Modelling of the Environmental Distribution and Fate of Persistent Organic Pollutants on a National, European and Global Scale (EPG 1/3/169).

Andy J. Sweetman, Konstantinos Prevedouros, Nick Farrar, Foday Jaward
and Kevin C. Jones

Department of Environmental Science, Institute of Environmental and Natural Sciences
Lancaster University, Lancaster, LA1 4YQ, UK
Phone: 01524-593972
Fax: 01524-593985
Email: a.sweetman@lancaster.ac.uk

Executive summary

The fate and behaviour of persistent organic pollutants (POPs) in the environment has attracted considerable scientific and political interest, arising from concern over human exposure to these chemicals and their discovery in pristine environments far from source regions. The ability of certain POPs to undergo long range atmospheric transport (LRAT) has resulted in the negotiation of protocols (e.g. UN/ECE, UNEP) for their reduction or elimination, to reduce the risks to regional and global environments. A number of chemicals are currently being investigated for inclusion on the UN/ECE POPs protocol list of priority compounds. The development of such protocols recognises the regional and global nature of many POP compounds. This implies that control of such chemicals requires multi-lateral agreements. However, the control and reduction of primary sources of such compounds is only part of the process as there may still be diffuse and secondary sources that need to be identified and quantified. Therefore a complete source inventory and an understanding is the multi-media fate and behaviour of individual POPs is essential if effective control is to be achieved.

Lancaster University has developed a number of modelling tools that can be used to investigate the potential environmental impact of existing and candidate POPs. The most recent model development is a regionally segmented multimedia fate model covering the European continent. This model has been designed to examine the environmental fate and behaviour of a wide range of chemicals and to investigate a number of emission scenarios and source reduction strategies. It can also be used as a predictive tool to identify potentially important sinks and for estimating the potential for long-range atmospheric transport. Models such as this can be helpful in understanding the movement from source to sinks. They can incorporate secondary or diffusive sources to land or water as well as directly to air. Whilst further refinement to model design and parameterisation is required, these models are already being used to direct research by identifying important fate processes and sinks that should receive further attention. In summary, fate models are important tools for policy making; by helping to prioritise chemicals, highlight research priorities and ultimately provide quantitative links between sources, environmental levels and exposure. Importantly, they can direct policy by identifying processes which may be subject to control and by providing quantitative information regarding the effectiveness of such control measures.

During the course of this contract scientific manuscripts have been prepared on a range of aspects of the work which have been submitted to various journals. These papers have been included in this report as they represent concise accounts of the work undertaken which have also been peer reviewed (or in the process of review) by the scientific community.

The model development work is complimented by a number of measurement exercises aimed at improving the description of key processes and providing datasets for calibration and validation. Although validation of models such as these is challenging an international group of experts has been formed coordinated by MSC-E in Moscow. Lancaster University is an active member of this group which is currently developing a framework which can be used to compare a number of POP fate models and to eventually provide meaningful validation with measurement data.

Physicochemical database and candidate POP compounds

A web based physicochemical and environmental fate database has been prepared for a wide range of POPs and related compounds. The database and the results of a range of screening model runs are available on the Lancaster University Environmental Science Department server (www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html). These databases contain a range of physicochemical data that can be used to provide an indication of environmental behaviour and to provide input to fate and behaviour models. The database is continually updated as new data becomes available

An important task, therefore, is to identify candidate POPs based on a knowledge of their physicochemical properties and their production and use patterns. To aid this process Lancaster hosts (on behalf of Defra) a web based physicochemical and environmental fate database for a wide range of POPs and related compounds. An equally important task is to continually update the emission inventory associated with these compounds. In some cases, this requires undertaking preliminary estimates as full inventories are not yet available. The current list of candidate POPs under discussion include the following:

Endosulfan, Hexachlorobutadiene, Pentachlorobenzene, Dicofol, Polychlorinated naphthalenes, Pentachlorophenol, Short-chain Chlorinated Paraffins and Pentabromodiphenylether.

Seasonal and long-term trends in atmospheric PAH concentrations: evidence and implications

The objective of this study was to examine seasonal and temporal trends of atmospheric PAHs, to shed light on the factors which exert a dominant influence over ambient levels. Urban centres in the UK have concentrations 1-2 orders of magnitude higher than in rural Europe and up to 3 orders of magnitude higher than Arctic Canada. Atmospheric monitoring data for selected polynuclear aromatic hydrocarbons (PAHs) have been compiled from remote, rural and urban locations in the UK, Sweden, Finland and Arctic Canada. Interpretation of the data suggests that proximity to primary sources 'drives' PAH air concentrations. Seasonality, with winter (W) > summer (S), was apparent for most compounds at most sites; high molecular weight compounds (e.g. benzo[*a*]pyrene) showed this most clearly and consistently. Some low molecular weight compounds (e.g. phenanthrene) sometimes displayed S>W seasonality at some rural locations. Strong W>S seasonality is linked to seasonally-dependent sources which are greater in winter. This implicates inefficient combustion processes, notably the diffusive domestic burning of wood and coal. However, sometimes seasonality can also be strongly influenced by broad changes in meteorology and air mass origin (e.g. in the Canadian Arctic). The datasets examined here suggest a downward trend for many PAHs at some sites, but this is not apparent for all sites and compounds. The inherent noise in ambient air monitoring data makes it difficult to derive unambiguous evidence of underlying declines, to confirm the effectiveness of international source reduction measures.

Modelling the atmospheric fate and seasonality of polycyclic aromatic hydrocarbons in the UK

This study into atmospheric fate and behaviour modelling of PAHs had three main objectives: 1). to investigate the balance between estimated national atmospheric emissions of 6 selected PAHs and observed ambient measurements for the UK, as a means of testing the current emission estimates; 2). to investigate the potential influence of seasonally dependent environmental fate processes on the observed seasonality of air concentrations; and 3). after undertaking the first two objectives, to make inferences about the likely magnitude of seasonal differences in sources. When addressing objective 1 with annually averaged emissions data, it appeared that the UK PAH atmospheric emissions inventory was reasonably reliable for fluorene, fluoranthene, pyrene, benzo[a]pyrene and benzo[ghi]perylene – but not so for phenanthrene. However, more detailed analysis of the seasonality in environmental processes which may influence ambient levels, showed that the directions and/or magnitudes of the predicted seasonality did not coincide with field observations. This indicates *either* that our understanding of the environmental fate and behaviour of PAHs is still limited, *and/or* that there are uncertainties in the emissions inventories. It is suggested that better quantification of PAH sources is needed. For 3- and 4-ringed compounds, this should focus on those sources which increase with temperature, such as volatilisation from soil, water, vegetation and urban surfaces, and possible microbially-mediated formation mechanisms. The study also suggests that the contributions of inefficient, diffusive combustion processes (e.g. domestic coal/wood burning) may be underestimated as a source of the toxicologically significant higher molecular weight species in the winter. It was concluded that many signatory countries to the UNECE POPs protocol (which requires them to reduce national PAH emissions to 1990 levels) will experience difficulties in demonstrating compliance, because source inventories for 1990 and contemporary situations are clearly subject to major uncertainties.

Modelling the fate of persistent organic pollutants in Europe: parameterisation of a gridded distribution model

A regionally segmented multimedia fate model for the European continent has been developed to provide fate and behaviour information for POP compounds on a continental scale. A manuscript has been prepared which describes the model construction and parameterisation together with an illustrative steady-state case study examining the fate of γ-HCH (lindane) based on 1998 emission data. The study builds on the regionally segmented BETR North America model structure and describes the regional segmentation and parameterisation for Europe. The European continent is described by a 5° x 5° grid, leading to 50 regions together with 4 perimetric boxes representing regions buffering the European environment. Each zone comprises seven compartments including; upper and lower atmosphere, soil, vegetation, fresh water and sediment and coastal water. Inter-regions flows of air and water are described, exploiting information originating from GIS databases and other georeferenced data. The model is primarily designed to describe the fate of Persistent Organic Pollutants (POPs) within the European environment by examining chemical partitioning and degradation in each region, and inter-region transport either under steady-state conditions or fully dynamically. A test case scenario is presented which examines the fate of estimated spatially resolved atmospheric emissions of lindane throughout Europe within the lower atmosphere and surface soil compartments. In accordance with the predominant wind direction in Europe, the model predicts high concentrations close to the major sources as well as towards Central and Northeast regions. Elevated soil concentrations in Scandinavian soils provide further evidence of the potential of increased scavenging by forests and subsequent accumulation by organic-rich terrestrial surfaces. Initial model predictions have revealed a factor of 5-10 underestimation of lindane concentrations in the atmosphere. This is explained by an underestimation of source strength and/or an underestimation of European background levels. The model presented can further be used to predict deposition fluxes and chemical inventories, and it can also be adapted to provide characteristic travel distances and overall environmental persistence, which can be compared to other long-range transport prediction methods.

Spatial mapping of POP chemicals using passive air samplers

During the summer of 2002 an ambient air passive sampling campaign for a range of persistent organic pollutants was carried out at the continental scale. This was achieved using a sampling system consisting of polyurethane foam disks, which were: prepared at Lancaster University; sealed to prevent contamination; sent out by courier to volunteers participating in different countries; exposed for 6 weeks; collected; re-sealed and returned to the laboratory for analysis. The study area covered most of Europe, a region with a history of extensive POPs usage and emission, and with marked national differences in population density, the degree of urbanisation and industrial/agricultural development.

The results have been split into two manuscripts covering different compounds groups/classes. Samplers were deployed at remote/rural/urban locations in 22 countries and analysed for PCBs, a range of organochlorine pesticides (HCB, HCHs, DDT, DDE), PBDEs, PAHs and PCNs. Calculated air concentrations were in line with those obtained by conventional active air sampling techniques. The geographical pattern of all compounds reflected suspected regional emission patterns and highlighted localised hotspots. PCB and PBDE levels varied by over 2 orders of magnitude; highest values were detected in areas of high usage and were linked to urbanised areas. HCB was relatively uniformly distributed, reflecting its persistence and high degree of mixing in air. Higher γ-HCH, DDT and DDE levels generally occurred in S and E Europe. Calculated air concentrations for PAHs and PCNs were also in line with those obtained by conventional active air sampling techniques. The geographical compound distribution reflected suspected regional emission patterns and highlighted localised hotspots. PAH and PCN levels varied by over 2 orders of magnitude; the implications for sources are discussed.

A further experimental passive air sampler was also sent out to selected participants during the European campaign which was designed to react more rapidly to changing ambient air concentrations of POP compounds. The use of polymer coated glass (POG) samplers for environmental sampling has been proposed and developed by Dr Frank Gobas (Simon Fraser University, British Columbia, Ca) and Dr Tom Harner (MSC, Toronto, Ca). Initially these devices were used to sample water and biota but have recently been adapted to measure POPs in ambient air. For the purposes of this study the POG was housed in a sampling chamber to allow deployment in a sheltered and controlled environment. The POG air sampler, composed of a rapidly equilibrating polymeric stationary phase (Harner *et al.* 2003), was deployed at 41 sites across 20 countries. Based on an estimated uptake rate of ~ $3m^3$ per day, samplers were theoretically exposed to approximately 21 m^3 of air. However, for some of the lighter compounds (i.e. high vapour pressure) equilibrium was achieved. In order to convert the amount of chemical recovered from the EVA a partition coefficient between EVA and air is required. These partition coefficients can be related to the octanol-air partition coefficient which in turn can be corrected for temperature as required.

Study into the factors controlling the uptake of POP chemicals by passive air samplers using controlled laboratory chambers

As previously mentioned, a number of passive sampler devices have been utilised to sample POP chemicals in the atmosphere including polyurethane foam, polymer coated glass, polyethylene and soil. However, in order to provide quantitative data that can be compared with concentration data measured by other techniques such as Hi-volume samplers, the uptake kinetics of the samplers needs to understood. As a result a laboratory study has been carried out to identify the key parameters controlling the exchange of chemicals between the atmosphere and the sampling device. For the purposes of this study SPMDs (semi-permeable membrane devices) were chosen although the sampling processes and mechanisms are broadly similar across all sampler types and hence the findings of this study are applicable elsewhere. The results suggested that both wind speed and temperature exert a effect on the depuration of phenanthrene from SPMDs. The effect of varying the wind speed across the SPMD controls the thickness of the boundary layer and hence the distance through which the phenanthrene has to diffuse. However, this effect appears to be limited to lower wind speeds above which the effect on the boundary layer is minimal. The effect of increasing the depuration rate by increasing temperature could also be related to diffusion through the boundary layer. As the temperature increases so does the molecular diffusion rate although this effect is limited – a 20°C increase in temperature results in a 13% increase in molecular diffusion. Temperature is also likely to control the diffusion rates in the triolein and through the polyethylene which would require further investigation.

POP multimedia model inter-comparison study (MSC-E, Moscow)

Multi-media POP fate and behaviour models are now widely available and are slowly being incorporated into risk assessment procedures. However, in order to improve accuracy and obtain comparable results the harmonization of model output is required. The intercomparison of different types of POP transport models has been included in the recommendations of the WMO/UNEP/EMEP Workshop on modelling of atmospheric transport and deposition of POP and HM, Geneva, November 1999. Later on, the work of intercomparison of POP long-range transport models was included to the EMEP work-programme. The recent OECD/UNEP Workshop on the use of multimedia models for estimating overall persistence and long-range transport, Ottawa, October 2001 also marked a necessity of intercomparison study of POP multimedia models of different complexity. MSC-E, Moscow, has initiated an intercomparison exercise that will take place over the next few years that hopes to achieve improved model harmonization.

Modelling of the Environmental Distribution and Fate of Persistent Organic Pollutants on a National, European and Global Scale (EPG 1/3/169).

Authors: Andy J. Sweetman, Costas Prevedouros, Nick Farrar, Foday Jaward and Kevin C. Jones

Prepared for Defra, AEQ Division
Project Manager: Alan Irving

Contents **Page**

Section

Section 1

Introduction

The fate and behaviour of persistent organic pollutants (POPs) in the environment has attracted considerable scientific and political interest, arising from concern over human exposure to these chemicals and their discovery in pristine environments far from source regions. The ability of certain POPs to undergo long range atmospheric transport (LRAT) has resulted in the negotiation of protocols (e.g. UN/ECE, UNEP) for their reduction or elimination, to reduce the risks to regional and global environments. A number of chemicals are currently being investigated for inclusion on the UN/ECE POPs protocol list of priority compounds.

Synthetic organic chemicals are released into the environment through a range of processes which include; release during the production process, release during use (e.g. pesticides), or accidental release during combustion processes (e.g. 'dioxins'). Once in the environment, some of these chemicals have been shown to exhibit detrimental effects on wildlife and some have been shown to bioaccumulate through food chains resulting in high concentrations in top predators e.g. man. If we are to achieve the sustainable use of chemicals then we need a validated process of risk assessment through which we can evaluate the impact of both existing chemicals and those which will be produced in the future. The process of risk assessment currently uses a combination of predictive models, and worst case scenarios, to calculate environmental concentrations based on a knowledge of chemical production/use and release and information on their likely behaviour in the environment. These can be compared to environmental quality standards (EQSs) which provide quantitative information on tolerable levels at which no harm to the environment (or man) is likely. In particular, the ability to link atmospheric concentrations to concentrations in other media, including accumulation through foodchains, is vital for our successful management of chemicals in the environment. The development of reliable and validated models is essential to ensure that the risk assessment process is effective and transparent to the regulated and the regulator. We currently have a suite of models and approaches which can be used and adapted to investigate these issues. These include a UK scale dynamic multi-media model, a European gridded steady state/dynamic model and an atmospheric fate and behaviour model which can be used to investigate seasonality in emissions and removal processes. The European model is currently being used to participate in an international model intercomparison exercise.

All of the models developed at Lancaster are undergoing a process of validation and further improvement as part of a new Defra contract entitled 'Research into the further development of regional and national modelling of persistent organic pollutants, and review of the UN/ECE POPs protocol EPG 1/3/203'.

The following table outlines a number of objectives and milestones that were identified at the beginning of this contract which are briefly discussed below.

The following milestones were set out in the project proposal.

Task	Details
1	Compilation of database to identify candidate POPs
2	Compilation of physicochemical database for 50 candidate POPs
3	Place database on website
4	Improvements to UK model
5	Construct European regional model
6	Adapt/improve global model where applicable.
7	Design and construct passive sampler deployment device
8	Deploy passive samplers across EUROPE
9	Air-surface exchange process study
10	UK temporal trends study
11	Investigate human model adaptation and incproporation

- The first three tasks involving the compilation of the physicochemical database, preliminary screening and web publishing were successfully completed. The database can be found at http://www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html and will be constantly updated and improved during the current contract with Defra.

- Task 4 was also completed with final improvements to the UK model which resulted in a manuscript being published in Environmental Toxicology and Chemistry. Sweetman, A.J., Cousins, I.T., Seth, R., Jones, K.C. and Mackay, D. (2002) A dynamic Level IV multimedia environmental model: Application to the fate of PCBs in the United Kingdom over a 40-year period. Environmental Toxicology and Chemistry, 21(5), 930-940. The model has been further developed and modified to examine the seasonality of PAH emissions and their fate in the UK atmosphere. Details of these studies can be found in sections 3 and 4 of this report.

- Task 5 involved the re-parameterisation of the BeTr North American model developed at Trent University, Canada, for Europe with the collaborative assistance of Professor Donald Mackay. This project has recently been completed and a manuscript prepared with γ-HCH as the test chemical. Details of the model can be found in section 5 and the manuscript will be published in Environmental Pollution later in 2003.

- Task 6 has involved collaborative research with other groups that are examining the global fate of POP chemicals. These include:

Prof. Don Mackay,	Trent University, Canada
Dr. Matt MacLeod,	Lawrence Berkeley National Laboratory, USA
Dr. Gerhard Lammel,	Max Planck Inst., Germany
Dr. Martin Scheringer,	ETH, Switzerland

This work is still on-going and will be reported under the new Defra contract.

- Task 7 and 8 have involved a European scale passive sampling campaign carried out during the summer of 2002. The analytical data has recently been completed. Two types of sampler were deployed across a number of widely dispersed sites and analysed for a range of POP chemicals. Details of the study are contained in sections 6, 7 and 8 of this report and are currently going through the peer review process for publication in the open literature. A further passive sampling study is being carried out under the current Defra contract which aims to quantify the spatial distribution of short-chain chlorinated paraffins in the UK atmosphere.

- Task 9 has been addressed in the development of the European model as the air-surface exchange of POP chemicals is a key part of transport description and an important factor in determining overall fate. However, this is an extremely important area of POPs research and a number of studies (both laboratory and modelling) are currently on-going which will be reported under the new contract.

- Task 10 was designed to use a range of methodologies, including modelling, to investigate temporal trends of POP chemicals in the UK environment. The UK atmospheric PAH study investigated the long-term trend data that is being provided by the TOMPs network and compared it to datasets from other countries. A further study using a range of modelling techniques has investigated the long-term trends of PBDEs in the UK and North American environments. In particular, this work focussed on sources of these compounds to the atmosphere. Details can be found in: Alcock, R.E., Sweetman, A.J., Prevedouros, K. and Jones, K.C. (2003) Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. Environment International, 29(6), 691-698

- The objective of Task 11 was to explore linking human exposure models to fate and exposure models such as the European model developed under this contract. The Lancaster group have been involved with developing terrestrial food chain transfer algorithms for POP chemicals with the aim of predicting human exposure. Currently this area of research is limited to local exposure resulting from point sourece emissions. The Environment Agency commissioned Lancaster University to develop a model framework to investigate the release of PCDD/Fs and PCBs from sources such as municipal waste incinerators (MWIs) and to quanitify the potential impact on human exposure at a local scale. Predicted environmental and foodstuff concentratations are then combined with dietary information and the intake predictions compared to the current TDI and UK typical ingestion rates provided by the Food Standards Agency. Whilst this model currently works on a local scale, the food chain transfer algorithms are applicable to larger scale models. A potential end point of regional scale models will be to incorporate such algorithms and provide an estimate of human exposure resulting from a particular emission scenario. However, further information would be required before this could be accomplished, such as the incorporation of regional differences in diet etc. This area is being investigated under the current contract with Defra.

Section 2

Physicochemical database and candidate POP compounds

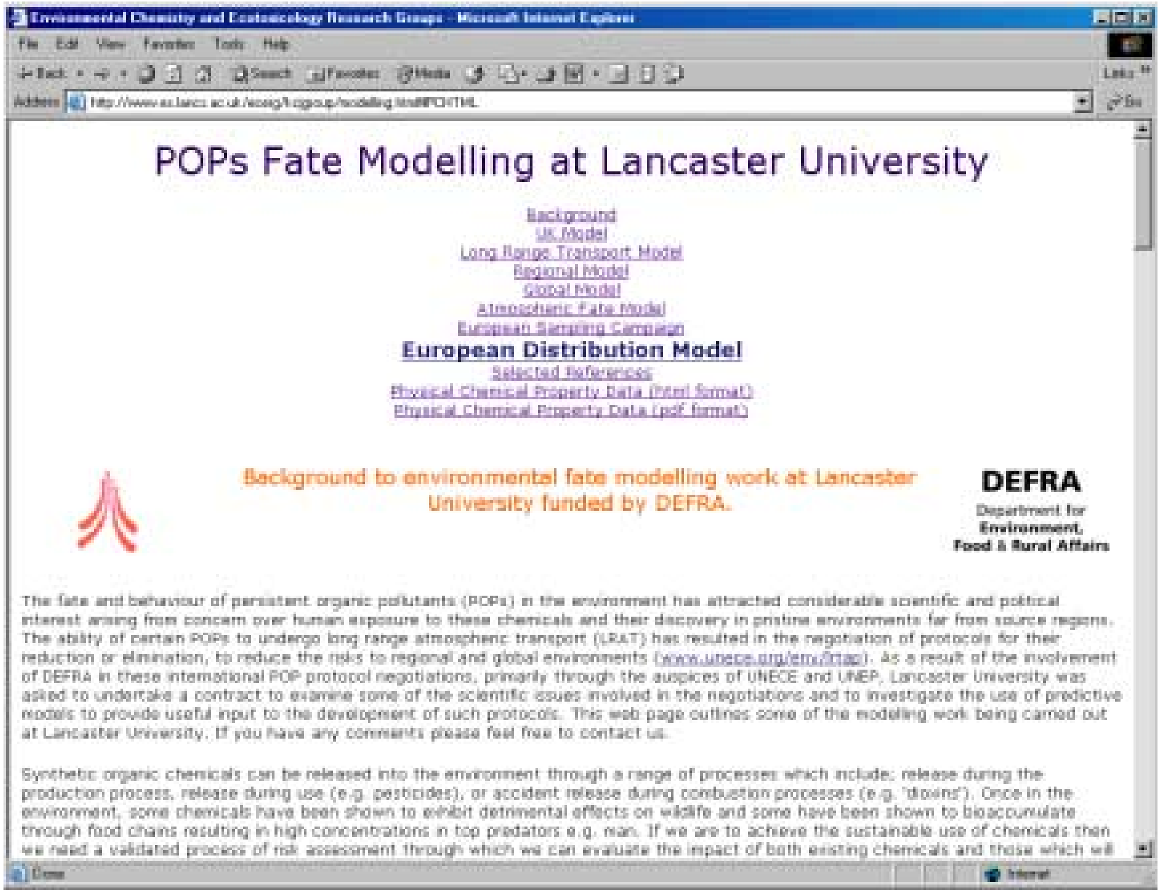
Introduction

Persistent organic pollutants have been the subject of internationally agreed protocols to ensure that their impact on humans and the environment are minimized. Under the UNECE Convention there are twelve POPs (or chemical groups) which have been targeted for elimination or reduction. They have been selected because of concerns over their persistence in the environment, their ability to undergo long range transport and their ability to bioaccumulate through food chains. As a result of these properties and their potential to exert toxic effects, efforts are being made to reduce environmental and human exposure. However, there are many chemicals being produced that may have similar properties and hence may be considered POPs. An important task, therefore, is to identify candidate POPs based on a knowledge of their physicochemical properties and their production and use patterns.

Compilation of database to identify candidate POPs

A web based physicochemical and environmental fate database has been prepared for a wide range of POPs and related compounds. The database and the results of a range of screening model runs are available on the Lancaster University Environmental Science Department server (www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html) with the current front page shown in Figure 1.

Figure 1 - Web page



POPs Fate Modelling at Lancaster University

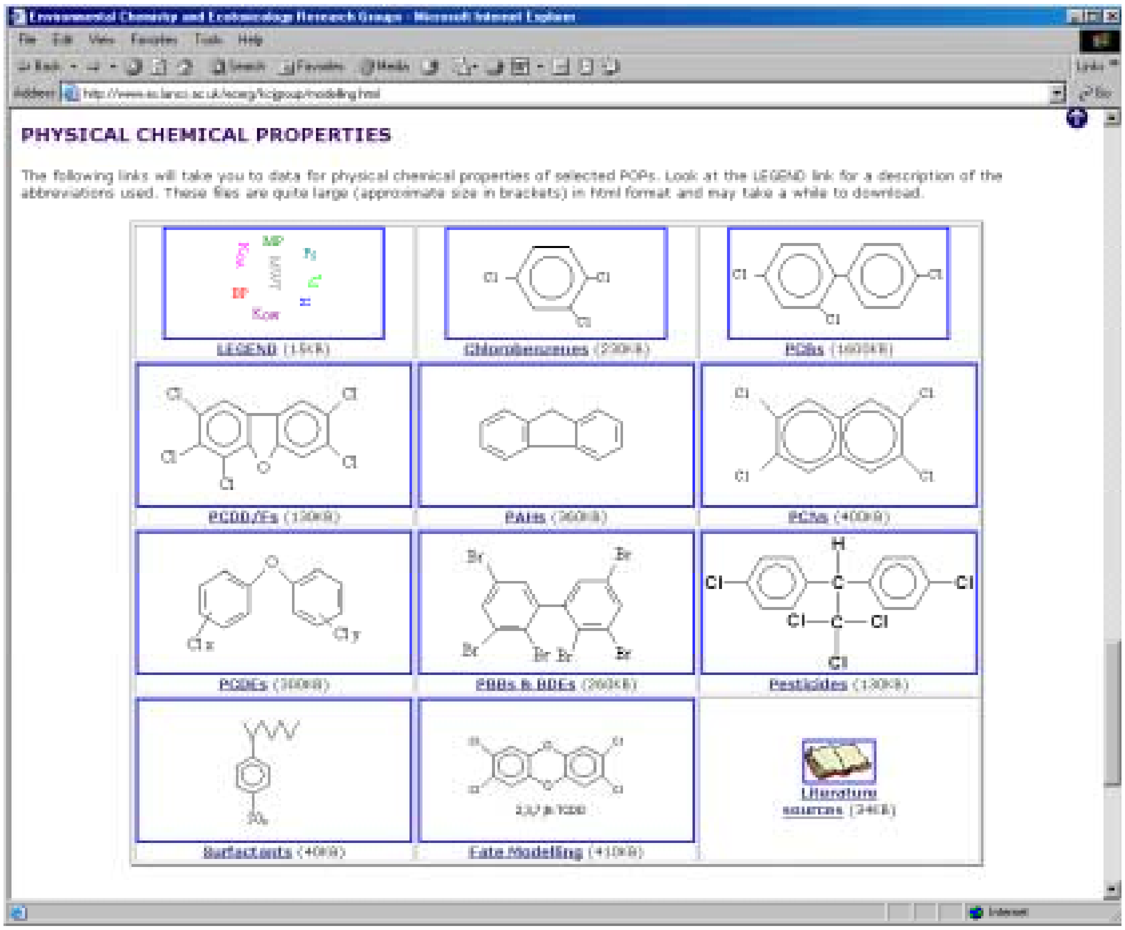
Background
UK Model
Long Range Transport Model
Regional Model
Global Model
Atmospheric Fate Model
European Sampling Campaign
European Distribution Model
Selected References
Physical Chemical Property Data (html format)
Physical Chemical Property Data (pdf format)

Background to environmental fate modelling work at Lancaster University funded by DEFRA.

DEFRA
Department for Environment, Food & Rural Affairs

The fate and behaviour of persistent organic pollutants (POPs) in the environment has attracted considerable scientific and political interest arising from concern over human exposure to these chemicals and their discovery in pristine environments far from source regions. The ability of certain POPs to undergo long range atmospheric transport (LRAT) has resulted in the negotiation of protocols for their reduction or elimination, to reduce the risks to regional and global environments (www.unece.org/env/lrtap). As a result of the involvement of DEFRA in these international POP protocol negotiations, primarily through the auspices of UNECE and UNEP, Lancaster University was asked to undertake a contract to examine some of the scientific issues involved in the negotiations and to investigate the use of predictive models to provide useful input to the development of such protocols. This web page outlines some of the modelling work being carried out at Lancaster University. If you have any comments please feel free to contact us.

Synthetic organic chemicals can be released into the environment through a range of processes which include; release during the production process, release during use (e.g. pesticides), or accident release during combustion processes (e.g. 'dioxins'). Once in the environment, some chemicals have been shown to exhibit detrimental effects on wildlife and some have been shown to bioaccumulate through food chains resulting in high concentrations in top predators e.g. man. If we are to achieve the sustainable use of chemicals then we need a validated process of risk assessment through which we can evaluate the impact of both existing chemicals and those which will



PHYSICAL CHEMICAL PROPERTIES

The following links will take you to data for physical chemical properties of selected POPs. Look at the LEGEND link for a description of the abbreviations used. These files are quite large (approximate size in brackets) in html format and may take a while to download.

These databases contain a range of physicochemical data that can be used to provide an indication of environmental behaviour and to provide input to fate and behaviour models.

Data includes:

F Fugacity ratio. The fugacity ratio represents the ratio of solid to liquid solubility or vapour pressure. F is calculated from MP and is unity for liquids.

LeBas (cm^3 mol^{-l}). Theoretical calculation of molar volume. Useful for developing quantitative structure activity relationships (QSPRs).

Aq.sol. (g m^{-3}). Aqueous solubility. Owing to the hydrophobic nature of many POPs their solubility in water is low, generally less than 1 mg l^{-1}. This makes measurement methods difficult and hence data is only available for selected congeners. However, both aqueous solubility and Kow are determined by the activity of contaminants in water which results in a strong correlation between these properties. When not reported a linear correlation between the sub-cooled liquid vapour pressure and Kow can be used to predict this property.

The solid vapour pressure is an important property for POPs as it describes their 'solubility' in air which partly determines their exchange with surfaces such as soil and water, but also their partitioning onto atmospheric particles. These processes will be responsible for determining their ability to undergo long range transport. Measurement techniques such as gas saturation are difficult and have only been carried out for a range of contaminants. For many POPs, vapour pressures are low ranging from 1 to 10-5 Pa which classifies them as semi-volatile.

Octanol-water partition coefficient - Kow (dimensionless). The octanol-water partition coefficient describes the equilibrium partitioning behaviour of a chemical between water and the lipid substitute octanol. POPs are hydrophobic in nature with Kow expressed on a log10 scale ranging from 3.6 for endosulphan to 8 for octachlorodibenzo-p-dioxin. Generally, values for Kow are determined experimentally but estimation methods structural properties can be employed. Much of the data in Table A 1 are taken from Mackay (2000). However, in order to provide values for some contaminants, particular for congeners within a contaminant group, we have used a quantitative structure property relationship (QSPR) which uses molecular volume (LeBas method) as the molecular descriptor.

H Henry's law constant (Pa mol. m-3). The Henry's law constant describes the equilibrium partitioning behaviour of a chemical between water and air phases and hence is an important descriptor of atmospheric-surface exchange. The data in Table A 1 has been calculated using the ratio between the sub-cooled liquid vapour pressure and sub-cooled liquid aqueous solubility.
H' Dimensionless Henry's Law Constant (calculated as H/RT)

Koa Octanol-air partition coefficient (dimensionless). The octanol-air partition coefficient describes the equilibrium partitioning behaviour of a chemical between air and the lipid substitute octanol. It has been shown to be a useful descriptor of atmospheric vapour-particle partitioning and surface-air exchange.

Reaction rate. Reaction or degradation rates are virtually impossible to assign single values as they vary not only with the intrinsic properties of the chemical but on the nature of the surrounding environment. Factors such as sunlight intensity, hydroxyl radical concentration and the nature of the microbial community, as well as temperature, affect a chemicals half life so it is impossible to a assign single reliable half-life. In the absence of measured atmospheric reaction rate data for individual congeners Mackay et al. (2000) have provided a semi-quantitative estimation of persistence in a range of environmental media.

Mackay, D., Shui, w- Y. and Ma, K-C.(2000) Illustrated handbook ofphysical-chemical properties and environmental fate for organic chemicals. Lewis Publ.

A number of compounds and compound groups are currently being considered as candidate POP compounds for possible inclusion on the UNECE protocol list. These inlclude:

1. Endosulfan: proposed by Germany

Organochlorine insecticide used for plant protection - primarily cotton, tobacco, tea also used in wood preservatives etc. Currently European total use is approximately 500 tonnes with highest usage in Southern Europe. Usage in the UK has declined according to Pesticide Survey Group from 1,660 kg in 2000 to 119 kg in 2001 - the main continuing use is on blackcurrants. Two isomers (alpha and beta), from which the α- isomer is considered to be more volatile. Large particle-bound fraction. Short atmospheric half-life (1-3 days), low Log Kow (<4). Predicted persistence 50-100h with only emissions to air. Predicted long-range transport distance ~ 200km. No data for the UK atmosphere at present. However, archived materials could provide useful clues to historical environmental levels.

2. Hexachlorobutadiene: proposed by the Netherlands

By-product formed during the manufacture of chlorinated hydrocarbons (tri-, tetrachloroethane, etc.). No current production in Europe. Past uses include; solvent, hydraulic fluid, use in rubber manufacture. Emissions may have also occurred from magnesium production. It is estimated that approximately 2 kg of HCBD are emitted per year into the European atmosphere, with 100 kg to water bodies (likely to find it's way into the atmosphere owing to high volatility). High vapour pressure and water solubility, low persistence but potentially high LRT. No UK data. Likely to be a localised issue (e.g. Weston village contamination).

3. Pentachlorobenzene: proposed by the Netherlands

Sources of PeCB include unintentional combustion and impurity in Quintoziene. Quintozene usage in the UK was stopped in 2002. Usage in 2000 and 2001 was about 4.5 tonnes. Currently not produced in UNECE countries. Uses have included; as a fungicide, flame retardant and dielectric fluid in combination with PCBs. It can also be found as impurity in hexachlorobenzene. Quintozene is still used in some Southern European countries. Secondary emissions may be important but this would need further investigation. Meets POP criteria for persistence, bioaccumulation. Volatile (vapour pressure greater than 2 Pa). Atmospheric levels at Alert (1988) greater than 30 pg m^{-3}. Likely to exhibit similar properties and behaviour to hexachlorobenzene. Again, no data available.

4. Dicofol: proposed by the Netherlands

Organochlorine pesticide used in the protection of fruit/vegetable crops. Production currently restricted to Spain and Italy. The use of dicofol is currently allowed in France and Belgium. UK-PSD licensed products expired during 2002 so there should be no more UK usage. Dicofol may contain DDT as an impurity (it must contain less than 0.1%). It also does not meet all the POP criteria. Short half-lives in water (3d) soil (30d) and air (3d) i.e. not that persistent. Low vapour pressure (10^{-5}- 10^{-6} Pa). No data available, although unlikely to be an issue for the UK.

5. Polychlorinated naphthalenes (PCNs): proposed by the Netherlands

Structurally similar to the PCBs. Hydrophobic, stable and good insulators. Uses include cable insulation, wood preservation and in capacitors. Used to be a HPV chemical. Production in the UK stopped by the end of the 1960s. Potential for LRT, bioaccumulation, although not enough information on persistence/degradation in various environmental media. Air concentrations have been measured as part of the HAPs program, with mean ΣPCN levels of 111 pg m^{-3} and 85 pg m^{-3} for Hazelrigg and Chilton, respectively. Totals are generally dominated by the tetra-chlorinated congeners.

6. Pentachlorophenol: proposed by Poland (draft)

PCP is a biocide which may contain other chlorophenols and PCDD/Fs as impurities. Major use is as a wood treatment. EU countries stopped producing PCP in 1992 but significant amounts have been imported until the end of the 1990s. The UK was one of the main importers: 30 tonnes in 1996 and 15 tonnes in 1999, mostly to manufacture sodium pentachlorophenyl laurate (PCPL). PCPL is used in the preservation of textiles, which are subject to degradation by fungi and bacteria (for heavy duty military transport and tent textiles). PCP has a low bioaccumulation potential, but is mobile and relatively persistent. The aquatic environment is most sensitive to PCP. Measured PCP concentrations in freshwater have been as high as 0.2 μg l^{-1} (1995) in the UK. Not much data available for the UK. Further inventory work is required to establish how much is currently in the environment (i.e. in treated wood) and the potential for on-going sources.

7. Short-chain Chlorinated Paraffins: proposed by Canada (draft)

The main uses of SCCPs are in metal working fluids, as plasticisers in paints, coatings and sealants, as flame retardant in rubbers and textiles, and in leather processing. Emissions can occur either during production or during their use in metalworking processes. OSPAR have reported that use of SCCPs in Europe has decreased from 13,000 tonnes in 1994 to 4,000 tonnes in 1998. Historical and current use in the UK is unknown – the UK is also a major exporter. SCCPs exhibit low vapour pressures, very low water solubilities and Log Kows ~6-7, and hence there is potential for bioaccumulation. They also exhibit short half-lives in air (~1-3 d) and decreasing vapour pressure with increasing in carbon chain length. We are currently planning a spatial mapping sampling campaign using passive air samplers. Levels in the UK atmosphere measured at Hazelrigg ranged from 5 to 1090 pg m^{-3} with a median value of 225 pg m^{-3}.

8. Pentabromodiphenylether: proposed by Finland/Sweden.

We have recently completed a manuscript which attempts to quantify historical production and use of pentabromodiphenylethers particularly, BDE-47. It has been published in a special issue of Environment International and represents our current understanding of PBDE production and environmental fate and behaviour. The results present some interesting thoughts about possible routes of human exposure.

Alcock, R.E., Sweetman, A.J., Prevedouros, K. and Jones, K.C. (2003) Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. Environment International, 29(6), 691-698

Table 1 contains a summary of available physicochemical data for selected POP candidate compounds.

Table 1 Summary physicochemical data for selected candidate POPs

Chemical	CAS No	MW (g/mol)	MP (°C)	Vp (Pa)	Sw (g/m^3)	Log Kow	T1/2 air (h)	T1/2 water (h)	T1/2 soil (h)	T1/2 sed (h)
α-endosulfan	959-98-8	406.95	109	0.0013	0.5	3.6	72	720	1200	1200
β-endosulfan	33213-65-9	406.95	213	0.006	0.3	3.8	72	720	1200	1200
Pentachlorobenzene	608-93-5	250.3	86	2.2	0.56	5	7200	7200	3600	3600
Pentachlorophenol	87-86-5	266.34	190	0.12	14	5.05	170	170	1700	550
Hexachlorobutadiene	87-68-3	260.7	-21	20	3.2	4.9	1700	550	550	550
Dicofol	115-32-2	370.5		0.0000016		5	72	72	720	1200
PCNs		162.5 - 404	-2- 200	5 - 10^{-5}	3 - 8 10^{-5}	3.9 - 8.3	24 - 10000	n/a	n/a	n/a
$C_{12}H_{20}Cl_6$		377	41.4	2.10E-03	2.46E-03	6.89				
$C_{12}H_{16}Cl_{10}$		520	101.1	1.80E-06	1.90E-04	7.81				
$C_{16}H_{31}Cl_3$		331	41.7	6.78E-02	9.80E-04	7.14				
$C_{16}H_{21}Cl_{13}$		681	190.9	8.47E-09	9.00E-06	8.88				
PeBDE (47)		485.5	80.5	8.18E-05	9.32E-03	6.67	256	3600	3600	14440

Section 3

Manuscript title:

Seasonal and long-term trends in atmospheric PAH concentrations: Evidence and implications

Authors and affiliations:

Konstantinos Prevedouros, Crispin J. Halsall, Kevin C. Jones, Robert G. M. Lee and Andrew J. Sweetman

Environmental Science Department, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

Eva Brorström-Lundén

IVL, Swedish Environmental Research Institute, Box 47086, SE-402 58 Göteborg, Sweden.

Submission journal:

Environmental Pollution. Elsevier Press. www.elsevier.com

Abstract

Atmospheric monitoring data for selected polynuclear aromatic hydrocarbons (PAHs) were compiled from remote, rural and urban locations in the UK, Sweden, Finland and Arctic Canada. The objective was to examine the seasonal and temporal trends, to shed light on the factors which exert a dominant influence over ambient PAH levels. Urban centres in the UK have concentrations 1-2 orders of magnitude higher than in rural Europe and up to 3 orders of magnitude higher than Arctic Canada. Interpretation of the data suggests that proximity to primary sources 'drives' PAH air concentrations. Seasonality, with winter (W) > summer (S), was apparent for most compounds at most sites; high molecular weight compounds (e.g. benzo[*a*]pyrene) showed this most clearly and consistently. Some low molecular weight compounds (e.g. phenanthrene) sometimes displayed S>W seasonality at some rural locations. Strong W>S seasonality is linked to seasonally-dependent sources which are greater in winter. This implicates inefficient combustion processes, notably the diffusive domestic burning of wood and coal. However, sometimes seasonality can also be strongly influenced by broad changes in meteorology and air mass origin (e.g. in the Canadian Arctic). The datasets examined here suggest a downward trend for many PAHs at some sites, but this is not apparent for all sites and compounds. The inherent noise in ambient air monitoring data makes it difficult to derive unambiguous evidence of underlying declines, to confirm the effectiveness of international source reduction measures.

Introduction

Polynuclear aromatic hydrocarbons (PAHs) are amongst the groups of compounds defined as 'persistent organic pollutants (POPs)' and subject to international atmospheric emissions controls under the 1998 United Nations Economic Commission for Europe (UNECE) protocol (*1,2*). PAHs are subject to long-range atmospheric transport (LRAT) and there are concerns over the carcinogenicity of some PAH compounds (*1-3*). Signatories to the 'POPs protocol' undertake to reduce atmospheric emissions of PAHs to the levels of the reference year 1990. Some countries have adopted, or are considering, air quality standards for selected PAHs; the United Kingdom has a proposed annually averaged standard for benzo[*a*]pyrene of 0.25 ng/m^3, for example. This value can be exceeded in both urban and rural areas (*4*).

These regulatory developments raise interesting scientific issues: a) are the major PAH sources and national emissions inventories well enough established, now and for the 1990 reference year, to ensure compliance with the 'POPs protocol'?; b) what are the trends in atmospheric concentrations of PAHs over the last decade or so?; c) how variable are PAH concentrations seasonally and spatially?; and, d) what are the implications of this variability for sources and compliance with an annually averaged air quality standard?

Despite several years of study, there is still considerable uncertainty over several aspects of the atmospheric sources and behaviour of PAHs. For example, whilst some inventories point towards domestic burning of coal and wood as the dominant source of PAHs to the atmosphere, others implicate emissions from vehicles, or metal smelting/process operations (*2,5*). Without reliable information on sources, it is difficult to conceive how a country can accurately assess whether it is reducing emissions in line with it's commitments to international agreements.

One useful approach to help distinguish between the dominant source categories is to examine ambient monitoring data. For example, if ambient air measurements display seasonality, this would provide clues about the dominant sources; some sources are seasonal (e.g. domestic heating; natural fire events), whilst others are not (e.g. industrial combustion, aluminium and coke production, petroleum refining). However, air concentrations are controlled by a complex array of variables, as depicted in Figure 1. Some of these factors may also influence the seasonality in ambient air measurements, notably secondary sources of PAHs into the atmosphere (i.e. possible volatilisation from soil, water, vegetation or/and urban surfaces); atmospheric loss/removal processes, such as wet deposition, reactions with OH radicals, scavenging by vegetation; 'dilution/advection factors', influenced by wind speed and direction and mixed boundary layer height. Finally, temperature changes drive the gas : particle distribution and atmospheric reaction rates of PAHs.

