclic aromatic hydrocarbons; among these are: smoking, eating grilled foods, exposure during night -home staying, or commuting periods (place and distance of residence). As part of the project conducted in order to quantify the urine hydroxylated metabolites of pyrene and benzo[*a*]pyrene in an exposed population of traffic police officers, in Bogota City, Colombia, South America, where breathing illness signs are significantly correlated with the TPM in some boroughs. As goals of this study were proposed the validation of the analytical method by HRGC-MS, the standardization of the samples collection and extraction and the analysis of the socio-demographic composition of the participants group.

For the analytical applied procedure, the required specificity, precision and linearity parameters are fulfilled (ZB-5ms GC Column, 30 m x 0.25 mm x 0.25 µm; standards from Aldrich-Sigma). For the exactness there was a 95% of recovering for 1-OH-Py and 93% for 3-OH-benzo[*a*]pyrene, which was acceptable in this kind of analysis with biological materials. The sample of 619 individuals was classified into five groups according a detailed survey and throughout statistical analysis by Odds Ratio, the level of prevalence show notable correlations with the outcome results. Related with the other factors, smoker subjects afforded the second higher levels of OH-derivatives, and this habit explain the higher levels of 3-OH-benzo[*a*]pyrene observed in control group where 80% of administrative workers are smokers, but with considerable distance from the street exposure individuals.

HUMA 21

Breast Cancer Resistance Protein Mediates the Efflux of Pyrene Conjugates in Human Intestinal Caco-2 Cells

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The human gastrointestinal tract represents the main portal for the entry of xenobiotics. The epithelium of the small intestine plays an important role in the detoxification of xenobiotics due to the expression of a number of phase I and phase II xenobiotic-metabolizing enzymes (XMEs) as well as several transport proteins of the ATP-binding cassette (ABC) superfamily.

In the present study, differentiated human intestinal Caco-2 cells were used as a model for the human small intestine to investigate the metabolism and excretion processes of the non-carcinogenic polycyclic aromatic hydrocarbon (PAH) pyrene and its metabolites. Pyrene represents a contaminant of the food chain because of its formation during cooking procedures like broiling or curing. Beyond this study should also identify XMEs involved in the biotransformation of pyrene, its metabolites as well as efflux proteins mediating the elimination of these metabolites from the intestinal Caco-2 cells.

In human intestinal Caco-2 cells pyrene is metabolized predominantly into the phase I metabolite pyrene-1-hydroxyde. This reaction is catalyzed mainly by the cytochrome P450 monoxygenases CYP1A1, CYP1A2 and/or CYP1B1 because of an increase in pyrene-1-hydroxyde after stimulation of CYP1A1 gene expression with typical inductors, e.g. β-naphtoflavone as well as a reduction of pyrene-1-hydroxyde after a treatment of Caco-2 cells with the typical CYP1A1/1A2/1B1 inhibitor β-naphtoflavone. Additionally, we detected phase II metabolites of pyrene-1-hydroxyde, pyrene-1-glucuronide and pyrene-1-sulfate and could identify human sulfotransferases (SULT) 1A2*1, 1A1*Arg, 1A3 as well as 1B1 catalyzing this sulfoconjugation.

Transport studies in Caco-2 cells grown in the Transwell system revealed a dominant excretion of pyrene-1-sulfate and pyrene-1-glucuronide to the apical side of Caco-2 cell monolayer representing the lumen of the gastrointestinal tract. A minor amount of conjugates was transported to the basolateral compartment ("blood side") of the Transwell chamber. An efflux of pyrene as well as pyrene-1-hydroxyde was not observed. By inhibiting the Breast Cancer Resistance Protein (BCRP/ABCG2) using the specific inhibitor Ko143 we could demonstrate that these phase II conjugates pyrene-1-sulfate and pyrene-1-glcuronide were excreted by this ABC-transporter to the apical side of cell monolayer. Furthermore, the transport rate was enhanced after treatment with several aryl hydrocarbon receptor (AhR) agonists like the chemoprotective compound oltipraz indicating an AhR-driven induction of gene expression of XMEs involved in pyrene metabolism or of BCRP gene expression [1].

In summary, human intestinal Caco-2 cells metabolize pyrene into the phase I metabolite pyrene-1-hydroxyde which is further conjugated by phase II enzymes (UDP-glucuronosyltransferases/sulfotransferases) into water-soluble metabolites pyrene-1-glucuronide and pyrene-1-sulfate. These conjugates are excreted predominantly apically over the Caco-2 monolayer by an active transport mechanism mediated by the BCRP. This finding corresponds to a transport into the lumen of the gut in the in vivo situation.

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HUMA 22

Effects of PAH Derivatives on Drug-Metabolizing Enzymes

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants in the urban area and adsorbed to the airborne particles. Through the chemical reaction in the atmosphere, PAHs generate several PAH derivatives, such as nitrated PAH, hydroxirated PAH and PAH quinones. PAHs are well known to activate the aryl hydrocarbon receptor (AhR) followed by the induction of drug-metabolizing enzymes mainly in the liver, while biological responses to PAH derivatives remain not to be fully understood. In this study we investigated the induction pattern of gene expression of phase I and II drug-metabolizing enzymes in the PAHs and PAH derivatives-exposed H4IIE cells, rat hepatocytes.

As shown in many studies indicating PAHs strongly induce phase I enzymes through AhR activation, dibenz[*ah*]anthracene and benzo[*a*]pyrene dramatically induced mRNA expression of phase I enzymes, such as *Cyp1a1, Cyp1a2* and *Cyp1b1*, while benz[*a*]anthracene and chrysene mildly induced these enzymes. Quinone derivative of benz[a]anthracene (1,2-benzanthraquinone) induced the similar level of phase I enzymes. Surprisingly, chrysene has a higher potential for the induction of phase I enzymes by quinone substitution at 1 and 4 positions. With regard to phase II enzymes, PAHs induced the phase II enzymes, (*Nqo1*) and (*Ugt*)*1a6*, and the relationship of induction potency among PAHs was similar to those of phase I enzymes, suggesting that these 2 genes are regulated mainly by AhR. On the other hand, expression of (*Sult*)*1a1* was up-regulated only by chrysene. In addition, neither PAHs examined in this study augmented the expression of (*Hmox1*). 1,2-Benzanthraquinone slightly induced the expression of *Sult1a1*. Exclusively, expression of *Ugt2b1* was greatly up-regulated by 1,4-chrysenequinone. Finally, we examined gene expression changes of drug-metabolizing enzymes by airborne particles. The extracts of airborne particles significantly up-regulated the expression of *Cyp1a1*, *Cyp1a2*, *Cyp1b1*, *Ugt1a6* and *Nqo1*, but not *Hmox1*, *Ugt2b1* and *Sult1a1*.

These results suggest that PAHs mainly induce phase I enzymes through AhR activation while PAH derivatives, especially quinones, induce both phase I and II enzymes through AhR and other transcriptional factors, which regulate the expression of *Sult1a1*, *Hmox1* and *Ugt2b1*. Furthermore, the organic chemicals adsorbed in the airborne particles suggest to exert biological effects mainly through AhR activation in the case of responses to drug-metabolizing enzymes.

Analytical Chemistry of PAC: Chromatography

Oral

CHRO 1

Supercritical Pyrolysis Products of Fischer-Tropsch Synthetic Jet Fuel and Model Fuels

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Prior to their combustion, fuels used in future high-speed aircraft will act as coolants, removing excess heat from engine components. The fuels, while acting in this role, will potentially be exposed to temperatures and pressures of up to 700 °C and 150 atm, conditions which are supercritical for jet fuels as well as most pure hydrocarbons. Such severe temperature and pressure conditions can cause the formation of polycyclic aromatic hydrocarbons (PAH), which are precursors to carbonaceous solid deposits. These solid deposits can block fuel-transfer lines and reduce heat transfer from the engine, hindering safe operation of the aircraft. It is therefore extremely important to understand the reaction pathways of PAH formation from fuels under supercritical conditions to prevent the formation of solid deposits in the pre-combustion environment.
A key component in gaining this understanding is the isomer-specific identification of the PAH products formed in the supercritical fuel pyrolysis environment. To this end we have employed high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorption detection and mass spectrometric (MS) detection in the analysis of PAH products from the supercritical pyrolysis of both a Fischer-Tropsch synthetic jet fuel, pyrolyzed at 710 °C and 42 atm in a bench-scale test rig, and single-component model fuels, pyrolyzed under isothermal, isobaric conditions in a laboratory-scale flow reactor. New PAH product identifications resulting from these analyses will be presented.

CHRO 2

The Quantification of Large PAH Products of the Catechol Co-Pyrolysis with 1,3-Butadiene and the Catechol Co-Pyrolysis with Propyne

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The combustion and pyrolysis of coal, wood and biomass produces the ubiquitous environmental pollutants polycyclic aromatic hydrocarbons (PAH). Interest in the formation pathways of PAH stems from the mutagenic and carcinogenic character of certain members of this class of compounds, particularly many of the $C_{24}H_{14}$ isomers as well as their role in the formation of soot particles.

To investigate PAH formation from solid fuels, catechol (ortho-dihydroxybenzene) is used as a model fuel for pyrolysis experiments as it is representative of aromatic structural moieties in coal, wood and biomass. Since C_3 and C_4 hydrocarbons species have been shown to be important intermediates in PAH formation and subsequent growth reactions, co-pyrolysis experiments of catechol have also been conducted with propyne (C_3H_4) and 1,3-butadiene (C_4H_6), respectively. For the purposes of this study, pyrolysis and co-pyrolysis experiments have been performed in an isothermal laminar-flow quartz-tube reactor at a temperature of 1000 °C and a fixed residence time of 0.3 s.

Analysis of the reaction products by reverse phase high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance detection has led to identification of over 100 two- to ten-ring PAH. The unequivocal identification of these products has been accomplished by matching UV absorbance spectra to spectra of reference standards or spectra published in the literature. Of the identified products of the pyrolysis and co-pyrolysis experiments, PAH with up to seven aromatic rings and molecular weights up to 300 have been quantified in a previous study. Here we present and discuss the yields of PAH with molecular masses greater than 300 from the pyrolysis and co-pyrolysis experiments. Comparisons of the yields offer important insight into the mechanisms leading to the formation of large PAH.

CHRO 3

Chromatographic Methods for the Detailed Analysis of Polycyclic Aromatic Sulfur Heterocycles

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Modern fuels are desulfurized in refineries to a sulfur content below 10 parts per million as demanded by legislation. A major class of sulfur compounds recalcitrant to the hydrodesulfurization are the so-called polycyclic aromatic sulfur heterocycles (PASH) that thus remain in the fuel. Clarifying the relationship between their structure and recalcitrance is an important goal for optimization of the desulfurization process and catalyst development.

Petroleum is the most complex mixture known, and every speciation method relies on a simplification of this complexity. The PASHs are best studied after first isolating them from all other groups of compounds in the crude oil through liquid chromatography. By using a silver(I)-containing silica gel we can achieve an efficient group separation of PASHs based on the number of aromatic C atoms. Three main fractions are isolated: benzothiophenes with two, dibenzothiophenes with three and benzonaphthothiophenes with four aromatic rings. These fractions were analyzed using the Orbitrap high resolution mass analyzer and the results are presented in so-called Kendrick plots with the double bond equivalents plotted against the Kendrick mass, so that the identification of compound groups is simplified. For instance, it is superbly clear how many saturated rings are attached to the aromatic system.

Furthermore, the dibenzothiophene fraction can easily be oxidized to the corresponding sulfoxides that can be separated in HPLC on a diphenyl phase according to the number of methyl substituents. These fractions are analyzed by gas chromatography. Due to the characteristic chemical shifts for dibenzothiophene sulfoxides, they can also be analyzed by 1H-NMR e.g. to determine the percentage and position of the side chains. This information gives further insights into the recalcitrance.

These phases may have use outside fossil fuel characterization, e.g. in environmental analysis.

CHRO 4

Measurement of Hydroxy-PAHs in Urine and Atmospheric Particulate Matter

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Humans are exposed to Polycyclic Aromatic Hydrocarbons (PAHs) through polluted air and diet. Broiled, smoked or grilled food contains higher amounts of PAHs compare to uncooked or boiled food. In air, PAHs are emitted from incomplete combustion of fuels and are adsorbed on fine particulate matter, which can be deposited in lungs, causing adverse health effects and cancer. When in the human body, PAHs are metabolized to hydroxy-PAHs and excreted via urine. By comparing the parent PAH composition of PM and the hydroxy-PAH composition of urine, the metabolic pathways of PAHs can be studied.

An analytical method was developed to measure 33 hydroxy-PAHs in urine and PM using gas chromatography/mass spectrometry (GC/MS). Urine samples were deglucuronized with β-glucuronidaze/aryl sulfoctase and solid phase extracted (SPE) with Plexa stationary phase. PM was extracted from filters with the use of Accelerated Solvent Extraction (ASE). The urine extracts and aliquots of PM extracts were mixed with an internal standard and derivitized with N-methyl-N-*tert*-buthyldimethylsilyl-trifluoroacetamide (MTBSTFA). The derivatized samples were analyzed in electron impact ionization mode with GC/MS. Stable isotope labeled surrogates were used to account for OH-PAH loss throughout the analytical method.

Recovery experiments were conducted using Plexa SPE columns and elution with a 1:1 mixture of Dichloromethane:Ethylacetate. Most of the OH-PAHs recoveries from urine ranged from 80 to 120%. Intra- and inter-day variability of the measurements was also investigated. The stability of the derivatized product was investigated as well. Results showed that the 33 OH-PAH formed stable products, over a two week storage period. The stability of OH-PAHs in frozen urine was also studied. Results showed that many OH-PAH were stable in frozen urine for one week period. However, the dihydroxynaphthalenes were not stable in frozen urine for one week period.

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CHRO 5

Multi-Channel Silicone Rubber Traps for PAH Air Emissions Monitoring

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Numerous sources of atmospheric polycyclic aromatic compounds (PAHs) are prevalent in South Africa, including emissions from an ageing vehicle fleet and from domestic fuel burning. Monitoring of these emissions is currently rather limited, as is the case in many developing countries. A means of sampling gas phase PAHs onto multi-channel silicone rubber traps was therefore developed. These traps are easy and cheap to manufacture and can be re-used after analysis. They consist of a 178 mm long glass tube (borosilicate or quartz; 4 mm i.d. and 6 mm o.d.) containing 22 polydimethylsiloxane (PDMS) channels (55 mm long; 0.64 mm o.d. and 0.3 mm i.d.). Due to the open structure of the trap, air can be drawn through it by portable sampling pumps and the gas phase PAHs partition into the PDMS. Particle bound PAHs can also be sampled simultaneously, by employing the same traps in a denuder configuration. Here particles are trapped on a downstream quartz fibre filter. A secondary trap post filter serves to sample any gas phase PAHs which may have broken through the primary trap or which may have blown off the particles.

The traps are analysed by direct thermal desorption into a GC-MS or a GCxGC-TOFMS, which reduces sample preparation costs and time, as well as the possibility for sample contamination. A novel method for screening PAHs has been developed[1] which is based on laser induced fluorescence (LIF) of PAHs sampled onto the silicone rubber traps. The method is non-destructive and therefore allows the subsequent comprehensive analysis of traps of interest by GC- or GCxGC-MS, if required.

In this manner, PAHs are quantified and chemical fingerprints of samples are determined, in order to assess potential environmental and human health effects. This paper will include results of the application of our technology to domestic fire emissions, for example.

[1] P.B.C. Forbes and E.R. Rohwer, Investigations into a novel method for atmospheric polycyclic aromatic hydrocarbon monitoring, Environmental Pollution, 2009, 157, 2529-2535.

CHRO 6

Laboratory Study for the Development and Application of Adapted Versions of POCIS to Sample Polycyclic Aromatic Hydrocarbons (PAH)

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Polar Organic Chemical Integrative samplers (POCIS) are nowadays widely used for the monitoring of emerging hydrophilic contaminants such as pesticides and pharmaceuticals. Even though their receiving phase has an affinity to aromatic groups, their accumulation capacity for polycyclic aromatic hydrocarbons is limited. Laboratory developments of adapted POCIS versions consisted of replacing the polyethersulfone membranes of the generic configuration (pharmaceutical configuration) with either nylon or polyethylene membranes. Promising results were obtained for a certain number of PAH tested, especially concerning the lag phase observed with the original POCIS and the sensitivity of the tool for hydrophobic compounds´ sampling.
After laboratory calibrations, a mesocosm field study was conducted in order to test the optimized tools in controlled environmental conditions. In-situ sampling rates were calculated, and water concentrations were estimated from the accumulated amounts of PAH in the adapted POCIS. The effects of an episodic contamination and a discontinuous exposure on the integrative capacity of this tool were also evaluated.

CHRO 7

Pressurized Fluid Extraction of Diesel and Air Particulate SRMs: Effect of Extraction Temperature and Pressure

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One use of Certified Reference Materials (of which Standard Reference Materials [SRMs] produced by the National Institute of Standards are a subset) is to evaluate new methods. During the original evaluation of pressurized liquid extraction (PLE) for its effectiveness in the certification of particulate SRMs [1], a sediment material, SRM 1944 New York/New Jersey Waterway Sediment, was used to evaluate the effect of the variables used for PLE, particularly temperature and pressure. Based on the data from that study, 100 °C and 2000 psi (13.8 MPa) were chosen as the PLE conditions used to extract PAHs from the air particulate and diesel particulate materials.

Since that study, Turrio-Baldassarri et al [2] investigated the extraction of PAHs and nitrated-PAHs from diesel particulate matter SRM 1650 by PLE. Using PLE with toluene as the extraction solvent at 195 °C and 2200 psi (15.2 MPa) with two 20 min static cycles, the authors [2] noted higher values compared to the certified values for several higher molecular mass PAHs, as well as 1-ntiropyrene in SRM 1650. Bergvall and Westerholm [3] found that increasing the number of extraction cycles and static extraction times increased extraction efficiencies for SRM 1649a, SRM 1650b, and SRM 2975. The optimal PLE conditions were reported [3] using toluene as the extraction solvent at 200 °C and 3000 psi (20.7 MPa), with five 30 min static cycles for SRMs 1650 and 2975 and four 5 min static cycles for SRM 1649. These conditions resulted in higher values compared to the certified values for several of the molecular mass 252 and higher PAHs.

The parameters used in this study for each material are summarized in Table 1. The presentation will focus on the effect of solvent, number of static cycles and static times, pressure, and temperature when using PLE for the extraction of PAHs and nitrated PAHs from two urban particulate SRMs, SRM 1648a and SRM 1649b and two diesel particulate SRMs, SRM 1650b and SRM 2975.

[1] Schantz, M.M.; Nichols, J.J.; Wise, S.A.; "Evaluation of Pressurized Fluid Extraction for the Extraction of Environmental Matrix Reference Materials"; Anal. Chem.; 69 (20): 4210-4219 (1997).
[2] Turrio-Baldassarri, L.; Battistelli, C.L.; Iamiceli, A.L.; "Evaluation of the Efficiency of Extraction of PAHs from Diesel Particulate Matter with Pressurized Solvents;" Anal. Bioanal. Chem.; 375: 589-595 (2003).
[3] Bergvall, C.; Westerholm, R.; "Determination of 252-302 Da and Tentative Identification of 316-376 Da Polycyclic Aromatic Hydrocarbons in Standard Reference Materials 1649a Urban Dust and 1650b and 2975 Diesel Particulate Matter by Accelerated Solvent Extraction-HPLC-GC-MS"; Anal. Bioanal. Chem.; 391: 2235-2248 (2008).

CHRO 8

Certified Reference Materials for PAC Measurements: Are the Needs Being Met?

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Since the first natural matrix certified reference materials (CRMs) for the determination of polycyclic aromatic compounds (PACs) were issued in the early 1980´s, NIST has developed and distributed over 30 Standard Reference Materials (SRMs) for use in the validation of methods for the determination of PACs. These materials include solutions of selected PACs and natural matrix materials including atmospheric particulate matter, diesel particulate matter, coal tar, marine sediment, mussel tissue, house dust, petroleum crude oil, and shale oil. With the exception of the two oil materials, all these materials have been up-dated with new issues or recertification of same materials.

For the first decade of SRM development, typically only 5 to 10 PAHs were targeted for value assignment because of limitations in the analytical methods; however, the number of PAHs with certified and reference values expanded significantly as new and improved analytical methods, including both LC and GC/MS methods, were developed with emphasis on differences in the chromatographic selectivity of both techniques. In the past decade, the assignment of values for PAHs has focused primarily on GC/MS measurements using several stationary phases of different selectivity to assign values for more isomeric PAHs, higher molecular mass PAH isomers (302 MW), alkyl-substituted PAHs, and for nitro-PAHs and PASHs. The current SRM matrices, which have been recently issued or recertified, (e.g., coal tar, air particulate, diesel particulate, sediments, mussel tissues, and house dust), typically have values assigned for 40 to 60 PAHs, nitro-PAHs, and PASHs as appropriate. The uncertainties associated with the certified values are typically 3% to 7% for the majority of the PAHs based on results from three to five sets of measurements from multiple methods.

After three decades of SRMs for PACs, it is an appropriate time to consider the question: Are these current materials meeting the measurement needs of the PAC community? The broader answer to this question could include the following inquiries: Are values for more PAHs needed in the existing materials? What other PACs need to be included in existing or future materials? Are the uncertainties associated with the current certified values sufficient for their use? Are the current matrices sufficient or are additional matrices needed? Should the certified values be based on smaller sample sizes? What should the next generation of SRMs for PAC measurements look like?

In addressing the last question, NIST is currently developing several new matrix SRMs with a focus on new PACs including three new human urine matrices for determination of hydroxylated PAHs and several materials intended to support oil spill remediation measurements (crude oil, coal tar, mussel tissue, and sediment) with a focus on petroleum-related PAH and alkyl-PAHs. In this presentation the current and in progress NIST SRMs, as well as CRMs provided by other sources, will be discussed relative to the questions posed above.

Poster

CHRO 10

Separation of Nitrogen Containing Aromatic Compounds in Crude Oil by Metal-Modified Stationary HPLC-Phases

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Polar petroleum compounds are responsible for the color, the odor and the viscosity of crude oil. Nitrogen Containing Aromatic Compounds (NCACs) in fuels derived from petroleum lead to undesirable emissions on combustion such as NO_x. They are also involved in gum-formation and fouling, deactivation of catalysts in refinery processes, etc. Due to this, the identification of such compounds is of special interest to petroleum chemists and engineers.
The extremely high complexity of petroleum requires a pre-separation according to functional groups before a compound identification can be realized. Present-day materials allow such separations but not of all compound classes. Therefore, the development of new stationary phases for liquid chromatography is necessary.
The chemical properties of metals like titanium, zirconium and hafnium make it likely that they might work well for the separation of NCACs. We investigated these metals bonded to a stationary silica phase and using a complex mixture containing different polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic sulfur heterocycles (PASHs), polycyclic aromatic oxygen heterocycles (PAOHs), indol-like aromatics, aromatic amines and quinoline-like aromatics. The PAHs, PASHs and PAOHs elute in the first fraction with non-polar solvents like cyclohexane. A somewhat more polar eluent like cyclohexane:dichloromethane displaces indol-like aromatics. In a third fraction, aromatic amines are isolated through elution with pure dichlormethane. The quinoline-like aromatics elute in the last fraction with a more polar eluent containing some tetrahydrofuran. The compounds are released on the change of eluent, leading to a fast separation.

CHRO 11

Standard Reference Materials Characterized for PAHs

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In the last 30 years, the National Institute of Standards and Technology has issued a wide range of Standard Reference Materials (SRMs) [1] characterized for PAHs. These include both solution SRMs that are useful for validating and calibrating the chromatographic separation and detection steps, as well as natural-matrix SRMs that are useful for evaluating and validating the complete analytical procedure [2]. For solution SRMs, there are solutions for parent PAHs (SRM 1647e and SRM 2260a), alkylated PAHs (SRM 1491a), deuterated PAHs (SRM 2269 and SRM 2270), and nitrated-PAHs (SRM 1587, SRM 1596,SRM 2264 and SRM 2265). For natural matrix SRMs, there are particulate matter (diesel, air, and house dust plus an extract of diesel particulate material), coal tar, sediment, mussel tissue, and crude oil materials. These SRMs have been value assigned for a wide range of PAHs, typically ranging from naphthalene through the molecular mass 302 isomers, using two or more independent methods of analysis. For many of the materials, selected alkylated PAHs have also been value assigned, often using only one method of analysis. For the diesel and air particulate materials, as well as the diesel extract, nitrated-PAHs have been characterized as well. These materials have been shown to be homogeneous for the PAHs and are suitable for use in developing methods for and characterizing other analytes of interest. The stability of the materials is monitored over time, and the Certificates of Analysis are updated periodically as new data are generated. This poster will summarize the wide-range of materials available as SRMs along with relevant information on the PAH-related analytes characterized in each material.

[1] For the Certificates of Analysis, see http://www.nist.gov/srm/
[2] Wise, S.A.; Poster, D.L.; Kucklick, J.R.; Keller, J.M.; Vander Pol, S.S.; Sander, L.C.; Schantz, M.M.; Standard Reference Materials (SRMs) for Determination of Organic Contaminants in Environmental Samples; Anal. Bioanal. Chem.; Vol. 386, pp. 1153-1190 (2006).

CHRO 12

Standard Reference Materials Related to Crude Oil Analysis

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The first crude oil Standard Reference Material (SRM) issued by the National Institute of Standards and Technology (NIST) was SRM 1582 Petroleum Crude Oil in 1984. SRM 1582 has certified values for six PACs: phenanthrene, fluoranthene, benz[a]anthracene, benzo[*a*]pyrene, perylene, and dibenzothiophene and non-certified (now designated as either reference or information values) for an additional seven analytes. Following the release of crude oil from the Deepwater Horizon (DWH) site in the Gulf of Mexico, there was renewed interest in quantifying the analytes associated with crude oil. In addition, crude oil was collected from the DWH site and provided to NIST by the National Oceanic and Atmospheric Administration (NOAA) to prepare an SRM for Gulf of Mexico Crude Oil, candidate SRM 2779. In quantifying the PAHs associated with crude oil, one of the big questions is the profile of the alkylated PAHs. Because few alkylated PAHs are available as pure standards, their response factors for quantification are typically estimated rather than measured; the response of the alkylated isomers, however, varies. To provide a common calibration solution for quantifying alkyl PAHs, NIST is collaborating with the Energy and Environmental Research Center (EERC) at the University of North Dakota to prepare a dichloromethane solution of a mixed coal tar and petroleum based-sample containing the entire range of alkyl clusters and parent PAHs, candidate SRM 1991. These three materials, SRM 1582, candidate SRM 2779, and candidate SRM 1991 are being characterized for a wide range of parent PAHs, alkylated PAHs (both selected individual alkyl PAHs and as groups of alkylated PAHs), and selected hopanes and steranes, in the crude oil samples using gas chromatography/mass spectrometry (GC/MS) on different stationary phases and multidimensional GCxGC with time-of-flight MS.

CHRO 13

Interlaboratory Studies Related to Crude Oil Analysis

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To support natural resource damage assessment (NRDA) in response to the Deepwater Horizon (DWH) oil spill in the Gulf of Mexico, a large number of coastal sediment and tissue samples (e.g., oysters) have been collected to define baseline environmental conditions prior to being exposed to oil. For the foreseeable future, subsequent analysis of oiled sediments and oil-exposed oysters will be required as well. To support these efforts, a large number of analytical laboratories are being used to support NRDA sample analyses. To compare the data among these laboratories, interlaboratory comparison studies are being coordinated by the National Institute of Standards and Technology (NIST) with sediment, crude oil, and bivalve tissue as the three matrices of interest. These studies are performance-based with each laboratory using its current methods for analysis of similar matrices that it would use for its program customers. The target analytes for each study are selected polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, hopanes, and steranes. For the sediment, crude oil, and mussel tissue studies, 33, 26, and 34 laboratories, respectively, returned data. In general, the agreement among the laboratories based on the relative uncertainty (95% confidence interval) around the consensus median averaged 30% for the PAHs, hopanes, and steranes, but higher (averaging 50%) for the alkylated PAH homolog groups. In the case of the PAHs, most variation among the interlaboratory data was noted for the more volatile compounds, naphthalene through biphenyl particularly in the sediment and tissue samples, possibly due to losses during the extraction or clean-up steps. The data have been compared based on extraction methods for the sediment and tissue samples and based on quantification methods for all three sample types. The interlaboratory comparability and method differences will be the focus of the poster.

CHRO 14

Analytical Method for Determining Polycyclic Aromatic Hydrocarbon (PAH) Pollutants in Plastic Materials by GC MS/MS

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Polycyclic aromatic hydrocarbons (PAH), such as benzo[*a*]pyrene and dibenz[*a,h*]anthracene, are known potent and persistent carcinogens. This abstract describes techniques with which consumer products were cleaned up and analyzed for PAH by using solvent extraction and GC MS/MS.
The determination and quantification of PAHs in rubber samples were done by GC MS/MS with the aid of isotopically labeled internal standards.
The Sixteen targeted PAHs were resolved, with sharp, symmetrical peak shapes, in less than twenty five minutes, with satisfactory resolution for the four known critical pairs; phenanthrene/anthracene, benz[*a*]anthracene/chrysene, benzo[*b/k*]fluoranthene, and indeno[*1,2,3-c,d*]pyrene / dibenz[*a,h*]anthracene. Postcolumn backflushing was applied to remove low-volatility material from the capillary column, reducing bakeout and maintenance time and increasing column life time.
Linear calibration curves were constructed from data obtained by 1 µl injections of standards. The calibration curve for all PAHs ranging from 2.5 ng ml^{-1} to 250 ng ml^{-1} showed excellent linearity with calibration coefficients greater than 0.996. The resulting detection limit were in the range of 0.01 to 0.08 ng ml^{-1} (based on S/N > 3:1 Peak to Peak) for all PAHs expect for benzo[*ghi*]perylene (0.23 ng ml^{-1}).

CHRO 15

Analysis of Water Accommodated Fractions using Head Space SPME for Volatile Organic Compounds: Obtaining Realistic Data of Oil Released into the Environment

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New approaches for Hazard and Risk Assessment of petroleum contaminated sites have been documented over the last few decades by the CONCAWE (CONservation of Clean Air and Water in Europe) and the TPHCWG (Total Petroleum Hydrocarbon Criteria Working Group). One of their main objectives was to propose a method for grouping individual petroleum hydrocarbons having similar physical and chemical properties, fate and toxicity potential in groups or blocks considered as "pseudo components". The ultimate goal was to define a Predicted Exposure Concentration "PEC" for each group and in each environmental compartment, since PECs for individual substances are hard to find for complex mixtures like petroleum rich in isomers and homologous groups.

In this context, analyzing petroleum composition would be of a great help to have a preliminary idea on compounds that might be found in a petroleum contaminated site. However, petroleum composition varies widely in a function of weathering and not all petroleum compounds can be found in the dissolved water phase. Characterizing the soluble fraction is crucial in risk assessment because this is the main bioavailable fraction for organisms in the ecosystem.

In this study, Water Accommodated Fractions were analyzed for aromatic and aliphatic volatile compounds using Head Space Solid Phase Micro Extraction technique (HS-SPME). Different WAFs with variable oil loading rates were analyzed and compositions were compared to the theoretical concentrations of compounds in gasoline.

CHRO 16

Fluorescence Enhancement of Polycyclic Aromatic Ketones

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We have reported that the fluorescence of a degassed solution of naphthanthrone, 6*H*-benzo[*cd*]pyren-6-one, (abbreviated to NT), is enhanced about one hundredfold after preliminary irradiation of the solution with strong light for half an hour [1,2]. This fluorescence enhancement is considered to due to association of NT with a solvent molecule. We have extended the study and investigated whether the fluorescence enhancement is observed for the other polycyclic aromatic ketones. Then, we have observed that phosphorescent molecules, having a carbonyl group, such as benzanthrone, 7*H*-benz[*de*]anthracen-7-one, 8,9-benzobenzanthorone, 7*H*-benzo[*hi*]chrysen-7-one, and 2-nirto-NT, exhibit the fluorescence enhancement and that fluorescent molecules such as anthracene and perylene show no enhancement. These findings support the association model. That is, in the model the association complex is formed by solute and solvent interactions via the triplet n π^* state of the solute, i.e., a ketone. Since the n π^* state of the ketone is electron-deficient at the oxygen atom, it attracts a nearest hydrogen atom of the solvent to form an associative complex. Such interaction is much more effective for the triplet state than for the singlet state because of longevity of the former. Therefore the phosphorescent molecules, that give rise to the triplet state, may exhibit the fluorescence enhancement. Although 2-nitro-NT is hardly fluorescent, its fluorescence is increased by one hundred times through degas and preliminary irradiation of the solution. Therefore the fluorescence enhancement process may be applicable to the environmental microanalysis of nitrated compounds which are weak fluorescent and mutagenic.
Furthermore, we have analyzed the chemical components of the solution, in which fluorescence enhancement had been occurred, by high performance liquid chromatography (HPLC). The chromatogram have revealed two peaks at retention times of 2.0 and 3.5 min: they were ascribed to a complex and NT, respectively. Since the retention time of the complex was shorter than that for NT, the former was found to be more hydrophobic than NT. This finding supports the validity of the association model, predicting that the association occurs at the carbonyl group of NT.

[1] Ohshima S., T. Ohtsuki, E. Kimura, M. Yamaguchi, T. Toyoshima, and M. Takekawa. 2008. Photochemical reaction of 6H-benzo[cd]pyren-6-one (naphthanthrone). Polycycl. Aromat. Comp. 28: 373-381.
[2] Yagishita M. and Ohshima S., 2009. Fluorescence Enhancement of 6H-benzo[cd]pyren-6-one (naphthanthrone): Effect of Concentration, Light Intensity, and Deutaration of Solvents. Polycycl. Aromat. Comp. 30: 287-297.

Evening Plenary

From Interstellar Polycyclic Aromatic Compounds and Ices to Astrobiology

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Tremendous strides have been made in our understanding of interstellar material in recent years thanks to significant, parallel developments in observational astronomy and laboratory astrophysics. Thirty years ago, the composition of interstellar dust was largely guessed at, the existence of icey materials in interstellar clouds was ignored, and the notion of large, abundant, gas phase, carbon rich molecules widespread throughout the interstellar medium (ISM) was considered impossible. Today the composition of dust in the diffuse ISM is reasonably well constrained to micron-sized cold refractory materials comprised of amorphous and crystalline silicates and amorphous carbon grains. In dense molecular clouds, the birthplace of stars and planets, these cold dust particles are coated with mixed molecular ices whose major components are also very well constrained. Finally, polycyclic aromatic hydrocarbons (PAHs) and related aromatic compounds--shockingly large molecules by the standards of interstellar chemistry—are known to be the most abundant class of interstellar molecules in space, and represent the single largest source of organic carbon in the universe. In this presentation, we will explore our understanding of interstellar PAHs and ices, and consider the contribution of these abundant and widespread materials to the chemical inventory of the primordial Earth, and the role they might have played in the chemistry that led to the emergence of life.

PAC in Environmental Forensics Investigations

Oral

Plenary Lecture 3

PAC in Environmental Forensic Chemistry

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Polycyclic aromatic compounds (PAC) are ubiquitous in soils and sediments worldwide, particularly in urbanized environments. They can be acutely toxic and have carcinogenic properties, and as a result, their occurrence is regulated under most countries' laws, and often require remedial activities or, at a minimum, long-term monitoring. Because of the significant costs associated with either of these actions it is usually necessary to identify the source(s) of PAC at contaminated sites before accepting or allocating liability for their presence or before designing a remedial strategy. It is particularly important to understand the anthropogenic source(s) of PAC at long-active industrial sites or in urban waterways where multiple PAC point sources (e.g., oil spills or coal-derived liquids) had existed over time and/or co-exist with persistent non-point sources (e.g., atmospheric deposition or runoff from the surrounding urban or industrial communities), and sometimes with naturally-occurring PAC.

Different PAC sources can distinguished using environmental forensic chemistry methods that include GC/MS-SIM analysis of unsubstituted "parent" and variously-alkylated homologues and/or individual isomers, as well as any associated compounds (e.g., non-PAC hydrocarbons such as *n*-alkanes or petroleum biomarkers) that often co-occur with PAC and provide additional evidence as to the source(s) of PAC. This presentation will review the three types of PAC found in environmental samples – petroleum-derived (*petrogenic*), combustion-derived (*pyrogenic*), and naturally-occurring (*biogenic*) – and the historical development of the analytical methods used to measure their concentrations in environmental matrices.

