



**1st Network Conference on Persistent Organic Pollutants:
Human Exposure and Impacts**

**The Manor House,
The University of Birmingham**

29 – 30 March 2006

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**Programme for NERC Knowledge Transfer Network 1st Conference
on Persistent Organic Pollutants: Human Exposure and Impacts**

The Manor House, University of Birmingham.

29th and 30th March, 2006

Wednesday, 29th March

The Hall, Library and Old JCR

10.00 - Reception, coffee, poster and trade exhibition

Session 1 (Chair, Stuart Harrad) - New JCR

11.00 – Welcome, Dr. Stuart Harrad

11.10 – PLENARY “BROMINATED FLAME RETARDANTS” - Mehran Alaei,
Water Science and Technology Directorate, Environment Canada, Burlington,
Ontario, Canada

12.10 – “Dietary Exposure to PBBs, PBDEs, and PBDD/Fs in the United Kingdom”,
Kyle D’Silva, Central Science Laboratory, York, U.K.

12.35 – “Analytical Protocols for the Determination of Polybrominated Flame
Retardants in Complex Matrix Samples”, John Upton, Varian Ltd., Yarnton, Oxford,
U.K.

13.00 – lunch (Dining Room)

Session 2 (Chair, Eric Aries) - New JCR

14.00 – PLENARY “POPs IN CITIES” - Miriam Diamond, Centre for Urban Health
Initiatives, Department of Geography, University of Toronto, Canada

15.00 – “PCBs and PBDEs in Indoor Environments: Levels and Implications”,
Sadegh Hazrati, Division of Environmental Health & Risk Management, University
of Birmingham, U.K.

15.25 - “Atmospheric Concentrations of PCBs and PBDEs on a Rural:Urban:Rural
Transect”, Stuart Harrad, Division of Environmental Health & Risk Management,
University of Birmingham, U.K.

The Hall, Library and Old JCR

15.50 – tea, poster and trade exhibition

New JCR, Session 4 (cont.)

16.15 – “The Measurement of Bioaccessible Benzo[*a*]pyrene in Contaminated Soils using a Physiologically-Based Extraction Test”, Joanna Wragg, British Geological Survey, Nottingham, U.K.

16.40 – “DDT in Great Lakes Air: Long-Range Transport or Home-Grown?”, Terry Bidleman, Centre for Atmospheric Research Experiments, Environment Canada, Toronto, Canada

The Hall, Library and Old JCR

17.10 – poster session and trade exhibition (to 18.40)

Dining Room

19.00 – Conference Dinner, followed by...

20.30 (approx.) to late – drinks reception in bar (sponsored by SAL Ltd.)

Thursday 30th March

Dining Room

07.30 – 08.15 – breakfast

Session 3 (Chair, Tanja Pless-Mulloli) - New JCR

8.30 – PLENARY “RISK ASSESSMENT AND TOXICOLOGY OF POPs: DIOXIN AS A MODEL, David Bell, University of Nottingham, Nottingham, U.K.

9.30 – “Dioxin profiles in two Spanish families in follow-up studies of accidental poisoning by consuming contaminate olive oil”- Andrew Smith, MRC Toxicology Unit, Leicester University, U.K.

9.55 – “An Assessment of Toxicity in profundal Lake Sediments due to the deposition of Heavy Metals and POPs from the Atmosphere”, Brian Rippey, School of Environmental Sciences, University of Ulster, U.K.

The Hall, Library and Old JCR

10.20 - coffee, poster and trade exhibition

New JCR, Session 3 (cont.)

10.45 – “The Fate of Chiral Organochlorine Compounds and Selected Metabolites in Intraperitoneally Exposed Arctic Char (*Salvelinus Alpinus*)”, Karin Wiberg, Dept. of Chemistry, Umeå University, Sweden

11.10 – “Stable Isotope ratios of POPs – a tracer that can lead to the origins of pollution”, Walter Vetter, Institute of Food Chemistry, University of Hohenheim, Germany.

11.35 – “Pharmaceuticals and Personal care Products (PPCP) – Candidate Environmental Pollutants with Increasing Impact”, Heinrich Hühnerfuss, Institute for Organic Chemistry, University of Hamburg, Germany

Dining Room

12.00 - lunch

Session 4 (Chair, Chris Wright) – New JCR

13.00 – PLENARY “STATE OF THE ART AND THE FUTURE FOR POPs ANALYSIS”, Jacob de Boer, RIVO, The Netherlands.

14.00 – “The Supelco “Dioxin Prep System – Florisil Version”: A Multilayer Silica Gel Column Connected in Series to an Activated Florisil Microcolumn for Rapid Determinations of PCDD/Fs and PCBs in Environmental Samples”, Eric Aries, Corus Research, Swinden Technology Centre, Rotherham, U.K.

14.25 – “Occurrence and Fate of the Cytostatic Drugs Cyclophosphamide and Ifosfamide in Wastewater and Surface Waters”, Ignaz Buerge, Plant Protection Chemistry, Swiss Federal Research Station (Agroscope), Wädenswil, Switzerland

14.50 – “Extraction of POPs from Environmental Samples using Accelerated Solvent Extraction (ASE)”, Frank Höfler, Dionex Europe, Olten, Switzerland

15.15 – Closing Remarks and Presentation of Prize (sponsored by LGC Promochem) for Best Student Presentation

15.30 – Coffee and Close

BROMINATED FLAME RETARDANTS

Mehran Alaei

Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Rd.,
P.O. Box 5050, Burlington, Ontario, L7R 4A6

Long before mankind learned to harness fire as a source of energy, he was horrified by the devastation caused by it. Fire is still a major source of damage to properties and loss of life. In Canada on average between 1986-1995, 67 000 fires were reported each year, which resulted 3700 injuries, 465 deaths, and over \$1.125 billion in damage to properties. Recent advances in technology have resulted in an increase in use of synthetic polymers, electronic equipment, and other ignitable materials loads in our commercial and residential habitat. This has drastically contributed to fire hazard. In order to reduce the chances of ignition and burning of these materials the application of flame-retardants has increased.

Flame-retardants are materials that are added to polymers (natural and synthetic) to significantly increase the resistance of a wide range of industrial and consumer products to fire. The idea of flame retardant materials dates back to about 450 BC, when the Egyptians used alum to reduce the flammability of wood. Today, there are more than 175 chemicals classified as flame-retardants. Flame-retardants are divided into four major groups: inorganic, halogenated organic, organophosphorus and nitrogen based flame-retardants which account for 50%, 25%, 20% and >5% of the annual production, respectively. Currently brominated flame-retardants (BFRs) are the second largest class of flame-retardants in use. The annual market demand for these compounds rose from 150,000 in 1994 to 204,000 metric tones in 2001. BFRs are divided into three subgroups: reactive, additive, and polymeric. Reactive flame-retardants, such as tetrabromobisphenol A (TBBPA), are chemically bonded into the plastics; additive flame-retardant compounds, such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are simply mixed together with the rest of the polymers; and polymeric, where brominated monomers, such as, brominated styrene is incorporated into the polymer.

Currently there are more than 75 different chemicals used as BFRs. However, only TBBPA, PBDEs, and HBCD are produced in large volumes. PBDEs were the first group of BFRs to be detected in the environment. In 1979, the presence of BDE-209 was measured in soil and sludge samples collected from areas surrounding PBDE manufacturing facilities in the U.S. Recent data indicated that levels of PBDEs are on the rise in North American environment. TBBPA has been observed in sewage sludge from across North America and in suspended solids from Detroit River. HBCD has been observed in biota and in abiotic environment in Europe and North America. Current isomer specific studies of HBCD indicated preferential bioaccumulation of α -HBCD.

In this presentation an overview of the levels and trends of PBBs, PBDEs, TBBPA, HBCD and other emerging BFRs in environmental matrices will be presented.

DIETARY EXPOSURE TO PBBs, PBDEs AND PBDD/Fs IN THE UNITED KINGDOM

Kyle D'Silva and Alwyn Fernandes,
Central Science Laboratory, Sand Hutton, York, Y041 ILZ

There is increasing concern over the toxicity and environmental distribution of a number of brominated organic contaminants including polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) used as flame retardants; and brominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs). Observed ubiquity, bio-accumulative characteristics and dioxin-like toxicity have led some of these compounds to be classified as POPs.

Dietary intake is a primary vector for human exposure to many POPs. Therefore, it is important to accurately determine the extent of human exposure to POPs in order to quantify their associated risk. In general a total diet study provides a good estimate of dietary contaminant intake for a country as a whole. In addition, total diet studies take into account the kitchen preparation of foods to assess the levels of contaminants in foods as consumed.

The modern United Kingdom Total Diet Study (TDS) is harmonised with a national food survey (NFS) program based on consumption surveys. The TDS is based on an analysis of retail foods prepared as if for consumption and combined into composite samples representative of a defined food group in amounts reflecting their relative importance in the typical UK diet. The food groups studied were bread, cereals, carcass meats, offal, meat products, poultry, fish, oils and fats, eggs, sugars and preserves, green vegetables, potatoes, canned vegetables, other vegetables, fresh fruit, fruit products, milk, dairy products, and nuts.

A robust analytical method for PBDEs, PBBs and PBDD/Fs was developed, validated and accredited (ISO17025). The method is outlined elsewhere [1]. Composite TDS samples from 1992, 1997, 2000 and 2001 were analysed for; 34 di- to hepta- bromo diphenyl ethers; 5 tetra- to hexa- bromo biphenyls and 11 laterally substituted tri- to heptabromo-dibenzofurans and dibenzo-p-dioxins.