In this paper, data from monitoring programmes were compiled and assessed, to evaluate the underlying trends and seasonality of PAH air concentrations. Data were considered for different compounds from a range of countries (UK, Sweden, Finland and Arctic Canada) and environments (urban, rural, coastal, remote). These datasets were selected because they provided time series over several years. They constitute some of the few consistent sources of measurement data available internationally. Our objective was to examine the spatial and temporal trends, to shed light on the factors which exert a dominant influence over ambient PAH levels, and to briefly consider the implications for sources and regulation.

Initial remarks on seasonality in air concentrations

Studies have been performed which provide data on the seasonality of atmospheric PAHs. Halsall *et al.* (*6*) reported data for 1991-1992 at 4 urban monitoring sites in the UK (London, Manchester, Cardiff and Stevenage). They noted only a small seasonal variation for the ΣPAH (vapour plus particulate) concentration and selected lighter compounds (e.g. phenanthrene), whilst benzo[*a*]pyrene and other heavy PAHs were an order of magnitude higher in winter than in summer. Gardner *et al.* (*7*) examined atmospheric PAH concentrations at a semi-urban (Castleshaw) and a rural (Esthwaite Water) site in northwest England. Lighter, vapour-phase compounds were again quite uniform, but particulate-bound species increased substantially in the colder months, when residential wood and coal-fired heating was most prevalent. Similar observations have been made at monitoring stations in Arctic Canada (*8*), where the mean ΣPAH concentration during the colder period (October-April) was an order of magnitude higher than that of the warmer season.

Environmental variables exert an influence on ambient PAH concentrations, but this can vary from place to place and between compounds. Lee and Jones (*9*) found significant positive correlations between phenanthrene, fluoranthene and pyrene concentrations and air temperature during an intensive sampling campaign over many months at Hazelrigg, a semi-rural site in the northwest of England. In contrast, benzo[*b*]- and benzo[*k*]fluoranthene were negatively correlated to air temperature. Phenanthrene and anthracene also exhibited a negative correlation with average daily wind speed, whilst wind direction and speed, humidity, precipitation and pressure were not correlated with any of the heavier PAHs. It has been suggested that volatilisation of the lighter compounds from soils/vegetation may contribute to the summer increase of concentrations (*9, 10*). Studies in urban Birmingham, UK, found most PAHs were significantly inversely correlated with temperature (*11*). However, when the data were 'corrected' to account for the seasonal variation in boundary layer height, this correlation disappeared for many of the PAHs. Positive relationships with temperature were then extracted for phenanthrene, fluorene and fluoranthene.

The picture that emerges about seasonality is therefore quite complex, with sources and environmental variables potentially exerting different influences on different compounds in different locations. Seasonality and ambient air trends were therefore investigated in more detail, using various datasets.

Selected datasets, locations and compounds

Sites in the UK, Sweden, Finland and Arctic Canada were selected for study. Their locations are shown in Figure 2 with some details provided below and in Table 1. Analytical details are available in the references cited in Table 1. When available, data were compiled for a range of compounds, namely: acenaphthene (Acen), fluorene (Fluo), phenanthrene (Phen), anthracene (Anthr), pyrene (Py), fluoranthene (Fla), benzo[*b*]fluoranthene (B[*b*]F), benzo[a]pyrene (B[a]P) and benzo[*ghi*]perylene (B[ghi]P). For consistency, through this study 'winter' has been represented by the January-March quarter and 'summer' by July-September. Data have been compiled accordingly.

UK sites: The UK Toxic Organic Micro-Pollutants Survey (TOMPs) has operated a network of sites since 1991, with samples collected at urban and rural locations every 2 weeks. In recent years, these samples have been bulked to give quarterly samples (January-March; April-June; July-September; October-December). The longest PAH time series available is for 2 city centres (London and Manchester) and the semi-rural Hazelrigg site (ca. 5 km from the Irish Sea and the small city of Lancaster). Hazelrigg may be influenced by the proximity of the major M6 motorway. Manchester and London concentrations were studied for the years of 1991-1998, whilst Hazelrigg provided measured data for 1993-2000. The time series for B[a]P was not continuous at Hazelrigg and therefore omitted from the study.

The prevailing wind directions tend to transport pollutants from the UK towards continental Europe and Scandinavia. Data recorded at Scandinavian sites may therefore represent possible 'recipients' of LRAT from the UK and Continental Europe (*16*).

Scandinavian sites: PAHs have been monitored at rural locations in Rörvik, Sweden and Pallas, Finland. Data are available for the years 1994-1999 at Rörvik and 1996-1999 at Pallas; Acen and Fluo were not monitored at these locations. Extreme winter temperatures are common in Pallas with rather temperate summers (see Table 1).

Arctic Canada: A monitoring site has been established at a remote site near Alert, Arctic Canada, with published data only for the first three years of the sampling campaign there beginning at 1992 (*15, 17*). The data are reported weekly, but quarterly arithmetic averages were calculated for this study. The data extend from 1992 to the end of 1996.

Statistical analysis of the data was performed, to test for significant differences in quarterly (seasonal) air concentrations within any given year (notably differences between winter and summer), and year-to-year. Winter-to-summer concentration ratios were calculated for the different sites, compounds and years.

Table 2 gives the typical ranges for most of the target compounds at each site for 1996 as a 'reference year'. It is clear from Table 2 that the sites differ substantially in PAH concentrations and represent a range along an 'urban', 'rural' and 'remote' gradient. As expected, Table 2 shows 'dilution' of ambient air concentrations at sites further away from major source regions. The PAH contamination at the Scandinavian sites is 1-2 orders of magnitude lower than the urban UK ones, whilst Alert concentrations are almost 1000 times lower. Elevated concentrations of some light PAHs (most notably Phen) appear at 'semi-rural' Hazelrigg. The sources are under investigation, but may be due to the proximity to a major highway (motorway). Table 2 suggests that proximity to source regions "drives" PAH air concentrations. This is reinforced by the findings of the statistical analysis discussed below.

Seasonality

A univariate analysis of variance was performed by the General Linear Model procedure, using the SPSS Version 10.1 statistical package. The quarterly air concentration was treated as the dependent variable, with the sequential seasonal data constituting the independent variable (covariate). The standard deviation of the mean concentration was also determined for each quarter, together with the Pearson correlation coefficient (r). Higher r^2 values (~0.75) were obtained for the heavier compounds. The standard deviation was, in most cases, higher that the mean value itself. The data were therefore logarithmically transformed to reduce skewness, a common practice when examining environmental datasets. A similar approach was used to examine PAH, PCB and pesticide air data for sites on Lake Superior, for example (*18*). The standard deviation/variability in the data was thereby reduced, making it less likely that outliers drive the observed trends. After transforming the data, the r^2 values increased up to 0.85 for the heavier PAHs, whilst the values for lighter compounds remained relatively small.

Urban UK – Manchester and London: The W:S ratios are summarised in Table 3 for the individual years and compounds, together with the 8-year average. The following observations can be made about the data: a) statistically significant seasonal concentration differences were observed at these sites for the heavier compounds, namely B[*b*]F, B[a]P and B[ghi]P. The winter concentrations, in some cases, exceeded the respective summer ones by more than an order of magnitude, notably in London; b) of the lighter compounds

(Acen, Fluo, Phen), only Fluo showed a distinct, though weaker, seasonal concentration pattern in both urban centres, with W:S ratios as high as 5 (Table 3). In contrast, Acen and Phen showed varying summer and winter trends (i.e. W:S <1 and >1); c) similar behaviour is shown by the intermediate compounds (Fla, Py and Anthr).

To minimize the influence of possible outliers, the 8-year average ratios were also calculated. These ratios are very similar for most of the compounds in London and Manchester. One exception to this was B[ghi]P; however, in London this compound gave a clear outlier in 1996 (see Table 3). If this value is excluded, the ratios are similar to that of other compounds. The similarities between the long-term seasonal ratios at these two urban sites are attributed to the influence of ongoing primary emission sources. Local site-specific factors, such as meteorology, may affect the year-to-year compound differences/ratios, which are smoothed out on the 8-year averages. Manchester, a smaller city than London, receives air masses originating both from the more polluted south and the relatively "clean" west and north. The higher year-to-year variability shown for most compounds at Manchester, compared to London, may be influenced by these factors.

W:S values >1 can result from either increased winter concentrations or decreased summer ones. The former would indicate a major influence of winter emission sources, such as domestic heating. The latter could be the result of increased depletion mechanisms. To help discriminate between these two possibilities, the contribution of the W and S quarters to the annual average concentration was assessed for each of the years 1991-1998 and is presented in Figure 3. This analysis showed that winter increases accounted directly for the changes in the W:S for the heavier compounds in both sites and most of the lighter ones in London. In summary, the similarity in seasonality implies similar controls on ambient levels at these urban locations. Given that urban centres have ongoing sources of PAHs (see Table 2), it seems likely that primary emissions exert the dominant influence over these trends.

<u>Semi-rural UK - Hazelrigg:</u> The statistical analysis performed for the Hazelrigg data also showed significant differences in concentrations between S and W for all heavy compounds, Py and Phen. There was also a significant difference between autumn and winter

concentrations for those compounds. Acen, B[*b*]F and B[ghi]P showed W>S, whilst Phen, Fla and Pyr showed S>W (see Table 3). Hazelrigg was the only site where elevated summer concentrations, as opposed to lower winter values, resulted in this observation for lighter compounds. Possible causes include enhanced volatilisation from vegetation/soils or greater traffic volume during summer on the nearby (~0.5 km) major motorway (people taking annual holidays, greater day length).

Rural Scandinavia - Rörvik and Pallas: At the coastal Rörvik site, all the compounds (Phen, Fla, Pyr, B[*a*]A, B[*b*]F, B[*k*]F and Anth) showed significantly different seasonal concentrations (p-values <0.001). At Pallas, weak seasonal differences were evident for the heavier compounds. As at the urban UK sites, the observed W : S ratio was >1, 'driven' by elevated winter concentrations. This is suggestive of the importance of elevated winter emissions, either locally or following LRAT, controlling ambient levels at these rural sites. Both locations may be influenced by emissions from continental/central Europe, or by local rural emissions, notably domestic burning of wood.

Interestingly, from Table 3 the W:S ratios of the heavier PAHs tend to increase moving away from the urban centres. For B[*b*]F, B[*a*]P and B[*ghi*]P the ratios are highest in order of R/P> H>L/M. Emissions from local domestic sources, where wood/coal are burnt during winter months for space heating (*3*) seems the most probable explanation, although scavenging by vegetation may contribute by reducing the summertime burden of these compounds at the rural sites.

Alert: It is important to note that winter temperatures at this site can reach –35°C, with summer temperatures only just exceeding zero (see Table 1). There are also important seasonal differences in the predominant air mass origins. Briefly, the Arctic lower atmospheric circulation during winter is characterized by the presence of two oceanic low (Icelandic and Aleutian) and two continental high (Asiatic and North American) pressure systems (*19*). This prevailing meteorology results in air mass movement from the polluted Eurasian land mass to impact the high Arctic (and, thus, Alert). This explains the high winter levels of particulate-bound pollutants measured at Alert (*20*). During summer, the dominant Asiatic high pressure system breaks down, greatly reducing air flow into the Arctic from southerly latitudes, resulting in clean air with very low pollutant levels. Indeed, PAH concentrations measured in the summer samples are often below detection limits (*17, 21*). Differences between winter and summer concentrations were sometimes 2-3 orders of magnitude for the multi-ringed compounds (see Table 2). A further analysis of the seasonality at this remote site was hindered by the extremely low summer values and for this reason Alert W: S ratios were omitted from Table 3.

Underlying trends

The underlying atmospheric trends of selected PAHs are shown in Figure 4. The X-axis represents the sequential quarters (seasons) for which data where available, whereas the natural logarithms of air concentrations are plotted in the Y-axis. Phen and BaP were used to represent low and high molecular weight compounds, but all other compounds revealed similar trends. The natural logarithm of air concentrations was selected in order to reduce the skewness/ scatter of the data. The following observations can be made:

1. London and Manchester show decreases in both the amplitude of the annual oscillation and the mean yearly value for most of the compounds studied. Concentrations exhibited a clear decreasing trend at both sites, excluding a peak in the autumn of 1994 for London. All heavy PAHs show statistically significant long-term trends, i.e. their rate of year-to-year seasonal concentration decrease follows the same pattern. Fluo also followed the pattern of its heavier counterparts. Examination of the data at a finer resolution showed 'spikiness', presumably the result of local emission events. Every early November in the UK, for example, fireworks are set off and bonfires lit across the whole country. Lee *et al.* (*22*) have found significantly elevated levels of combustion-derived polychlorinated-dibenzo-p-dioxin and dibenzofuran (PCDD/Fs) as a result of such events and similar observations have been made for PAHs (*23*).
2. At Hazelrigg, Fla and Py concentrations appear to have increased since 1998. There are no significant or consistent trends (up or down) for the other compounds, with large year-to-year variability.

3. No underlying trends were apparent at Rörvik and Pallas, although the available datasets are shorter here. Bignert *et al.* (*24*) highlighted the importance of long-term, continuous environmental datasets and the difficulties of interpreting shorter-term datasets. This emphasises the need for consistent multi-year monitoring programmes.
4. A decrease of concentrations is evident in Alert over the 1992-1996 period for most of the studied compounds and is the subject of an ongoing study (*25*). Over time concentrations at Alert were represented only by the months of November to March for the existing five years of data. Most of the summer data fell below the method detection limit and were, thus, omitted from further analysis.

Derivation of half-lives for declines in atmospheric concentrations

To gain further insight regarding the long-term concentration trends, the natural logarithm of the quarterly air concentration was regressed with season. Linear trendlines were then calculated for all 6 sites under study for the years 1991-1999 (or however long samples were available). If Y is the air concentration and X the time in quarters, half-lives for declines in atmospheric concentrations can then be calculated from the slope of the line, A (if a significant decrease is observed) according to the following first-order rate equation:

$\mathrm{Ln}\, Y = A\, X + B$ (eqn 1)

$t_{1/2} = -\mathrm{Ln}\, 2/ A$ (eqn 2)

The calculated half-lives (in years) are summarized in Table 4, together with the regression statistics (r square and p values). Half-lives have only been calculated for the datasets that are the least "uncertain". In other words, when the p-values were low, the confidence of the calculated half-lives being statistically significant was high and, thus, the selected datasets represent the long-term concentration trends more reliably. In the case of increased p-values, the scatter/uncertainty in the data is so high that a half-life term is not meaningful. This was the case for most compounds at Rörvik and Pallas as well as most light PAHs in Alert.

Most of the data are 'noisy', influenced by the short time-series available, and reveal site-by-site and compound differences. Some trends are apparent, however: generally, the trends for PAH air concentrations are downwards, though exceptions are apparent (see Table 4). It has taken approximately 4-8 years for London air concentrations to drop by 50% during the 1990s, whilst there is a greater inconsistency (and longer half-lives) in the other major urban centre of Manchester. Fla, Py and B[*a*]A at Hazelrigg showed increasing trends over the time periods available and are symbolised with (+) in Table 4. In contrast, rates of decline at Alert through the years 1992-1996 were extremely rapid, especially for the heavier congeners. Air concentrations at this site are believed to be mainly driven by primary emissions and LRAT. Local meteorology is likely to exhibit a profound effect for this remote site, as discussed above. It will be interesting to see how the trends develop over a longer time period at this location.

Implications of the study

Signatories to the UNECE POPs protocol undertake to reduce national PAH emissions to 1990 levels. However, as discussed and despite efforts at source identification (*2, 26*), many countries will experience difficulties in demonstrating compliance, because source inventories for 1990 and contemporary situations are subject to major uncertainties. Ambient monitoring data can provide a powerful tool to demonstrate underlying trends directly and – by implication - source reduction. However, this requires reliable and long-term (many years) datasets because – as this study has demonstrated – site-by-site differences in levels and trends can be substantial and subject to considerable short-term (seasonal; year-on-year) variability.

This study indicates that primary sources continue to drive atmospheric PAH concentrations in the urban centres. LRAT carries these primary emissions to rural/remote locations, where they can exert an important influence, with some evidence for this affecting the sites of Hazelrigg and Rörvik. PAH concentrations in such areas can also be strongly influenced by local diffusive combustion-derived emissions. The remote site at Alert revealed strong seasonality, but illustrates the importance of considering the seasonal dependency of local meteorology.

A convenient categorisation of PAH sources considers domestic, industrial, mobile (vehicle), agricultural and natural atmospheric emissions. A recent European Commission (EC) report concluded that 'major source components are changing with time as a result of regulation and economic development' (*26*). Industrial sources are increasingly regulated in Europe, whilst mobile sources have been subject to more stringent regulation, but not specifically for PAHs. These factors may collectively contribute to the declining urban PAH concentrations reported here, although it is perhaps more appropriate to see this as part of the steady drop in atmospheric PAH concentrations from the 1950/60s observed from long-term trend records in sediment cores and archived samples (*27-29*). Agricultural (stubble) burning has also been controlled in the UK and many other European countries for some years now.

If further declines in ambient PAH concentrations are desirable, they will be increasingly difficult to achieve. This study indicates that seasonally-dependent diffusive domestic combustion sources provide a major component of the primary emissions of PAHs nationally/regionally. This heightens concern that the targets set by the UNECE protocol may be difficult to demonstrably meet, because such sources are – by their very nature – difficult to quantify, control and reduce. For example, the EC concluded that 'it is likely that the continued burning of solid fuels for domestic heating as a source is unlikely to decrease unless new measures are introduced' (*26*). Our study therefore lends support to the conclusion that 'from a cost-benefit perspective, actions to reduce PAH emissions should focus on domestic burning of wood and coal' (*30*). Such measures include optimisation of stoves, replacement of open fireplaces with optimised stoves, information campaigns to promote best practice for combustion, and switching to alternative fuels (*30*).

Studying the seasonality and long-term trends of air concentrations for semi-volatile organic compounds such as PAHs is subject to a number of uncertainties and rather poorly understood environmental processes. The influence of volatilisation from soil, water, vegetation and urban surfaces is still not well understood. Multi-media modelling may be useful in helping to assess the influence/relative importance of seasonally dependent depletion/loss mechanisms, the controlling influence(s) of these mechanisms and of different emission scenarios.

Acknowledgements

This study was supported by Defra (Department for Environment, Food and Rural Affairs) funding No. EPG 1/3/169. We thank Dr Knut Breivik (NILU) for critical comments and advice, and Drs Pierrette Blanchard and Hayley Hung of MSC Downsview, Canada, for access to the Northern Contaminants database for PAH data from Alert.

Literature cited

(1) United Nations Economic Commission for Europe (UN ECE) ECE/EB.Air/60, 1998

(2) Vestreng, V.; Klein, H. 2002. Emission data reported to UNECE/EMEP: Quality Assurance and Trend Analysis and Presentation of WebDab. MSC-W Status Report 2002. EMEP-MSC-W Note 1/2002. Meteorological Synthesizing Centre – West. Oslo, Norway. 101 pp.

(3) International Agency for Research on Cancer (IARC) Monograph: Volume 34. Evaluation of the Carcinogenic Risk of Chemicals to Humans: PAH Compounds, Part 3. 1998.

(4) Lohmann, R.; Northcott, G. L.; Jones, K. C. *Environ. Sci. Technol.* 2000, 34, 2892-2899.

(5) Wild, S. R.; Jones, K. C. *Environ. Pollut.* 1995, 88, 91-108.

(6) Halsall, C.J.; Coleman, P.J.; Davis; B.J., Burnett, V.; Waterhouse, K.S.; Harding-Jones, P.; Jones, K.C. *Environ. Sci. Technol.* 1994, 28, 2380-2386.

(7) Gardner, B., Hewitt, C.N., Jones, K.C. *Environ. Sci. Technol.* 1995, 29, 2405-2413.

(8) Macdonald, R.W.; *et al.* *Sci. Total Environ.* 2000, 254, 93-234.

(9) Lee, R.G.M.; Jones, K.C. *Environ. Sci. Technol.* 1999, 33, 705-712.

(10) Lee, R. G. M.; Hung, H.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol.* 1998, 32, 2172-2179.

(11) Dimashki, M.; Lim, L.H.; Harrison, R.M.; Harrad, S., *Environ. Sci. Technol.* 2001, 2264-2267.

(12) Halsall, C.J.; Lee, R.G.M.; Coleman, P.J.; Burnett, V.; Harding-Jones, P.; Jones, K.C. *Environ. Sci. Technol.* 1995, 29, 2368-2376.

(13) Coleman, P.J.; Lee, R.G.M.; Alcock, R.E.; Jones, K.C. *Environ. Sci. Technol.* 1997, 31, 2120-2124.

(14) Brorström-Lundén, E.; Lindskog, A.; Mowrer, J. *Atmos. Environ.* 1994, 28, 3605-3615.

(15) Fellin, P.; Barrie, L.A.; Dougherty, D.; Toom, D.; Muir, D.; Grift, N.; Lockhart, L.; Billeck, B. *Environ. Toxicol. Chem.* 1996, 15, 253-261.

(16) van Jaarsveld, W. A. J.; van Pul, W. A. J.; de Leeuw, F. A. A. M. *Atmos. Environ.* 1997, 31, 1011-1024.

(17) Halsall, C.J.; Barrie, L.A.; Fellin, P.; Muir, D.C.G.; Billeck, B.N.; Lockhart, L.; Rovinsky, F.YA.; Kononov, E.YA.; Pastukhov, B. *Environ. Sci. Technol.* 1997, 31, 3593-3599.

(18) Buehler, S.S.; Basu, I.; Hites, R.A. *Environ. Sci. Technol.* 2001, 35, 2417-2422.

(19) Raatz, W.E. In *Pollution of the Arctic Atmosphere*; Sturges, W.T., Ed.; Elsevier Science Publishers: London, 1991; pp. 13-42.

(20) Barrie, L.A. *Atmos. Environ.* 1986, 20, 643-663.

(21) Sirois, A.; Barrie, L.A. *J. Geoph. Res.* 1999, 104, 11599-11618.

(22) Lee, R. G. M.; Green, N. J. L.; Lohmann, R.; Jones, K. C. *Environ. Sci. Technol.* 1999, 33, 2864-2871.

(23) N. Farrar; Lee, R.G.M.; Smith, K.; Jones, K.C.; unpublished data.

(24) Bignert, A.; Olsson, M.; Persson, W.; Jensen, S.; Zakrisson, S.; Litzén, K.; Eriksson, U.; Häggberg, L.; Alsberg, T. *Environ. Pollut.* 1998, 99, 177-198.

(25) Halsall, C.J.; Attwell, S.; Tych, W., Hung; H., Blanchard, P.; Li, H.; Fellin, P.; Stern, G., unpublished data.

(26) European Union, 2001. Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position Paper. Office for Official Publications of the European Communities. L-2985 Luxembourg. ISBN 92-894-2057-X.

(27) Jones, K. C.; Sanders, G.; Wild, S. R.; Burnett, V.; Johnston, A. E. *Nature* 1992, 356, 137-140.

(28) Sanders, G.; Jones, K. C.; Hamilton-Taylor, J.; Dörr, H. *Environ. Toxicol. Chem.* 1993, 12, 1567-1581.

(29) Wild, S. R.; Jones, K. C.; Johnston, A. E. *Atmos. Environ.* 1992, 26A, 1299-1307.

(30) European Commission DG Environment, 2001. Economic Evaluation of Air Quality Targets for PAHs. http://europa.eu.int/comm/environment/index

List of figures

List of tables

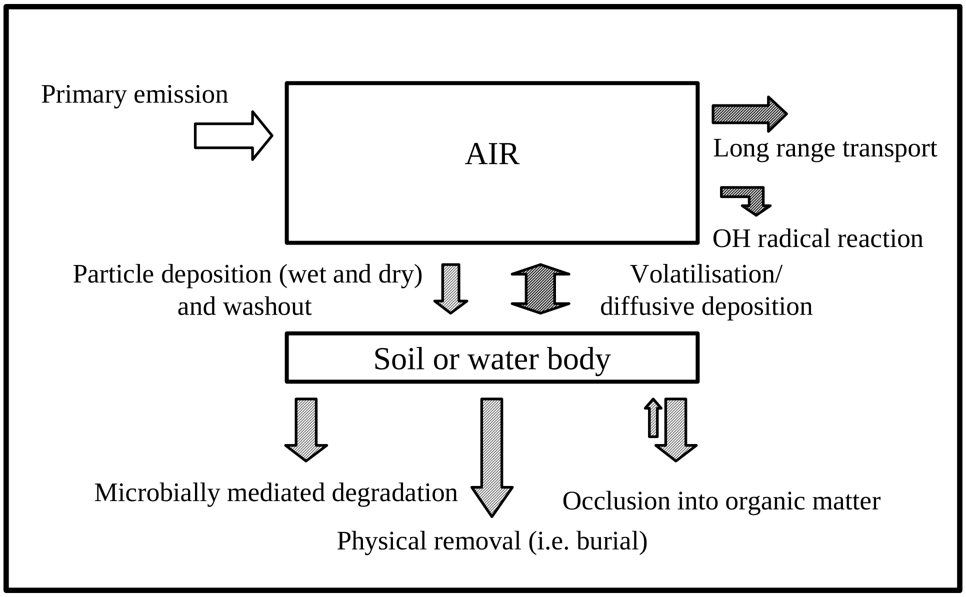


Figure 1

Figure 2

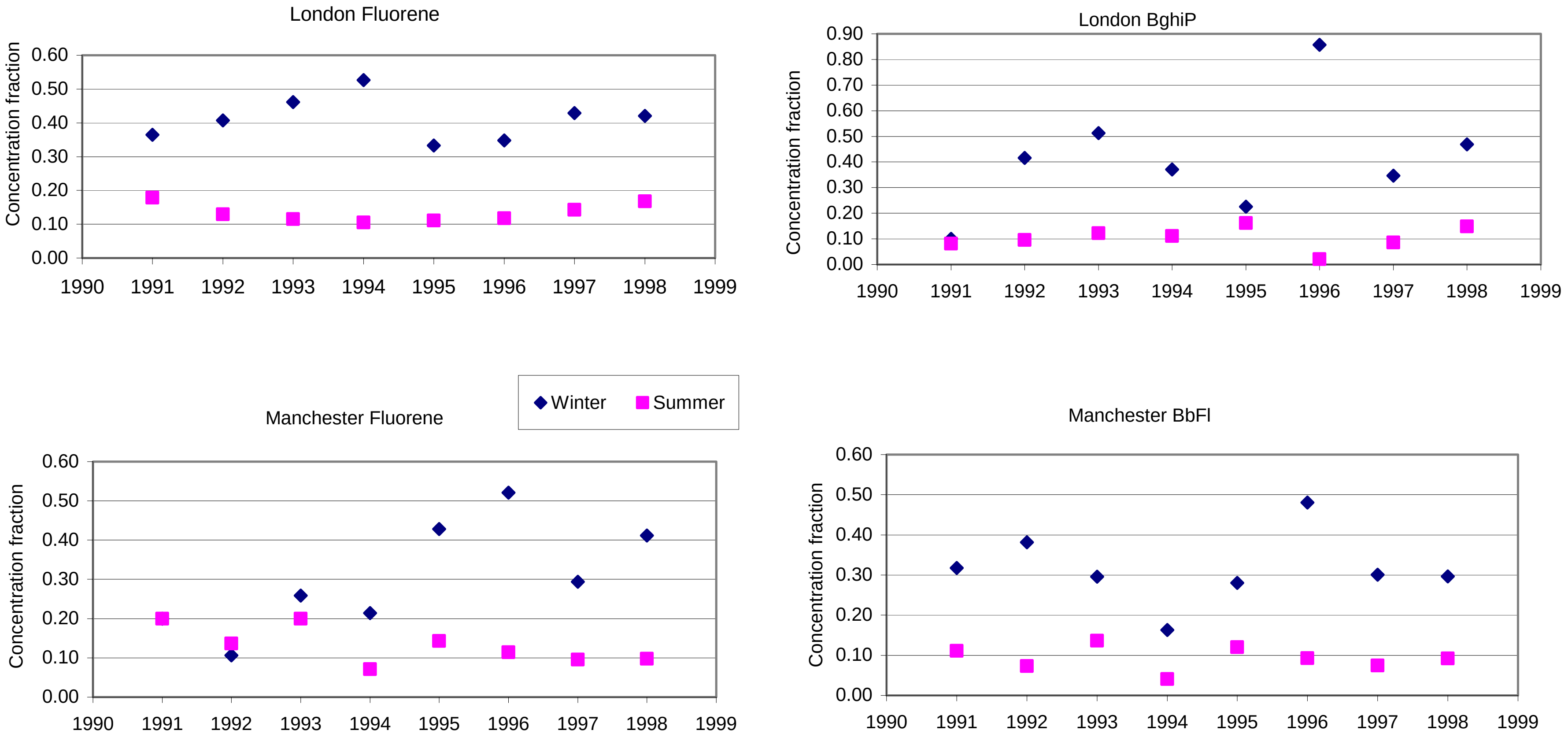

London Fluorene
Concentration fraction
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
London BghiP
Concentration fraction
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
Manchester Fluorene
Concentration fraction
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
◆ Winter
■ Summer
Manchester BbFl
Concentration fraction
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999

Figure 3

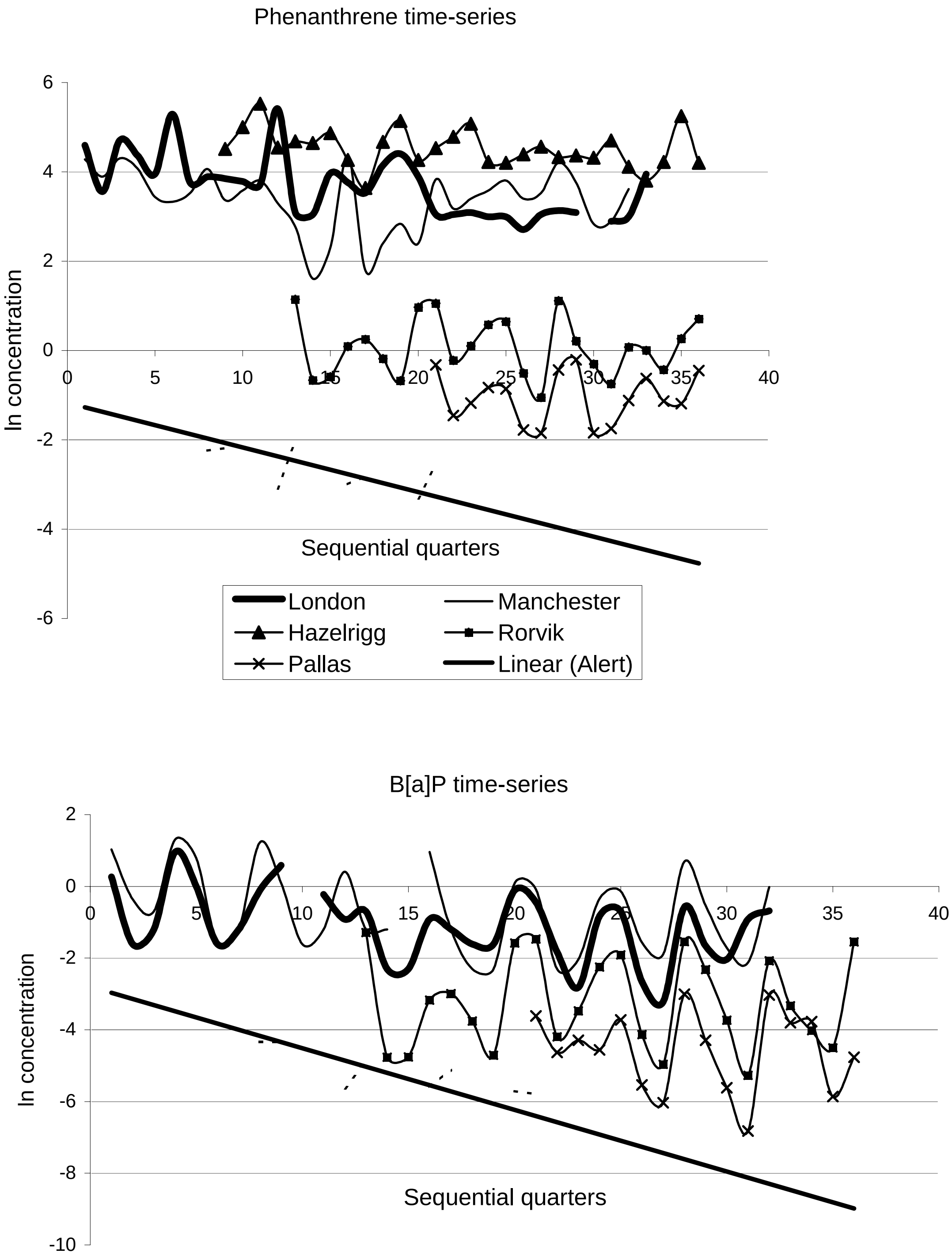

Phenanthrene time-series
ln concentration
6
4
2
0
-2
-4
-6
0
5
10
15
20
25
30
35
40
Sequential quarters
London
Manchester
Hazelrigg
Rorvik
Pallas
Linear (Alert)
B[a]P time-series
ln concentration
2
0
-2
-4
-6
-8
-10
0
5
10
15
20
25
30
35
40
Sequential quarters

Figure 4

Table 1

Site	Coordinates	Location	Duration of study	Frequency of record	Typical annual temperature and T range (°C)	Reference
London	51° 30′, 0°10′W	Rooftop	1991-1998	Quarterly	10, (5-25)	12, 13
Manchester	53°30′N, 2°13′W	Rooftop	1991-1998	Quarterly	10, (5-20)	12, 13
Hazelrigg	54°2′N, 2°45′W	Field	1993-2000	Quarterly	10, (5-20)	12, 13
Rörvik	57°14´N, 14°35´E	4m above ground	1994-1999	Monthly	7.5, (-17-22)	14
Pallas	67°58´N, 24°08´E	4m above ground	1996-1999	Monthly	-1.6, (-30-24)	14
Alert	82°47´N, 62°30´W	4m above ground	1992-1996	Weekly	-18, (-35-5)	15

Table 2

	London	Manchester	Hazelrigg	Rörvik	Pallas	Alert
Acen	0.7-1.5	1-4	0.5-2	N/a	N/a	0.001-0.02
Fluorene	3-9	4-20	5-20	N/a	N/a	0.01-0.3
Phenanthrene	20-22	20-50	70-160	0.8-3	0.2-0.7	0.02-0.08
Anthracene	1-2	1-4	5-15	0.01-0.1	0.002-0.01	0.002-0.003
Fluoranthene	4-6	5-10	5-10	0.3-1.7	0.1-0.3	0.005-0.07
Pyrene	2.5-5	3.5-8	5-10	0.1-1	0.05-0.2	0.004-0.05
B[a]A	0.2-0.9	0.2-1.6	0.3-0.7	0.01-0.2	0.005-0.02	N/d-0.020
Chrysene	0.5-2	0.4-6	0.25-1	0.05-0.5	0.03-0.04	N/d -0.050
B[b]F	0.2-1.5	0.2-1.5	0.05-1	0.04-0.8	0.02-0.05	N/d -0.012
B[k]F	0.1-1	0.1-1	0.02-0.4	0.01-0.3	0.01-0.02	N/d -0.01
B[a]P	0.05-0.6	0.1-1	N/a	0.01-0.2	0.01-0.03	N/d -0.004
B[ghi]P	0.3-10	0.2-0.8	0.02-0.5	0.02-0.15	0.01-0.04	N/d -0.013

N/a: Not analysed

N/d: Not detected

Table 3

YEAR		1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	Average
Acen	M	0.5	0.7	1.2	1.0	1.0	2.6	3.2	3.2			1.7
	L	1.7	1.4	1.4	0.7	0.6	1.8	1.8	1.4			1.4
	H			0.4	3.3	1.0	4.4	4.1		0.9		2.3
Fluo	M	1.0	0.8	1.3	3.0	3.0	4.6	3.1	4.2			2.6
	L	2.0	3.1	4.0	5.0	3.0	3.0	3.0	2.5			3.2
	H			0.6	2.3	0.9	3.7	3.0	1.7	0.6	1.3	1.8
Phen	M	1.0	0.9	0.6	1.6	0.4	1.5	1.3	2.4			1.2
	L	0.9	1.2	1.1	0.4	0.4	1.0	1.0	1.2			0.9
	H			0.4	0.8	0.2	0.6	0.7	0.7	0.2		0.5
	R				5.6	2.5	2.6	5.5	2.6	0.8		3.3
	P						2.3	2.7	4.7	1.8		2.9
Fla	M	1.4	1.3	0.7	7.0	1.0	1.3	1.1	1.7			2.0
	L	1.7	1.5	2.0	1.0	0.7	1.2	0.9	0.9			1.2
	H			0.7	2.1	0.1	0.9	0.6	0.8	0.2	0.3	0.7
	R				10.7	4.1	4.3	8.2	3.9	2.7		5.7
	P						1.8	4.7	6.9	3.5		4.2
Py	M	1.5	1.3	0.8	3.3	1.0	1.4	1.2	1.8			1.5
	L	1.6	1.8	2.3	1.0	0.8	1.4	1.1	1.0			1.4
	H			0.5	0.7	0.1	0.7	0.6	0.6	0.2	0.3	0.4
	R				8.4	3.4	4.8	9.0	4.3	2.9		5.5
	P						2.3	4.2	7.2	2.3		4.0
Anthr	M	1.6	1.4	0.8	8.3	3.0	2.1	1.9	1.8			2.6
	L	1.8	2.0	2.0	1.0	0.7	1.5	1.5	1.5			1.5
	H			0.6	0.3	0.2	0.8	0.6	0.5	0.2	0.2	0.4
	R				9.8	5.2	4.7	8.3	2.6	1.6		5.4
	P						1.9	2.6	28.6	1.1		8.6
B[b]f	M	2.9	5.3	2.2	4.0	2.3	5.2	4.1	3.2			3.6
	L	3.7	2.4	3.7	2.3	1.7	6.8	6.7	1.9			3.6
	H			10.0	7.0		16.8	10.0	7.4	2.6	1.9	8.0
	R				25.1	5.5	13.3	19.1	12.0	3.7		13.1
	P						1.9	2.8	6.6	9.0		5.1
B[a]P	M	5.6	7.3	3.7		3.0	7.1	5.8	4.9			5.3
	L	4.3	3.3	2.3	5.0	1.5	10.7	12.5	1.5			5.1
	H	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
	R				>30	>5	>7	>20	>19	>34		
	P						>2	>10	>12	>7		
B[ghi]P	M	4.0	3.5	1.8	1.0	1.0	4.4	4.4	4.6			3.1
	L	1.2	4.4	4.2	3.3	1.4	41.4	4.1	3.2			7.9
	H			5.0	1.0	1.0	26.5		12.0		>10	9.1

M: Manchester, L: London, H: Hazelrigg, R: Rörvik, P: Pallas

Numbers in bold are assumed outliers

Values >1 signify winter > summer

Table 4

	London			Manchester			Hazelrigg			Rörvik			Pallas			Alert		
	$t_{1/2}$	r^2	p	$t_{1/2}$	r^2	p	$t_{1/2}$	r^2	p	$t_{1/2}$	r^2	p	$t_{1/2}$	r^2	p	$t_{1/2}$	r^2	p
Acen	4.2	0.454	<0.001		0.121	0.424				n/a	n/a	n/a	n/a	n/a	n/a	3	<0.1	0.12
Fluo	3.2	0.619	<0.001	5.0	0.344	0.048	1.5	0.5	<0.001	n/a	n/a	n/a	n/a	n/a	n/a		<0.1	0.66
Phen	3.8	0.538	<0.001	11.5	0.169	0.207	10.0	0.686	0.005		<0.1	0.6		<0.1	0.84		<0.1	0.48
Anthr	3.5	0.768	<0.001		0.499	0.426	9.0	0.507	0.136	5	<0.1	0.11		<0.1	0.99	0.8	0.22	<0.001
Fla	7.5	0.574	<0.001	9.0	0.227	0.154	+	0.3	0.014	8	<0.1	0.23		<0.1	0.73		<0.1	0.56
Py	7.0	0.647	<0.001		0.302	0.422	+	0.482	0.004		<0.1	0.89		<0.1	0.6		<0.1	0.65
B[a]A	9.2	0.683	0.014	8.5	0.458	0.154	+	0.269	0.123		<0.1	0.7		<0.1	0.19		<0.1	0.71
Chrys	8.0	0.567	0.023		0.4	0.768		0.025	0.512		<0.1	0.63		<0.1	0.54		<0.1	0.92
B[b]F	5.9	0.623	0.002	8.1	0.841	0.002	3.2	0.745	0.001		<0.1	0.61		<0.1	0.8		<0.1	0.64
B[a]P	4.1	0.74	<0.001	4.1	0.828	<0.001	n/a	n/a	n/a		<0.1	0.95		<0.1	0.9	1.3	<0.1	0.28
B[ghi]P	4.2	0.617	0.001	2.9	0.758	<0.001	2.2	0.654	<0.001		<0.1	0.4		<0.1	0.84	1	<0.1	0.1

N/a: data not available, + : Positive slope

Section 4

Manuscript title:

Modelling the atmospheric fate and seasonality of polycyclic aromatic hydrocarbons in the UK

Authors and affiliations:

Konstantinos Prevedouros, Kevin C. Jones and Andrew J. Sweetman

Environmental Science Department, Institute of Environmental and Natural Sciences,
Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

Submission journal:

Environmental Toxicology and Chemistry. SETAC press. www.setac.org

Abstract

This paper presents the results from an exercise in atmospheric compound fate modelling, which had three main objectives: 1). to investigate the balance between estimated national atmospheric emissions of 6 selected PAHs and observed ambient measurements for the UK, as a means of testing the current emission estimates; 2). to investigate the potential influence of seasonally dependent environmental fate processes on the observed seasonality of air concentrations; and 3). after undertaking the first two objectives, to make inferences about the likely magnitude of seasonal differences in sources. When addressing objective 1 with annually averaged emissions data, it appeared that the UK PAH atmospheric emissions inventory was reasonably reliable for fluorene, fluoranthene, pyrene, benzo[a]pyrene and benzo[ghi]perylene – but not so for phenanthrene. However, more detailed analysis of the seasonality in environmental processes which may influence ambient levels, showed that the directions and/or magnitudes of the predicted seasonality did not coincide with field observations. This indicates *either* that our understanding of the environmental fate and behaviour of PAHs is still limited, *and/or* that there are uncertainties in the emissions inventories. It is suggested that better quantification of PAH sources is needed. For 3- and 4-ringed compounds, this should focus on those sources which increase with temperature, such as volatilisation from soil, water, vegetation and urban surfaces, and possible microbially-mediated formation mechanisms. The study also suggests that the contributions of inefficient, diffusive combustion processes (e.g. domestic coal/wood burning) may be underestimated as a source of the toxicologically significant higher molecular weight species in the winter. It is concluded that many signatory countries to the UNECE POPs protocol (which requires them to reduce national PAH emissions to 1990 levels) will experience difficulties in demonstrating compliance, because source inventories for 1990 and contemporary situations are clearly subject to major uncertainties.

Introduction

There is considerable interest in the atmospheric sources, behaviour and potential carcinogenic/mutagenic effects of polycyclic aromatic hydrocarbons (PAHs) [1-3]. They are amongst the compounds subject to international atmospheric emissions controls under the 1998 United Nations Economic Commission for Europe (UNECE) protocol [4]. Signatories to the 'POPs protocol' have undertaken to reduce atmospheric emissions of PAHs to the levels of the reference year 1990. In addition, some countries have adopted, or are considering, air quality standards for selected PAHs [2]; the United Kingdom has a proposed annually averaged standard for benzo[a]pyrene of 0.25 ng/m^3, for example. This value can be exceeded in both urban and rural areas, during the winter months [5].