Numerous case studies exemplifying (1) how petrogenic PACs derived from different crude oils (spilled versus seeped) or coals can be recognized and distinguished, (2) how petroleum refining (e.g., distillation, cracking, and hydrodesulfurization) predictably effects PAC distributions in refined petroleum such as heavy fuel oils and diesel fuels, and (3) how environmental weathering (e.g., evaporation, water-washing, and biodegradation) can alter PAC distributions will be given. Other case studies focused on pyrogenic PACs derived from (1) historic manufactured gas plant operations (e.g., coal tar *versus* carbureted water gas tar *versus* oil gas tar), (2) wood treatment (creosote) operations, (3) skeet shooting range operations, and (4) urban fill and runoff will also be given.

FORE 1

Tool Comparisons for the Sampling of Polycyclic Aromatic Hydrocarbons (PAH): Field Monitoring in Arcachon´s Bay

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Biomonitoring organisms have been used over the past few decades for surveying water quality, identifying pollution sources, as well as for monitoring the effectiveness of site remediation. However, bioaccumulation factors vary widely between species, and depend on environmental conditions and physiological characteristics of the species used. This variability in bioaccumulation factors induces uncertainty in the estimation of water concentrations based on the accumulated amounts of PAH in the organisms. In addition, biological species cannot be deployed in all environments, and some of them have the capacity to metabolize xenobiotics. For these reasons and many others, the use of passive sampling devices for the monitoring of hydrophobic chemicals has emerged, and many studies have reported the coupling of monitoring organisms and Semi Permeable Membrane Devices (SPMDs) for the sampling of PAH in the aqueous system.
In this study, the performances of three types of passive samplers (SPMDs, Polar Organic Chemical Integrative Samplers (POCIS), and adapted versions of POCIS) for the sampling of dissolved concentrations of PAH were evaluated through a field exposure in Arcachon´s Bay, a lagoon situated in the south west of France, on the Atlantic Ocean. Diploid and Triploid oysters were deployed in parallel to passive samplers in four sites, among which a harbor and pleasance harbors. Distribution profiles between passive and biological sampling were compared, and the interests and limits of the application of adapted versions of POCIS were also assessed.

FORE 2

Determination of 16 EPA-PAHs in Surface Water Containing Suspended Particulate Matter Using SPE-Disk Followed by GC-MS

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Many priority and priority hazardous substances which may occur in surface water sorb on suspended particulate matter (SPM). The SPM can interfere with conventional analytical methods like liquid-liquid-extraction (LLE), because it is insufficiently extracted by these methods. Therefore, SPM is often separately analyzed after filtration of the water sample. If the fraction of sorbed analytes is low compared to the total analyte concentration, it is often totally ignored. However, the European Directive 2000/60/EC (Water Framework Directive, WFD) not only demands for a wide ranging monitoring of priority and priority hazardous substances in surface water, but also requires investigation of the "whole water sample", which means the water sample including SPM [1, 2]. Until now most used methods can not totally satisfy these demands and are associated with a high expenditure of time, work and costs.

The aim of this work was to refine an existing solid-phase-extraction-disk (SPE-disk) method for the determination of the 16 EPA polycyclic aromatic hydrocarbons (PAHs) [3] including further priority substances (in total: 54) considering the WFD. A SPE-disk method allows the extraction of analytes both dissolved in the water and sorbed on SPM in one analysis step. In contrast to normal SPE cartridges (diameter: 6 - 13 mm), SPE-disks (47 or 50 mm) rarely tend to plug due to their higher diameter. Additionally, by using SPE-disks the consumption of organic solvents can considerably be reduced compared to LLE or Soxhlet extraction.

Method development included the choice of phase materials and the optimization of parameters like the enrichment flow, the eluent and the contact time. Special emphasis was put on the drying step which can decisively reduce the amount of residual water in phase material after sample enrichment. The residual moisture in SPE-disks depends on the drying time, the applied pressure and the used phase material. In spite of constant conditions the amount of residual water may fluctuate up to 49 % after drying and therefore influences the choice of both organic eluent and GC-MS analysis. Residual moisture particularly influences the sensitivity of GC-MS analysis for the lower volatile PAHs.

The optimized method provides conditioning of SPE-disks by acetone and water followed by enrichment of 1 L unfiltered water sample containing SPM up to 1000 mg/L within 20 min. SPM is separated from the aqueous phase and collected on top of the SPE-disk. Following a 30 min drying step, the analytes are desorbed by elution from the phase material and SPM in one single step using acetone. Then a volumetric standard is added to the eluate. After concentrating, the eluate is analyzed by GC-MS within 35 min. The overall processing time is about 2 h for one sample including sample preparation and GC-MS analysis for more than 50 analytes. By use of this method the expenditure of time, work and costs was reduced distinctly in contrast to conventional methods such as Soxhlet extraction.

[1] Directive 2000/60/EC
[2] Directive 2008/105/EC
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FORE 3

Combinatorial Library Building to Obtain Mass Spectral Patterns of PAH and PASH by GC-GC/MS and Spectral Deconvolution

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Forensic investigations rely on analyzing complex environmental samples by selective ion monitoring of target compounds. We have shown that this approach results in severe overestimation of alkylated PAH if only their molecular ion signal is extracted or underestimation if a single fragmentation pattern per homolog is used. In this work, we employed automated sequential, multidimensional GC-GC/MS to detect the C1 to C4 alkylated PAH and PASH in crude oil and coal tar to obtain retention times and mass spectra for these compounds. In most cases, an unresolved chromatogram was present even though small sample portions were transferred from the first column to the second. Nonetheless, the Ion Fingerprint Deconvolution algorithms untangled the spectra so that fragmentation patterns were "clean" and could be used to build a library of target compound fragmentation patterns. The library building process consisted of taking four to five ions from the mass spectra of known compounds and then searching for these ions in each heartcut. Once found, the criterion for acceptance was that all ions co-maximized, independent of whether peak relative abundances matched those of known compounds, and that at least two peaks per homolog pattern were found in the samples. When all ions were present and co-maximized, new patterns were those whose relative abundances were different from one another and found in consecutive heartcuts. For those homologs where no mass spectra were available, the mechanism of fragmentation was postulated, with the resulting ions used to search the heartcuts. PASH fragmentation mechanisms are presented in another paper at this conference. These patterns were used to quantify PAH and PASH in a "fresh" and "weathered" coal tar.

FORE 4

PAH Forensics - Tool for Investigation of Subsurface Processes

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PAHs as groundwater contaminants are mostly not easily accessible via simple analytical methods like isotope fractionation for testing in-situ biodegradation. But due to the huge differences in properties (biodegradation, sorption) of the 16 standard PAH substances, transport and natural biodegradation in groundwater result in a characteristic change of the PAH composition (i.e. fingerprint) which could be used in environmental forensics to elucidate subsurface processes. This was investigated in two remediation cases.
In the first case residual tar oil below a building caused an extended PAH plume in groundwater showing high concentrations. In a pilot test it was tried to interrupt PAH transport by initiation of a biological highly reactive zone. This should be achieved by the installation of a dense network of groundwater wells and frequent injections of nitrate solutions. It was expected that the addition of nitrate as electron acceptor should increase PAH biodegradation rates. It was found that the nitrate injection caused a change of the redox environment but in contrast to the expectations this ham-pered the previous active natural biodegradation resulting in an increased mobility of the PAH at the location of the pilot test. At the same time a "wave" of increased PAH concentrations passed the plume, which, however, could not be allocated to the disruption of the natural biodegradation. Later performed detailed site investigation using direct push technologies (ROST) revealed a free product phase trapped in a geological depression. It is assumed that the mechanical energy introduced into the subsurface by the construction of numerous monitoring wells needed for the pilot test has mobilized these PAH.
On the second site, a tar oil contamination caused a PAH plume in groundwater of several hundred meter length. Due to the fact that locally higher PAH concentrations compared to the bulk distribu-tion were observed, it was suspected that the waste deposit located in this area contribute to the PAH mass flux in groundwater. Investigations of the PAH fingerprint across the groundwater plume and of the vertical distribution of soil bound PAH indicated that the waste deposit did not elute PAH into the groundwater although being substantially contaminated. These investigation results were supported by various other investigations like e.g. soil elution tests and the distribution of heterocyclic aromatic compounds (so-called NSO aromatics) which are usually also associated with tar oil.

FORE 6

Quantification of PAH and PASH in Coal Tar by GC/MS and GCxGC/MS, with Spectral Deconvolution

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Forensic investigations rely on analyzing complex environmental samples by selective ion monitoring of target compounds. We have shown that this approach results in severe overestimation of alkylated PAH if only their molecular ion signal is extracted or underestimation if a single fragmentation pattern per homolog is used. In previous work, we described how to build a comprehensive library of retention times and mass spectra for PAH and PASH from coal tar using GC-GC/MS and spectral deconvolution.

In this paper, we describe the analytical results for GCxGC/MS and GC/MS in terms of measurement precision, accuracy, sensitivity, and selectivity when multiple fragmentation patterns per alkylated homolog are used. The Ion Fingerprint spectral deconvolution software quantified PAH, PASH, and their alkylated homologs in "fresh" and "weathered" coal tar samples from a former manufactured gas plant site. GCxGC/MS is a multidimensional chromatography technique that employs a conventional length first column and a much shorter, 0.75 m second column. Because the stationary phases differ in polarity, separation is sufficient to provide visual images of homolog differences between the fresh and weathered samples. We deconvolved this data, produced by an Agilent quadrupole mass filter, and confirmed results by GC/MS. Based on these results, one can postulate as to which compounds are more likely to be lost during weathering from evaporation, dissolution and degradation. Discussion will center on the use of current forensic diagnostics in the context of understanding how samples weather in the environment.

FORE 7

Effects of Weathering on Aromatic Compounds in Beach Tars from the Deepwater Horizon Disaster, Gulf of Mexico Coast, USA

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Operators aboard the Deepwater Horizon drilling platform lost control of the Macondo No. 1 well about 90 km southwest of the Louisiana coast on April 20, 2010, leading to a catastrophic release of ca. 550 Gg of crude oil over the next 86 days [1]. Oil from the spill soon found its way to nearby coastal areas, leaving tarry deposits on beaches and marshes. Oil was reported on the beach at Gulf Shores, Alabama (180 km northeast of the well) on June 5 and the relatively fresh sample discussed herein (GSA) was collected that same day. Oil reached the beach at Grand Isle, Louisiana (180 km east of the well) by May 24, 2010 and the sample (GIL) was collected on Jan. 15, 2011, i.e., about six months after the flow of oil was staunched at the well site. These two tar samples were analyzed directly, without preparation or clean-up, using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) in order to evaluate the usefulness of this technique for rapid forensic characterization of beach tars at spill sites. In this case, the pyrolysis temperature of 610 °C primarily induced vaporization of compounds present with relatively minor formation of pyrolytic artifacts. The analyses revealed a complex suite of polycyclic aromatic compounds, along with acyclic alkanes and both saturate and aromatic biomarkers.
The total ion current trace of the fresher sample (GSA) exhibits a series of C_{16} - C_{32} n-alkanes above a pronounced hump due to an unresolved complex mixture (UCM) of hydrocarbons, whereas in the case of the more weathered sample (GIL), only the UCM is visible, indicating an advanced stage of biodegradation. Distributions of hopanes, tricyclic terpanes, and steranes in both samples show little evidence of degradation and correlate well, indicative of a common origin. The monoaromatic and triaromatic steroid distributions are also very similar in both samples. Differences are evident in the relative proportions of alkylated phenanthrene and dibenzothiophene isomer clusters, as well as in the proportions of individual isomers, particularly among the dimethyl. In contrast, the C0 – C3 alkylchrysenes display only minor differences between the two samples. Given that the biomarkers indicate that both samples are of about the same thermal maturity, the observed variations most likely arise due to differences in the severity of degradation. Such alterations must be considered when undertaking forensic evaluations of weathered oil. The Py-GC/MS technique appears to adequately resolve the essential similarities and differences between the two samples.

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FORE 8

Source Apportionment and Significance of PAH Associated with the Triassic-Jurassic Boundary Mass-extinction Event

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The leading "suspect" for the Triassic-Jurassic (T/J) boundary mass-extinction event, which occurred 200 million years ago, is the eruption of the Central Atlantic Magmatic Province (CAMP), triggering the release of large quantities of CO_2 and SO_2 to the atmosphere. In response, the T/J boundary marks a dramatic decline in forest vegetation and a change towards a pioneering, low-growing vegetation that was entirely composed of ferns and fern allies. The T/J boundary beds also contain elevated levels of high molecular-weight polycyclic aromatic hydrocarbons (PAH), such as coronene. Here, we present new high-resolution PAH quantification data from the recently drilled Schandelah-1 core and compare our data with those obtained from the nearby Mariental-1 core. We discuss two working-hypotheses for the source of the PAH: (1) Volcanic activity and thermal metamorphism of organic rich sediments. The PAH formed when ascending lava from the CAMP heated surrounding sediments, such as coal beds, releasing large quantities of additional carbon, sulfur, and other toxic compounds into the atmosphere. PAH thus can be used to fingerprint volcanic activity. (2) Widespread wild fires. The PAH may have been released through increased wild fire activity as a result of climate changes. Evidence for the latter hypothesis comes from abundant charcoal in some outcrops, although the exact relationships between charcoal and PAH abundance are not always obvious.

Poster

FORE 11

Tool Comparisons for the Sampling of Polycyclic Aromatic Hydrocarbons (PAH): Field Monitoring in Arcachon´s Bay

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Biomonitoring organisms have been used over the past few decades for surveying water quality, identifying pollution sources, as well as for monitoring the effectiveness of site remediation. However, bioaccumulation factors vary widely between species, and depend on environmental conditions and physiological characteristics of the species used. This variability in bioaccumulation factors induces uncertainty in the estimation of water concentrations based on the accumulated amounts of PAH in the organisms. In addition, biological species cannot be deployed in all environments, and some of them have the capacity to metabolize xenobiotics. For these reasons and many others, the use of passive sampling devices for the monitoring of hydrophobic chemicals has emerged, and many studies have reported the coupling of monitoring organisms and Semi Permeable Membrane Devices (SPMDs) for the sampling of PAH in the aqueous system.

In this study, the performances of three types of passive samplers (SPMDs, Polar Organic Chemical Integrative Samplers (POCIS), and adapted versions of POCIS) for the sampling of dissolved concentrations of PAH were evaluated through a field exposure in Arcachon´s Bay, a lagoon situated in the south west of France, on the Atlantic Ocean. Diploid and Triploid oysters were deployed in parallel to passive samplers in four sites, among which a harbor and pleasance harbors. Distribution profiles between passive and biological sampling were compared, and the interests and limits of the application of adapted versions of POCIS were also assessed.

FORE 12

PAH Source Assignment in Estuarine and Marine Sediments

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A number of diagnostic ratios have been applied as tools to distinguish provenance of hydrocarbons in sediments. In the present work the effectiveness of such ratios as source indicators under tropical conditions is evaluated using aliphatic and aromatic hydrocarbons determined in recent and historical sediments from some regions in Brazil. The study include samples of two heavily populated and industrialized bays, an oil spill contaminated mangrove and an uncontaminated oil basin in Brazil. In Todos Santos (NE Brazil - TSB) a Bay with 1000 km^2 of area, onshore oil exploration occurred in the past. Guanabara Bay (Rio de Janeiro, Brazil) with 340 km^2 of area houses the second major industrial complex in Brazil, and provides support for activities related to petroleum exploration, transport and processing.

We found that searching for source indications (petrogenic, pyrogenic, fuel or biomass combustion) is not trivial [1], especially under the high temperatures and microbiological activity in tropical marine environments. It turned out that substantive alteration of the original hydrocarbon composition often produced misleading results and that source evaluation in sediments required more complex approaches. Some diagnostic ratios, as the pyrolytic ratio [2] give reliable indications after an oil spill. Degradation of naphthalenes, dibenzothiophenes and fluorenes, however, change PAH source assignment.

In all investigated cases not related to spills, petrogenic source is rarely indicated by diagnostic ratios [3]. Environmental forensics requires broader approaches which will be discussed in the present work. Although a lesser fraction in oils, often so-called pyrolytic PAH which are persistent may derive from oil residues

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FORE 13

Assessment of Polycyclic Aromatic Hydrocarbons Contamination of Groundwater in El-Agamy District, West Alexandria, Egypt

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To assess the status of polycyclic aromatic hydrocarbon (PAH) contamination in the extent and nature of El-Agamy district groundwater, Alexandria, Egypt, sixteen collected groundwater samples from private wells which are currently or formerly used as drinking water supply, were investigated for PAHs with 2-6 benzene rings by gas chromatography-mass spectrometry (GC-MS). The analytical results of the groundwater samples pointed out to the continuous input of contaminants from sewage water of the septic tanks and from road runoff to uncovered wells. Total concentration of PAHs ranged from ND to 1880 µg/l with mean concentration 146.61 µg/L. The majority of the analyzed groundwater samples (88%) have exceeded the maximum permissible limit of PAH in drinking water. Most of the water samples have a high LMW/ HMW PAH and high percentage of 2-6 rings which indicating the petrogenic origin. The n-alkanes and PAHs in the study area are most likely of mixed sources. The resulted data will provide a foundation for a proper management strategy for pollution prevention and control of toxic contaminants that will lead to more effective reduction in risk and more efficient conservation for this valuable natural resource.

Atmospheric Reactions of PAC

Oral

ATMO 1

PAH Sources and Atmospheric Transport in China and the Western U.S.

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The objectives for this research were to 1) determine the significance of combustion source control measures in reducing PAH concentrations during the 2008 Beijing Olympics as a model for air pollution control in other Chinese megacities and 2) study the atmospheric transport of PAHs to remote sites in the Western U.S. and identify their regional and long-range sources. Size fractionated particulate matter (PM) samples were collected in Beijing before, during and after the 2008 Olympics, during both source control and non-source control periods, and analyzed for a wide range of PAHs, nitro-PAHs, oxy-PAHs, and high molecular weight (MW 302) PAHs. In addition, air samples were collected from three different remote sites in the Pacific Northwestern U.S. and analyzed for parent PAHs.
The lifetime excess cancer risk due to exposure to the carcinogenic PAHs was estimated to range from 6.5 to 518 per million people for the source control period concentrations and from 12.2 to 964 per million people for the non-source control period concentrations. This would correspond to a 46% reduction in inhalation cancer risk due to source control measures, if these measures were sustained over time. The total excess inhalation cancer risk would be underestimated by 23% if the 5 MW 302 PAHs were not included in the risk calculation.
The trans-Pacific and regional North American atmospheric transport of PAHs in biomass burning emissions were measured in air masses from April to September 2003 at two remote sites in western North America. During this time period, both remote sites were influenced by PAH emissions from forest fires in Siberia and regional fires in Oregon and Washington State. Concurrent samples were taken at both sites on June 2 and August 4, 2003. On these dates, one site had elevated gas phase PAH and retene concentrations ($p < 0.05$) and the other site had elevated retene and particulate phase PAH concentrations due to trans-Pacific transport of emissions from fires in Siberia. In addition, during the April to September 2003 sampling period, CPO and MPO were influenced by emissions from regional fires that resulted in elevated gas phase PAH concentrations. These data suggest that the trans-Pacific and regional atmospheric transport of biomass burning emissions results in elevated PAH concentrations in western North America.

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ATMO 2

Source Apportionment of Atmospheric Particulate PAH in French Rural Sites

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Polycyclic Aromatic Hydrocarbons are atmospheric pollutants mainly formed and emitted during combustion of organic matter. Studied for already quite some time, they are recently subject to European regulations in terms of air quality monitoring (EU Directives 96/62/EC and 2004/107/EC). Concentrations exceeding the regulatory target value (annual average concentration of 1 ng m^{-3} for BaP) are observed by the certified air-quality monitoring agencies in urban area or near industrial and vehicular traffic activities. However due to the development of new energy sources some rural sites can also be impacted by high PAH concentration. In addition specific meteorological conditions (e.g. temperature inversion layer) can lead to pollutant accumulation in atmosphere. In this context improving air quality requires method development of allowing to identify the influence of pollutant source on the PAH atmospheric levels.
As part of field campaigns conducted in several rural site (coastal, plain, valleys) the source apportionment of PAH was performed using some diagnostic ratio. The qualitative approach is based on the comparison of ambient data and source profiles and involves the construction of ratios of species concentrations (Robinson et al. E.S.T., 2006). In addition this approach allows the assessment of chemical stability and aging. For example plot of two particulate PAH ratios (benzo[*ghi*]perylene (BghiP) and indenopyrene (IP) normalized by elemental carbon (EC) concentration measured on atmospheric particles allows to identify the strong influence of biomass burning in winter. This study shows also the higher impact of vehicular emission in summer. Limitations of these methods based on diagnostic ratio and their potential use in discriminating PAH source will be also discussed

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ATMO 3

Source Apportionment of Polycyclic Aromatic Hydrocarbons Transported in Air over Central Europe

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For source apportionment of airborne polycyclic aromatic hydrocarbons (PAHs) two methods are commonly used, among others, i.e. so-called diagnostic ratios (DRs) of chosen pairs of individual PAHs (because of its simplicity) and positive matrix factorization (PMF), which makes use of a number of PAHs (fingerprint). Methods' application is limited due to overlapping DR ranges for various PAH source categories, difficulties in the allocation of factors obtained by PMF to source categories, inconsistent data published in the literature and degradation of PAHs during atmospheric transport. The latter can significantly alter the PAH fingerprint and result in the loss of source signature.

A critical study on both source apportionment methods applied on an extensive dataset of total PAH air concentration data measured at the Central European background site Košetice between 1996-2009 has been conducted. Reference PAH DRs and profiles were obtained from an extensive literature search on PAH emission factors relevant for Central European PAH sources as well as from ambient sampling conducted at sites with well known and significant local PAH sources in the Czech Republic, Serbia and Bosnia and Hercegovina. The influence of PAH degradation during transport in air on source apportionment was explored and accounted when using PMF.

Using DRs and the mass balance model some PAHs' ozone and OH radical reaction rate coefficients´ uncertainties could be narrowed down. The current knowledge on PAH reactivity in air, both in the gaseous and particulate phases, was found insufficient for DRs based source apportionment at receptor sites. Caution is recommended when using both methods for PAH source apportionment especially at background sites.

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ATMO 4

Source Apportionment of Particulate-PAHs Using ^{13}C Molecular Isotopic Approach

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Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous organic compounds widely found in all environmental compartments. The main concern of PAHs is that some of them are reported to have carcinogenic and mutagenic properties. In the atmosphere, they are mainly emitted as by-products of organic matter and fossil fuel incomplete combustion such as, domestic heating, automobile fuel combustion, wood burning and other industrial processes. Once released into the atmosphere, they are present on both gaseous and particulate phases and may be submitted to photodegradation and/or chemical oxidation by O_3, OH or NO_x.

In order to differentiate and apportion PAH sources, several approaches of source assessment are proposed in the literature like, for instance, the molecular PAH concentration ratios. Recently, the use of ^{13}C molecular isotopic composition has been developed to improve the molecular approach, commonly used to characterize atmospheric particulate-PAH sources. The first step of the method consists in measuring the ^{13}C/^{12}C isotopic composition of particulate PAHs from specific sampling sites (urban, rural, traffic), well characterized emissions (ship soot, kerosene burner, coal fly ash…) or reference materials (urban dust, diesel soot) . It is important, in a second step, to check the influence of atmospheric physico-chemical processes on the PAH isotopic composition values such as the heterogeneous reactivity with atmospheric oxidants, photolysis and particle transport.

In this work, will be presented and discussed the last results of our group on the use of molecular isotopic composition as an interesting source tracer of atmospheric particulate-PAHs, ^{13}C/^{12}C PAH ratios being measured by using gas chromatography/combustion/isotopic ratio mass spectrometry (GC/C/IRMS).

ATMO 5

High Resolution Investigations of Aromatic Compounds in Particulate Matter - Characterization and Source Apportionment by GC-APLI-UHR-TOF-MS

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Particulate matter (PM) is composed of primary particles that are directly emitted into the atmosphere by natural or anthropogenic sources, and by secondary particles that are produced in the atmosphere from volatile organic compounds and other precursors. Organic matter is a main fraction of atmospheric aerosols, contributing 10 - 70% to their mass. PM and the associated organic compounds including polycyclic aromatic compounds (PAC) are of great concern because of their health effects [1]. The main sources of PAC in the atmosphere are fossil fuel combustion, domestic heating, various industrial processes, incineration and energy production [2].
The aim of the study is an improved understanding of the environmental fate of PM associated PAC.
Commonly, analyses of PM associated PAC are performed by gas chromatography – mass spectrometry (GC-MS) [3, 4]. For increased PAC resolution in the complex matrix of PM and increased sensitivity, GCxGC-MS has been used [5, 6]. Here, for the first time, GC-atmospheric pressure laser ionization (APLI)-MS will be applied to PAC analysis of PM. APLI has been developed explicitly for aromatic compounds and is highly selective and sensitive for PAC (<amol, [7]).

In a first step, PM has been collected with a Berner type impactor (five grain size fractions) with a sample integration time of 24 hours. High sensitivity of the GC-APLI required a dilution of 1:100 of the extract. Results of first PM samples show significantly increased amounts of detected aromatic compounds compared to GC-MS analyses. The compounds will be identified by use of ultra high resolution time-of-flight (UHR-TOF-)MS.
In following steps, a new sampling strategy with one hour resolution can and will be used to receive more information about PAC patterns, sources, transport and fate.

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ATMO 6

Uptake and Photo-Oxidation of Fluorene at the Air/Water Interface

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Polycyclic aromatic hydrocarbons (PAH) are abundant pollutants of our combustion-driven society. They are well known due to their carcinogenic character and many of them can be found as pollutants in the atmosphere. Atmospheric PAH partition between particulate matter and the gas phase. PAH such as naphthalene, phenanthrene and fluorene are among the group of volatile PAH found in the gas phase. These volatile PAH have additionally the potential to accumulate at the air/water interface of atmospheric hydrometeors such as fog droplets or snow, finding ample surface area for adsorption.

To assess this adsorptive process at the air/water interface we investigate the uptake of fluorene onto thin water films of varying thickness in a thin-film reactor. By determining the adsorption at different temperatures, ranging from ambient to below freezing, we are able to determine the interfacial partition coefficient and its temperature dependence. The adsorption at the air/water interface is energetically favorable for PAH, and presents therefore a potentially different environment for their degradation than in the gas- or water phase.

Although PAH exhibit substantial chemical stability as aromatic compounds, they are nonetheless susceptible to photo-oxidation and therefore degradation in the atmosphere. Fluorene reacts in the presence of air under UV-B light to oxygenated compounds, namely 9-fluorenone, 9-fluorenol and 6H-benzo[*b,d*]pyran-6-ol. By following the kinetics of these reaction products in thin films of varying thickness, the contribution of the interfacial degradation can be assessed.

ATMO 7

Effect of NO$_2$ Concentration on the Nitro-PAH Yields and Isomer Distribution Patterns from the Gas-Phase OH Radical-Initiated Reactions of Selected Dimethyl- and Ethyl-Naphthalenes

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In urban areas, polycyclic aromatic hydrocarbons (PAHs) such as alkylnaphthalenes are emitted by vehicle exhaust and other sources of incomplete combustion. Dimethylnaphthalenes (DMNs) and ethylnaphthalenes (ENs) are found predominantly in the gas-phase and can undergo gas-phase reactions with OH radicals during daylight hours and with NO$_3$ radicals during evening and nighttime. The dominant atmospheric loss process for these compounds is the daytime OH radical reaction which proceeds by initial addition to the aromatic ring to form an OH-PAH adduct. This adduct can then react with either NO$_2$ or O$_2$ to form products including nitro-PAHs, which are considered potential human carcinogens.

Although the yields of nitro-PAHs formed from the gas-phase OH radical-initiated reactions of PAHs are relatively low, ambient measurements of nitro-PAHs have been made in both the gas and particle phase, and ambient daytime profiles of nitro-PAHs are often consistent with laboratory studies of OH + PAH conducted at high [NO$_2$]. This suggests that the OH-PAH adducts, at least in part, react with NO$_2$ in urban atmospheres. In this study, we measured the yield of dimethylnitronaphthalenes (DMNNs) from the OH radical-initiated reactions of 1,7- and 2,7- DMN over an [NO$_2$] range of 0.03-1.30 ppmV. The dominant nitro-isomers formed were 1,7-DM-5NN and 2,7-DM-4NN for the reactions of 1,7-, and 2,7-DMN with OH radicals, respectively. Yields at high [NO$_2$] were 0.26% and 0.011% for 1,7- and 2,7-DMNNs respectively, and our data suggests that the OH-DMN adducts react equally with NO$_2$ and O$_2$ at an [NO$_2$] of ~60-80 ppbV, which is typical of urban polluted atmospheres and similar to that reported for OH-naphthalene adducts [1].

We also examined isomer distributions of alkylnitronaphthalenes produced from the reaction of OH radicals with a mixture of ENs and DMNs as a function of [NO$_2$]. While slight variations in isomer distributions were observed as a result of decreasing [NO$_2$], 1,7-DM-5-NN was consistently the dominant isomer formed and the isomer distribution patterns were similar to those observed in ambient Mexico City samples.

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ATMO 8

Characterization and Mutagenicity Assessment of PM2.5 and PM10 PAH at Agra, India

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The average concentration of total concentrations of PAHs in $PM_{2.5}$ and PM_{10} were from 0.003 to 0.114 $\mu g\ m^{-3}$ (with a mean value of 0.035 $\mu g\ m^{-3}$) and from 0.022 to 0.251 $\mu g\ m^{-3}$ (with a mean value of 0.075 $\mu g\ m^{-3}$) respectively. $PM_{2.5}$ and PM_{10} contained mainly carcinogenic and mutagenic PAHs, among which Pyr, Chy, Phen were higher in $PM_{2.5}$ and BbF, Chy and Fla were in higher concentration in PM_{10}. Among the 16 PAH compounds estimated, the concentration of Chy (0.161 $\mu g\ m^{-3}$) was highest in case of PM10 followed by the concentration of Benzo (b) fluoranthene (0.161 $\mu g\ m^{-3}$). In $PM_{2.5}$, the highest concentration of PAH was found in Chy (0.078) followed by Pyr (0.075). DbA, BghiP, IP were absent both the $PM_{2.5}$ and $PM_{10.}$ The relative percentage of low molecular weight (LMW) PAH (Molecular weight 128 - 202) containing two to four ringed PAHs (Nap, Acy, Ace, Flu, Phen, Anth, Fla, Pyr) were higher (77%) in PM 2.5 than PM 10 (59%). High molecular weight (HMW) PAH (molecular weight 228 - 278) containing five to seven ringed PAHs (BaA, Chy, BbF, BkF, BaP, DbA, BghiP and IP) were higher in PM_{10} (41%). The *Salmonella* assay revealed the mutagenic properties of organic air pollutants adsorbed on suspended particles of PM_{10} and $PM_{2.5}$ fractions of the collected samples. Positive results were found for the standard compounds (sodium azide) while the negative controls showed insignificant growth of colonies. From the slope of the regression line, it is evident that all the samples are mutagenic without metabolic activation, proved that pollutants that are able to affect the genetic material directly (direct mutagens) were present in the samples tested. Particulate matter collected from the air pollution sources contains condensed organic matter that is extractable by organic solvents. A number of studies have shown that the organic extractable matter from air particles and different combustion sources are carcinogenic in animals and mutagenic in short-term bioassay tests .The number of spontaneous revertant colonies for both $PM_{2.5}$ and PM_{10} with both the strains TA 98 and TA 100 is given in Table below.

Table: Revertant colonies for both $PM_{2.5}$ and PM_{10} with both the strains TA 98 and TA 100

Concentration (µl)	Rev/plate TA 98 PM$_{2.5}$	Rev/plate TA 98 PM$_{10}$	Rev/Plate TA 100 PM$_{2.5}$	Rev/Plate TA 100 PM$_{10}$
10	25	19	59	20
20	31	23	63	60
30	49	40	68	85
40	80	67	90	113
50	99	75	148	125
60	114	82	160	133

Ames test indicated that both strains TA 98 and strain TA 100 showing a positive response both in $PM_{2.5}$ and PM_{10}, indicating the presence of both frame shift mutagens as well as mutagens capable of causing base pair substitutions.

Poster

ATMO 10

Innovative Analysis of Oxygenated PAH Derivatives on PM_{10} through Pressurized Solvent Extraction High Resolution Magnetic Sector Mass Spectrometry

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In the last years, particulate matter (PM) has become worldwide a major research issue receiving increasing attention because of its significant impact on human health. For example, in Flanders, it has been estimated that out of the five healthy living months that each inhabitant loses because of environmental pollution 71% is attributed to the inhalation of PM_{10} [1]. The mechanisms through which PM toxicity proceed are still a matter of discussion but there are major indications that next to the morphological characteristics of the particle, also the chemical composition plays an important role. Among the wide range of organic compounds that are associated with PM, the rather non-polar fraction has attracted most attention so far, with particular focus on polycyclic aromatic hydrocarbons (PAHs). Less focus is put on PAHs derivatives formed through atmospheric reactions with oxidative species as well as UV induced photoreactions. This contribution particularly deals with oxy-PAHs which deserve major attention since they can participate in redox cycles and generate reactive oxygen species in target cell populations. Attention will be paid to possible formation paths, analytical method development and ambient concentration levels. Nevertheless their importance, literature data on oxy-PAHs concentrations on ambient particulate matter are scarce, at least partially because of the limited availability of analytical methods [2].

A new high performance liquid chromatography - high resolution mass spectrometry based method is presented for the analysis of 11 three to five ring oxy-PAHs (including phenanthrene-9,10-dione and benzo[*a*]pyrenedione isomers) sorbed onto airborne particulate matter (PM_{10}). The use of accurate masses for selective and sensitive (oxy-) PAHs analysis is quite new and as far as we know magnetic sector mass spectrometry operated in multiple ion detection (MID) mode is not reported yet for the analysis of these compounds. The different steps in the analytical method were systematically evaluated including sample preparation, separation and detection steps.

For sample extraction, pressurized liquid extraction (PLE) was evaluated as an advanced sample extraction technique and was compared to the more frequently used ultrasonic extraction (UE). Ethyl acetate was proven to be a very good extraction solvent for the target analytes and both techniques showed high recoveries from spiked quartz fiber filters (PLE: >82%; USE: >67%). The effect of the matrix on both recovery and ionization process (enhancement or suppression) was systematically investigated resulting in high recoveries (>76%) and no significant disturbance of the ionization process. After optimization of the analytical method, method detection limits (MDL, S/N = 10) in the range from 1 to 160 pg/m³ were obtained.

Finally, the method was used for the analysis of real PM samples which were collected in both urban and rural locations in the Antwerp area, Belgium. Concentration levels (2 pg/m³ to 2 ng/m³) obtained were compared to other studies. Overall, a seasonal effect was observed with the median of the oxy-PAHs concentrations during winter being a factor of 3 to 4 higher than during summer. However, the oxy-PAH/parent PAH ratio is about 20 times higher during summer, indicating the importance of photochemical activity in the atmosphere.

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ATMO 11

Long-range Transport Potential of Polycyclic Aromatic Hydrocarbons in Air - Insights from Measurements from in Europe, Africa and Antarctica

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Despite the fact that the occurrence of PAHs in the atmospheric environment has been studied for decades the atmospheric chemistry, deposition processes and, consequently, the long-range transport potential are not well understood. The reason is partitioning between the gas and the aerosol particulate phase, its sensitivity to temperature, humidity and particulate phase composition, and sampling artefacts', wash-out efficiency's and reactivity's sensitivities towards particulate phase composition. Furthermore, most PAHs are subject to re-volatilisation upon deposition to soils (multihopping). Are remote environments contaminated by regional or intercontinental atmospheric transport of PAH?