This is the first structured comprehensive study of dietary exposure to this range of contaminants. PBBs and PBDD/Fs were determined in only about a dozen samples; BB-153 dominating the biphenyl profile. Tri- to tetra-BDFs dominated the profile of bromodioxins. Dietary exposures were calculated using accurate NFS consumption statistics for each composite food group, for each sampling year. Dietary exposure was consistently low for PBBs (Σ PBB 0-0.1 ng/day) and PBDD/Fs (Σ PBDD/Fs WHO-TEQ* 0.3 pg/day in 1992, to WHO-TEQ 6.5 pg/day in 2000).

PBDEs were detected above the LOQ in every foodstuff sample tested. Dietary exposure to PBDEs appears to have reached a maxima in the late 1990s (Σ PBDE 163.1 ng/day in 1997) and has shown a marked decrease in more recent years (Σ PBDE 78.4 ng/day in 2001). This trend is in agreement with recent trends of PBDEs in breast milk from Sweden [2]. Further work must be conducted to see if the trend continues with more recent samples.

1. Fernandes, A., White, S., D'Silva, K., and Rose, M., *Talanta.*, 63 (5), **2004**, p.1147-1155.
2. Lind, Y., Darnerud, P. O., Atuma, S., Aune, M., Becker, W., Bjerselius, R., Cnattingius, S., and Glynn, A., *Environmental Research.*, 93 (2), **2003**, p.186-194.

* Interim TEQ based on PCDD/F analogue TEFs

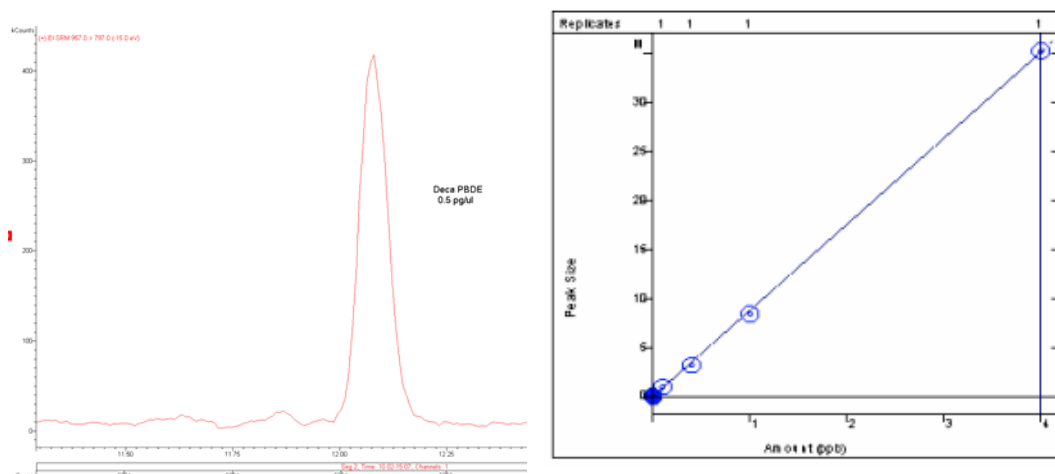
ANALYTICAL PROTOCOLS FOR THE DETERMINATION OF POLYBROMINATED FLAME RETARDANTS IN COMPLEX MATRIX SAMPLES

J Upton and E Lewis,
Varian Ltd, Oxford Industrial Park, Yarnton, Oxford, OX5 1QU

Polybrominated Diphenylether flame retardants, PBDEs, are widely recognised as being present within the environment and are potentially hazardous to health. The growing demand for the routine analysis of such compounds has pushed existing analytical methodologies to their limits due to two main factors. Firstly, and not uniquely to PBDEs, they need to be determined with a high degree of confidence at very low concentrations within complex environmental matrices. Secondly, the molecular weight of the highly brominated species means that conventional GC/MS methodology often does not produce acceptable chromatographic performance.

This work outlines a cost effective analytical approach in which negative pressure chromatography is used to effect an optimal chromatographic profile for a range of PBDEs, including the deca-PBDEs, in under 12 minutes. This optimal chromatography is complemented by quadrupole based MS/MS to achieve both a very selective and a very sensitive detection protocol. The work looks at both EI-MS/MS and NCI-MS/MS in terms of selectivity, sensitivity and the applicability to congener specific or formulation type interpretation.

Detection limits and matrix examples are presented in context alongside both the current and proposed legislative aspects.



POPs IN CITIES

**Miriam Diamond,
Department of Geography and Centre for Urban Health Initiatives
University of Toronto
Toronto, Canada**

Cities are home to two-thirds of the world's population and nearly three-quarters of the population of developed countries. As such, it is not surprising that the largest mass of chemicals, including hazardous chemicals, is incorporated within the built environment of cities. In addition to this standing stock of chemicals, the wide range of human activities undertaken in cities results in emissions to virtually every medium. Consequently, concentrations of many contaminants are typically 10 fold higher in urban than nearby rural sites. This 10-fold difference occurs for legacy as well as current use POPs, where the cities still retain a significant repository of legacy POPs such as PCBs.

The built environment influences the fate and hence exposure pathways of contaminants. The built environment is typically a highly simplified system characterized by impervious surfaces, an altered hydrologic regime that maximizes water movement, and extremes in microclimatic conditions. Surface films, which coat impervious surfaces and change their functionality, promote contaminant mobility by acting as a sink/source of atmospherically deposited contaminants in relation to air and water. Thus, the built environment tends to maximize the mobility of contaminants, notably through export via air to downwind locations (i.e., agricultural areas) and movement via stormwater to surface waters (and eventually the aquatic food web). Conversely, a small fraction of total emissions is retained in media within cities (e.g., soils).

Contaminant emissions from, and enhanced mobility in cities control our exposure pathways to contaminants. Our greatest exposure to legacy POPs such as PCBs, which have been released and transported from cities for decades, is through our food supply. However, for current use POPs such as PBDEs, exposure is closer to the source of emission (e.g., dust). Over time, contaminant fate processes are expected to shift exposure from these proximal sources to our food supply. This consideration has important implications for public health and regulatory initiatives.

Finally, we need to relate contaminant sources, emissions, transport processes and exposures to potential health effects. Current emissions that generate air pollution, for example, have the potential to cause immediate to intergenerational health effects. Interestingly, despite the higher contaminant concentrations in urban areas, city-dwellers tend to experience better health than their rural counterparts, in part due to access to health care. However, a closer analysis of health effects shows that socio-economic status is a critical mediator of health impacts, with those of lower socio-economic status having the poorest health outcomes. Future studies need to understand contaminant sources, transport and exposure pathways in cities within a context of temporal and socio-economic factors to better understand the importance and most effective regulatory measures that will reduce exposure and potential health effects from POPs.

POLYCHLORINATED BIPHENYLS (PCBs) AND POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN INDOOR ENVIRONMENTS: LEVELS AND IMPLICATIONS

**Sadegh Hazrati and Stuart Harrad,
Division of Environmental Health & Risk Management, School of Geography,
Earth & Environmental Sciences, University of Birmingham.**

Although human exposure to POPs is widely considered to occur almost exclusively *via* the dietary pathway; the application of PCBs in building materials and PBDEs in products employed indoors (*i.e.* furniture, electronic and electrical equipment) along with the high proportion of time spent in such environments (*i.e.* typically more than 90%), highlight the potential role of contaminated indoor environments as major sources for human exposure *via* dust digestion or inhalation. To investigate levels and behaviour of PCBs and PBDEs in indoor air, PUF disk passive air samplers were deployed in 59 different indoor microenvironments including 24 homes, 24 offices and 11 private cars for sampling periods of approximately one month. Furthermore, 3 offices and 4 homes were monitored over a period of 12 months in which detailed sampling was conducted on a monthly basis in two separate rooms (*i.e.* living room and bedroom) of the same homes and the same office buildings.

Σ PCB concentrations varied from 1.2 to 99.3 (mean = 17.2) ng m^{-3} , 0.60 to 9.8 (mean = 2.6) ng m^{-3} , and 0.41 to 2.5 (mean = 1.3) ng m^{-3} in offices, homes and cars, respectively. Σ PBDE concentrations ranged between 10 and 1,416 (mean = 166) pg m^{-3} , 4 and 168 (mean = 44) pg m^{-3} , and 11 and 8,203 (mean = 1568) pg m^{-3} in offices, homes, and cars respectively. Offices and cars were identified to be the most contaminated microenvironments within the studied locations for PCBs and PBDEs, respectively.

Comparison of target pollutants in two microenvironments of the same home/office buildings revealed statistically significant differences in Σ PCB ($p=0.0139$) and Σ PBDE concentrations ($P=0.0002$) in the two different rooms of one home. Similar differences were observed for Σ PBDE concentrations in one of the office buildings studied ($p=0.0047$). These intra-building variations may be due to the presence of different source types and numbers in each microenvironment.

One-way variance analysis showed statistically significant seasonal variability in analyte concentrations in some locations. These include one office (highest in summer) for PCBs and one home (highest in summer) and one office for PBDEs (where concentrations fell 3-4 fold after replacement of an older PC). For the other monitoring locations, differences in pollutant concentrations were not statistically significant but the ratio of the maximum to minimum concentration over the whole monitoring period varied from 1.5 to 2.1 for PCBs and from 1.6 to 7.8 for PBDEs.