Despite these regulatory developments, there are still major uncertainties over our understanding of the atmospheric sources and behaviour of PAHs. National and regional source inventories are still at best expert estimates, as there are numerous diffusive and poorly quantified sources of these compounds [2,3]. Some inventories point towards domestic burning of coal and wood as the dominant source of PAHs to the atmosphere, others implicate emissions from vehicles, or metal smelting/process operations, for example. Without reliable information on sources, it will be difficult for signatory countries to accurately assess whether they are reducing emissions in line with their commitments to international agreements.

One useful approach to help distinguish between the dominant source categories is to examine ambient monitoring data. For example, if ambient air measurements display seasonality, this would provide clues about the dominant sources; some sources are seasonal (e.g. domestic heating; natural fire events), whilst others are not (e.g. industrial combustion, aluminium and coke production, petroleum refining). Seasonality of ambient PAHs is often observed [6]. However, air concentrations are controlled by a complex array of variables, some of which may also influence the seasonality in ambient air measurements. Examples include: secondary sources of PAHs into the atmosphere (i.e. possible volatilisation from soil, water, vegetation or/and urban surfaces); atmospheric loss/removal processes, such as wet deposition; reactions with OH radicals; scavenging by vegetation; 'dilution/advection factors', influenced by wind speed and direction; and mixed boundary layer height. Finally, seasonal temperature changes drive the gas : particle distribution and atmospheric reaction rates of PAHs.

Modelling is a useful tool in helping to assess the influence/relative importance of seasonally dependent sources and environmental fate processes on ambient concentrations. Hence, it can be helpful in identifying which variables are likely to exert an influence on the seasonality of ambient PAH monitoring data, thereby providing clues as to the dominant processes and the reliability of emission inventories. This paper presents the results from a modelling exercise, which had three main objectives:

1. to investigate the balance between estimated national atmospheric emissions of PAHs and observed ambient measurements for the UK, as a means of testing the current emission estimates;
2. to investigate the potential influence of seasonally dependent environmental fate processes on the observed seasonality of air concentrations;
3. after undertaking 1 and 2, to make inferences about the likely magnitude of seasonal differences in sources.

A dynamic atmospheric fate model was developed and applied to a range of compounds with contrasting physico-chemical properties and fate characteristics. Six PAHs were selected for study, namely: fluorene (Fluo), phenanthrene (Phen), fluoranthene (Fla), pyrene (Py), benzo[*a*]pyrene (B[*a*]P) and benzo[*ghi*]perylene (B[*ghi*]P). The years 1993-1997 were chosen as the study period, as source inventory and ambient data is available for that time, with 1996 selected as a 'model year'. Based on the results of these objectives, the likely dominant sources of PAHs to the UK atmosphere are discussed, along with the environmental processes controlling them.

PAH emissions for the UK

PAHs are generally produced as a result of incomplete combustion processes, in oxygen deficient conditions. A convenient categorisation of PAH sources considers domestic, industrial, mobile (vehicle), agricultural and natural atmospheric emissions. Most source inventories focus on these 'primary' or fresh releases of PAHs, although secondary sources - re-cycling of previously emitted 'reservoirs' in soils, vegetation and sediments - may also be important, particularly for lower molecular weight species [7,8]. Accidental fires are another source, which are very difficult to quantify and often not included in inventories.

A recent report concluded that 'major source components are changing with time as a result of regulation and economic development' [3], which adds to the problems of attaining a reliable source inventory. Industrial sources are increasingly regulated in Europe, whilst mobile sources have been subject to more stringent regulation, but not specifically for PAHs. Agricultural (stubble) burning has also been controlled in the UK and many other European countries for some years now.

Annual UK source inventories for PAHs are carried out for the Department for Environment Food and Rural Affairs (Defra) and published in the National Atmospheric Emissions Inventory (NAEI), details of which can be found at (http://www.aeat.co.uk/netcen/airqual/naei/annreport/naeiapp5.html). The focus of the NAEI inventory is primary sources; more information about the inventory methodology can be found at (http://www.aeat.co.uk/netcen/airqual/naei/annreport/annrep99/). The major primary PAH sources to the UK atmosphere according to the NAEI are detailed in Table 1, together with the average 1993-1997 annual emissions for each of the six compounds under study and the percentage contribution of each source to the total [9-12]. The sources considered in Table 1 are segregated into 'seasonal' and 'non-seasonal', for use later in the paper.

Model structure and environmental input

The atmospheric/box model described herein was written in ModelMaker version 4.0 (®Cherwell Scientific Ltd). PAHs are introduced into the UK atmosphere via primary emissions and advection, whilst their environmental fate is governed by wet and dry deposition, reactions with OH radicals and advection out of the region. Revolatilisation from ground surfaces was considered to be not of major importance for the UK and the inclusion of further environmental compartments (e.g. soil or water) into the model framework was deemed that would unnecessarily increase the degree of complexity. Hence, the ambient air temperatures generally cannot support the outgassing of PAHs previously deposited in such bodies. Furthermore, the losses to other environmental media can be described in the following differential equation; an analysis of the influence of vegetation is included towards the end of the paper.

$$\text{Vair}\ \frac{dCair\_g}{dt} = \text{Eair}+(\text{Gadv}*\text{Cair\_adv})-(\text{Gadv}*\text{Cair\_g})-(\text{Gadv}*\text{Kp}*\text{TSP}*\text{Cair\_g})-(\text{Wg}*\text{SA}*\text{Cair\_g})-(\text{Ur}*\text{Q}*\text{Kp}*\text{Cair\_g}*\text{TSP}*\text{SA})-(\text{Vg}*\text{Cair\_g}*\text{SA})-(\text{Up}*\text{Kp}*\text{Cair\_g}*\text{TSP}*\text{SA})-(\text{Vair}*(0.693/\text{half\_life})*\text{Cair\_g}) \qquad (1)$$

Where:
Eair: Emissions (g/h)
G_{ADV}: Advective flow (m^3/h)
Cair_adv: Background concentration (g/m^3)
Cair_g: Concentration in air of gaseous phase (g/m^3)
Wg= Ur*H Scavenging ratio for gaseous phase (m/h)
Q: Scavenging ratio for particle phase
Ur: Precipitation rate (m/h)
Vg/Up: Dry gaseous/particle deposition velocity (m/h)
Vair: Atmospheric volume of the UK (m^3)
Kp: Particle- vapour partition coefficient (m^3/g)
SA: Surface area (m^2)
TSP: Total suspended particulate(g/m^3)
Half_life (h): Atmospheric half-life due to reactions with OH radicals

The prevailing wind direction for the UK is from the south-west, so relatively 'clean' air arrives from the Atlantic/Irish Sea [7]. Sweetman *et al.* [13] estimated that the UK currently exports approximately 25% more PCBs than it receives. However, PAHs are less prone to long-range atmospheric transport (LRAT) than PCBs due to their shorter atmospheric life-times [14]. Air concentrations measured at Mace Head, a remote site on the west coast of Ireland, provided the background/advective input to the UK "box" (Table 2), whilst the average atmospheric residence time was calculated to be 3 days [15]. It must be hereby acknowledged that the UK boundary layer was considered well mixed so that advection could be determined by one "background" concentration at the border. Nevertheless, important seasonal parameters such as temperature, wind speed, cloudiness, etc. do show an inhomogeneous pattern in their annual mean. For this reason, seasonal changes in the boundary layer height as well as in the wind velocity will be considered in a later part of this paper.

The relationship between the vapour: particle partition coefficient (Kp) and the octanol: air partition coefficient (Koa) derived by Harner and Bidleman [16] was used:

$$\log Kp = \log Koa + \log f_{om} - 11.9 \qquad (2)$$

The organic fraction of the aerosol was assumed to be 20%, therefore (2) can be written as

$$\log Kp = \log Koa - 12.6 \qquad (3)$$ or

$$Kp = 10^{(\log Koa - 12.6)} \qquad (4)$$

Kp and TSP were used to calculated the particulate fraction φ:

$$\phi = \frac{Kp * TSP}{1 + Kp * TSP} \qquad (5)$$

The selected values for the model input parameters are presented in Table 2. Dimensionless Henry's law constants H' and Log Koa were calculated using the Bamford *et al.* [17] and Harner and Bidleman [16] regression parameters respectively for the temperature of 10°C. Mackay *et al.* [18] provided H' for the heavier two PAHs and Behymer and Hites [19] the half-lives due to reactions with OH radicals for Fluo, Phen and Fla. The same reaction rate with Fla was assumed for Py; B[*a*]P and B[*ghi*]P were assigned values almost an order of magnitude lower. The Behymer and Hites [19] photolysis experiment revealed half-lives >200h for selected particle-bound PAHs. Due to lack of studies concerning the particle-bound fraction of the PAHs under study that can undergo degradation by reactions with OH radicals, only the degradation of their gaseous component was considered. This might be valid for the lighter PAHs (small phi values), but might produce discrepancies for the heavier PAHs, which are bound almost exclusively into particles. The particle-bound fraction degradation due to this loss mechanism was neglected but could become important for the overall fate of the heavier congeners. The particle size and other morphological characteristics may also play an important role. The chemical degradation due to other reactants (e.g. NOx) could also be significant for some PAHs with the formation of nitro-PAHs and their subsequent removal with deposition (REFs: Dimashki et al., 2000)

Sensitivity to input parameters

The sensitivity of the model output to changes in the input parameters was tested as follows. All meteorological and deposition parameters were varied by a factor of 3; half-lives due to reactions with OH radicals were modified by a factor of 2. Table 3 summarises the influence of varying the input parameters. Temperature, rainfall and dry particle deposition velocity changes did not significantly affect the predicted concentrations for the 3 and 4-carbon ring PAHs (Fluo, Phen, Fla, Py). High dry gaseous deposition velocities caused a 5-10% decrease in the predicted Fluo and Phen concentrations, and a 10-20% change in Fla and Py concentrations. Reactions with OH radicals were found to be the most sensitive model parameter for the low and intermediate molecular weight compounds. Other researchers have also emphasized the importance of OH radical reactions for PAHs and other POPs [20-23]. However, the predicted concentrations of the high molecular weight species were insensitive to reactions with OH radicals; rather, they were relatively sensitive to changes in dry and wet particle deposition velocities.

Model results and discussion

Figures 1a and 1b present the concentrations predicted by the model for the six compounds under study, together with typical summer (July-September) and winter (January-March) air concentrations from four measurement stations during the mid-1990s. These stations are part of the UK Toxic Organic Micro-Pollutants Survey (TOMPs) network, set up in the early 1990s [24, 25]. High Muffles, Stoke Ferry and Hazelrigg are considered to be rural/semi-rural sites, whilst London provides an urban 'signal' and, thus, elevated air concentrations (Figures 1a and 1b). One site, Hazelrigg, has unusually high concentrations of Phen, especially in the summer [7] the source of this is not known at present (see below). These sites are believed to provide a reasonable representation of the spatial variability of the UK. Tremolada et al. [26] conducted a study of PAHs in pine needles collected at 28 sites across the country in the summer of 1994, using them as passive air samplers. The ratios of the highest: lowest measured concentrations were 20, 10 and 8 for Fluo, Py and B[*ghi*]P, for example, when some notable outliers were excluded. This variability is broadly captured by the TOMPs air monitoring data .

When the annually averaged NAEI emission inventory estimates were used as the input data for the model, the predicted air concentrations were generally within a factor of 3 of measured values for Fluo, Fla, Py, B[*a*]P and B[*ghi*]P (see Figures 1a,b). On the basis of the calculations for these 5 compounds and given the likely variability in rural air concentrations across the UK noted above, it would appear that the NAEI emission inventory estimates provide an acceptable agreement with measured ambient air concentrations. In general, the model underpredicts the concentrations of the lighter compounds and there is a tendency to overpredict the concentrations of the heavier compounds. Possible reasons for these trends might include the representation of the particle-bound fraction as depicted by equations 2-5, the possible degradation of the particle-bound fraction (more relevant for the high MW PAHs but still not well studied in literature) and a possible underestimation of the input due to advection. It is worth mentioning that the model predicts that 85% of BghiP is likely to be particle-bound, whereas only 1% of Phenanthrene is found attached to particles.

One compound - Phen - was an outlier. The model underestimated the concentrations of this compound by a factor of 5-60. The greatest discrepancy was for the Hazelrigg site (see earlier). It is considered that there may be other sources of Phen to the atmosphere, which are not considered by the NAEI. Secondary (re-cycling) [7] and natural sources may be important for this compound. Wakeham et al. [27] suggested possible natural sources may include the dehydrogenation of steroids, and the microbially-mediated alteration of retene, derived from abietic acid, which is found in plant lipids and soils. Another explanation may be the overestimation of KOH that might be leading to the fast depletion of Phen in the model algorithms.

Comments on compound fates and mass balances

It is appropriate to comment on the compound fate and mass balances generated by the model. The modelled input and output fluxes (kg/day) of the selected compounds are depicted in Table 5. It is shown that primary emissions generated within the UK dominate (>97%) over advective inputs (<3%) received by the UK atmosphere.

Reactions with OH radicals appear to be the most important PAH depletion process for the lighter PAHs, with 52% of Fla and Py, and as much as 75% of Phen lost from the modelled environment via this route. B[*a*]P and B[*ghi*]P are predominantly particulate-bound, which significantly reduces the losses by this mechanism (<5%). However, dry and wet particle deposition becomes much more important for these high molecular weight compounds. The predominance of the gaseous-phase component for the lighter PAHs results in a relatively high dry gaseous deposition flux. The model predicts that between 22% (Phen) - 51% (B[*a*]P) of the total PAH burden entering the UK atmosphere will be advected out of the UK's atmosphere. In other words, the UK is a net exporter of PAHs. The proportion of the input flux advected is generally higher for the high molecular weight compounds, which resist atmospheric reaction. This is despite the fact that these compounds are POPs which are not particularly susceptible to LRAT; their predicted characteristic travel distances [28] are generally on the order of 100-500 km, but actual travel distances will be highly influenced by aerosol size [29], mode of introduction into the environment [30] and temperature [28].

Seasonality in environmental parameters

Given the uncertainties in the emission inventories and the model parameterisation, this first exercise suggested that Objective 1 of the paper – to test predicted ambient concentrations from the annual NAEI against measured values - had been met satisfactorily. It was therefore appropriate to proceed with Objective 2 - namely to investigate the potential influence of seasonally dependent environmental fate processes on the modelled/projected seasonality in air concentrations. The purpose of this section is therefore to address the question: can these seasonally-dependent environmental parameters – acting individually or in combination – generate sufficient seasonality in modelled air concentrations to match the *observed* seasonality on ambient UK data?

The influences of the following seasonally dependent variables are considered in this section: rainfall; wind speed and boundary layer height; temperature and OH radical concentrations; vegetation. These variables were addressed using the model, with the exception of vegetation. Typical values for UK winter/summer environmental conditions were used; throughout this section the emissions were assumed to be constant. The two seasons were treated as two separate steady-state scenarios with different conditions for each. In later stages of the paper the effect of seasonal emissions will also be presented.

Rainfall Rainfall exerts its influence by scavenging PAHs from the atmosphere – influencing the particle-bound species to a greater extent than the vapour phase compounds. This variable was considered by employing the following winter : summer conditions: winter maximum 140 mm; summer minimum 10 mm. *Scenario 2* in Table 6 shows the predicted impact of seasonally varying rainfall conditions. The rainfall information was then converted into a rain rate (m/h) in a monthly basis. However, it is a small effect even for the particle-dominated high molecular weight species.

Wind speed and boundary layer height These variables influence the advection and 'dilution' of PAHs in the atmosphere. The UK atmospheric boundary layer is generally assumed to fluctuate between 500 m (winter) and 1500 m [31], although it is highly variable with meteorological conditions. Average wind speed does vary somewhat between seasons, but by less than a factor of 2 [32].

Clearly, all other factors being equal, varying the boundary layer height between the values mentioned above would generate an effect on air concentrations of a factor of 3, with the higher values in winter. The mild seasonal wind effect would offset this somewhat; as *scenario 3* in Table 6 shows, these factors exert a similar influence on the winter: summer ratios of all of the PAH compounds.

OH radical concentrations and temperature effects on reaction processes Temperature exerts a seasonal influence in two ways – through controlling compound gas: particle partitioning (and hence deposition processes) and the reaction rates with hydroxyl radicals. The mean ambient air temperatures were assumed to fluctuate according the mean monthly England and Wales temperature variation, whereas winter OH radical concentrations were assumed to be 2×10^5 molecules cm^{-3}, with summer values an order of magnitude higher [21]. These OH radical concentrations were coupled with temperatures of 5°C for winter and 25°C for summer to derive reaction half-lives for the winter and summer scenarios. *Scenario 4* in Table 6 therefore considers the combined influence of temperature and OH radical concentrations. It predicts higher atmospheric concentrations in the winter, with the enrichment most marked for the lighter compounds.

A sentence about log Koa (higher in winter) and TSP (higher in summer) seasonality ?

One other seasonally-dependent environmental variable is worthy of consideration – namely vegetation - although it has not been included in the modeling exercise.

<u>Vegetation</u> There is a complex interplay between the atmosphere and vegetation, with respect to POPs [33]. It is generally accepted that the bulk of the PAH burden associated with vegetation is derived from the atmosphere, rather than from soil (see [34]). Compounds can be scavenged from the gas and particle phases of the atmosphere by vegetation [35], reactions can occur on vegetated surfaces, and - through volatilisation and cuticular shedding - may enter the atmosphere [36]. The rates of these processes differ with environmental conditions, plant species and ecosystems. Although there has been discussion about various approaches by which vegetation can be included in multi-media fate models (e.g. [33, 37]), it is complex and there is as yet no consensus about how this should be done; there are also large uncertainties over model parameterisation. A vegetation compartment was therefore not included in the model used here. However, vegetation may be expected to exert some seasonal influence on the atmospheric burden of PAHs and it is therefore important to discuss its potential influence.

The UK land mass is ca 25% arable land (with seasonally variable crop coverage), 40% grassland, 6% deciduous forest, 6% coniferous forest and 10% heath/peat lands [38].

There is therefore a standing crop of vegetation during winter, with most growth occurring in spring/summer. Grass growth is most active in the UK during spring and early summer, when it can reach ca. 100 kg DM/ha/day [39]. Smith et al. [40] investigated the seasonality and species differences in the air-plant transfer of PAHs to grasses. In general, they found that plant concentrations of the lower molecular weight PAHs were about 3-10 times higher during winter than summer; this is offset by lower biomass during winter. In contrast, the scavenging coefficients (m^3 air scavenged per g plant dry weight) of heavier PAHs changed little throughout the year. The mass of vegetation which can scavenge compounds from the atmosphere will vary seasonally. The leaf area index (LAI – m^2 vegetation surface/m^2 land surface) is commonly used, to assess the vegetation coverage. This obviously differs with vegetation type; typical values for broad-leaved forests (in summer), evergreen needle forests and grasslands are ~4-8, 5-10 and ~1.5, respectively [41].

Given the dominance of grassland in the UK, the estimated PAH burdens associated with UK vegetation during the winter and summer were calculated, using typical UK grassland data, as described previously by Thomas et al. [39]. The results are given in Table 7. This shows that the estimated UK burden of Fluo, Phen; Fla and Py in vegetation is higher in the winter, by factors of 2-6, whilst there is little difference between the seasons for B[*a*]P and B[*ghi*]P. The burdens are of the order of 10s-100s kg per compound. As Table 5 showed, the typical input fluxes of these compounds to the UK atmosphere are of the order of 100s kg/day. The burdens in UK vegetation at any one time therefore only represent the equivalent of the total UK atmospheric emissions from a day or so, and therefore do not – by themselves – represent a sufficiently large portion of the emission to significantly impact air concentrations on a seasonal basis. However, one area of uncertainty concerns the role of vegetation as a site for photolytic destruction of PAHs. If the rates of supply of compounds from air to leaf are sufficiently rapid, this could presumably be an important seasonally dependent loss process for photo-reactive PAHs. A study by Niu et al. [42] reported the following photolytic degradation half-lives (hours) on spruce needles under summer conditions in southern Germany: Fluo, 41; Phen, 75; Fla, 26; Py, 37; B[*a*]P, 33; B[*ghi*]P, 46. They concluded that 'photolysis of some PAHs on surfaces of spruce needles may play an important role on the fate of PAHs in the environment'. However, for the overall mass balance of PAHs in the UK environment, this is probably not the case. For example, if it is assumed that the masses of PAHs on vegetation each day throughout the year are represented by the values given in Table 7, that photolysis rates of the order of those given above apply, and that the atmosphere can replenish the PAHs lost via this process, then total annual losses will be of the order of tens kg/compound. This is a very small fraction of the estimated annual atmospheric emissions given in Table 1.

<u>Summary of modeled/projected seasonal differences in air concentrations</u> As the preceding sections have shown, there is a complex inter-play of environmental factors potentially influencing air concentrations seasonally. The seasonally-dependent environmental variables considered separately above will tend to result in winter:summer ratios >1. *Scenario 5* in Table 6 considers them collectively, again assuming constant emissions. The model predicts that environmental factors would result in comparatively high (~4-6) winter:summer ratios for the 3- and 4-ringed PAHs – largely driven by the enhanced summer reaction rates. In contrast, the predicted winter:summer ratios of the 5- and 6-ringed species are ~1.5-2. It has also been argued that seasonal differences in vegetative cover are unlikely to exert a significant effect on air concentrations, if the influence of vegetation is simply that of 'scavenging' compounds from the air. Photolytic reactions on leaf surfaces may enhance removal of PAHs from the environment, particularly during the summer, but this effect is not predicted to be large.

It is now appropriate to compare the effects of these modeled/projected environmental processes with the *observed* seasonality in air concentrations at UK sites during the 1990s.

Comparisons with the measured seasonality in UK air concentrations

Data on the *observed* seasonality at 6 UK sites during the 1990s are given in Table 6. The full datasets have been published elsewhere (London, Manchester, [6]; Hazelrigg, [7]; Esthwaite Water, [43]; High Muffles, Stoke Ferry, NAEI website). The winter:summer ratios vary between compounds and locations. This variation can be large; for example, the Fluo ratio varies between 0.5 and 4.6 across the 6 sites. However, the general trend is that the high molecular weight compounds have high winter:summer ratios. Values for B[*a*]P and B[*ghi*]P ranged between 5-16 and 4.4->10, respectively.

These considerably exceed the modeled ratios from *scenario 5*, which were only 1.8 and 1.6, respectively. In contrast, the measured ratios for the 4-ringed species were 0.6 – 1.3 (Fla) and 0.2 – 1.5 (Py), whilst the modeled ratios from *scenario 5* were much higher, at ~4 for both compounds. There were also substantial discrepancies for the 3-ringed species; Phen had measured values of 0.3 – 1.1 and a modeled value of 6.1; Fluo had measured values of 0.5 – 4.6 and a modeled value of 4.5.

These discrepancies between measured and modeled values are important. Earlier in the paper it appeared that the estimated annual UK emissions could be used to predict annually averaged air concentrations reasonably well, for all the compounds except Phen (Table 4). In other words, it appeared as if the emissions inventory is reliable and the model was well parameterized. However, from this section – where seasonality in environmental processes is explored – it becomes clear that these good agreements should probably be regarded as largely coincidental. Seasonality in air concentrations is predicted for the different compounds when constant emissions are assumed. However, the directions and/or magnitudes of the predicted compound seasonalities do not coincide with field observations. This indicates *either* that our understanding of the environmental fate and behaviour of PAHs is still limited, *and/or* that there are uncertainties in the emissions inventories.

Implications for sources

At the beginning of the paper, and in Table 1, it was noted that some source categories are seasonal. The model was therefore employed to investigate the seasonality in emissions required to generate the *observed* seasonality in air concentrations. It was run with the environmental conditions of scenario 5, but with variable winter:summer emission scenarios. The results are given in Table 8.

Table 8 highlights that summer emissions of the 3- and 4-ringed species would need to be higher than those in winter, by between factors of 1-16 (but perhaps typically around 4-7), to account for the observed ambient seasonality. Potential seasonal sources, which might be expected to generate elevated summer emissions are: volatilisation from soils, vegetation, water bodies and urban surfaces [7, 8, 44]; emissions from creosote/wood treatment usage [10]; natural and some diffusive anthropogenic combustion sources (e.g.

burning of garden refuse); and microbially-mediated natural formation (notably for Phen, but possibly for other compounds too; [27]). These emission categories are all generally relatively enriched in low molecular weight PAHs (see references above). However, emission factors from such sources, and their contributions to inventories are relatively poorly studied and extremely difficult to estimate [45].

In contrast, B[*a*]P and B[*ghi*]P emissions would need to be >4 times higher in winter than summer, to match the observed ratios in air concentrations (Table 8). The most obvious seasonally-dependent sources likely to generate elevated winter emissions are domestic burning of coal and wood for space heating [43]. These combustion processes are relatively inefficient and generate PAH emissions enriched in the high molecular weight species [5].

Traffic is an important contributor to the national emission inventory (Table 1). However, seasonal variability in emissions from this source is also difficult to assess; in general, vehicle usage is greater in the summer, but the contribution of 'cold start' emissions will presumably be higher in the winter [46]. In conclusion, this study suggests that the fate of PAHs is controlled by a combination of seasonal environmental processes and a higher contribution of seasonal emission sources than proposed by the current emissions inventories.

Concluding remarks

Constructing reliable emissions inventories for POPs is notoriously difficult (e.g. [45]). Models are therefore often used to test the reliability of emission estimates against ambient data. When this exercise was conducted in a simplified fashion in the early part of the paper, it appeared that the UK PAH atmospheric emissions inventory was reasonably reliable for most of the compounds studied. However, more detailed analysis of the seasonality in environmental processes, which influence ambient levels, showed that the directions and/or magnitudes of the predicted seasonality did not coincide with field observations. This indicates *either* that our understanding of the environmental fate and behaviour of PAHs is still limited, *and/or* that there are uncertainties in the emissions inventories. Fate models are therefore useful tools in helping to assess the influence/relative importance of seasonally dependent depletion/loss mechanisms, the controlling influence(s) of these mechanisms and of different emission scenarios.

The approach used in the paper suggests that better quantification of PAH sources is needed. For 3- and 4-ringed compounds, this should focus on those sources which increase with temperature, such as volatilisation from soil, water, vegetation and urban surfaces, and possible microbially-mediated formation mechanisms. These sources and processes are of considerable academic interest, and have been relatively poorly studied to date. The study also suggests that the contributions of inefficient, diffusive combustion processes (e.g. domestic coal/wood burning) may be underestimated as a source of the toxicologically significant higher molecular weight species in the winter. With a better quantification of seasonal emission variations, fate models such as the one presented before can better be validated and important questions on the model uncertainties/ assumption better addressed. As the present study clearly indicated, model weaknesses and missing information on chemical properties can be identified when modeling and (seasonal) monitoring are combined. Furthermore, a number of inconsistencies might not be detected on an aggregated/annual level, but only when seasonal (or even diurnal, where possible) variability is taken into account.

Signatories to the UNECE POPs protocol undertake to reduce national PAH emissions to 1990 levels [4]. Many countries will experience difficulties in demonstrating compliance, because source inventories for 1990 and contemporary situations are clearly subject to major uncertainties. This heightens concern that the targets set by the UNECE protocol may be difficult to demonstrably meet, because such sources are – by their very nature – difficult to quantify, control and reduce.

Acknowledgements

This study was supported by Defra (Department for Environment, Food and Rural Affairs) funding under project EPG 1/3/169.

References

1. International Programme on Chemical Safety (IPCS), 1998. Environmental Health Criteria 202. Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons. World Health Organization: Geneva.

2. European Union. 2001. Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position Paper. Office for Official Publications of the European Communities. L-2985 Luxembourg. ISBN 92-894-2057-X.

3. European Commission DG Environment. 2001. Economic Evaluation of Air Quality Targets for PAHs. http://europa.eu.int/comm/environment/index

4. United Nations Economic Commission for Europe (UN ECE). 1998. ECE/EB.Air/60.

5. Lohmann R, Northcott GL, Jones KC. 2000. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the U.K. atmosphere. *Environ Sci Technol* 34:2892-2899.

6. Halsall CJ, Coleman PJ, Davis BJ, Burnett V, Waterhouse KS, Harding-Jones P, Jones KC. 1994. Polycyclic aromatic hydrocarbons in UK urban air. *Environ Sci Technol* 28:2380-86.

7. Lee RGM, Jones KC. 1999. The influence of meteorology and air masses on daily atmospheric PCB and PAH concentrations at a UK location. *Environ Sci Technol* 33:705-12.

8. Diamond ML, Priemer DA, Law LN. 2001. Developing a multimedia model of chemical dynamics in an urban area. *Chemosphere* 44:1655-1667.

9. Gevao B, Jones KC, Hamilton-Taylor J. 1998. Polycyclic aromatic hydrocarbons (PAH) deposition to and processing in a small rural lake, Cumbria UK. *The Sci of the Tot Environ* 215:231-42.

10. Gevao B, Jones KC. 1998. Kinetics and potential significance of polycyclic aromatic hydrocarbon desorption from creosote-treated wood. *Environ Sci Technol* 32:640-646.

11. Harrison RM, Smith DJT, Luhana L. 1996. Source Apportionment of Atmospheric Polycyclic Aromatic Hydrocarbons collected from an urban location in Birmingham, UK. *Environ Sci Technol* 30:825-32.

12. Wild SR, Jones KC. 1995. Polynuclear Aromatic Hydrocarbons in the United Kingdom environment: A preliminary source inventory and budget. *Environ Pollut* 88:91-108. Elsevier Science Limited.

13. Sweetman, AJ, Cousins IT, Seth R, Jones KC, Mackay D. 2002. A dynamic level IV multimedia environmental model: application to the fate of polychlorinated biphenyls in the United Kingdom over a 60-year period. *Environl Toxicol Chem* 21:930-940.

14. Bennett DH, Scheringer M, McKone TE, Hungerbühler K. 2001. Predicting Long-Range Transport: A Systematic Evaluation of Two Multimedia Transport Models. *Environ Sci Technol* 35:1181-1189.

15. Sweetman AJ, Alcock RE, Wittsiepe J, Jones KC. 2000. Human exposure to PCDD/Fs in the UK: the development of a modelling approach to give historical and future perspectives. *Environ Intern* 26:37-47.

16. Harner T, Bidleman TF. 1998. Octanol-Air Partition Coefficient for Describing Particle/Gas Partitioning of Aromatic Compounds in Urban Air. *Environ Sci Technol* 32:1494-1502.

17. Bamford HA, Poster DL, Baker JE. 1999. Temperature dependence of Henry's law constants of thirteen Polycyclic Aromatic Hydrocarbons between 4 and 31oC. *Environ Toxicol Chem* 18:1905–1912.

18. Mackay D, Shiu WY, Ma KC. 1992. Illustrated Handbook of Physical-Chemical properties and environmental fate for organic chemicals, vol.2: Polynuclear aromatic hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Lewis Publishers: Ann Arbor, MI.

19. Behymer TD, Hites RA. 1988. Photolysis of PAHs adsorbed on fly ash. *Environ Sci Technol* 22:1311-1319.

20. Atkinson R, Arey J. 1994. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. *Environmental Health Perspectives* 102:117-126.

21. Halsall CJ, Sweetman AJ, Barrie LA, Jones KC. 2001. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmos Environ* 35: 255-267.

22. Alcock RE, Sweetman AJ, Jones KC. 2001. A congener-specific PCDD/F emissions inventory for the UK: Do current estimates account for the measured atmospheric burden? *Chemosphere* 43:183-194.

23. Totten LA, Eisenreich SJ, Brunciak PA. 2002. Evidence for destruction of PCBs by the OH radical in urban atmospheres. *Chemosphere* 47:735-746.

24. Halsall CJ, Lee RGM, Coleman PJ, Burnett V, Harding-Jones P, Jones KC. 1995. PCBs in U.K. urban air. *Environ Sci Technol* 29:2368-2376.

25. Coleman PJ, Lee RGM, Alcock RE, Jones KC. 1997. Observations on PAH, PCB, and PCDD/F trends in U.K. urban air, 1991-1995. *Environ Sci Technol*, 31:2120-2124.

26. Tremolada P, Burnett V, Calamari D, Jones KC. 1996. Spatial distribution of PAHs in the UK atmosphere using pine needles. *Environ Sci Technol*, 30:3570-77.

27. Wakeham SG, Schaffner C, Giger W. 1980. Polycyclic aromatic hydrocarbons in Recent lake sediments-II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta* 44:415-429.

28. Beyer A, Wania F Gouin T, Mackay D, Matthies M. 2003. Temperature dependence of the characteristic travel distance. *Environ Sci Technol* 37:766 – 771.

29. Offenberg JH, Baker JE. 2002. The influence of aerosol size and organic carbon content on gas/particle partitioning of polycyclic aromatic hydrocarbons (PAHs). *Atmos Environ* 36:1205-1220.

30. Beyer A, Mackay D, Matthies M, Wania F, Webster E. 2000. Assessing long-range transport of Persistent Organic Pollutants. *Environ Sci Technol* 34:699-703.

31. Williams ML. 1996. Atmospheric dispersal of pollutants and the modelling of air pollution. In *Pollution: causes, effects and control*, Harrison, R.M. Ed. 3rd edition, the Royal Society of Chemistry: Cambridge, UK, pp. 221-240.

32. Palutikof J, Holt T, Skellern A. 1997. Wind: resource and hazard. In *Climates of the British Isles: present, past and future.* Hulme, M., Barrow, E. Eds. Routledge: London, UK, pp. 220-242.

33. Cousins IT, Mackay D. 2001. Strategies for including vegetation compartments in multimedia models. *Chemosphere* 44:643-654.

34. Smith KEC, Jones KC. 2000. Particles and vegetation: implications for the transfer of particle-bound organic contaminants to plants. *Sci. Total Environ* 246:207-236.

35. Bennett DH, McKone TE, Matthies M, Kastenberg WE. 1998. General formulation of characteristic travel distance for semivolatile organic chemicals in a Multimedia environment. *Environ Sci Technol* 32:4023-4030.

36. Riederer M. 1995. Partitioning and transport of organic chemicals between the atmospheric environment and leaves. In *Plant Contamination, Modeling and Simulation of*

Organic Chemical Processes. Trapp, S., McFarlane, J.; Eds.; Lewis Publishers: Boca Raton, FL, pp. 153-190.

37. McLachlan MS, Horstmann M. 1998. Forests as filters of airborne organic pollutants: a model. *Environ Sci Technol* 32:413-420.

38. Countryside Information System. 2000. Accounting for nature: assessing habitats in the UK countryside.

39. Thomas G, Sweetman AJ, Ockenden WA, Mackay D, Jones KC. 1998. Air-pasture transfer of PCBs. *Environ Sci Technol* 32:936-942.

40. Smith KEC, Thomas GO, Jones KC. 2001. Seasonal and species differences in the air-pasture transfer of PAHs. *Environ Sci Technol* 35:2156-2165.

41. Barber JL. 2003. Studies on the air-plant transfer of persistent organic pollutants. Lancaster University.

42. Niu J, Chen J, Martens D, Quan X, Yang F, Kettrup A, Schramm K-W. 2003. Photolysis of polycyclic aromatic hydrocarbons adsorbed on spruce [Picea abies (L.) Karst.] needles under sunlight irradiation. Currently in press (*Environ Pollut).*

43. Gardner B, Hewitt CN, Jones KC. 1995. PAHs in air adjacent to two inland water bodies. *Environ Sci Technol* 29:2405-13.

44. Harner T, Bidleman TF, Jantunen LMM, Mackay D. 2001. Soil-air exchange model of persistent pesticides in the United States cotton belt. *Environ Toxicol Chem* 20:1612–1621.

45. Breivik K, Sweetman AJ, Pacyna JM, Jones KC. 2002. Towards a global historical emission inventory for selected PCB congeners –– a mass balance approach: 2. Emissions. *Sci Total Environ,* 290:199-224.

46. Ludykar D, Westerholm R, Almén J. 1999. Cold start emissions at +22, -7 and –20°C ambient temperatures from a three-way catalyst (TWC) car: regulated and unregulated exhaust components. *Sci. Total Environ* 235: 65-69.

Measurements of nitro-PAH in the atmospheres of two cities, *Atmospheric Environment, Volume 34, Issue 15, 2000, Pages 2459-2469*
Marwan Dimashki, Stuart Harrad and Roy M. Harrison

Table 1. Selected atmospheric emission sources, average 1993-1997 annual discharge (t) and % of total

	Fluo		Phen		Fla		Py		B[a]P		B[ghi]P	
Source	Discharge	% of total	Discharge	% of total	Discharge	% of total	Discharge	% of total	Discharge	% of total	Discharge	% of total
Road Transport	15	6.3%	16.2	2.1%	9.8	2.7%	9.8	4.5%	6.6	20.4%	19.6	56.0%
Domestic Coal	31.2	13.2%	12.6	1.6%	5.6	1.5%	5.6	2.5%	2.9	9.0%	1.4	4.0%
Domestic Wood	7	3.0%	22	2.9%	6	1.6%	7	3.2%	1.2	3.6%	1	2.9%
Creosote Use	23	9.7%	20	2.6%	3	0.8%	3	1.4%	0.1	0.2%	0	0.0%
Natural Fire events	1	0.4%	4.2	0.5%	1.2	0.3%	1	0.5%	3.0	9.3%	1	2.9%
Seasonal Sources	77.2	32.6%	75	9.8%	25.6	6.9%	26.4	12.0%	13.8	42.4%	23	65.7%
Anode Baking	112.2	47.4%	594	77.7%	296.6	80.3%	164.2	74.6%	12.1	37.4%	6.8	19.4%
Aluminium Production	13	5.5%	69.2	9.1%	34.6	9.4%	19.4	8.8%	1.5	4.6%	1	2.9%
Industrial Coal	31.4	13.3%	15	2.0%	7	1.9%	6.4	2.9%	3.8	11.9%	1.6	4.6%
Coke Production	3	1.3%	10	1.3%	4	1.1%	3	1.4%	1.0	3.1%	0	0.0%
Industrial Wood	0	0.0%	0	0.0%	0	0.0%	0	0.0%	0.0	0.1%	0	0.0%
Other Sources	0	0.0%	1	0.1%	1.4	0.4%	0.8	0.4%	0.1	0.4%	0	0.0%
Non Seasonal Sources	159.6	67.4%	689.2	90.2%	343.6	93.1%	193.8	88.0%	18.7	57.6%	9.4	26.9%
Total UK Emission	236.8		764.2		369.2		220.2		32.4		32.4	

Table 2. Physicochemical properties and environmental input

Compound	Fluo	Phen	Fla	Py	B[a]P	B[ghi]P
Bulk volume of air (m^3)	$2.34*10^{14}$					
Cair_adv (pg/m^3)	142	227	50	45	4.4	1
TSP ($\mu g/m^3$)	60					
T (K)	283					
Rainfall (mm)	70					
OH_T1/2 (h)	29.6	14.3	35.2	35.2	200	200
Scavenging ratio	70000					
Up (m/h)	10.8					
Vg (m/h)	2.16					
H'	$1.39*10^{-3}$	$6.34*10^{-4}$	3.48*10-4	$2.74*10^{-4}$	$1.86*10^{-5}$	$3.03*10^{-5}$
Log Koa	7.6	8.3	9.7	9.5	11.1	11.6

Table 3. Sensitivity analysis

Compound	Fluo	Phen	Fla	Py	B[a]P	B[ghi]P
3*Temperature	A	A	A	A	A	A
3/Temperature	A	A	A	A	A	A
3*Rainfall	A	A	A	A	D	D
3/Rainfall	A	A	A	A	C	C
3*Up	A	A	A	A	D	C
Up/3	A	A	A	A	D	D
3*Vg	B	B	C	C	A	A
Vg/3	A	A	A	A	A	A
3*Q	A	A	A	A	D	D
Q/3	A	A	A	A	C	C
2*half life	D	D	D	D	A	A
half life/2	D	D	D	D	A	A

A: 0-5%
B: 5-10%
C: 10-20%
D: >20%

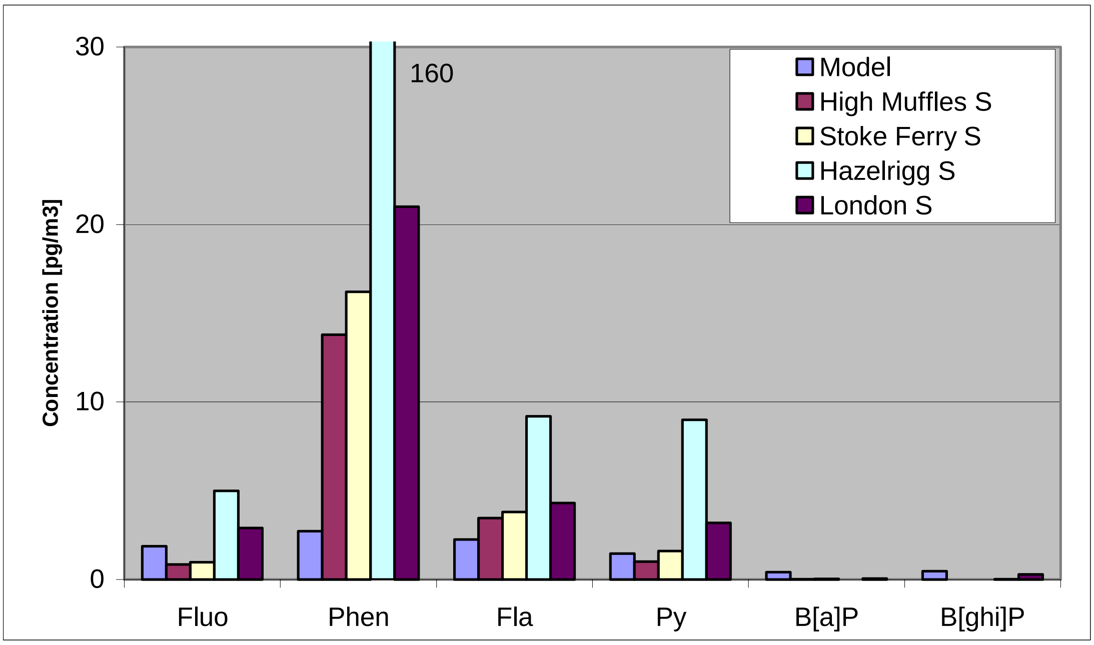


Figure 1a. Summer predicted and measured concentrations

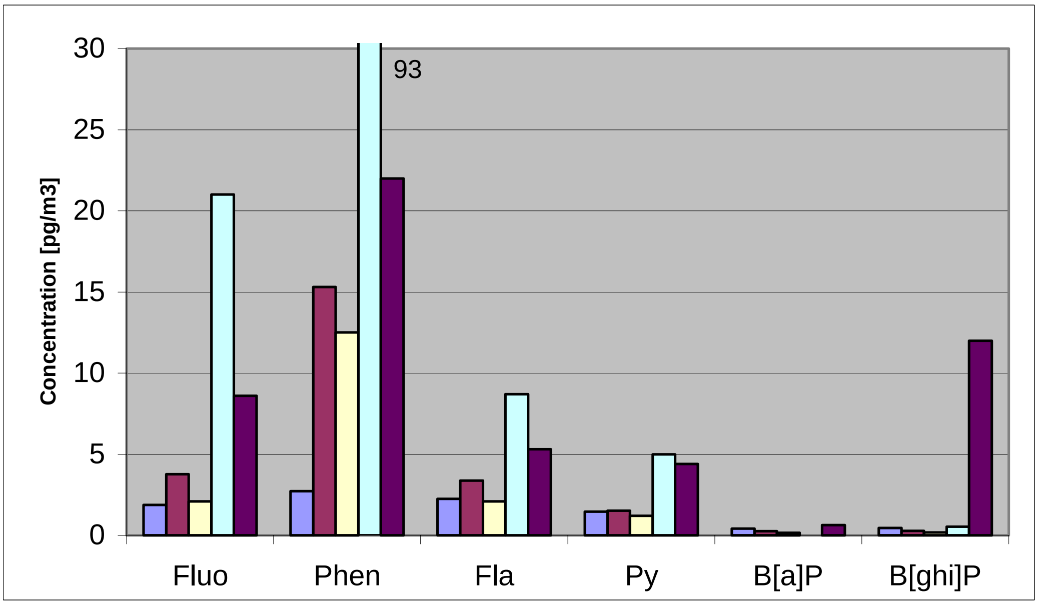


Figure 1b. Winter predicted and measured concentrations

Table 5. Compound fluxes (kg/d) predicted by the model and the % contribution of each flux to the total UK atmospheric inputs/losses

	Fluo		Phen		Fla		Py		B[a]P		B[ghi]P	
	Flux	% contribution	Flux	% contribution	Flux	% contribution	Flux	% contribution	Flux	% contribution	Flux	% contribution
Inputs												
Emission	403.2	97.3%	964.8	98.2%	444.0	99.1%	288.0	98.8%	64.1	99.5%	76.1	99.9%
Advection in	11.1	2.7%	17.7	1.8%	3.9	0.9%	3.5	1.2%	0.3	0.5%	0.1	0.1%
Total in	414.3	100.0%	982.5	100.0%	447.9	100.0%	291.5	100.0%	64.4	100.0%	76.2	100.0%
Outputs												
OH radicals	245.7	59.3%	737.0	75.0%	232.7	52.0%	154.0	52.8%	3.0	4.6%	1.3	1.7%
Advection out	145.8	35.2%	211.8	21.6%	175.4	39.2%	113.9	39.1%	32.9	51.1%	35.6	46.7%
Dry gas deposition	22.7	5.5%	32.8	3.3%	25.5	5.7%	16.9	5.8%	1.8	2.9%	0.8	1.1%
Dry particle deposition	0.1	0.0%	0.5	0.1%	8.7	2.0%	4.1	1.4%	16.4	25.4%	23.6	31.0%
Wet gas deposition	0.0	0.0%	0.0	0.0%	0.0	0.0%	0.0	0.0%	0.0	0.0%	0.0	0.0%
Wet particle deposition	0.0	0.0%	0.3	0.0%	5.5	1.2%	2.6	0.9%	10.3	16.0%	14.9	19.5%
Total out	414.3	100.0%	982.4	100.0%	447.9	100.0%	291.5	100.0%	64.4	100.0%	76.2	100.0%

Table 6. Modelled and measured winter-to-summer concentration ratios

	Fluo	Phen	Fla	Py	B[a]P	B[ghi]P
Model scenarios						
Scenario 1 (a)	1.0	1.0	1.0	1.0	1.0	1.0
Scenario 2 (a)	1.0	1.0	1.1	1.0	1.2	1.1
Scenario 3 (a)	1.2	1.1	1.2	1.2	1.3	1.2
Scenario 4 (a)	4.3	5.9	3.7	3.8	1.5	1.2
Scenario 5 (a)	4.5	6.1	4.0	4.1	~1.8	~1.6
High Muffles (rural)	4.5	1.1	1.0	1.5	9.6	>8
Stoke Ferry (rural)	2.2	0.8	0.6	0.7	5.0	>5
Esthwaite water (rural)	0.5	0.3	0.7	0.2	16	N/a
Hazelrigg (rural)	4.2	0.6	0.9	0.6	N/a	>10
London (urban)	3.0	1.0	1.2	1.4	>10	>10
Manchester (urban)	4.6	1.5	1.3	1.4	7.1	4.4

N/a: data not available

a = see text and below for details

Scenario 1: Constant emissions and environmental conditions

Scenario 2: Constant emissions but seasonal rainfall seasonal changes

Scenario 3: Constant emissions but seasonal variations in boundary layer height and wind speed.