Levels and sources of 16-25 2-6-ring unsubstituted PAHs were studied in remote environments, i.e. far from potential sources, based on air (active and passive) and snow sampling: Free tropospheric air which had not been within the continental planetary boundary layer for weeks was sampled at Zugspitze, Alps (2650 m a.s.l., 20007). Air which had no or hardly any contact to source areas was sampled on Mt. Kenya (3600 m a.s.l.), in the Sahel (Tombouctou, Mali) and the savannah (Molopo, Rep. of South Africa), 2008. Air transported over Antarctica in 2003-2005 was studied based on the analysis of a snow pit dug on the Ekström Shelf Ice in the Weddell Sea (70°44'S).

The investigation of gas-particle partitioning in a Mediterranean climate (near and in Banya Luka, Bosnia and Hercegovina, 2008) suggested doubling of the particulate mass fraction of semivolatile PAHs per 13 K temperature decrease. Another process must be significant for phase partitioning, less temperature sensitive than adsorption, most likely absorption into organic matter and/or sorption to black carbon.

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ATMO 12

Concentration, Photochemistry and Mutagenicity of PAHs During the Beijing Olympic Games

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During the 2008 Beijing Olympics, the Chinese government implemented intensive regional source reduction measures to improve air quality in Beijing. In general, the source control measures were aimed at reducing air pollution emissions such as, SO_2, NO_x and atmospheric particulate matter (PM). A wide range of combustion sources, including vehicles, trucks, factories, and coal combustion for power generation, were controlled leading up to the Olympics, with the most stringent combustion source control measures occurring during the Olympic period (August 8-24, 2008) [1]. The control measures period extended after the Olympic period to September 20 but the source control measures were less strictly implemented [2]. PM samples (aerodynamic diameter <2.5 μm) were collected in Beijing for a 2 week period prior to the Olympics, during the Olympics and a 4 week period following the Olympics [3] and analyzed for black carbon (BC), organic carbon (OC), lower molecular weight (MW <300) and higher MW (MW 302) Polycyclic Aromatic Hydrocarbons (PAHs), nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs). In addition, the direct and indirect acting mutagenicity of the crude $PM_{2.5}$ extracts were measured.
Significant reductions in BC (45%), OC (31%), MW < 300 PAH (26% - 73%), MW 302 PAH (22% - 77%), NPAH (15% - 68%) and OPAH (25% - 53%) concentrations were measured during the source control and Olympic periods. The PAH, NPAH, and OPAH composition of the PM2.5 was similar throughout the study, suggesting similar sources during the different periods. During the source control period, the parent PAH concentrations were correlated with NO, CO, and SO_2 concentrations, indicating that these PAHs were associated with both local and regional emissions. However, the NPAH and OPAH concentrations were only correlated with the NO concentrations, indicating that the NPAH and OPAH were primarily associated with local emissions. The relatively high 2-nitrofluoranthene/1-nitropyrene ratio (25 - 46) and 2-nitrofluoranthene/2-nitropyrene ratio (3.4 - 4.8), suggested a predominance of photochemical formation of NPAHs through OH-radical-initiated reactions in the atmosphere. On average, the ∑NPAH and ∑OPAH concentrations were 8% of the parent PAH concentrations, while the direct-acting mutagenicity (due to the NPAH and OPAH) was 200% higher than the indirect-acting mutagenicity (due to the PAH). This suggests that NPAH and OPAH make up a significant portion of the overall mutagenicity of $PM_{2.5}$ in Beijing.

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ATMO 13

Heterogeneous Reactions of O_3, OH Radicals and N_2O_5 with Chinese Particulate Matter to Simulate Trans-Pacific Atmospheric Transport

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In the atmosphere, polycyclic aromatic hydrocarbons (PAHs) partition between the gas and particulate phases depending on their chemical and physical properties and ambient temperature. In general, PAHs with more than four aromatic rings are found primarily in the particulate phase, allowing them to undergo long range atmospheric transport. The reactivity of particulate-bound PAHs is considered to vary, to some extent, with the composition of particle [1]. Previous heterogeneous reaction studies on particulate matter (PM) have used graphite, diesel soot, wood smoke and in-house soot samples [2-4]. However, in this study, PM from Beijing, China, with an aerodynamic diameter < 10 μm, was exposed to O_3, OH radicals, and N_2O_5 to simulate heterogeneous reactions that may occur during trans-Pacific transport. The PM samples were collected on pre-baked quartz fiber filters over 24 h periods at an urban site in Beijing, China. The filters were cut into two portions. The first portion was quantitatively analyzed for PAHs, nitrated-PAHs (NPAHs) and oxygenated-PAHs (OPAHs) and represented the unreacted masses. The second portion was placed in a ~7000-L indoor all-Teflon chamber and exposed to either O_3, OH radicals, or N_2O_5. The concentrations of O_3, OH radicals, and N_2O_5 used in chamber experiments, combined with the duration of the exposures, simulated trans-Pacific atmospheric transport of the PM [5]. The quantitative analysis of both the unreacted and reacted portions of the filter was done using gas chromatography coupled with mass spectrometry, with electron ionization for PAHs and negative chemical ionization mode for NPAHs and OPAHs.

The reaction of PAHs on PM with O_3 resulted in a 16% - 48% loss in parent PAH concentrations. As expected, no significant NPAH products were observed in the O_3 reaction.

For the OH-radical exposure, the parent PAH masses on PM decreased by 1% to 42%. Only 1-nitropyrene and 6-nitrobenzo[a]pyrene concentrations were found to increase significantly, while 9-nitroanthracene and 7-nitrobenzo[a]anthracene masses were found to decrease significantly upon exposure.

The N_2O_5 was the most effective oxidant in transforming the particulate-bound PAHs, reducing the masses by 5% to 57%. Of the parent PAHs, benzo[a]pyrene showed the largest percent decrease in concentration on the PM. The concentrations of 1-nitropyrene, 1-nitrotriphenylene, 6-nitrochrysene, 2-nitrotriphenylene and 6-nitrobenzo[a]pyrene increased significantly, while the concentration of 9-nitroanthracene decreased significantly. For all three exposures, there was no observed increase in the concentrations of 2-nitropyrene and 2-nitrofluoranthene, two nitro-PAHs formed via gas-phase radical-initiated reactions, suggesting that the increase in other nitro-PAHs was due to the occurrence of heterogeneous reactions of PAHs with gas-phase species. Overall, these exposures simulating trans-Pacific transport did not significantly change the NPAH profile.

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ATMO 14

Atmospheric Formation of Hydroxynitrofluoranthene from a Photochemical Reaction of Particle-Associated 2-Nitrofluoranthene

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Nitrated polycyclic aromatic hydrocarbons (NPAHs) are a class of mutagens/carcinogens found in the atmosphere, and some of them exhibit stronger mutagenicity/carcinogenicity than their parent PAHs. 1-Nitropyrene (1-NP) is a representative NPAH formed through combustion processes of fossil fuel such as diesel fuel combustion. On the contrary, 2-nitrofluoranthene (2-NF), generally the most abundant NPAH in the atmosphere, is believed to be the product of the atmospheric reactions of parent fluoranthene in the presence of nitrogen oxides, especially those initiated by OH radicals or NO_3 radicals. Recently, we found that 1-NP is easily transformed to hydroxynitropyrenes (OHNPs) by UV irradiation, and that five isomers of OHNP (1-hydroxy-x-nitropyrenes (1-OH-x-NPs); x = 2, 3, 5, 6, and 8) existed in ambient airborne particles [1]. The mutagenicity of OHNPs was investigated by several groups, and they concluded that most of OHNP isomers showed lower activity than the parent 1-NP. However, we have found that OHNPs act as endocrine disruptors which may cause dysfunction of human and wildlife endocrine systems, abnormalities associated with the developing reproductive systems, and deficiencies of immune systems [2,3]. Thus, to clarify the environmental concentration level, sources and behavior of hydroxylated NPAH is urgently required from a human health point of view. In this study, therefore, we demonstrated the formation of hydroxynitrofluoranthene (OHNF) via a photochemical reaction of 2-NF, one of the most abundant NPAHs, using a UV irradiation system. Moreover, we detected an OHNF isomer in soluble organic fractions of ambient airborne particles collected in Kanazawa, Japan. The atmospheric concentration of the OHNF isomer was estimated to be less than 2 fmol/m^3, which was comparable to that of 1-OH-3-NP, but lower than that of 1-OH-6-NP by factor of 10.

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ATMO 16

Gas-phase and Heterogeneous Reaction Chemistry of PAHs in the Atmosphere and the Formation of Oxy- and Nitro- Derivatives: A Review

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The presence of oxy- and nitro-PAH compounds in the ambient atmosphere has been widely reported for over 20 years. These compounds are of interest as they have the potential to be more toxic than their parent PAH due to direct acting mutagenicity in the case of nitro-PAH, or the formation of reactive oxygen species in the case of oxy-PAH. Furthermore, as well as being emitted from anthropogenic combustion sources such as vehicular exhausts, industrial activities and agricultural burning, these compounds have been shown to be formed via atmospheric reactions of PAH compounds with oxidative species such as OH and NO_3 radicals, NO_x and O_3. This combined input of direct emissions and reaction products presents a degree of uncertainty regarding the relative contribution of primary and secondary sources of oxy- and nitro-PAH compounds to the observed atmospheric burden. It is therefore important to have a good understanding of the nature and extent of the atmospheric reactions that produce these compounds. This paper closely examines the research that has been conducted regarding the reaction chemistry of these processes, compiling and reviewing the current literature investigating the reaction kinetics (rate order constants, product yields, reaction mechanisms and specific isometric products) involved in the atmospheric conversion of PAH compounds to oxy- and nitro-derivatives. A significant amount of research has been carried out in this field, both for reactions of PAH in the free gas-phase and heterogeneous reactions of PAH associated with organic and inorganic particle surfaces. However, this research has not been subject to scientific review for over 15 years. Here we present an overview of the key findings from the suite of data derived from laboratory experiments simulating atmospheric conditions both for gas-phase and heterogeneous PAH reactions. Additionally, an assessment of some of the key factors (e.g. PAH molecular structure, PAH concentration, oxidant type, reactant concentration, particle type, surface coating etc) that influence the extent and nature of these reactions is also made and the importance of these factors is discussed.

ATMO 18

Atmospheric Occurrence of Particle-Associated Nitrotriphenylenes via Gas-phase Radical-initiated Reactions in Southern Osaka, Japan

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Diurnal concentrations of nitrotriphenylenes (NTPs) and selected nitro polycyclic aromatic hydrocarbons (NPAHs) in airborne particles collected at Osaka, Japan were monitored with high time resolution. The variation in concentration of 1-nitropyrene (1-NP) was accompanied with that of NO_x (NO and NO_2) and CO, i.e. their concentrations were high early in the morning and late in the evening. This result indicates that the occurrence of 1-NP was significantly affected by the primary emission, especially the automotive emission. On the contrary, the concentrations of 2-nitrofluoranthene (2-NF) and 2-nitrotriphenylene (2-NTP) increased in the nighttime, suggesting that neither 2-NF nor 2-NTP was emitted from primary sources, but formed by atmospheric nitration of the parent fluoranthene and triphenylene (TP). Rate constants of gas-phase reactions of TP with OH and NO_3 radicals were predicted using a relative-rate method in CCl_4 liquid phase-system which was previously reported [1]. Based on the ambient concentration of 2-NTP and the obtained rate constant for the reaction of TP with the radicals, the atmospheric loss rate of 2-NTP relative to 2-NF was successfully determined. Mutagenicity of soluble organic fractions of airborne particles elevated in the nighttime, when anthropogenic activities were expected to be low, and this period was consistent with the period of time when 2-NF and 2-NTP concentrations were the highest. NPAHs formed via the atmospheric reactions may significantly contribute to the ambient mutagenicity.

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ATMO 19

Particulate Nitro/oxy-PAHs Size Distribution and PAHs on Sampling Degradation in Two Sites Around Paris

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Polycyclic aromatic hydrocarbons (PAHs) are emitted both in gas and particulate phases during incomplete combustions. Due to the mutagenicity and carcinogenicity of some of them, their monitoring is of prime interest. Particularly for the Benzo[*a*]pyren (B[*a*]P) which is commonly used as a tracer for this compounds family due to his high toxicity. B[*a*]P, which is present at 90% in particulate phase (<$PM_{2.5}$) can react with many gaseous oxidants such as ozone, nitrogen dioxide [1] to form nitrated and oxygenated derivatives which are also associated mostly with ultrafine particles. This reactivity leads to quantification problems [2]. Indeed results obtained do not reflect the real B[*a*]P air concentration.

These reactions may occur before the sampling (in the air) or during the sampling (on the filter). The aim of this study, based on chamber and field experiments, is to identify the major degradation place, oxidants responsible of these degradations and products formed, in order to propose solutions to quantify correctly B[*a*]P.

Several field campaigns were carried out. One of these was conducted in the south-west of Paris as part of the European MEGAPOLI project; another was realized in a traffic site. Two types of instruments were used:

- Two high volume samplers: one equipped with a conventional PM_{10} head, and the other with a specific PM_{10} head with a MnO_2 denuder system (Megatec Digitel DA-80, 30m3/h, 12 h sampling);
- The other sampler was a 12-stage Micro Orifice Uniform Deposit Impactor (MOUDI, 1,8m3/h, 24 h sampling).

Filters obtained with high volume samplers were used to evaluate the on-filter degradation of PAHs during sampling. To do so, PAHs, oxy-PAHs and nitro-PAHs were quantified. Results obtained show differences between the two sampling systems (with and without denuder) for several compounds and the comparison with other physical and chemical data obtained during the field campaign should give valuable information about the most significant factors responsible of these differences.

Moreover, using the MOUDI, a size distribution of particulate nitro- and oxy-PAHs will be obtained. Thanks to these results, information about the primary or secondary origin of these derivatives will be available.

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ATMO 20

Computational Study of the Thermodynamics of Atmospheric Nitration of PAHs via OH-Radical-Initiated Reaction

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Nitrated polycyclic aromatic hydrocarbons (NPAHs) are an important class of PAH derivatives that are more toxic than their parent PAHs [1] and are emitted from direct emission and secondary emission to the atmosphere. The secondary emissions, particularly the OH-radical initiated and NO_3-radical-initiated reactions, have been shown to influence the NPAH concentrations in the atmosphere. Gas-phase reactions are thought to be the major sources of NPAHs containing four or fewer rings [2]. Besides NPAHs, PAHs lead to a number of other products including oxygenated, hydroxy substituted and ring-opened PAH derivatives [3]. For some PAHs, the OH-initiated and NO_3-initiated reactions result in the formation of different NPAH isomers, allowing the ratio of these isomers to be used in the determination of direct or secondary emission sources.

Previous studies have shown that the PAH gas-phase reactions with OH radical is initiated by the addition of OH radical to the aromatic ring to form hydroxycyclohexadienyl radicals [4]. In the presence of NO_2, these reactive intermediates readily nitrate with the elimination of water [4]. The hydroxycyclohexadienyl-type radical intermediates are also prone to react with other species in the atmosphere or revert back to the original compound [3].

The objective of this study was to investigate the thermodynamics of PAH nitration through day-time OH-radical-initiated reactions. The theoretical investigation were carried out using Density Functional Theory (B3LYP) and the 6-31G(d) basis set, as implemented in Gaussian03. A number of different PAHs were studied including fluoranthene, pyrene, as well as the molecular weight 302 PAHs such as dibenzo[*a,l*]pyrene. Computations were compared to previous studies and also used to predict unknown NPAHs formed by OH-radical-initiated reaction. All intermediates for the OH-radical addition and the following nitration were computed. We have discovered that the thermodynamic stability of the intermediates involved in the PAH oxygenation and nitration pathways are critical in explaining the atmospheric abundances of NPAHs. Specifically, we have found that the experimentally most abundant species had the most stable intermediates. Interestingly, the overall free energy of reaction was not a factor in determining the relative abundances of NPAHs.

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ATMO 21

Effect of Salinity and pH on the Kinetics of the Photo-Oxidation of Benzene with Hydrogen Peroxide

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Hydroxyl radicals are one of the most dominant oxidative species in the atmosphere, reacting even with stable aromatic compounds. Hydroxyl radicals can be produced by the dissociation of hydrogen peroxide in the presence of UV-B light. Correspondingly, benzene serves as a model aromatic compound due to its basic aromatic structure, and its oxidative products, phenol and biphenyl, are straightforward to follow. The oxidation pathway of benzene to phenol has been studied extensively, but less consideration has been given to the alternative pathway of benzene to biphenyl.

The photo-oxidation of benzene in the presence of hydrogen peroxide is monitored in a bulk phase reactor containing a UV-B lamp, maintained at room temperature. Salinity and pH are varied in order to represent the typical environmental conditions near the shoreline, and in particular, to pinpoint their effect on the formation of biphenyl, which has been studied to a lesser extent. It should be noted that Skudaev et al. [1] observed that chlorine is formed in a system in the presence of UV light containing concentrated hydrogen peroxide and concentrated hydrochloric acid, but this system is not representative of the natural environment. Nevertheless, the formation of biphenyl and potentially polychlorinated biphenyls is tested under these adverse conditions and extended to the less extreme environmental conditions to monitor the product formation trend.

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ATMO 22

PAH and Oxy-PAH Processing during a Fog Event

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Polycyclic aromatic hydrocarbons (PAH) are an abundant group of significant organic pollutants in the atmosphere. PAH can react with reactive atmospheric species in the environment to yield oxygenated polycyclic aromatic compounds (OPAC). This PAH transformation is strongly dependent on atmospheric conditions and events such as rain, snow, fog, etc. Especially fog, with its abundance of air/water surface, can provide a very unique setting for the transformation of PAH. Hence, it is of interest to study the processing of PAH and OPAC during a fog event, by investigating their population on various atmospheric species such as the fog water, the gas phase, and particulate matter ($PM_{2.5}$ and PM_{10}) present during a fog event.
Two field campaigns were conducted in the central valley of California in order to study the processing of PAH and OPAC during a fog event.
The first campaign was conducted in January 2010 at Fresno, capturing two major fog events, while the second campaign was conducted in January 2011 at Davis, where a total of five fog events were sampled. Different atmospheric matter, such as fog water, gas phase, and particulates were sampled in three to four hours time intervals during a fog event, and in six to eight hours time intervals before and after a fog event. All samples were extracted with dichloromethane and analyzed with a gas chromatograph coupled to a mass spectrometric detector in single-ion monitoring mode. The analysis focused on the 16 PAH, defined by US EPA as priority pollutants and 18 OPAC, including several of the known oxidation products of these PAH. The evaluation of the concentrations of these PAH and OPAC in the sampled atmospheric matter before, after, and during the fog events provides substantial information on the fate of polycyclic aromatic compounds during a fog event.

PAC in Food

Oral

FOOD 1

Clean-up Strategy for the Analysis of PAH in Food of Animal Origin

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Polycyclic aromatic hydrocarbons (PAHs) are well-known environmental contaminants and 15 of which exert both genotoxic and carcinogenic properties. These compounds can be found in food at residue levels, result of a contaminated environment or the type of food processing applied such as smoking or roasting. In addition, Butler et al. has demonstrated that food is the major exposition route of the general population to benzo[a]pyrene (B[a]P). To protect human health, many competent Authorities has established maximum residue levels in food. In Europe, a MRL is fixed for B[a]P, considered as a marker for PAH contamination, and in 2012 the legislation will concern 3 more PAH: benzo[*a*]anthracene B(a)A, benzo[*b*]fluoranthene (B[b]F) and Chrysene (Chr). Therefore, food samples will have to be analysed to demonstrate compliance with these limits.

The analysis of PAH has been mostly focussed on environmental matrices and little is published about food. In 2008, Windal et al. reported a method for the analysis of the 16 European polycyclic aromatic hydrocarbons (PAHs) in vegetable oils and plant extract using a donor acceptor complex chromatography (DACC). This DACC clean-up is highly specific to PAHs and was then, tested for different type of food matrices. The applicability of this technique to all food matrices was hampered by some co-extracts not separated by the column and interfering with the fluorescence detection of the PAHs.

This research deals with the evaluation of different type of clean-up addition to the DACC to enable easy determination of the 16 PAHs. All the tests were performed with fish oil because this matrix, one of the most difficult food matrixes, displayed after DACC clean-up many interferences.

First, we compared the GPC (Gel Permeation Chromatography) on a polymeric phase to the DACC clean-up. In terms of the solvent consumption and clean-up efficiency, DACC demonstrated better performances and was therefore kept in the protocol. Then, different types of SPE were tested as a post DACC clean-up step. Phenyl and C18 cartridges were used as chemical filters: the DACC Acetonitrile eluate was directly loaded. In the opposite, normal phase such as silica and SupelMIP® required a solvent exchange prior to loading.

We will show that chemical filters are not efficient for the removal of interferences. For the normal phase SPE cartridges, the SupelMIP® gave better results than silica.

All SPE options could not eliminate early eluting interferences which hamper the determination of benzo[*c*]fluorene (B[c]F). However, in the elution range of the 4 PAHs under legislation in the next future, several co-eluting interferences have been efficiently removed.

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FOOD 2

Analysis of PAH in Food - Meeting the Prospective Requirements

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Polycyclic aromatic hydrocarbons (PAH) constitute a large group of more than several hundred chemical compounds, many of them known to be carcinogenic and genotoxic. Food could be naturally contaminated with PAHs either by uptake from the environment or during processing procedures such as frying, drying, smoking, grilling or roasting where PAHs are generated at significant levels [1,2,3].
In 2008, the EFSA published an opinion where they concluded that benzo[*a*]pyrene, until now the only regulated one in food, is not a suitable indicator for the occurrence of carcinogenic PAH in food. In addition, the sum of four PAH is proposed in order to better protect consumer health. In 2012, an amendment of the European Regulation 1881/2006 is anticipated towards the four PAH benzo[*a*]pyrene, chrysene, benzo[*b*]fluoranthene and benz[*a*]anthracene[4,5].
The accurate quantification of PAHs in food with GC-MS requires special attention for both separation on the stationary phase and differentiation by mass ions. Different stationary phases, an unpolar Agilent J&W HP-5ms (5% phenyl/ 95% dimethylpolysiloxane phase), a mid polar Agilent J&W VF-17ms (50% phenyl/ 50% dimethylpolysiloxane phase) and an Agilent J&W Select PAH were evaluated for the accurate analysis of the 15 + 1 EU priority PAHs in food with a special focus on critical pairs such as chrysene/ triphenylene and the three benzo[*b/j/k*]fluoranthenes. Influence of the column choice on the accurate quantification is discussed for examples from different kind of food matrices [6,7,8].
Furthermore, the hitherto applied method using a classical GPC clean-up was improved. The developed automated Online-SPE-GC-MS method enables the analysis of PAH in food in a significant reduced analysis time and no manual handling between clean-up and measurement without loosing robustness and accuracy. Method performance criteria are presented as well as advantages and disadvantages of the different clean-up procedures.

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FOOD 3

Applicability of Different GC-Columns in the Analysis of the "PAH4" in Meat Products

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Polycyclic aromatic hydrocarbons (PAHs) are common contaminants in several kinds of food. Spices, tea leaves, and cocoa beans are often contaminated by the drying process (e.g. over open fire or dispersed over a tarred ground). Smoking and barbecuing of meat products is another important source for PAHs in food. Currently, in the European Union, only maximum levels for benzo[*a*]pyrene (BaP) exist in accordance with Section 6 of the Annex to Regulation (EC) No 1881/2006 for several foodstuffs (e.g. edible oils and fats, smoked products, bivalve mollusks, baby food etc.). For smoked meats and meat products the maximum level of BaP is 5.0 μg/kg wet weight. The European Food Safety Authority (EFSA) argued for a more suitable marker for PAH contamination in food on 9 June 2008. Two options were discussed: "PAH4" (BaP, benzo[*a*]anthracene, chrysene and benzo[*b*]fluoranthene) and "PAH8" (PAH4 + benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene, dibenzo[*a,h*]anthracene, and indeno[1,2,3-*c,d*]pyrene). As "PAH8" does not provide much more information about the level of contamination in food than "PAH4", the European Commission works on an amendment to Regulation (EC) No 1881/2006, which will include new maximum levels for BaP and "PAH4". Consequently, a reliable analytical method for "PAH4" is required.
HPLC coupled with FL detection is commonly used for PAH analysis. The main disadvantage of this method is the non-applicability of 2H or 13C labeled internal standards, which behave nearly the same as the native analytes during sample preparation. For the isotopic dilution analysis, a mass selective detector is needed, usually coupled with gas chromatography (GC). Often, capillary columns with non -polar phases like 5% phenyl / 95% methyl polysiloxane and related materials are used, however, the separation of some substances belonging to the"PAH4"group is not possible. Chrysene (CHR) co-elutes on most phases with triphenylene (TP), which is not included in the "PAH4". Wrong positive results of chrysene may cause unjustified legal consequences for the food producer. CHR was classified by the IARC in group 2B as "possibly carcinogenic to humans" whereas TP was "not classifiable as to its carcinogenicity to humans" (group 3)[2].
JIRA et al.[1] developed a method for separating CHR and TP with a highly arylene modified phenyl-arylene polymer column. This method is not suitable for routine analysis due to very long retention times (> 67 min). The investigation of 25 smoked meat products showed different ratios of TP/CHR (0.12 - 2.70), demonstrating the need for a faster separation of these critical components. Another problem is the separation of benzo[*b*]fluoranthene from the benzo[*j+k*]fluoranthenes.
At the MRI, several capillary columns with different dimensions and mid-polar phases were tested to find a fast, reliable, and cost-efficient method to analyze the "PAH4" in smoked and barbecued meat products, e.g. silarylene phases, equivalent to 50% phenyl / 50% dimethylarylenepolysiloxane or to 50% phenyl / 50% methylpolysiloxane. The smoked samples were produced within the FEI research project AiF 16460 N.

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FOOD 4

PAH in Barbecued Meat from Restaurants and by Home-Grilling in Denmark

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Barbecuing or grilling is known to result in the formation of polycyclic aromatic hydrocarbons (PAH). Thirty home-grilled meat samples (beef, pork and chicken) and 86 commercial grilled meat samples (beef, pork, chicken, salmon, lamb and calf) were analyzed for 23 PAH including PAH 4 (benzo[a]pyrene (BaP), benzo[*a*]anthracene, benzo[*b*]fluoranthene and chrysene). PAHs were extracted by Pressurized Liquid Extraction followed by clean-up by GPC (Bio Beads, S-X3) and SPE (500mg, Silica) and finally analyzed by GC-MS. Home-grilled beef were found to contain highest concentrations of BaP (up to 24 µg/kg) whereas commercially barbecued hamburgers were found to contain BaP up to 13.7 µg/kg. Chicken was found to contain the lowest BaP concentrations (0-0.1µg/kg). The highest concentration of BaP for chicken was 3.1 µg/kg detected in a commercially barbecued marinated chicken with skin. The sum of PAH 4 ranged from below the detection limit to the highest concentration for a home-grilled beef (64 µg/kg).
Worst case estimates revealed a margin of exposure (MOE) of approximately 18,000 for both BaP and the sum of PAH 4 for grilled meat only. The European Food Safety Authority (EFSA) has previously recommended that care should be taken due to high risk by intake for MOE < 10,000.

FOOD 5

Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Food with GC-MS/MS

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Polycyclic Aromatic Hydrocarbons (PAH) comprise of a large group of chemical compounds known to be cancer-causing agents. Humans are exposed to PAH by various pathways. The major route of exposure is the consumption of food. Food can be contaminated from environmental sources, industrial food processing especially by smoking processes of fish or meat and from domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling [1]. The European Commission Regulation (EC) No 1881/2006 sets maximum levels for benzo[*a*]pyrene in different food groups. So far, it was assumed that benzo[a]pyrene is a good marker for the "total-PAH content". In 2008, the European Food Safety Authority (EFSA) published an opinion on suitable indicators for the occurrence and toxicity of PAH in food. The EFSA´s CONTAM Panel concluded that benzo(a)pyrene is not a good marker for the occurrence of PAH in food. Instead the sum of four PAH (PAH4) (benzo[*a*]pyrene, chrysene, benz[*a*]anthracene and benzo[*b*]fluoranthene) or eight PAH (PAH8) (benzo[*a*]pyrene , benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, chrysene, dibenz[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene) PAH are considered to be the most suitable indicators of PAHs in food1. Benzo[*a*]pyrene is the only PAH presently regulated in food in the EU, but it is intended to set harmonized maximum levels for PAH4 in addition to benzo[a]pyren. The Commission Regulation (EC) No 333/2007 lays down sampling methods and performance criteria for methods of analysis for the official control of benzo[*a*]pyrene levels in food. In this Regulation the minimum limit of detection (LOD) for benzo[*a*]pyren is specified at a level of 0.30 µg/kg in food. To reach this low concentration generally a meticulous clean-up of the samples is mandatory. Different clean up steps are mentioned after a fat extraction for example: liquid/liquid-extraction after an acid/basic treatment, different chromatographic columns like silica gel or florisil, a size exclusion chromatography or solid phase extraction (SPE) columns with different phases. A special SPE phase is the MIP-SPE column. Molecularly imprinted polymers (MIPs) are a class of highly cross-linked polymer-based molecular recognition elements engineered to bind a target compound or a class of structurally related target compounds with high selectivity. After sample clean up the measurement on HPLC coupled with a fluorescence detector (HPLC/FLD) or GC coupled with a mass spectrometry detector (GC-MS) are generally used. For GC analysis it is important to separate critical pairs such as chrysene/triphenylene and the benzo[*b/k/j*]fluoranthenes. Selective GC phases like "Varian Select PAH" are available for this separation. Normally a single quadrupole mass detection system is used for the PAH quantification. To reach lower LOD and more selectivity, a GC-triple quadruple mass spectrometer (GC-MS/MS) system was used for the detection. However the PAH are very stable and are hardly fragmented by nitrogen as a collision gas even at a high collision energy. Instead the matrix is mainly destroyed in the collision cell. The MRM traces for each PAH are the molecule ion itself. Through this operation, LOD lower than 0.02 µg/kg were reached which is a magnitude lower than with a single quadrupole and without changing the sample preparation and the sample concentration.

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FOOD 6

Preparation of Test Material and Evaluation of a Pproficiency Test for Official Food Control Laboratories on the Determination of PAH in Baby Food

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In the context of our tasks as National Reference Laboratory for Polycyclic Aromatic Hydrocarbons, a proficiency test on the determination of PAH in baby food was organised in 2010. Official food control laboratories in Germany and also in Austria were invited to participate in the test. The test material was produced at the NRL. Certain amounts of PAH were added to a blank matrix, which had been obtained by mixing commercially available products of cereal-based instant baby food. To a total batch of approx. 4 kg of blank matrix, 16 PAH (15 PAH according to Recommendation 2005/108/EC [1] plus benzo[*c*]fluorene) were added, resulting in concentration levels between 0.6 and 3.5 µg/kg. Homogenisation was achieved by tumbling the mixture in a stainless steel barrel. The material was divided into subsamples of 20 g. 12 test portions for homogeneity testing were chosen at random and a certain number of test portions was set apart for continuous stability testing. For all tests necessary to characterise the material, the analytical method validated at the National Reference Laboratory for PAH was used. In brief, this method comprises pressurised liquid extraction, clean-up with SPE on a polymeric sorbent and determination with GC-MS.
Homogeneity was tested according to the procedures laid down in DIN/ISO 13528 and the "International Harmonized Protocol" [2,3]. Presuming a target standard deviation of 22%, the sufficient homogeneity of the test material could be verified by both approaches and for all 16 analytes. The results of stability testing confirmed that no special precautions were necessary when handling the material.
Sample dispatch for the proficiency test took place in September 2010, and the participants were asked to present their data within a timeframe of five weeks. In total, 21 laboratories submitted results for the proficiency test. All laboratories except one analysed at least for benzo[*a*]pyrene (BaP), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF) and chrysene (CHR) (group "PAH4"). The laboratories were free to use their method of choice, but method details had to be reported, showing a preference of HPLC-fluorescence to GC-MS-based detection.
The evaluation of the test was done applying methods of robust statistics as described in standard DIN 13528 A 45 [4]. The individual performance was assessed with the help of z-scores. As to the quantitative results, the dispersion of data for the PAH4 group appeared to be acceptable, with a relative robust standard deviation ranging from 13.2% for BbF to 26.7% for BaA. In total, the performance of one laboratory had to be rated as unsatisfactory because of a result for BaP outside the limits of tolerance. The methods applied in the test may be considered to be comparable, as no significant effects in the distribution of data could be attributed to certain analytical procedures.

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[4] DIN 38402 A 45: Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: Allgemeine Angaben (Gruppe A) Teil 45: Ringversuche zur externen Qualitätskontrolle von Laboratorien

FOOD 7

Sweets for My Sweets, PAHs for My Honey ....

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Upcoming EU legislation introduces maximum levels for PAHs in cocoa butter products. The maximum level for benzo[*a*]pyrene is set to 5 µg/kg fat and a maximum content of 30 µg/kg will be tolerated for the sum of the future four EU marker PAHs.

The implementation of this piece of legislation will provide some difficulties due to the complexity of the chocolate matrix. It contains a large number of fluorescent substances, which hampers especially the analysis based on HPLC with fluorescence detection (FLD). Hence selectivity becomes an issue. This presentation reports on the development of an analysis method based on liquid chromatography hyphenated to atmospheric pressure photo ionisation tandem mass spectrometry (LC-APPI-MS/MS) for the determination of EU marker PAHs in plain chocolate. In-house method validation revealed depending of the analyte repeatability relative standard deviations of about 4.0 % to 7.0 % and intermediate precision relative standard deviations between 4.3 % and 8.5 % respectively. The expanded measurement uncertainty of the determination of benzo[*a*]pyrene by this method was below 15.0 %. Trueness of the results was evaluated by applying certified reference material and a suitable proficiency test material. In addition to method validation data issues such as stability of the ion source will be discussed.

The method, which has proven suitable for the monitoring of PAH contents of chocolate, was applied for the analysis of about 200 chocolate samples collected in different EU countries. The analysis results revealed that the vast majority of chocolate samples complied with the new maximum levels.

Sweets for My Sweets, PAHs for My Honey ....

Poster

FOOD 10

Quantification of Polycyclic Aromatic Hydrocarbons in Meat Samples

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Polycyclic aromatic hydrocarbons (PAHs) are the products of pyrolysis or incomplete combustion of organic material at high temperature. PAHs are introduced into the environment from both natural and anthropogenic sources, but anthropogenic sources have been introduced as the major source for distribution of these compounds into the environment and food. Anthropogenic sources including; vehicle exhaust emissions from gasoline and diesel engines, waste incineration, wood and coal combustion, and coke production industries are well known for releasing if PAHs into the environment and causing subsequent pollution for water and soils and foods. Food can be contaminated by PAHs that are present in air, soil or water or are formed during processing (during drying or smoking) and cooking (during grilling, roasting or frying).
In this work, different methods (Soxhlet, Sonication, Micro Waive, and Solid-Phase Extraction) were used for separation, clean up, and pre-concentration of PAHs. The recovery of PAHs from methods was studied and then used for pre-concentration of PAHs. The samples of beef and chicken meat pieces were chopped into small uniform size pieces were collected from the markets located in different areas of Tehran (Iran).
The determinations were carried on an Agilent HPLC equipped with a fluorescence detector and an UV detector. The amount of PAHs formed during cooking or processing of meats was studied. Principle component analysis (PCA), as a fast and efficient method for evaluating the effect of temperature in PAHs, is proposed.