Given an average adult respiration value of $20 \text{ m}^3 \text{ d}^{-1}$, and assuming that people spend 67.9%, 23.8%, 2.9% and 5.4% of their time at home, in the workplace, on public transport and private cars, and outdoors, respectively, mean daily exposure from inhalation of $118.9 \text{ ng day}^{-1}$ for Σ PCB and 2.3 ng day^{-1} for Σ PBDE may be estimated. However, the wide variability of concentrations in indoor environments along with the intra-building and seasonal variability in PCB and PBDE concentrations mean that inhalation exposure could be much higher during some periods for some people.

**ATMOSPHERIC CONCENTRATIONS OF POLYCHLORINATED
BIPHENYLS (PCBs) AND POLYBROMINATED DIPHENYL ETHERS
(PBDEs) ON A RURAL:URBAN:RURAL TRANSECT**

**Stuart Harrad and Stuart Hunter,
Division of Environmental Health & Risk Management, School of Geography,
Earth & Environmental Sciences, University of Birmingham.**

Outdoor air samples were collected using PUF disk passive samplers from 10 sites within the West Midlands conurbation in the UK. Sampling sites were located at intervals of between 3 and 17 km across the conurbation on a southwest (upwind) to northeast (downwind) transect, ranging from 48 km upwind to 31 km downwind. In this way, a mix of rural, suburban, and urban sampling locations were studied. Samples (n=11 at each site) were collected at approximately monthly intervals at each site between August 2003 and October 2004. A total of 78 individual tri-through hepta-PCBs were monitored, along with PBDEs 28, 47, 99, 100, 153, and 154. For both PCBs and PBDEs, an “urban pulse” effect was observed, *i.e.* concentrations at the city centre were markedly higher than those elsewhere on the transect. This effect was more pronounced for PCBs than for PBDEs. This is possibly due to the higher gradient of indoor:outdoor air concentrations for PCBs. The impact of urbanisation is further illustrated by the fact that for both Σ PCB and Σ PBDE there is a significant ($p<0.001$) negative correlation between distance from the city centre and atmospheric concentrations. This effect was not seasonally-dependent. Examination of seasonal variation in concentrations revealed that for most locations, Σ PCB was positively related to air temperature, with the greatest temperature-dependence observed at the city centre site. In contrast, for Σ PBDE, a correlation with temperature was only observed at the city centre site. This implies different sources and/or emission pathways to outdoor air for the 2 compound classes.

THE MEASUREMENT OF BIOACCESSIBLE BENZO(A)PYRENE (BaP) IN CONTAMINATED SOILS USING A PHYSIOLOGICALLY BASED EXTRACTION TEST

**Joanna Wragg, Ian Harrison and Mark Cave,
British Geological Survey, Keyworth, Nottingham, NG12 5GG**

Polycyclic aromatic hydrocarbons (PAHs) are common soil contaminants both in the UK and worldwide, being present at old coal gas manufacture sites and in commercial products such as creosote. The determination of the amount of the total concentrations of PAHs in soils, and other media, is important due to the mutagenic and carcinogenic nature of many of the individual compounds that make up this class of contaminant (Weissenfels et al., 1992; Harvey, 1996). In addition to the measurement of the total concentrations of these potentially harmful contaminants, the need to determine the bioaccessible concentrations, the fraction of contaminant available for uptake in the human gastrointestinal tract, is becoming increasingly important in the UK.

Benzo(a)pyrene (BaP) is a 5 member ring PAH with the chemical formula $C_{20}H_{12}$. Because of its high molecular weight, this contaminant degrades in the environment at a slow rate and as a result is deemed to be a persistent organic pollutant. B(a)P poses a potential risk to human health because of its resistance to degradation and its potential mutagenic and carcinogenic effects.

The aim of this work was to estimate the amount of B(a)P available for uptake in the gastrointestinal tract, via oral ingestion of PAH contaminated soils. Soils, collected from a contaminated gas works site in the north of England, were subjected to a modified physiologically based extraction test (PBET). The PBET method, originally developed for inorganic contaminants, was modified for the determination of organic contaminants, which were quantified by subsequent HPLC analysis. A summary of the difficulties encountered with PAH contamination will be given along with the procedures used to overcome these problems. The results of the modified method will be given for a variety of contaminated soils.

Harvey, R.G. Polycyclic aromatic hydrocarbons. New York: Wiley-VCH, 1996.

Weissenfels, W.D., Klewer, H.-J., Langhoff, J., 1992. Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particules: influence on biodegradation and biotoxicity. *Appl. Microbiol. Biotechnol.* 36. 689-696.

DDT IN GREAT LAKES AIR: LONG-RANGE TRANSPORT OR HOME-GROWN?

**Terry Bidleman and Celine Audette,
Centre for Atmospheric Research Experiments, Environment Canada, Egbert,
ON, Canada**

**Fiona Wong, Ralf Staebler and Pierrette Blanchard,
Environment Canada, Downsview, ON, Canada**

**Henry Alegria,
Chemistry Department, California Lutheran University, Thousand Oaks, CA,
USA**

**Perihan Kurt-Karakus and Kevin Jones,
Department of Environmental Sciences, Lancaster University, Lancaster, UK**

Atmospheric transport of DDT to the Laurentian Great Lakes is still occurring, more than 30 years after its ban in Canada and the U.S. Possible sources are transport from Mexico-Central America and emission of old residues in soils. Atmospheric measurements of DDTs in southern Mexico and at Integrated Atmospheric Deposition Network (IADN) stations in the Great Lakes region were compared, with particular emphasis on the proportions of DDT compounds as indicators of source and residue age. Concentrations of total DDT in the air of southern Mexico were 1-2 orders of magnitude greater than those at IADN stations. Among the IADN stations, the Illinois Institute of Technology site in Chicago stood out as the one with highest total DDT concentrations. The possibility of DDT emissions from soil residues was confirmed by measuring fluxes from an agricultural soil in southern Ontario. Ratios of p,p'-DDT to its metabolite p,p'-DDE (DDT/DDE) in air were compared with those predicted from emission of soil residues in the Great Lakes region and southern U.S.A. DDT/DDE ratios decreased in the order: Mexico-Central America > IADN air samples ~ predicted emissions from agricultural soils in the midwest U.S.A. and Ontario > predicted emissions from southern U.S. agricultural soils. Results suggest that midwest soils and urban areas contribute to maintaining atmospheric DDT levels in the Great Lakes region.

RISK ASSESSMENT AND TOXICOLOGY OF POPs: DIOXIN AS A MODEL

**David R Bell,
School of Community Health Sciences, University of Nottingham, University
Park, Nottingham, NG7 2RD**

The poly-halogenated dioxins and polychlorinated biphenyls (PCBs) are a class of chemicals which are both persistent, and cause toxic effects through their action on a common cellular receptor, the AhR. Because of this common mode of action, the chemicals in this grouping are regulated through a common risk assessment, and related to the toxicity of the prototypical and potent congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin through chemical-specific Toxic Equivalent Factors (TEFs).

Although dioxins have a fearsome reputation, there are no reports of acute human lethality from dioxin poisoning. Whilst dioxin in sufficiently high dose can be acutely toxic in human, the evidence for adverse effects in human at lower doses, such as carcinogenicity, is controversial. Consequently, the risk assessment for dioxins in the EU and UK is based on experiments conducted in animal models.

Current risk assessments are based on the most sensitive endpoint of toxicity in animal models, which was determined to be the developmental exposure of the developing rat fetus, resulting in defects in the adult male reproductive capacity. I present a review of the literature on this effect, and present the results of a study evaluating the effects of developmental dioxin exposure on the reproductive tract of male rats.

Part of this work was funded by the Food Standards Agency under contract no T01034 (Risk Assessment of Dietary Dioxins).

**DIOXIN PROFILES IN TWO SPANISH FAMILIES IN FOLLOW-UP
STUDIES OF ACCIDENTAL POISONING BY CONSUMING
CONTAMINATED OIL**

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In 1991 we reported studies of a family living in the region of Sevilla in Spain who were poisoned in 1982 by consuming cooking olive oil that had been contaminated apparently by hexachlorobenzene. Mother, father and six children all developed differing severities of chloracne the only proven human consequence of dioxin poisoning but not of hexachlorobenzene. One additional child was exposed *in utero* [1]. Preliminary gas chromatography analysis confirmed the presence of hexachlorobenzene but also showed the presence of pentachlorophenol and the more chlorinated dibenzo-*p*-dioxin and dibenzofuran congeners. Detailed GC-MS of recovered oil confirmed the presence of chlorinated dibenzo-*p*-dioxins and furans especially the 1243678-hepta- and octachloro compounds. Analysis of a pooled serum sample from some of the patients showed a similar distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. In 1990 another family, unrelated, were discovered in the same region that had also developed chloracne from contaminated cooking oil. Individual samples of serum were obtained from all members of both families and analysed. The patterns of congeners were not identical between families. In 1996 all members of the first family plus 2 grandchildren and most members of the second family were re-examined. The differences in levels after the six years are presented. Serum levels in most, but not all, patients had fallen. Dioxins were apparently passed from a daughter in family one, subsequently married after exposure as an 11 year old, to her own daughters. Since in some experimental animals immune competence has been compromised by dioxin immune competence was also assessed including lymphocyte subpopulations. No long-term abnormalities of immune competence compared to control subjects were detected. We also detected an abnormal porphyrin in urine in some Austrian patients exposed to TCDD 25 years previously possibly indicating disturbed liver function [2]. This was found in the urine of some members of family 1 in 1990 and 1996. Contact with the families has been lost.