Scenario 4: Constant emissions but seasonal variations in temperature and OH radical concentrations.

Scenario 5: Constant emissions but seasonal variations in all environmental conditions

Table 7. Estimated amount of selected PAHs incorporated into UK grasslands during the winter and summer (see text for details)

Summer	Grass concentration (g/g DW)	Standing yield (g DM/m^2)	PAH (g per m^2)	UK Grassland area (m^2)	PAHs in UK grass (kg)
Fluo	6.00E-09	100	6.00E-07	1.41E+11	85
Phen	1.70E-08		1.70E-06		240
Fla	1.20E-08		1.20E-06		169
Py	9.00E-09		9.00E-07		127
B[a]P	4.50E-09		4.50E-07		63
B[ghi]P	4.50E-09		4.50E-07		63
Winter					
Fluo	2.50E-08	50	1.25E-06	1.41E+11	176
Phen	1.60E-07		8.00E-06		1128
Fla	1.40E-07		7.00E-06		987
Py	7.50E-08		3.75E-06		529
B[a]P	1.00E-08		5.00E-07		70
B[ghi]P	7.00E-09		3.50E-07		49

Table 8. Data on observed winter:summer air concentrations compared to model predictions of the seasonal differences in emissions required to generate them.

Compound	Observed ratios in winter:summer air concentrations[a]	Winter (W):summer (S) emission conditions required to generate the observed air concentrations
Fluo	0.5 - 4.6	S 1-11 x higher than W
Phen	0.3 - 1.5	S 4 -16 x higher than W
Fla	0.6 – 1.3	S 3 - 9 x higher than W
Py	0.2 – 1.5	S 3-16 x higher than W
B[a]P	5 - 16	W >4 x higher than S
B[ghi]P	4.4 - >10	W >4 x higher than S

[a] Data summarised from Table 6.

Section 5

Manuscript title:

Modelling the fate of persistent organic pollutants in Europe: Parameterisation of a gridded distribution model

Authors and affiliations:

Konstantinos Prevedouros, Kevin C. Jones and Andrew J. Sweetman

Environmental Science Department, Institute of Environmental and Natural Sciences,
Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

Matthew MacLeod

Lawrence Berkeley National Laboratory, One Cyclotron Road 90R3058, Berkeley, CA
94720.

Submission journal:

Environmental Pollution. Elsevier Press. www.elsevier.com

Abstract

A regionally segmented multimedia fate model for the European continent is described together with an illustrative steady-state case study examining the fate of γ-HCH (lindane) based on 1998 emission data. The study builds on the regionally segmented BETR North America model structure and describes the regional segmentation and parameterisation for Europe. The European continent is described by a 5° x 5° grid, leading to 50 regions together with 4 perimetric boxes representing regions buffering the European environment. Each zone comprises seven compartments including; upper and lower atmosphere, soil, vegetation, fresh water and sediment and coastal water. Inter-regions flows of air and water are described, exploiting information originating from GIS databases and other georeferenced data. The model is primarily designed to describe the fate of Persistent Organic Pollutants (POPs) within the European environment by examining chemical partitioning and degradation in each region, and inter-region transport either under steady-state conditions or fully dynamically. A test case scenario is presented which examines the fate of estimated spatially resolved atmospheric emissions of lindane throughout Europe within the lower atmosphere and surface soil compartments. In accordance with the predominant wind direction in Europe, the model predicts high concentrations close to the major sources as well as towards Central and Northeast regions. Elevated soil concentrations in Scandinavian soils provide further evidence of the potential of increased scavenging by forests and subsequent accumulation by organic-rich terrestrial surfaces. Initial model predictions have revealed a factor of 5-10 underestimation of lindane concentrations in the atmosphere. This is explained by an underestimation of source strength and/or an underestimation of European background levels. The model presented can further be used to predict deposition fluxes and chemical inventories, and it can also be adapted to provide characteristic travel distances and overall environmental persistence, which can be compared to other long-range transport prediction methods.

Introduction

The fate and behaviour of persistent organic pollutants (POPs) in the environment has attracted considerable scientific and political interest, arising from concern over human exposure to these chemicals, and their discovery in areas far from source regions. The ability of certain POPs to undergo long-range atmospheric transport (LRAT) has resulted in the negotiation of protocols for their reduction or elimination, to reduce the risks to regional and global environments (www.unece.org/env/lrtap). The assessment of candidate POP chemicals for future addition to these protocols is based on an assessment of a number of criteria, for example, atmospheric half life, aquatic bioconcentration and presence of chemical in remote locations. These factors are inter-linked within a multimedia environment and the interactions between processes needs to be fully understood. For example, a chemical may have a high potential for aquatic food chain bioaccumulation, but if emitted to soil may remain there owing to its high affinity for soil organic matter. As a result, the development of predictive models can assist our understanding of chemical fate and behaviour in a multi-media environment. Ideally these models support the development of a thorough understanding of the release of a contaminant (both quantity and emission route), its migration pathways through the multi-media environment, the dynamics of inter-compartmental exchange and its ultimate fate. Frequently, there are gaps in the information that is available for chemicals and models are used to assess whether identified sources can account for observed contaminant levels in the environment and to identify key pathways and processes based on a knowledge of physicochemical parameters and emission estimates.

An important part of the evaluation of potential POP compounds is the assessment of their potential to undergo long-range transport from source regions. Transport in air is generally the most important mechanism, but water borne transport can be significant for some chemicals. A range of model approaches has been developed to provide an assessment of chemicals' potential for LRT. These models provide rankings of transport potential for chemicals using a characteristic distance they are likely to travel or a measure of the fraction of the global environment they are likely to affect. For example, most predictive models indicate that HCB has a very high potential for LRAT, whereas B(a)P is unlikely to be transported appreciable distances (Fellin et al., 1996). The model results for relatively well-characterized chemicals are supported by measurements/observations and expert judgement, and enable 'new' compounds examined using models to be placed in context.

Generic multi-media models are used to provide an assessment of LRT potential in a standardised environment and are useful for screening-level LRAT assessments (Bennett et al., 1998; Beyer et al., 2000; Scheringer et al., 2000). Global and/or hemispheric models have also been developed using highly simplified descriptions of environmental conditions (Van de Meent, 1993; Wania and Mackay, 1995; Scheringer et al., 2000). However, there is clearly a need to concurrently develop models with region specific parameterisation (e.g. MacLeod et al., 2001) that can be directly evaluated against environmental monitoring data, given sufficient information about contaminant sources. Region specific models provide information on chemical fate and behaviour with a more realistic description of the environment, and can also provide estimates of LRAT. Such models can include region specific deposition parameters (e.g. snow and ice scavenging), regional variations in temperature driven processes, and spatially variable descriptions of emissions and environmental compartment properties.

A regionally segmented model, BETR North America, has recently been developed for North America that describes the continent as 24 watershed-based, linked regional environments(MacLeod et al. (2001), Woodfine et al., (2001)). The present study builds on the BETR North America model structure and describes a regional segmentation and parameterisation for Europe. There is considerable incentive to develop such a model for the European continent; Europe is (and has been) a major global source area of POPs and reasonably sophisticated source inventory data are available. Given the complex political and economic state of the region, there is an incentive for a model that can be used as a tool to support management decisions. This paper presents details of the adaptation and restructuring of the BETR North America model to describe the European continent, along with a preliminary case study for γ-hexachlorocyclohexane (γ-HCH or lindane). The potential use of a continental-scale model for regulatory purposes is discussed, particularly for the UNECE POPs protocol.

Model segmentation and parameterisation

The European continent is described in the model by a 50 cell grid (5° x 5°), together with 4 perimetric boxes representing the Atlantic, Mediterranean, Eurasian and Arctic "buffer zones" around Europe that directly impact (or are impacted by) contaminant levels in the European environment. Each grid represents an area of approximately 500 km by 500 km, with the whole grid covering an area from 38.7°N to 61.1°N latitude and –10.1° to 39.4° longitude. Figure 1 shows the model segmentation which covers a total area of 14 million km^2.

The selection of the spatial-scale and boundaries of regions in a geographically explicit model for POPs requires balancing several factors. Owing to their semi-volatile and persistent nature, many POP chemicals have been shown to travel distances in excess of 500 km. The atmospheric half-life criterion for consideration for inclusion on the UNECE POPs protocol list is two days. Assuming a mean wind speed of 3 $m\ s^{-1}$, this could result in a travel distance in excess of 520 km which would facilitate exchange between neighbouring grid cells. Further, the atmospheric residence time in each grid cell is approximately 28 hours, which provides sufficient time for reaction and deposition processes to occur before advection flushes the atmospheric compartment. The gridded approach was also chosen to facilitate the input of atmospheric transport data from global circulation prediction models' and is consistent with our emphasis on assessing long-range atmospheric transport. For the purposes of this study data from the European Centre for Medium-Range Weather Forecasts (ECMWF) global circulation model has been used, which divides the atmosphere into a series of layers of equal atmospheric pressure and provides wind velocities, humidity and temperature on a gridded basis. The BETR North America segmentation, in comparison, is determined by water drainage basins, in order to minimize the water flow between adjacent regions (Woodfine et al., 2001).

The gridded segmentation adopted for the European model allowed the most consistent adaptation of the ECMWF data to the multimedia framework, and is consistent with our focus on assessing atmospheric transport. The drawback of this approach relative to segmentation based on watershed boundaries is that parameterisation of the flow-patterns of surface water within the continent is much more difficult. Gridded segmentation still allows assessment of atmospheric deposition to surface waters, which may be of particular concern in remote areas such as parts of Scandinavia.

The bulk of the model domain (represented by the 50 grid cells) describes a surface area of 14 million km^2, 40% of which is covered by sea and only 1.2% by freshwater (rivers and lakes). The major sea bodies are the North, Baltic and Black Seas as well as a large part of the Mediterranean. Only 0.4% of the total land area is defined as urban. In order to transform the three-dimensional space occupied by Europe into a two-dimensional map, all landcover and environmental data was projected using a polar stereographic projection. This starts from the North Pole and preserves the shape of its segments, creating an increasing distortion of the surface area with distance from the centre of the projection. Thus, the area of individual regions in the 5 x 5 degree grid range between 2-3 10^5 km^2. In order to address the issue of the degree of spatial resolution required in continental-scale models, investigations were carried out to ascertain whether a given chemical is likely to spend enough time in each model segment to allow reactions and other processes such as deposition to occur. Assuming a constant wind speed of 3 m s^{-1} produces an atmospheric advective residence time of around 24-48 hours depending on the size of the region. This compares to vegetation deposition half times ranging from 26 to 58 hours and deposition half-times to seas/coastal waters of between 22 – 38 hours for γ-HCH. A higher degree of spatial resolution is therefore deemed unnecessary and will only increase the model complexity. Furthermore, it is likely that only a small fraction of the most persistent compounds emitted in Europe will react/degrade within the borders of Europe; Hexachlorobenzene, α-HCH and PCP are typical examples of such chemicals with extremely high characteristic travel distances (CTD) (Fellin et al., 1996; Wania and Mackay, 1999; Beyer et al., 2003).

The air and water flow connections between the 54 regions is specified using 54 by 54 spreadsheet matrices, with a 55th region representing an area outside the model region to ensure an air mass balance. Matrices for upper and lower air, fresh and coastal water and water runoff define the flows between adjacent regions, as well as within each individual model segment. This data was gathered by exploiting information originating from Arc Info/View databases and other georeferenced data. The lower air matrix, see Figure 2, shows the flow rates of air (m^3 h^{-1}) leaving region I and entering region J. The following section provides information on the parameterisation and compilation of the flow balances, together with the selected environmental datasets.

Starting from the centre of each region, one-day forward trajectories were calculated using the British Atmospheric Data Centre ECMWF trajectory service (http://badc.nerc.ac.uk/data/ecmwf-trj/). The trajectories were calculated using 6-hourly operational analyses of the three components of the wind and surface pressure, which were then interpolated on to a 1.5° x 1.5° grid. The data was linearly interpolated in time and space. The output data from the trajectories consisted of latitude, longitude and pressure of the trajectory every 30 minutes. Air was allowed to move freely to all other regions within the two atmospheric heights of 500m and 2000m above sea level. The endpoints of those trajectories were then computed, producing an average wind rose for all the model segments for the period of study (1997-2001). The wind roses were then converted into a connectivity flux matrix for each atmospheric height, using a matrix technique described by Woodfine et al. (2001). Figure 3 presents the average 5-year wind rose of model region 19 (northwest UK), which shows the predominance of southwesterly winds.

The gridded approach to the model structure requires that the flow of fresh water through rivers is calculated at each interface between adjacent cells. This also applies to the movement of coastal water and currents in the oceans/seas. Although there is a network of gauging stations along most of the major river systems they are of course not located at the precise intersections of the grid. Consequently, the water flow was estimated for each river system and its associated stations taking into account the proximity of the gauging station to the borderline and its elevation. Two datasets were used to quantify the water movement between adjacent regions as well as the water running off at each region's oceanic compartment (if any). Freshwater bodies were assumed to have an average depth of 20 m. The data used for the fresh water balance were extracted from:

i. A database of monthly averaged European river discharge measurements from 160 gauging stations derived from UNESCO archives. The period covered by each dataset varied from station to station. These data were checked against information obtained

from the Global Runoff Centre in Kobletz (Germany) and through the US National Geophysical Data Centre in Boulder, Colorado (Vorosmarty et al. 1998).
ii. The FRIEND European Water Archive Project with data from more than 5000 stations providing gauged daily flows, catchment areas and site elevations, with participation from more than 30 European countries. For the purposes of this study only stations with catchment areas greater than 5000 km^2 were selected, resulting in another 160 stations. These data were provided by UK Centre for Ecology and Hydrology (CEH).

In order to close the water mass balance for each region an evaporation/transpiration rate was calculated for each cell using the following equation:

Evap./Transp. rate (m^3yr^{-1}) = Net discharge (m^3yr^{-1}) – Precipitation (m^3yr^{-1}) (1)
Where,
Net discharge = Water outflow from a region – Water inflow into the region (2)

Figure 4 illustrates the water balance for region 16 (Denmark) and compares riverine inputs into coastal waters, input from precipitation and coastal water residence time.

Coastal water exchange between neighbouring cells (where appropriate) has been calculated using the coastline length between adjacent oceanic regions, the average depth of each oceanic region (determined by using world bathymetry data, Smith and Sandwell, 1997) and mean current flow and direction using World Data File-Drifter data (Hansen and Poulain, 1996). An opposite flow equivalent to 10% to the dominant flow has also been included to account for seasonal changes in the movement of oceanic water.

Monthly averaged global climate data from the International Institute for Applied System Analyses (IIASA; Laxenburg, Austria) which includes precipitation and temperature data were used in the model (Leemans and Cramer, 1991). The dataset uses standardized climate records from up to eight different sources, interpolated and smoothed to fit a one-half degree latitude/longitude terrestrial grid surface. These data were incorporated into the model by averaging the data over each grid.

In the context of this model this parameter refers to the volume of the water within a particular region that runs off to its own coastal water compartment per unit time. Again, the data was extracted from the two datasets used for freshwater flow calculations.

The land cover description of the model classifies forests, agriculture, horticulture and grassland into a single generic vegetation compartment in order to retain simplicity. The current parameterisation of the generic vegetation has been adapted from Cousins et al. (2001). Chemicals can be deposited onto vegetation surfaces via diffusion, wet and dry deposition, rain dissolution, as well as root uptake from soil. Runoff from the leaf surface, litterfall and volatilisation can re-mobilize the previously deposited chemicals. In the absence of measured data for most POP chemicals, the degradation half-life within vegetation has been assumed to be the same as in the atmosphere. However, there is some evidence that this may overestimate the importance of this loss processes.

Information on vegetation and other land features, together with the organic carbon content of European soils, was extracted from the European Land Cover map developed by the Stockholm Environment Institute, based at York University in the UK. The dataset provides geo-referenced information on 15 regions covering most of the European continent. In order to incorporate these data into the model each region had to be projected and statistically assessed to provide summary data for the 54-region model design. Land cover data for Turkey was not included in this dataset so parameterisation for regions 48-50 (see Figure 1) was extrapolated based on the properties of neighbouring regions.

Model structure

MacLeod et al. (2001) and Woodfine et al. (2001) describe the compartmental structure, advective and reactive processes and regional links of the BETR North America (NA) model. The approaches used in the construction of the European model were similar. If further details of the compartmental construction are required the reader is directed to MacLeod et al. (2001) and Woodfine et al. (2001). The fate of POPs within the

European model is described by seven mass balance equations for each region, resulting in 378 equations for all 54 grids. The steady state equations are summarised in Table 1, in both linear algebra and matrix algebra formats. The system of seven equations and the seven unknown fugacities can be solved analytically using either linear or matrix algebra, for which a Gauss elimination algorithm was used (MTEC 2000). In the first iteration of the model, the analytical solutions to the steady-state regional mass balance equations yield compartmental fugacities in all regions due to local sources of contaminant only. The total emission rate to the four compartments that receive advective transfers from other regions are then calculated, and a new steady-state solution is determined. The steady-state solution for the linked set of regional models is approached by iteration until compartmental fugacity in all of the compartments does not change from its value in the previous iteration by more than 1 part in 1E+15, which is consistent with the expected rounding error for the calculations. The linear algebra and matrix algebra solution methods yield the same solutions to a high precision, and thus serve as verification that the steady-state model is solved without errors.

The model can also be run under dynamic conditions which can be used to simulate changing emission scenarios. Historical emissions of POP compounds typically follow distinct release patterns. For example widespread production and subsequent release of PCBs throughout the 1950s and 1960 was followed by a rapid reduction in production through the 1970/80s. This type of emission pattern is common for many chemicals of commerce and can be simulated using the dynamic version of the model. This introduces added parameterisation and the associated uncertainties, but potentially yields a more realistic description of compound environmental fate.

The following section describes a case study which uses the steady state solution and provides an illustration of the potential use of the European model.

Lindane as a case study

γ-HCH or lindane was selected as a case-study chemical to test the continental atmospheric transport algorithms and to evaluate the model against available measurement data for the year of 1998. It is emphasised that this is an illustrative example of how the model might be applied to describe the continental-scale dynamics of persistent chemicals. This example uses the model's steady-state description of the processes governing the fate of lindane. A fully dynamic emission inventory coupled with dynamic model runs is likely to provide a better indication of the predictive capabilities of the model, and model calculations of this type are planned for the future. Lindane was selected for this steady-state evaluation partly due to its extensive and long-term environmental monitoring, its relatively well-documented emission estimates and its spatially confined emission sources. It is also included on the UNECE POPs protocol list of chemicals that are considered to undergo LRAT and exhibit high overall environmental persistence, based on measurement data documenting its ubiquity in the environment.

Lindane has been extensively used worldwide as an agricultural insecticide (Li et al., 1998), with most of the European countries having banned or severely restricted its use since the mid-1990s. European estimates suggest that as much as 135,000 tonnes was applied over the period 1970-1996 (Breivik et al., 1999); with the major emissions originating from France, Spain and the Netherlands. Breivik and co-workers estimated that approximately 650 tonnes/year were still being emitted in 1998 and have also calculated the contribution of each European country. For the purposes of this illustration, lindane emission estimates for 1998 have been used and integrated into the model's regional structure, as presented in Figure 5. For the purposes of this initial evaluation of the performance of the model, all emissions were assumed to be to the lower atmosphere compartment of the model.

In addition to the direct application of lindane there may also have been diffuse emission sources such as from disused chemical factories or/and emissions from dumps (Manz et al., 2001) revolatilisation from soils and other lindane-treated surfaces, as well as significant amounts "imported" into the European environment from the West and East. For this reason, two types of model runs have been considered. The first assumes no background lindane concentration in any of the environmental compartments under consideration. In this way, the atmospheric transport of the selected chemical can be tested under the current model parameterisation. The second evaluated scenario applies an estimated background concentration to simulate advection into Europe. The ambient air levels can, thus, be supported and the predicted spatial distribution of atmospheric lindane concentrations may better resemble the distribution obtained by various sampling campaigns. Steady-state concentrations for both scenarios in air and other environmental media have been predicted and compared to measured data from the same time period (1998). As a result, both the validity of the existing emission inventories (inherently uncertain in nature) and, to a lesser degree, the performance of the model can be tested. Furthermore, compartmental distributions, deposition fluxes and chemical inventories have been predicted. The model can also be adapted to provide CTDs and overall environmental persistence of γ-HCH, which can then be compared to other LRAT-predictive models. It should be emphasised that the model described herein is only at its initial testing stage and results should be treated with caution. In addition, while the model predicts average regional lindane concentrations monitoring data from only one station in some of the segments was taken into account, making direct comparisons between the model and data difficult.

Case study results and discussion

Predicted steady-state concentrations for each of the seven environmental compartments were calculated, with the lindane distribution in the lower air and soil compartments presented in Figures 6a and 6b. Figure 6a reveals, as expected, that the highest lower-air concentrations are the ones closest to the major emission source regions of France and Spain. The emission estimates used in this scenario support concentrations as high as 23 pg m^{-3} with an estimated spatial variability of up to 2 orders of magnitude. Figure 6a also presents relatively high concentrations towards the Central and Northeast Europe, an observation that agrees with the calculated wind roses and the predominant West-North West wind direction in Europe. The lowest concentrations are found in Southeast and Northwest Europe. These findings suggest that the current model description of the atmospheric transport of POPs produces realistic results and can provide the basis for further testing scenarios.

A slightly different pattern emerges in the case of the soil concentration/distribution (Figure 6b.). In this case, lindane is transported through air and water and is mainly deposited in the immediate vicinity of the major emission regions. High concentrations are, therefore, found in soils west and east of France. Another feature in Figure 6b is the increased concentrations (through atmospheric deposition) in Scandinavian and other Northern European soils. This is attributed to the organic-rich terrestrial surfaces underlying these heavily forested regions that have a high capacity for sorption of mainly gaseous-phase POPs from the atmosphere. Previous studies (McLachlan and Horstmann, 1998; Wania and McLachlan, 2001) have also highlighted the influence of forests on increasing the net atmospheric deposition to the terrestrial environment. The lowest soil concentrations are, again, found in the South and East. A factor of 100 difference in soil concentrations was evident, with a maximum of 15 pg g^{-1} in the grid representing Belgium, the Netherlands and Northeast France. Since no background concentrations or historical release trends were taken into account, the actual concentration values for all compartments are likely to be underestimated.

A mean value of 50 pg m^{-3} was used as an initial/background air concentration throughout Europe in order to reduce the spatial variability and compare model predicted concentrations to measured data. The model predictions using the background concentration data are shown in Figure 7. The results show rapid "depletion" of the concentrations with distance from source due to the advection, degradation and other processes together with an average factor of 5 underestimation of air concentrations. This would suggest that either one (or both) of the following may be occurring:

a. The selected initial concentration is too small to support the measured ambient air levels, or/and
b. The source term is underestimated, for example, diffusive sources are not currently considered

The output also reveals a similar picture to Figure 6a, with the possible exception of higher concentrations towards the east. A greater influence from the local emission sources, together with the selected background value of 50 pg m^{-3} which sustains elevated ambient air levels, are the main reasons for these trends. They are also responsible for the much smaller spatial variability, which reduces to one order of magnitude (2.6 - 26 pg m^{-3}). This finding supports the well-documented transport potential of γ-HCH (Beyer et al., 2003). Table 2 presents the predicted lower air concentrations for selected "inner" European model regions, geographically relevant measurement data for 1998 and the location of the station and its reference. In general measured and predicted concentrations fall within one order of magnitude at most sites.

Van Jaarsveld et al. (1997) have also modelled the atmospheric transport and deposition of lindane on a European scale, using a Lagrangian-type model and emission inventories for 1990. Their results are very similar to the model output presented here, with an underestimation of atmospheric lindane steady-state concentrations. They concluded that the under prediction was likely to have resulted from inaccuracies in the emission inventory. High deposition of lindane to sea bodies emphasised the role of seas as buffers for lindane, whilst re-emission to the atmosphere only appeared to occur under very low ambient atmospheric concentrations. The transport potential of lindane outside the continent was also highlighted. LRAT is predicted to be of primary importance following the predominant wind direction i.e. West to East. According to the model results, the Arctic is likely to be the recipient of long-range lindane transport primarily via oceanic transport. Atmospheric concentrations of lindane in the "Arctic Box" air are relatively low, suggesting that the transport potential via the atmosphere from continental Europe is likely to be minimal. Modelling the global fate of α-HCH, Wania and Mackay (1999) also highlighted the small advective inflow into the Arctic environment via atmospheric transport.

Future model improvements and concluding remarks

A linked European scale multimedia model has been developed which describes the fate and behaviour of POPs under steady-state or dynamic conditions. Results for a steady-state solution for lindane have been presented which illustrate the apparent success of the re-parameterisation process. Future efforts will be directed towards dynamic runs, utilising fully dynamic emission patterns and exploring the use of air trajectories over shorter time-scales. It is anticipated that future improvements of the model include in a more sophisticated parameterisation of the vegetation compartment and further investigations into model parameter sensitivity. The model is intended to provide a more environmentally realistic representation of fate and behaviour of POP chemicals within Europe with particular emphasis on transport processes. Models such as these can provide useful information identifying key processes and potential sinks, predictions of long-range transport and ultimately aid policy decisions by providing information on the potential impact of proposed source reduction strategies.

Acknowledgements

We wish to thank Professor Donald Mackay and the Canadian Environmental Modelling Centre for their invaluable help and hospitality. The authors also wish to acknowledge the assistance provided by Sam Pepler of the British Atmospheric Data Centre, Dr Duncan Whyatt of Lancaster University and Defra Air Quality Division Funding No. EPG 1/3/169.

Literature cited

Breivik, K., Pacyna, J.M., Münch, J. (1999) 'Use of α-, β- and γ- hexachlorocyclohexane in Europe, in 1970-1996'. Sci. Total Environ., 239: 151-163.

Bennett DH, McKone TE, Matthies M, Kastenberg WE. 1998. General formulation of characteristic travel distance for semivolatile organic chemicals in a Multimedia environment. *Environ Sci Technol* 32:4023-4030.

Beyer A, Mackay D, Matthies M, Wania F, Webster E. 2000. Assessing long-range transport of Persistent Organic Pollutants. *Environ Sci Technol* 34:699-703.

Beyer A, Wania F Gouin T, Mackay D, Matthies M. 2003. Temperature dependence of the characteristic travel distance. *Environ Sci Technol* 37:766 – 771.

Cousins IT, Mackay D. 2001. Strategies for including vegetation compartments in multimedia models. *Chemosphere* 44:643-654.

Fellin, P., Barrie, L.A., Dougherty, D., Toom, D., Muir, D., Grift, N., Lockhart, L., Billeck, B. (1996). Air monitoring in the arctic: results for selected organic pollutants for 1992. *Environmental Toxicology and Chemistry,* 15, 253-261.

Hansen, D.V. and Poulain, P.-M. (1996) 'Quality control and interpolations of WOCE-TOGA drifter data. J. Atmos. Oceanic Technol., 13, 900-909.

Lakaschus, S., Weber, K., Wania, F., Bruhn, R., Schrems, O. (2002) 'The air-sea equilibrium and time trend of Hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica'. *Environ Sci Technol* 36: 138-145.

Leemans R. and Cramer, W. (1991). 'The IIASA database for mean monthly values of temperature, precipitation and cloudiness of a global terrestrial grid. International Institute for Applied Systems Analysis (IIASA). RR-91-18.

Li, Y.F., Bidleman, T.F., Barrie, L.A., McConnell, L.L. (1998) 'Global hexaclorocyclohexane use trends and their impact on the arctic atmospheric environment'. Geophys. Res. Lett., 25(1): 39-41.

Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E. (1996) 'Evaluating the environmental fate of a variety of types of chemicals using the EQC model'. Environ.Toxicol.Chem.: Vol 15, pp. 1627-1637.

MacLeod, M., Woodfine, D.G., Mackay, D., McKone, T., Bennet, D., Maddalena, R. (2001) 'BETR North America: A Regionally Segmented Multimedia Contaminant Fate Model for North America'. ESPR 8 (3) PP. 156-163.

Manz, M., Wenzel, K.D., Dietze, U., Schüümann, G. (2001) 'Persistent organic pollutants in agricultural soils in central Germany'. The Science of the Total Environment, Vol. 277, 1-3, 187-198.

McLachlan, M.S. and Horstmann, M. (1998) 'Forests as Filters of Airborne Organic Pollutants: A Model'. Environ. Sci. Technol. 32, 413-420.

Scheringer, M., Wegmann, F., Fenner, K., Hungerbuhler, K. (2000) 'Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model'. Environmental Science and Technology 34, 1842–1850.

Smith, W.H.F. and Sandwell, D.T. (1997) 'Global Seafloor Topography from satellite altimetry and ship depth soundings. Science, Vol. 277, 1956-1962.

UNECE report

Van de Meent, D. (1993) 'SIMPLEBOX- a generic multimedia fate evaluation model' Report number 672720001. National Institute of Public Health and the Environment (RIVM), Bilthoven, the Netherlands.

Van Jaarsveld, J.A., Van Pul, W.A.J., De Leeuw, F.A.A.M. (1997) 'Modelling transport and deposition of persistent organic pollutants in the European region'. Atmospheric Environment, Vol. 31, No 7, pp. 1011-1024.

Vorosmarty, C.J., Fekete, B.M., Tucker, B.A. (1998). Global River Discharge Database (RivDis), v. 1.1. http://www-eosdis.ornl.gov.

Wania, F., Mackay, D. (1995). 'A global distribution model for persistent organic chemicals'. The Science of the Total Environment, 160/161, 211-232.

Wania, F., Mackay, D. (1999) 'Global chemical fate of a-hexachlorocyclohexane. 2. Use of a global distribution model for mass balancing, source apportionment, and trend prediction'. Environmental Toxicology and Chemistry, Vol. 18, No.7, 1400-1407.

Wania, F. and McLachlan, M.S. (2001) 'Estimating the Influence of Forests on the Overall Fate of Semivolatile Organic Compounds Using a Multimedia Fate Model'. Environ. Sci. Technol. 35, 582-590.

Woodfine, D., MacLeod, M., Mackay, D., Brimacombe, J.R. (2001) 'Development of Continental Scale Multimedia Contaminant Fate Models: Integrating GIS'. ESPR 8 (3) PP. 164-172.

Table 1. Model mass balance equations

Steady-state Mass Balance Equations

(1) Upper Air	$f(1)\cdot DT(1) = E(1) + f(2)\ \ D(2,1)$
(2) Lower Air	$f(2)\ \ DT(2) = E(2) + f(1)\ \ D(1,2) + f(3)\ \ D(3,2) + f(4)\ \ D(4,2) + f(5)\ \ D(5,2) + f(6)\ \ D(6,2)$
(3) Vegetation	$f(3)\ \ DT(3) = E(3) + f(1)\ \ D(1,3) + f(2)\ \ D(2,3) + f(6)\ \ D(6,3)$
(4) Fresh Water	$f(4)\ \ DT(4) = E(4) + f(1)\ \ D(1,4) + f(2)\ \ D(2,4) + f(6)\ \ D(6,4) + f(7)\ \ D(7,4)$
(5) Coastal Water	$f(5)\ \ DT(5) = E(5) + f(1)\ \ D(1,5) + f(2)\ \ D(2,5) + f(4)\ \ D(4,5)$
(6) Soil	$f(6)\ \ DT(6) = E(6) + f(1)\ \ D(1,6) + f(2)\ \ D(2,6) + f(3)\ \ D(3,6)$
(7) Sediment	$f(7)\ \ DT(7) = E(7) + f(4)\ \ D(4,7)$

Matrix Algebra Format

$$\left|\begin{array}{ccccccc|c}
f(1) & f(2) & f(3) & f(4) & f(5) & f(6) & f(7) & RHS \\
\hline
DT(1) & -D(2,1) & -D(3,1) & -D(4,1) & -D(5,1) & -D(6,1) & -D(7,1) & E(1) \\
-D(1,2) & DT(2) & -D(3,2) & -D(4,2) & -D(5,2) & -D(6,2) & -D(7,2) & E(2) \\
-D(1,3) & -D(2,3) & DT(3) & -D(4,3) & -D(5,3) & -D(6,3) & -D(7,3) & E(3) \\
-D(1,4) & -D(2,4) & -D(3,4) & DT(4) & -D(5,4) & -D(6,4) & -D(7,4) & E(4) \\
-D(1,5) & -D(2,5) & -D(3,5) & -D(4,5) & DT(5) & -D(6,5) & -D(7,5) & E(5) \\
-D(1,6) & -D(2,6) & -D(3,6) & -D(4,6) & -D(5,6) & DT(6) & -D(7,6) & E(6) \\
-D(1,7) & -D(2,7) & -D(3,7) & -D(4,7) & -D(5,7) & -D(6,7) & DT(7) & E(7)
\end{array}\right|$$

Legend

f(x) - Fugacity of chemical in compartment x, Pa
E(x) - Emission rate to compartment x, mol/h
V(x) - Volume of compartment x, m^3
Z(x) - Fugacity capacity of compartment x, $mol/m^3 \cong Pa$

Table 2. Predicted and measured lower air concentrations

Region No	Region	Lower Air (pg/m^3)	Measured (pg/m^3)	Reference
4	W Norway	3.88	60; 6.7	UNECE; Lakaschus et al., 2002
6	E Sweden	5.01	25	Brorström-Lundén[1]
7	W Finland	4.79	10.4	Brorström-Lundén[1]
16	Denmark	4.94	25; 69, 11	UNECE; Lakaschus et al., 2002
19	Scotland	4.32	30	Lakaschus et al., 2002
26	Poland Ch	6.57	57	Holoubek[1]
39	N Spain	6.23	5.8	Lakaschus et al., 2002
41	S Portugal	4.00	7	Lakaschus et al., 2002
51	Arctic	5.12	8; 4.9	UNECE; Lakaschus et al., 2002

[1] Personal communication

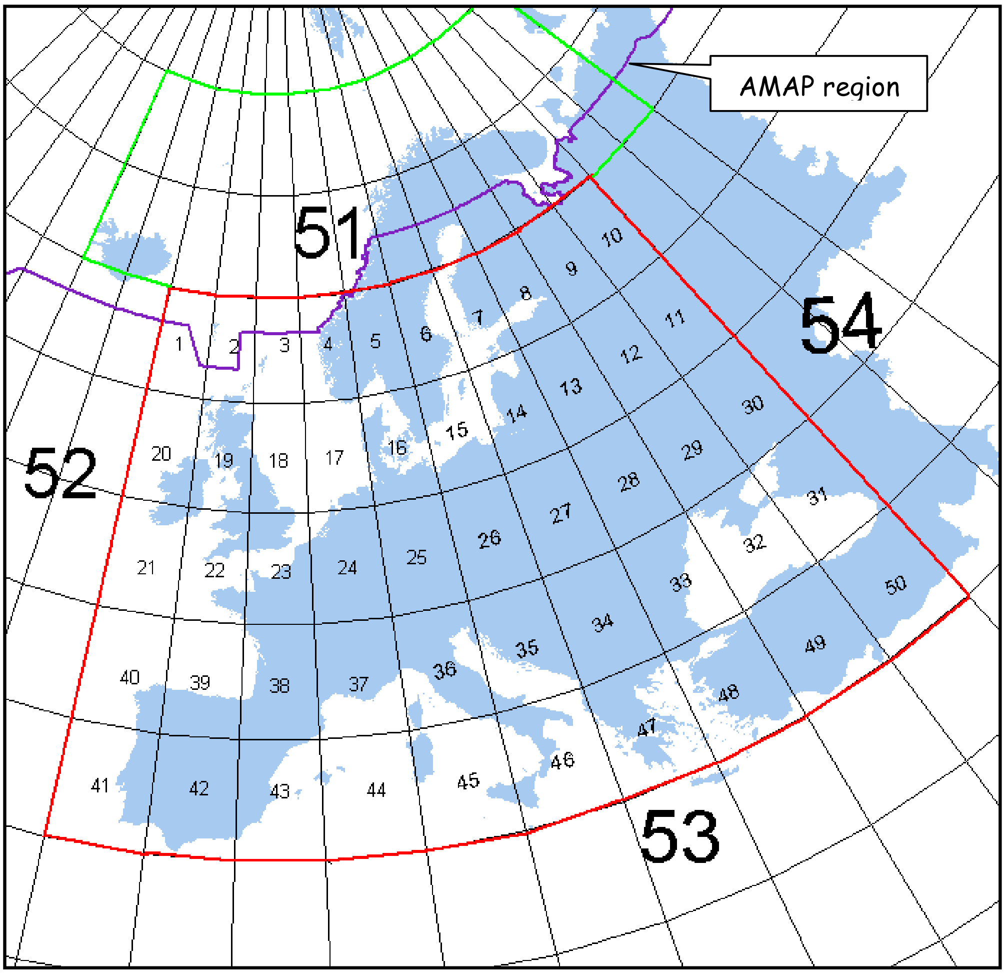
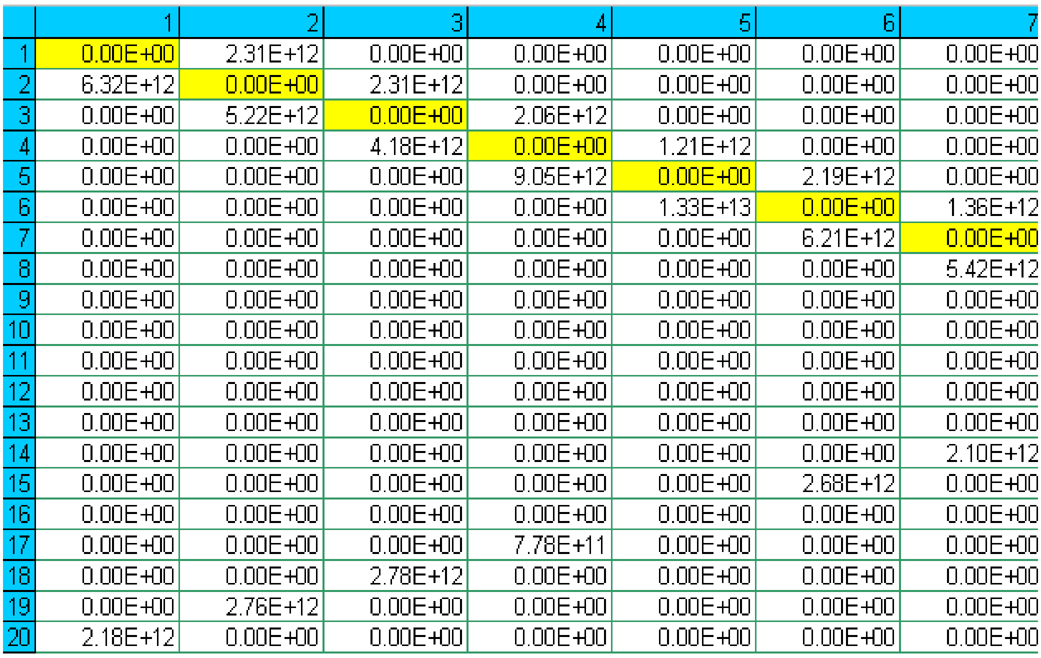


Figure 1. Europe regional segmentation showing 50 inner cells and 4 perimetric zones. Area 51 represents the Arctic region

Region I

Region J



	1	2	3	4	5	6	7
1	0.00E+00	2.31E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2	6.32E+12	0.00E+00	2.31E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3	0.00E+00	5.22E+12	0.00E+00	2.06E+12	0.00E+00	0.00E+00	0.00E+00
4	0.00E+00	0.00E+00	4.18E+12	0.00E+00	1.21E+12	0.00E+00	0.00E+00
5	0.00E+00	0.00E+00	0.00E+00	9.05E+12	0.00E+00	2.19E+12	0.00E+00
6	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.33E+13	0.00E+00	1.36E+12
7	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.21E+12	0.00E+00
8	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.42E+12
9	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
13	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
14	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.10E+12
15	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.68E+12	0.00E+00
16	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
17	0.00E+00	0.00E+00	0.00E+00	7.78E+11	0.00E+00	0.00E+00	0.00E+00
18	0.00E+00	0.00E+00	2.78E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00
19	0.00E+00	2.76E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20	2.18E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Figure 2 Part of the 54 by 54 lower air flow matrix – flows from region i to j m3 hr^{-1}

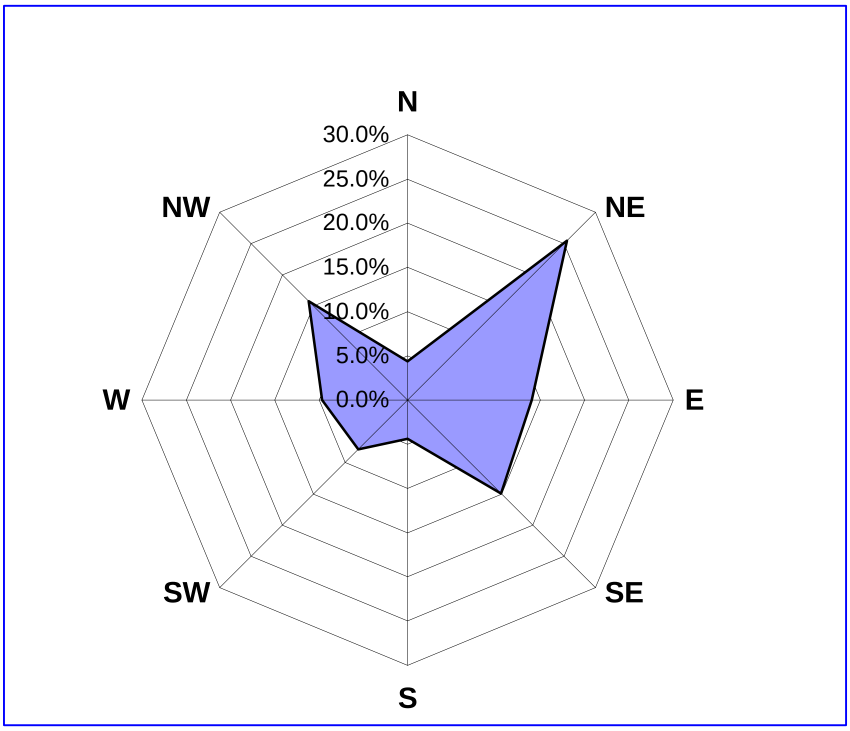


Figure 3. Average 1997-2001 wind rose for Northwest UK

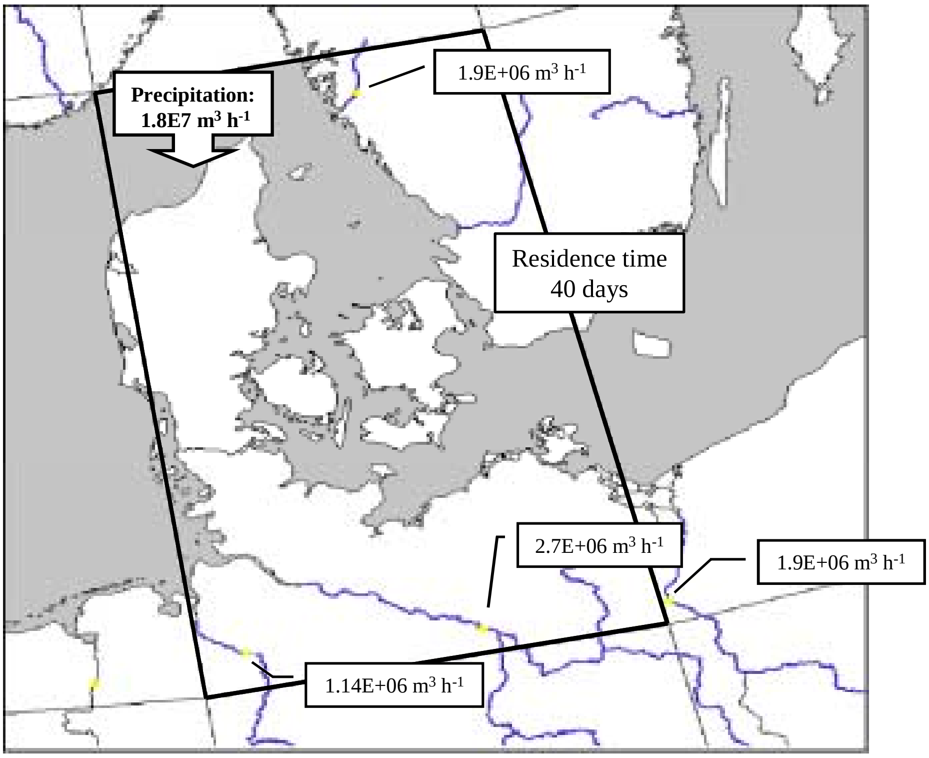


Figure 4. Water flows for region 16.