FOOD 11

Method for the Determination of PAH at Low Levels in Baby Food by GC-MS - Results of a Validation Study

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In the European Union, Regulation (EC) No 1881/2006 [1] currently undergoes an update and new maximum limits for polycyclic aromatic hydrocarbons will apply from 1 January 2012. For food intended for infants and young children, the Regulation foresees a maximum limit of 1.0 µg/kg benzo[*a*]pyrene as before, but also a maximum limit of 1.0 µg/kg for the sum (referred to as "PAH4") of benzo[*a*]pyrene (BaP), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF) and chrysene (CHR). Analytical methods used for official food control have to meet at least the criteria for BaP laid down in Regulation (EC) No 333/2007 [2]. However, lower limits of quantification are highly favourable when analysing baby food. The analytical method established and validated at the National Reference Laboratory (NRL) for PAH consists of three basic steps: (1) pressurised liquid extraction (PLE) with cyclohexane and silica added to the extraction cell; (2) clean-up with SPE on a polymeric sorbent; (3) determination by GC-MS with isotopically labelled standards. The method was validated according to the matrix-comprehensive alternative approach laid down in Commission Decision 2002/657 [3]. This approach is not obligatory when analysing for contaminants, but covers the requirements of Regulation No 333/2007. Eight different products of commercially available instant baby food of different brands and different composition (fat content) were included in the study to account for variations of the matrix. During the validation study, certain experimental conditions were varied systematically (two operators, conditions of PLE, different lots of SPE sorbent, different instruments). The validated range covers a concentration interval of 0.4 to 2.0 µg/kg for each analyte (i.e. approx. half to double the maximum limit of BaP). The dispersion of results appears to be acceptable with a within-laboratory reproducibility of 6 - 7% for BaA, BaP and BbF and 10% for CHR at concentration levels of 0.8 µg/kg. The method appeared to be robust against variations of the experimental conditions and no significant interferences of matrix components occurred.
The limits of detection (LOD) and limits of quantification (LOQ) were determined as foreseen in Regulation (EC) No 333/2007 (calculated from the standard deviation of the mean of blank determinations); the LOQ was below 0.25 µg/kg for all analytes of the PAH4 group. In addition to the validation, the performance of the method was verified by participation in two international laboratory intercomparison studies (proficiency tests). The evaluation of these studies on the basis of z-scores points to a minor laboratory bias: in one test a z-score of -0.36 and in the second test a z-score of -0.51 were the most deviating results for the four key analytes. In the context of our tasks as NRL, the analytical method presented here was applied to characterise a test material intended for use in a proficiency test with respect to homogeneity and stability. The outcome of this proficiency test will be presented in a separate contribution.

[1] Commission Regulation (EC) No 1881/2006, OJ L 364, 20.12.2006, p. 5-24
[2] Commission Regulation (EC) No 333/2007, OJ L 88, 29.03.2007, p. 29-38
[3] Commission Decision 2002/657/EC, OJ L 221, 17.8.2002, p. 8-36

FOOD 12

PAHs in Grilled Hamburgers Sampled in Sweden 2008-2011.

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Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of three or more condensed aromatic rings. PAHs are formed during incomplete combustion processes. Food can be contaminated from environmental sources, industrial food processing and during home food preparation.

As PAHs represents an important class of carcinogens their presence in food should be as low as possible. Maximum levels of benzo[*a*]pyrene (BaP) in a range of foodstuffs are specified in a Commission Regulation (EC No 1881/2006). For smoked meat and smoked meat products the maximum level is 5.0 µg/kg. High levels of PAHs can be found in some types of heat treated meat (grilling, barbecuing) if not appropriate processing conditions and equipments are used. Heat treated meat and heat treated meat products are not covered by existing regulation. Work is ongoing to set new maximum levels for BaP alone as well as to include the sum PAH 4 (benzo[*a*]antracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene and chrysene). Heat treated meat and heat treated meat products are proposed to be included in the regulation from September 1 2012 with maximum level 5.0 µg/kg for BaP and 30.0 µg/kg for PAH 4.

A survey in Sweden of grilled and fried hamburgers was performed in 2008. Minced hamburgers (meat only) were spiked with perdeuterated PAHs as internal standards and saponificated in methanolic KOH solution at 70°C. Extracted with cyclohexane and washed several times with a mixture of methanol and water. Cleaned-up on two sets of SPE columns and injected in an Agilent 6890 gas chromatograph connected to an Agilent 5975 mass selective detector. A 30m DB-35ms fused silica column was used for separation. The analytical method (1) complies with the criteria for official control of BaP according to Commission Regulation (EC) No 333/2007. High levels of BaP up to 16.6 µg/kg were found from one fast food restaurant using electric grilling of hamburgers. Level of BaP was well above maximum level in Commission Regulation for smoked meat products. The high PAH levels probably depends on pyrolysis of fat dripping down on the electric heater. Fast food restaurants selling fried hamburgers showed very low levels of BaP. Follow up samples in 2011 from the fast food restaurant showed that the level of PAHs are now much lower and comply with proposed regulation for heat treated meat products. Grilled hamburgers are consumed more regularly than most other categories of food currently represented in regulation. It´s important that consumers who eat at fast food restaurants regularly should be protected by a maximum level of PAHs in the same way as consumers of smoked meat products.

[1] S. Wretling, A. Eriksson, G.A. Eskhult, B. Larsson. Polycyclic aromatic hydrocarbons (PAHs) in Swedish smoked meat and fish. Journal of Food Composition and Analysis 23 (2010) 264-272.

FOOD 13

Low Levels of PAHs in the Swedish Diet

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Polycyclic aromatic hydrocarbons (PAHs) representing an important class of carcinogens and their presence in food should be as low as possible. Food can be contaminated from environmental sources, industrial food processing and during home food preparation.

Maximum levels of benzo[*a*]pyrene (BaP) in a range of foodstuffs are specified in a Commission Regulation (EC No 1881/2006). Work is currently ongoing to set new maximum levels for BaP alone as well as to include the sum PAH 4 (benzo[*a*]antracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF) and chrysene (CHR)). National Food Administration in Sweden has since 1999 analyzed organic pollutants and nutrients in market baskets. Food is a significant source of PAHs to which humans are exposed so when a new survey started in 2010 analysis of PAHs was included for the first time. The proportion of the different foodstuffs in the market basket was based on purchase statistics and divided into twelve food groups. Samples were representative of about 90% of a total dietary intake of an average Swedish consumer. Food samples, in total around 150, were purchased in May and September 2010 at five supermarket chains in the city of Uppsala. Samples were immediately homogenized and stored in freezer until analyzed.

Composite samples from the twelve food groups were spiked with perdeuterated PAHs as internal standards and saponificated in methanolic KOH solution at 70 °C. Extracted with cyclohexane and washed several times with a mixture of methanol and water. Cleaned-up on two sets of SPE columns and injected in an Agilent 6890 gas chromatograph connected to an Agilent 5975 mass selective detector. A 30m DB-35ms fused silica column was used for separation. The analytical method [1] complies with the criteria for official control of BaP according to Commission Regulation (EC) No 333/2007.

In this presentation we show some of our data of PAH levels in food market baskets. PAH values for 25 PAHs were obtained. The levels of BaP, BaA, BbF, CHR and the sum of PAH 4 will be presented for the twelve food groups and compared against corresponding food groups sampled in 1999. The samples from 1999 had been stored at -70°C and were analyzed together with samples from 2010. Based on the calculated PAH levels the daily intake for the Swedish consumer is very low.

[1] S. Wretling, A. Eriksson, G.A. Eskhult, B. Larsson. Polycyclic aromatic hydrocarbons (PAHs) in Swedish smoked meat and fish. Journal of Food Composition and Analysis 23 (2010) 264-272.

FOOD 14

Lowering of PAH Levels in Smoked Meat Using a Cellulosic Covering

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Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of three or more condensed aromatic rings. PAHs are formed during incomplete combustion processes. Food can be contaminated from environmental sources, industrial food processing and during home food preparation.
As PAHs represents an important class of carcinogens their presence in food should be as low as possible. Maximum levels of benzo[*a*]pyrene (BaP) in a range of foodstuffs are specified in a Commission Regulation (EC No 1881/2006). For smoked meat and smoked meat products the maximum level is 5.0µg/kg. Work is ongoing to set new maximum levels for BaP alone as well as to include the sum PAH 4 (benzo[*a*]antracene, benzo(a)pyrene, benzo[*b*]fluoranthene and chrysene). A two step procedure is foreseen for smoked meat products. From September 1 2012 the maximum levels are proposed to be included in the regulation with maximum level 5.0 µg/kg for BaP and 30.0 µg/kg for PAH 4, and then from January 1 2014 lowered to 2.0 µg/kg for BaP and 12.0 µg/kg for PAH 4.
Yearly official control programme of BaP levels in Swedish foods including smoked meat have been carried out since 2006. The analytical method [1] used complies with the criteria for official control of BaP according to Commission Regulation (EC) No 333/2007. Minced meat was spiked with perdeuterated PAHs as internal standards and saponificated in methanolic KOH solution at 70°C. Extracted with cyclohexane and washed several times with a mixture of methanol and water. Cleaned-up on two sets of SPE columns and injected in an Agilent 6890 gas chromatograph connected to an Agilent 5975 mass selective detector. A 30m DB-35ms fused silica column was used for separation.
High levels of BaP were found in meat products produced by traditional "sauna" smoking, where the food is directly exposed to hot smoke from a burning log fire. It is well known that PAHs occur in curing smoke and can deposit on the surface of, and migrate into the meat being smoked. Level of BaP was well above maximum level in Commission Regulation for smoked meat products and the new maximum levels will be very difficult to comply with. Traditional "sauna" smoked products are marked as special delicacies with accentuation on the traditional handicraft production methods employed and on their local origin. The smoke-houses in Sweden differ in size and equipment and it is not possible to make general statements on exact measures needed to lower the concentrations of PAHs in the products. A possible way to lower the PAH levels and comply with proposed maximum levels in smoked meat will be presented. Cellulosic covering on the meat during smoking results in a product that smells and taste as without covering, but color and surface will be different and not easy accepted by the consumer.

[1] S. Wretling, A. Eriksson, G.A. Eskhult, B. Larsson. Polycyclic aromatic hydrocarbons (PAHs) in Swedish smoked meat and fish. Journal of Food Composition and Analysis 23 (2010) 264-272.

FOOD 15

Feed Ingredients Mainly Contributing to Polycyclic Aromatic Hydrocarbon and Polychlorinated Biphenyl Residues

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Animal nutrition constitutes an important issue for the animal production industry. Products intended for animal feed may contain undesirable substances which could endanger animal health or, because of their presence in livestock products, human health or the environment [1]. In this sense, several incidents related with the presence of persistent organic pollutants, particularly with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), have happen in food and feed additives [2]. Simple, fast, quantitative and economic methods for determinig PAHs and PCBs in potentially polluting feed ingredients were developed and evaluated by constructing calibration curves, measurement of recovery and precision, and the limits of detection. The methods involved liquid-liquid extraction (LLE), clean-up and detection by liquid chromatography with fluorescence detection (LC-FD) for PAHs and gas chromatography (GC) coupled to electron capture detection (ECD) for PCBs, using tandem mass spectrometry (MS/MS) as confirmatory technique. The overall method quantification limits range from 0.020 to 4.0 µg/Kg for PAHs and from 0.20 to 0.75 µg/Kg for PCBs, analyte recoveries are between 70 and 105% with relative standard deviations (RSD) lower than 20%.
Once the method was optimized, it was applied to 26 feed ingredients. As expected, the samples of animal origin as shell powder and fish oil showed the highest PCBs concentrations of 56 and 29 ng/g, which are equivalent to toxicological concentrations of 123 and 18 ng WHO-TEQDL-PCBs/Kg, respectively. Nevertheless the highest B[a]P levels (8.9 and 8.2 µg/Kg) were detected in additives (calcium phosphate) and fibre foods (alfalfa). Principal component (PC) and discriminant analysis were used to find the pattern pollution of the selected contaminants in feed ingredients.

[1] Ábalos, M., Parera, J., Abad, E., Rivera, J. (2008). PCDD/Fs and DL-PCBs in feeding fats obtained as co-products or by-products derived from the food chain. Chemosphere, 71, 1115-1126.
[2] Llerena, J.J., Abad, E., Caixach, J., Rivera, J. (2003). An episode of dioxine contamination in feeding stuff: the choline chloride case. Chemosphere, 53, 679-683.

FOOD 16

Bees, Honey and Pollen as Sentinels for Environmental PAH Contaminants ?

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Assessment of environmental health may be investigated with sentinel species. Honeybees are in particular commonly presented as a good sentinel for monitoring the environmental pollution due to their biological characteristic. Three beehive matrices (honey, bees and pollen), sampled from six different apiaries from West France, were analysed for the presence of 19 polycyclic aromatic hydrocarbons, with a special attention to the "PAH4" indicator (PAH4 representing the sum of the concentrations of benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthène and chrysene). Analysis were performed using liquid/liquid extraction or pressurized-liquid extraction (depending of the matrix), followed by a purification on a solid phase extraction on a copolymeric stationnary phase, and subsequent GC-MS/MS measurement. Quantification was performed by isotopic dilution approach (use of ^{13}C-internal standard), with two specific diagnostic signals monitored for each target compound.
Samples were collected from four different periods during two beekeeping seasons (2008 and 2009). Honey samples presented the lowest measured PAH concentration levels (min = 0,03 µg kg^{-1}; max = 5,80 µg kg^{-1}; mean = 0.82 µg kg^{-1}). Bee samples presented higher levels of PAH4 contamination (min= 0,32 µg kg^{-1}; max = 73,83 µg kg^{-1}; mean = 7,03 µg kg^{-1}). A wide dispersion of the observed values was however noticed in bees, that have been related to the existence of four main episodes of high concentrations. The analysis of pollen samples revealed the existence of only one major episode with also highly variable PAH4 concentration levels (min = 0,33 µg kg^{-1}; max = 129,41 µg kg^{-1}; mean = 7,10 µg kg^{-1}).
Our study demonstrates that PAH4 concentrations are significantly influenced by the landscape context for all beehive samples. Bees seems to be the best beehive matrix for monitoring environmental PAHs contamination. In the future, it would be particularly informative to analyse samples collected from urban apiaries, PAH contamination increasing with anthropogenic activities.

[1] Veyrand, B., Brosseaud, A., Sarcher, L., Varlet, V., Monteau, F., Marchand, P., Andre, F., Le Bizec, B. "Innovative method for determination of 19 polycyclic aromatic hydrocarbons in food and oil samples using gas chromatography coupled to tandem mass spectrometry based on an isotope dilution approach". J. Chrom. A 1149 (2007), 333-344

FOOD 17

Feeds Based on Constituents and their Corresponding Footprints of Residual Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls

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Food safety is central to any society, having important economic, social and environmental implications. International comparisons have shown that the European Union is the world´s largest producer of food and drink products [1]. It is not surprising therefore that the Agro-food sector has major importance/influence on the economy of Europe. The first link in the agro-food chain is animal feed, and therefore the risks associated to them, as is the case of the distribution of carcinogenic polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), are of paramount importance [2]. Simple, fast, quantitative and economic methods for PAHs and PCBs potentially polluting feeds were developed. The methods were evaluated by constructing calibration curves, measurement of recovery and precision, and the limits of detection. The methods involved liquid-liquid extraction (LLE), clean-up and detection by liquid chromatography with fluorescence detection (LC-FD) for PAHs and gas chromatography (GC) coupled to electron capture detection (ECD) for PCBs, using tandem mass spectrometry (MS/MS) as confirmatory technique. The overall method quantification limits range from 0.020 to 4.0 µg/Kg for PAHs and from 0.11 and 0.30 µg/Kg for PCBs, analyte recoveries are between 70 and 105% with relative standard deviations (RSD) lower than 20%. Based on the results, most of the target PAHs and PCBs were detected in the selected feed samples. Only maximum levels of dioxin-like PCBs (DL-PCBs) in animal feed are to be found in Commission Directive 2006/13/EC of 3 February 2006 amending Annexes I and II to Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal. For B[a]P only is regulated their presence by oils and fats, muscle meat of fish and processed cereal-based foods [3]. The highest B[a]P values were detected in fibre feeds unlike PCBs that were mainly detected in feeds from animal origin. Molecular patterns of PAHs were used to study their distribution in the selected samples by cluster analysis, separating them in two groups: contaminated by atmospheric or pyrolytic sources. The complete data set of 27 feed samples x 10 PAH and 14 PCB concentrations were analyzed by Principal Component Analysis (PCA) to find out what feeds were controlling PAH and PCB contamination.

[1] http://ec.europa.eu/enterprise/sectors/index_en.htm
[2] denHartog, J. (2003). Feed for food: HACCP in the animal feed industry. Food Control, 14, 95-99.
[3] Commission Regulation (EU) No. 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

FOOD 18

The Effect of the Smoking Technique on the Polycyclic Aromatic Hydrocarbons in Rainbow Trout

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Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants formed primarily by incomplete combustion in food processing methods such as drying, grilling, smoking and roasting, resulting in food contamination.
In this study, PAHs were determined in warm smoked and cold smoked rainbow trouts. The aims were i) to compare the effect of the smoking technique on PAH concentrations (traditional wood chip smoke and liquid smoke) and ii) to compare the distribution of PAHs in different edible parts of rainbow trouts (fillets, pieces, skin). To accomplish these tasks, 40 warm smoked and 10 cold smoked rainbow trout samples representing both smoking techniques were taken at the chosen smoke house. The samples collected included both fillets and pieces with skin in which the skin was removed and analysed separately.
The determination of PAHs was conducted by using an ISO 17025 accredited method. In brief, the extraction of PAHs was performed by pressurised liquid extraction (PLE) to remove fat and other interferences. An additional purification step (SPE) was needed before the final detection and quantification of the analytes by gas chromatography-tandem mass spectrometry (GC-MS/MS). The target analytes of the study included 15+1 EU PAH with special attention to PAH4 compounds.
Our preliminary results for the warm smoked rainbow trout indicate that the liquid smoking technique generates less PAH4 compounds than traditional wood chip smoking technique, as expected. There are no remarkable differences in the distribution of PAH4 compounds in fillets and pieces whereas in the skin the concentrations are noticeable higher. Our preliminary results for the cold smoked rainbow trouts show lower PAH4 concentrations compared to warm smoked samples. The comparison between liquid smoke and traditional wood chip smoke indicates the liquid smoking technique generating less PAH4 compounds in cold smoked rainbow trouts.
Based in our results it seems like the effect of the liquid smoking technique on PAH concentrations is to generate lower PAH4 concentrations both for warm and cold smoked rainbow trouts. A full report of PAH concentrations in warm and cold smoked rainbow trouts as well as their distribution in fillets, fish pieces and skin will be addressed and discussed in the poster presentation.

PAC and Fuels

Oral

FUEL 1

The Identification of Five-Ring PAH Products of the Supercritical Pyrolysis of *n*-Decane and Implications for PAH Formation in this Reaction Environment

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The fuels used in the next generation of high-speed aircraft will have to operate under very high pressures (beyond the critical pressures of most hydrocarbons) and will have to sustain very high heat loads in order to meet aircraft cooling requirements. Critical to the development of the fuel systems in these aircraft is an understanding of the fuel pyrolysis reaction mechanisms under the conditions that the fuels will be operating. Of particular interest are the reactions leading to polycyclic aromatic hydrocarbons (PAH), which can serve as precursors to fuel-line solid deposits, a problem of critical importance to avoid, for safe aircraft operation.

Alkane components of jet fuels have proven to be particularly prone to solids production, so in order to better understand the reactions responsible for PAH and solids formation from alkanes, we have conducted supercritical pyrolysis experiments with the model fuel *n*-decane (critical temperature, 345 °C; critical pressure, 20.8 atm) at temperatures up to 570 °C, pressures up to 100 atm, and a fixed residence time of 140 sec. The highly alkylated PAH products from these experiments have been fractionated according to ring number by normal-phase high-pressure liquid chromatography (HPLC), and the fractions have each been analyzed by reversed-phase HPLC. This fractionation/analysis technique has led to the identification of over 60 unsubstituted PAH, along with 270 alkylated derivatives of these PAH, among the products of supercritical *n*-decane pyrolysis. The present work focuses on three families of five-ring PAH products - seven unsubstituted $C_{20}H_{12}$ PAH and their alkylated derivatives, five unsubstituted $C_{21}H_{14}$ PAH, and six unsubstituted $C_{22}H_{14}$ PAH and their alkylated derivatives - many of which have never before been identified as products of *n*-decane. These PAH belong to the same isomer families as five-ring PAH products of supercritical 1-methylnaphthalene pyrolysis and/or supercritical toluene pyrolysis and therefore provide insight into the reaction mechanisms at work in the supercritical *n*-decane pyrolysis environment.

FUEL 2

Benzocarbazoles: An Ancillary Tool in Migration Assessment of Saudi Arabian Carbonate Oil Fields

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Generally, oil is expelled from the source rock kitchen and migrates laterally and vertically to structural or stratigraphic traps where it accumulates over geologic times. Tracking the route in which petroleum has migrated can lead to the discovery of additional reserves along the migration pathway. A great deal of migration modeling is routinely accomplished with simulation software packages based on several geological considerations, including the location of the source rock kitchens and traps. Modeling efforts should always be constrained by, or checked against real field data. Geochemical approaches that can potentially provide indications on migration directions and distances have been investigated for many years. One of these approaches is the use of naturally occurring functional organic molecules (geotracers) in crude oil to track migration pathways. The benzocarbazole ratio (benzo[a]carbazole/ benzo[c]carbazole (BCR)), for example, has been suggested as one of the potentially useful migration parameters (e.g., [1]) that continue to be examined in different geological sittings and petroleum systems. In this study we are assessing the use of these "odometers" in a fully carbonate source-carrier-reservoir petroleum setting in Saudi Arabia.

The analytical challenge lies initially in the separation and quantification of benzocarbazoles in oils of low carbazole concentrations, such as the subject crude oils. We have, therefore, adopted a selective sample preparation method for the isolation of nitrogen heterocycles, viz. solid phase extraction and high performance liquid chromatography, prior to the analysis of carbazole derivatives by gas chromatography-mass spectrometry. The BCR in this petroleum system shows a systematic decrease over a migration route exceeding 200 km laterally and 5 km vertically. Although the ratio might be complicated by maturity variations along the presumed migration pathway, it provides a circumstantial evidence of long-range migration of oil from a distant source rock kitchen. It is believed that during migration, the rod-shaped benzo[a]carbazole is selectively adsorbed onto the solid phase of the carrier beds compared to the sub-spherical benzo[c]carbazole, resulting in geochromatography (or preferential fractionation) of the two isomers. The presentation will discuss the absolute and relative concentration of carbazole isomers and their application in this petroleum system.

[1] Larter, S.R., Bowler, B., Li, M., et al.: "Benzocarbazoles as Molecular Indicators of Secondary Oil Migration Distance," Nature, Vol. 383, 1996, pp. 593-597.

FUEL 3

HPLC/UV/MS Analysis of Polycyclic Aromatic Compounds in Extracts of Wood Soot from Henan, China

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Polycyclic aromatic compounds (PAC) are an important class of environmental pollutants formed during the incomplete combustion of organic fuels. These compounds are ubiquitous in the environment, and some have been found to be mutagenic and/or carcinogenic. High rates of esophageal cancer in the Henan Province of China have led to the suspicion that PAC from domestic coal and wood combustion are a potential cause. To investigate the viability of this hypothesis, soot samples from wood-burning homes in Henan Province, China, have been collected and extracted with dichloromethane, and the solutions have been concentrated in a Kuderna-Danish apparatus. Analyses of the concentrated wood-soot extracts by high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection and mass spectrometric (MS) detection have led to the identification of 78 aromatic products. The PAC components have been unequivocally identified by matching their UV absorbance spectra with those of authentic reference standards or with those published in the literature. In cases where different solvents are involved, MS data are utilized and appropriate solvatochromic corrections are applied. Extract components for which reference standards and published UV spectra are not available have been identified from the components´ UV and mass spectra, in conjunction with the application of Clar´s annellation theory. The PAC identified in the wood-soot extracts range in size from 2 to 11 aromatic rings and constitute several structural classes: oxygen-containing aromatics, bi-aryls, benzenoid polycyclic aromatic hydrocarbons (PAH), fluoranthene benzologues, indene benzologues, cyclopenta-fused PAH, ethynyl-substituted PAH, and alkylated PAH,. Many of the identified PAH are 5- and 6-ring PAH (e.g., $C_{24}H_{14}$ PAH) that are known to be potent mutagens and/or carcinogens. This finding suggests that PAC could be a contributing factor in the high rate of esophageal cancer in Henan Province. The HPLC/UV/MS evidence supporting the component identifications will be presented.

FUEL 4

Aqueous and Nonaqueous Capillary Electrophoresis Coupled to TOF-MS for the Analysis of Polycyclic Aromatic Sulfur Heterocycles in Diesel Fuels

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Polycyclic Aromatic Sulfur Heterocycles (PASHs) are a class of compounds which are found in fossil fuels and refined petroleum based products. Because of the limited separation efficiency of HPLC and problems with volatility while separating high molecular PASHs with GC, capillary electrophoresis was investigated as an alternative. Coupled to a time-of-flight mass spectrometer for detection, it was identified as a highly efficient method to separate this class of compounds.

The neutral PASHs are converted to ions, needed for capillary zone electrophoresis, through S-methylation. Standard PASHs that are expected to be present in industrially desulfurized fuels were successfully analyzed on the CE-TOF-MS instrument with both aqueous and nonaqueous electrolyte systems.

The practicability of this method with respect to real world samples is demonstrated by analyzing the PASH fractions of desulfurized diesel fuels. The compounds are isolated from the fossil fuels by ligand exchange chromatography on a Pd(II) containing phase and, after methylation, separated and identified using CE-TOF-MS.

FUEL 5

Characterization of Deactivating Species of Zeolite Catalysts

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The species responsible for the deactivation of zeolite catalysts may be very diverse: organic or inorganic, simple or very complex, present as impurities in the feed of the reactor or formed during reaction, etc. As a consequence of this diversity, these species may deactivate the catalytically active sites in different ways: By competing with reactant molecules for chemisorptions on these sites, by reacting with them, by sterically blocking their access, etc. [1]. Obviously, the first step to understand and prevent the negative effect of these species is to determine their main characteristics, i.e. amount, elemental composition, distribution in size and in chemical nature, location, etc.

An important remark is that in most zeolite-catalysed processes, carbonaceous deposits, generally denomined as "coke", are the main species responsible for deactivation [2-4]. Typically, "coke" consists of polyaromatic molecules. The formation of carbonaceous compounds is primarily a chemical process: "coke" must be a stable reaction product under the operating conditions. Generally, this process is very complex involving various successive steps. Among these steps, the intramolecular condensation reactions play a key role. These reactions, which are exothermic, are often reversible under the operating conditions; hence the concentration of the condensation products is limited by thermodynamic equilibrium. However, these condensation products generally undergo almost irreversible secondary reactions. Thus, "coke" molecules formed during the catalytic transformation of hydrocarbons are often very stable polyaromatic compounds, which in addition to condensation reactions, require for their formation stabilization reactions: dehydrogenation or hydrogen transfer reactions, etc; [1]. Another essential particularly of "coke" is the requirement to be non-desorbed, which means that the formation of "coke" molecules requires not only chemical steps, but also their retention within the pores or the outer surface of the catalyst [1]. The retention of "coke" molecules may be due (i) to their steric blockage (trapping) within the micropores, (ii) to their strong chemisorptions generally on the active sites often coupled with confinement effects and (iii) to their low volatility (gas-phase reaction). These three possibilities can occur independently or in association. In both aspects of "coke" formation, chemical process and retention, the characteristics of the catalyst-reaction system couple play a decisive role. Thus, the composition, location of "coke" and rate of formation are determined by:

- The features of the reaction system: type and rate of the desired and secondary transformations, size and shape of reactant and product molecules, operating conditions, characteristics of the reactor.
- The features of the catalyst nature, concentration, strength and location of the active sites, size and shape of pores and opening.

Some examples concerning the formation and the nature of coke deposited over zeolites as the function of pore structure, temperature and nature of the reactants will be presented. Furthermore, the deactivating effect of the coke molecules formed from the cracking of n-heptane over various zeolites will be shown and discussed.

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FUEL 6

Studying Effects of Hydrotreatment on PAC Compositions in Refinery Streams using GCxGC-FID/SCD and GCxGC-ToFMS

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Hydrotreatment using adequate or tailor made catalysts is a vital process in most refinery operations performed to improve product quality and meet environmental specifications. Such operations in-clude hydrodenitrogenation (HDN), hydrodesulphurisation (HDS), hydrodearomatisation (HDA), hydrocracking (HYC) etc., and depending on the catalyst(s) in use and processing conditions the feed oil undergoes various compositional changes. Unravelling compositional changes on a molecular level during processing is important for 1) evaluating and understanding and 2) improving the effect and efficiency of the applied catalyst(s). In this study we have utilised the increased resolution and peak capacity of GCxGC equipped with FID/SCD or ToF-MS detectors to monitor PAC compositional changes in various refinery streams (middle and heavy distillates) experienced during hydrotreating processes. We shall present examples on the kinetics of dibenzothiophenes removal and their conversion to biphenyls and cyclohexylbenzenes (HDS), the partly saturation of tri- and tetraaromatics to corresponding naphthenoaromatics (HDA) and the build-up of HPNAs in unconverted oil during full HYC conversion.

FUEL 7

Polycyclic Aromatic Hydrocarbons as Models for Asphaltenes

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The increasing demand for fuels derived from petroleum and the dwindling supply of light crudes has raised the pressure on upgrading non-conventional sources of this important raw material. Many of the problems in its production, transport and conversion are attributed to asphaltenes, defined by their solubility class and corresponding to complex mixtures containing, mainly high molecular weight polyaromatic hydrocarbons (PAHs), naphthyl rings, aliphatic side chains, and heteroatoms (N, S, O). Although the structure of isolated asphaltenes is not known, there are reports in the literature based on powder X-ray diffraction that indicate interlayer distances of 3.5 to 3.7 Å [1]. Thus, a convenient approach to investigate the physic-chemical behavior of the structures in this mixture is to study PAHs that represent these properties as asphaltene models.

PAH molecules can associate in three distinct orientations: face-face (FF), face-tail (FT) and tail-tail (TT). In general, the FF orientation is considered the most stable owing to π-π; overlap between molecules. However, in the case of PAHs made up of few aromatic rings FF and FT orientations can be equally favorable, since the energy barriers for interconversion are low [2-4] and there are crystals containing several layers of PAHs in FT orientation [5-8]. Little is known about how these layers form clusters, the shape of these clusters and how many layers they are made up of.

The objective of this work is to understand how these structures are arranged geometrically and how a solvent affects the association/dissociation process. Associations among PAHs to form dimers were studied by molecular mechanics (MM) in vacuum and by molecular dynamics (MD) in solvents. All calculations were run on the Materials Studio program v.5.0 [9] using the COMPASS force field.

The PAH structures used in this study are: benzene, indene ,tetralin, 1,4-dipropylbenzene, 1,4-dihexylbenzene, naphthalene, 1,5-dipropylnaphtalene, 1,5-dihexylnaphtalene, 1H-phenalene, tetralin, 2,3-dihydro-1H-phenalene, anthracene, 1,5-dipropylanthracene, 1,5-dihexylanthracene, phenelene , pyrene (Py), 2-methylpyrene (MPy), 2,7-dipropylpyrene, 2,7-dihexylpyreny, 2-pyrenol (2PyOH), 1-hydroxymetilpyrene (1HMP), 2,7-dihydroxypropylpyrene, 2,7-dihydroxyhexylpyrene, hexa-peri-hexabenzocoronene (HBC) and hexa-hexyl-HBC(C_6-HBC), considering three possible orientations: FF, FT e TT.

All structures were submitted to an energy minimization process by MM in vacuum, using the steepest descent algorithm and a convergence level of 1.10^{-3} kcal/mol/Å. Structures C_6-HBC, 2PyOH, 1HMP, MPy and Py were studied in n-heptane and toluene solvents. These PAHs/solvent systems were submitted to NVT MD simulations, using periodic boundary conditions, for 500 ps, at 298 K.

PAH results in vacuum demonstrated that the increasing number of aromatic rings, the insertion of aliphatic side chains, saturated rings and polar functional groups increases the stabilization of the system. In addition, when saturated rings and polar groups are directly connected to the aromatic nucleus, the stabilization is larger.

For solvated PAHs, it was possible to observe an interlayer distance around 3.6 Å in n-heptane and larger distances in toluene, as observed experimentally.

Thus, the use of theoretical calculations to study PAHs by MM and MD led to results that are consistent with those from X-ray diffraction.

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Poster

FUEL 12

Extractable Polycyclic Aromatic Hydrocarbons (PAHs) in Coals of Various Rank and Origin

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Coal is a complex heterogeneous material composed of a number of distinct organic constituents called macerals and variable quantities of inorganic substances. The structure of coal can be simplified as a two component system, which includes a macromolecular network (an insoluble phase) and a "mobile" (soluble) phase, both of which contain polycyclic aromatic hydrocarbons (PAHs) [1]. Several previous studies investigated PAHs from the "mobile" phase in coals, and mainly emphasized the influence of coal rank on the PAH concentration and composition (e.g., [3]). The influence of coal origin has not been systematically studied to date.

The aim of our study was therefore to assess the differences in concentrations and compositions of PAHs from the "mobile" phase in coals of different rank, elemental composition, and origin. This was achieved by investigating a broad range of PAHs (including alkylated compounds) and applying principal component analysis to a set of fifty coal samples from eleven coal basins around the world.

The results of this study showed that the bell-shaped curve of PAH concentrations plotted against increasing coal rank (described by [2]) was in our study only observed in samples from a single basin. No clear relationship between PAH concentrations and coal rank was identified when the entire set of coals was investigated. We hereby revealed that, while the relationship between PAH concentrations and coal rank may be apparent in samples within a single coal basin, there is no evidence for such a relationship on a multiple-basin scale.

Variations in PAH compositions with coal rank were examined using (1) the ratio of the concentrations of low molecular weight (2-3 ring) PAHs to the concentrations of all (2-6 ring PAHs), and (2) the ratio of the concentrations of C_0-C_1 napthalenes and phenanthrenes to the concentrations of C_0-C_4 naphthalenes and phenanthrenes. The examination of the PAH compositions revealed that low molecular weight (2-3 ring) PAHs remain dominant compounds irrespective of coal rank and origin. Among them, monomethylated compounds are the most abundant in the coals with vitrinite reflectance >1.6%, while di- and trimethylated compounds dominate in the less mature coals (vitrinite reflectance <1.6%).

The relationship between PAH composition and coal rank and origin was further evaluated using principal component analysis (PCA). The PCA provided a graphical separation of the investigated coals into seven groups according to their rank and origin, and therefore additionally illustrated the dependency of the PAH composition and concentration on both, rank and origin of coals.

Our study demonstrated that the investigation of the influence of both coal rank and origin on PAH concentration and composition requires a detailed analysis of various compounds (PAHs from the "mobile" phase) and bulk parameters (elemental and maceral composition, Rock Eval parameters) and is more effective if multiple analytical techniques are applied, together with adequate statistical analyses.

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FUEL 15

Temperature-Dependent Global Kinetic Rate Parameters for the Production of Polycyclic Aromatic Hydrocarbons from the Supercritical Pyrolysis of n-Decane

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The fuels that will be used in future high-speed aircraft will act as a coolant for removing excess heat from the engine before being subjected to combustion. The fuel, while acting as a coolant, will be exposed to temperatures and pressures of up to 700 °C and 150 atm, conditions which are supercritical for jet fuels as well as most pure hydrocarbons. Such severe temperature and pressure conditions lead to fuel decomposition, which can lead to the formation of polycyclic aromatic hydrocarbons (PAH), precursors to carbonaceous solid deposits. These carbonaceous solid deposits can block the pre-combustor fuel transfer lines, hindering safe operation of the aircraft. Therefore, it is extremely important to understand the reaction pathways of PAH formation under supercritical conditions to prevent the formation of solid deposits in the pre-combustion environment. Experiments have been performed with n-decane (critical temperature, 345 °C; critical pressure, 21.1 atm), a representative aliphatic component of actual jet fuels, under supercritical conditions in an isothermal silica-lined stainless-steel tubular reactor heated in a fluidized alumina bath. Experiments were conducted at a constant pressure of 100 atm and temperatures, held constant during each experiment, ranging from 530 to 570 °C. PAH produced during n-decane pyrolysis are a complex mixture of unsubstituted and highly alkylated compounds, therefore a two-dimensional high pressure liquid chromatography (HPLC) technique was used to separate the PAH products, and ultraviolet-visible diode-array detection and mass spectrometry were used for identification and quantification.

The HPLC analysis of the PAH products revealed a gradual rise in PAH yields from 530 to 550 °C, followed by a steep rise in yields from 550 to 570 °C. The experimentally measured yield versus temperature data are found to conform to a first-order global kinetic model. The values of the pre-exponential factor AT and the activation energy Ea which appear in the temperature-dependent expression for the kinetic rate constant, $k = AT\exp[(Ea/RT)]$, were obtained. Comparisons of the observed yields of the PAH products and a curve of the yields determined by the calculated parameters will be shown in the current work.