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AN ASSESSMENT OF TOXICITY IN PROFUNDAL LAKE SEDIMENT DUE TO THE DEPOSITION OF HEAVY METALS AND PERSISTENT ORGANIC POLLUTANTS FROM THE ATMOSPHERE

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The concentrations of seven heavy metals and four groups of POPs (OCs, PCBs, PAHs, PBDEs) were determined in surficial sediment from the profundal area of ten lakes in the United Kingdom and two sediment toxicity tests completed (chironomid survival and emergence and cladoceran survival and reproduction). The lakes are contaminated by heavy metals and POPs deposited from the atmosphere and were chosen to represent the range of contamination found in the UK. The results showed that between 5 and 7 of the lakes, depending on the chemical or chemical group, are contaminated by Pb, Zn, Cd, As, PCBs, PAHs and PBDEs. The toxicity quotient suggested that the contaminants of concern are Pb, Ni, As and PAHs, and not the other metals nor OCs and PCBs. The toxicity tests showed that there was toxicity in the sediment of four of the lakes. A comparison of the relationship between the incidence of toxicity and the Probable Effect Concentration Quotient for seven heavy metals (PEC-Q Mean-metals) in the UK lake sediments with the general relationship for freshwater sediment indicated that metals in the sediments of Scoat Tarn, Agden Reservoir and Llyn Llagi are likely to be responsible for the toxicity found, with PAHs also contributing in Agden Reservoir. An investigation of the relationship between PEC-Q Mean-metals and biological effects in freshwater sediment was made using a data set of six studies and this suggests that effects are likely if PEC-Q Mean-metals is greater than approximately 2. As the highest PEC-Q value measured in the UK lake sediments was 1.1, biological effects in the profundal sediment of these lakes due to deposition of heavy metals from the atmosphere may not be likely, although this finding is inconsistent with the laboratory toxicity found in the sediment of three of the lakes.

**THE FATE OF CHIRAL ORGANOCHLORINE COMPOUNDS AND
SELECTED METABOLITES IN INTRAPERITONEALLY EXPOSED
ARCTIC CHAR (*SALVELINUS ALPINUS*)**

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The fate of chiral organochlorine (OC) compounds and selected metabolites in exposed Arctic char (*Salvelinus alpinus*) was investigated. The contaminants α -hexachlorocyclohexane (α -HCH), *cis*-chlordane, $^{13}\text{C}_4$ -heptachlor, *o,p'*-DDT and the atropisomeric chlorinated biphenyls (CBs) CB-95, CB-132, CB-136, CB-149 and CB-174 were solved in peanut oil and injected into the peritoneal cavity. The exposed fish were sampled three times during a 5-week period, and the OC residues and detected metabolites (heptachlor-*exo*-epoxide) were quantified in muscle and liver tissues by chiral and achiral gas chromatography (GC) - mass spectrometry and GC-electron capture detection. Peak concentrations were reached after 1-2 weeks, and thereafter the levels declined. At the end of the experiment, liver concentrations had decreased 76-92% relative to peak concentrations, while muscle concentrations showed moderate decline (5-38%) with the exception of α -HCH (91%). Hydrophobicity and steric hindrance were shown to influence the assimilation process, and a significant linear relationship between the product of the steric hindrance coefficients and the inverse of the octanol-water partition coefficients (K_{ow}) versus peak concentration was found for the CBs ($r^2=0.86$, $p=0.02$). The assimilation of the contaminants into muscle and liver tissues generally resulted in racemic mixtures, while elimination was enantioselective for α -HCH, *cis*-chlordane and *o,p'*-DDT, CB-132 and CB-136. The chiral heptachlor metabolite $^{13}\text{C}_4$ -heptachlor-*exo*-epoxide was formed in the fish. The enantiomeric composition of the formed metabolite indicated racemic formation, while the elimination process appeared to be enantioselective.

STABLE ISOTOPE RATIOS OF POPs – A TRACER THAT CAN LEAD TO THE ORIGINS OF POLLUTION

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Several organohalogen compounds are persistent organic pollutants (POPs) or persistent, bioaccumulative and toxic chemicals (PBTs) whose use and environmental fate and effects are under close inspection by scientists, residue control authorities, and (eco)toxicologists. Nowadays, the *occurrence* of PBTs in the environment is well-documented but their *origin* if somewhat away from a specific production source can only be estimated when the PBT was produced in different countries. In such a case determination of stable isotopes by MS or NMR can be a valuable tool to elucidate a specific product as the source of pollution in a sample. Stable isotope ratio mass spectrometry (IRMS) is able to determine minute mass-dependent effects in structurally identical compounds owing to lower mobility and higher binding energies of the heavier isotopes [1]. Consequently, IRMS has been applied in different disciplines of natural sciences for the differentiation of structurally identical compounds that may stem from different sources. Initial studies in the field of PBTs focused on the determination of $^{13}\text{C}/^{12}\text{C}$ and $^{37}\text{Cl}/^{35}\text{Cl}$ ratios [2-5].

In this presentation we discuss the progress of our attempts to use isotopic data to distinguish PBTs with the same structure that differ only in their way or place of production. We used EA-IRMS and GC-IRMS to identify differences in the $\delta^{13}\text{C}$ values of two products of technical toxaphene. Investigation of the $\delta^{13}\text{C}$ value of two key toxaphene congeners in a sample from the Antarctic indicated that long-range transport and food-chain enrichment do not alter the stable carbon isotope ratio significantly. However, an assignment of the residues in the Antarctic to the one or the other source could not be established. Therefore, more isotopic data was required.

While standard IRMS equipment does allow for $\delta^{13}\text{C}$ value determinations, a direct determination of $\delta^2\text{H}$ values is not possible due to the formation of hydrochloric acid instead of H_2 [6]. To overcome this drawback, we constructed a chromium reactor and incorporated it into the IRMS system. This novel system was used to demonstrate that toxaphene and hexachlorocyclohexane isomers (HCHs) from different sources differ in their $\delta^2\text{H}$ content. Surprisingly large differences for DDT and metabolites were also determined. Quantification of individual ^2H isotopomers by NMR was used as an accompanying technique for the explanation of some of the results.

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PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCP) – CANDIDATE ENVIRONMENTAL POLLUTANTS WITH INCREASING IMPACT

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The fact that the population in Europe is ageing is well known and when people get older the demand for health care increases too. As a consequence, pharmaceuticals are increasingly consumed which in turn, via the domestic waste water pipes, reach the sewage treatment plants (STP). Finally, the non-transformed parent compounds and/or the respective transformation products are being dumped into the aquatic ecosystem thus giving rise to a new class of environmental pollutants. As an example, the transformation of ibuprofen was monitored both for a STP without a biological treatment step (Tromsø, Norway) and for a STP exhibiting a state-of-the-art biological treatment unity (Hamburg, Germany). The different concentration patterns of the parent compound and the two transformation products hydroxyibuprofen and carboxyibuprofen will be presented herein. Furthermore, the different enantioselective transformation pathways of ibuprofen and its two transformation products occurring within these two STPs, within the adjacent rivers and the marine environment were documented using enantioselective gas chromatography. Additional pharmaceuticals monitored during this project included triclosan, diclofenac, propranolol, metoprolol, sertraline, paroxetine, carbamazepine and clofibric acid.

Furthermore, personal care products such as musk compounds and their transformation products were investigated. Musk is an odoriferous animal product and one of the oldest-known ingredients of perfumes. Laboratory synthesis of surrogates permitted cheap synthetic chemicals to replace the animal products. In particular, nitro musks like musk xylene (MX) and musk ketone (MK) have been widely used as fragrance ingredients in soaps, laundry detergents and cosmetics. In view of the increasing public concern on nitro musks and their metabolites in various environmental compartments, polycyclic musk fragrances on the basis of indane and tetraline structures play an increasing role, in particular, galaxolide[®] (HHCb) as well as tonalide[®] (AHTN) gain a prominent importance.

In the present study, the concentrations and the transformation pathways both for nitro musks and polycyclic musks were followed from the inflow into and the outflow out of the STPs, within the STP pond and the adjacent rivers until the marine environment. In the case of the chiral polycyclic musks, our study also included the enantioselective transformation pathways in these different compartments. As a tracer compound that can be unequivocally related to domestic sewage, caffeine was identified, quantified and traced back from the marine environment until the domestic sewage pipe outflows.

STATE OF THE ART AND THE FUTURE FOR POPs ANALYSIS

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In spite of bans and other regulations to prevent further contamination of the environment and our food, persistent organic pollutants (POPs) are still being found at significant levels in many matrices. In some areas some of the POPs such as polychlorinated biphenyls (PCBs) tend to decrease. However, other 'new' POPs have been found recently. Examples are various brominated flame retardants, and the perfluorinated compounds. Over the last 30-40 years analytical methods have been improved both in selectivity and sensitivity. Whereas in the 1970s mg/kg concentrations were close to detection limits, nowadays ng/kg concentrations do not pose serious problems anymore for most chemists. On the other hand progress is often not as fast as we would wish. From international interlaboratory studies it appears that laboratories need several years to develop reliable methods for 'new' contaminants such as decabromodiphenylether or hexabromocyclo-dodecane. The first international interlaboratory study on perfluorinated compounds showed very high coefficients of variation for most of the target compounds in environmental matrices. It is in particular the phase between the first set-up of a method and the full validation of it that requires a considerable amount of time and effort of the analytical chemist. Step-wise designed interlaboratory studies help the chemist to improve the quality of his/her method. However, a world-wide lack of certified reference materials hinders a proper validation.