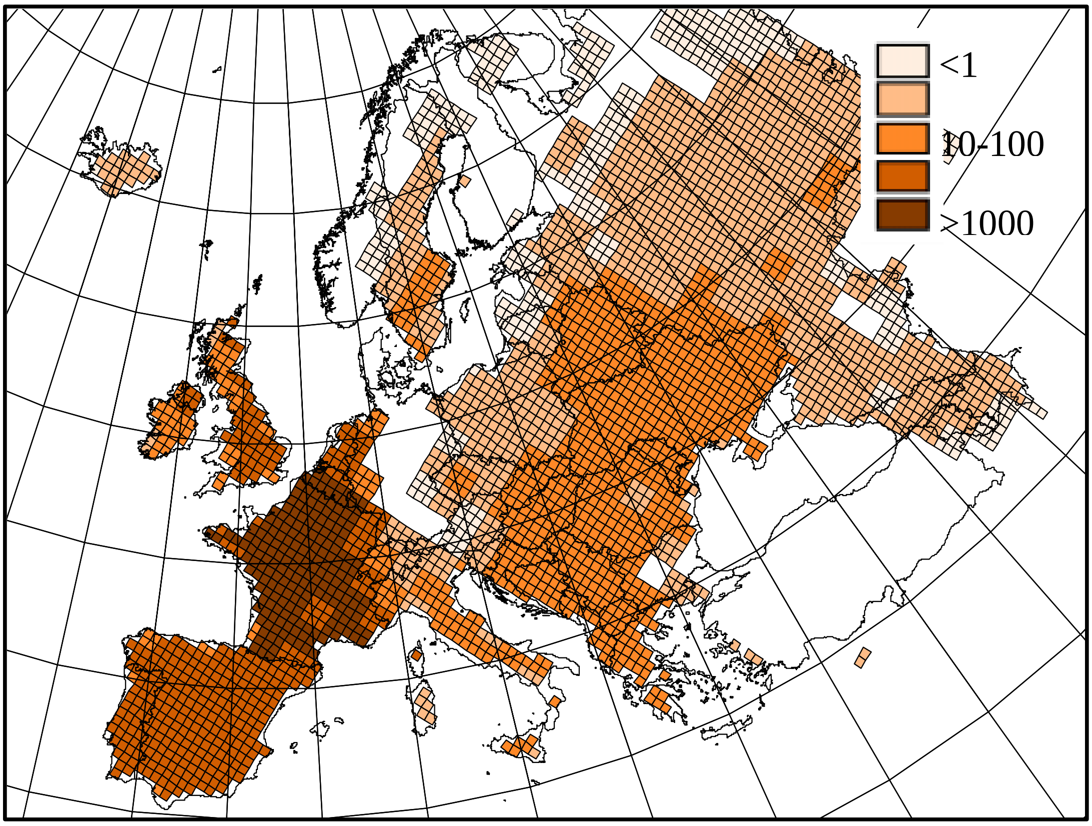


Figure 5. 1998 lindane emissions (kg)

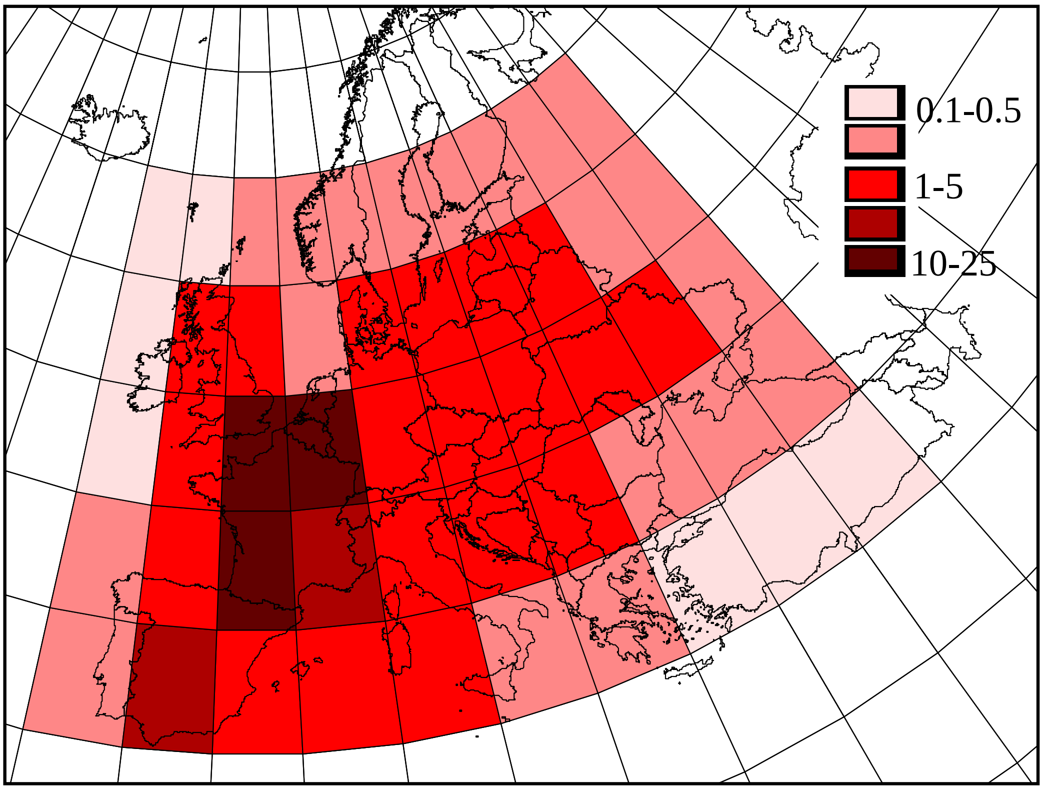


Figure 6a. Lower air distribution (pg m^{-3})

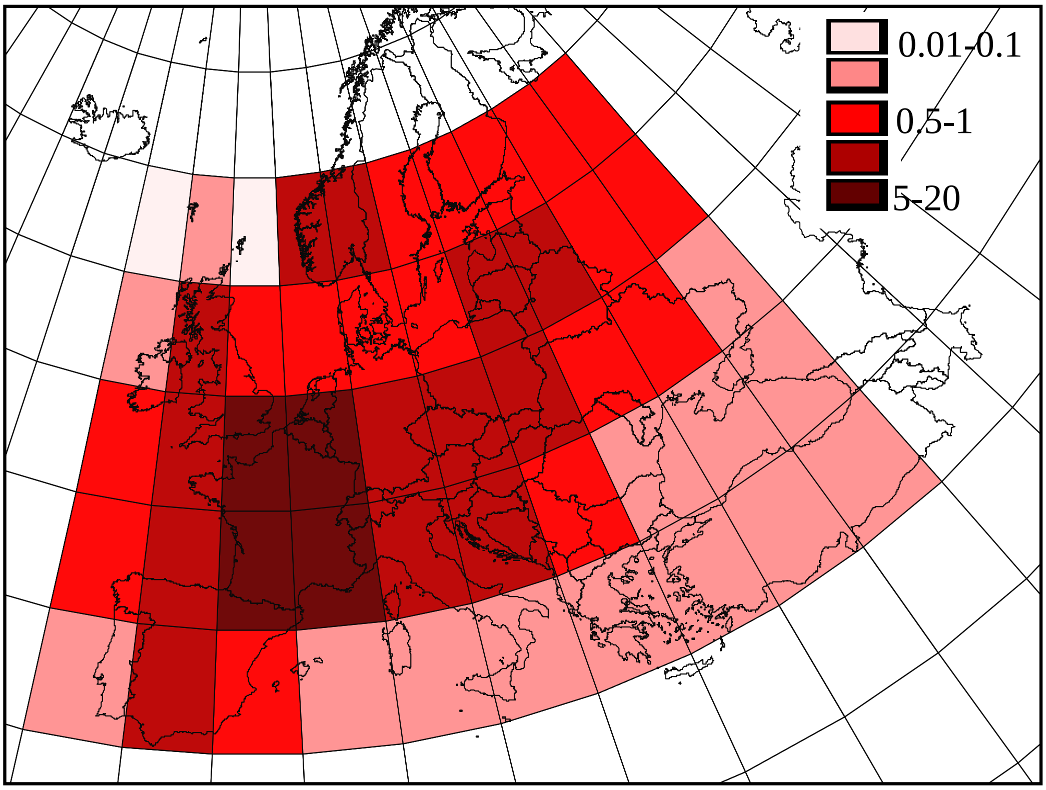


Figure 6b. Soil distribution (pg g^{-1})

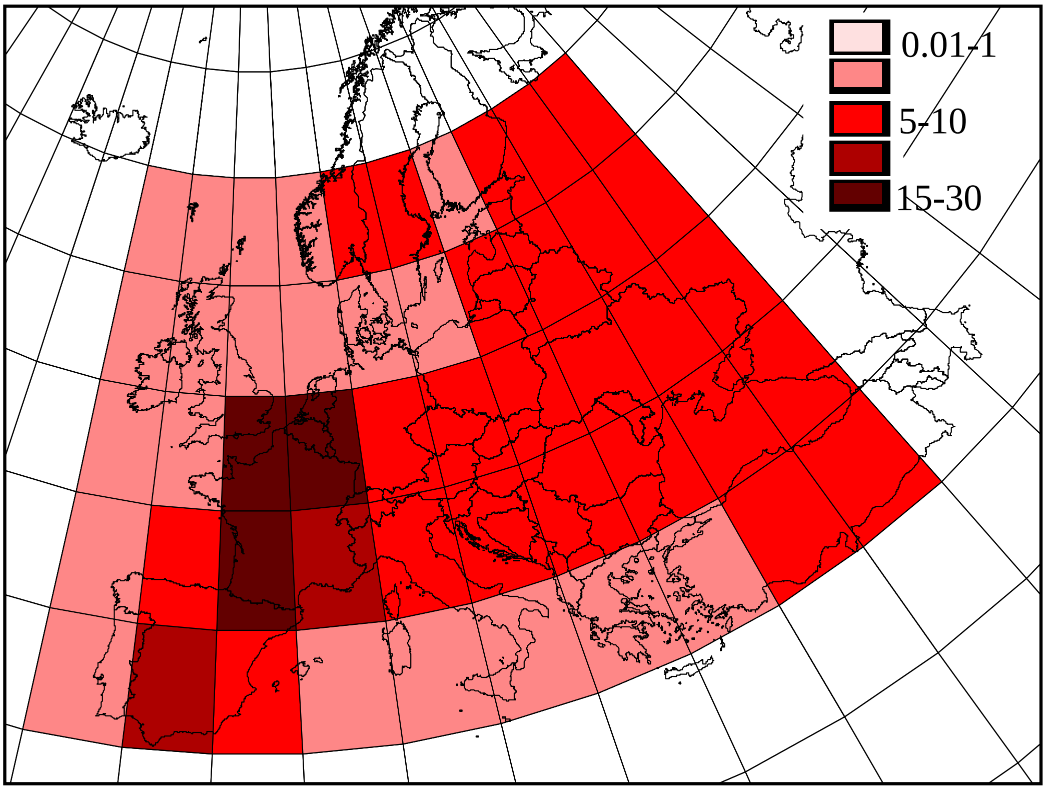


Figure 7. Lindane lower air concentration with background (pg m^{-3})

Section 6

Manuscript title:

Atmospheric PCBs, PBDEs and OC pesticides across Europe: results of a passive sampling programme

Authors and affiliations:

Foday M Jaward, Nick Farrar, Andy Sweetman and Kevin C Jones

Environmental Science Department, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

Tom Harner

Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada, M3H 5T4

Submission journal:

Environmental Science and Technology. American Chemical Society (in press).

Abstract

This study presents concurrently sampled ambient air data for a range of persistent organic pollutants at the continental scale. This was achieved using a passive air sampling system, deploying polyurethane foam disks, which was: prepared in one laboratory; sealed to prevent contamination; sent out by courier to volunteers participating in different countries; exposed for 6 weeks; collected; re-sealed; returned to the laboratory for analysis. Europe was the study area - a region with a history of extensive POPs usage and emission, and with marked national differences in population density, the degree of urbanisation and industrial/agricultural development. Samplers were deployed at remote/rural/urban locations in 22 countries and analysed for PCBs, a range of organochlorine pesticides (HCB, HCHs, DDT, DDE) and PBDEs. Calculated air concentrations were in line with those obtained by conventional active air sampling techniques. The geographical pattern of all compounds reflected suspected regional emission patterns and highlighted localised hotspots. PCB and PBDE levels varied by over 2 orders of magnitude; highest values were detected in areas of high usage and were linked to urbanised areas. HCB was relatively uniformly distributed, reflecting its persistence and high degree of mixing in air. Higher γ-HCH, DDT and DDE levels generally occurred in S and E Europe.

Introduction

Persistent organic pollutants (POPs) are stable in the environment, undergo long-range atmospheric transport (LRAT), and can bioaccumulate through food chains. This has focussed international regulation on reducing emissions to air (*1,2*), and risk assessment/modelling efforts on their ambient distribution (*3*). Research on POPs currently focusses on uncertainties over their ambient sources, atmospheric transport and fate, and air-surface exchange, to improve understanding of the complex array of factors controlling air concentrations. These vary spatially and temporally, and ultimately influence the global fate of POPs and their entry into food chains. Ideally, *simultaneous* measurements of air concentrations in different locations are needed to assess the relative importance of sources, atmospheric processes, the LRAT potential of POPs, and to validate models. Such spatial mapping studies could be on a range of scales, from around potential point sources, across cities, or even nationally, regionally and globally (*4-9*). However, such surveys at multiple sites are not feasible with conventional high volume (active) air samplers, which are expensive and require power. Several interesting studies have therefore made use of 'environmental media', such as leaves and pine needles (*4,8,10,11*), tree bark (*12,13*) and butter (*5*), to map the spatial distribution of POPs, on the assumption that their POPs concentrations broadly reflect ambient levels. However, there are often issues of sample comparability, exposure time and potential confounding factors with such media, which can produce uncertainties in data interpretation.

There are therefore considerable incentives to develop passive air sampling techniques (*14-17*). These should be simple to use, cheap, versatile and capable of being deployed in many locations concurrently. Passive samplers can be designed and calibrated, to allow reliable estimates of air concentrations to be made, or to allow semi-quantitative comparisons of the levels and patterns of POPs. Several designs are possible and – indeed – are desirable. For example, it would be useful to have samplers to integrate ambient concentrations over time scales as short as hours/days or a long as weeks/months/years. The shorter timescales facilitate studies of contaminant dispersal, fluxes and transport processes and can provide data for dispersion/transport modelling. Longer timescales would allow source/sink regions to be identified and underlying trends in ambient levels to be investigated.

A range of different passive sampling devices has been utilised in the last few years. To date, most work on passive samplers has focussed on integrating concentrations over weeks/months, using samplers with a high 'capacity' to retain POPs, such as semi-permeable membrane devices (SPMDs) (*14,18-20*), polyurethane foam (PUF) disks (*15,16*) and XAD resins (*21-23*). These operate as 'kinetic samplers' where it is necessary to know the sampling/uptake rate, rather than as equilibrium samplers (*24*). PUF disks are a particularly attractive sampler, because they are cheap, easy to handle and can be used to sample over periods of several weeks. PUF is the sampling medium routinely deployed in conventional (active) high volume air samplers, and so there is also information already available about how POPs partition to it, its capacity etc. (*25*). PUF disks of 14 cm diameter and 1.2 cm thickness have been tested as passive samplers previously; they sample POPs at a rate of a few m^3 of air/day (*16*). With appropriate instrumental detection limits and low blanks, this allows detection of many classes of POPs, following exposure periods of weeks in ambient air. The sampling period used in this study was 6 weeks, so the PUF disk was still operating in the 'kinetic' phase (*16*), where uptake of gas phase compounds occurs at the same rate for the range of target compounds and is practically independent of temperature.

In previous studies, we have demonstrated the utility of passive samplers at the local scale (*16,19*) and to conduct urban-rural (*15*) and latitudinal (*6,7*) transects. However, in this study we wanted to demonstrate the feasibility of obtaining ambient data on a continental scale, thereby helping to shed light on large-scale source/sink/transport potential issues for these compounds. Europe was the study area - a region with a history of extensive POPs usage and emission, with marked national differences in population density, the degree of urbanisation and industrial/ agricultural development. There are major differences between European countries in their production, usage, emission and regulatory controls on POPs. It was hoped that this would provide an interesting test area with which to demonstrate the feasibility of the large-scale deployment of passive sampling techniques. For the study to be most effective, it is clearly necessary to synchronise the start and finish dates of sample deployment. We therefore developed a sampling system that could be: prepared in one laboratory; sealed to prevent contamination; sent out by courier to volunteers participating in different countries; exposed; collected; re-sealed; returned to the laboratory to be analysed there together with the same methods. This obviously provides scope for a relatively cheap but large-scale deployment exercise. An additional objective was to obtain ambient data in a form that could subsequently be used to test a European scale multi-media model (*26-28*). The model utilises information on air mass flows between different regions of Europe, and can integrate air concentration data integrated over time scales of the order of weeks.

One of the benefits of such a study is in being able to make comparisons between compound classes which may have different properties, or between compound classes which are relatively well known/understood, and those which are not. Data are therefore presented for polychlorinated biphenyls (PCBs), selected organochlorine (OC) pesticides, and polybrominated diphenyl ethers (PBDEs) obtained from the same sample deployment.

These are all chemicals subject to LRAT, which have been measured in the atmosphere of remote regions, far from source areas (*29-34*). PCBs and OC pesticides have been subject to international regulations (*2*), whilst the patterns of production and use of PBDEs are changing rapidly; they have been little used in some countries, widely used in others, and recently restricted in others (*35-37*). They are being considered as 'candidate POPs' under the international protocol (*1*). Production, usage and emission information (of variable quality) is available for these POPs in European and national inventories (e.g. *38-40*).

PCBs, OC pesticides and PBDEs enter the environment by different routes. PCBs are associated with industrialised countries and urban source areas (*38,39*). Current atmospheric levels of PCBs in the environment are due to either primary anthropogenic emissions (e.g. intentional production and disposal or accidental releases of products or materials containing PCBs), volatilisation from environmental reservoirs (e.g. sea, soil) or incidental/ unwanted formation of some congeners (e.g. in combustion processes) (*38*). OC pesticides are released into the atmosphere by spray drift, post-application volatilisation and wind erosion of soil. These emissions are influenced by numerous physical and chemical factors (*41-43*). A substantial portion of hexachlorobenzene (HCB) measured in the atmosphere is thought to come from volatilisation of 'old' (agricultural) HCB applied to soils in the past, along with combustion and other poorly quantified sources (*41*). PBDEs have been extensively used in Europe and North America as flame retardants in various products, such as furnishing foam, plastics, textiles, wire and cable insulation, electrical and electronic connectors etc. They reduce the risk of fire, by interfering with the combustion of the polymeric materials (*44-46*). They presumably enter the environment by volatilisation from these products (*35*).

This study reports the first attempt to monitor the distribution of PCBs, PBDEs and OC pesticides in the European atmosphere, using a passive sampler network. The data are discussed, in terms of the sources and properties of the compounds.

MATERIALS AND METHODS

Air Sampling, Extraction and Analysis

The samplers have been described previously (*16*); they were deployed in sheltered chambers, as shown in Figure 1. A pre-cleaned and weighed PUF disk (14 cm diameter x 1.35 cm thick; density 0.0213 g cm^{-3}) was suspended in the centre of the two dishes between washers using solvent-rinsed tweezers. Samplers were then transferred to the sampling locations in airtight containers to avoid contamination during transit. Those deployed outside the UK were sent by courier. A total of 71 samplers were successfully deployed over a 6 week period (15th June to 30th July 2002), across 22 countries (see Figure 2). Local volunteers were given guidance on choice of deployment location; 25 were in urban locations and 46 in rural/remote locations. At the end of the deployment period, the samplers were retrieved by the volunteers, re-sealed in their original transport containers and returned by courier to Lancaster University. On receipt in Lancaster, the disks were removed and stored in sealed, solvent cleaned brown glass jars at –20 °C until extraction.

The samplers were spiked with a range of $^{13}C_{12}$–labelled PCB congeners *($^{13}C_{12}$ PCB 28, 52, 101, 138, 153, 180, 209)* and three PCCD/F congeners (*$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF, 1,2,7,8-TCDF and 1,3,6,8-TCDD*) to monitor the extraction and cleanup procedures. They were extracted for 18 hours with DCM in a Buchi extraction unit. The extract was rotary evaporated and transferred with hexane to a 15 ml amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 ml and cleaned on a 9 mm id chromatography column with 1 g alumina (BDH neutral Alumina), 2 g silica gel (Merck Silica 60) and 1 cm baked sodium sulphate (all baked at 450 °C overnight) and then passed through gel permeation chromatography (GPC) using 6 g of Biobeads SX 3. A further three labelled PCB congeners, $^{12}C_{12}$ PCB 30, $^{13}C_{12}$ PCB 141 and $^{13}C_{12}$ PCB 208 were added to the sample prior to injection as internal standards. The samples were reduced to a final volume of 25 μl.

The samples were analysed for PCBs and OC pesticides (except HCHs) by GC-MS on a Fisons MD800 operated in electron ionisation mode using selected ion monitoring (*18,47*). PBDEs and HCHs were analysed separately with a Thermo Trace GC-MS operated in negative chemical ionisation source in selected ion monitoring mode using ammonia as the reagent gas. GC temperature programme and monitored ions are given elsewhere (*44*). A total of 29 PCB congeners (tri*-PCB 18, 22, 28, 31;* tetra*-PCB 41/64, 44, 49, 52, 60/56, 70, 74;* penta*-PCB 87, 90/101, 95, 99, 110, 118, 123;* hexa*-PCB 138, 141, 149, 151, 153/132, 158;* hepta*-PCB 170, 174, 180, 183, 187*); 8 PBDE congeners (*28, 47, 49, 75, 99, 100, 153, 154*) and 7 OC pesticides (*α-HCH, γ-HCH, HCB, α-chlordane, γ-chlordane, opDDD, opDDE, ppDDD, ppDDT*) regularly detected in samples were quantified using an internal standard method.

Quality Control/Quality Assurance (QA/QC)

All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks consisted of pre-extracted PUF disks extracted and analysed in the same way as samples. There was no difference between concentrations of analytes in the laboratory and field blanks, indicating contamination was minimal during transport, storage and analysis. Practical detection limits were 0.03-0.64 ng/sample for PCBs (depending on congener), 0.06-1.5 ng/sample for PBDEs and 0.05-1.7 ng/sample for pesticides for the six-week deployment period. Recoveries were 60-85% for PCBs and OC pesticides and 75-110% for PBDEs. Reported values are not recovery corrected. Method recoveries were determined, by spiking six PUF disks with a working standard containing all analysed PCB and PBDE congeners, and pesticides. These PUF disks were extracted and cleaned in the same way as samples. Recoveries were found to be between 80 and 115%. Instrument efficiencies were monitored using quality control standards after every six samples run on the instrument. Peaks were only integrated where the signal to noise ratio was ≥ 3; otherwise, they were considered non-detect. Mean recoveries of surrogates per sample were found to be > 75% for all compounds.

RESULTS AND DISCUSSION

Introductory remarks

Table 1 presents a summary of the data arising from the study. Data on the detection limits (DL) and measured range in samples are given as ng compound/sample.

Also shown is: the percentage of samples above the detection limit (%>DL); the ratio of the highest/lowest measured values (H/L ratio), calculated for those compounds that were routinely above the detection limits; and the estimated range of air concentrations (pg/m^3) (see below). Further details of sampling sites and compounds detected in individual samples are available in the Supporting Information (Table S1).

A number of compounds were detected in all the samples, namely PCBs, γ-HCH, HCB and pp-DDT. The PBDEs were detected in about half of the samples. A longer exposure time would have ensured that a greater air volume was sampled, and raised the frequency of their detection.

Some observations on comparisons between compound distributions

The variation in persistent contaminant concentrations in the atmosphere yields information, which can be related to aspects of their sources-sinks and persistence (*48*). For example, the concentrations of chlorofluorocarbons (CFCs) in the atmosphere are virtually the same around the world (*49*). Because of their high persistence and volatility, they have become extremely well mixed in the air. Other chemicals may show marked source-sink gradients, resulting in substantial differences in air concentrations between locations. Differences between locations also shed light on the relative transport potential of compounds. The dataset obtained here demonstrates contrasting behaviour for different POPs. For example, the ∑PCBs and ∑PBDEs show differences of over two orders of magnitude, between the highest and lowest locations. The highest values are in urban centres of high past/present use, whilst the lowest values are from remote parts of Europe. This is powerful evidence that there are continuing primary emissions of these compound classes (*6*). In contrast, the distribution of HCB through the European atmosphere is very consistent, only varying by a factor of ~6 between the samples (see Table 1). HCB is much more volatile than PCBs and PBDEs, and very stable in the atmosphere (*50*). As a result, it is predicted to have an atmospheric characteristic travel distance (CTD) of ~100,000 km (*50*), about two orders of magnitude greater than that of PCBs (*50*) and PBDEs (*37*).

Comparing derived air concentrations with measured concentrations

When the PUF disks are deployed in the sampling chambers (Figure 1), they give typical sampling rates of ca. 3-4 m^3 air per day (*16*). Hence a 6-week deployment 'samples' ca. 130-170 m^3. The ambient concentrations (pg/m^3) represented by the measured ng/sampler values were therefore derived and are shown in Table 1. In summary, this indicates that European $\sum$PCB concentrations broadly lie in the range of 10s – a few thousand pg/m^3, perhaps typically being in the low 100s pg/m^3. This is exactly in line with data obtained with conventional high-volume air samplers. Some of the UK's air monitoring stations where PCB data are obtained were used to deploy samplers for this study. The data were consistent with expectations. For example, inner city sample sites, such as London and Manchester, are typically 1000-2000 pg $\sum$PCB/m^3, whilst those at semi-rural UK sites are a few hundred pg/m^3 (*51*). HCB (10s pg/m^3) and HCH (10s-100s pg/m^3) values of the survey are also very consistent with measured results from other studies (*43,52,53*). Based on work by Bailey (*41,54*), average ambient concentrations in the northern hemisphere atmosphere of ca. 50 pg/m^3 are expected, for example. Table 1 suggests $\sum$PBDE values in the range ~0.1-10s pg/m^3. PBDEs have been reported for the remote west coast of Ireland at ca. 0.1-5 pg/m^3 and in rural/semi-rural England up to 10s pg/m^3 (*55*).

In summary, the data presented so far give confidence that the samplers are capable of reflecting the spatial variations and absolute values of these POPs in the European atmosphere. It is therefore appropriate to examine the spatial patterns in more detail.

General comments on spatial trends

A wide range of sample sites was utilised. Remote/background locations included sites at Mace Head (western Ireland), Iceland and Svalbard (Norway) (sites 39, 19 and 28, respectively). Additionally, low concentrations were often detected in samples from the south west of the European region – Portugal and south west Spain (sites 32, 33 and 60). These areas experience relatively clean air, coming off the Atlantic Ocean. In contrast, a number of samplers were deployed in major urban centres, notably London, Manchester, Paris, Madrid, Barcelona, Stockholm, Milan and Moscow (site numbers 65, 68, 40, 57, 62, 36, 54, and 21 respectively).

PCBs The spatial variation in PCBs is shown in Figure 3, where the length of the bars is proportional to the ng PCB/sampler. The full dataset is in Table S1. As expected, the predominant gradient was between urban-rural-remote locations. The lowest levels were measured in rural/remote sites, such as in Ireland, Norway, Cyprus, Greece, Portugal and Sweden. The highest levels occurred at urban sites in Russia, France, Italy, Sweden, UK and Eastern Europe (Croatia, Hungary, Estonia). Europe is the area of the world where PCB usage has been most concentrated (*38,39*). It is interesting that Eastern European levels are amongst the highest. Manufacture and use is believed to have continued in Eastern Europe after bans were imposed in some western European countries (*38,39*). As noted earlier, the urban-rural gradient in PCB concentrations extends over at least two orders of magnitude, emphasising that diffusive atmospheric emissions from urban locations continue to contaminate the regional atmosphere, over 30 years after international restrictions on usage were first introduced.

HCB Bailey (*41,54*) assembled information from a variety of sources to give a picture of global HCB emissions in the mid-1990s. He suggested that no single overwhelming source dominated but, rather, emissions resulted from (largely past) pesticide applications, manufacturing and combustion. Pacyna et al. (*40*) focussed on European emissions, concluding that emissions had reduced from a total of ~200 t/year in 1970 to ~40 t/year in 1993. They estimated that by the mid-1990s, the greatest contributors to the European inventory were Russia, Spain, the Ukraine, France and Germany.

As noted earlier, HCB levels throughout the survey were very consistent (Table 1), reflective of the atmospheric persistence of HCB. Ambient levels are declining (*40*) as primary sources have reduced and may be being maintained by emissions from it's former use as a fungicide. As the sources of HCB are diffuse and its volatility is relatively high, it is perhaps not surprising that the ambient levels, revealed by this study are very consistent (see Figure 4). Slightly elevated concentrations at individual sites are probably due to local sources. For example, the highest value was obtained at a location in rural Germany (site 44) where local agricultural usage of HCB in glasshouses has been high.

Other studies in Europe, using latitudinally deployed SPMDs as long-term air samplers exposed for 2 years, found higher HCB concentrations in colder, northerly latitudes (*56,57*). In other words, HCB can undergo 'cold condensation' onto solid phases from the atmospheric gas phase. In contrast, Hellstrom (*58*) studied pine needles sampled across Europe in the late 1980s. There was no evidence of increasing HCB concentrations northwards and evidence that the needles had not reached equilibrium with the air, prior to sampling (*59*). It should be noted that there is no indication from Figure 4 of a latitudinal increase in HCB on the samplers in this study. These observations may support the contention that the samplers were still operating in the (kinetic) uptake phase (*17*), which is not influenced by temperature, and had not attained air-sampler equilibrium after 6 weeks of exposure. Theoretical predictions, from knowledge of compound K_{OA}, suggest that HCB would be beginning to approach equilibrium after this exposure time (*16*).

HCHs Figure 5 presents the spatial distribution data for α-HCH and γ-HCH. A greater proportion of non-detect values occurred for the α isomer (see Table 1) and measured concentrations ranged between 1.7-17 ng/sample. The distribution of α-HCH was reasonably homogenous, although some of the higher values were observed in samples from eastern locations (samples sites 16 and 17 in Kazakhstan; 8, 9, and 12 in Poland; 15 in Hungary; 13 in Estonia and 20 and 21 in Russia). Most non-detect values were in the northerly latitudes. The use of the technical mixture reduced substantially in much of Europe during the 1970s (*53*). The ongoing distribution of α-HCH probably reflects diffuse emissions from past usage in Europe and limited ongoing usage in some parts of the continent, for example, Russia.

Values of γ-HCH show greater variability (see Figure 5). Highest concentrations occurred in the south and east of Europe, notably Spain, parts of France, Italy and the Balkans region. Some ongoing usage of γ-HCH continues on vegetable and tomato crops in these countries (*11,53,60*). In Hellstrom's (*58*) study with pine needles sampled in the late 1980s, the highest γ-HCH concentrations were also observed in the southernmost part of the transect.

DDT and DDE The spatial distribution of DDT and its stable metabolic breakdown product, DDE, are shown in Figure 6. Most European usage of DDT occurred in Eastern Europe, Spain, Italy and France (*61*). Various countries introduced bans and restrictions on DDT usage through the 1970-80s (*40*).

DDT was routinely detected in the samples and showed a very wide range in concentrations – ca. 400-fold – between the highest and lowest values (see Table 1). This was influenced by a couple of very high 'outlier' samples. The highest levels were recorded in Russia and Italy. In both cases, low DDE/DDT ratios were measured, suggestive of a fresh DDT signal. The elevated Russian sample could be due to limited local usage of old stocks of DDT, despite the restrictions on its use (*52*). The high Italian sample was obtained in the north, near Milan. DDT has been produced in a factory in that area, as a precursor of dicofol (*61*). It exerts a strong signal on ambient residues in the surrounding area, which is likely reflected in this sample (site number 54). As expected, the lowest values were in the north and west of Europe (Figure 6).

PBDEs Figure 7 presents the spatial distribution data for the Σ_8PBDEs. PBDE production and use has been a relatively recent phenomenon, with the resultant environmental emissions peaking much later than for the organochlorine substances discussed earlier (*35-37*). It is therefore not surprising that there should be a large 'gradient' between samples collected in source regions and remote regions; as noted in Table 1, the ratio of highest/lowest sample is ~700. An overriding feature of Figure 7 is the focus of the most elevated samples in the UK. The UK has a history of PBDE production and has been a major user of PBDE based flame retardants, owing to particularly stringent fire regulations (*35-37,55*). The UK is clearly a regional source area for PBDEs to the European atmosphere. In contrast, levels reaching Europe from the west (i.e. over the Atlantic) are low (see Figure 7).

Other high values were detected in urban centres in mainland Europe – samples from Milan, Bilthoven (Netherlands), Geneva, Athens, and Seville, for example. Lower levels were detected in the samples from France and Germany. Non-detectable/very low values occurred in the remote/background sites, especially in Iceland, Ireland (Mace Head), Norway, and Sweden. Values in Eastern Europe were generally low. As expected from previous studies, PBDE-47 and 99 were the dominant contributors to the pattern, contributing ca. 75 % to the Σ_8PBDE. These are the dominant congeners in the Bromkal 70-5DE commercial product, where they constitute ~70-80% of the mixture (*46,62*).

Concluding remarks

In general, the geographical pattern of all the compounds studied reflected the suspected regional emission patterns. The samples also highlighted localised hotspots;

great care therefore needs to be taken over the choice of site locations. The study demonstrates that it is possible to map local, regional and global sources of POPs using passive air samplers. Reconnaissance studies of this nature can provide information on trends and identify unknown sources. The trends of PCBs and PBDEs are linked to urbanised source areas. The levels of α-HCH and HCB were relatively uniform throughout Europe, while the levels of γ-HCH and the DDT and DDE were higher in southern and eastern locations. Predicted concentrations of compounds reported in this study are comparable to concentrations reported by other authors indicating that quantitative data, suitable for modelling purposes, can be obtained.

Acknowledgements

We are grateful to the UK Department of the Environment, Food and Rural Affairs (Defra) Air Quality Division for financial support. We thank: numerous colleagues and friends who helped in deploying the sampling devices; colleagues at Lancaster University especially, Dr Gareth Thomas, Dr Robert Lee, Dr Rainer Lohmann, and Mrs Victoria Burnett for their analytical support and meaningful consultations, and Costas Prevedouros for assistance with data handling. FMJ is grateful to the Commonwealth Commission for PhD funding.

REFERENCES

(1) UNECE, *Protocol on Persistent Organic Pollutants under the 1979 Convention on Long-Range Transport Air Pollution.* 1998, United Nations Economic Commission for Europe (ECE/EB.Air/60).

(2) UNEP, *Preparation of an Internationally Legally Binding Instrument for Implementing International Action on Certain Persistent Organic Pollutants.* 1998, United Nations Environment Programme, UNEP/POPs/Inc.1/6.

(3) Klecka, G.; et al. *Evaluation of persistence and long-range transport of organic chemicals in the environment. In SETAC Special Publication Series.* 2000. Pensacola, Florida.

(4) Calamari, D.; Tremolada, P.; Di Guardo, A.; Vighi, M. *Environ. Sci. Technol.* 1994, *28*, 429-434.

(5) Kalantzi, O. I.; Alcock, R. E.; Johnston, P. A.; Santillo, D.; Stringer, R. L.; Thomas, G. O.; Jones, K. C. *Environ. Sci. Technol.* 2001, *35*, 1013-1018.

(6) Meijer, S. N.; Ockenden, W. A.; Steinnes, E.; Corrigan, B. P.; Jones, K. C. *Environ. Sci. Technol.* 2003, *37*, 454-461.

(7) Ockenden, W. A.; Sweetman, A.; Preston, H. F.; Steinnes, E.; Jones, K. C. *Environ. Sci. Technol.* 1998, *32*, 2795-2803.

(8) Tremolada, P.; Burnett, V.; Calamari, D.; Jones, K. C. *Environ. Sci. Technol.* 1996, *30*, 3570-3577.

(9) Jones, K. C.; Barber, J. L., *Sample matrices, site selection and sampling techniques In: Proceedings of the UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stocholm Convention.*. 2003, UNEP: Geneva. p. 185-199.

(10) Tremolada, P.; Burnett, V.; Calamari, D.; Jones, K. C. *Chemosphere* 1996, *32*, 2189-2203.

(11) Villa, S.; Finizio, A.; Diaz, R. D.; Vighi, M. *Water, Air, Soil Pollution* 2003, *146*, 335-349.

(12) Simonich, S. L.; Hites, R. A. *Science* 1995, *269*, 1851-1854.

(13) Simonich, S. L.; Hites, R. A. *Environ. Sci. Technol.* 1997, *31*, 999-1003.

(14) Ockenden, W. A.; Jaward, F. M.; Jones, K. C. *The Scientific World* 2001, *1*, 557-575.

(15) Harner, T.; Ikonomou, M.; Shoeib, M.; Stern, G.; Diamond, M. *Organohalogen Compounds*. 2002, 57, 33-36.

(16) Shoeib, M.; Harner, T. *Environ. Sci. Technol.* 2002, *36*, 4142-4151.

(17) Harner, T.; Farrar, N. J.; Shoeib, M.; Jones, K. C.; Gobas, F. A. P. C. *Environ. Sci. Technol.* 2003, *37*, 2486-2493.

(18) Ockenden, W. A.; Preston, H. F.; Thomas, G. O.; Sweetman, A.; Jones, K. C. *Environ. Sci. Technol.* 1998, *32*, 1538-1543.

(19) Lohmann, R.; Corrigan, B.; Howsam, M.; Jones, K. C.; Ockenden, W. *Environ. Sci. Technol.* 2001, *35*, 2576-2582.

(20) Wennrich, L.; Popp, P.; Hafner, C. *J. Environ. Monit.* 2002, *4*, 371-376.

(21) Billings, W. N.; Bidleman, T. F. *Environ. Sci. Technol.* 1980, *14*, 679-683.

(22) Billings, W. N.; Bidleman, T. F. *Atmos. Environ.* 1983, *17*, 383-391.

(23) Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. *Environ. Sci. Technol.* 2003, *37*, 1352-1359.

(24) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. *Environ. Sci. Technol.* 2003, 3A-9A.

(25) Patton, G. W.; Walla, M. D.; Bidleman, T. F.; Barrie, L. A. *J. Geophys. Res. - Atmospheres* 1991, *96*, 10867-10877.

(26) MacLeod, M.; Woodfine, D. G.; Mackay, D.; McKone, T.; Bennet, D.; Maddalena, R. *Environ. Sci. Pollut. Res.* 2001, *8*, 156-163.

(27) Woodfine, D. G.; MacLeod, M.; Mackay, D.; Brimacombe, J. R. *Environ. Sci. Pollut. Res.* 2001, *8*, 164-172.

(28) Prevedouros, K.; MacLeod, M.; Jones, K. C.; Sweetman, A. J. *Environ. Pollut.* 2003, *in press*,

(29) Fuoco, R.; Colombini, M. P.; Ceccarini, A.; Abete, C. *Microchemical Journal* 1996, *54*, 384-390.