FUEL 18

Coal and Petroleum-derived PAHs in Size-fractionated Urban Particulate Matter

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This study investigates urban particulate matter (PM) collected in June 2009 and 2010 from filter bags of the air-conditioner system installed in Prague´s Congress Centre, close very busy arterial highway D1, and located in the city centre. Distributions of polycyclic aromatic hydrocarbons were investigated in four particle size fractions: 0,507-0,119 mm, 0,063-0,119 mm, <0,063 mm and sub-fraction <0,025 mm, using GC/MS and Py-GC/MS. The results were compared with NIST standard reference material (SRM 1649a) and with the most used coal for local furnace from Sokolov basin.

PAHs were found in all examined PM fractions sampled in 2009. They comprise compounds with 3-6 condensed rings and are dominated by fluoranthene, pyrene, chrysene and benzo[$k+b$]fluoranthene. All these compounds are known to be associated with combustion sources and pyrogenic nature and usually predominance of fluoranthene and pyrene in distribution is connected with coal-fired domestic furnace [1]. The PAH distribution in fraction showed a similar pattern, dominated by benzo[$k+b$]fluoranthene with the concentration 6.53 µg/g. The highest PAH concentrations occur in the coarsest size fraction, while the finest samples had lower PAH concentrations. The variations of the concentrations found in different size fractions are controlled by the presence of organic matter in different size fractions and larger concentrations of PAHs are associated with char, coke, charcoal and soot particles as was confirmed by optical and scan electron microscope analyses.

Ratios were used to infer sources of PAHs [2]. Flu/Flu+Pyr, BaA/178, and InP/InP+BghiP ratios are consistent with a mixture of vehicle emissions and of biomass and coal combustion, and differ a little according grain size: the coarsest fractions approach more the liquid fossil fuel combustion signs and the finest more coal and biomass combustion.

There is difference between PAHs specified by GC/MS and Py-GC/MS. In the pyrolysis products were also identified PAHs but only in small amounts (<1.0%) and only in the finest PM fractions < 0,063 mm and sub-fraction <0,025 mm. The results imply, that by Py-GC/MS (at 500 °C) are released only the aromatic compounds from the particle surface, and GC/MS after sample extraction record the PAHs encapsulated also inside of the particles.

On the contrary the fractionalised sample collected in 2010 contained minor amount of organic compounds, corresponding with lower soluble organic matter (1.8-2.6%), and there only phenanthrene was quantified (1.51 µg/g). The other PAHs were presented in minority amounts (< 0.5 µg/g). This result is interesting because the sample was collected after the same period of time and in the same season.

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Behavior of PAC in the Environment

Oral

ENVI 1

Harmonisation and Evaluation of Sampling Techniques in the Aquatic Environment (HESTIA) - Trend Monitoring of Polycyclic Aromatic Hydrocarbons and Heavy Metals in the Danube River

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Directive 2008/105/EC (Environmental Quality Standards Directive) defines the good chemical status to be achieved by all Member States in 2015 and gives, together with the Water Framework Directive 2000/60/EC (WFD), the legal basis for the monitoring of priority substances in water, sediment and biota. Besides compliance checking of priority pollutants with environmental quality standards (EQS), monitoring should address the assessment of compliance with the no deterioration objective of the WFD. This should ensure that concentrations of priority substances are below detection limits, declining or stable and there is no obvious risk of increase. Representative sampling techniques are required for assessment of compliance with EQS, as well as for trend monitoring of priority pollutants. Sampling techniques that enable the measurement of time weighted average (TWA) concentrations over a period of several weeks provide a promising alternative to frequent spot sampling of water for obtaining representative measurements of concentrations of trace pollutants in water bodies. This study presents the comparison of various sampling techniques available for temporal trend monitoring of hydrophobic organic pollutants (polycyclic aromatic hydrocarbons; PAHs) and heavy metals (Ni, Cd, Pb, Hg) in the water column. The tested sampling techniques included passive sampling, time proportional suspended sediment traps and time proportional water sampling. The sampling was performed from July to December 2010 at a single sampling site located in the online monitoring station in the Danube river at Wolfsthal, Austria. Priority pollutants were sampled using passive samplers (SPMDs for PAHs and DGTs for heavy metals, respectively), a suspended particle trap, and an automatic continuous water sampler during ten consecutive 14-day sampling periods. Subsamples of water from the automatic sampler were collected twice a week and immediately transported to two laboratories for independent processing and analysis. Pooled samples representative of a two week time period were prepared in each laboratory and analysed for total contaminant content. Results from water samples obtained by two laboratories were compared. The suspended particulate matter analysis provided the particle bound contaminant content in the water column, while the dissolved concentration was measured using passive samplers. The results obtained using different techniques are compared to recommend an optimum sampling approach for trend monitoring of priority pollutant in the Danube River between Austria and Slovakia.

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ENVI 2

Polycyclic Aromatic Hydrocarbons (PAHs) in Shanghai: Distribution and Soures of PAHs in Surface Sediments and Soils

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous toxic pollutants in the environment and have a great impact on human health. Concentrations, spatial distribution and sources of PAHs were investigated in surface sediments (the Yangtze Estuary, the Huangpu River and the Suzhou River) and surface soils in Shanghai, China. Total PAH concentrations ranged from 107 to 1,707 ng/g-dw in sediments, and from 104 to 37,385 ng/g-dw in soils.

Sedimentary PAH concentrations of the Huangpu River were higher than those of the Yangtze Estuary. The concentration of the Suzhou River was close to the average concentration of the Huangpu River. PAHs source analysis suggested that, in the Yangtze Estuary, PAHs at locations far away from cities were mainly from petrogenic sources. At other locations, both petrogenic and pyrogenic inputs were significant. In the Huangpu and Suzhou Rivers, pyrogenic input outweighed other sources. The pyrogenic PAHs in the upper reaches of the Huangpu River were mainly from the incomplete combustion of grass, wood and coal, and those in the middle and lower reaches were from vehicle and vessel exhaust.

An isopleth map of total PAH concentrations in surface soils clarified the regional variability and identified regional hot spots in the urban and industrial areas of Shanghai. These hot spots all suffer from high PAH pollution, suggesting that local human activities (e g. vehicular traffic, petrochemical industry and coal combustion) may be the main contributors. Coal or oil fired power plants and their locations seem to be a significant factor controlling the PAH concentrations in surface soil. The total PAH concentrations are not correlated with soil total organic carbon. We successfully applied hierarchical cluster analysis (HCA) and principal components analysis (PCA) based on a centered log ratio procedure to explore the characteristics and possible sources of soil PAHs. The high PAH contamination in the Shanghai surface soil is mainly attributed to the contribution of pyrogenic sources (vehicular traffic pollution and combustion of coal and biomass). Furthermore, we applied PAH percentages by ring number, isopleth maps of total concentrations of 18 PAHs and source diagnostic ratios of PAHs to help assign the pyrogenic sources in Shanghai soils.

ENVI 3

Recent Sedimentary Record of Anthropogenic Contaminants, PAHs and Trace Metals, in the Eastern Mediterranean Sea (Levantine Basin)

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As part of a study on the contamination of the Lebanese coast by polycyclic aromatic hydrocarbons (PAH), we investigated changes in PAHs and metals deposition in recent sediments from the Levantine basin. A 53 cm long sediment core was collected from sea bottom at an offshore location facing the south of Lebanon at ~300 m water depth. It was kept frozen and precisely sliced every 0.5 cm down to 40 cm and every 1cm down to the bottom. Sedimentation rate was calculated from unsupported ^{210}Pb activity then layers were dated. Unsubstituted and alkyl-substituted PAHs were analysed by GC-MS. Complimentary analyses were performed for granulometry determination, nitrogen and organic carbon content and their isotopic composition ($^{13}\delta C_{org}$ and $^{15}\delta N_{tot}$). Distribution of trace metals, redox tracers and lead isotopic ratios were assessed as additional indicators of anthropogenic inputs.

The core exhibits slow sedimentation that suggests a weak influence of lateral inputs from the continental sources. It is homogeneously constituted of silt and clay particles (<µm), which allows interpretations to be less dependant on grain size. Iron´s and aluminium´s relative abundances confirm granulometric analysis as their presence is closely correlated to the earth silicate matrices. PAHs show a clear upcore increase in the first 20 cm indicating increasing contamination in the recent past (one hundred fifty years). However, the concentrations in the surface layer did not show an increase and are found to be significantly lower than those from the Dyphamed site, a remote station in the western Mediterranean (at ~3000 m water depth). The diagnostic ratio of methylphenanthrene over phenanthrene (MP/P) also underlines a change in PAH sources that matches the increase in PAH concentrations. We also note that six-ring PAHs (m/z = 302), which are particularly mutagenic show an increase by 10 fold through this same period of time.

Trace metals enrichment roughly starts at 20 cm upward and corroborates with findings from the PAH profiles. Lead isotopes also show a shift in lead sources at the upper section of the core suggesting a possible industrial input. Globally, though it presents very low levels of contamination, this core provides a good means to reconstructing a historical record of contaminant input in the Levantine basin.

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ENVI 4

Study on the Degradation of Polycyclic Aromatic Hydrocarbons (PAHs) in the Excrement of Annelids

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To investigate the fate and behavior of polycyclic aromatic hydrocarbons (PAHs) through feeding and excretion of annelids in tidal flat, we have measured the concentration of PAHs in annelid's excrement. Two interesting phenomena were found [1]. Firstly, the PAH concentrations range from 61.2 to 286.9 ug/kg-dry for the excrement of *Marphysa sanguinea*; the concentrations are about 100 times as high as those of the sediment. Secondly, the concentration of the "fresh" fecal pellets of *M. sanguinea* reduces to about half in 2h when they are allowed to stand on the sediment in the sun. The reduction is attributed to the decomposition of PAHs by microorganisms and/or enzymes included in the excrement of *M. sanguinea*, but the reason still remains uncertain. In the present study, we aimed to clarify the cause leading to the rapid decomposition of PAHs in the excrement of *M. sanguinea*.

The reduction in PAHs is confirmed to occur within the fecal pellet excreted by *M. sanguinea*. If the reduction arises from some chemical changes caused by enzymes or microorganisms in the body of *M. sanguinea* and continues after excretion, the PAH concentration of the excrement within the body should be higher than that of the excrement just excreted. Thus we examined whether the decrease would occur when the excrement stayed in annelid's body. The analysis by use of GC-MS revealed that the PAH concentration for the excrement in the body 22 - 1023 µg/kg-dry and that for the excrement just excreted 29 - 1446 µg/kg-dry. Therefore it is suggested that the reduction of PAHs in the excrement begin to reduce after the annelid has excreted on the sediment.

The PAH concentration of the fresh fecal pellets of *M. sanguinea* was reduced to 74% while they were allowed to stand for 1h. This finding is consistent with the previous result: The PAH concentration was reduced to half when the excretion had stood for two hours. To investigate the rate of the PAH reduction in more detail, we are taking more extensive measurements in which the duration of standing is changed to shorter times such as 15 and 30 minutes.

Furthermore, the influence of freezing the excrement was examined to trace the reduction in the PAH concentration for the excrement of *M. sanguinea*. Even if the fecal pellet frozen and thawed was allowed to stand for about 4h, no reduction occurred. This finding suggests that the cause of the PAH reduction is inactivated by freezing.

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ENVI 5

Ubiquitous Distribution of Heterocyclic PAHs in the Large River Systems in Northern Germany

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PAHs and heterocyclic PAHs are known as the predominant contaminants in groundwater at tar contaminated sites. Beyond these local sources, especially concentrations and the distribution of heterocyclic PAHs in environmental samples, such as rivers, in particular have received less research attention. Concentrations in samples of this type are assumed to be far below those from highly polluted areas, making a sensitive analytical method for the reliable quantification necessary. An analytical method for aqueous samples in low ng/l range, sediment samples and suspended matter in the range of 1 µg/kg was developed. GC-MS and LC-MSMS were used in the simultaneous analysis of 86 heterocyclic PAHs, phenols, classical EPA-PAHs and alkylated PAHs. In preliminary experiments liquid-liquid extraction (LLE) for water samples was used at the beginning of the project. However, a high LLE-sample throughput is impractical. Therefore, a combined extraction strategy using solid phase extraction (SPE) and subsequent fractionation by pH variation on Lichrolut EN cartridges was developed. Aqueous samples were directly enriched, whereas ultrasonic extraction was adopted for solid samples with subsequent transfer of evaporated extracts onto the SPE cartridges. The given procedure separates basic nitrogen-heterocycles and possesses a suitable clean-up prior to LC-MSMS analysis for this fraction. Sensitive quantitation of phenols, PAHs, sulfur- and oxygen-heterocycles is realized by GC-MS. Mean recovery of the analytes was found to be >80%. Reproducibility of the method expressed as mean RSD was found to be below 5% for GC-MS and 10% for LC-MSMS. The method combines the benefits of GC-MS and LC-MSMS analysis and is applicable to highly contaminated groundwaters at tar-contaminated sites, river waters and sediments representing background concentrations. The method was successfully validated for EPA-PAHs sampled from river sediments by a threefold extraction of a standard reference material.
The methods were applied to numerous environmental samples taken from river waters, river sediments and particulate matter. Results from two sampling campaigns in Lower Saxony are discussed. A first campaign was performed in 2009 for the water phase, sediment and suspended matter from 26 rivers. A second compaign was implemented in 2010 with the research vessel Ludwig Prandtl in the estuaries of the rivers Weser and Elbe. Only a few general results are presented here and details and interpretations are given in the presentation. Out of the 86 compounds analyzed in the first sampling campaign, only 3- and 4-phenylpyridine, phenanthridinone and 2-hydroxycarbazole were never found to be above the detection limit in any sample. Due to high blank concentrations, cresoles were not quantified. Main heterocycles found in sediment samples were dibenzofuran (up to 39 µg/g C), dibenzothiophene (up to 11 µg/g C) and carbazole, 4-methylquinoline and acridine (in the range of 4-8 µg/g C). However, homocyclic PAHs prevailed in sediment samples. Unlike the case with solid samples, comparable sum concentrations of heterocyclic and homocyclic compounds were found in the aqueous phase, dominated especially by acridine and quinoline with concentrations of up to 20 ng/L. The interpretation of results for the second campaign is still under way and will be discussed in the presentation.

ENVI 6

Oxygen-containing Polycyclic Aromatic Hydrocarbons in Soils: Sources, Patterns, Relation to Parent-PAHs and Vertical Distribution

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Oxygen-containing derivatives of PAHs (OPAHs) are more toxic than parent-PAHs because they are direct-acting mutagens unlike their parent-PAHs which require enzyme activation to exhibit their mutagenicity. OPAHs can also generate reactive oxygen based free radicals responsible for causing oxidative stress associated with adverse health conditions. Predictions based on their higher water solubility indicate that OPAHs might be more mobile in soils than their much studied and regulated parent-PAHs. Considerable knowledge gaps exist about the sources, concentrations, composition pattern, and fate of OPAHs in soils. In this presentation, we will report the results of extensive studies of the concentrations and vertical distributions of OPAHs in soils under different land-use types (rural-background, urban and industrial), from diverse geographical regions: Manaus (Brazil), Bangkok (Thailand), Angren (Uzbekistan), Bratislava (Slovakia), Mainz and Berlin (Germany). The results show that OPAHs are ubiquitous in soils, with their composition pattern dominated by the carbonyl-OPAHs (9-fluorenone, 9,10-anthraquinone, 1-indanone and benzo[*a*]-anthracene-7,12-dione) which also dominate in atmospheric samples. The concentrations of these dominating OPAHs were higher (sometimes 100 fold) than those of their parent-PAHs. Evidence of faster transport of some carbonyl-OPAHs in field soils by leaching as indicated by higher subsoil/topsoil ratios of OPAH than of PAH and correlation of these ratios with the octanol-water partition coefficient is provided. The concentration of OPAHs strongly correlated with their $\sum$parent-PAHs ($r = 0.92$-0.98, $p < 0.01$) suggesting that OPAHs like their parent compounds might be dominantly derived from combustion sources. OPAHs can also originate from biological, photooxidation and chemical transformation of parent-PAHs. We further examine the ratios of OPAHs to parent-PAHs as indication of differences in intensity of transformations of parent-PAHs to OPAHs between tropical ad temperate zones soil. Experimental plans to use compound-specific stable isotope analysis (C, H) to distinguish combustion-derived from biologically produced OPAHs will be discussed.

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ENVI 7

Influence of Humic Acids on Pyrene Sorption by Carbon Nanotubes

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Understanding the interactions between organic contaminants and carbon nanotubes (CNTs) is essential for evaluating the materials´ potential environmental impact and their application as sorbent. Although a great deal of work has been published in the past years, data are still limited in terms of compounds, concentrations, and conditions investigated. This can be mainly explained by limitations associated with the generally-applied batch sorption test set ups. The present study focuses on the effects of humic acids (HA) on the sorption of Polycyclic Aromatic Hydrocarbons (PAHs) onto CNTs. The presence of HA may have two opposite effects on sorption. On the one hand, competition between HA and PAHs can result in a decrease in sorption to CNTs. On the other hand, HA are known to disperse CNTs and we showed in a previous study that sorption capacity is directly related to surface area. The presence of HA may thus increase sorption of PAHs through an increase in the available surface area. The balance between these phenomena remains unclear as classical separation techniques (e.g. centrifugation or filtration) are not adequate to efficiently separate the CNTs and liquid phase under conditions where CNTs are partially dispersed. We previously validated a passive sampling method to study sorption of PAHs1. The method is applicable to dispersed CNTs and we here use it to investigate the influence of HA on the sorption of pyrene. Sorption isotherms were determined over a wide concentration range. Changes in isotherm shapes were interpreted in terms of sorption mechanisms for a range of HA concentrations (0-200 mg/L).
Changes in the sorbent properties as a function of HA concentration are essential to understand and distinguish the various processes involved. CNTs settling behaviour, size distribution in suspension, and particle diameter in the supernatant were determined by UV-vis spectrometry, particle size analysis (CIS-1), and dynamic light scattering, respectively. Preliminary results confirmed the strong dispersing effect of HA on CNTs. The size range of CNTs decreased from 0-60 μm down to 0-8 μm in suspensions containing 0 and 200 mg/L HA, respectively. The speed of settling also decreased with increasing HA concentration, however, after 2 d, particles remaining in the supernatant had similar diameters for all HA concentrations (200 nm), as compared to the control without HA (650 nm). Together with the isotherm analysis, these results will allow a better understanding of the interactions between PAHs and CNTs in complex environmental matrices.

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ENVI 8

Characterization of Aqueous Fullerene (nC60) after UV-assisted Dispersion and during Sorption Experiments with Phenanthrene

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Due to their unique physico-chemical properties, there has been a growing interest in research on carbon-based nanomaterials (CNM) in the past decades. CNM are characterized by a large surface area to volume ratio and electron delocalization. They have been proposed and proven to be strong sorbents for the removal of organic pollutants in various adsorptive separation techniques in environmental science [1] or analytical chemistry [2]. As the production of these materials is expected to further increase in the future, the question of their fate and potential impact in the environment has also become a major concern [3]. While it seems that there is consensus that CNM will eventually reach the environment, their environmental behavior and the impact of their presence on the fate of other pollutants is a controversial issue among researchers. Once CNM reach natural systems, they are likely to undergo changes that may directly change their environmental behavior, such as oxidation from sunlight, or other, non-covalent surface modifications due to the presence of NOM [4].
A detailed investigation of the phase transition of organic sorbates on CNM is difficult, because CNM tend to form aggregates of various sizes due to their hydrophobicity. Nevertheless, sorption of polycyclic aromatic hydrocarbons (PAHs) on CNM has already been studied to some extent. A large range of distribution coefficients for phenanthrene on fullerene dispersed in aqueous solution (nC60), ranging from log Kd 2.3 to 4.7, has been reported in the literature. It was concluded that the degree of nC60 aggregation, i.e., particle size, and the sorption capacity of such materials are directly related [5].
Classical methods used for phase separation (e.g., centrifugation or filtration) may not be adequate to completely separate nC60 and the aqueous phase under conditions where nC60 are partially dispersed. This may explain why a systematic study relating the extend of sorption and the degree of aggregation of nC60 was not reported to date. We here present the results of a study based on a passive sampling technique with polyoxymethylene (POM-SPE), which was successfully applied to investigate sorption of PAHs on multi-walled carbon nanotubes in a previous study [6]. The aims were (i) to induce a photo-catalyzed surface oxidation of nC60 to mimic a possible environmentally relevant change in fullerene properties and (ii) to study the impact on the sorption of phenanthrene over a four order of magnitude wide concentration range. In addition, nC60 were characterized before and during the batch experiments in terms of size distribution by dynamic light scattering and morphology by scanning electron microscopy. Sorption isotherm analysis and characterization data will be combined and allow a better understanding of the interactions likely to occur in natural environments.

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Poster

ENVI 11

PAHs Associations in Fire-Affected Soils

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The emissions during wildfires are considered to be PAH source in the environment, but there is lack of information devoted to this subject. Especially PAH content and composition in fire-affected soils needs further investigations. The objective of the present study was to determine PAHs associations indicating type of burnt vegetation.

Our research was conducted in three nature reserves of Russia: Norskii (Amur Region), Khakasskii (Republic of Khakassia), Polistovskii (Pskov Region). The study sites are characterized by different vegetation, soils and fire regime. Samples of the soils studied were collected at depths of 0-5, 5-10, 10-20, 20-30 in Khakasskii and Polistovskii reserves and at depths of 0-5, 5-15 and 15-40 cm in Norskii reserve.

The soil samples were analyzed for 12 PAH compounds: fluorene, naphthalene, phenanthrene, chrizene, pyrene, anthracene, benz[*a*]antracene, benz[*a*]pyrene, benz[*ghi*]perylene, retene, coronene, benz[*e*]pyrene. Soil samples were air-dried, triturated, and sieved through a sieve with 0,25-mm mesh. Each sample was than extracted with n-hexane. Identification and quantification was carried out by high resolution Shpol‧skii spectrofluorometry. Spectrofluorometer Fluorolog-3-22 (Horiba Jobin Ivon) was used for quantitative analysis.

PAH concentrations in soils after wildfires were relatively low and rarely exceeded 100 ng/g in mineral soils, and 200 ng/g in peat soils, which was much lower than PAH concentrations in urban or industrial areas. Still PAHs associations of background soils differed from associations of burnt sites.

Background mineral soils of different regions had similar PAHs associations. Fluorene, pyrene, naphthalene prevailed in background soils of all regions. It could be explained by their presence in atmospheric deposits. Background peat soils (Polistovskii reserve) differed from mineral soils, major PAH of peat sites included pyrene and naphthalene.

In addition to background PAH the soils subjected to forest fires contained higher concentrations of chrizene, benz[*a*]antracene, retene, phenantrene, benz[*ghi*]perylene. Coniferous wood combustion tended to give higher absolute PAH concentrations then deciduous wood burning because of resinous component.

Peat-fire affected soils showed prevalence of pyrene, naphthalene and benz(a)antracene, phenantrene, chrysene, benz[*a*]pyrene. The highest concentrations of PAH were detected at depths of 5-10 and 10-20 cm. This phenomenon could be caused by PAH formation in situ during peat heating.

Grass combustion during natural fires favoured the accumulation of low weight PAH (fluorene, naphthalene) in soils, and did not cause considerable changes in PAHs association.

So PAHs associations of fire-affected soils have indication significance, they depend on soil type and type of burnt vegetation.

ENVI 12

Diurnal Variation of Chlorinated Polycyclic Aromatic Hydrocarbons in Urban Air, Japan

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Concentrations of chlorinated polycyclic aromatic hydrocarbons (ClPAHs) with 3- to 5-ring were quantified in three-hour integrated air samples obtained serially over a three day period in December 2009 in Shizuoka City, Japan. The gaseous and particulate ClPAHs were collected from the PUF and quartz fiber filter attached in high-volume air samplers, respectively. Twenty species of ClPAHs were detected in the both gas and particle phase, whereas PAHs with larger 4-ring were detected in only the particle phase. The concentrations of total ClPAHs in gas and particle phase ranged from 47 to 250 pg/m^3 and from 21 to 94 pg/m^3, respectively. The diurnal variation of total ClPAHs concentrations in the both gas and particle phase trended to be slightly higher in nighttime than in daytime. The similar trend was also observed in the ambient PAHs. Significant correlation ($p < 0.01$) was observed in between total concentrations of ClPAHs and PAHs in particle phase. The diurnal compositions showed characteristic pattern for some kind of ClPAH; the compositions of 9-chlorophenanthrene in gas phase and 6-chlorobenzo[*a*]pyrene in particle phase trended to elevate in daytime than in nighttime. On the other hand, the opposite pattern, i.e. elevate in nighttime than in daytime, was observed in much of ClPAHs and PAHs. To evaluate the atmospheric behaviors and emission sources of ClPAHs, the concentrations of inorganic compounds such as Cl-, NO_3- and SO_4^{2-} were also investigated in the particle samples. Only a few particulate ClPAHs showed significant correlations to those inorganic compound concentrations. For most ClPAHs, the concentrations did not showed significant correlation to climate conditions such as wind speed, temperature and humidity. These facts indicate that atmospheric behaviors and sources of ClPAHs are associated to those of PAHs, whereas some ClPAHs might act distinctively in the air.

ENVI 13

Comparison of PAH in Sediment Samples vs. Suspended Particulate Matter of the Elbe-Basin System

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Polycyclic aromatic hydrocarbons (PAH) are ubiquitous in the environment. They occur in high structural diversity. PAH have gained serious attention in the scientific community due to their persistence and toxic potential. Under the Water Framework Directive (WFD) the monitoring of priory substances like PAH is an important tool to observe the reduction of contamination to achieve the good ecological and chemical status by the year 2015. EQS are set for several PAHs at 1000 ng/g d.w.
The Federal Institute of Hydrology (BfG) and the Environmental Specimen Bank
(ESB) of the Federal Environmental Agency (FEA) are collecting monitoring data of PAH. The BfG is sampling sediments at about 20 sampling locations (surface sediments - grab samples on annual base) in the river course and in important tributaries (Saale, Mulde, Havel, Schwarze Elster) since 1992. The ESB is collecting suspended particulate matter (SPM) at five sampling locations along the Elbe River Basin and two major tributaries, the Saale (Wettin) and the Mulde (Dessau) on a monthly basis since 2005.
For the years 2005 to 2008 the contamination of surface sediments is compared with SPM. The PAH contamination of surface sediments and SPM (as yearly homogenates) along the monitoring sites are in a good agreement. The comparability of the investigation is made by an appropriate technique of samplings. Surface sediments have to be freshly deposited and fine grained. In addition TOC values and the grain size distribution of the sediments were measured.
In 2002 and 2005 additional dated sediment cores were taken within the ESB. In agreement with the the surface sediments sampled by BfG a slight trend of decreasing concentrations is obvious for recent years. In relation to early data on surface sediments from 1992 a clear trend of decreasing concentrations and a shift in contaminant pattern is deduced. The EQS are still exceeded in many cases.
The specific load of the aquatic systems is fairly constant throughout the system, with decreasing concentrations in the lower reaches of the Elbe system.
The ratios of specific PAH indicate mostly pyrogenic sources. Some comparisons indicate different processes like tidal pumping in Hamburg, rapid deposition during flood events (e.g. Barby) and changes in contamination pattern in recent years relative to early results from the 1990s and before. The problem in using dated sediment long cores (>10 years) in river systems is addressed.

ENVI 15

Overview of Atmospheric PAH Pollution in Brazil

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Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental contaminants considered as priority pollutants by the U.S. EPA and EEA, because some PAHs are carcinogenic and/or mutagenic. There is concern about atmospheric PAHs since the atmosphere is the major pathway for the transportation of PAHs through global environment and there is a significant risk of human exposure through inhalation of air, especially in areas containing high concentrations of PAHs.

PAHs have received increasing attention in studies of air quality in Brazil and, currently, there are data of atmospheric concentrations of several PAHs from different cities (such as the Megacities of São Paulo and Rio de Janeiro). In this study, an overview of the data of atmospheric PAHs obtained at different locations in Brazil and published in around 70 papers in the last 30 years are discussed. The concentrations of certain PAHs, especially of the well known carcinogen benzo[a]pyrene (BaP) and the total concentrations of PAHs (ΣPAHs) were used to compare different locations.

The ΣPAHs observed in different Brazilian cities varied widely. ΣPAHs ranged from 1.31 to 25.9 ng/m³ in São Paulo (SP); 0.69 to 85.9 ng/m³ in Rio de Janeiro (RJ); 0.15 to 73.9 ng/m³ in Porto Alegre (RS); 2.97 to 7.08 ng/m³ in Curitiba (PR); 1.37 to 40.9 ng/m³ in Salvador (BA); 23.73 to 46-17 ng/m³ in Tubarão (SC); 8.94 to 85.32 ng/m³ in Campo Grande (MS) and 0.013 to 6.89 ng/m³ in the Amazon Forest (MT). Besides the characteristics of the studied city the variation of ΣPAHs seems to be also related to other factors such as a) the number of samples evaluated; b) the period and local of sampling; c) the number of studied PAHs, and d) the kind of sample (TSP, MP10) and even the analytical method, that have to be taken in consideration for the comparison. The use of PAH ratios allowed identifying the main sources of PAHs at each site, that resulted consistent with the main economic activities of each region. Thus, the major source of PAHs in the cities of São Paulo, Rio de Janeiro, Porto Alegre, Curitiba and Salvador was the vehicular exhaust, while in Tubarão, the coal combustion and in Campo Grande and Amazon Forest, the biomass combustion.

The mean levels of BaP also varied widely in Brazilian cities, showing values ranging from 0.57 (Curitiba) to 0.99 ng/m³ (Rio de Janeiro). High values were found in Tubarão (14.45 ng/m³) and in Campo Grande (1.91 ng/m³).Many of these values are comparable to those found in large European cities (1.9 ng/m³) and North America (0.98 ng/m³), but lower than those found in Beijing, China (35.0 ng/m³), that emits the highest levels of PAHs in the world. Only in Alta Floresta (0.17 ng/m³), the concentration of BaP was below the concentration limit (0.25 ng/m³) considered as the air quality standard for the UK.

Our results show that the atmospheric composition and main sources of PAHs vary among different areas and cities around Brazil, although the concentrations of BaP were comparable to those found in large urban centers worldwide.

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ENVI 17

Photo-Induced Production of Halogenated Derivatives of Polycyclic Aromatic Hydrocarbons Under Mimic Conditions of Tidal Flats

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In this study, six types of PAHs (naphthalene: NA; phenanthrene: PHE; anthracene: ANT; fluoranthene: FLR; pyrene: PYR; benz[*a*]pyrene: B[a]P) were irradiated with the natural sunlight under field conditions of tidal flats, varying compositions of solid phase. MnO_2 as a co-existing material in the sediments was dosed to sea sands at the concentration of 2,000 µg/g, simulating environmentally relevant manganese (Mn) level in sediments from a tidal flat of southeastern Japan. We had already revealed that among manganese oxides, MnO_2 could act as a photo catalyst on the halogenation of PYR. Here the main purposes of the experiment were to i) reveal the chemical structures of halogenated derivatives produced by photochemical reaction on the surface of the solid phase, ii) explore the effect of Mn as a co-existing material in sediments on the halogenation efficiencies of PAHs and iii) clarify photochemical reactivity of each PAH by comparison of the production amounts. Five g of sea sands spiked with each PAH (25 µg) and artificial seawater (2.5 mL) were irradiated with the natural sunlight for 3 hr. After extractions, the irradiated samples were analyzed by GC/MS to identify the photochemical products. An analytical result revealed productions of 12 types of halogenated PAHs, including 9,10-dichloroanthracene, 1-chloropyrene and 6-chloroB[a]P. In comparison with chlorinated PAHs, the productions of brominated PAHs were lower, since seawater contains chloride ion abundantly. In the MnO_2 added group, the production of haroganated B[a]P was significantly higher than those of control group. It might be due to photocatalytic activity of MnO_2. On the other hands, the dosage of MnO_2 to the sea sands decreased the productions of halogenated ANT and halogenated PYR. Since we had found that MnO_2 could act as a photo catalyst, these results suggest that effects of the addition of MnO_2 on haloganation vary with many factors such as a type of PAHs, dosage amounts of MnO_2 and its form in the sediment. None or only negligible halogenated derivatives were found in the sample where NA and PHE were irradiated. The most abundant halogenated PAHs was 6-ClB[a]P, showing 1600 pM of the production. In general, the production amounts seemed to increase with the increasing of molecular weight. Nevertheless, the halogenated derivatives of ANT and PYR were higher than those of PHE and FLR, respectively. It implies the photo reactivity of PAHs depend on molecular descriptors. We calculated the absolute hardness for each parent PAH and checked the correlation between the descriptors and production amounts of halogenated derivatives. As a result, we found a negative correlation between the hardness and the production amount. Therefore, the hardness would be a useful indicator for the prediction of photo-induced haloganation of PAHs in the coastal environment.

ENVI 20

Wet Deposition and Scavenging Efficiency of Gaseous and Particulate Phase Polycyclic Aromatic Hydrocarbons by Rain at a Central European Suburban Site

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The concentration of 15 3-6-ring polycyclic aromatic hydrocarbons (PAHs) in rainwater and in air before the onset of rain was monitored over 18 months in the years 2006-2008 in a suburban area of Brno, Czech Republic (360,000 inhabitants), 308 m a.s.l. and approximately 30 m above ground. In air and rainwater PAHs were measured in both phases, i.e. gas and particulate and dissolved and particulate, respectively. The rainwater samples were collected by an automatic wet-only sampler. Ambient air samples from 15 to 24 h before the precipitation event and the onset of rain were collected using a medium volume sampler.
Washout of the PAHs by rain was quantified with the aim to identify common trends and differences. In the analysis of mostly stratiform precipitation events a large variability among PAHs and across individual precipitation events was found with regard to the particle-associated fraction in rainwater and to scavenging ratios. The dynamics of phase changes, turbulent motions, transient hydrometeor growth, shrinking and deposition velocities, vdep, introduce a strong non-linearity of pollutant transfer from air to precipitation samples, which can explain a large variation in particle and gas scavenging. The contribution of particle scavenging to total PAH scavenging varied between 7 and 98% among events.
Estimates of the scavenged fraction in the column of air subject to precipitation suggest that typically only a few percent or less of the airborne PAHs are washed out during a precipitation event. Scavenging efficiency seems to be influenced by mass size distribution. It is concluded that wet deposition of PAHs is less efficient than dry deposition.

ENVI 22

Effects of Weathering on Distribution of Polycyclic Aromatic Compounds in the Terrestrial and Marine Sedimentary Rocks

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Polycyclic aromatic compounds (PACs) are major constituents of sedimentary rocks, coals, crude oils and other organic matter (OM) types, but their distributions strongly depend on OM source, depositional conditions and possible occurrence of pyrolytic and/or diagenetic processes (e.g. [2]). The concentrations of most of the PACs decrease with the degree of weathering in both terrestrial and marine OM type. Low molecular weight aromatic compounds, as for example naphthalene, dibenzofuran and dibenzothiophene, decrease sharply already in the partially weathered samples. Some higher molecular weight PAHs, like. benzo[*a*]pyrene and perylene also disappear in the early stage of weathering while others, e.g. benzo[*e*]pyrene or chrysene and triphenylene, are more resistant to the oxidation processes [1]. Interestingly, certain PAHs like fluoranthene and benzo[*b*]fluoranthene increase in concentration in the partially weathered zones of marine shales and terrestrial fossil wood due to their formation from phenyl-derivatives (1-phenylnaphthalene and 9- or 1-phenylphenanthrene) and subsequently decrease in the highly weathered samples [1]. The results presented here may aid in the correct recognition of the signs of weathering in surface and drill core samples and improve the understanding of the PACs transformations that occur during weathering.