Pressure on laboratories from authorities asking for faster methods has pushed research on acceleration of extraction and clean-up. The European research project DIFFERENCE has shown that considerable time can be gained by the application of accelerated solvent extraction (ASE) or pressurised liquid extraction (PLE) in combination with a clean-up. The use of a fat retainer in a proper ratio in the extraction cell was a major step forward in this field and saves the technician at least a day during a series of dioxin or PCB analyses.

Ongoing research on chromatographic methods has offered new GC methods such as comprehensive two-dimensional gas chromatography (GCxGC) which is now robust enough for routine use in the analysis of complex mixtures of contaminants, and new LC methods such as UPLC and various combinations of HPLC and MS detection (triple-quad and others), that can be used for the determination of flame retardant and perfluorinated compounds.

**THE SUPELCO “DIOXIN PREP SYSTEM - FLORISIL VERSION” : A
MULTI-LAYER SILICA GEL COLUMN CONNECTED IN SERIES TO AN
ACTIVATED FLORISIL MICRO-COLUMN FOR RAPID
DETERMINATIONS OF PCDD/Fs AND PCBs IN ENVIRONMENTAL
SAMPLES**

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In 2003, Supelco launched in the UK a new sample preparation kit for rapid clean-up of dioxins, namely polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The so-called “Dioxin Prep System” was composed of a multi-layer silica gel column and of a dual-layer carbon cartridge connected in series. This system aimed at shortening considerably sample preparation time while maintaining high accuracy for performing PCDD/F analysis. Before this system became commercially available, Hall Analytical Laboratories and the Environment Department of Corus R, D and T (particularly its Trace Organic Analysis Laboratory) were invited by Supelco to evaluate it alongside their existing UKAS ISO 17025 accredited procedures. Results showed that the 'Dioxin Prep System' could significantly reduce the sample preparation time while maintaining high accuracy for performing the analysis of PCDD/Fs (2 days of sample pre-treatment vs. 3-4 days using a standard analytical procedure)¹.

In 2004, Corus and Hall Analytical agreed to collaborate with Supelco on the development of an enhanced version of the “Dioxin Prep System” that would allow fast analyses of polychlorinated biphenyls (PCBs) as well as PCDD/Fs. This new sample preparation kit is now composed of a multi-layer silica tube connected in series to a new designed micro-column packed with activated Florisil (1 g), which is provided for each sample in sealed ampoules. A vacuum manifold also provides a steady and efficient means to control the flow rate during the sample preparation.

Analytical developments were carried out by both Corus UK and Hall Analytical to set up and validate an experimental procedure suitable for the analysis of PCDD/Fs and PCBs using the so-called "Dioxin Prep System - Florisil Version". This was achieved using synthetic standard and certified reference materials. The methodology involves an extraction of environmental samples using accelerated solvent extraction (Dionex ASE 200). Sample extracts are loaded onto the silica and Florisil columns connected in series. A waste fraction containing PCBs is eluted with *n*-hexane, whereas PCDD/Fs are retained on the activated Florisil adsorbent. PCDD/Fs are then eluted from the Florisil micro-column using dichloromethane and analysed by HRGC - HRMS. For PCBs, a final basic alumina chromatographic step is used to separate them from interfering compounds such as saturated hydrocarbons, that may have an adverse effect on the final HRMS analysis stage if present in significant concentrations in the samples².

Both laboratories validated the methodology for the determination of the 17 toxic 2,3,7,8-PCDD/Fs and the 12 'dioxin-like' PCBs using a range of certified reference materials including soils, sediments, sewage sludge, fish tissue, stationary source emission samples, and intercalibration samples from Orebrö University. For all matrices, results were in very good agreement with the certified values and recoveries of ¹³C₁₂-PCDD/F or PCB internal standards were typically within the range 70% to 100%. For both laboratories, the use of the Supelco Dioxin Prep System - Florisil Version resulted in a significantly quicker turn-around than standard US EPA methods. Therefore, when it becomes commercially available, this sample preparation kit could constitute one of the fastest analytical solutions for the sample preparation of PCDD/Fs and PCBs from environmental matrices.

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OCCURRENCE AND FATE OF THE CYTOSTATIC DRUGS CYCLOPHOSPHAMIDE AND IFOSFAMIDE IN WASTEWATER AND SURFACE WATERS

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Cyclophosphamide and ifosfamide are important cytostatic drugs used in the chemotherapy of cancer and in the treatment of autoimmune diseases. Their mechanism of action, involving metabolic activation and unspecific alkylation of nucleophilic compounds, accounts for genotoxic effects described in literature and is reason for environmental concern. Occurrence and fate of cyclophosphamide and ifosfamide were studied in wastewater treatment plants (WWTPs) and surface waters in Switzerland, using a highly sensitive analytical method based on solid phase extraction and liquid chromatography-tandem mass spectrometry. The compounds were detected in untreated and treated wastewater at concentrations of < 0.3 - 11 ng/L, which corresponded well with concentrations, predicted from consumption data and typical renal excretion rates. Weekly loads determined in influent and effluent wastewater were comparable and suggested a high persistence in WWTPs. Furthermore, no degradation was observed in activated sludge incubation experiments within 24 h at concentrations of ≈ 100 ng/L. The elimination behavior in lake water was also studied with a set of incubation experiments in the laboratory. Extrapolated to natural conditions in surface waters, a slow hydrolytical degradation (half-lives in the order of years) is, apart from water exchange, the most important elimination process. Degradation by photochemically formed HO \cdot radicals may be of some relevance only in shallow, clear, and nitrate-rich waterbodies, but is expected to be important in advanced oxidation of, e.g., hospital wastewater. Concentrations finally measured in surface waters ranged from ≤ 50 to 170 pg/L and were thus by several orders of magnitude lower than the concentrations at which acute ecotoxicological effects have been reported in literature (mg/L range). However, due to lack of studies on chronic effects on aquatic organisms and data on occurrence and effects of metabolites, a final risk assessment can not be made.

EXTRACTION OF PERSISTENT ORGANIC POLLUTANTS POPs FROM ENVIRONMENTAL SAMPLES USING ACCELERATED SOLVENT EXTRACTION (ASE)

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Accelerated Solvent Extraction (ASE) is a modern extraction technique that significantly streamlines sample preparation. A common organic solvent as well as water is used as extraction solvent at elevated temperature and pressure to increase extraction speed and efficiency. The entire extraction process is automated and performed within 15 minutes with a solvent consumption of 18 mL for a 10-g soil sample.

For many matrices and a variety of analytes, ASE has proved to be equivalent or superior to sonication, Soxhlet, and reflux extraction techniques whilst requiring less time, solvent, and labour.

ASE has been mainly applied for the extraction of environmentally hazardous compounds from solid matrices such as soil, waste, and sludges. Within a short time ASE was approved by the U.S. EPA for the extraction of base, neutral and acidic semivolatile pollutants (BNAs), polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyles (PCBs), pesticides, herbicides, petroleum hydrocarbons, and polychlorinated dibenzodioxins and – furanes from solid samples in method 3545A. Especially for the extraction of polychlorinated dibenzodioxins and furanes the extraction time with ASE is reduced to 20 minutes compared to 18 hours using Soxhlet. For matrices with a high carbon content ASE demonstrated to achieve higher dioxin and furan extraction yields than the classical Soxhlet methods while the pattern of the congeners was unchanged.

For all 12 persistent organic pollutants according to the Stockholm Convention on POPs ASE is successfully used today. Especially for difficult to extract matrices such as pine barks or soils with high organic carbon content, ASE can deliver superior results than sonication or Soxhlet extraction.

Poster Presentation

HEXABROMOCYCLODODECANE DOES NOT ALTER GLOBAL DNA METHYLATION LEVELS IN THE THREE-SPINE STICKLEBACK (*GASTEROSTEUS ACULEATUS*)

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The use of brominated flame-retardants (BFRs) has raised a lot of concern in recent times. Unfortunately, there are only limited toxicological data on the impact of these newly identified environmental contaminants on living organisms. Structurally the BFRs are similar to dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs), environmental contaminants with known carcinogenic potentials. Hexabromocyclododecane (HBCD) is one of such BFRs, whose effect needs to be thoroughly investigated to provide a platform for appropriate risk assessment. Hence the effect of HBCD on global DNA methylation levels (an epigenetic event) in stickleback (*Gasterosteus aculeatus*) was measured using the isocratic reverse-phase high-performance liquid chromatography method. The effect of this contaminant at environmentally applicable and adverse effect levels (30ng/L and 300ng/L respectively) was tested in female stickleback liver (an anadromous species of fish) after exposure of the animals to the test compound for 30 days. Both groups of HBCD treatments as well as the DNA demethylating agent, 5 Aza 2 'deoxycytidine (5AdC, positive control) caused a decrease in global genomic methylation levels but these effects were not statistically significant. DNA hypomethylation is a frequent cause of chromosomal instability and proto-oncogene activation, which play key roles in the carcinogenic process. In fact, one of the most frequent and consistent observations in tumourigenic cells is the presence of generic DNA hypomethylation in association with hypermethylation of selected tumour suppressor genes in the genome. Hence, it is possible that HBCD might have caused some gene-specific effects, which can only be revealed when the hypermethylation or hypomethylation status of these individual genes are analysed. The next stage of our research will address these concerns.