(30) Bidleman, T. F.; Jantunen, L. M.; Falconer, R. L.; Barrie, L. A. *Geophysical Res. Letters* 1995, *22*, 219-222.

(31) Bidleman, T. F.; Walla, M. D.; Roura, R.; Carr, E.; Schmidt, S. *Marine Pollution Bulletin* 1993, *26*, 258-262.

(32) Larsson, P.; Jarnmark, C.; Sodergren, A. *Marine Pollution Bulletin* 1992, *25*, 281-287.

(33) ter Schure, A. F. H.; Larsson, P. *Atmos. Environ.* 2002, *36*, 4015-4022.

(34) Oehme, M.; Haugen, J.-E.; Kallenborn, R.; Schlabach, M. *Organohalogen Compounds* 1994, *20*, 523-528.

(35) Alcock, R. E.; Sweetman, A. J.; Prevedouros, K.; Jones, K. C. *Environ. Int.* 2003, *in press*,

(36) Alaee, M.; Arias, P.; Sjodin, A.; Bergman, A. *Environ. Int.* 2003, *in press*,

(37) Gouin, T.; Harner, T. *Environ. Int.* 2003, *in press*,

(38) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. *Sci. Total Environ.* 2002, *290*, 199-224.

(39) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. *Sci. Total Environ.* 2002, *290*, 181-198.

(40) Pacyna, J. M.; Breivik, K.; Munch, J.; Fudala, J. *Atmos. Environ.* 2003, *in press*,

(41) Bailey, R. E. *Chemosphere* 2001, *43*, 167-182.

(42) Bidleman, T. F. *Water, Air, Soil Pollution* 1999, *115*, 115-166.

(43) Walker, K.; Vallero, D. A.; Lewis, R. G. *Environ. Sci. Technol.* 1999, *33*, 4373-4378.

(44) Gouin, T.; Thomas, G. O.; Cousins, I.; Barber, J.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol.* 2002, *36*, 1426-1434.

(45) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. *Sci. Total Environ.* 2001, *275*, 1-17.

(46) Sjodin, A.; Jakobsson, E.; Kierkegaard, A.; Marsh, G.; Sellstrom, U. *J. Chromatogr. A* 1998, *822*, 83-89.

(47) Thomas, G. O.; Sweetman, A. J.; Parker, C. A.; Kreibich, H.; Jones, K. C. *Chemosphere* 1998, *36*, 2447-2459.

(48) Junge, C. E. *Tellus* 1974, *26*, 477-488.

(49) Stanley, L. J.; Hites, R. A., *Chlorinated Organic Contaminants in the Atmosphere*, in *Organic Contaminants in the Environment: Environmental Pathways and Effects*, K.C. Jones, Editor. 1991, Elsevier Applied Science Publishers: London and New York. p. 338.

(50) Beyer, A.; Mackay, D.; Matthies, M.; Wania, F.; Webster, E. *Environ. Sci. Technol.* 2000, *34*, 699-703.

(51) Halsall, C. J.; Lee, R. G. M.; Coleman, P. J.; Burnett, V.; Harding-Jones, P.; Jones, K. C. *Environ. Sci. Technol.* 1995, *29*, 2368-2376.

(52) Iwata, H.; Tanabe, S.; Ueda, K.; Tatsukawa, R. *Environ. Sci. Technol.* 1995, *29*, 792-801.

(53) Li, Y. F.; McMillan, A.; Scholtz, M. T. *Environ. Sci. Technol.* 1996, *30*, 3525-3533.

(54) Bailey, R. E., *Hexachlorobenzene Concentration Trends in the Great Lakes, Second Edition. Report prepared for the HCB/BaP Working Group of the Great Lakes Binational Toxics Strategy*. 2001, Environmental Chemistry Consultants: Midland. p. 1-29.

(55) Lee, R. G. M.; Thomas, G. O.; Jones, K. C. *Organohalogen Compounds*. 2002, 58, 193-196.

(56) Ockenden, W. A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Sweetman, A. J.; Jones, K. C. *Environ. Pollut.* 2003, *121*, 75-80.

(57) Meijer, S. N.; Ockenden, W. A.; Sweetman, A.; Breivik, K.; Grimalt, J. O.; Jones, K. C. *Environ. Sci. Technol.* 2003, *37*, 667-672.

(58) Hellstrom, A., *Uptake of Airborne Organic Pollutants in Pine Needles: Geographical and Seasonal Variations, PhD Thesis*. 2003, Swedish University of Agricultural Sciences: Uppsala.

(59) Kylin, H.; Sjodin, A. *Environ. Sci. Technol.* 2003, *37*, 2350-2355.

(60) Van Jaarsveld, J. A.; Van Pul, W. A. J.; Leeuw, F. A. A. M. D. *Atmos. Environ.* 1996, *31*, 1011-1024.

(61) Di Guardo, A.; Zaccara, S.; Cerabolini, B.; Acciarri, M.; Terzaghi, G.; Calamari, D. *Chemosphere* 2003, *52*, 789-797.

(62) Sundstrom, G.; Hutzinger, O. *Chemosphere* 1976, *5*, 187-190.

List of Tables and Figures

Table 1. Summary data for the passive air sampling programme

Table S1. Supporting Information for all compounds and sampling sites

Figure 1. Schematic representation of the PUF disk sampling device

Figure 2. Map showing sampling sites

Figure 3. Spatial distribution of PCB (ng/sample – June 15 to July 30, 2002)
Key: Largest bar = 280 ng/sample (site 21)

Figure 4. Spatial distribution of HCB (ng/sample – June 15 to July 30, 2002)
Key: Largest bar = 8.9 ng/sample (site 44)

Figure 5. Spatial distribution of α- and γ-HCH (ng/sample – June 15 to July 30, 2002)
Key: Largest bar α-HCH = 17 ng/sample (site 16)
Largest bar γ-HCH = 65 ng/sample (site 61)
Figure 6. Spatial distribution of ppDDE and ppDDT (ng/sample – June 15 to July 30, 2002)
Key: Largest bar ppDDE = 4.2 ng/sample (site 21)
Largest bar ppDDT = 32 ng/sample (site 21)

Figure 7. Spatial distribution of PBDE (ng/sample – June 15 to July 30, 2002)
Key: Largest bar = 43 ng/sample (site 68)

Table 1. Summary data for the passive air sampling programme. Data on the detection limits (DL) and measured range in samples is given as ng/sample. Also shown is: the ratio of the highest/lowest measured samples (H/L ratio), the percentage of samples above the detection limit (%>DL), and the estimated range of air concentrations (pg/m^3).

Compound	**DL**	**%>DL**	**Measured range**	**H/L ratio***	**Air conc+**
PCB-28	0.64	58	0.67-38		<5-230
PCB-52	0.03	100	0.20-36		1.6-210
PCB-90/101	0.03	100	0.35-21		2.8-120
PCB-118	0.03	100	0.12-15		0.9-90
PCB-138	0.03	100	0.19-15		1.5-90
PCB-153/132	0.03	100	0.24-18		1.9-110
PCB-180	0.03	94	0.03-4.1		<0.25-20
$\sum_{29}$PCB			2.5-280	>100	20-1700
α-HCH	1.72	57	1.7-17		<14-100
γ-HCH	0.13	100	1.1-65	60	9-390
HCB	0.13	99	1.4-8.9	6	11-50
pp-DDE	0.05	87	0.05-4.2		<0.4-25
pp-DDT	0.13	100	0.08-32	400	0.6-190
PBDE-28	0.06	82	0.06-4.5		<0.5-30
PBDE-47	0.95	55	0.97-13		<8-80
PBDE-49	0.06	30	0.07-2.0		<0.5-12
PBDE-75	0.06	54	0.07-0.58		<0.5-3
PBDE-99	1.47	45	1.6-21		<10-120
PBDE-100	0.29	41	0.31-3.5		<2-20
PBDE-153	0.09	55	0.09-2.4		<0.7-15
PBDE-154	0.10	44	0.10-1.5		<0.8-10
$\sum_{8}$PBDE			0.06-43	>700	0.5-250

* this ratio has only been calculated for compounds where ~100% of samples gave detectable levels.

+ derived as described in the text. < values utilise the %<DL data.

Figure 1. Schematic representation of the PUF disk sampling device

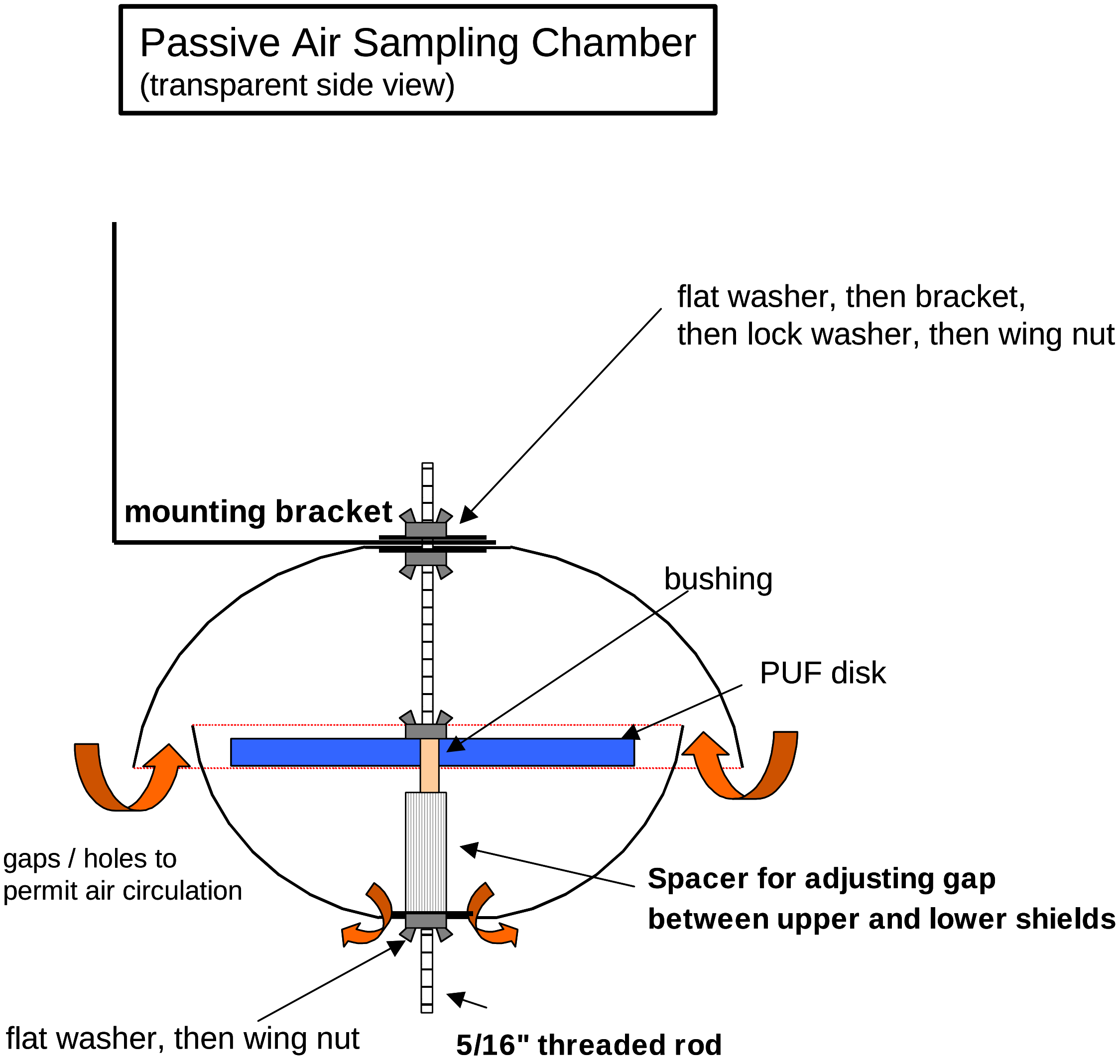


Figure 2. Map showing sampling sites

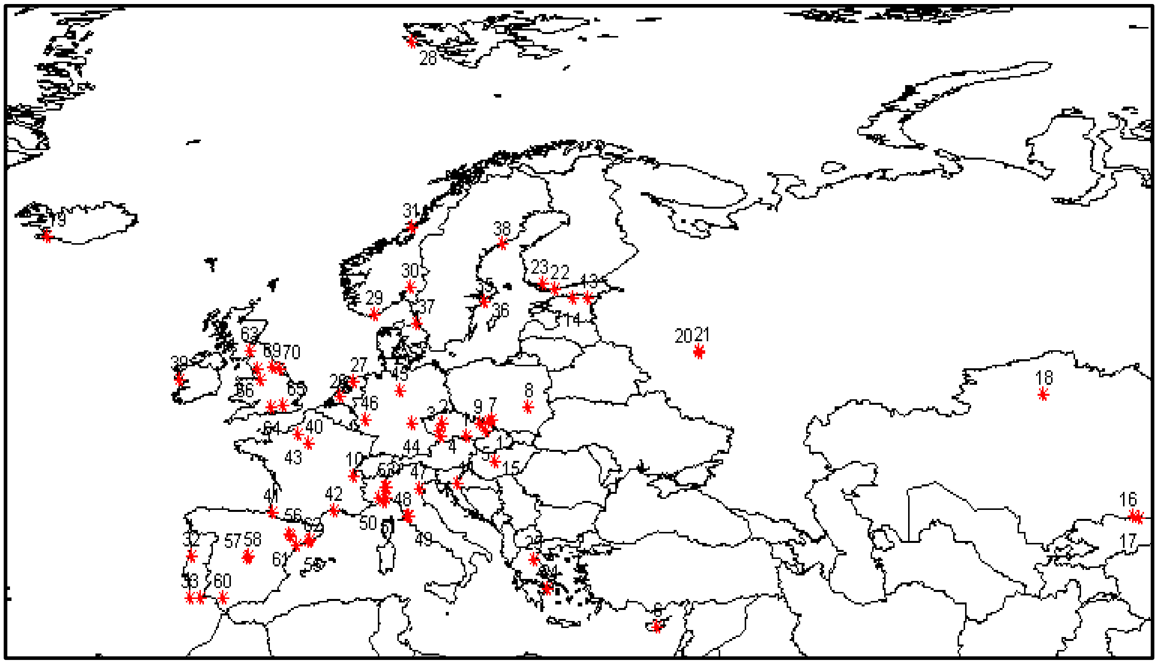


Figure 3. PCB

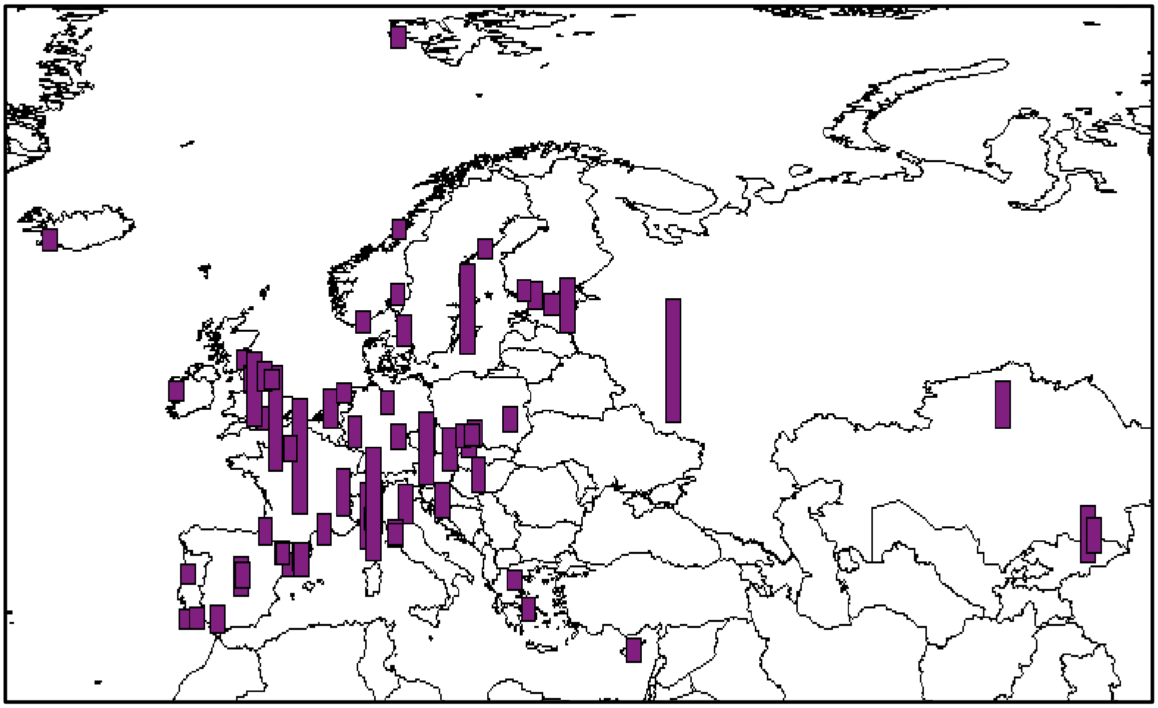


Figure 4. HCB

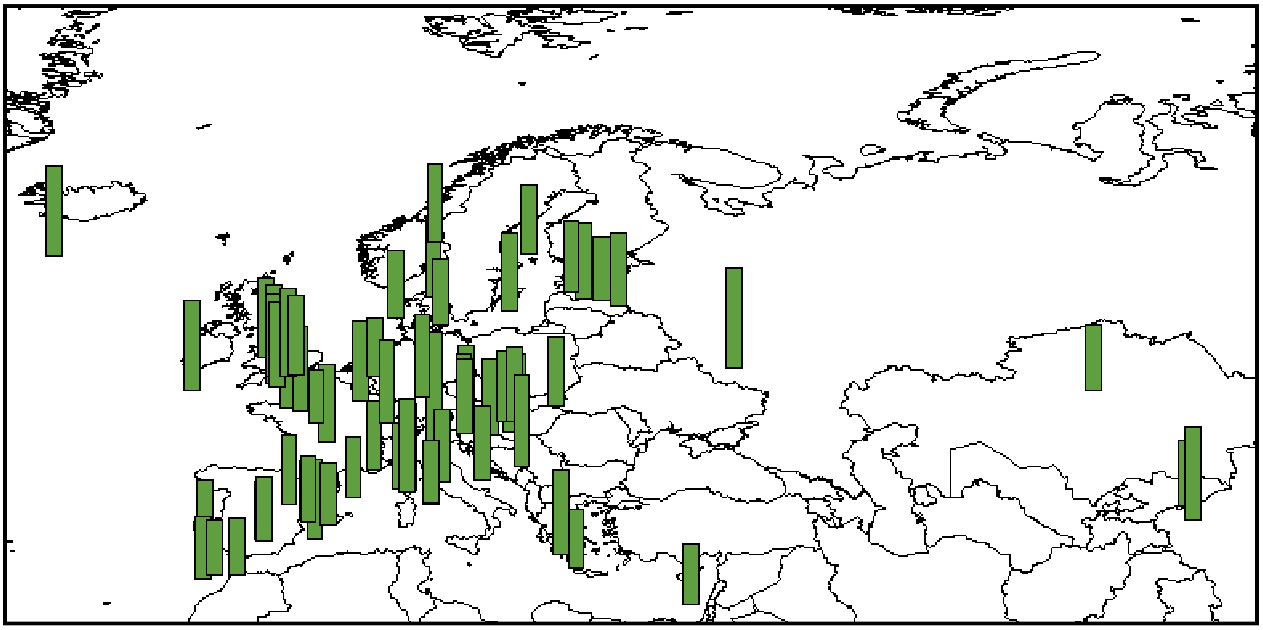


Figure 5 α-HCH and γ-HCH

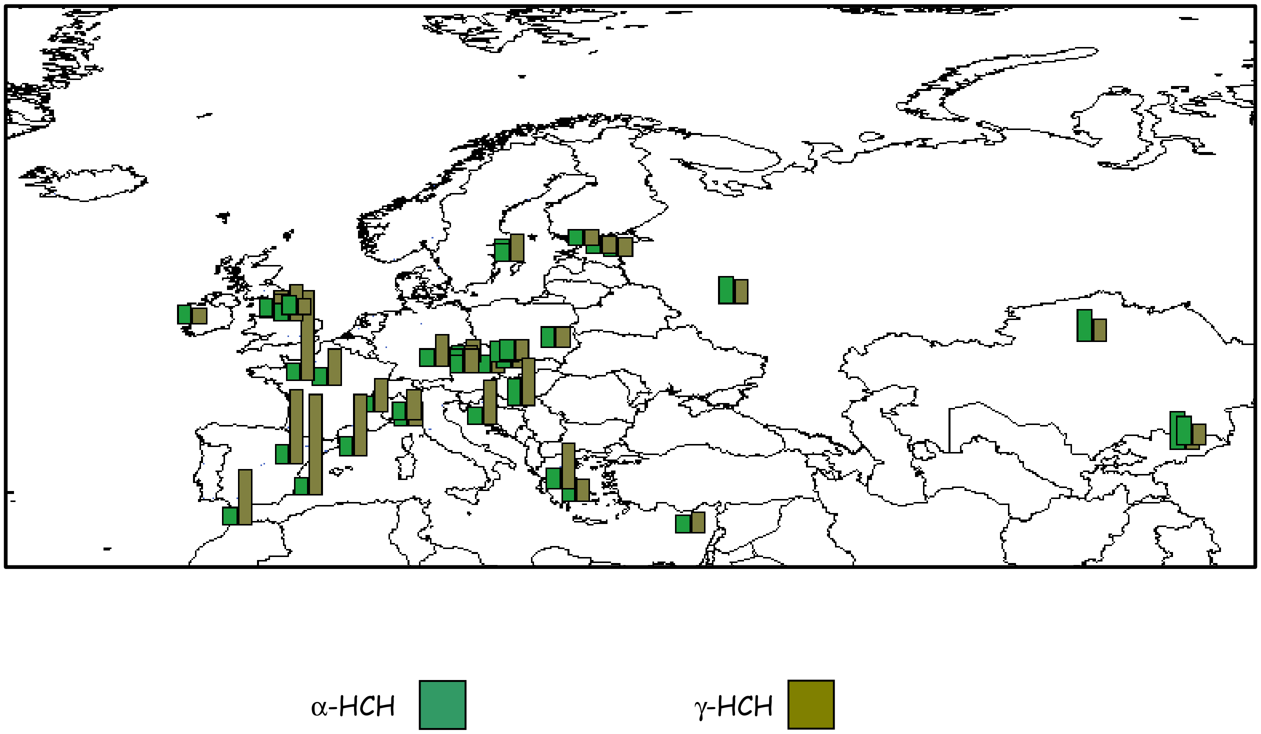


Figure 6. ppDDE and ppDDT

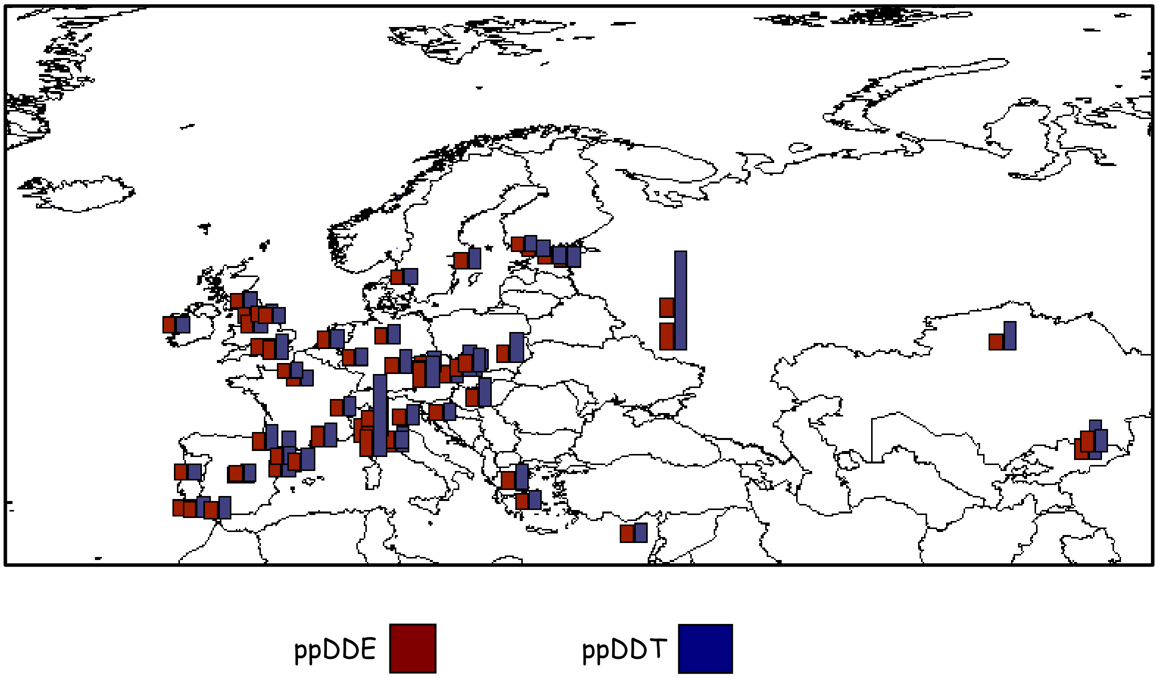
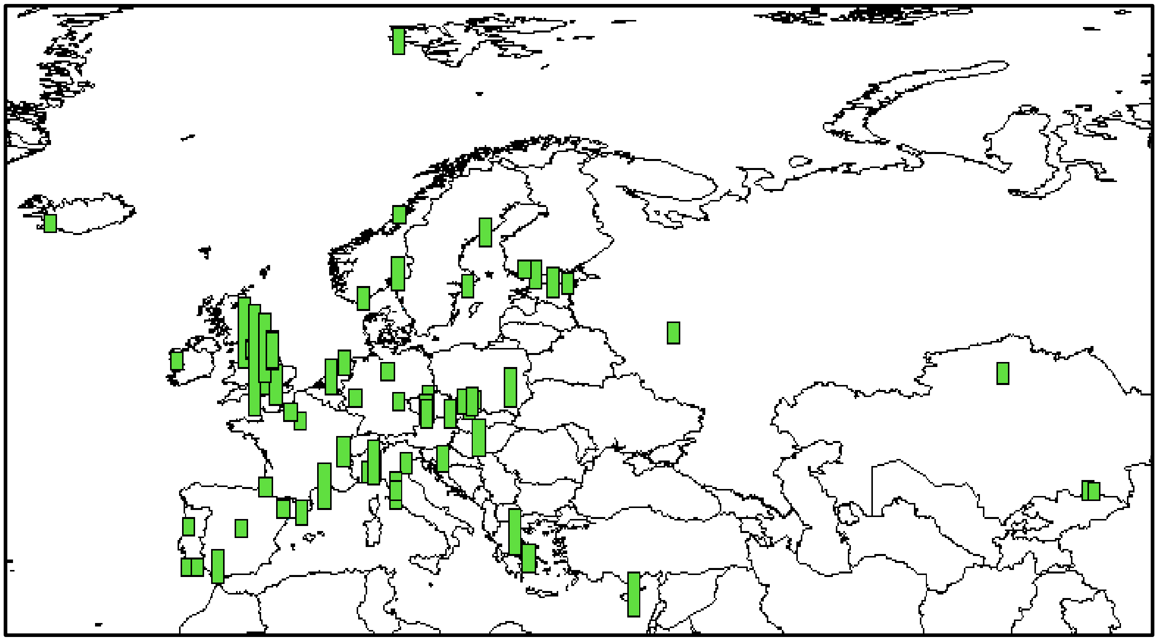
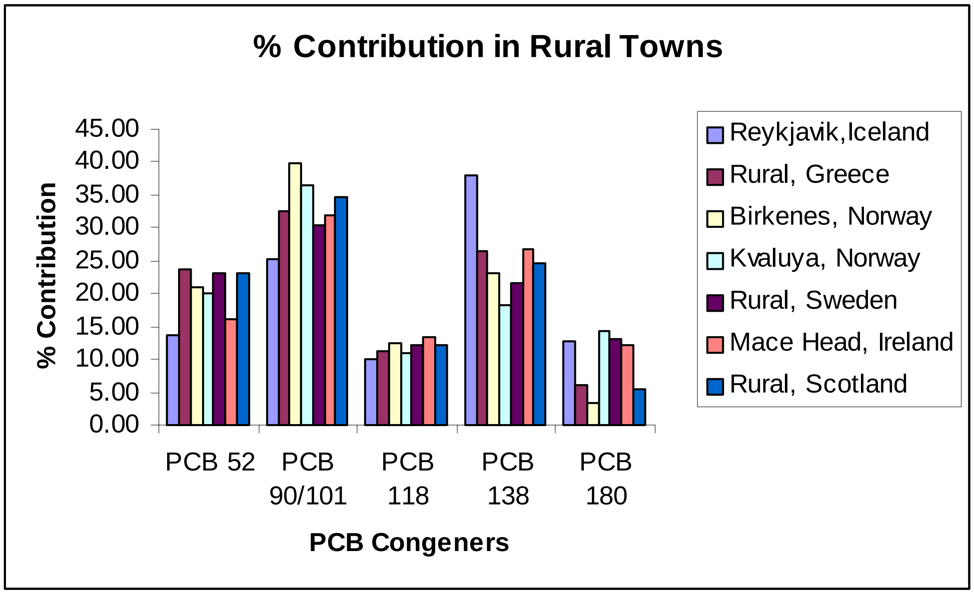
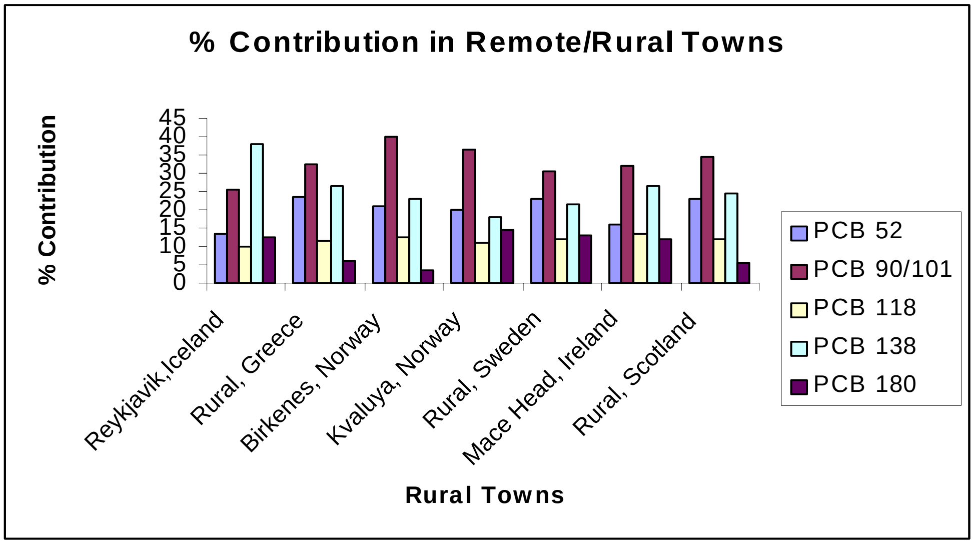


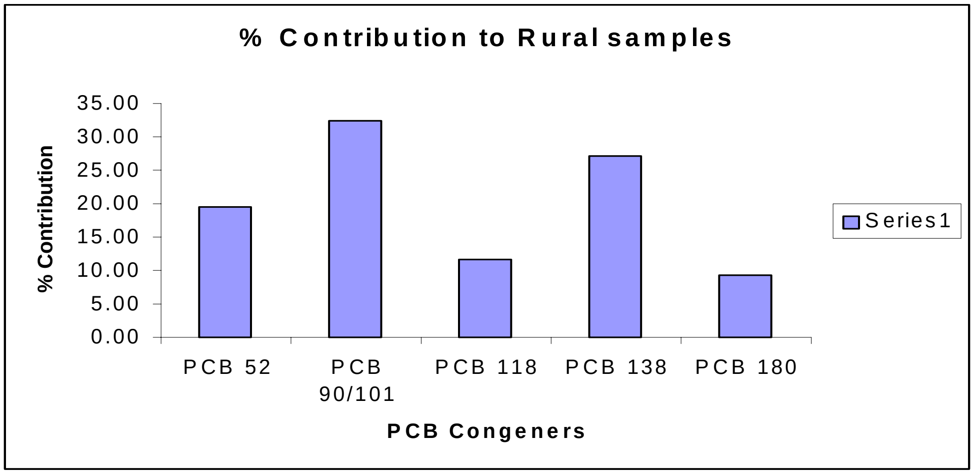
Figure 7 PBDE

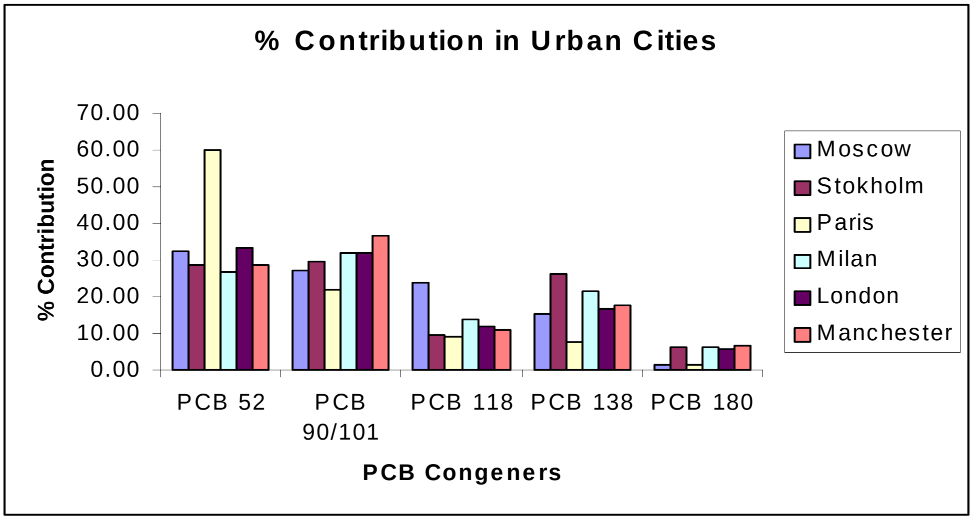


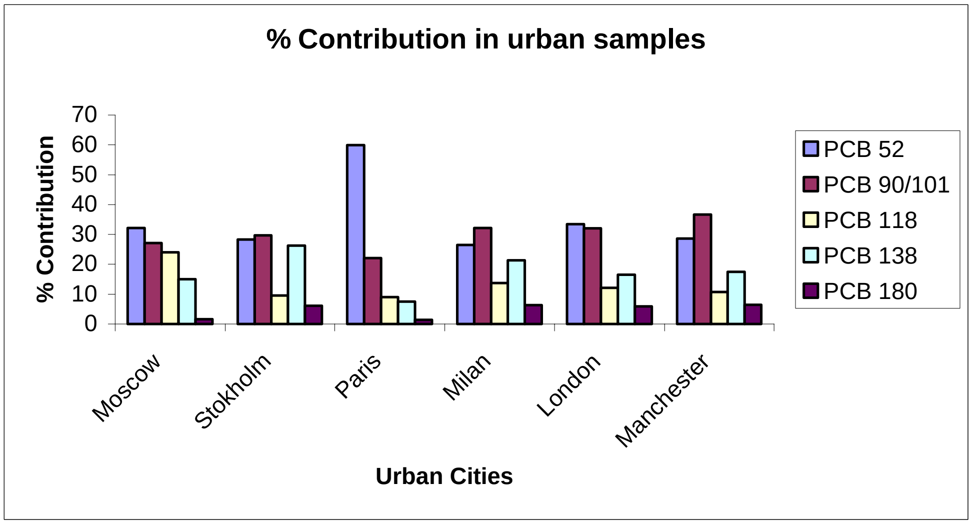
Supporting information

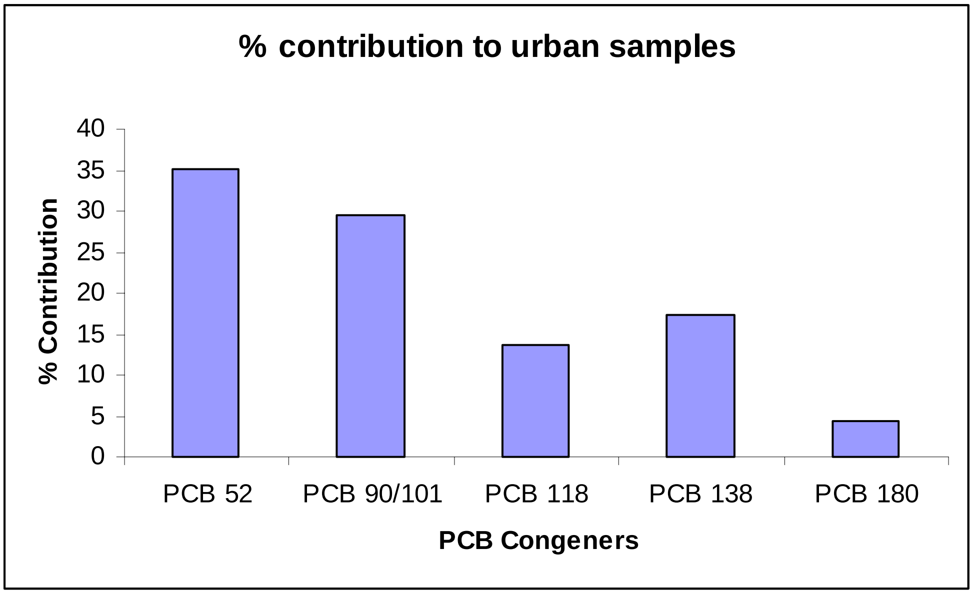







% Contribution in Urban Cities
% Contribution
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
PCB 52
PCB 90/101
PCB 118
PCB 138
PCB 180
PCB Congeners
Moscow
Stokholm
Paris
Milan
London
Manchester


% Contribution in urban samples
% Contribution
70
60
50
40
30
20
10
0
Moscow
Stokholm
Paris
Milan
London
Manchester
Urban Cities
PCB 52
PCB 90/101
PCB 118
PCB 138
PCB 180


% contribution to urban samples
% Contribution
40
35
30
25
20
15
10
5
0
PCB 52
PCB 90/101
PCB 118
PCB 138
PCB 180
PCB Congeners

Section 7

Manuscript title:

Passive air sampling of PAHs and PCNs across Europe

Authors and affiliations:

Foday M Jaward, Nick Farrar, Andy Sweetman and Kevin C Jones

Environmental Science Department, Institute of Environmental and Natural Sciences,
Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

Tom Harner

Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Toronto,
Ontario, Canada, M3H 5T4

Submission journal:

Environmental Toxicology and Chemistry. SETAC Journal.

Abstract

This study presents concurrently sampled ambient air data for a range of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs) at the continental scale. This was achieved using a passive air sampling system, deploying polyurethane foam disks, which was: prepared in one laboratory; sealed to prevent contamination; sent out by courier to volunteers participating in different countries; exposed for 6 weeks; collected; re-sealed; returned to the laboratory for analysis. Europe was the study area - a region with a history of extensive POPs usage and emission, and with marked national differences in population density, the degree of urbanisation and industrial/agricultural development. Samplers were deployed at remote/rural/urban locations in 22 countries. Calculated air concentrations were in line with those obtained by conventional active air sampling techniques, for both compound classes and for compounds existing predominantly in the gas and particle phases. The geographical compound distribution reflected suspected regional emission patterns and highlighted localised hotspots. PAH and PCN levels varied by over 2 orders of magnitude; the implications for sources are discussed.

Introduction

Persistent organic pollutants (POPs) are stable in the environment, undergo long-range atmospheric transport (LRAT), and can bioaccumulate through food chains. This has focussed international regulation on reducing emissions to air [1, 2], and risk assessment/modelling efforts on their ambient distribution [3]. Research on POPs currently focusses on uncertainties over their ambient sources, atmospheric transport and fate, and air-surface exchange, to improve understanding of the complex array of factors controlling air concentrations. These vary spatially and temporally, and ultimately influence the global fate of POPs and their entry into food chains. Ideally, simultaneous measurements of air concentrations in different locations are needed to assess the relative importance of sources, atmospheric processes, the LRAT potential of POPs, and to validate models. Such spatial mapping studies could be on a range of scales, from around potential point sources, across cities, or even nationally, regionally or globally [4-8]. However, such surveys are usually not feasible with conventional high volume (active) air samplers, which are expensive and require power. Several interesting studies have therefore made use of 'environmental media', such as leaves and pine needles [4, 8-10], tree bark [11, 12] and butter [5], to map the spatial distribution of POPs, on the assumption that their POPs concentrations broadly reflect ambient levels. However, there are often issues of sample comparability, exposure time and potential confounding factors with such media, which can produce uncertainties in data interpretation.

There are therefore considerable incentives to develop passive air sampling techniques [13-15]. These should be simple to use, cheap, versatile and therefore deployed in many locations concurrently. Passive samplers can be designed and calibrated, to allow reliable estimates of air concentrations to be made, or to allow semi-quantitative comparisons of the levels and patterns of POPs. Several designs are possible and – indeed – are desirable. For example, it would be useful to have samplers to integrate ambient concentrations over time scales as short as hours/days or a long as weeks/months/years. The shorter timescales facilitate studies of contaminant dispersal, fluxes and transport processes and can provide data for dispersion/transport modelling. Longer timescales would allow source/sink regions to be identified and underlying trends in ambient levels to be investigated.

A range of different passive sampling devices has been utilised in the last few years. To date, most work on passive samplers has focussed on integrating concentrations over weeks/months, using samplers with a high 'capacity' to retain POPs, such as semi-permeable membrane devices (SPMDs) [13, 16, 17], polyurethane foam (PUF) disks [14] and XAD resins [18-20]. These operate as 'kinetic samplers' where it is necessary to know the sampling/uptake rate, rather than as equilibrium samplers [21]. PUF disks are a particularly attractive sampler, because they are cheap, easy to handle and can be used to sample over periods of several weeks. PUF is the sampling medium routinely deployed in conventional (active) high volume air samplers, and so there is also information already available about how POPs partition to it, its capacity etc. [22]. PUF disks of 14 cm diameter and 1.2 cm thickness have been tested as passive samplers previously; they sample POPs at a rate of a few m^3 of air/day [14]. With appropriate instrumental detection limits and low blanks, this allows detection of many classes of POPs, following exposure periods of weeks. The sampling period used in this study was 6 weeks, so the PUF disk was still operating in the 'kinetic' phase [14], where uptake of gas phase compounds occurs at the same rate for the range of target compounds and is practically independent of temperature.

In previous studies, we have demonstrated the utility of passive samplers at the local scale [14, 17] and to conduct urban-rural [23] and latitudinal [6, 7] transects. However, in this study we wanted to demonstrate the feasibility of obtaining ambient data on a continental scale, thereby helping to shed light on large-scale source/sink/transport potential issues for these compounds. Europe was the study area - a region with a history of extensive POPs usage and emission, with marked national differences in population density, the degree of urbanisation and industrial/agricultural development. There are major differences between European countries in their production, usage, emission and regulatory controls on POPs. It was hoped that this would provide an interesting test area with which to demonstrate the feasibility of the large-scale deployment of passive sampling techniques. For the study to be most effective, it is clearly necessary to synchronise the start and finish dates of sample deployment. We therefore developed a sampling system that could be: prepared in one laboratory; sealed to prevent contamination; sent out by courier to volunteers participating in different countries; exposed; collected; re-sealed; returned to the laboratory to be analysed there together with the same methods. This obviously provides scope for a relatively cheap but large-scale deployment exercise. An additional objective was to obtain ambient data in a form that could subsequently be used to test a European scale multi-media model [24-26]. The model utilises information on air mass flows between different regions of Europe, and can integrate air concentration data integrated over time scales of the order of weeks.