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ENVI 23

Correlation Patterns of PAHs and Heterocyclic PAHs in Sediment Samples from Northern Germany - Point Sources and Diffuse Immissions

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PAHs are extensively investigated and classified as priority hazardous substances within the Water Framework Directive of the European Union (EU-WFD, besides anthracene five representative compounds and in addition naphthalene and fluoranthene, classified as priority compounds). Unlike the highly lipophilic PAHs much less is known about the related class of heterocyclic PAHs. To investigate the general importance of especially heterocyclic PAHs numerous environmental samples taken 2009 from river waters, river sediments and particulate matter were analyzed in our group (sampling campaigns in Lower Saxony, Germany). For comparison purposes a special point source in the River Lippe (from a highly contaminated site in Lünen, Ruhr area, Germany) was used. In a first step concentrations from sediment samples (bulk fraction normalized to carbon content) were used. Analytical data for 81 compounds (16 EPA PAHs, 12 phenols, 21 N-heterocycles, 7 O-heterocycles, 5 S-heterocycles and 20 related PAHs such as methylated compounds or hydroxy- or keto-derivatives) at 35 EU-WFD sampling points in Lower Saxony, 2 particulate matter sampling stations and 5 sampling points before, at and behind the local source in Lünen were used (in sum 3400 concentrations). The following main questions were addressed:

- Which correlations exist between the compounds at different sampling points (more than 6500 potential correlations were examined).
- Which compounds out of the chosen spectrum of 81 substances were never found and are assumed to be not important (with respect to an analytical screening)?
- Which heterocyclic PAHs were found to be most important in sediment samples?
- Do correlations exist between heterocyclic PAHs and homocyclic PAHs? Is it possible to define priority compounds which can be used e.g. as markers?
- High concentrations were determined at the local point source (but in general not for all compounds).

Besides the question of the influence of such a point source on the background concentration the difference in compound patterns was investigated using cluster analysis.
Due to the high dynamic in concentrations logarithmic values were used and only linear correlations are discussed here. 22 compounds were found without correlation (defined as R >0.9) with any other compound. This group includes 3 compounds with very high blank concentrations (cresols and 2,3,6-trimethylphenol) and 11 compounds never detected above detection limit in any sample (3- and 4-phenylpyridine, phenanthridinone and 2-hydroxycarbazole) or only in less than 3 samples (e.g. 1,8-dimethylnaphthalene, 2-methylbenzofuran, 2,3-dimethylbenzofuran, xanthene, 8-methylquinoline). Compounds found at least in more than 17 samples but without any correlation to other compounds include for instance acenaphthylene, indene, benzofuran, or 2-naphthol. Due to their high solubility most phenols were found only in few samples and in addition with bad correlations.
Not surprisingly superb correlations (R >0.99) were found for numerous EPA-PAHs as for pyrene (with fluoranthene) or for isomers such as 1,2-dimethylnaphthalene (with 1,4-dimethylnaphthalene). Correlations for heterocycles with R >0.97 were found for instance for 1-benzothiophene (with naphthalene), dibenzofuran (with fluorene) or dibenzothiophene (with phenanthrene).
Details, first interpretations and the comparison between concentrations at the local source with background samples are discussed on the poster.

ENVI 24

Detection of Enzyme Function and Toxicity Potency of Polycyclic Aromatic Hydrocarbons (PAHs) in Avian Embryo Hepatic System using a Tritium Release Assay

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In this study we present a new toxicity assay which can be a practical method elucidating possible mechanisms behind avian toxicity of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs) or for other research purposes. The input of PAHs into the atmospheric, aquatic and terrestrial system has been accelerating and accumulating since the beginning of early industrialization. PAHs are well-known to be potentially carcinogenic to humans and ecotoxicological effects of PAHs have been shown in a diverse suite of studies, including microorganisms, reptiles, birds and mammals with documented effects on toxicity and tumor formation. Relatively few studies address questions concerning the health impact of PAHs in avian species, but some laboratory studies show that PAHs are highly embryotoxic to birds when injected into eggs. We have designed a method to investigate the effects of PAHs on the β-oxidation of fatty acids in hepatic embryonic tissue from chicken (*Gallus domesticus*). Using this assay previous results suggest a small but significant increase in β-oxidation of fatty acids in chicken embryonic liver tissue after in ovo exposure to some PFCs. The focus for this study is exposure to 16 PAHs injected on day 4 into the air cell. This is then followed by in vitro incubation of the embryonic livers on day 10 with a tritiated fatty acid mixture (palmitate 16:0). The fatty acids undergo oxidation and repetitive cleavage of carbons before entering the tricarboxylic pathway and cycles of β-oxidation. As a result of this lipid oxidation tritiated water is produced. The radioactive water (^3H_2O) is collected and measured in a scintilator counter. Studies presenting effects on the fatty acid metabolism in avian embryos due to exposure of PAHs are absent. Using our assay the effects of PAHs on the enzyme function regulating the hepatic fatty acid metabolism can be studied in vitro. This approach could be a very useful trying to find out the mechanisms behind avian toxicity including disturbance of fatty acid oxidation and lipid homeostasis. To the best of our knowledge, this is the first time such study has been performed.

ENVI 27

PAH Measurements in Road Tunnels by Moss Bags and Particulate Samplings

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Over the last few years there have been extensive researches on the use of biological matrices to monitor contamination degree and different kinds of vegetal organisms have been proposed and applied in these researches. Mosses are often used in biomonitoring studies because of their capability to accumulate pollutants directly from air. Many studies used mosses to biomonitor air metal deposition, whereas only recently their use to estimate air polycyclic aromatic hydrocarbon (PAH) depositions is gaining in importance.

In the current study, the moss bag technique and air samplings were applied to monitor PAHs derived from road transport inside two tunnels (QG and CH) of Naples urban area, characterized by elevated traffic flows (almost 2000/3000 veh/h). Tunnel environment is particularly suitable for studying traffic pollution exposure because of the high concentration levels, the single pollution source and the slower deposition process, not taking the wet deposition place.

Moss bags containing *Hypnum cupressiforme* Hedw., sampled in a mixed wood of a remote area far from direct PAH emission sources, were exposed at 3 m height above ground level for 15 days in both tunnels. At QG tunnel a comparison between two different exposure times (15-30 days) was also carried out.

In order to estimate the moss feasibility in ambient air monitoring, 19 PAHs with different molecular weight were detected in moss samples exposed in bags and compared with those bounded to particulate collected in air samples, during some rush hours, inside the tunnels. Total number (PN) and size distribution of particles, ranging from 7 nm to 10 μm, were collected on 12 dimensional stages and measured directly in air by an Electrical Low Pressure Impactor. For PAHs evaluation, collecting particulate filters were grouped in three dimensional groups: particles with aerodynamic diameter lower than 100 nm, between 100 nm and 1 μm, higher than 1 μm.

PAH extraction was carried out by Soxhlet in cyclohexane and the quantitative analyses by GC-MS, for both matrices.

The results did not show any significant difference between the two tunnels for PAH concentrations and PN (mean value 220 ng/Nm^3 and 6×10^5 particles/cm^3, respectively). Moreover, both for PAHs and PN the highest values were measured in the first dimensional group (diameter lower than 100 nm). The contribution of PAHs deriving from the second and third dimensional groups was comparable.

On the other hand, the results showed a higher total PAH concentration in mosses exposed for 15 days at CH than at QG tunnel, with values of 7700 versus 5500 ng/g d.w., respectively. The longer exposure time in QG tunnel resulted in a further PAH accumulation with values about 2-fold higher in mosses exposed 30 days compared to those exposed 15 days.

The analyses of PAH profile in the mosses highlighted phenanthrene, fluoranthene and pyrene as the most representative PAHs. The same relative abundance of single PAHs measured in air and moss samples in both tunnels indicated moss suitability for PAH monitoring in road tunnels.

ENVI 28

Reactions of PAC´s under Oxidative and Reductive Conditions for the Investigation of Potential Bound Residues

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Numerous xenobiotics, such as PAC´s and their derivatives, directly influence the ecosystem. Some of these compounds in addition undergo chemical and/or microbial transformations after exposure to aquatic and/ or terrestrial systems.
In addition it is known that a number of xenobiotics undergo physical or chemical transformation to form bond residues. The investigation of these bond residues is extremely difficult because the matrix of soil, solid organic matter/dissolved organic matter in water is extremely complex and the concentration of the compounds of interest is very low [1].
Recently we have shown that electrochemistry coupled to mass-spectrometry (EC-MS) might be a tool to perform chemical reactions of a xenobiotic and catechol, a model substance for soil organic matter (SOM). Changing the reaction conditions for the EC-cell, we also found that we either can receive a product of the xenobiotic itself and the reaction of a metabolite generated under oxidative conditions [2].
Starting from this basis we took a look at the model for soil organic matter and choose some chemicals as model substances for the organic part to find out where typical reaction-sites for bond residues might be. With these chemicals we generated oxidative and reductive degradation products and performed reactions with the SOM model substance. The structures of reaction products have been elucidated. The results of the various reactions will be presented.

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ENVI 29

Influence of Two Tar-Contaminated Sites on Adjacent Rivers: Quantitation of PAHs, Heterocyclic PAHs and Phenols in the Aqueous Phase

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Over the past century, the anthropogenic use of coal as important resource of industrial products often resulted in soils and groundwater contamination at manufacturing plant sites. Tars and tar oils are formed as byproducts during coking processes and are known to be of high toxicological relevance. The major portion of a typical coke oven coal tar is represented by unpolar, homocyclic aromatic compounds, such as the well known EPA-PAHs. Additionally, even more polar compounds such as phenols and heterocyclic aromatic compounds are present at low mass percentages of up to 10%. Over the last decade, these polar compounds played an increasing role in the groundwater-soil system of tar-contaminated sites and were subject of governmentally funded research projects in Germany (KORA, RUBIN). As an extension of these projects, the presented work investigates the importance of tar-contaminated sites as point sources to adjacent rivers. Therefore, a sensitive method for the quantitation of 86 heterocyclic PAHs, phenols and homocyclic PAHs was developed and applied to groundwater samples on the river bank of tar-contaminated sites and samples from related rivers.
Groundwater samples and river water samples were taken at two tar-contaminated sites and their adjacent rivers in Germany:

- Former coal mining and coke oven plant site (A): 5 sampling points on the adjacent river, 3 groundwater wells on the river bank of the contaminated site.
- Former steel works site (B): 3 sampling points on the adjacent river, 5 groundwater wells on the river bank of the contaminated site, 1 reference well outside the contaminated zone.

All water samples were acidified on-site to pH 1-2 by adding hydrochloric acid and stored at 4°C until preparation. The following solid phase extraction procedure (groundwater: 100 ml, river water: 1000 ml) was performed using Lichrolut EN SPE Cartridges (Merck, Germany) with a vacuum extraction manifold. River samples were initially filtrated using 1.6 µm glass fiber filter pads to prevent clogging of the cartridges. After loading, the cartridges were eluted in two fractions under acidic (fraction 1: neutral analytes) and basic conditions (fraction 2: basic PANHs). Quantitative analysis of the resulting and finally concentrated extracts were performed by GC-MS for fraction 1 and LC-MSMS for fraction 2. The method provides a reliable reproducibility (5-10% RSD) and a mean recovery of more than 80%. Limits of detection achieved are in the low ng/l range. For further information, a schematic overview of the sample preparation procedure will be presented on the poster. The analysis of groundwater samples from the river bank of site (A) show high sum concentrations of up to 10 mg/l in two wells and minor concentrations of 0.4 mg/l in the third well. Main contaminants found are the homocyclic aromatics indane, indene, 1-methylnaphthalene and acenaphthene. Especially, sulfur- and oxygen heterocycles, such as 1-benzothiophene and dibenzofurane were found in high concentrations as well. Increased concentrations of the compounds mentioned were also found in the river adjacent to the contaminated site (A). Measurements of samples from the former steel works side (B) and further data processing is still under way.

ENVI 30

Behaviors of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Airborne Particulates of Hanoi Capital-Vietnam

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Airborne particulates were collected for two weeks in August 2010 and February 2011 at two representative sites (site I and site T) in Hanoi city, one of typical traffic jam cities caught by motorbikes in the world. Fifteen polycyclic aromatic hydrocarbons (PAHs) having two to six rings and eleven nitropolycyclic aromatic hydrocarbons (NPAHs) having three to five rings in airborne particulates were determined by high-performance liquid chromatography with fluorescence and chemiluminescence detections, respectively. The result shows that the predominant PAHs were six-ring PAHs: benzo[ghi]perylene (BghiPe); indeno[1,2,3-cd]pyrene (IDP) and five-ring PAHs: benzo[b]fluoranthene (BbF); benzo[a]pyrene (BaP). These PAHs are highly carcinogenic and/or mutagenic compounds. The mean concentration of total fifteen PAHs at sites I and T ranged from 18.0 – 85.7 pmol m^{-3} and 31.1 – 51.0 pmol m^{-3}, repectively. The highest concentrated NPAH at site I was 9-nitroanthracene (9-NA) (annual concentration was 297 ± 134 fmol m^{-3}), while it was 1-nitropyrene (1-NP) (annual concentration was 331 ± 103 fmol m^{-3}) at site T. Several diagnostic ratios of NPAHs and PAHs indicate that the major contributor of PAHs and NPAHs at site T was vehicles and the main source at site I was mixed contributors of motorbikes and industries. Moreover, the contribution ratio of 6-ring PAHs to the total concentration of PAHs was larger at both sites of Hanoi city than those of several cities in Japan and China, suggesting that the larger ratio of the 6-ring PAHs might be an useful marker to estimate the motorbike contribution

ENVI 31

Predicting Physico-chemical Properties of Propylated Aromatics with COSMO-RS

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At the fourth Conference of the Parties (COP4) to the Stockholm Convention on Persistent Organic Pollutants (POPs), a moratorium concerning production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) was announced by all Parties, except for some exemptions.
These exceptions indicate the need for available alternatives for most diverse uses. The key to the performance of the aforementioned fluorosurfactants is their extremely low surface tension, which currently cannot be matched with other surfactants. Up to know, it has been difficult for other than fluorinated alternatives to gain a foothold on the market.
One alternative being discussed [1] is summarized as "propylated aromatics" with the trade name Ruetasolv®. These aromatic surfactants are based on propylated naphthalenes and biphenyls which can be used as water repelling agents for a variety of applications, such as corrosion protections, marine paints, resins, inks, coatings, plasticizers, or electrical, electronically and mechanical applications. Besides being colourless liquids with boiling points around 570 K and having rather low aqueous solubilities, they are very hydrophobic substances which have a remarkable compatibility with almost all raw materials on one hand and pose a considerable bioaccumulation potential on the other.
Information on environmental and toxicological effects are still scarce; the same holds for accurate physico-chemical property data, most prominent vapour pressure, aqueous solubility and log K_{OW}, which belong to the fundamental parameters for predicting transport, distribution and fate of organic substances in the environment. While vapour pressures of propylated aromatics can be measured fairly easy with current vapour pressure measurement systems, given the availability of pure samples, this is not the case for the very low water solubilities, where a large experimental error might be expected. Here, modern in-silico prediction methods may supply missing data with reasonable accuracy.
Traditional approaches for correlating or predicting thermodynamic properties are primarily based on dividing the molecules into various groups (GCMs). COSMO-RS, the conductor-like screening model for realistic solvation [2], combines quantum chemistry, dielectric continuum models, electrostatics surface interactions and statistical thermodynamics and can predict thermodynamic properties of neutral and charged molecules in liquid phase. The method is based on a very small number of adjustable parameters only, which are completely independent of any molecular or structural information [3].
In this work, vapour pressures, aqueous solubilities, Henry constants and log K_{OW} values have been calculated for a set of propylated aromatic compounds with COSMO-RS in its COSMOtherm implementation. The data are compared with results from other, publicly available prediction methods. On the base of the obtained data, the predicted partitioning of propylated aromatic compounds in an evaluative environment is discussed.

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ENVI 33

Determination of Polycyclic Aromatic Hydrocarbons in the Pseudofeces of Mactra Veneriformis

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The concentration of polycyclic aromatic hydrocarbons (PAHs) in a sediment, bivalve (*Mactra veneriformis*), pseudofeces of *M. veneriformis*, and excrements of *M. sanguinea* collected on the coast of Tokyo Bay (Chiba, Japan) were measured by gas chromatography / mass spectrometry. The total PAH concentrations were about 2.4 for *M. veneriformis*, 2.9 for the pseudofeces of *M. veneriformis*, and 3.3 mg/kg-dry for the excrement of *M. sanguinea*. These concentrations were about 30 to 40 times higher than that in the sediment. The composition of the PAHs in the excrements of *M. sanguinea* was similar to that in the sediment, which was dominated by phenanthrene (Phe), fluoranthene (Flu), and pyrene (Pyr). On the other hand, the PAH composition of the pseudofeces of *M. veneriformis* was similar to that of suspended matter in the sea water, which was dominated by Phe, anthracene, and Flu. These findings suggest that the source of PAHs is different between *M. sanguinea* and *M. veneriformis*: the former, a deposit feeder, feeds on the sediment surface, but the latter, a filter feeder, takes feed through water. Moreover, *M. veneriformis* was found to concentrate PAHs in their body; strongly hydrophobic PAHs such as chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, and perylene were significantly accumulated. This is understandable by taking into consideration that the bivalve's body has a high n-octanol / water partition coefficient (log P_{ow} > 5.5).

ENVI 34

Impact of Emission Reductions between 1980 and 2020 on Atmospheric Benzo[a]pyrene Concentrations

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Benzo[a]pyrene (BaP) has been proven to be toxic and carcinogenic. Since 2010 the European Union officially established target values for BaP concentrations in ambient air. In this study BaP concentrations over Europe have been modelled using a modified version of the Chemistry Transport Model CMAQ which includes the relevant reactions of BaP. CMAQ has been run using different emission datasets for the years 1980, 2000, and 2020 as input data. In this study the changes in BaP concentrations between 1980 and 2020 are evaluated and regions which exceed the European annual target value of 1 ng/m³ are identified, i.e. the PoValley, the Paris metropolitan area, the RhineRuhr area, Vienna, Madrid, and Moscow. Additionally the impact of emission reductions on atmospheric concentrations of BaP is investigated. Between 1980 and 2000 half of the BaP emission reductions are due to lower emissions from industrial sources. These emission reductions, however, only contribute to one third of the total ground level BaP concentration reduction. Further findings are that between 2000 and 2020 a large part (40%) of the BaP concentration reduction is not due to changes in BaP emissions but caused by changes in emissions of criteria pollutants which have an impact on the formation of ozone.

ENVI 38

PAHs Associated to TSP and PM$_{10}$ at Niteroí City, Rio de Janeiro, Brazil

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants of concern because some of them are well-known pro-carcinogenic and/or mutagenic compounds that have been related to several kinds of human cancer. The three major PAH exposure pathways to human beings are inhalation of contaminated air, ingestion of contaminated food and/or water and dermal contact, but the former one seems to represent the most important exposure pathway in urban areas. PAHs are distributed between the gaseous and particulate phases of the atmosphere, but the particulate shows different composition with regard to the mean aerodynamic diameters of the particles. This study presents the evaluation of PAHs associated to samples of total suspended particulate (TSP) and particulate matter <µm (PM$_{10}$) that were collected during a short study carried out at the central area of Niterói City. This medium city is located in the Rio de Janeiro State, Brazil and belongs to the metropolitan area of Rio de Janeiro City, which is considered to be one of the Megacities of the world. This study also partly addresses to fill the lack of data of atmospheric PAHs in medium Brazilian cities and also in tropical cities. Twenty PAHs, including those considered as priority pollutants by the U.S. EPA and perylene, benzo[*e*]pyrene, coronene and naphtho[2,3-*a*]pyrene were evaluated by HRGC-MS in samples of TSP and PM$_{10}$ collected at the central area of Niterói City. The sampling point faced an eleven lane traffic system and it was located in open area 5 meters above ground and around 200 m away of Guanabara Bay margin. The chromatographic system consisted of a 7890 gas chromatograph interfaced to a 5975 mass spectrometer (both from Agilent, USA). Samples and standards were injected under splitless conditions. The injection volume was 1 µL and an injector temperature of 300 °C was employed. He was used as carrier gas and the ion source temperature was kept at 230 °C. A DB-5MS capillary column (30 m x 0.25 mm x 0.25 µm) (J & W Scientific, USA) was used under optimized conditions. PAH quantification was performed by the method of internal standards and presented a linear dynamic range adequate for the determination of PAHs in both set of samples. The extraction of PAHs from the filters was performed according to a previously developed method.1 Samples of TSP and PM10 (n = 7) were collected during a typical week of the fall in the State of Rio de Janeiro, Brazil (June 09 to 15, 2011), which showed mild temperatures (20-25 °C) and moderate humidity (40-70%). benzo[*b*]fluoranthene (0.30 to 3.65 ng/m³) and benzo[*e*]pyrene (0.15 to 2.99 ng/m³) predominated in both TSP and PM10. The total concentrations of PAHs (∑PAHs) found in TSP varied between 1.9 and 10.2 ng/m³ and between 1.1 and 11.3 ng/m³ in PM$_{10}$. The values of ∑PAHs in both type of samples were comparable in almost all studied days, but the values of ∑PAHs associated with PM$_{10}$ seemed to be larger than that of ∑PAHs associated with TSP, possibly due to the dilution of MPA by larger particles, such as those of salt-spray.

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ENVI 39

Impact of Rainwater Management on the Behaviour and Mobility of Pollutants in a Small Urban Headwater Catchment

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Storm water runoff in settlement areas is often polluted by contaminants which originate from impervious surfaces. Due to catchment specific natural and anthropogenic influenced runoff formation, the receiving small urban waters are characterised by a high dynamic of their hydrographs and corresponding chemographs (concentrations of different substances as a function of time). Chemographs reflect the runoff generation processes during flood events and the concomitant transport of xenobiotics as an integral of the watershed's chemical and hydrological processes. Thus, the transport and mobility of xenobiotics in small urban catchments is highly dynamic first of all at storm event scale and provides important information about flow paths and sources of pollutants [1, 4, 3].

In line with restructuring of the former military terrain Trier-Petrisberg, covering an area of approximately 0.4 km^2, the combined sewer system in the headwater catchment has been replaced by a separated sewer system. The runoff from roofs, traffic and green areas is managed by a semi-central infiltration-based retention system [5,6]. The receiving water Brettenbach is a tributary of the Olewiger Bach, which flows in its lower part through the inner city of Trier and drains into the Moselle River. Low flow of the Brettenbach is about 2 l s-1, whereas flood waves reach maximum discharges of 32 l s^{-1}. The bigger flood waves consist of three identified substreams, one natural component and two substreams resulting from the retention basin overflows, and usually pass the stream gauge within 36-48 hours.

To date, the 16 Polycyclic Aromatic Hydrocarbons (PAH) identified by the United States Environmental Protection Agency, Dissolved Organic Carbon (DOC) and nutrients have been analysed in altogether eleven sampled flood waves. Small PAH (2-3 aromatic rings) are measured in all samples in very low concentrations. Medium PAH (4-5 aromatic rings) and bigger PAH (6 aromatic rings) are analysed in higher concentrations in the pre-wave and at the end of the flood wave. In comparisons bigger PAH are measured in lower concentrations than medium PAH. Conformities between PAH chemographs and nutrient as well as DOC chemographs show that the first peak of the PAH concentration is due to xenobiotic input from the source area of the Brettenbach. The second peak at the end of the flood wave is caused by stormwater runoff from the settlement area, which has already passed the retention basins. Even though the PAH concentration is lower at the end of the flood wave, the absolute load deriving from stormwater runoff of the settlement area is higher.

The maximum concentrations and loads of pollutants during flood events depend on resuspension of compounds from surfaces [2]. In the flood waves of the Brettenbach, two flush effects are measurable. First of all the PAH wash-off deriving from the source area of the small brook. The second peak at the end of the flood wave is ascribed to flushing of PAH from roofs and traffic areas.

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ENVI 40

Monitoring Polycyclic Aromatic Compounds in New Hampshire Lichen Using Gas Chromatography Mass Spectrometry

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Lichens are a group of organisms that have been shown to exhibit bioaccumulation of specific contaminants and pollutants after exposure to soil or air pollution[1-3]. The broad goal of our research is to investigate lichens as biomonitors of polycyclic aromatic hydrocarbon distribution in our local environment. A biomonitor is a biological species that can provide a measureable response to a change or impact on an ecosystem. To accomplish this goal analytical instrumentation and simple extraction methods will be applied to quantify PAH in lichen and to evaluate pollutant distribution in proximity to sources of contamination. Understanding the distribution and fate of PAH pollutants in our environment can increase our knowledge of human impact in our local environment and potentially benefit human health by recognizing areas of concern. The Environmental Protection Agency and other researchers have reported several PAH to display carcinogenic and mutagenic properties [4-6]. Therefore developing sensitive methods to measure these chemicals at Keene State College will provide important resource for environmental testing in the southern New Hampshire region.

Fruticose and foliose lichen will be preferred as their higher surface to volume ratio is more susceptible to bioaccumulation of pollutants. Lichen samples are collected from the field are separated from substrate and dried at 35 ºC for 3-4 days [1,7]. Previous studies use organic solvent partitioning methods (soxhlet), sonication extraction, and classic solid phase extraction to extract PAH content from lichen [7,8]. These methods can be expensive, time consuming, and solvent intensive; all unattractive to an undergraduate research lab. A simplified commercial partitioning and dispersive solid phase extraction technique (QuEChERS) will be employed to facilitate analyzing larger numbers of lichen samples. QuEChERS has been previously shown to be an effective method for PAH extraction from biological matrices.[9,10] PAH quantitative analysis will be accomplished using gas chromatography-mass spectrometry (GC-MS) with a 16 PAH calibration curve and three deuterated PAH internal standards. Full resolution of each PAH is provided by temperature programming and selected ion monitoring detection.

Lichen sampled from expected sites of contamination in Keene, New Hampshire have shown the presence of 12 PAH compounds in a single lichen species. Fluoranthene, pyrene, and benzo[*a*]anthracene are three of the most abundant PAH detected in the sample of Flavoparmelia caperata. Benzo[*a*]anthracene is a PAH with known carcinogenicity [5,6]. Mass content of accumulated PAH will be presented for sampled lichen and spiked samples will be used to calculate extraction efficiencies to assess the sample preparation methods. Sample preparation and quantitative analytical methods will be applied to analyzed samples from the Ashuelot River and Mill Creek, where distance to pollution source, lichen species type, and other environmental factors are considered. Mill Creek is a known site of PAH contamination from past industrial activities. Quantitative profiles from local lichen species will be used to assess PAH accumulation in samples collected in proximity to expected sources of pollution, and to demonstrate the usefulness of GC-MS methods for environmental monitoring of PAH in lichen.

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Analytical Chemistry of PAC: Mass Spectrometry

Oral

MASS 1

Determination of Polycyclic Aromatic Hydrocarbon Hydroxides in the Airborne Particles using Gas Chromatography/Tandem Mass Spectrometry

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Polycyclic aromatic hydrocarbons (PAHs) which show carcinogenicity and mutagenicity are one of the atmospheric pollutants produced by combustion of fossil fuels derived from automobiles and industrial activities. It was reported that PAHs secondarily generate PAH derivatives through atmospheric reactions and they exist in the atmosphere mainly being adsorbed to the airborne particles such as diesel-, gasoline-engine exhaust particles and yellow sand. One of the PAH derivatives, PAH hydroxides (PAHOHs) have been suspected of acting as endocrine disruptors that have the potential for estrogenic/antiestrogenic activity. Especially PAHOHs having 4 aromatic rings showed strong estrogenic activity and their activities were found to depend on several physical parameters [1]. There are several reports of chemical analysis of PAHOHs in the airborne particles using gas chromatography with mass spectrometry (GC-MS) [2] and high-performance liquid chromatography (HPLC)[3], and some PAHOHs having 2 or 3 rings were identified. However, 4 or 5 ringed PAHOHs, which showed strong estrogenic activity, have never been identified and quantified in the atmosphere.
In this study, we established an analytical method using GC-MS/MS (Thermo Fisher Scientific, San Jose, CA, USA) with DB5-MS capillary column (60×0.25 mm i.d., 0.25 μm, Agilent Technologies, Santa Clara, CA, USA) for simultaneously determining 45 kinds of PAHOHs having 2 to 5 rings. PAHOHs have weak volatility and insufficient thermal stability, therefore derivatization of their phenol is needed for the analysis by GC-MS/MS. To separate structural isomers with the same mass spectrometric behavior, two types of silylation, trimethylsilylation (TMS) and t-butyldimethylsilylation (TBDMS) were used to derivatize PAHOHs. The developed method was applied to airborne particles collected in several urban cities. As a result, 27 kinds of PAHOHs including 4 and 5 ringed compounds were detected. Some of them were newly identified PAHOHs in the airborne particles. Especially 3 ringed compounds, 2- and 3-hydroxypheanthrene were detected with relatively high concentration in the sample of urban city. Furthermore 3-hydroxychrysene and 4-hydroxybenz[*a*]anthracene, which have strong estrogenic activity in the atmosphere, were abundant in the 4 ringed compounds. This result supposed that PAHOHs are related to the estrogenic activity induced by airborne particles.
The monitoring of PAHOHs in airborne particles should be important to evaluate exposure to the endocrine disruptors from atmospheric environment.

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MASS 2

Gas Chromatographic Retention Behavior of Polycyclic Aromatic Sulfur Hydrocarbons

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Polycyclic aromatic sulfur hydrocarbons (PASH) are in all fossil fuels and their waste products. Although PASH poses environmental risks, most researchers ignore them because little analytical information is available. This paper discusses the retention characteristics and mass spectra for 119 three to six ring PASH. Stationary phases studied included: 14%-cyanopropyl/86%-polydimethylsiloxane (DB-1701ms), trifluoropropylpolysiloxane (Rtx-200ms), 5%-phenyl/95%-dimethyl (Rxi-5ms), and 50%-diphenyl/50%-dimethyl (Rxi-17Sil-ms). The most striking result is that the retention indices across all columns are highly correlated; the Pearson correlation coefficient is ~ 0.99. Results demonstrate the stationary phases are similar even though some consider these phases to have different polarity.

Like PAH, the majority of PASH produce fragmentation ions whose relative abundances (RA) are low compared to the molecular ion. Doubly charged ions at one-half the molecular ion m/z are also common. For structural isomers, the greater the number of rings the more consistent is the spectra. For monomethylated PASH the base ion is the molecular ion. The PASH analog of the benzylium/tropylium species is the second most abundant m/z. Subsequent fragmentation leads to the loss of sulfur to produce the methyl biphenylene cation. For dimethylated PASH the second most abundant ion is the loss of hydrogen or methyl, which is location dependent. Substitution on both rings results in the M-1 cation but if on the same ring, cleavage of •CH3 and shift of hydrogen produces the benzylium/tropylium cation with much higher relative abundance than when the groups are on both rings. The loss of •CH3 produces the benzylium/tropylium species for ethylated C2 PASH without rearrangement and is the dominant fragmentation pathway. The work described here guided GC-GC/MS method development aimed at building a retention time and MS library for all of the C_1 to C_4 substituted PASH found in crude oil and coal tar.

MASS 3

Analysis of Dissolved Polycyclic Aromatic Compounds (PACs) in Seawater by Stir Bar sorptive Extraction (SBSE) and Thermal Desorption GC/MS.

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The latest oil spills which have occurred in recent years have shown an increasing demand for detailed assessments of the chemical contamination induced in the water column. This is particularly true for the Deepwater Horizon incident, for which the chemical dispersion of the oil was largely used as an emergency response. Even at low concentrations due to dilution processes, hydrocarbons are known to generate impacts, and sanitary questions can be raised.

When spilled at sea, a crude oil is subjected to weathering processes such as evaporation, emulsification, photo-oxidation and dispersion in the water column which occur under natural conditions. Concerning dispersion, many oil compounds are dissolved in seawater as polycyclic aromatic compounds (PACs) which represent a category of molecules known as highly toxic and that can cause both short- and long-term effects. Therefore, it is of major interest to be able to characterize any contamination of the water column by this family of chemical compounds, both quantitatively and qualitatively. This implies the availability of reliable and sensitive analytical techniques. In this context, Cedre has developed new protocol of analysis by stir bar sorptive extraction technique (SBSE) and thermal desorption coupled to capillary gas chromatography-mass spectrometry (SBSE-TD-GC-MS) fully dedicated to the analyses of 29 polycyclic aromatic hydrocarbons (PAHs) and 17 polycyclic aromatic sulphur heterocyclic (PASHs). This protocol was validated by analysing the PAHs and PASHs dissolved in three different aqueous phases: at lab, water accommodated fraction (WAF) and water soluble fraction (WSF); in field, natural seawater collected in a harbour area (Brest, France). Results show that these molecules can be detected in all aqueous fractions and quantified at 0.1 ng/L, which underline the high sensibility of the SBSE method.

MASS 4

Improving the Chromatographic Resolution of PAHs in GC×GC/TOF-MS

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Polycyclic aromatic hydrocarbons (PAHs) are a class of complex organic chemicals containing two or more aromatic rings and are formed by incomplete combustion of organic material [1]. Measurements of PAHs in environmental matrices require difficult analytical chemistry procedures, largely because of the complexity of environmental samples. In addition, numerous structural isomers are often present, and in some matrices there may be heteroatoms attached to the PAH (nitrogen, halogens, oxygen). Hence, analytical methods must include processes for isolation of compounds that are part of complex phases, and separation and detection techniques for multi-component mixtures [2]. Gas Chromatography is a useful technique for the separation and determination of PAHs. However, one-dimensional GC is unable to effectively separate the multitude of compounds that are present in environmental samples. With the introduction of comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GC×GC/TOF-MS) the ability to separate numerous compounds of interest has improved [3]. Because the potential peak capacity of a multidimensional chromatogram is the arithmetic product of the peak capacities of the constituent dimensions, extremely large peak capacities can be obtained if the constituent dimensions are independent of each other. A high degree of correlation can reduce a multidimensional separation to what is, in effect, a one-dimensional separation with peaks distributed along a diagonal [4]. In order to maximize orthogonal separation and resolution in GC×GC/TOF-MS, three different combinations of GC columns were tested for the separation of a standard mixture containing 103 parent-PAHs, methylated-PAHs, nitro-PAHs, chloro-PAHs, bromo-PAHs and high molecular weight PAHs. For a primary column, Rtx-5 and liquid crystal GC columns were tested, and for a secondary column, DB-17 and nano-stationary phase GC columns were tested. For all three combinations, distribution of PAHs in a two-dimensional space, increment of the average resolution, and skewness of the data were evaluated. Correlations between retention time and molecular properties, such as vapor pressure, molecular weight, partition coefficients and shape descriptors for each PAH in each column combination were also examined.

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MASS 5

Resonance Enhanced Multi-Photon Ionization Time-of-flight Mass Spectrometry for Monitoring the Pattern and Dynamic Behaviour of Polyaromatic Compounds in Combustion and Pyrolysis Off-Gases from Solid Fuels

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Combustion and pyrolysis off-gases are characterized by enormous complexity of molecular organic species and show often a highly dynamic behavior. Investigation of organic compounds in such matrices on a real-time basis thus requires a fast, yet selective and sensitive analytical technique. Resonance enhanced multi-photon ionization time-of-flight mass spectrometry (REMPI-TOF-MS) using UV-photons is a sound method for selective analysis of (poly)aromatic species, thus meeting these requirements. This technique allows direct monitoring of thermally evolved gases from combustion and pyrolysis without fragmentation, masking out matrix molecules such as nitrogen and oxygen. Transfer of evolved gases to the TOF-MS is carried out via heated sampling lines containing a deactivated quartz capillary and filters to account for the particle load.

REMPI-TOF-MS has been applied for on-line monitoring of combustion and pyrolysis gases of different solid fuels such as wood and coal. For instance, combustion off-gases from a firewood boiler could be consistently monitored for changes in their aromatic pattern. Thereby, typical products of incomplete combustion such as naphthalene and phenanthrene on one hand and thermal decomposition products of lignin such as guiacol on the other hand tended to show different time courses depending on the combustion conditions. During smouldering phases at the beginning, guiacol exhibited high signals due to the predominating pyrolytic conditions. When full scale combustion started, the guiacol signal dropped and PAH signals increased. An attempt at quantification has also been made by measuring an external toluene standard. Subsequently the signals of selected aromatic compounds, for which the relative ionisation cross sections with respect to toluene were determined in the laboratory, have been converted into concentration values.

In coal pyrolysis the changes of the molecular aromatic pattern either as function of pyrolysis temperature or employed coal sort, i.e. different lignites and black coals, could be determined. With the help of cluster and principal component analysis it could be shown that every coal displayed an unique PAH pattern. This could be of interest for the monitoring of coal gasification processes to instantaneously revealing the coal quality by detecting specific marker compounds in the off-gases.