Key Words: Hexabromocyclododecane *Gasterosteus aculeatus*, DNA Methylation, Liquid Chromatography, Epigenetics

PARTICLE CHARACTERISATION IN URBAN ENVIRONMENT

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Particulate matter in the urban environment has been causing adverse health effects, direct and indirect impact on the environment. Aerosol particles in the atmosphere can cause light scattering which has a direct effect on climate and visibility. It can also indirectly affect the climate by acting as cloud condensation nuclei. Toxic particulates are produced from absorption and reaction of particles with other pollutants in the atmosphere. Additionally fine particles usually contain inflammatory, carcinogenic and mutagenic compounds and increased exposure to these particles can cause acute or chronic health complications.

Identifying the source of these particles, its composition, physical and chemical properties will help to provide a clear connection to its impact on the environment and the human health. Individual particles have different chemical morphology and these data will provide information on the formation and reaction mechanism of these particles, also the source it originates from as well as its atmospheric history. Over the years, numerous studies have been conducted to characterise PM₁₀ and some work on PM_{2.5}. However, there is an emerging interest to identify the effects of very fine particles such as nano-particles. Characterisation of particles is crucial for the purpose of assessing its impact on the environment which can be done by collecting detail information on shape, size and chemical composition of individual particles.

The main objective of this three year research project is to produce a comprehensive particle characterisation in the urban environment. Different sampling and analysing techniques will be investigated as part of the extensive experimental work to be conducted. Preliminary samples will be collected from selected urban locations using an ambient cascading impactor sampling device. The samples will then be analysed using scanning electron microscopy with energy-dispersed analysis of X-rays (SEM/EDX). This technique has already proven to provide information on the morphology, phase and elemental composition of individual particles. Furthermore, this research will related the findings to better understand of behaviour of finer particles such as nano-particles in the urban environment.

Poster Presentation

HALOGENATED ORGANIC CONTAMINANTS IN POLAR BEARS (URSUS MARITIMUS)

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As an indicator of global environmental pollution, the polar bear has proven to be one of the most central Arctic species for both scientists and the public. As an apical predator the polar bear provides pollution indications for a number of arctic species used as prey, as well as for the humans consuming these mammals. This is principally due to their remote and sparsely populated Arctic habitat; typically pristine environments with no significant local human population or contaminant source, but also due to the bears position at the apex of their food chain. The spread of anthropogenic contaminants to these areas is likely to be through natural vectors or through the migration of prey species.

A small number of adipose tissue samples were taken from adult, sub-adult and juvenile bears. The bears were found dead or shot in Svalbard, Norway between 1996 and 1999. The samples were analysed for: 17 laterally substituted PCDD/Fs, 25 PCBs, 34 PBDEs and 5 PBBs, using previously described methods [1].

Organohalogen residues were detected at various levels in the order: oPCBs >> PBBs > PBDEs >> nPCBs > PCDD/Fs. PCBs, PCDD/Fs, PBDEs and PBBs were detected in every sample of polar bear tissue. Differing contaminant profiles were observed. In all but one sample hexabromobiphenyl BB-153 was the most dominant BFR congener, at an average concentration of 47.8ng/g whole weight. This was highly unexpected because PBBs have not been in widespread use for the last three decades. It has been reported that BB-153 has a remarkably long half-life in humans of approximately 29 years [2]. It is possible that polar bears have a similarly slow metabolic rate for this compound. PBDEs were dominated by the presence of BDE-47 but closely followed by BDE-153 – a distinctive congener profile, dissimilar to most common commercial PBDE formulations.

Of the chlorinated compounds determined, ortho-PCBs dominated, with PCB-153 showing the highest levels at an average of 3600ng/g. All animals tested were found to have remarkably similar dioxin WHO-TEQ burdens, with little evidence for trends. Contaminant profiles were significantly different in samples taken from a juvenile coy; cub of year, which are believed to subsist principally on maternal milk. The juvenile tissue showed elevated proportions of PBDEs and non-ortho-PCBs when compared to the other animals tested. To our knowledge this is the first study to report this range of contaminants in Polar Bears. Reasons for the persistence of BB-153 are unknown.

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**GLOBAL TRENDS IN CHIRAL SIGNATURES AND CONCENTRATIONS
OF POLYCHLORINATED BIPHENYLS (PCBs) IN MATCHED AIR AND
SOIL SAMPLES**

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Chiral signatures of PCBs 95, 136 and 149 are reported for matched air and soil samples from selected sites in the UK and elsewhere. Air samples were collected using passive air samplers (PUF disks) with soil samples being collected at the end of the sampling campaign. Passive air samplers are ideal for this study as their portability, low cost and lack of requirement for a power supply means that they offer wide spatial coverage in a cost-effective manner. Furthermore, although their use for deriving concentrations requires detailed calibration exercises, this is not necessary for the determination of chiral signatures where one simply measures the relative amount of each enantiomer in the sample. Air and soil samples were purified and subjected to enantioselective GC/MS analysis, with results adding weight to the existing evidence that the major source of PCB to the atmosphere arises from new emissions from remaining stocks of PCBs rather than via the re-volatilisation of PCBs from soil and other environmental surfaces as has been previously suggested. In most soils, the enantiomeric fraction (EF) of PCBs deviates from racemic i.e. the EF is *not* 0.500. By comparison, in air samples, the chiral signatures were racemic or near-racemic, thus mirroring the signatures found in commercial PCB formulations. EFs in soil ranged from 0.449 to 0.517 for PCB 95, 0.459 to 0.525 for PCB 136 and 0.463 to 0.530 for PCB 149. In air samples, the EFs ranged from 0.486 to 0.499 for PCB 95, 0.486 to 0.499 for PCB 136 and 0.486 to 0.506 for PCB 149. Concentrations of PCBs in samples were also derived. Those in air samples ranged from 0.288 to 1.534 ng Σ PCB/m³ while those in soil samples ranged from 0.233 to 5.01 μ g/kg (dry weight).

Poster presentation

POPs IN ALLIGATOR LIVERS FROM LAKE APOPKA, FLORIDA, USA

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Reproductive disorders in American alligators (*Alligator mississippiensis*) inhabiting Lake Apopka, Florida, have been observed for several years. Such disorders are hypothesized to be caused by endocrine disrupting contaminants occurring in the Lake due to pesticide spills and runoff from bordering agricultural lands, and various studies have resulted in identification of several POPs, some of them known endocrine disrupters. However, no previous study has attempted to determine the enantiomer composition of any of the chiral pollutants identified, although it is known that enantiomers of chiral pesticides often differ in their biological activity, including endocrine disruption. In this report, livers of alligators inhabiting Lake Apopka were extracted and analyzed using chiral gas chromatography-mass spectrometry for identification of organochlorine pesticides; in so doing, the enantiomer fractions of any chiral pesticides identified were also measured. In summary, p,p'-DDE was the most prominent such compound identified, being found in all samples at concentrations ranging from 4 to 779 ng/uL. Trans- and cis-nonachlor were next most concentrated; they were also found in all samples, with the trans-isomer being 2 to 3 times higher than the cis. p,p'-DDD was also found in all samples. Only a few chiral organochlorine pesticides were identified, and they each occurred in only 1 to 3 samples. Their enantiomer fractions were mostly non-racemic. An especially interesting compound identified was p,p'-dichlorobenzophenone, a known metabolite of p,p'-dicofol; the latter was not detected but is known to have been used and spilled near Lake Apopka, and is highly toxic to fish and aquatic invertebrates. The metabolite occurred at low concentrations (<1ng/uL except one sample of 3.6ng/uL) in all but 1 (non-detected) sample. However, as well as being a metabolite, this compound is also known to be formed by thermal degradation of p,p'-dicofol during gas chromatography. Efforts are underway to determine whether the p,p'-dichlorobenzophenone identified in these samples occurred via metabolism or thermal degradation of dicofol during GC.

Poster Presentation

DEVELOPMENT OF AN ANALYTICAL TECHNIQUE TO ASSESS BIOACCESSIBLE BENZO(A)PYRENE IN CONTAMINATED SOILS

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Benzo(a)pyrene, or B(a)P, belongs to a family of over 100 compounds collectively known as polycyclic aromatic hydrocarbons (PAHs). These consist of two or more fused aromatic rings and arise as complex mixtures with numerous anthropogenic and biogenic origins. Mainly generated through incomplete combustion of fossil fuels they are distributed throughout the environment.

Sixteen of their number, including B(a)P, were chosen by the US EPA to be analyzed in the environment since:

most information is available on these PAHs

they are suspected of being more harmful than most other PAHs

they exhibit harmful effects representative of PAHs

chance of exposure to these is greater than to other PAHs

these PAHs had the highest concentrations at hazardous waste sites.

B(a)P, considered the most toxic of the sixteen, has been identified by the UK Environment Agency as a carcinogenic marker substance and a Soil Guideline Value (SGV) for this compound is being considered by DEFRA. B(a)P is resistant to biodegradation and may be regarded as a persistent organic pollutant. Accordingly, its determination in soils is necessary particularly as substantial B(a)P concentrations can be encountered in the soils in and around sites where coal tar, creosote and allied products have been produced (*e.g.* gasworks).

Additionally, the need to determine the bioaccessible concentration, (*i.e.* the fraction of B(a)P available for uptake in the human gastrointestinal tract), is being accorded increasing significance in the UK.