One of the benefits of such a study is in being able to make comparisons between compound classes which may have different properties, or between compound classes which are relatively well known/understood, and those which are not. Data are therefore presented for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs) obtained from the same sample deployment. These are chemicals subject to LRAT, which have been measured in the atmosphere of remote regions, far from source areas [27]. PAH emissions are subject to international regulations [2], with the stated objective for signatory countries being to reduce their emissions to 1990 levels [28]. PCNs are being considered as 'candidate POPs' under the international protocol [29]. Production, usage and emission information (of variable quality) is available for these compounds in European and national inventories (e.g. [22, 28-30]. Several of the PCN congeners exhibit dioxin-like toxicity [31].

PAHs are byproducts of incomplete combustion, and thus, these compounds have many current sources, including motor vehicles, domestic burning of coal and wood for space heating, power generation via combustion of coal and oil, incineration, wood burning, cooking, smoking and burning of natural gas [28, 32, 33]. The highest ambient levels occur in winter months (consistent with the increase in combustion-derived PAH emissions in colder periods) and tend to be concentrated in urban areas, which can in turn influence the PAH concentrations in rural areas [34]. PCNs, however, have both combustion and industrial/formulation sources. They have been used in similar applications to PCBs such as capacitor fluids, engine oil additives, cable insulation and wood preservation [30]. PCNs have also been found in incinerator emissions, as contaminants in PCB formulations, and metal refining [35-38]. Recently Helm et al. [39] have reported PCNs in air as combustion related products.

This study reports the first attempt to monitor the distribution of PAHs and PCNs in the European atmosphere, using a passive sampler network. The data are discussed, in terms of the sources and properties of the compounds.

MATERIALS AND METHODS

Air Sampling, Extraction and Analysis

The samplers have been described previously [14]; they were deployed in sheltered chambers, as shown in Figure 1. A pre-cleaned and weighed PUF disk (14 cm diameter x 1.35 cm thick; density 0.0213 g cm^{-3}) was suspended in the centre of the two dishes between washers using solvent-rinsed tweezers. Samples were then transferred to the sampling locations in airtight containers to avoid contamination during transit. Those deployed outside the UK were sent by courier. A total of 71 samplers were successfully deployed over a 6-week period (15th June to 30th July 2002), across 22 countries (see Figure 2). Local volunteers were given guidance on choice of deployment location; 25 were in urban locations and 46 in rural/remote locations. At the end of the deployment period, the samplers were retrieved by the volunteers, re-sealed in their original transport containers and returned by courier to Lancaster University. On receipt in Lancaster, the disks were removed and stored in sealed, solvent cleaned brown glass jars at –20 °C until extraction.

Samples were spiked with a range of 13C12–labelled PCB congeners (13C12 PCB 28, 52, 101, 138, 153, 180, 209) and deuterated PAHs (1-methylnaphthalene-d^{8}, fluorene-d^{10}, anthracene-d^{10}, pyrene-d^{10}, p-terphenyl-d^{14}, benzo[a]pyrene-d^{12}, indeno[123-cd] pyrene and benzo[ghi]perylene-d^{12}) to monitor the extraction and cleanup procedures. The samples were extracted for 18 hours with DCM in a Buchi extraction unit, rotary evaporated and transferred with hexane to a 15 ml amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 ml and cleaned on a 9 mm id chromatography column with 1 g Alumina (BDH neutral Alumina), 2 g silica gel (Merck Silica 60) and 1 cm baked sodium sulphate (all baked at 450 °C overnight) to prevent the column from going dry or trapping air bubbles and then passed through gel permeation chromatography (GPC) using 6 g of Biobeads SX 3. Deuterated PAH internal standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d^{10}, fluoranthene-d^{10}, benzo[a]anthracene-d^{12}, perylene-d^{12} and 1,3,5-triphenylbenzene) were added to the fractions and the volume of sample reduced to 100 µl for PAH analysis.

PAHs were analysed with a HP 5890 series II GC equipped with a 30 m HP5MS column (0.25 mm i.d., 0.25 µm film thickness) and 3 m long deactivated HP retention gap (0.53 mm i.d.). This was connected to a HP 5972 MSD operating in selected ion monitoring mode. GC temperature programme and monitored ions are given elsewhere [40, 41]. Twelve PAHs (fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benz[e]pyrene, benzo[a]pyrene, indeno[123-cd]pyrene and benzo[ghi]perylene) routinely detected in samples were quantified. The sum of these constitutes the å12PAHs.

After checking that the chromatograms were satisfactory, two labelled PCB congeners, $^{12}C_{12}$ PCB-30 and $^{13}C_{12}$ PCB–141 in dodecane were added as internal standards and the final volume reduced to 25 μl. The samples were analysed for PCNs by GC-MS on a Fisons MD800 operated in electron ionisation mode using selected ion monitoring [16, 42]. A total of 13 PCN congeners (PCN-19, 24, 15, 23, 29, 35, 38(40), 46, 61, 57, 62, 53/55 and 59) regularly detected in samples were quantified. The sum of these constitutes the $\sum$13PCNs.

Quality Control/Quality Assurance (QA/QC)

All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks consisted of pre-extracted PUF disks which were extracted and analysed in the same way as samples. There was no difference between concentrations of analytes in the laboratory and field blanks, indicating minimal contamination during transport, storage and analysis. Practical detection limits were ~0.5 ng/sample for PAHs (depending on compound) and 0.03-1.4 ng/sample for PCNs for the six-week deployment period. Recoveries were 70-81% for PAHs and 60-85% for PCNs. Reported values are not recovery corrected. Method recoveries were determined by spiking six PUF disks with a working standard containing all analysed PAH and PCN congeners. These PUF disks were extracted and cleaned in the same way as samples. Recoveries were found to be between 80 and 105%. Instrument efficiencies were monitored using quality control standards after every six samples run on the instrument. Peaks were only integrated where the signal to noise ratio was > 3; otherwise, they were considered non-detect.

RESULTS AND DISCUSSION

Introductory remarks

Table 1 presents a summary of the data arising from the study. Data on the detection limits (DL) and measured range in samples are given as ng compound/sample. Also shown is: the percentage of samples above the detection limit (%>DL); the ratio of the highest/lowest measured values (H/L ratio), calculated for those compounds that were routinely above the detection limits; and the estimated range of air concentrations (pg m^{-3}) (see below).

A number of compounds were detected in all the samples, namely lighter PAHs (fluorene to chrysene). Heavier PAHs were detected ~ 70-90% of samples. Tri-PCNs (PCN 19, 24, 15 and 23) were detected in about 15% of the samples, while tetra-(PCN 29, 35, 38(40) and 46) and penta-(PCN 61, 57, 62, 53/55 and 59) were detected in ~25 and 30% of samples respectively. Air concentrations of PCNs are typically an order of magnitude lower than those of PAHs. A longer exposure time would have ensured that a greater air volume was sampled, and raised the frequency of their detection.

Some observations on comparisons between compound distributions

The variation in persistent contaminant concentrations in the atmosphere yields information, which can be related to aspects of their sources-sinks and persistence [43]. For example, the concentrations of chlorofluorocarbons (CFCs) in the atmosphere are virtually the same around the world [44]. Because of their high persistence and volatility, they have become extremely well mixed in the air. Other chemicals may show marked source-sink gradients, resulting in substantial differences in air concentrations between locations. Differences between locations also shed light on the relative transport potential of compounds. The dataset obtained here demonstrates contrasting behaviour for different compounds. For example, the å12PAHs and ∑13PCNs show differences of over two orders of magnitude between the highest and lowest locations (see Table 1). The very high H/L ratio for ∑13PCNs (>1100) and ∑12PAHs (>160) indicates important ongoing sources of both compound classes [6, 45]. Generally the highest values were observed in urban centres and more heavily industrialised countries, whilst the lowest values occurred in remote parts of Europe. This is powerful evidence that there are continuing primary emissions of these compounds [6].

Comparing derived air concentrations with measured concentrations

When the PUF disks are deployed in the sampling chambers (Figure 1), previous studies have shown they give typical compound sampling rates of ca. 3-4 m^3 air per day [14]. Hence a 6-week deployment 'samples' ca. 130-170 m^3. The ambient concentrations (pg/m3) represented by the measured ng/sampler values were therefore derived using this (3.5 m^3/day) sampling rate and are shown in Table 1. In summary, this indicates that European air concentrations of å12PAHs broadly lie in the range of 0.5 – ~60 ng m^{-3}, typically being in the low tens ng/m3. This compares well with data obtained with conventional high-volume air samplers.

More information was obtained with which to evaluate sampler performance. A direct comparison of passive and active sampling data was made by deploying the samplers at 4 UK sites (London, Manchester, Middlesborough and Pickering; sites 65, 68, 69 and 71, respectively) where PAH monitoring data are routinely obtained for bulked 3 monthly periods. Figure 3 shows that the passive/active sampling data are usually well within a factor of 2 for individual compounds. Given the differences in sampling duration, methodology and analyst, this is considered very good and certainly sufficient for this kind of survey. For example, the passive sampler-derived $\sum$12PAH air concentrations for London and Manchester are in the general range ~25-35 ng $\sum$PAH m^{-3}, in line with other data from these and other urban sites where tens - ~150 ng m^{-3} have been reported [46-48]. Air concentrations derived for $\sum$PCNs broadly lie in the range of 0.2 – 200 pg m^{-3}, again in line with data obtained with conventional samplers. Data have been reported for European marine air, rural and urban areas, in the range of 0.8-200 pg m^{-3} [27, 45, 49]. However, for both classes of compounds, the concentrations derived in this study tended to be somewhat lower than reported in other studies. This is probably because: a. the samplers were deployed in the summer when ambient levels are lower; b. atmospheric levels of these compounds are generally decreasing, reflecting a decrease in emissions [26, 48, 50].

Observations on sampler performance of gas and particle phase compounds

One of the challenges of using passive air samplers for POPs is that both gas and particle phase species can be important. Most attention to date has focussed on passive sampling of PCBs and other organochlorines, for which the gas phase predominates [6, 7, 15-17, 19, 20]. Some sampler designs, such as semi-permeable membrane devices - are more efficient at sampling the gas phase than the particle phase [17]. The full range of gas-particle partitioning is observed across the PAH analytes; phenanthrene is almost exclusively in the gas phase at ambient temperatures, for example, while benzo[a]pyrene and benzo[ghi]perylene are almost exclusively in the particle phase [51]. The PAH data therefore provides a useful test of the ability of the PUF disks to sample both phases in air, with similar efficiency. The results are extremely encouraging in this respect. As noted in the previous section, PAHs sampled with the PUF disks gave derived air concentrations in good agreement with those obtained by traditional active sampling. This applied to the lighter, predominantly gas phase compounds and the heavier, particulate bound PAHs, as can be clearly seen from the data presented in Figure 3. No systematic bias was seen in the passive:active sampling data with molecular weight. In contrast, SPMDs are poor at sampling high molecular weight PCDD/Fs and PAHs – the particle phase species [17].

Ambient particle phase PAHs are present across a range of particle sizes, but are typically on aerosols 0.1-1.5 µm in diameter in the environment, away from roads and other point sources [52-54]. The obvious implication of the findings here is that the PUF disks are effective at trapping these very fine particles, which move in air essentially as gases, rather than as coarse particles (> 10 µm), which are subject to gravitational settling.

In summary, the data presented so far give confidence that the samplers are capable of reflecting the spatial variations and absolute values of these POPs in the European atmosphere. It is therefore appropriate to examine the spatial patterns revealed by the survey in more detail.

General comments on spatial trends

A wide range of sample sites was utilised. Remote/background locations included sites at Mace Head, western Ireland, Iceland and Svalbard, Norway (sites 39, 19 and 28, respectively). Additionally, low concentrations were often detected in samples from the south west of the European region – Portugal and southwest Spain (sites 32, 33 and 60). These areas receive clean air, coming off the Atlantic Ocean. In contrast, a number of samplers were deployed in major urban centres, notably London, Manchester, Paris, Barcelona, Stockholm, Milan and Moscow (site numbers 65, 68, 40, 57, 36, 48, and 21 respectively).

PAHs. Figure 4 shows the full dataset for $\sum 12$PAHs. The highest PAH levels were detected in Moscow (70 ng m^{-3}), the industrial area of Middlesborough (UK) (40 ng m^{-3}) and the Czech

Republic (30 ng m^{-3}) (sample sites 21, 69 and 4 respectively) while the lowest levels (0.4-1.3 ng m^{-3}) were measured in the most remote sites (Ireland, Iceland, Norway) and generally in the northern and southern parts of Europe. Similar maps were prepared for individual compounds (not shown, but available on request from the authors). These highlighted that high/low samples were strongly correlated between compounds (i.e. source(s) areas are common for the full range of PAHs). Illustrative data are given in a correlation matrix in Table 2; all correlations between PAHs were significant at the $P<0.001$ level).

Attempts have been made to compile atmospheric inventories for selected PAHs (benzo[a]pyrene, benzo[b]fluoranthene) at the European scale [55]. These are obviously subject to considerable errors, due to lack of comparable national reporting and uncertainties/variabilities in emission factors etc. The benzo[a]pyrene inventory indicates highest loadings in Eastern Europe (e.g. Poland, parts of Russia, Czech Republic), and the more populated/industrialised areas of western Europe (e.g. parts of the UK; Netherlands). This is broadly consistent with the survey results.

PCNs. The most elevated å13PCN levels were detected in urban/industrialised areas in Poland (220 pg m^{-3}), London (180 pg m^{-3}) and Moscow (140 pg m^{-3}) (sample sites 9, 65 and 21 respectively). Increased concentrations of PCNs in the Northern Atlantic and Arctic have been associated with air systems which have originated or moved over the UK/Europe [27, 45]. This may be indicative of ongoing use of PCNs or leakage and volatilisation from past uses in Europe [49]. High levels were also measured in Eastern Europe while lowest levels/non detects occurred in the remote sites (Ireland, Iceland, Norway) and generally in the northern and southern parts of Europe.

As noted earlier, PCNs can originate from technical mixtures and from combustion sources [37-39]. Previous studies have identified a wide range of congeners in the technical formulations; PCN-19, 24, 15, 23, 42, 33/34/37, 47, 38(40) and 46 are typically the most abundant [27, 49]. In contrast, PCN-29 and PCN-35 have been reported in combustion emissions [39, 56]. Helm and Bidleman [39] present important data on the most abundant congeners for urban Toronto air. They observed an abundance of penta and hexa-PCNs

(PCN-52/60, 61, 57, 62, 53, 59, 69 and 71/72), while Lee et al [49] reported primarily tri and tetra-PCNs (PCN-24, 23, 42, 33/34/37, 47, 29, 35, 38(40) and 46) as major constituents in the UK atmosphere. It is important for regulatory/source reduction purposes to better understand the major sources of PCNs to the atmosphere.

Of the 13 PCNs detected in the samples studied here, eleven (PCN-19, 24, 15, 23, 38(40), 46, 61, 57, 62, 53/55 and 59) are typically related to technical mixtures [39, 56]; only two (PCN 29 and 35) are reported as being derived principally from combustion sources [39, 56]. Figure 5a is a map of the distribution of the sum of the technical ($\sum$11PCN) congeners. Figure 5b shows the distribution of congener PCN-29. The first impression from Figure 5 (a and b) is that combustion source areas and technical mixture sources areas broadly coincide; UK and eastern European locations are both prominent, for example (note that in Figure 5a a few samples dominate the scaling). However, a more detailed analysis shows that there are some differences. The highest samples for the 'technically-derived' $\sum$11PCN congeners were in Poland, London and Moscow (sites 9, 65 and 21 respectively). In contrast, PCN-29 was highest in sites in Hungary, Barcelona and (again) London (sites 15, 62 and 65 respectively).

The correlation analyses presented in Table 2 provide further information. It needs to be borne in mind, however, there were many non-detect values for PCN congeners (see Table 1). Table 2 shows that there are correlations between the congeners dominant in the technical mixtures (e.g. PCN-19, 24, 23, 38, 61, 57, 62, 53, 59 tend to correlate with each other). However, of the 'combustion constituents', PCN-29 does not correlate with any other compound, whilst PCN-35 correlates with all the other PCNs. It should be noted that PCN-35 also occurs in technical mixtures whilst PCN-29 apparently does not [39, 54]. This raises questions about the utility of PCN-35 as a combustion 'indicator'. Ambient levels of PCN-35 are presumably influenced by emissions from technical products and combustion. Figure 5c shows the proportional contribution that 'combustion indicator' PCN-29 makes to the $\sum$13PCN. It contributed most (28%) at site 62 (Barcelona), followed by the Hungary site (site 15) (20%). Generally, however, it contributed < 5% to the $\sum$13PCN. One striking feature of Table 2 is that the strongest PCN correlations are between the later congeners (e.g. PCN-35 to PCN-59 correlate with each other at the $p<0.001$ level), while they are less well correlated with the lower molecular weight PCNs (i.e. PCN-19 to PCN-23, correlations are usually $p< 0.05$ and $p< 0.01$).

Almost without exception, there are no significant correlations between PCNs and PAHs (see Table 2). One implication of this observation is that although 'combustion' is a source of PCN-29 (and other PCNs) [39, 54], and the full suite of PAHs, the specific combustion sources are different. A hypothesis consistent with these observations is that combustion-derived PCNs (e.g. PCN-29) are mostly emitted from efficient, high temperature combustion sources (i.e. incinerators; [35, 36]) which are not an important source of PAHs, [32, 33] whilst inefficient, low temperature combustion sources are responsible for the bulk of the PAH burden emitted to atmosphere [32, 33].

Concluding remarks

In general, the geographical pattern of the compounds studied reflected the suspected regional emission patterns. The samples also highlighted localised hotspots; great care therefore needs to be taken over the choice of site locations. The study demonstrates that it is possible to map local, regional and global sources of POPs using passive air samplers. Reconnaissance studies of this nature can provide information on trends and identify unknown sources. The trends of PAHs are linked to urbanised source areas; sites in the UK and parts of eastern Europe gave some of the highest values. Predicted concentrations of compounds reported in this study are comparable to concentrations reported by other authors indicating that quantitative data, suitable for modelling purposes, can be obtained.

Acknowledgements

We are grateful to the UK Department of the Environment, Food and Rural Affairs (Defra) Air Quality Division for financial support. We thank: numerous colleagues and friends who helped in deploying the sampling devices; colleagues at Lancaster University especially, Dr Gareth Thomas, Dr Robert Lee, Dr Rainer Lohmann and Mrs Victoria Burnett for their analytical support and meaningful consultations. FMJ is grateful to the Commonwealth Commission for PhD funding.

REFERENCES

1. UNECE. 1998. Protocol on persistent organic pollutants under the 1979 convention on long-range transport air pollution, United Nations Economic Commission for Europe (ECE/EB.Air/60).

2. UNEP. 1998. Preparation of an internationally legally binding instrument for implementing international action on certain persistent organic pollutants, United Nations Environment Programme, UNEP/POPs/Inc.1/6.

3. Klecka G, et al. 2000. Evaluation of persistence and long-range transport of organic chemicals in the environment. In SETAC special publication series, Pensacola, Florida.

4. Calamari D, Tremolada P, Di Guardo A, Vighi M. 1994. Chlorinated hydrocarbons in pine needles in Europe: Fingerprint for the past and recent use. Environ Sci Technol 28: 429-434.

5. Kalantzi OI, Alcock RE, Johnston PA, Santillo D, Stringer RL, Thomas GO, Jones KC. 2001. The global distribution of PCBs and organochlorine pesticides in butter. Environ Sci Technol 35: 1013-1018.

6. Meijer SN, Ockenden WA, Steinnes E, Corrigan BP, Jones KC. 2003. Spatial and temporal trends of POPs in Norwegian and UK background air: Implications for global cycling. Environ Sci Technol 37: 454-461.

7. Ockenden WA, Sweetman A, Preston HF, Steinnes E, Jones KC. 1998. Toward an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time integrated passive samplers. Environ Sci Technol 32: 2795-2803.

8. Tremolada P, Burnett V, Calamari D, Jones KC. 1996. Spatial distribution of PAHs in the U.K. atmosphere using pine needles. Environ Sci Technol 30: 3570-3577.

9. Di Guardo A, Zaccara S, Cerabolini B, Acciarri M, Terzaghi G, Calamari D. 2003. Conifer needles as passive biomonitors of the spatial and temporal distribution of DDT from a point source. Chemosphere 52: 789-797.

10. Kylin H, Sjodin A. 2003. Accumulation of airborne hexachlorocyclohexanes and DDT in pine needles. Environ Sci Technol 37: 2350-2355.

11. Simonich SL, Hites RA. 1995. Global distribution of persistent organochlorine compounds. Science 269: 1851-1854.

12. Simonich SL, Hites RA. 1997. Relationships between socioeconomic indicators and concentrations of organochlorine pesticides in tree bark. Environ Sci Technol 31: 999-1003.

13. Ockenden WA, Jaward FM, Jones KC. 2001. Atmospheric sampling of persistent organic pollutants: Needs, applications and advances in passive air sampling techniques. The Scientific World 1: 557-575.

14. Shoeib M, Harner T. 2002. Characterisation and comparison of three passive air samplers for persistent organic pollutants. Environ Sci Technol 36: 4142-4151.

15. Harner T, Farrar NJ, Shoeib M, Jones KC, Gobas FAPC. 2003. Characterisation of polymer-coated glass as a passive sampler for persistent organic pollutants. Environ Sci Technol 37: 2486-2493.

16. Ockenden WA, Prest HF, Thomas GO, Sweetman A, Jones KC. 1998. Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices. Environ Sci Technol 32: 1538-1543.

17. Lohmann R, Corrigan B, Howsam M, Jones KC, Ockenden W. 2001. Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: Field application in a spatial survey of PCDD/Fs and PAHs. Environ Sci Technol 35: 2576-2582.

18. Billings WN, Bidleman TF. 1980. Field comparison of polyurethane foam and Tenax-GC resin for high-volume air sampling of chlorinated hydrocarbons. Environ Sci Technol 14: 679-683.

19. Billings WN, Bidleman TF. 1983. High volume collection of chlorinated hydrocarbons in urban air using three solid adsorbents. Atmos Environ 17: 383-391.

20. Wania F, Shen L, Lei YD, Teixeira C, Muir DCG. 2003. Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. Environ Sci Technol 37: 1352-1359.

21. Mayer P, Tolls J, Hermens JLM, Mackay D. 2003. Equilibrium sampling devices. Environ Sci Technol: 3A-9A.

22. Patton GW, Walla MD, Bidleman TF, Barrie LA. 1991. Polycyclic aromatic and organochlorine compounds in the atmosphere of northern Ellesmere-Island, Canada. J Geophys Res - Atmospheres 96: 10867-10877.

23. Harner T, Ikonomou M, Shoeib M, Stern G, Diamond M. 2002. Passive air sampling results for polybrominated diphenyl ethers along an urban-rural transect. Organohalogen Compounds. 57: 33-36.

24. MacLeod M, Woodfine DG, Mackay D, McKone T, Bennet D, Maddalena R. 2001. BETR North America: A regionally segmented multimedia contaminant fate model for North America. Environ Sci Pollut Res 8: 156-163.

25. Woodfine DG, MacLeod M, Mackay D, Brimacombe JR. 2001. Development of continental scale multimedia contaminant fate models: Integrating GIS. Environ Sci Pollut Res 8: 164-172.

26. Prevedouros K, MacLeod M, Jones KC, Sweetman AJ. 2003. Modelling the fate of persistent organic pollutants in Europe: Parameterisation of a gridded distribution model. Environ Pollut in press.

27. Harner T, Kylin H, Bidleman T, Halsall C, Strachan WMJ, Barrie LA, Fellin P. 1998. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in arctic air. Environ Sci Technol 32: 3257-3265.

28. European Commission. 2001. Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position paper, Luxembourg.

29. Van de Plassche EJ, Schwegler AMGR. 2002. Polychlorinated naphthalenes, Ministry of Housing, Spatial Planning and the Environment, Directorate-General for Environmental Protection, Nijmegen.

30. Crookes MJ, Howe PD. 1993. Environmental hazard assessment: Halogenated naphthalenes; report tsd/13, Department of the Environment, London, 1993.

31. Hanberg A, Wærn F, Asplund L, Haglund E, Safe S. 1990. Swedish dioxin survey: Determination of 2,3,7,8-TCDD toxic equivalent factors for some polychlorinated biphenyls and naphthalenes using biological tests. Chemosphere 20: 1161-1164.

32. Lohmann R, Northcott GL, Jones KC. 2000. Assessing the contribution of diffuse burning as a source of PCDD/Fs, PCBs, and PAHs to the U.K. atmosphere. Environ Sci Technol 34: 2892-2899.

33. Wild SR, Jones KC. 1995. Polynuclear aromatic hydrocarbons in the United Kingdom environment: A preliminary source inventory and budget. Environ Pollut 88: 91-108.

34. Cortes DR, Basu I, Sweet CW, Hites RA. 2000. Temporal trends in and influence of wind on PAH concentrations measured near the Great Lakes. Environ Sci Technol 34: 356-360.

35. Oehme M, Mano S, Mikalsen A. 1987. Formation and presence of polyhalogenated and polycyclic compounds in the emissions of small and large scale municipal waster incinerators. Chemosphere 16: 143-153.

36. Schneider M, Stieglitz L, Will R, Zwick G. 1998. Formation of polychlorinated naphthalenes on fly ash. Chemosphere 37: 2055-2070.

37. Yamashita N, Kannan K, Imagawa T, Miyazaki A, Giesy JP. 2000. Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preparations. Environ Sci Technol 34: 4236-4241.

38. Theisen J, Maulshagen A, Fuchs J. 1993. Organic and inorganic substances in the copper slag "Kieselrot". Chemosphere 26: 881-896.

39. Helm PA, Bidleman TF. 2003. Current combustion-related sources contribute to polychlorinated naphthalene and dioxin-like polychlorinated biphenyl levels and profiles in air in Toronto, Canada. Environ Sci Technol 37: 1075-1082.

40. Smith KEC, Green M, Thomas GO, Jones KC. 2001. Behaviour of sewage sludge-derived PAHs on pasture. Environ Sci Technol 35: 2141-2150.

41. Smith KEC, Thomas GO, Jones KC. 2001. Seasonal and species differences in the air-pasture transfer of PAHs. Environ Sci Technol 35: 2156-2165.

42. Thomas GO, Sweetman AJ, Parker CA, Kreibich H, Jones KC. 1998. Development and validation of methods for the trace determination of PCBs in biological matrices. Chemosphere 36: 2447-2459.

43. Junge CE. 1974. Residence time and variability of tropospheric trace gases. Tellus 26: 477-488.

44. Stanley LJ, Hites RA. 1991. Chlorinated organic contaminants in the atmosphere. In Jones KC, ed, Organic contaminants in the environment: Environmental pathways and effects. Elsevier Applied Science Publishers, London and New York, pp. 1-338.

45. Harner T, Lee RGM, Jones KC. 2000. Polychlorinated naphthalenes in the atmosphere of the United Kingdom. Environ Sci Technol 34: 3137-3142.

46. Halsall CJ, Coleman PJ, Davis BJ, Burnett V, Waterhouse KS. 1994. Polycyclic aromatic hydrocarbons in U K urban air. Environ Sci Technol 28: 2380-2386.

47. Coleman PJ, Lee RGM, Alcock RE, Jones KC. 1997. Observations on PAH, PCB, and PCDD/F trends in U. K. urban air, 1991-1995. Environ Sci Technol 31: 2120-2124.

48. Vana M, Dejmal K, Machalek P, Holoubek I. 2001. Emep assessment report - Czech Republic.

49. Lee RGM, Burnett V, Harner T, Jones KC. 2000. Short-term temperature-dependent air-surface exchange and atmospheric concentrations of polychlorinated naphthalenes and organochlorine pesticides. Environ Sci Technol 34: 393-398.

50. Gevao B, Harner T, Jones KC. 2000. Sedimentary record of polychlorinated naphthalene concentrations and deposition fluxes in a dated lake core. Environ Sci Technol 34: 33-38.

51. Lohmann R, Harner T, Northcott G, Thomas GO, Jones KC. 2000. A comparative study of the gas-phase partitioning of PCDD/Fs, PCBs and PAHs. Environ Sci Technol 34: 4943-4951.

52. Gardner B, Hewitt CN, Jones KC. 1995. PAHs in air adjacent to two inland water bodies. Environ Sci Technol 29: 2405-2413.

53. Peters AJ, Lane DA, Gundel LA, Northcott GL, Jones KC. 2000. A comparison of high volume and diffusion denuder samplers for semi-volatile organic contaminants in the atmosphere. Environ Sci Technol 34: 5001-5006.

54. Kaupp H, McLachlan MS. 1999. Atmospheric particle size distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) and their implications for wet and dry deposition. Atmos Environ 33: 85-95.

55. Pacyna JM, et al. 1999. POPCYCLING project: Technical report/the emission database/the POPCYCLING-Baltic model/the environmental database. NILU, P.O. Box 100, N-2027 Kjeller, Norway. CD-Rom

56. Meijer SN, Harner T, Helm PA, Halsall CJ, Johnston AE, Jones KC. 2001. Polychlorinated naphthalenes in U.K. soils: Time trends, markers of source, and equilibrium status. Environ Sci Technol 35: 4205-4213.

List of Tables and Figures

Table 1. Summary data for the passive air sampling programme

Table 2. Correlation matrix for PAHs and PCNs

Figure 1. Schematic representation of the PUF disk sampling device

Figure 2. Map showing sampling sites

Figure 3. PAH concentrations for UK sites obtained by active high volume (12 weeks) and PUF (6 weeks) samplers.

Figure 4. Spatial distribution of PAH (ng/sample – June 15 to July 30, 2002)
Key: Largest bar = 10400 ng/sample (site 21, Moscow)

Figure 5. Spatial distribution of PCNs a) associated with the technical mixtures $\sum_{11}$PCN; b) the 'combustion indicator' PCN-29 (see text for details) (ng/sample – June 15 to July 30, 2002); c) Proportional contribution that 'combustion indicator' PCN-29 makes to the$\sum_{13}$PCN.

Key to Figure a: Largest bar = 33 ng/sample (site 9, Poland)

Key to Figure b: Largest bar = 1.6 ng/sample (site 15, Hungary).

Key to Figure c: Largest bars = 28% (site 62, Barcelona) and 20% (site 15, Hungary)

Table 1. Summary data for the passive air sampling programme. Data on the detection limits (DL) and measured range in samples are given as ng/sample. Also shown is: the ratio of the highest/lowest measured samples (H/L ratio), the percentage of samples above the detection limit (%>DL), and the estimated range of air concentrations (pg m^{-3}).

Compound	DL	% > DL	Measured range	H/L ratio*	Air conc+
Fluorene	0.50	100	13-1240	95	100-7300
Phenanthrene	0.50	100	31-4400	142	240-26000
Anthracene	0.50	99	<0.5-198	790	<4-1200
1-methylphenanthrene	0.50	100	1-780	780	7-4600
Fluoranthene	0.50	100	2-2240	1120	12-13200
Pyrene	0.50	100	2-1240	620	12-7300
Benzo[a]anthracene	0.50	89	<0.5-100		<4-600
Chrysene	0.50	100	1-220	220	6-1300
Benzo[e]pyrene	0.50	92	<0.5-55		<4-320
Benzo[a]pyrene	0.50	66	<0.5-43		<4-250
Indeno[123-cd]pyrene	0.50	69	<0.5-23		<4-130
Benzo[ghi]perylene	0.50	86	<0.5-48		<4-280
$\sum_{12}$ PAH			64-10400	>160	500-61200
PCN 19	0.27	17	<0.27-1		<2-6
PCN 24	1.4	18	<1.39-9		<11-55
PCN 15	0.38	13	<0.38-1.5		<3-10
PCN 23	1.3	11	<1.26-4		<10-25
PCN 29	0.18	23	<0.18-1.6		<1.5-10
PCN 35	0.11	18	<0.11-0.67		<1-4
PCN 38(40)	0.26	24	<0.26-2.3		<2-14
PCN 46	0.03	35	<0.03-0.57		<0.2-3.5
PCN 61	0.09	42	<0.09-1.7		<1-10
PCN 57	0.49	23	<0.49-5.4		<4-30
PCN 62	0.13	28	<0.13-1.6		<1-10
PCN 53/55	0.16	34	<0.16-2		<1-12
PCN 59	0.28	38	<0.28-4.2		<2-25
$\sum_{13}$ PCN			0.03-34	>1100	0.2-200

* Note: this ratio has only been calculated for compounds where ~100% of samples gave detectable levels (i.e. the %>DL = 99+).

+ Note: derived as described in the text. < values take account of the %<DL column.

Table 2. Correlation matrix for selected PAHs and PCNs

	Fluo	Phen	Anthr	1-MP	Fla	Py	B(a)Anthr.	B(a)P	B(e)P	B[ghi]P	**PCN19**	**PCN24**	**PCN23**	**PCN29 [C]**	**PCN35 [C]**	**PCN38**	**PCN61**	**PCN57**	**PCN62**	**PCN53**	**PCN59**
Fluorene	.	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Phenanthrene	* * *	.	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	*	*	ns	ns	ns	ns
Anthracene	* * *	* * *	.	* * *	* * *	* * *	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	ns
1-methyphenanthrene	* * *	* * *	* * *	.	* * *	* * *	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	ns	*	ns	*	*	ns
Fluoranthene	* * *	* * *	* * *	* * *	.	* * *	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	* *	ns	ns	ns	ns	ns
Pyrene	* * *	* * *	* * *	* * *	* * *	.	* * *	* * *	* * *	* * *	ns	ns	ns	ns	ns	* *	*	ns	ns	ns	ns
Benzo[a]anthracene	* * *	* * *	* * *	* * *	* * *	* * *	.	* * *	* * *	* * *	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Benzo[a]pyrene	* * *	* * *	* * *	* * *	* * *	* * *	* * *	.	* * *	* * *	ns	ns	ns	ns	ns	*	*	ns	ns	ns	ns
Benzo[a]pyrene	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	.	* * *	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Benzo[ghi]perylene	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	* * *	.	ns	ns	ns	ns	ns	*	*	ns	ns	*	*
PCN19	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.	* * *	ns	ns	*	*	*	*	*	ns	ns
PCN24	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	* * *	.	ns	ns	* *	*	*	* *	*	*	ns
PCN23	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.	ns	* *	* *	*	* *	* * *	* *	* *
PCN29 [C]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.	ns	ns	ns	ns	ns	ns	ns
PCN35 [C]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	* *	* *	ns	.	* * *	* * *	* * *	* * *	* * *	* * *
PCN38	ns	*	ns	ns	*	*	ns	*	ns	*	*	*	* * *	ns	* * *	.	* * *	* * *	* * *	* * *	* * *
PCN61	ns	*	*	*	ns	*	ns	*	ns	*	*	*	*	ns	* * *	* * *	.	* * *	* * *	* * *	* * *
PCN57	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	* *	* *	ns	* * *	* * *	* * *	.	* * *	* * *	* * *
PCN62	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	*	* *	* * *	ns	* * *	* * *	* * *	* * *	.	* * *	* * *
PCN53	ns	ns	ns	*	ns	ns	ns	ns	ns	*	ns	*	* *	ns	* * *	* * *	* * *	* * *	* * *	.	* * *
PCN59	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	* *	ns	* * *	* * *	* * *	* * *	* * *	* * *	.

KEY:

fluorene (Fluo), phenanthrene (Phen), anthracene (Anthr), 1-methyphenanthrene, (1-MP), fluoranthene (Fla), pyrene (Py), Benzo[a]anthracene (B(a)Anthr.), Benzo[a]pyrene B(a)P, Benzo[e]pyrene B(e)P, and benzo[*ghi*]perylene (B[ghi]P).

p<0.001 * * *, p<0.01 * *, p<0.05 *, ns not significant - correlations performed in SPSS version 11.

Figure 1. Schematic Representation of the PUF Disk Sampling Device

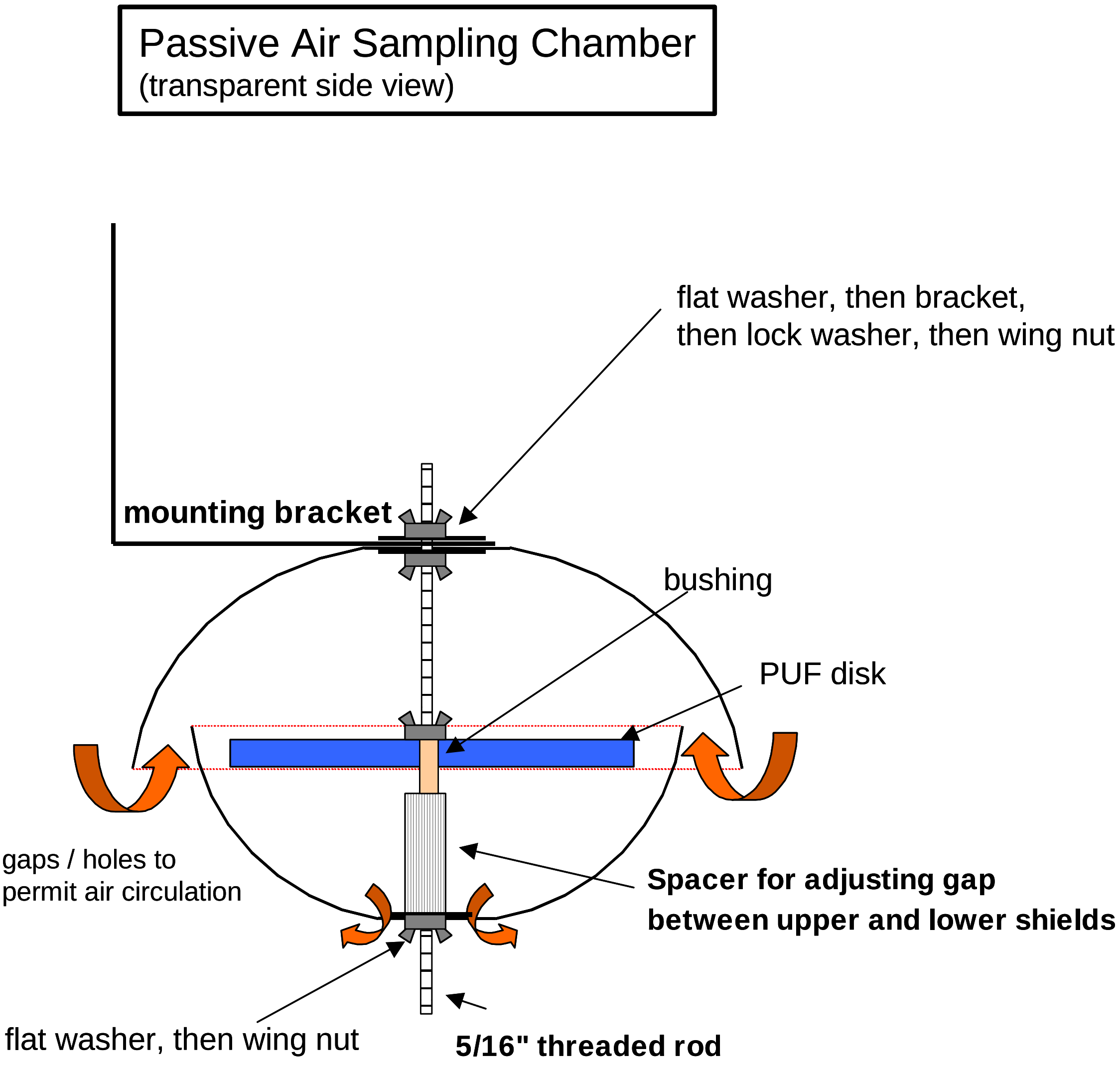


Figure 2. Map Showing Sampling Sites

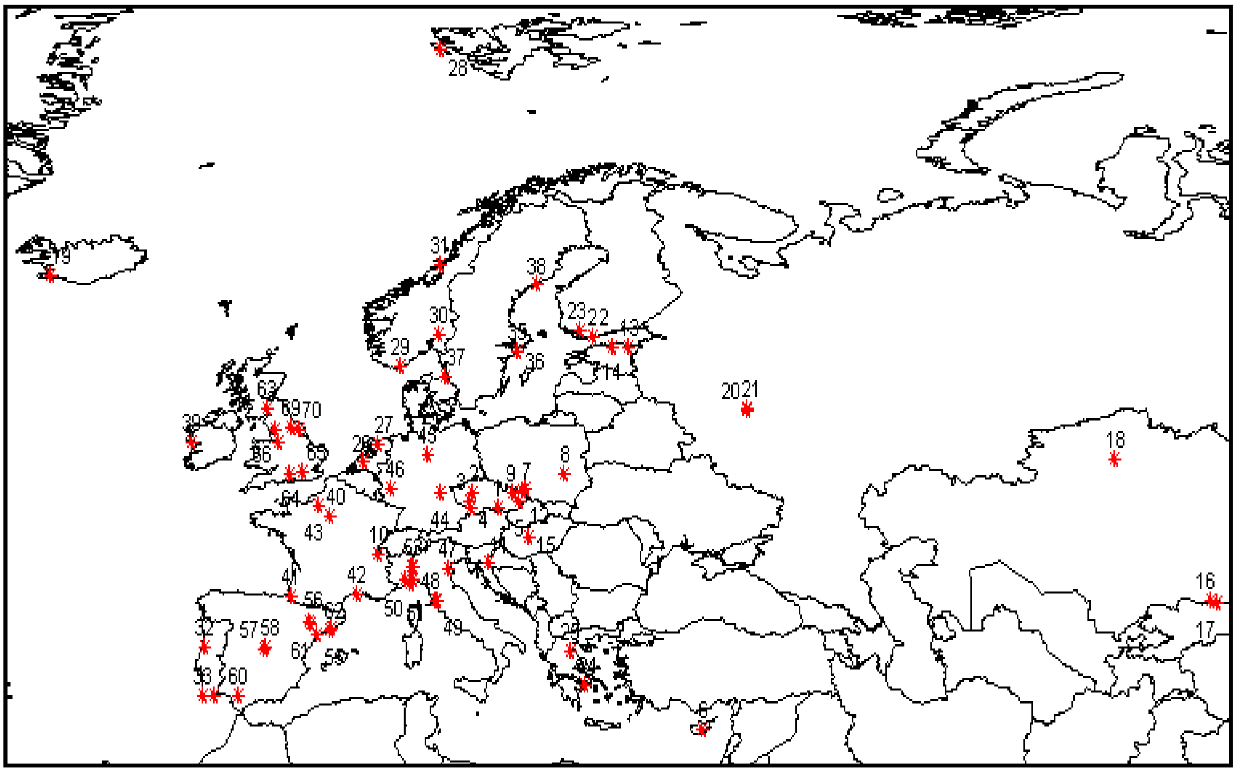


Figure 3. PAH Concentrations for UK sites by Hi-Vol (12 weeks) and PUF samplers (6 weeks)