MASS 6

Investigation of Aromatic Hydrocarbons in Crude Oil Fractions Using Laser Ionization High Resolution Mass Spectrometry

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Introduction
Due to the complex nature of crude oil, it is almost impossible to obtain a complete view without using sample preparations which are time, labor and cost consuming. As a result of these problems many different fractionation methods have been established. Due to the significantly more complex organic compounds in the heavy portion, methods such as the SARA have been developed. The SARA method describes the separation of crude oil in the so-called resins (resin-R), asphaltenes (asphalt-A), saturated (saturates-S) and aromatic (aromatic-A) hydrocarbon fractions. The percentage composition of these fractions shows a very big an impact on the physical and chemical properties of the oil.

Methods
For the extraction a slightly modified version of the SARA methodology was used to study two heavy crude oils. In a further step the separated fractions were analyzed using a home-built APLI source connected to a 12T LTQ FT-ICRMS. The samples were dissolved in toluene at a concentration of 100 ppm. The diluted samples were injected and evaporated through an APCI nebulizer. The generated cloud was ionized with a UV (248 nm, KrF*) laser beam, positioned between the MS orifice and the exit of the ion source. Narrow SIM mode (30 Da windows with overlapping of 5 Da) and 400 K of resolution were used for the data acquisition.

Results
The two crude oil samples analyzed presented very different results. Starting with the mass balance, samples A and B presented principally different amounts of volatiles (A: 9% and B 23%) and asphaltene compounds (A:10% and B 2%) while the amount of saturates, aromatics and resins were comparable.
Wide ranges of heteroatom containing groups were found in the analyzed fractions of both samples with hydrocarbons and O-containing groups were found in all fractions. In sample A the N-containing compounds were found in all fractions and S-compounds were only in the resin fraction. For sample B, in the asphaltenic fraction N-compounds were not found and S-compounds were found in low amounts and in the resin S-compounds were not found at all while NOS compounds were observed only in this fraction. In comparison sample A presented a higher intensity of hydrocarbon and NOx compounds than sample B.
For both samples the different fractions presented very distinct compounds. Saturate compounds were found in lower DBE than aromatic compounds; however both fractions presented similar KM distributions. Resin compounds were found in a large range of DBE and KM distribution. Even in the overlapping regions of DBE and/or KM between the fractions the compounds observed were different for each fraction.

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MASS 7

Extending the Mass Range for Semi-Quantitative Analysis of Heavy Petroleum Cuts by Combination of FT-ICR MS with Mass Spectral Segmenting-Stitching and High Temperature SIMDIST

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To improve upgrading and processing of petroleum, a detailed analysis of the feed and product streams is desirable. However, a quantitative analysis of high and non-boiling petroleum fractions has not been accomplished yet at the molecular level. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with atmospheric pressure photo ionization (APPI) is an established tool for the qualitative analysis of aromatic compounds in petroleum heavy ends [1]. In recent work we have explored the technique´s potential for semi-quantitative analysis [2, 3]. However, ion transfer into the ICR cell and space charge effects in the cell limit the broadband detectable mass range as well as the dynamic range, respectively. For this work, we have combined a rarely used FT-ICR MS measurement protocol (recording of several overlapping mass spectral segments that are then combined together) with abundance correction based simulated distillation (SIMDIST) curves.

A quadrupole mass filter before the ICR cell was used to select 110 Da wide mass spectral segments. Multiple segments across the whole mass range of the samples with a 55 Da overlap between each two neighboring segments were measured with high mass resolution. Mass calibration was based on identified signals in the low mass segment and extended through the overlap between segments to the high mass end of the spectrum.

For highly complex samples such as petroleum fractions, measuring mass spectral segments significantly reduces the number of ion species in the ICR cell, thus reducing space charge effects and alleviating suppression of less abundant ion species. A wider dynamic range and increased mass resolution are obtained. The number of identified peaks in a stitched mass spectrum increased by a factor of 3.2 compared to a full range broadband spectrum. In the same instance, the average mass resolution was improved by a factor of 1.7. High temperature SIMDIST curves were used to calculate the true molecular weight distributions of the samples. These distributions were used to correct the mass spectral intensities in the combined spectrum. The resulting corrected mass spectra semi-quantitatively represent the aromatic sulfur and hydrocarbon composition in petroleum heavy ends.

This approach results in high resolution mass spectra with enhanced dynamic range and representative molecular weight distribution across the full mass range of heavy petroleum fractions.

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MASS 8

Mechanistic Study on Temperature Dependence of Ion Formation in Atmospheric Pressure Photoionization of PAH Compounds

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Atmospheric pressure photo ionization (APPI) is a powerful technique for analysis of polycyclic aromatic compounds. Analysis of polycyclic aromatic compounds is very important for environmental, drug and crude oil analyses. As a dopant or solvent, toluene is commonly used in APPI analysis. Toluene is especially important for the polycyclic aromatic compounds because they are soluble in toluene. Despite its importance, ionization mechanism of APPI using of toluene solvent was not thoroughly investigated. In this study, role of toluene molecules for the APPI process was investigated. Especially, the source and position of hydrogen involved in the formation of protonated ions and mechanisms for the generation of molecular and protonated ions were studied. In our present study, protonated ions were commonly observed by APPI analysis with toluene only solvent. First part of our study was focused on finding the origin of the proton generated during the ionization process (either sample or solvent) and to find out which hydrogen is used to produce proton (either methyl group hydrogen or aromatic ring hydrogen). The APPI spectra demonstrate that the proton came from the toluene molecules and the hydrogen in methyl group of toluene molecules is used to produce protonated ion. Additionally, the direct connection between methyl group and aromatic ring is observed to be important for the protonation process. In the second part, we attempted to find out the mechanisms involved for the generation of molecular and protonated ions. To study the ionization mechanism, ratio between molecular and protonated ions were monitored at various APPI source temperatures. 1/T dependent exponential relationship between molecular and protonated ion was shown for the first time. For polycyclic aromatic compounds such as anthracene, pyrene and benzo[*b*]fluoranthene, molecular ion formation was dominant at lower temperature (2000 °C). However, protonated ions became gradually dominant as the source temperature was increased. This strongly suggests that ionization may occur via two steps. At the first step, analytes become molecular ion by charge exchange reaction. In the second step, the molecular ions are converted to protonated ions by hydrogen radical transfer. Therefore, the protonated ions are generated not by protonation but rather by hydrogen radical transfer. The ionization process could stop at the first step to produce molecular ion or be continued by the second step to produce protonated ions.

$[M]^{+\cdot} + S \rightarrow [M+H]^{+} + [S-H]^{\cdot}$ is likely to be the main mechanism to produce protonated ions by toluene solvent.

Theoretical calculations at molecular level are now under progressing to verify the results.

Poster

MASS 10

Quantification of PAHs, N-PAHs, O-PAHs and X-PAHs in Standard Reference Materials Using GC×GC/TOF-MS

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds in the environment and originate from incomplete combustion of organic matter during energy and industrial processes. PAH derivatives can also be formed as byproducts of transformation reactions in the environment. Identifying sources and understanding the environmental fate of PAHs has been the subject of extensive studies due to the carcinogenic and mutagenic properties of some isomers [1, 2, 3]. Some PAHs derivatives, such as 1-nitropyrene, have higher mutagenic and carcinogenic potential than its parent PAH [4, 5]. Other PAH derivatives, such as halogenated PAHs [6] and PAHs with molecular weight greater than 300 [7], are being studied due to their potential persistence, bioaccumulation, and toxic effects.

The objective of this research was to develop a single analytical method to measure up to a total of 103 PAHs (a mixture of parent PAHs, nitro PAHs, oxygenated PAHs, halogenated PAHs and high molecular weight PAHs) in a single chromatographic analysis. A method based on comprehensive two-dimensional gas chromatography/time of flight mass spectrometry (GC×GC/TOF-MS) was developed and used due to GC×GC´s superior sensitivity and separation over one-dimensional [8]. Using a 30 m. Rtx-5 column in the first dimension and a 1 m. DB-17 column in the second dimension, standard PAHs solutions were analyzed by GC×GC/TOF-MS. A six-point calibration curve was developed for a standard mixture of a total of 103 different PAHs. Two standard reference materials were used for method validation, NIST-SRM1975 (Diesel Particulate extract) and a Chinese Coal Fly Ash standard reference material [9]. The results obtained correspond well to the certified values for both standard reference materials within a 95% confidence interval. Distribution of PAHs in the two SRM´s is described

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MASS 11

Ultrahigh Resolution Mass Spectrometry on Polycyclic Aromatic Compounds in Reference Materials

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Certified Reference Materials (CRM) have found a variety of uses in routine analytical practice. Especially when dealing with environmental or public health issues, certified values for typical pollutants in real world samples can be extremely valuable. One of the most important group of these substances are polycyclic aromatic compounds (PAC). Several institutions around the world - among them the National Institute of Standards and Technology (NIST) in the USA and the Institute for Reference Materials and Measurements (IRMM) in Europe - offer CRMs with certified values for PACs, particularly polycyclic aromatic hydrocarbons (PAH).
While these hydrocarbons are important pollutants and abundant in almost all environmental samples, there are also a great number of heterocyclic aromatic compounds that may pose significant health risks. Furthermore, only a relatively small number of typical PAHs have been certified so far.
The certification has mostly been done by separating the analytes using gas or liquid chromatography and identifying and quantifying them by mass spectrometry or fluorescence spectroscopy. By using ultrahigh resolution mass spectrometry instead it is possible to take a much closer look at the general composition of environmental samples. Especially Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) has proven effective in analyzing PACs in several CRMs and crude oil samples even without prior chromatographic separation.
Due to the extremely high mass resolution and sensitivity of this technique it has now become possible to generate separate mass spectra for PAHs and heteroatomic PACs from one single data set/measurement even for very low concentrations of a given analyte. In addition, a novel ionization technique, Atmospheric Pressure Laser Ionization (APLI), can be employed to selectively ionize aromatic compounds in a gentle manner i.e. without fragmentation that often leads to unnecessarily complex mass spectra. Nonaromatic compounds such as alkanes, that are also abundant in many real world samples, are not ionized. Further it is possible to gain information on many alkylated PACs. Alkylation patterns may be helpful in determining the source of a contamination, e.g. in environmental samples or identifying the exact oil well from which a crude oil was taken.
Two harbor sediments, one soil and one dust sample from an urban area, a diesel particulate matter, one coal tar extract and one crude oil as examples for commercial reference materials were examined using FT-ICR MS. In addition to these materials, measurements were taken on one crude oil from Azerbaijan and one from the Mexican Gulf as well as another coal tar sample. The distribution of PACs in these samples will be discussed.

MASS 12

Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Complex Plastic Sample Matrices with Comprehensive Two-Dimensional Gas Chromatography-Mass Spectrometry (GCxGC-qMS)

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PAH are known to be absorbable by skin contact [1] and they occur in consumer products as contaminants from extender oils and soot. Since there are no specific regulations for PAH in these products, their levels should be as low as reasonably achievable (ALARA) to avoid health risks [2].

We analysed many commodities and toys for their PAH contents according to ZEK 01.2-08 [3]. This document implies risk analysis, categorisation, test and evaluation for the 16 compounds listed by EPA. Due to complex matrices (for example in acrylnitril butadiene styrene materials (ABS)), analyte identification especially for PAH with molecular mass fragments between m/z 166 and m/z 228 is difficult even in cases with a additional purification step on a silica phase. To separate the PAH from matrix comprehensive two-dimensional gas chromatography/mass spectrometry (GCxGC-MS) was used. The GCxGC-MS analysis was performed using a rapid scanning quadrupole GC-MS (GCMS-QP2010 Ultra, Shimadzu (100 scan/s, 20000 amu/s).Using in the first dimension a Zebron TM ZB-5HT 30 m x 0.25 mm I.D. , 0.25 µm connected to a VF-17µs 1 m x 0.1 mm x 0.1 µm the separation of the analytes from matrix signals was achieved in the second dimension (polar) which was not possible using one dimenionsal GC (both clean-up step with silica gel).

Several samples of different colours were analysed. Fluoranthene and pyrene could be qualified as main PAH-contaminants in the samples analysed. The extracted ion contour plot of the mass m/z 202 (fluoranthene) as an example shows, that overlaying polymeric matrix of analogue mass can be separated easily in the second dimension.

As a conclusion, comprehensive two-dimensional gas chromatography is suitable not only to separate complex analyte mixtures, but also matrix interferences from target compounds in complex matrices. The analysis of different polymeric matrices can be performed to categorize matrix interference and to quali- and quantificate the PAH contaminants in consumer products.

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MASS 15

Ultra-Sensitive Gas Chromatographic Analysis of PAHs with a Temperature-Controlled APLI-Source

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PAHs are ubiquitous environmental pollutants of high carcinogenicity and mutagenicity. Atmospheric pressure laser ionization (APLI) coupled to LC or GC using orthogonal TOF-MS is a powerful tool for the selective and ultra-sensitive analysis of PAHs. In this work we present a novel temperature-controlled multipurpose ion source (TC-MPIS) which allows the swift coupling of LC and GC to the
same MS. Furthermore, in LC the use of an eluent with a high water content does not lead to any condensation within the ion source enclosure, as occasionally observed with other systems. The sensitivity of GC-APLI-(TOF)MS for the analysis of PAHs was increased further by carefully studying the influence of the dry-gas flow as well as different types of capillary caps.
An Agilent GC7890A was coupled to a new home-built temperature-controlled multi-purpose ion source of a Bruker micrOTOF MS via a home-built rigid transfer line held at 320 °C. To reduce contaminations of the injector unit an activated carbon filter was inserted into the carrier gas line upstream of the injector.
A mixture of 16 PAHs was separated with GC-APLI-(TOF)MS and the limit of detection was determined for each PAH. Even at higher retention times, the TIC is not inceasing considerably, demonstrating the advantage of using APLI as compared to more conventional GC-MS methods. GC-typical signals originating from column bleeding at elevated temperatures, which often complicate the analysis of highboiling compounds, are strongly suppressed because the compounds bleeding out lack chromophores amenable to APLI. In order to optimize the sensitivity for GC-APLI the influence of the dry-gas flow of the used Bruker micrOTOF MS was investigated. The experiments show that the highest sensitivity was obtained without dry gas. The lowest limit of detection for all PAHs investigated was determined for chrysene with 0.05 ng/L or 220 zmol on column.
The temperature-controlled multi-purpose ion source can be operated in LC- and also GC-mode. Particularly in LC-MS, the elevated temperature prevents condensation inside the source enclosure, which was clearly evident when using eluates with a high content of water or with a high flow rate.

MASS 16

Novel Derivatization Strategies for Biomarker Analysis using APLI MS

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For a couple of years we have developed the hyphenation of HPLC, GC, and CEC with APLI and high resolution TOF-MS for the analysis of essentially non-polar poly-aromatic hydrocarbons. For these compounds APLI is outstandingly sensitive. However, only aromatic compounds are amenable to APLI. This selectivity has both advantages (selectivity in a complex matrix) and disadvantages (severe restriction of the analytical compound range). To overcome these limitations, we have already reported on a derivatization strategy that facilitates ionization of polar non-aromatic compounds in complex matrices without hyphenated techniques or stable-isotope labeled standards (SILS). In this contribution, the derivatization approach is considerably broadened and particularly extended towards various biomarkers.
All experiments were performed using a novel temperature-controlled multipurpose ion source (TC-MPIS) coupled to a Bruker micrOTOF in combination with direct-syringe injection or HPLC separation for the analysis of the derivatized compounds.
We present a number of methods for highly efficient derivatization of i) fatty alcohols, ii) fatty acids, and iii) complex organic alcohols such as hydroxyl-propylpyridine and 5-hydroxy-cytosine. The target compounds were either present in complex matrices (pre-separation with HPLC) or were delivered individually by direct syringe injection. The concentration range was generally in the femto-molar regime. In all cases the derivatization reagent was a functionalized anthracene marker. The synthesis of the marker as well as the derivatization approaches are described in detail. We demonstrate that the introduction of the laser ionization marker leads to nearly identical response factors for all derivatized analytes. Thus stable isotope labeling is not required for quantitative measurements, rendering the entire analysis procedure much simpler.

MASS 17

Development of a Multipurpose Ion Source for LC-MS and GC-API MS

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Over the past decade, multimode ion sources operating at atmospheric pressure (i.e., more than one ionization method is operative in the ion source enclosure)have received considerable interest. Simultaneous operation of different ionization methods targeting different compound classes within one analysis run has several advantages,including enhanced sample throughput and thus significant laboratory cost reductions. Potential drawbacks are enhanced ion suppression and other undesirable effects of the simultaneous operation of ionization methods. In this contribution we present an alternative approach—the development and characterization of a widely applicable, multipurpose ion source operating at atmospheric pressure. The optimized source geometry allows rapid changing from LCAPI methods (ESI, APCI, APLI) to GC-API methods (APCI, APLI, DA-APLI) along with the appropriate coupling of chromatographic equipment required. In addition, true multimode operation of the source is demonstrated for LCESI/APLI and LC-APCI/APLI.

MASS 18

Analysis of GSH Conjugates of Bay- and Fjord-Region Dihydrodiol Epoxides of Benzo[*a*]pyrene and Dibenzo[*a,l*]pyrene and their Transport in Enterocyte-like Caco-2 Cells

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The gastrointestinal tract is a main route of exposure to polycyclic aromatic hydrocarbons (PAH) due to the ingestion of PAH contaminated food. Numerous PAH are carcinogenic and are predominantly metabolised to biologically active bay- and fjord-region dihydrodiol epoxides that are capable to form stable DNA adducts leading subsequently to mutations and cell transformation. Detoxification of dihydrodiol epoxides through glutathione (GSH) conjugate formation catalysed by glutathione S-transferases (GST) and their subsequent removal from the cell by transport proteins of the ATP-binding cassette (ABC) superfamily is an important process to control DNA adduct levels [1].
Caco-2 cells were selected to serve as a model system to investigate both the intestinal metabolism of PAH and transport of its metabolites [2]. In the present study specific LC-ESI-MS/MS methods were established in order to determine GSH conjugates of the carcinogenic PAH benzo[*a*]pyrene (BP) and dibenzo[*a,l*]pyrene (DBP) using non-labeled compounds. Using reference materials of these GSH conjugates and 1-methylpyrenylglutathione as an internal standard a solid phase extraction (SPE) step with RP 18 material was established with subsequent determination of the conjugates by LC-MS/MS. LC-MS/MS analysis operated in the selected reaction monitoring mode (SRM) appeared to have the best specificity and sensitivity for the analysis of the GSH conjugates whose molecular ions are fragmented during this process to their associated daughter ions. Besides the SRM mode, additional mass spectrometric scan modes like the daughter scan mode were used for structure determinations of the GSH conjugates. Limits of quantification were 0.04 ng/ml and 0.05 ng/ml for the GSH conjugates of bay- and fjord-region dihydrodiol epoxides of BP and DBP, respectively, and were determined by spiking the blank medium with the reference GSH conjugates.
Caco-2 cell cultures were incubated with either the racemic PAH dihydrodiols or the bay- and fjord region dihydrodiol epoxides (5-10 µM). The LC-MS/MS analysis revealed the presence of two GSH conjugate diastereomers of each PAH in the culture medium. These findings indicate that both enantiomers of (±)-anti-BPDE and (±)-anti-DBPDE are substrates for GST and the formed GSH conjugates are actively excreted from Caco-2 cells into the culture medium. In the TranswellTM-system the conjugates reached both, the basolateral and the apical compartment corresponding in vivo to an excretion into the blood stream and into the intestinal lumen, respectively.
Presently, the established method is used to study the detoxification of PAH dihydrodiol epoxides by GSH conjugation and the transport of these conjugates in Caco-2 cell culture. Pre-treatments of the cell system with specific inhibitors are performed to elucidate the involved transport protein(s). Initial results with TranswellTM-system experiments point to an equal excretion of GSH conjugates of PAH dihydrodiol epoxides into the blood stream and the intestinal lumen.

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MASS 19

Investigating the Role of Extraction Methods on the Analysis of Polycyclic Aromatic Compounds in Crude Oil by FT-ICR Mass Spectrometry

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Introduction
Crude oil is a very complex mixture which represents a challenge for researchers to elucidate its structure. The presence of heteroatomic polycycles in crude oil causes a lot of technical problems. Therefore, a thorough knowledge of types and of polycyclic aromatic compounds in crude oils is essential for the optimization of refining processes and the speciation. High resolution mass spectrometry is a very significant tool for the compositional determination of solid deposits in crude oils, Nevertheless, the use of complementary analytical approaches as a prior step to mass spectrometric measurements can elucidate the complexity of investigated samples and can cause selectivity as well as suppression of compounds.

Method
Two distinctive extraction methodologies were applied on crude oil and on a solid deposit fraction. In regard to crude oil, two crude oils with different Nitrogen content and fouling properties were used in this study. Nitrogen compounds were extracted from the crude oils through the addition of pure ethanol solution and ethanol solution containing Al^{3+}, Fe^{3+} and H^+ ions. In a further step, the samples were derivatized using methyl iodide in the presence of silver tetrafluoroborate.
A solid deposit of a crude oil was dissolved in six organic solvents of different polarities. The isolated N-species were characterized using Fourier Transform Ion Cyclotron resonance Mass Spectrometry, the instrument used in this study was a 12T LTQ-FT-ICR MS (Thermo-Scientific, Bremen Germany).

Results
The results indicate that the metal ion extraction exclusively extracts nitrogen species in the investigated crude oils. To confirm the selectivity of the extraction method applied, we methylated all the extracted samples obtained. Similar results were observed using pH 1. However, after extraction using both metal ions and acidic conditions, nitrogen compounds were found. For a better understanding the samples were derivatized to be able to study additional compounds that are not ionizable by ESI and again the extracted samples are showing the extracted nitrogen species. This shows that the ion extraction methods applied, employing both metal ions and acid pH, were indeed very selective for nitrogen species and show similar results.
Data analysis of the obtained mass spectra of the solvent extracted samples show a variation to the used solvent. In positive mode measurements N1 class was the dominating one for all the extraction procedures, which can be most likely pyridinic in nature. The presence of classes such as N_1O_1, N_1S_1, and O_1S_1 was also notable. On the other hand, classes such as O_1 and O_2S_1 could be detected in DMSO for instance, but not in toluene extraction. The ratios of classes to each other also differ between classes. For example, the N_2/N_1 ratio in dimethylsulfoxide is 0.44, whereas it is about 0.02 in dichloromethane extraction according to the number of isobaric masses.

MASS 20

Quantification of Carcinogenic 4-6 ring Polycyclic Aromatic Hydrocarbons in Human Urine by Solid-Phase Microextraction Gas Chromatography-Isotope Dilution Mass Spectrometry

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Polycyclic aromatic hydrocarbons (PAHs) are pollutants found in living and working environments. The aim of this study was to develop a solid-phase microextraction gas chromatography-isotope dilution mass spectrometry (SPME/GC-IDMS) method for the quantification of ten 4-6-ring PAHs in urine samples. Seven of the selected PAHs have been classified as carcinogenic. Under the final conditions, analytes were sampled with a 100 μm polydimethylsiloxane SPME fiber for 60 minutes at 80°C and desorbed in the injection port of the GC at 270°C. Fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene were separated using a highly arylene modified phase capillary column and quantified by MS using eight deuterated PAHs as surrogate internal standards. Limits of quantification (LOQ) were in the 0.5 - 2.2 ng/L range. Validation showed linear dynamic ranges up to 340 ng/L, inter- and intra-run precisions <20%, and accuracies within 20% of spiked concentrations. Matrix effect evaluation and the use of controls charts to monitor process performances showed that the isotope dilution approach allowed for the control of bias sources. Urinary PAHs were above or equal to LOQ, depending on different compounds, in 58 - 100% (min - max), 40 - 100% and 5 - 39% of samples from coke-oven workers (n = 12), asphalt workers (n = 10) and individuals not occupationally exposed to PAHs (n = 18), respectively. Chrysene was the most abundant PAH determined with median levels of 62.6, 6.9 and <0.6 ng/L, respectively. These results show that the method is suitable for quantifying carcinogenic PAHs in specimens from individuals with different levels of PAH exposure.

Contaminated Sites: Risk Assessment and Remediation

Oral

CONT 1

Colon Extended-PBET Increases Bioaccessibility of Soil-Bound PAH

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Assessment of the risk to human health posed by contaminated land may be seriously over-estimated if reliant on total pollutant concentration. *In vitro* extraction tests, such as the physiologically-based extraction test (PBET), imitate the physico-chemical conditions of the human gastro-intestinal tract and offer a more practicable alternative for routine testing purposes. However, even though passage through the colon accounts for approximately 80% of the transit time through the human digestive tract and the typical contents of the colon *in vivo* are a carbohydrate-rich aqueous medium with the potential to promote desorption of organic pollutants, PBET comprises stomach and small intestine compartments only. Through addition of an eight-hour colon compartment to PBET and use of a carbohydrate-rich fed-state medium we demonstrated that colon-extended PBET (CE-PBET) increased assessments of soil-bound PAH bioaccessibility by up to 50% in laboratory soils and a factor of 4 in field soils. We attribute this increased bioaccessibility to a combination of the additional extraction time and the presence of carbohydrates in the colon compartment, both of which favour PAH desorption from soil. We propose that future assessments of the bioaccessibility of organic pollutants in soils using physiologically-based extraction tests should have a colon compartment as in CE-PBET.

CONT 2

Funnel-and-Gate Biobarrier for Groundwater Remediation: Pilot Test and Field Constrcution

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At a former tar factory site near the city centre of Offenbach, Germany, a funnel-and-gate system is constructed as a biobarrier. Biodegradable pollutants are removed in the bioreactor. If any contaminants are remaining, an additional activated carbon filter can be installed. The concept was developed taking into consideration the site-specific hydrogeological data, sorption isotherms, ferrous iron removal, and process modeling. This presentation focusses on lab studies to determine the operation parameters of the microbiological in-situ reactor and the construction of the field scale biobarrier.

An initial microbiological screening revealed that sufficient numbers of pollutant degrading bacteria were present at the site. Also denitrifying bacteria, but no nitrifying bacteria were detected. Degradation of BTEX, PAH, and heterocyclic compounds (e.g. benzofuran, benzothiophene, dibenzofuran, dibenzothiophene, carbazole) was studied with the autochthonous microflora. Laboratory column studies – operated for a period of 300 days - revealed that ethylbenzene was degraded after addition of nitrate as electron acceptor. The addition of increasing amounts of H_2O_2 up to a concentration of 180 mg/l resulted in increasing biodegradation of the pollutants. The main compounds were eliminated in the following sequence: naphthalene, m-, p-xylene, benzene, o-xylene, benzothiophene, benzofuran. The consumption of electron acceptors could be correlated with COD removal.

In a subsequent on-site pilot study, average influent concentrations were 8,100 µg/l benzene, 12,000 µg/l BTEX, 4,400 µg/l other monoaromatic hydrocarbons, 4,400 µg/l naphthalene, 2,000 µg/l heterocyclic hydrocarbons and 470 µg/L other PAH. Biodegradation of the pollutants was >99 % at a residence time of 72 hours. Also toxicity (bioluminescence test) was significantly reduced. In the bioreactors, a fast dissociation of H_2O_2 was observed resulting in losses of oxygen and temporary gas clogging. Therefore, a repeated addition of moderate concentrations of H_2O_2 proved to be more favourable than the addition of high concentrations at a single dosing port.

CONT 3

Natural Attenuation at an Abandoned Manufactured Gas Plant Site: Pollutant Profiles and Biodegradation of NSO-heterocycles, BTEX and PAH

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Abandoned manufactured gas plant (MGP) sites and landfills containing gasworks residues are important emittants of tar oil pollutants. Due to their toxicity and higher polarity, additionally to BTEX and PAH, NSO-heterocyclic aromatic compounds, containing nitrogen, sulphur or oxygen, are increasingly included in monitoring programmes.

At the MGP site considered in this study, 22 groundwater sampling points are distributed across the centre of contamination and the plume, thus enabling a comprehensive monitoring of the affected area. From October 2010 till March 2011 the most polluted source area was excavated. Groundwater samples are taken regularly and analysed by GC MS. Maximum pollutant concentrations range from 750 µg/L of BTEX to 6600 µg/L of EPA - PAH. Beside BTEX and PAH, 35 NSO - heterocycles with a maximum total concentration of 1000 µg/L were analysed. The main heterocyclic contaminants are benzofuran, benzothiophene, dibenzofuran, and carbazole. Batch experiments with groundwater from the centre of contamination revealed aerobic biodegradation of BTEX, PAH, and NSO-heterocycles. Results from batch experiments were compared with contaminant ratios in the plume. Naphthalene shows a much faster elimination in batch experiments than acenaphtene despite the high initial concentration of naphthalene. Corresponding to these findings the ratio of acenaphthene to naphthalene increases within the plume indicating a faster naphthalene biodegradation also under field conditions. Concerning NSO-heterocycles, a similar effect was observed in the field e.g. for the ratio of dibenzofuran and 2-methyldibenzofuran. Dibenzofuran is one of the four dominant heterocyclic pollutants in the centre of contamination whereas 2-methylbenzofuran concentrations are less pronounced. In the plume, the concentrations of both compounds decrease but there is a faster decrease of dibenzofuran. Changing pollutant ratios in the field are to be compared with the redox zonation, i.e. the microbial electron acceptors availability, and biodegradation kinetics in microcosm studies that are in progress.

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CONT 4

Toxicity and Bioavailability of Geogenic Polycyclic Aromatic Compounds from Coal

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Coals contain native polycyclic aromatic compounds (PAC) that are generated during the diagenetic process of coal formation from biological precursor materials [1, 2]. The amount of PAC depends on the various properties of coal, e.g. origin, coal rank or parent material. In abundant areas of the world soils and sediments are highly contaminated with unburned coal particles as a result of longtime mining activities, transport and usage of coal and overburden material [3]. A large part of PAC in coal-rich soils could be ascribed to coal particles [4]. It is assumed that the coal-derived PAC are of low environmental concern because coal acts as a very strong geosorbent for hydrophobic substances resulting in very low bioaccessibility indicating low environmental risk and reduced remediation costs. The highly varying properties of different coals and heterocyclic aromatic compounds (NSO-PAC) have not yet received much attention in investigations. Furthermore, the assumed low/no availability of coal-derived PAC is commonly not considered in tasks of assessment and remediation of contaminated soils and sediments containing coal particles.

In this investigation, eight coals of varying origin, coal rank and chemical properties were subjeceted to bioassays to study the toxicity and in particular bioavailability of coal-bound PAC. Apart from polycyclic aromatic hydrocarbons (PAH), NSO-PAC have been taken into account. NSO-PAC often show high toxicity and higher mobility compared to PAC.

Contact assays using ground coal as a substrate were performed (fish embryo assay with Danio rerio, nematode contact assay with Caenorhabditis elegans and a bioaccumulation test with Lumbriculus variegatus). The results were compared to the results of the same test systems performed with the fractionated solvent extracts in liquid medium and additional tests (Neutral red retention assay, EROD assay, Ames fluctuation assay) to assess the toxic potential of the compounds present in the extracts. Quantification of PAC and identification of unknown compounds were performed by gaschromatography-mass spectrometry and gaschromatography coupled with atmospheric pressure laser ionisation-ultra high resolution mass spectrometry (GC-APLI-UHR-QTOF-MS), respectively.

The PAH-fraction of nearly all coal extracts exhibited very strong cytotoxic, dioxin-like and mutagenic activity in the different test systems. The heterocyclic fractions caused lower but also noticeable effects. The results of the fish embryo contact assay show that the whole coal samples did not cause any effect, while the organic extracts of both fractions led to embryo mortality already at very low concentrations.

We conclude that the toxic compounds are not bioavailable to fish embryos when exposed in a contact assay despite a very high toxic potential provided by the solvent extracts.

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CONT 5

TERQ: Toxicological Exposure Risk Quantification for Heterocyclic PAC and Aromatic Amine Contamination in Case of DNBA Site Remediation

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Toxic Heterocyclic Poly Aromatic Compounds (HET-PAC) as acridine, carbazole, dibenzofurane, etc. and Aromatic Amines (AA) as aniline, toluidines, etc. are mostly by-products of PAH-contaminations, as from former Gasworks Plants, Cookeries, Tar-oil-transforming Facilities, etc. Since the 19th Century HET-PAC & AA were distilled from tar-oils for production of pigments, as dye-products for textiles and leather, inks, paints, photo-chemistry, etc., and thousands of contaminated Sites showing those Pollutants are exist.
In the past HET-PAC were to rarely investigated on those contaminated sites and AA even nearly never. The reason is, that only since 4 to 5 years HET-PAC are sometimes analyzed and AA must be even extracted under alkaline conditions, which is for the most laboratories not very usual. For this reason, very often nothing is known concerning these compounds on contaminated sites and the associated health effects.
The goal of TERQ (Toxicological Exposure Risk Quantification) is the transparent assessment of toxicological Health Risks for actual and future site use scenarios. Site specific Remediation Goals (SS-RG) are defined (as acceptable residual concentrations for acceptable risks, as the maximum Individual Carcinogenic Risk: ICR = 10-5 in France, Germany, Italy, Spain, etc.) even for Pollutant "Cocktails". The SS-RG exceeding can be mapped for Remediation Definition.
Case Studies from France & Germany are showing, that for this kind of HET-PAC & AA Pollutions Natural Bio-Attenuation Reactors are often exist in Aquifers. Site specific technical-economic Feasibility Studies show, that in case of DNBA-Remediation (Dynamized Natural Bio-Attenuation) the changing to aerobic groundwater hydro-chemical Conditions cleans-up very rapidly the aquifer for low Remediation Costs.

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CONT 6

Biological Mechanism-Specific Tests: A Necessary Complement to Chemical Analysis in Risk Assessment of PAH-Contaminated Soils

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Contaminated sites are a worldwide problem. In Sweden some of the most contaminated areas are being remediated. Polycyclic aromatic hydrocarbons (PAHs) are fairly common in industrial areas and generic guideline values in risk assessment are usually based on chemical analysis of the 16 EPA priority pollutants, even though often hundreds of PAHs and PAH metabolites exist in the soils.
We wanted to elucidate to what extent the actual toxicological risks of soil samples from successful remediation projects could be reflected by these 16 PAHs and also examine the toxicity contribution of some other PAHs and PAH metabolites.
In this study we therefore compared chemical GC-MS analysis and biological H4IIE-luc analysis of a number of remediated soils containing PAHs. The H4IIE-luc bioassay is an Ah receptor based assay that detects all compounds that activate the Ah-receptor, one important mechanism for PAH toxicity. AhR agonistic potencies (REPs) of 16 individual PAHs, 10 oxy-PAHs and four azareenes were investigated using the H4IIE-luc bioassay. The REPS was then used in mass balance analysis to estimate the contribution of instrumentally identified and quantified compounds to the overall observed response in the bioanalysis. The REP approach is an application of the concept of dose-addition and is based on additive behaviour of the compounds, therefore the toxicity of composed mixtures of selected PAHs were also investigated using the concentration addition model (CA) looking for additivity. Additive behaviour of PAHs is important for a successful application of the REP approach in risk assessment of PAH-contaminated samples.
Results from the mixture studies support the use of bioassay derived potency factors (REPs) in risk assessments of PAH-contaminated environmental samples. REPs seem to be a good and necessary complement to chemical analysis. Our results from the soil analysis show the possibility of missing toxicologically relevant PAHs or other AhR agonists in a soil with the chemical analysis methodology mostly used today. All soils tested showed a large proportion of biologically active AhR agonists that could not be explained by chemical analysis of the priority PAHs. It is therefore reasonable to include mechanism-specific tests in risk assessment and in the classification of remediated PAH-contaminated soils. This could minimize the risk these soils can pose to humans and the environment and enable greater safety in subsequent reuse of remediated soils.