The overall aim of this work was to assess, *via* the oral ingestion route, the bioaccessibility of B(a)P in a variety of soils collected from a contaminated gas works site in the north of England. The method employed was a physiologically based extraction test (PBET) modified for the determination of organic contaminants.

The subsequent analysis of the PBET extracts by HPLC with fluorescence detection represented an appreciable analytical challenge. Several techniques for sample preparation were examined and the relative merits and drawbacks of these are presented.

Poster presentation

DEGRADATION OF POLY-AROMATIC HYDROCARBONS (PAHs) FROM CONTAMINATED SOIL BY COMPOSTING

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Persistent organic chemicals and in particular poly-aromatic hydrocarbons (PAHs) are of environmental concern, especially when it comes to remediation of polluted soils. Bioremediation has been shown to be most effective at degrading PAHs. With this approach PAHs are mineralised by micro-organisms and not “locked up in the soil”. Locking-up may reduce the overall risk but leaves the long-term fate of those contaminants uncertain. To achieve good mineralization rates of PAHs composting conditions must be optimal for the micro-organisms that use PAHs as a carbon source or degrade PAHs co-metabolically or by unspecified oxidative metabolism. In this study the use of different fungi under different physical and chemical conditions is investigated using small-scale compost vessels to assess PAH degradation. Species included are the basidiomycetes *Pleurotus ostreatus*, *P. eryngii* and *Trametes versicolor*. The processes are characterised by measuring chemical and physical conditions and changes and by microbiological analysis. Nutrient concentrations and sources like chicken manure, cattle manure, and fertilizer, and physical conditions like the temperature profile, are manipulated and the impact on the microbial community successions and PAH degradation rates are characterised and determined using phosphor lipid fatty acid analysis (PLFA) and polymerase chain reaction – denaturing gradient gel electrophoresis (PCR-DGGE). Interdependencies of the microbial communities, physical and chemical conditions, and PAH degradation rates reveal the timescale in which the degradation rate of PAHs is highest and principal component analysis shows microbial groups associated with the given conditions and PAH degradation rates.

Poster Presentation

PREVENTATIVE AND REMEDIATION STRATEGIES FOR CONTINUOUS ELIMINATION OF POLY-CHLORINATED PHENOLS FROM FOREST SOILS AND GROUND WATERS

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Pentachlorophenol (PCP) and its salts sodium pentachlorophenate (NaPCP) and pentachlorophenyl laurate (PCPL) have been used as herbicides, fungicides and wood preservatives worldwide. As such they can be detected in all ecosystems. Listed as a priority toxic substance by the European Union, PCP has been limited to professional and industrial use, with the majority of consumption in the United Kingdom, France, Spain and Portugal. PCP bioaccumulation in plants and animals of terrestrial and aquatic environments can lead to unpredictable physiological responses. Fungal species diversity is reduced through the use of chlorophenolic agro-forestry additives favouring the dominance of tolerant species. Chloroanisoles are produced through fungal methylation of chlorophenols within cork.

Cork slabs, direct from forests, are often contaminated with PCP and chloroanisoles suggesting that cork forest ecosystems are important step in contamination exposure. The University of Paisley, Scotland, and ITQB, Portugal, are working together to determine the fate of PCP and its toxic degradation products (e.g. tetra-, tri- and dichlorophenols) in cork forests ecosystems with focus on the interaction mechanisms with the forest litter and soil. Project kick off has focused on the influence of physical and chemical factors on the PCP sorption/desorption isotherm. The PCP fungal degradation/transformation mechanism is being assessed with deriving PCP risk to higher trophic levels through their bioaccumulation and biomagnification

Poster presentation

POLYBROMINATED DIPHENYL ETHERS IN HOUSEHOLD DUST IN BIRMINGHAM, UK

**Catalina Ibarra de Moore and Stuart Harrad,
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University of Birmingham**

Polybrominated diphenyl ethers (PBDEs) have been used widely as flame retardants in electronic components, plastics, textiles and building materials. The ubiquitous nature of PBDEs is verified by finding them in different locations and in animal and human samples. Levels of PBDEs have been analyzed in blood, fat and human milk samples and the concentrations found in humans in the USA are more than ten fold higher than in Europe. Their presence in humans means that it is important to identify routes of exposure to the general population and the fact that North American and European dietary exposure is similar, suggests that sources in addition to diet are important. In particular, inhalation and ingestion of indoor air and dust could account for a significant proportion of the SPBDE in people. In this study we analyzed vacuum dust collected from different households in Birmingham where the air was previously analyzed using a passive air sampler. Analysis of dust extracts by gas chromatography/mass spectrometry was performed to determine the levels of 9 PBDE congeners (BDEs 28, 47, 49, 66, 85, 99, 100, 153 and 154). Data from the first batch of samples (n=7) shows Σ PBDE concentrations to range from 20.9 to 625.4 ng/g dust (geometric mean: 244 ng/g, median: 108 ng/g). BDE 99 was the major congener detected in all the samples, followed by BDE 47. The levels reported in this study, compared to existing PBDE analysis performed in North America and Europe, are very similar to concentrations found in Germany where SPBDE ranged from 17-550 ng/g dust (median: 74 ng/g). Concentrations reported in USA ranged from 530 – 29,000 ng/g dust (median: 4,200 ng/g) in Atlanta, GA, and from 780 – 30,100 ng/g dust in Washington, DC (mean: 5,900 ng/g, median: 4,250 ng/g). In a recent study completed in Ottawa, Canada, SPBDE ranged from 170 – 170,000 ng/g dust (mean: 2,000 ng/g, median: 1,800 ng/g). The concentrations of Σ PBDE in indoor dust registered in North America are more than 20 times higher (in some cases 200 times higher) than the concentrations reported in this study (Fig. 1). Given recent evidence that PBDE concentrations in UK indoor air are of similar magnitude to those in Canada, this study provides preliminary evidence that the difference in North American and European human body burdens may be attributable to higher concentrations in North American dust.

Poster presentation

CHARACTERIZATION OF COMBUSTION RESIDUES FROM MUNICIPAL SOLID WASTE INCINERATORS

A Phongphiphat et al

Particulate matter generated from combustion processes is raising environmental concern because they are mainly fine particulates (PM_{2.5}) that can penetrate and deposit deep in the lung. In particular are the combustion residues from municipal solid waste incinerators (MSWI) since they contain toxic substances such as heavy metals, PCDD/Fs, and other products of incomplete combustion. This research study focuses on the behaviour of trace elements emitted from the incineration processes. Five samples of combustion ash/deposits collected at different locations of a MSWI were analysed. The analytical tests included i) unburnt carbon content, ii) size distributions, iii) surface morphology and iv) elemental composition. The samples consisted of i) bottom ash which accounts for approximately 88% of total ash from the incinerator, ii) superheater deposit, iii) heat exchanger ash, iv) economiser ash, and v) the fabric filter ash.

More than 57% (by weight) of the particles in the bottom ash were larger than 4.75 mm. 14.3% of the samples were smaller than 850 µm. The superheater deposit composed of agglomerate crusts. The mean diameter of the heat exchanger and economiser ash particles were 344.11 µm, and 366.09 µm respectively. The mean diameter of fabric filter particles was 75.04 µm. PM₁₀ contents of the bottom ash, superheater deposit, heat exchanger, economiser and bag filter ash samples were 0.2%, 4.5%, 3.3%, 2.4%, and 22.1% respectively. SEM analysis revealed that the superheater deposits consisted of spherical particles with diameters ranging from 20 µm to 60 µm. Majority of particles in the heat exchanger ash samples has irregular shape with diameter larger than 100 µm. Light weight particles (i.e. paper ash) were first detected in the heat exchanger ash. Particles in the economiser ash samples were larger than 300 µm. Fabric filter ash contained various types of particles with diameters ranging from 10 µm to 500 µm. Unburnt carbon content in the bottom ash was about 4% which showed good combustion efficiency. Ca, Si, and Al were dominant inorganic elements found in all samples. Other major elements were S, K, Na, Fe, Mg, P, Zn, and Ti. EDS results of all samples showed that the most common constituents of spherical particles were Ca, Si, Al, Fe and Zn. Various combinations of elemental composition were found in irregular shaped particles such as (1) Ca-Si-Al-Fe, (2) solely Si (possibly SiO₂), and (3) Si-K-Al. In superheater deposit, Ca-S particles, Ca-Ti particles, and particles with Cl were also found. In fabric filter ash, particles containing Ca-Cl were dominants due to hydrated lime injection. Metals showed different partitioning behaviours depending on their physical and chemical characteristics. Less volatile elements including Al, Cu and Fe were mostly found in the bottom ash. In contrast, more volatile elements such as Cd, Pb, and As condensed on the fly ash particles when the flue gas temperature cooled down and were highly enriched in fabric filter ash. Fabric filter ash contained high concentration of C and Ca due to the hydrated lime and activated carbon injection. This resulted in high concentrations of Cl and S which presented in the forms of Ca-based compounds. The results from this study provide fundamental understanding about the formation and characteristic of particulates in the MSWIs.

Poster presentation

HEAVY METALS AS PERSISTENT TRACE POLLUTANTS: QUANTIFICATION OF EMISSIONS SOURCES

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The Stockholm Convention sought to protect public health and the environment from Persistent Organic Pollutants. It defined POPs as “chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife”. In this context, it is interesting to consider anthropogenic sources of heavy metals. These too, can remain in the environment (in harmful form) for long periods, undergo wide distribution in the ecosystem, bio-accumulate, and exhibit severe toxic effects (at similar extremely low concentrations). In addition, sources of POPs can also be significant sources of heavy metals.