CONT 7

Genotoxicity, Embryotoxicity and Dioxin-like Activity of Selected Heterocyclic Aromatic Hydrocarbons Typically Found at Taroil-Contaminated Sites

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Polycyclic aromatic hydrocarbons containing nitrogen, sulphur or oxygen heteroatoms (NSO HET) are a class of widely distributed environmental contaminants that have been detected in air, soil, marine and freshwater systems. Particularly high concentrations can be measured in the vicinity of taroil-contaminated sites. However, only few publications are available investigating the ecotoxicity of NSO-HET using in vitro bioassays on mechanism-specific effect.
In context of the BMBF project KORA and a RWTH Aachen University Seedfunds project, a number of NSO-HET (indole, benzothiophene, benzofuran, 2 methylbenzofuran, 2,3 dimethylbenzofuran, quinoline, 6 methylquinoline, carbazole, dibenzothiophene, dibenzofuran, acridine, xanthene) were tested for genotoxicity, embryotoxicity and dioxin-like activity by means of the micronucleus assay with RTL-W1 cells, the zebrafish embryo toxicity test and the DR-CALUX, respectively. To account for the physico-chemical properties of the substances, the assessment was also based on measured compound concentrations in the assay medium, not only on nominal concentrations.
All of the tested compounds exhibited a high or very high embryotoxicity even at environmentally relevant concentrations in the µg/L-range. Compounds with very high toxicity towards zebrafish embryos were also found to have genotoxic and dioxin-like properties. Chemical analyses revealed that an assessment based on nominal concentrations underestimates the toxicity of the investigated compounds up to 450-fold.
The results of the presented studies clearly demonstrate the ecotoxicological relevance of NSO-heterocyclic PAHs. This group of chemicals should also be accounted for in bioanalytical and chemical analysis-based mass balance calculations since they may be involved in the often encountered unexplained dioxin-like activity and genotoxicity of environmental samples.

Poster

CONT 10

Immobilized Bacterial Consortium RRM-V3 on Rain Tree Leaves for Biodegradation of Pyrene/Phenanthrene in Contaminated Soil

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Bioremediation of contaminated environments by augmenting active microorganisms was often failed due to the loss of bioactivity and low survival rate of the introduced strains [1, 2]. As there have been reports on agricultural materials in helping maintaining survival rate as well as biodegrading activity of many microorganisms [2, 3, 4], here we report immobilization of a bacterial consortium RRM-V3, effective phenanthrene/pyrene degraders isolated from rain tree (Samanea saman Merr.) leaves collected in downtown Bangkok, on rain tree leaves and determination of their PAHs degrading ability and survival rate. It was observed that the bacterial cell number was increased from 8 to 10 log CFU/g of immobilizing material after 3 days of immobilization. Scanning electron micrographs revealed that bacterial cells were attached to the immobilizing material. Analysis by denaturing gradient gel electrophoresis indicated that the major bacterial species in the consortium remained unchanged. RRM-V3 in either free cells or immobilized form could degrade both phenanthrene/pyrene at the concentration of 0.05g each/L to undetectable level within 3 days when cultivated in liquid medium. Application of the immobilized RRM-V3 consortium to soil spiked with phenanthrene/pyrene at 0.05 g each per gram of soil resulted in complete degradation of both compounds within 7 days. We also found that addition of non-sterile rain tree leaves to this PAHs-spiked soil could enhance the ability of indigenous bacteria in the soil to degrade both compounds but with less efficiency than that of the bioaugmentation with the immobilized cells. Furthermore, it was observed that RRM-V3 in free cells or after acclimatized in soil slurry could remove both compounds in soil at slower rate than that of the immobilized cells on rain tree leaves. We, therefore, concluded that immobilized bacterial consortium RRM-V3 on rain tree leaves was an efficient method for bioremediation of PAHs contaminated in soil.

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CONT 11

NBA: Natural Bio Attenuation: Feasibility-Study for the Application of Monitored Natural Bio-Attenuation (MNBA) and/or Dynamized Natural Bio-Attenuation (DNBA) - Case Study HAH, BTEX, PAH

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The Conditions of Natural Bio-Attenuation in the hydro-geological Downstream of an industrial Tar Impregnation Facility Site in Hanau / Germany, contaminated with HAH: Heterocyclic Aromatic Hydrocarbons, BTEX: Monocyclic Aromatic Hydrocarbons and PAH: Polycyclic Aromatic Hydrocarbons were investigated to understand the physical, chemical and microbiological Conditions of the ground water´s aquifer natural Bio-Reactor. Additional to the long term Monitoring concerning HAH, BTEX, PAH and PAH metabolites (as PAH carboxylic acids, etc.), detailed investigations were undertaken to understand the Natural Bio-Reactor´s 3D-Zones of Electron-Acceptor Using (as Oxygen, Nitrate, Sulphate, Iron and Manganese). Additionally PCR- and Isotope-Fractioning-Technologies permitted together with Electron-Acceptor and Electron-Donator Relationship-Calculations to quantify the Pollutant´s microbiological Degradation-Rates. The Isotope-Fractioning Technology was implemented by using the Bac-Trap®-Technology with help of the UFZ-Institute [1,2].
Additionally microbiological Eco-toxicity Tests to identify the Natural Bio-Rector´s Zones which have to be optimized concerning the microbiological Pollutant Degradation-Rates were realized with help of the Planreal-Laboratory. The results showed, that some zones in the Site´s contaminated down-gradient Groundwater needs some Enhancement in Form of In-Situ-DNBA (Dynamized Natural Bio-Attenuation or ENA). Two different DNBA-Technologies were tested with Field-Tests to bring Oxygen into the Groundwater: Bio-Air-Sparging and iSOC® (In-situ submerged oxygen curtain). After a testing time of 8 Months the results showed a very strong and rapid degradation of HAH, BTEX and even more heavy PAH as Phenanthrene. The microbiological Phenanthren Degradation via the Bac-Traps® was even found the first time.
The Natural Bio-Degradation without "Dynamization" (or Enhancement) destroyed even totally all Naphthalene in all Sites down gradient. Based on the DNBA-Field-Tests, the Site´s down gradient Groundwater Clean-up strategy is now based on MNBA (Monitored Natural Bio-Attenuation) with local Enhancement by DNBA via Bio-Air-Sparging which showed on-site better results than the iSOC-Technology. These Technology is clearly cheaper than traditional Pump&Treat.
In-Situ-PAH-Degradation from 750 ìg/l to less than detection limits was obtained in the ground water. These results were so satisfying, that the Authorities signed-off for a Remediation Strategy in a combined Scenario MNBA + enhancement by DNBA. The following Graphic is showing the In-Situ PAH-Degradation in Groundwater during 8 Month:

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CONT 14

Natural Attenuation Investigations of NSO-Heterocyclic Aromatic Compounds in Groundwater Studied at a Former Manufactured Gas Plant Site

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A study at a former manufactured gas plant site in the Northern Ruhr Area (Germany) proved the decreasing content of monoaromatic hydrocarbons (BTEX) and polycyclic aromatic hydrocarbons (PAH) as a result of microbial degradation under sulphate-reducing conditions [1]. Monitored Natural Attenuation (MNA) can be an option in remediation tasks at contaminated abandoned industrial sites and sulphate-reduction often seems to be an important precondition for it [2,3]. Another group of common compounds at former manufactured gas plant sites are NSO-heterocyclic aromatic compounds (NSO-PAC), which are characterized by increased polarity and reduced sorption to soil particles compared to PAH [3]. This is expected to lead to higher mobility in groundwater. Although toxicity of many NSO-PAC is often comparable to that of PAH and they are found concomitantly, to date, investigations at a regular basis and conclusive risk assessment is still lacking [5,6,7]. Regarding NSO-PAC contamination of groundwater, the applicability of MNA is a question of great concern.
In this study, an existing analytical method for NSO-PAC in water [5] was optimized and applied to groundwater samples from five different sample collections (October 2009 – March 2011) at the former manufactured gas plant site studied before [1]. The method is based on extraction by solid phase extraction and analysis by gas chromatography-mass spectrometry. The samples were analyzed for selected NSO-PAC including metabolites which specifically indicate microbial degradation of corresponding parent compounds [5].
Highest concentrations of NSO-PAC were found in groundwater welsl in the center of the contamination source. Concentrations of ∑NSO-PAC (including 10 NSO-PAC commonly found at tar oil-contaminated sites) reached up to 5,379 µg/l in October 2009 and 7,367 µg/l in March 2011, respectively. Highest single compound concentrations in the same wells were found for benzothiophene (3,600 µg/l in October 2009) and quinoline (4,200 µg/l in March 2011), respectively. Concentrations of NSO-PAC generally descreased downstream. Identified metabolites were quinolinone and methylquinolinones. Highest measured concentrations were (234 µg/l for quinolinone and 81 µg/l for methylquinolinones) which were detected downstream of the contamination source.
On the one hand, decreasing concentrations of quinoline and methylquinoline downstream could be ascribed to sorption and dilution of NSO-PAC, on the other hand the occurrence of quinoline and methylquinoline metabolites indicate microbial degradation. Further investigations about the identification of other known metabolites of NSO-PAC at the site will be performed by ultra-high resolution time-of-flight mass spectrometry.

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CONT 15

Comparative Effects of Several Cyclodextrins on the Extraction of PAHs from a Real Contaminated Soil

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Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) attracting extensive attention worldwide. Soils from many sites, such as areas of coal storage, coke oven plants, manufactured gas plants and areas of coal tar spillage present a high contamination level by PAHs. Due to their low solubility in water, the presence of PAHs in the soil matrix constitutes a long-term source of groundwater contamination, and their toxic, mutagenic and carcinogenic properties are responsible that the remediation of PAH-contaminated soil becomes a major environmental concern. In order to enhance the desorption rate of organic pollutants, various extracting agents have been used. Recently, cyclodextrins (CDs) have been proposed as an alternative agent to enhance the water solubility of hydrophobic compounds and thus their availability for biodegradation. The objectives of the present work were: to identify the level of PAHs of an aged-contaminated soil sample from a former chemical industry plant and to evaluate the ability of a natural cyclodextrin (β-cyclodextrin, BCD) and three chemically modified cyclodextrins: 2-hydroxypropyl-β-cyclodextrin (HPBCD), partially methylated-β-cyclodextrin (PMBCD), and hydroxypropyl-γ-cyclodextrin (HPGCD) to extract the sixteen PAHs considered as priority pollutants by US-EPA. A real contaminated soil from the surrounding area of a deserted chemical industry situated in Asturias (North of Spain) was analyzed exhaustively in order to know its PAHs content. Then extraction experiments using an aqueous solution or solutions of one of the four CDs selected were carried out on this soil.
The results presented in this study show that according to Spanish legislation the analyzed soil had to be considered as a contaminated soil. Its total PAHs content was about 1068.77 ± 100.81 mg Kg^{-1}, being phenanthrene, anthracene and naphthalene the most abundant compounds (25.3, 24.7 and 17.1% of the total PAHs content of the soil, respectively). After the extractions experiments using CDs solutions, it was observed that the percentages of PAHs obtained were always higher than when the aqueous solution was used, although the three chemically modified cyclodextrins achieved higher extractions percentages than the natural cyclodextrin (BCD). From the sixteen selected PAHs, the highest extraction percentages was always obtained for the 3-rings PAHs, what is related with the more appropriated size and shape of this compounds with respect to the cavity dimensions of the CDs studied.

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Nanoporous Polymeric Material for Remediation of PAHs Polluted Water

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A new nanoporous polymer was prepared using non-covalent molecular imprinting technique to remediate PAHs contaminated water. The molecularly imprinted polymer (MIP) microspheres sized from 10 to 20 mm were synthesized in acetonitrile using four PAHs mix as the template, methacrylic acid as the functional monomer, and ethylene glycol dimethacrylate as the cross-linking monomer. The removal efficiency of the nanoporous polymeric material (NPM) for mixed PAHs (benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*k*]fluoranthene and chrysene) was studied using adsorption equilibrium experiments. The linear adsorption isotherm and the independent adsorption in binary isotherm indicated that the selected PAHs are mainly adsorbed onto the NPM by a partition mechanism. The adsorption capacity of the NPM (4.25 mg g^{-1}) is 3-fold higher than the commercially used activated carbon. Washing with methanol/acetic acid, the NPM can be regenerated after adsorption of PAHs. No significant decline in the PAHs removal efficiency of the NPM was observed even when the adsorption-regeneration process was repeated for 25 cycles. This study demonstrated that the NPM has potential to remediate PAHs polluted water.

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Application of Spent Fungi-Substrate in Biodegradation of Soils Polluted by PAHs

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The persistence of PAHs in the environment is mainly due to their low solubility in water and stable polycondensed aromatic structure [1]. 16 of these compounds have been identified by US Environmental Protection Agency as hazardous contaminants. Therefore, soils contaminated with PAHs have risks to human and ecological health. Regulations in different countries are increasing the requirements about the limits of pollutants. The importance of this kind of contamination is the publication of guidelines to soil treatment for different countries (Canada, United Kingdom, The Netherlands …). During the last years, different techniques have been developed to treat a contaminated soil in situ: phytoremediation, electrokinetic remediation, solvent extraction, chemical oxidation, thermal technologies and bioremediation. One of the more promising techniques is bioremediation.

Biodegradation of PAHs has been extensively studied, mainly with bacteria. White rot fungi have been proposed to promote biodegradation of PAHs. Compared to bacteria, some white rot species are better able to colonize soil and to complete with the autoctonous microflora. Bioremediation of soils by ligninolytic fungi can be carried out by inoculating the fungus grown on agroindustrial waste like wheat straw, corn cob, or other similar lignocellulosic material. This form of inoculation allows a generous settlement in the ground, sustaining their growth for a long time, given its carbon contribution and encourages the production of ligninolytic enzymes, since these materials tend to mimic their natural environment.

Taking into account these facts, the inoculum to bioremediation process could be obtained by solid state fermentation (SSF). Among them, the possibility of using agro-industrial wastes as a support-substrate and the reproduction of the natural living conditions of the white-rot fungi are outstanding. Among the different existing wastes from the alimentary industry, orange-wastes, a common by-product from the orange and other citrus juices industry, is especially suitable for the production of laccase [2]. Moreover, these agroindustrial wastes could be used as soil nutrient. Several researchers [3-4] have reported that the re-use of industrial orange wastes as organic soil fertilizers as low-cost technology for the recycling nutrients contained in these wastes.

The aim of the present work was to investigate the potential of orange peelings as raw material for the production of laccase by *T. versicolor* and *P. ostreatus* under SSF conditions and to degrade model polycyclic aromatic hydrocarbons (PAHs). Best results in laccase production were obtained with *T. versicolor* cultures (3.000 U l^{-1}), however, *P. ostreatus* (2.700 U l^{-1}) showed higher ability to degrade the tested PAHs phenanthrene and pyrene.

Finally, orange peelings were used as biofertilizer and the oxidative ability of the spent fungus and substrate obtained in SSF was used in the remediation of polluted soil. The results obtained confirm this hypothesis. Thus, the decontamination achieved in soils polluted with PYR was around 43% (after 30 days) by addition of spent fungus and substrate from SSF.

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Benzo[*a*]anthracene Remediation by *Trichoderma longibrachiatum* In Batch and Continuous Mode

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Polycyclic aromatic hydrocarbons (PAHs) are an important kind of xenobiotic, persistent pollutants in soil, slurry and air. Microbial degradation of PAHs is considered to be the major decomposition process, and represents a potential solution to the environmental problems. Usually, low-molecular-weight PAHs (two or three aromatic rings) as sole carbon and energy sources are readily degradable, but high-molecular weight PAHs, containing four or more aromatic rings, are regarded as recalcitrant, thermodynamically stable and more difficult to degrade [1]. Benzo[*a*]anthracene, a tetracyclic PAH, has been widely used as an indicator and a model compound to study biodegradation of PAHs [2]. Bacterial and fungal isolates have been reported to grow on or mineralize PAHs, such as strains of *Bacillus subtilis* and *Pseudomonas aeruginosa, Penicillium sp.*, *Diaphorobacter sp.* and *Pseudoxanthomonas sp.*, saprotrophic soil filamentous fungi and yeasts [3]. Indigenous microbial strains to a particular habitat have been shown to outcompete other artificially introduced strains in bioremediation investigations of oil contaminated sites. A detailed knowledge of the indigenous microbial ecology would therefore be an important prerequisite of the design and implementation of any bioremediation scheme [1].
In the present work, several samples from wastes polluted with polycyclic aromatic hydrocarbons (PAHs) and heavy metals were investigated as potential sources of PAH-degrading microorganisms. After isolating twelve potential degrading-strains, one of them was assured to be best in the preliminary tests. Genetic identification by sequencing was carried out for these strains, and it was identified as *Trichoderma longibrachiatum*.
The degradation ability of this strain was determined in liquid cultures with 100 µM of benzo[*a*]anthracene. *T. longibrachiatum* cultures showed the higher degradation values (around 97%) after 9 d, furthermore in a second batch the time was reduced to 6 d. The results show the enormous potential of the microorganisms isolated in the degradation of high-molecular weight PAHs.
In order to analyze the viability of an industrial application, a continuous treatment with different benzo[*a*]anthracene concentration was carried out. A new bioreactor configuration based on expanded-bed bioreactors was developed. *T. longibrachiatum* was pre-cultured on cubes of nylon sponge, and the cultivation was carried out in a column reactor in continuous mode at three different residence times. It is noticeable that the continuous was able to operate without operational problems, and attaining high degradation levels depended on the residence time. It points out the relevance as well as the novelty of the results obtained in the present work.

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Effects of Geosorbents on the Bioavailability of Polycyclic Aromatic Hydrocarbons (PAH) to Humans by Oral Uptake

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To assess the health risk resulting from human uptake of contaminated soil from hand-to-mouth activity, it is necessary to know the oral bioavailability of the contaminants [1]. Soil-bound contaminants cannot only be mobilized by water from soil but rather by digestion juices and become available for absorption through the intestinal wall [2]. With a physiologically based extraction model (PBET) it is possible to simulate the human digestive system [3].

Previous studies showed a strong variability of the bioavailable fraction (23 – 68 %) of polycyclic aromatic hydrocarbons (PAH) in natural site samples [3]. The reasons for these variations are not known. We assume that quality and quantity of present geosorbents in the samples play an important role. We investigate systematic effects of different geosorbents (sand, clay, peat and char coal) on the bioavailability of PAH from these matrices. It is generally known that the sorption of PAH in an aquatic environment depends on the type and amount of organic carbon present [4]. However, it is unclear if the sorbents show comparable effects on a digestion juice system. The aim of the study is to show the differences in bioavailability of PAH from commonly occurring geosorbents by using them as single materials. The results are expected to lead to a better understanding of the variations in PAH bioavailability in natural site samples.

In this study the sorbents were ground (grain size < 0.06 mm) and spiked with a mix of 16 deuterated EPA-PAH, resulting in a concentration of 100 mg/kg for each compound. The PBET-model according to German DIN 19738 [5] was used. For simulating the human gastrointestinal tract, synthetic salvia, gastric and intestine juice were successively added to the spiked samples. The chime was stirred at 37 °C for 8.5 hours at varying pH-conditions comparable to human mouth, stomach and intestine digestion phases.

After the mobilization of contaminants from the sorbents, the liquid and solid phases were separated by centrifugation and filtration. The contaminants were extracted by liquid-liquid- extraction and analyzed by gas chromatography – mass spectrometry.

The four different sorbents showed systematic effects on bioaccessibility, as expected. Measured bioaccessibilities were: 24,16% (sand), followed by 4,84% (clay), 1,97% (peat) and 0,047% (char coal). Pyrene often had highest bioaccessibilities.

It could be proved that sorption of PAH in the human gastrointestinal tract depends on the characteristics of the sorbent and on the type and amount of organic matter present in soil. The effects are similar to those in an aquatic environment.

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CONT 20

Identification and Quantification of Polycyclic Aromatic Compounds in a Subbituminous Coal from Schöningen, Germany

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Polycyclic aromatic compounds (PAC) are prevalent organic environmental contaminants. It is well known that some polycyclic aromatic hydrocarbons (PAH) have mutagenic or carcinogenic properties and thus are considered as potentially hazardous to human health [1]. Due to the large number of potentially toxic compounds and their ubiquitous distribution, the identification of PAC sources is of essential importance. Apart from other PAH sources, unburnt coal particles can carry increased geogenic and anthropogenic PAH concentrations which has been shown in flood sediments of the River Saar (Germany) [3, 4]. Many studies about PAH from coal utilization and combustion processes exist [2], however, less is known about the environmental impact of geogenic coal-bound PAH.

Results from a current study showed surprisingly increased toxic effects by an extract of the aromatic fraction from a subbituminous coal from Schöningen (Germany) after various tests such as Ames-Fluctuation Test and EROD Assay despite very low concentrations of 16 EPA-PAH [5]. The aim of this study is the identification and quantification of PAH in this coal extract (which could be responsible for the toxic effects of the extract).

For PAH analysis, finely ground coal from Schöningen (Germany) has been extracted using accelerated solvent extraction. Subsequently, the extract was divided into three fractions of different polarity by open column chromatography (aliphatics, PAH and NSO-PAC).The analysis of PAH was carried out using one-dimensional gas chromatography-mass spectrometry and gas chromatography coupled with atmospheric pressure laser ionization - ultra high resolution quadrupole time-of-flight mass spectrometry (GC-APLI-UHR-QTOF-MS). Concentration of the sum of 40 commonly known toxic PAH were as low as 4.8 mg/kg (dry weight). Furthermore, 16 EPA-PAH accounted for less than 42% of these concentrations. By GC-APLI-UHR-QTOF-MS measurements large quantities of compounds with *m/z* 324 and *m/z* 274, identified as alkylated picenes and chrysenes, with a total concentration of 522.9 mg/kg were detected. To date, toxicity studies with varying results have only been carried out with the parent compound picene [6]. The results will be discussed in the presentation.

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CONT 21

A Preliminary Study on Adsorption of PAH from Water by (Lightweight Expanded Clay Aggregate) LECA

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Polycyclic aromatic hydrocarbons (PAH) are present in industrial effluent as a result of combustion processed of organic compounds. Petroleum, coal and shale oil contain extremely complex mixtures of these PAH. The refinery process of petroleum can also result in the formation of PAH. Control of levels of environmental exposure of PAH from process water, airborne particulates as well as accidental oil spillage is an issue of crucial importance. Adsorption is one of the methods of industrial waste remediation employed over the years.
In this study, LECA was explored as a possible adsorbent for 'PAH (phenanthrene, fluoranthene and pyrene) removal from water. LECA was exposed to PAH for varied durations. In all cases, 0.2 g of LECA with average particle size of 4.0 mm was shaken with 100 ml of a solution containing 2.0×10^{-5} mg/ml of PAH. An approximate range of 16-70 % removal of the starting material was observed from 1-20 h duration of LECA exposure. Amount of PAH was determined comparison of peaks areas of GC-MS. The research is ongoing to ascertain the effects of amount of adsorbent and possible best fit isotherms for the LECA- PAH interaction.

Black and Brown Carbon Metrology for Climate

Oral

BLAC 1

Soot, Elemental Carbon (EC), Black Carbon (BC), and Brown Carbon (BrC): A Transmission Electron Microscopy Perspective

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Carbonaceous materials are widespread in natural environments. Their occurrence in many forms has led to confusion about their nature and terminology. Sorting out the differences is a necessary first step for carbon metrology and is important for assessing the effects of atmospheric carbonaceous species on climate and public health. Moreover, communication is greatly facilitated if we clearly define the terms for the atmospheric carbonaceous species, and confusion is inevitable if we do not. Common terms include black carbon (BC), brown carbon (BrC), elemental carbon (EC), soot, and light-absorbing carbon (LAC), although many other terms also occur. BC is widely used by atmospheric scientists for describing strongly light-absorbing carbonaceous materials, which include soot and certain organic substances. On the other hand, according to the International Steering Committee for Black Carbon Reference Materials, BC is a general term that includes chars, charcoals and soots. EC is used for aerosol particles that are assumed to be "pure" carbon without reference to either optical or structural properties. In some cases EC is applied to samples that others would call soot or BC. BrC has been defined based on optical properties of light-absorbing organic particles such as humic-like substances (HULIS) and atmospheric "tar balls."
Transmission electron microscopy (TEM) provides a powerful means for assessing the morphology, internal (crystallographic) structure, size, and composition of particulate species of carbon. We suggest that a TEM-based definition is convenient for those carbonaceous particle types that have distinctive morphological and structural features. In addition, knowledge of the elemental composition can facilitate the further categorization of such particles. For example, soot can be defined as a particle type that consists essentially of carbon and that has a structure of bent graphene layers that are wrapped into spherules that resemble "nano-onions." The nano-onions aggregate and form branching or compact fractal clusters. Tar balls are defined as spherical, typically unaggregated particles that lack the nanostructural order of soot. They consist mostly of C and O, and can contain N and traces of S, Si, and other elements. Primary biogenic particles can be identified on the basis of their distinctive morphologies and compositions. Although perhaps impractical for monitoring purposes, TEM can be used for rapid spot checks of morphologically distinct carbonaceous particles, similar to asbestos measurements. With additional TEM work, novel types of carbonaceous particles might be identified. In any case, the terminology of light-absorbing carbonaceous materials needs to be clarified. Clear understandings and definitions are needed to improve communication and minimize confusion among atmospheric scientists.

BLAC 2

Towards the Development of Black Carbon Reference Materials: Summary of a Workshop

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On June 30, following the 10th International Conference on Carbonaceous Particles in the Atmosphere, a workshop was convened for the purpose of discussing the way forward to develop black carbon (BC), soot, reference materials for instruments that measure atmospheric BC in applications such as air quality monitoring, environmental and health effects studies, climate change and other areas related to airborne BC. The major focus was to develop ideas and make recommendations on how to improve measurements of BC properties through the use of reference materials for validating measurement techniques, calibrating instruments and intercomparing sensing techniques. In particular there continues to be significant differences among instruments that measure the organic and elemental carbon mass concentrations of BC particles and their optical and cloud forming properties. The scientific community has yet to reach consensus on the best methodologies for comparing measurements of BC or how to calibrate the different sensing techniques.
Attending the workshop were almost 50 researchers with expertise in thermal optical analysis of EC/OC, photoacoustic and incandescent spectrometry and filter transmittance through light absorbing particles. During participants focused on: 1) summarizing the current state of technology for measuring BC, 2) identifying the best candidates for BC reference materials and 3) formulating a viable plan for moving the state of BC measurement science forward through the development of reference materials that will be accepted by the scientific community.
This presentation will summarize the findings and recommendations of workshop.

BLAC 3

Black Carbon Measurement by Thermal-Optical Analysis: Optimizing the Technique for Combustion Carbon's Light Absorption rather than its Oxidative Resistance

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Thermal-optical transmission analysis (TOT) is a principal method for measuring refractory (elemental) carbon (EC) in atmospheric particulate matter (PM). In TOT, heating of the sample at multiple temperatures to correct for the presence of particulate organic carbon (OC) has led to a variety of temperature programs ("protocols"), which often produce conflicting results on the same sample. The most widely used protocol, NIOSH 5040, was developed for the analysis of refractory carbon in mine dust. While TOT is widely used to determine light-absorbing combustion (black) carbon (BC) in climate change studies with the assumption that EC and BC are technically identical, temperature protocols based solely on BC absorptivity, i.e., involving the Beer-Lambert Law, have not been developed. BC determination by Beer-Lambert is itself problematic because the specific absorption cross section of PM varies with the presence and spatial arrangement of light-scattering phases in individual particles.

NIST has developed a TOT temperature protocol that is closely based on the Beer-Lambert Law, but that does not require an absolute specific absorption cross section for BC. Empirical response-surface modeling was used to optimize the protocol so that two criteria are met. First, the specific absorption cross section for carbon that the instrument detects as native BC (apparent cross section) is maximized so that OC is not measure as BC. Second, the apparent specific absorption cross sections for native BC and for OC that is pyrolyzed by the method are equivalent. This presentation discusses the optimization criteria, how the temperature protocol was derived from empirical models, optical anomalies of the instrument, and advantages of employing relative rather than absolute absorption cross sections. In addition, results are presented from a comprehensive U.S. EPA comparison of the NIST and NIOSH methods, along with the IMPROVE method commonly associated with thermal-optical reflection.

Although this work was reviewed by the U.S. EPA and approved for publication, it may not necessarily reflect official Agency policy.

BLAC 5

Elemental and Organic Carbon Determination by Proton Elastic Scattering Techniques

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Ion Beam Analysis (IBA) techniques are a reliable tool to study the composition of atmospheric aerosols in a fast, non-destructive way. In particular, Elastic Backscattering Spectrometry (EBS) and Particle Elastic Scattering Analysis (PESA) with MeV energy proton beams - based on the detection of protons elastically scattered by the target nuclei in the backward and in the forward directions, respectively - allows obtaining quantitative information about the concentration of C and other low-Z atoms like H, N and O in atmospheric aerosol samples collected on Teflon filters.

These nuclear techniques do not allow a direct measurement of Elemental Carbon (EC) and Organic Carbon (EC). Nevertheless, the detection of all the light elements may help to infer some information on the aerosol chemical composition. The H concentration obtained by PESA may be used to give an estimate of particulate Organic Matter (OM) and OC. Then, EC can be obtained as the difference between total Carbon measured simultaneously by EBS and OC estimated by PESA.

The basics of these ion beam techniques will be illustrated, together with the current data analysis procedure. The feasibility of the quantification of EC and OC following this approach in particulate matter samples collected on Teflon filters, where this information can not be obtained by standard thermo-optical analyses, will be discussed.

BLAC 6

Data and Mechanism for Carbonaceous Aerosols

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The effects of brown and black carbon aerosols on climate and the environment are well known, and range from pollution-causing to climate-forcing. However, despite their importance, quantitative information, for example, on the chemical reactions leading to second organic aerosol formation or the optical properties (extinction, absorption, and scattering) of brown and black carbon, is sparse. The U.S. National Institute of Standards and Technology has begun a program to collect and disseminate reference data on the mechanisms by which secondary organic aerosols are formed and on the optical properties of brown and black aerosolized carbon. I shall present an overview of the unique instruments that we have developed and recent results, including data on the size-dependent optical properties of aerosols in a range of chemical states.

BLAC 7

Discriminating Diesel Exhaust and Wood-Smoke - Optical Detection of Carbonaceous Aerosols as a Tool for Source Apportionment of Air Pollution

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Anthropogenic climate change has driven the regulatory bodies to promote biomass over fossil fuel due to the low net contribution to atmospheric CO_2 of biomass combustion. Biomass combustion has, however, variable efficiency and can emit large concentrations of aerosolized particulate matter. Recent studies have shown that wood-smoke originating from domestic heating represents a major local and an overlooked regional air pollutant in the EU.

The source specific dependence of carbonaceous aerosol optical absorption on the wavelength enables on-line discrimination of fossil fuel and biomass combustion. Application of a technique, called the "Aethalometer model" and based on this difference, will be demonstrated in several case-studies for local source apportionment. The spatio-temporal heterogeneity of air pollution challenges its abatement and a highly time resolved method is advantageous for this purpose.

BLAC 8

Radiocarbon Analysis of Black and Brown Carbon: What Can We Learn?

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Carbonaceous aerosols are a large fraction of the air-borne particulate matter causing substantial negative impacts on global climate and human health. In spite of this general importance, the knowledge of emission sources of carbonaceous aerosols is very limited. Furthermore, optimum procedures for the distinction of optically absorbing (black and brown carbon) and non-absorbing (organic carbon) sub-fractions are currently discussed controversially. Thermo-optical methods simultaneously take advantage of different chemical and optical properties of these sub-fractions so that their usage seems to be very promising. The complexity of the atmospheric components and pyrolytic artifacts during analysis, however, hamper the verification of the best procedure.

The analysis of the long-lived radioisotope radiocarbon (^{14}C) in carbonaceous aerosols may help to improve this situation with respect to two aspects. First, radiocarbon determination allows the apportionment of fossil from non-fossil sources, as ^{14}C has completely decayed in fossil fuels, whereas modern materials have the contemporary radiocarbon level. Second, isotope analysis provides additional insights into the quality of separation of organic carbon and black carbon with thermo-optical techniques, as both sub-fractions typically have substantially different 14C levels. These two aspects will be highlighted.

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BLAC 9

The Use of Approximated Quantum Chemical Methodologies as a Practical Tool for Studying Intermolecular Interactions in Aromatic Clusters

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Aromatic-aromatic interactions play an important role in many chemical and biological systems. They control, among others, structures of DNA and proteins, the packing of aromatic crystals, the formation of aggregates, the binding affinities in host-guest systems, and conformational preferences of poly- aromatic macrocycles and chain molecules. In addition, under the right conditions, they can play in important role in the formation of soot particles and other organic aerosols resulting from combustion processes.

As the species formed by a direct consequence of the intermolecular interactions, the geometrical structures and binding energies of aromatic clusters provide fundamental understanding of aromatic π-π interactions. For this reason aromatic dimers and higher clusters, produced by supersonic jet expansion has been the focus of substantial experimental and computational efforts. Experimental information on the interaction potentials is however sparse (and not always in agreement with each other), being limited only to the T-shaped dimer of benzene and the cyclic trimer of naphthalene. Recently, it has been suggested that in order to help in the interpretation of experimental data, a way forward would be the integration of measurements with accurate quantum chemical calculations.

During the past 25 years, the area of computational chemistry has witnessed significant advances in the development of accurate and efficient ab initio quantum chemistry methodologies that together with the advent of powerful computational architectures, has allowed the use of these methods in the study of a large variety of chemical processes on a routine basis. Despite these major advances, the application of accurate ab initio quantum chemistry methodologies to the study of the mechanisms, energetics, and dynamics governing the cluster formation of aromatic hydrocarbons has been limited to small systems given their relatively high computational expense.

In this talk, the implementation and validation of computational efficient and reliable quantum chemistry methodologies able to properly describe the physics and chemistry of the intermolecular interactions between aromatic hydrocarbons will be discussed. Examples illustrating the applicability as well as the limitations of these models in the case of benzene, naphthalene and anthracene micro-clusters will presented

Poster

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UV-VIS Spectroscopy of Astrophysically Relevant PAHs

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Mid-infrared (MIR) emission bands related to aromatic C-H and C-C vibrational modes were found in several astrophysical environments, ranging from planetary nebulae, reflection nebulae, circumstellar disks to even active galactic nuclei [1]. Inferred from their presence, polycyclic aromatic hydrocarbons (PAHs) are believed to be an important component of interstellar dust. They belong to the most abundant molecules in the interstellar medium (ISM). Unfortunately, the MIR bands do not permit an identification of specific PAH molecules. Based on energetic arguments, these bands were attributed to rather large molecules (20 - 100 C atoms). In astrophysical environments, PAHs exist as free-flying neutrals, ions, or clusters. In addition, they can contribute to the formation of carbonaceous dust [2]. Besides the MIR emission bands, specific absorption features in the UV and visible spectral range observed in the ISM, i.e., the 217.5 nm UV bump and the diffuse interstellar bands (DIBs), are proposed to be connected to PAHs.
Mixtures of polycyclic aromatic hydrocarbons (PAHs) have been produced by means of laser pyrolysis. The main fraction of the extracted PAHs was primarily medium-sized, up to a maximum size of 38 carbon atoms per molecule. The use of different extraction solvents and subsequent chromatographic fractionation provided mixtures of different size distributions. UV-VIS absorption spectra have been measured at low temperature by matrix isolation spectroscopy and at room temperature with PAHs as film-like deposits on transparent substrates. In accordance with semi-empirical calculations, our findings suggest that large PAHs with sizes around 50 - 60 carbon atoms per molecule could be responsible for the interstellar UV bump at 217.5 nm [3]. We also investigated how the electronic absorption bands of selected PAHs are altered upon ionization by interstellar UV photons. The main effects were found to be a broadening in the UV combined with slight red shifts. The position of the complete pi-pi* absorption structure around 217.5 nm, however, remains more or less unchanged which could explain the observed position invariance of the interstellar bump for different lines of sight. This favors the assignment of this feature to neutral and ionized PAHs [4].

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Plenary Discussion Platform

U.S. EPA's 16 PAH Priority Pollutants – Where They Came From

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Very little is written or published about where EPA's 16 PAH Priority Pollutants came from or how and why these particular compounds were selected as representatives of PAHs. Now, over thirty years later questions are being asked (quite appropriately) whether some of these compounds are still useful or whether others might be better. Environmental analysis today is <u>very</u> different from the way it was back then. Because the present is almost always linked to the past, in order to evaluate the current list you must also understand the context and the epochal times during which the list was developed. This paper presents a personal history of what was happening in the late 1960s and early 1970s that led to the 1976 legal settlement known as the EPA Consent Decree. It also details what, where, when, how, and (very importantly) **why** each of the 16 EPA PAHs were selected as representatives of PAHs used for environmental analyses as part of the Consent Decree.

U.S. EPA's 16 PAH Priority Pollutants – Where They Came From