Many of the difficulties associated with POPs research are also common to trace heavy metal contamination. These include difficulty of accurate detection and quantification at low level, questionable source apportionment, uncertainty regarding environmental and toxicity effects, and complex distribution mechanisms through the natural world.

An on-line continuous emission monitoring system, based around Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) was developed to detect metals in thermal industrial processes, which are the main sources of airborne heavy metals. This self-contained mobile laboratory was transported by road to a UK energy-from-waste plant, where measurements of metal concentrations both before and after flue gas clean-up were conducted, with a temporal resolution of one minute.

The measurements revealed high and variable concentrations of numerous metals, including toxic heavy metals in the un-cleaned flue gas, which contained a high particulate loading, and required extensive clean-up. Metal concentrations could be linked both to changing waste feed composition, and to changes in furnace operating conditions.

Measurements in the flue gas emitted to atmosphere, following gas clean-up showed that metal concentrations were vastly reduced, and no longer exhibited any significant temporal variation. All metals detected were at concentrations below relevant regulatory limits, demonstrating that the clean-up processes in place were effective in minimising atmospheric discharge of potentially harmful persistent heavy-metal pollutants from this waste-to-energy plant.

The work demonstrates the ability of the mobile laboratory to make time-resolved measurements of these important micro-pollutants, and so assist in accurately quantifying time-resolved metal concentrations, and understanding what factors lead to higher emissions. Such information should help to lead to improved and informed control strategies, and waste disposal practices.

Poster presentation

ENVIRONMENTAL BEHAVIOUR OF PBDEs IN TERRESTRIAL MAMMALS: BIOGMAGNIFICATION vs METABOLISM

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PBDEs are highly lipophilic and persistent chemicals, which bioaccumulate in fatty tissues of biota and biomagnify throughout the food chain (de Wit 2002). Because PBDEs have a high toxicological potential (Darnerud 2003), their theoretically expected biomagnification throughout the food chain can have health consequences for terrestrial top-predators, such as foxes. The aim of this study was to investigate the biomagnification potential of PBDEs in terrestrial food chains with mice and foxes as representatives of both prey and predator, respectively.

BDEs 28, 47, 99, 100, 153, 154, and 183 were determined in mice and fox muscle, liver and adipose tissue. PBDE-analysis revealed low levels in all the tissues of both mice and foxes. Median sum of PBDE-levels in mice and fox were 8.5 ng/g lw and 2.4 ng/g lw, respectively. The low levels in mice were expected, seeing the herbivorous character of the animals. However, it was unexpected that the levels in the mice (prey) were higher than in the fox, a carnivorous top-predator. Small rodents, such as the mice of the present study, are the main constituents of the fox's diet (> 80%). However, foxes do not have a strict dietary pattern and can adapt easily to available food sources in their territory. Nevertheless, these small rodents can provide valuable information on the PBDE exposure of foxes.

However, it was demonstrated previously that foxes are more likely to possess strongly developed metabolic processes, as was shown for PCBs (Georgii et al., 1994). Due to the structural similarity of PCBs and PBDEs, the latter may also be subjected to extensive metabolic transformation. This can explain the low levels found in fox. Based on the present data, we can conclude that there is no biomagnification of PBDEs from mice to foxes. The hypothesis of extensive metabolism is confirmed by the PBDE-profile change from mice to fox; the congener-profile in fox is entirely dominated by higher brominated BDEs, such as BDE 153 and 183 (and 209 if it is > LOQ), while in the prey, BDEs 47 and 99 dominated. The use of fox as a biomonitoring tool for environmental biological PBDE pollution can therefore lead to an underestimation of the exposure and should be advised against.

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Poster presentation

ENDOSULFAN IN THE ARCTIC SEA: AN ASSESSMENT OF AIR-WATER EXCHANGE

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Keywords: Endosulfan, Arctic, Air-sea exchange, Spatial distribution

Endosulfan (ES) is an organochlorine pesticide (OCP) that exists as two isomeric forms (α - and β -ES) and has widespread global use. Concern arises due to the ubiquitous occurrence of ES in the Arctic and understanding its transfer between key compartments in the Arctic is crucial for quantifying ES loadings to this environment. In this study, detailed survey data of levels in air and seawater were collated based on both published and unpublished monitoring and campaign-based projects over the years 1993-2000. Comparisons were made with γ -HCH and a fugacity approach applied to examine air-water transfer over different regions of the Arctic Ocean. Surface seawater concentrations for α - ES ranged between 400 and 8800 pg/L with evidence of higher concentrations towards the western Arctic. Calculated fugacity ratios (FR) utilising air concentrations from land-based monitoring stations, indicated notable regional differences in air-water transfer. For example, the FRs of α - ES ranged from <1 in the Canadian Archipelago to >1 in the Bering Sea and <1 to >1 in the Greenland and White Seas respectively. These results indicate that the equilibrium status of α -ES in some of the marginal coastal seas is different from other regions of the Arctic Ocean and the implications of this are discussed in relation to γ -HCH.

Poster Presentation

MULTI RESIDUE ANALYSIS OF EU BLACK LIST PRIORITY POLLUTANTS IN DRINKING AND SURFACE WATER USING SOLID PHASE EXTRACTION AND GC TANDEM QUADRUPOLE MSMS

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EU council directive 76/464/EC¹ lists 132 compounds that have restricted levels in drinking and surface waters. Of these compounds, 109 are amenable to gas chromatographic analysis. Currently published methods² involve the use of two injections, one using selected ion recording as a screen, followed by a full scan injection for confirmation. The use of tandem quadrupole GC-MS/MS allows the analyst to combine the screening and confirmatory injections into one run, whilst also allowing a reduction of the chromatographic separation required for confirmation of some of the target compounds.

The EU list has many similarities with the target compound lists of USEPA water quality methods such as 625³ and 8270⁴ it should be noted that the list analysed in this method is by no means an exhaustive one.

A method will be shown that combines a single solid phase extraction/clean up with GC-Tandem Quadrupole detection using multiple reaction monitoring (MRM). The method describes and compares both a confirmatory approach, monitoring two MRM transitions per compound, and a screening approach monitoring one MRM transition per compound. Method limits of detection; based upon spiked drinking water extracts; will be shown to be in the <0.1µg/L concentration range for the vast majority of target compounds.

The method is a demonstration of the throughput increase that can be achieved with the combination of less selective extraction/clean up and a more selective detection technique, such as Tandem Quadrupole MSMS.

- [1] Directive 76/464/EEC, Dangerous Substances Discharged into the Environment, Official Journal of the European Union no. L 129, Brussels, 1976.
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- [3] USEPA method 625, Base/Neutral and Acid Organics in Wastewater, U.S.EPA National Exposure Research Laboratory (NERL) microbiological and Chemical Exposure Assessment Research Division (MCEARD), Cincinnati, OH
- [4] USEPA method 8270, Semi volatile Organic Compounds by GC/MS, U.S. EPA Office of Solid Waste (OSW) Methods Team, Ariel Rios Bldg. (5307W), 1200 Pennsylvania Ave. NW, Washington, DC 20460

Poster presentation

METABOLIC FATE OF DECABROMODIPHENYL ETHER IN PREGNANT WISTAR RATS

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Decabromodiphenyl ether (DBDE) is widely used as a flame retardant, for industrial applications such as TV sets, office equipment and textiles. DBDE (commercial mix) world-wide demand was estimated over 50 000 tons, as reported in 2001. It is now the only BDE mix which use remains authorised within the EU. DBDE readily debrominates, into lower-molecular weight BDEs. Its presence in biological samples is difficult to assess, mainly due to analytical difficulties (hydrophobicity, weak solubility in organic solvents and high molecular weight). In human, DBDE has been found in breast milk and in tissues: serum, adipose tissue, but also foetal liver. Little is known about its metabolic fate in animals models. Though hydroxylated and methoxylated metabolites have been identified in rat, the corresponding metabolic profiles of DBDE residues in tissues are unavailable. Hence, the distribution and the proportion of metabolites in tissues remain unknown. We have started a study of the metabolism of DBDE in pregnant wistar rats to address these different questions, based on the development of suitable extraction and analytical methods, with the aim to achieve the radio-HPLC separation and structural identification of DBDE metabolites. DBDE was synthesised by brominating ^{14}C ring-labelled diphenyl ether and was purified by SPE to reach a high degree of purity (>99,8%). Rats were daily dosed with 7,8 mg/kg (7 MBq/kg) DBDE by oral route from gestational days 16 to 19, and were killed on day 20 of gestation. Most of the radioactivity was recovered in faeces and in the digestive tract, but significant concentrations of residues were found in tissues (liver, adrenals, ovaries, kidneys, placentas) ranging from 2.4 to 34 $\mu\text{g/g}$ fresh weight. Radio-HPLC metabolic profiling of faeces extracts showed that more than 97% of the faecal radioactivity was associated with unchanged DBDE. In liver, which contained $6.2\% \pm 0.9\%$ of the radioactivity distributed to animals during the 4-day experiment, several metabolites were detected, and unchanged DBDE accounted for about 90%. Foetuses (whole litter) contained *ca.* 0.4% of the radioactivity distributed to mothers, demonstrating that either DBDE or its metabolites can cross the placental barrier in rat. Results obtained for the liver and several other tissues indicate that following oral exposure, DBDE is absorbed and undergoes biotransformation in rat.

1st Network POPs Conference

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