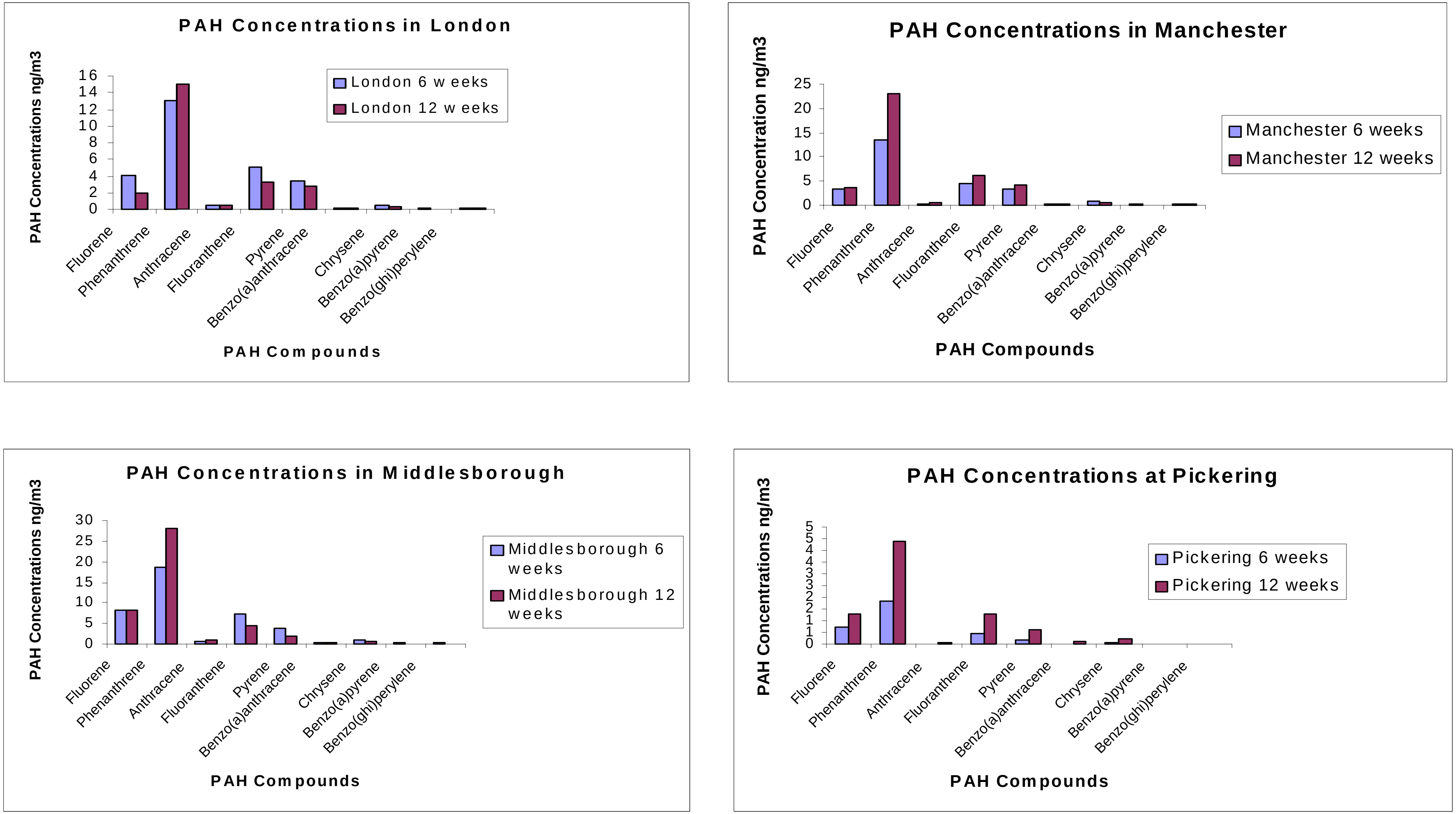


Figure 4. $\sum_{12}$PAH

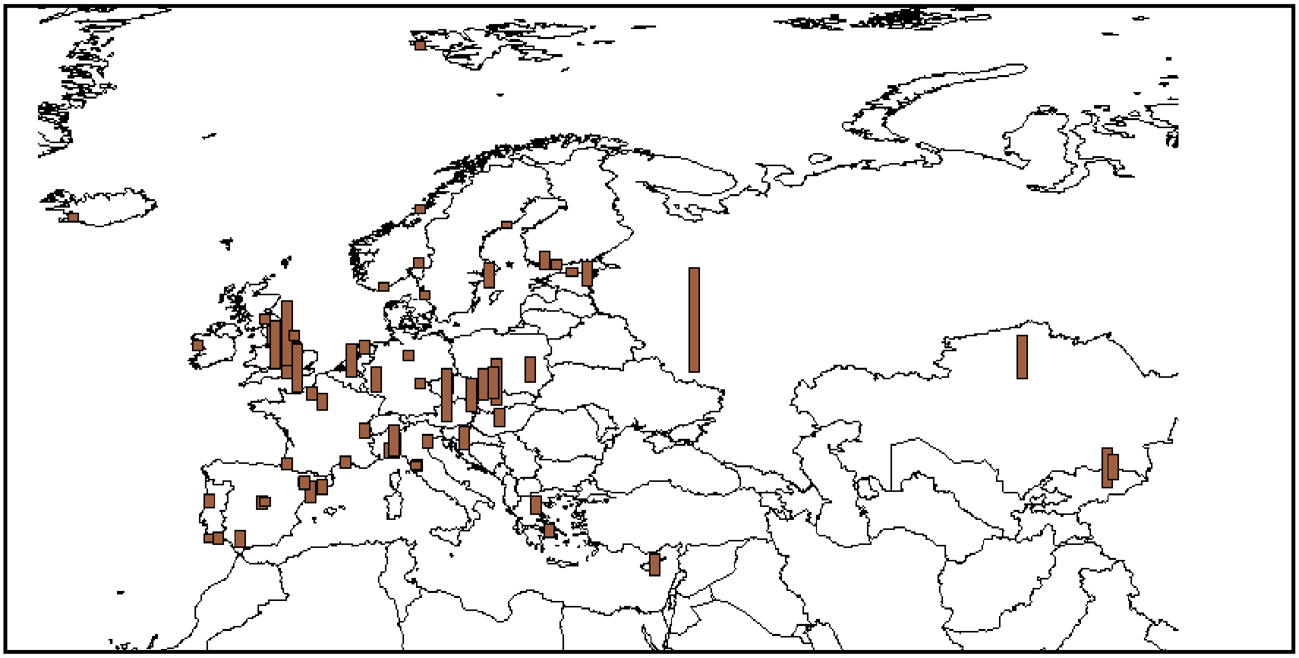


Figure 5a. $\sum_{11}$PCN (technical-related)

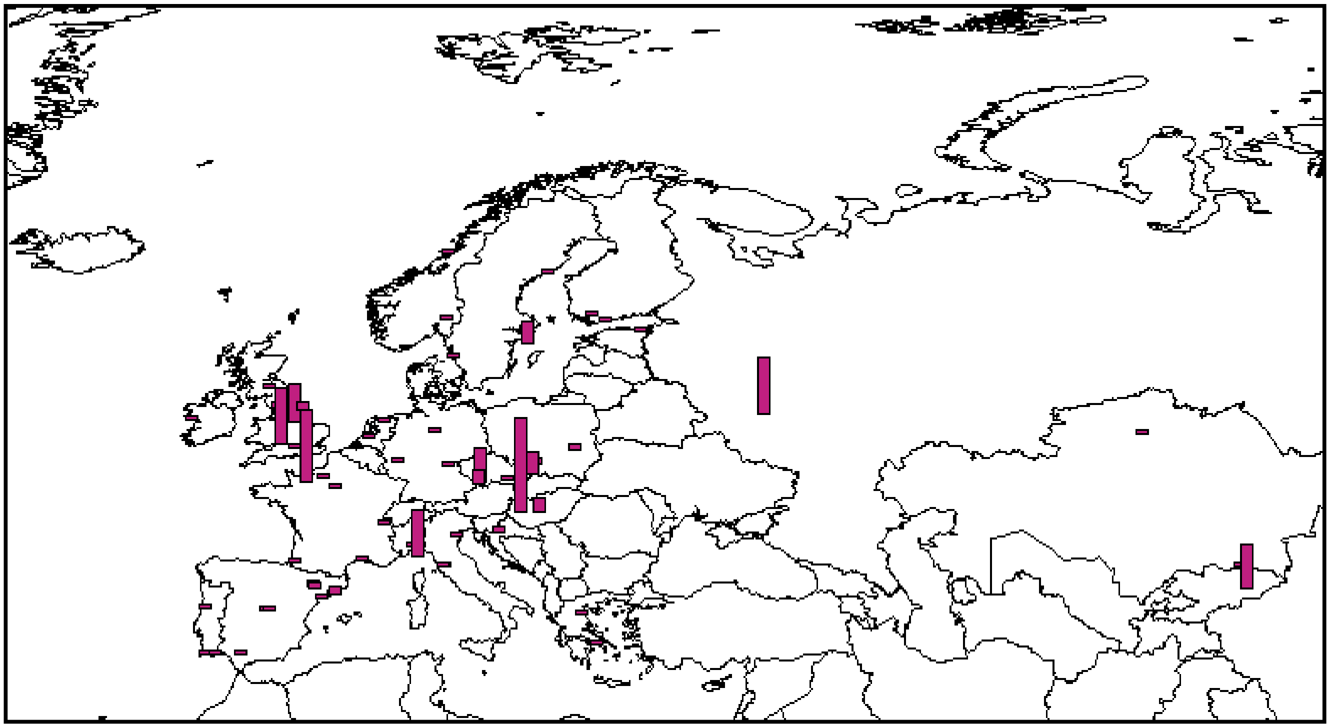


Figure 5b. PCN-29 ('combustion-indicator')

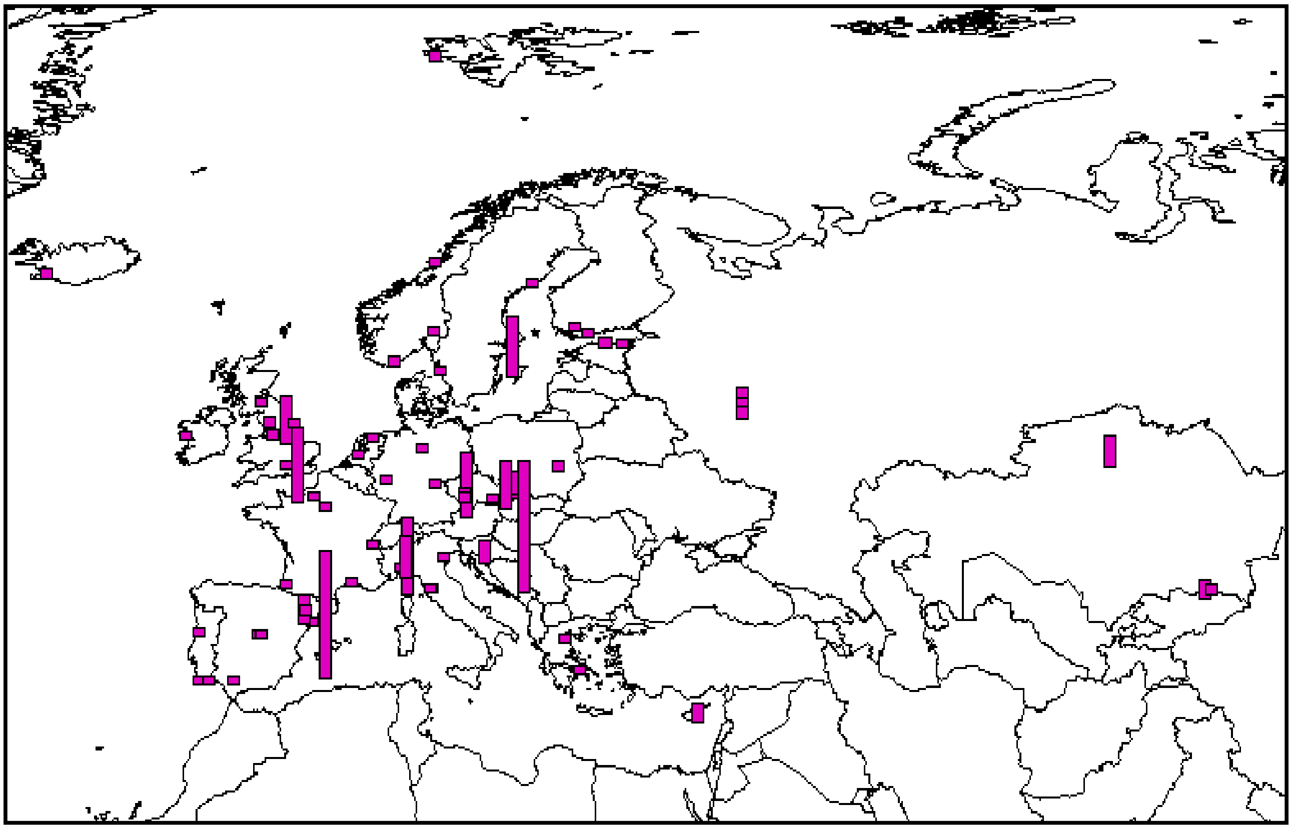
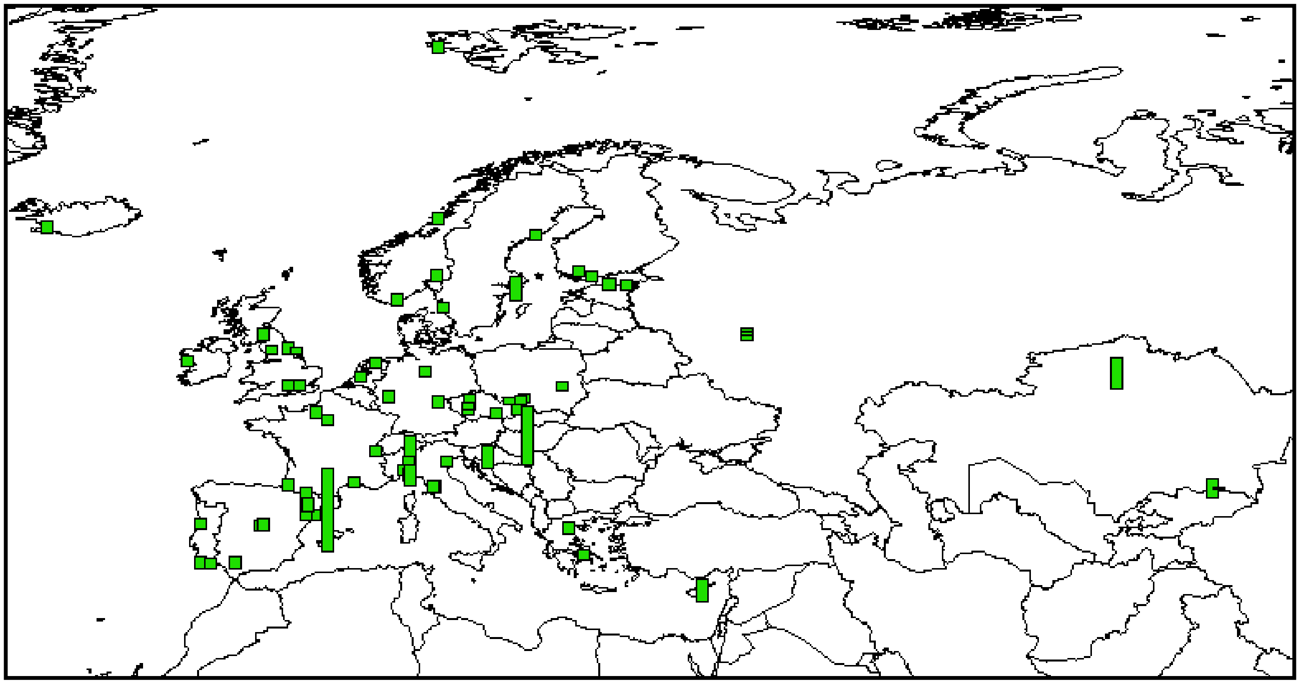


Figure 5c. Proportional contribution that 'combustion indicator' PCN-29



Section 8

Manuscript title:

Passive sampling across Europe campaign using short term air sampling using polymer coated glass samplers (POG)

Authors and affiliations:

Nick Farrar, Foday M Jaward, Andy Sweetman and Kevin C Jones

Environmental Science Department, Institute of Environmental and Natural Sciences,
Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

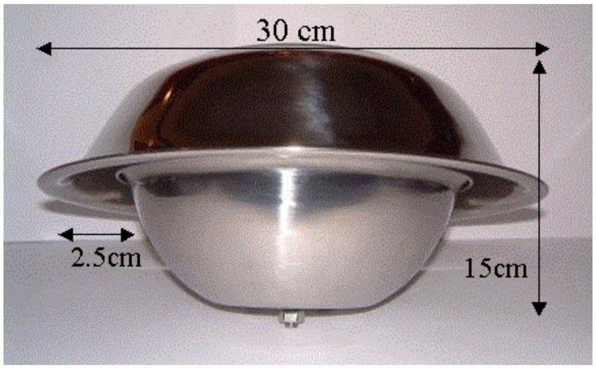
Tom Harner

Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Toronto,
Ontario, Canada, M3H 5T4

Submission journal:

Environmental Science and Technology. American Chemical Society.

The use of polymer coated glass (POG) samplers for environmental sampling has been proposed and developed by Dr Frank Gobas (Simon Fraser University, British Columbia, Ca) and Dr Tom Harner (MSC, Toronto, Ca). Initially these devices were used to sample water and biota but have recently been adapted to measure POPs in ambient air. For the purposes of this study the POG was housed in a sampling chamber to allow deployment in a sheltered and controlled environment. The sampling device consisted of two stainless steel dishes one inverted with the external diameter of largest bowl being 30cm, and the small bowl 20cm. The gap between the two which allows air to flow over the sampling surface is 2.5cm. For the PUF sampler the two dishes are attached via a central threaded spindle, whilst for the POG an aluminium strap is used (Fig b). A hook to suspend the sampler is attached through a 3mm hole drilled through the top of the thread.



Passive samplers were deployed throughout Europe to aid in the validation of a multi-segmented, fugacity-based model which was designed to replicate the movement of persistent organic pollutants on a regional scale. A short term air sampler, composed of a rapidly equilibrating polymeric stationary phase (Harner *et al.* 2003), was deployed to 41 sites across 20 countries, from the 15th – 22nd of June 2002. Based on an uptake rate of ~ $3m^3$ per day, samplers were theoretically exposed to approximately 21 m^3 of air. However, for some of the lighter compounds (i.e. high vapour pressure) equilibrium was achieved. In order to convert the amount of chemical recovered from the EVA a partition coefficient between EVA and air is required. These partition coefficients can be related to the octanol-air partition coefficient which in turn can be corrected for temperature as required.

Sample preparation and extraction was identical to that used by Harner and co-workers. Clean-up methodology was based on chromatographic separation (silica and alumina based system) and size exclusion chromatography (gel permeation). Analysis was carried out using GS-MS.

Results

PCBs.

Ten congeners have been routinely reported as they were consistently above the detection limits of the sampler and analytical methodology; PCB 18, 28, 49, 52, 110, 101, 118, 153, 138 and 180. Any data presented as **∑**PCB is based entirely on the summation of these congeners only. Blank levels were exceptionally low, with average blanks for each congener (except PCB 28) being below the commonly used instrument detection limit of 1 pg/μl. Average blank values were subtracted from the values at each site.

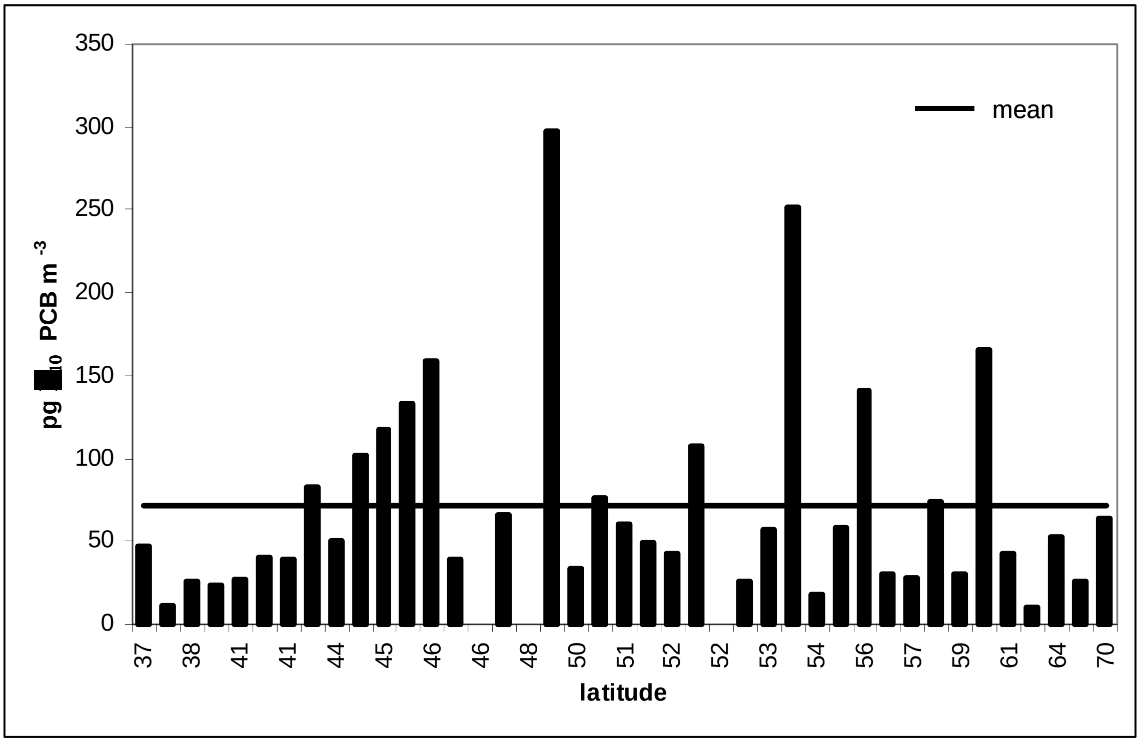


Figure 1. ∑PCB levels at each site across Europe, showing an average concentration of 70 pg m3.

PCB	Site Average	Min	Max	[Range] (pg/m^3)
18	5.8	0.7	19.7	4.2 - 112
28	9.4	0.5	57.4	0.92 - 116
49	5.8	0.2	51.6	0.2 - 50
52	10.2	0.8	78.6	0.7 - 73
110	14	1.2	62.3	0.06 - 3
101	16.8	1.8	68.2	0.09 - 3
118	9.2	0.5	42.8	0.02 - 2
153	16.4	1.8	75.7	0.09 - 4
138	16.3	1.9	74.2	0.1 - 4
180	6.6	1.2	27.6	0.06 - 1.3

Table 1. Congener specific data, taking into account all 41 sites. All concentrations are presented as ng / g EVA.

- Figure 1 illustrates the ∑PCB levels recorded at each of the sites, clearly indicating that ten sites were above the average of 70 pg m^{-3}. Information regarding the location of each site can be seen in the appendix.

- Sites showing the five highest PCB concentrations were France, Germany, Sweden, Croatia and Russia .

- Other higher than average sites tended to be located within Central Europe, with the exception of one site in Russia.

- High concentrations of PCBs were often associated with urban centres.

- Of the ten PCBs recorded, 18, 28, 49 and 52 (i.e. the lightest congeners) contributed the most, on average accounting for >90% of the total.

- The PCB congeners showing the greatest spatial range were PCB 28, 49, 52 and 118 with concentrations ranging by a factor of over 100.

- PCBs were detected at all sites.

- Air concentrations suggest ∑PCBs range from 10 (Norway: POG 14) – 300 (France: POG 24) pg/m^3, which is similar to data presented in the literature by Lee, 1999. However, comparing data gathered from other urban sites is quite tricky, due to large variation. For example, data from urban Germany suggests levels of approximately 600 pg / m^3 (Ballschmitter, 1991), whilst London produces levels of 1300 pg/m^3 (Halsall, 1995).

PBDEs

Due to ambient atmospheric levels of PBDEs being generally quite low and 21 m^3 of air sampled, only small amounts of PBDE were sequestered into the polymer matrix. Consequently, only four PBDEs are reported; 75, 71, 47, and 99. With respect to blank levels, PBDEs 75, 71 and 99 were undetectable, but PBDE 47 was quite high, with an average blank being ~ 5 ng / g of EVA. Although levels in some samples were below the commonly used LOD, the response was well above that associate with the blanks. All calculations based on ∑PBDE take into account only the four detectable PBDEs. Air concentration values have been calculated assuming a sampling rate of 3 m^3 per day.

Table 2. Data associated with specific PBDEs. All concentrations are in ng / g EVA.

PBDE	Site Average	Min	Max	% Contribution to ∑PBDE	[Range] (pg/m^3)
75	5.4	1.5	10.2	14.4	0.9 - 6.3
71	7.5	2.0	18.2	19.9	1.3 - 11.3
47	15.5	0.6	56.7	41.2	0.4 - 35.3
99	9.2	2.3	29.3	24.5	1.4 - 18.2

- PBDEs were not detected at all sites, except PBDE 99. 14% of sites did not show any PBDE 75, 17% of sites had no detectable amounts of PBDE 71 and due to the high blanks, 65% of sites had no detectable levels of PBDE 47. If it wasn't for the high blank, PBDE 47 would be found at all sites. was detected at every site.

- Figure 2 shows that 13 sites were above the average concentration of 5.8 pg m^{-3}. Again, these sites represented urban areas in central Europe, in particular, Germany (POG 27) and Italy (POG 34) Spain (POG 36) and Sweden (POG 20).

- PBDE 47 showed the largest maximum value of 35 pg m^{-3} (POG 37 – Sevilla, Spain).

- UK values of PBDEs fell below the European average and in some cases being similar to levels recorded at Macehead (PBDE 71 and 99). This may have been due to prevailing winds originating in the west. See Figure 3.

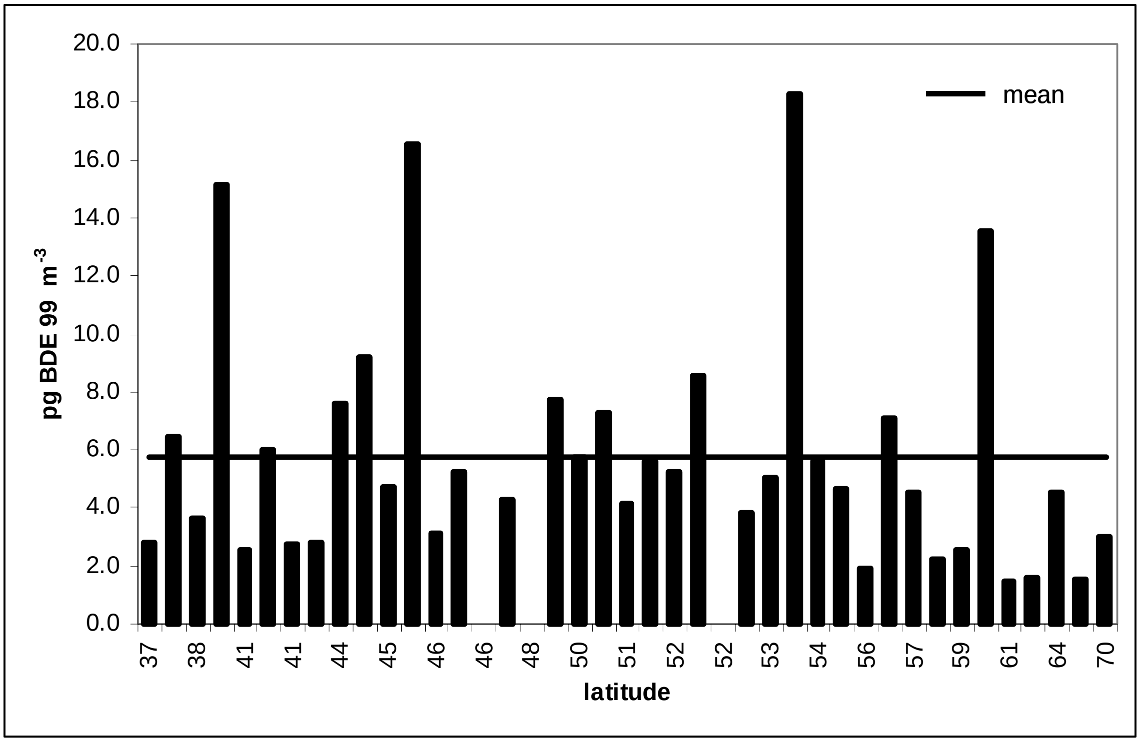


Figure 2. BDE-99 levels at each site across Europe, showing an average concentration of 6 pg m^{-3}.

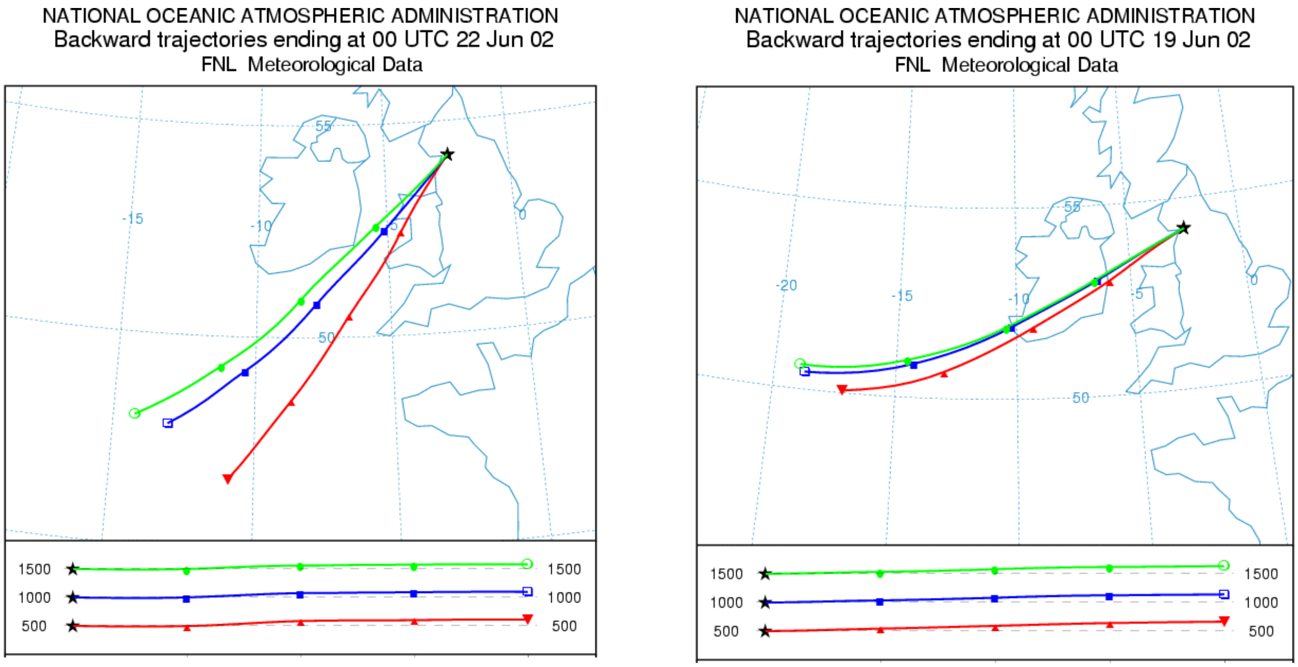


Figure 3. Backwards air trajectories at Hazelrigg for two days during the campaign

- Calculated air concentration data suggest that the levels of PBDEs are realistic, with ∑PBDE for each site ranging from 3.0 (Sweden: POG 19) – 50 (Germany: POG 27) pgm^{-3}. Levels were similar to those reported in an USA study, where samples from Lake Superior were 5 pg m^{-3} and Chicago produced levels of ~ 50 pg m^{-3}. (NB: See next section for PAH comparisons for the same region).

- PBDE 47 showed its maximum calculated air concentration of 35 pg m^{-3} in Spain (POG 37).

PAHs

All samples were quantified for a total of 14 PAHs (table 3), blank corrected and normalised for the mass of EVA.

- Heavier weight PAHs (i.e. *benzo(a)- & benzo (e)-* pyrene) were detectable at only a few sites and were generally regarded as being non detectable for the majority of sites. The only detectable levels were found in Germany and Italy, where concentrations were approximately 5 ng g^{-1} EVA (approximately 3 ng m^{-3}).

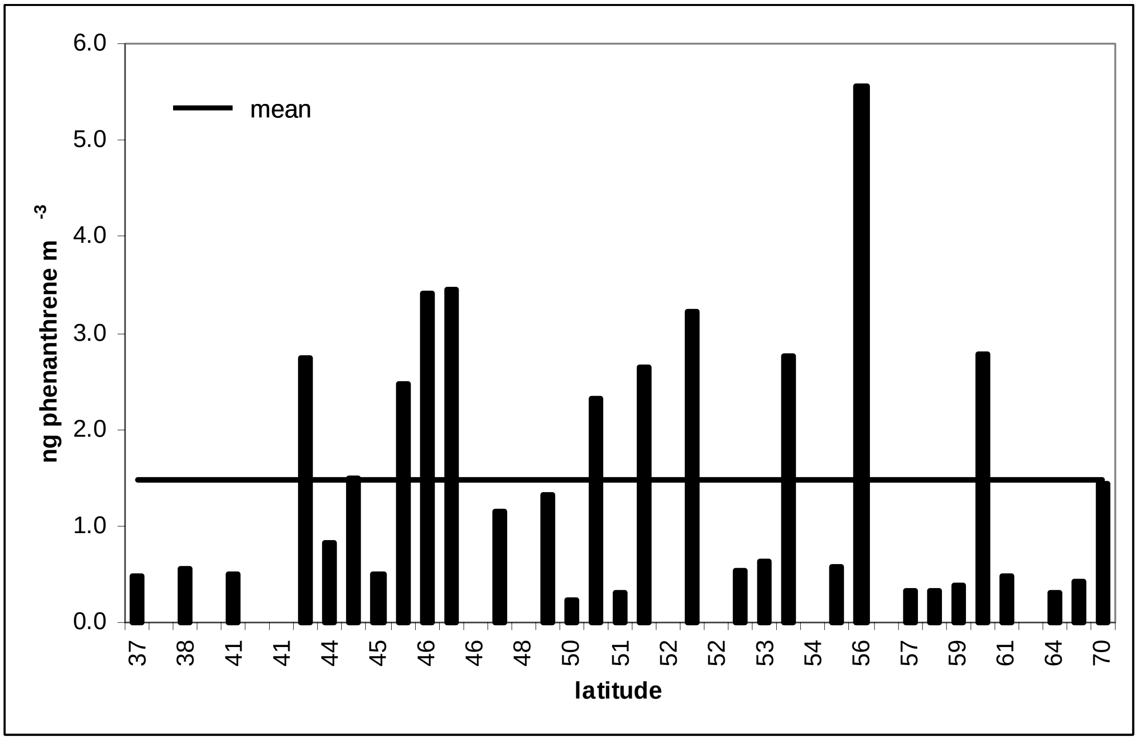


Figure 4. Phenanthrene levels at each site across Europe, showing an average concentration of 1.5 ng m^{-3}.

- Figure 4 shows that the phenanthrene concentrations varied of the 34 sites under scrutiny, 14 locations had ∑PAH levels that were deemed to be above the average of 130 ng / g EVA.

- In addition to high levels seen in central Europe, countries such as Russia and Kazakhstan were also noted as providing greater than average levels of PAH.

- High levels were again associated with large urban centres, although POGs 29 and 30 were regarded as being rural. This can be explained by their location in central Europe, perhaps being subjected to winds from various directions / origins.

- Based on a combination of equilibrium partitioning for the lighter PAHs and an uptake of 21m^3 (one week deployment) for the heavier compounds, ng per sampler data was converted to air concentrations (table 3). ∑PAH for each site varied from 8.3 (Belgium) – 940 (Switzerland) pg m^{-3}.

- Buehler *et al.* (2001)[1] reported ∑PAH air concentrations in the Great Lakes region ranging from 1.1 to 6.7 ng m^{-3} and an urban site (Chicago) as high as 113 ng m^{-3}. Data from the POG samplers shows concentrations lower than this range.

-

Table 3. PAH data from across Europe. All concentrations are in ng / g EVA.

PAH	Site Average	Min	Max	[Range] (pg m^{-3})
Naphthalene	54.2	6.8	116.3	6 - 103
2-methylnaphthalene	28.6	0.3	66.4	
1-methylnaphthalene	20.1	0.9	35.8	
Biphenyl	19.4	2.4	95.9	0.7 - 29
2,6-dimethylnaphthalene	22.6	2.9	160.6	
Acenaphthylene	1.8	0.1	5.0	0.01 - 0.2
Acenaphthene	385.0	30.3	810.6	2.4 - 64
2,3,6-trimethylnaphthalene	61.6	5.7	417.7	
Fluorene	30.9	9.4	249.6	0.5 - 14
Phenanthrene	159.2	25.0	601.7	0.2- 5.6
Anthracene	24.4	1.4	414.2	0.06 - 16.7
1-methylphenanthrene	35.0	3.1	226.0	
Fluoranthene	225.4	7.9	1106.8	0.01- 1.1
Pyrene	127.5	10.0	714.3	0.02 - 1.7
Benzo(a)anthracene	7.1	0.1	102.7	<0.01 - 0.04
Chrysene	21.2	0.4	97.5	0.3 - 61

---

[1] Buehler, S. S., Basu, I. and Hites, R. A. (2001) A Comparison of PAH, PCB, and Pesticide Concentrations in Air at Two Rural Sites on Lake Superior Environ. Sci. Technol., 35(12), 2417-2422.

Conclusions

PCBs, PBDEs and PAHs are seen to be widely distributed throughout Europe, with highest levels being associated with urban centres. When presented as a concentration (pg/m^3), some compounds (particularly PAH) did not compare very well with data recorded using active sampling techniques. However, such techniques produce data which is derived from both the particulate and vapour phase, and it is possible that the heavier weight PAHs which may play a more dominant role in other studies were not sampled very effectively using the POG passive sampler (due to the chamber restricting particulate loading). This may describe why PBDEs were seen to compare well with data from Chicago, whilst PAH were significantly out.

Appendix (Concentrations are all pg m^{-3})

No	Country	Total PCB	Total PBDE	Total PAH	Location
1	Switzerland	66.1	15.8	940.2	Rural / Urban
2	Croatia	158.7	10.2	341.2	urban
3	Estonia	73.4	8.3	42.9	
4	Russia	141.0	7.9	101.3	urban
7	Kazakhstan				urban
8	Iceland				urban
9	Belgium	83.0	11.9	70.7	
10	Finland	25.2	7.7	21.2	rural / semi-rural
11	Greece	60.8	7.0	8.3	
13	Netherlands	42.4	3.1	29.8	urban
14	Norway	25.5	11.4	198.6	rural
15	Norway				rural
16	Portugal	107.2	27.0	48.6	rural
17	Portugal	9.8	5.8		rural (coast)
18	Sweden	64.1	5.9	86.2	semi rural
19	Sweden	26.5	4.4	67.6	
20	Sweden	47.2	5.2	90.6	urban
21	Sweden	58.7	9.4	83.7	
22	Sweden	30.3	2.6	56.4	semi rural
23	EIRE	165.8	39.4	99.9	rural
24	France	27.7	9.3	47.2	
25	France	52.9	8.4	44.8	semi rural
26	France	57.4	11.5	103.8	
27	Germany	297.0	22.8	94.4	
28	Germany	50.4	15.3	82.6	rural
29	Germany	39.6	8.2	145.9	rural
30	Germany	252.0	46.3	117.2	urban
31	Germany	33.6	9.4	65.2	urban
32	Italy	25.7	12.9	122.0	urban
33	Italy	76.5	17.6	97.0	urban
34	Italy	49.6	15.4	129.8	urban
35	Spain	116.9	12.4		rural
36	Spain	101.9	16.1		urban
37	Spain	132.6	43.5		rural
38	Spain	40.2	15.8		rural
39	UK	23.2	21.1		semi - rural
40	UK	11.0	45.8		rural
41	UK	39.2	6.4		semi rural

Section 9

Study into the factors controlling the uptake of POP chemicals by passive air samplers using controlled laboratory chambers

Introduction

A number of passive sampling devices have been utilised to sample POP chemicals in the atmosphere including polyurethane foam, polymer coated glass, polyethylene and soil. However, in order to provide quantitative data that can be compared with concentration data measured by other techniques such as Hi-volume samplers, the uptake kinetics of the samplers needs to understood. As a result, a laboratory study has been carried out to identify the key parameters controlling the exchange of chemicals between the atmosphere and the sampling device. For the purposes of this study SPMDs (semi-permeable membrane devices) were chosen although the sampling processes and mechanisms are broadly similar across all sampler types and hence the findings of this study are applicable elsewhere.

SPMDs were originally designed to study bio-availability in water, although more recently they have also been used as passive air samplers. Whilst sampler uptake kinetics in water have been extensively studied, the dominant factors which control their sampling rates in air reqiures further investigation. The purpose of this study was to investigate the effects of wind speed and temperature on SPMD uptake and sampling rates. Ideally the uptake phase should be investigated but this presents problems associated with generating a constant concentration in the air used to contaminate the sampler. As a result, the depuration rate from SPMDs fortified with a known amount of chemical, as opposed to uptake rate, has been investigated. This of course assumes that the uptake and depuration kinetics are directly related and one can be deduced from the other. The three ringed PAH phenanthrene was chosen for this study because of its intermediate volatility and availability as a ^{14}C analogue. Using radio-labeled compounds for this type of study increases accuracy and reduces the analytical time .

Experimental Method

The experimental apparatus used for the study consisted of three parts; the trap, the chamber and the inlet - see Figure 1. The chamber was approximately 12 cm x 3.5 cm x 1.5 cm. with dimples along the top and bottom sides to ensure a turbulent flow and minimisation of the stagnant boundary layer.

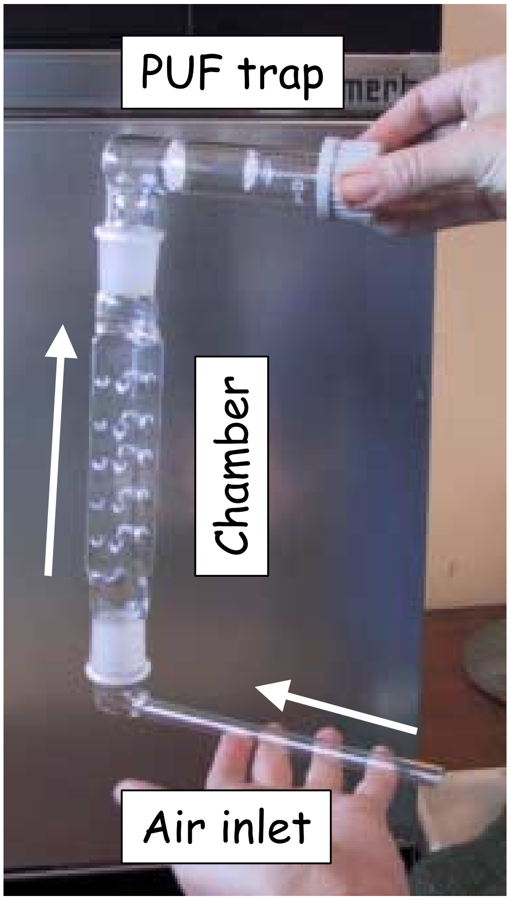


Figure 1 – SPMD experimental chamber showing inlet and trap

The chamber was submerged in a water bath to maintain a constant temperature and the inflowing air was equilibrated with the water bath temperature by passing it through 2m of immersed copper tubing. The trap was designed to hold a 5 cm micro PUF plug and was L-shaped which allowed the top to be positioned out of the water, enabling easy removal of the PUF plugs. After the trap, a gas meter recorded the volume of air (m^3) leaving the chambers. Each chamber had its own pump to pull air through it. The design of the chambers allowed 3 chambers to be run simultaneously in the water bath with one chamber run as a background sample allowing the laboratory air to be monitored for possible contamination.

The SPMDs were made from low density polyethylene (LDPE) membrane bags; 9cm long containing 100μL of triolein thus keeping membrane area : triolien volume consistent with commercially available samplers. The triolein was spiked with 49 ng of ^{14}C labelled phenanthrene ensuring that the amount (in terms of mass) would be above the background air concentration and that depuration would be the dominant process. Before assembly and spiking the SPMDs were soaked in hexane for several hours to remove any contaminating film and maintain the condition of the membrane. The traps were replenished with fresh PUF plugs at regular intervals in order to provide a time series of volatilisation/depuration.

Extraction Method for PUF ^{14}C Phenanthrene

After collection, each PUF plug was placed in a solvent rinsed glass jar with foil lined lids and stored in a freezer until extracted. The PUF plugs were extracted in using cellulose thimbles using a Soxhlet apparatus for 4 hours with 100 mL of DCM. Subsequently, the samples were reduced under a stream of nitrogen to approximately 15 mL, transferred to 25 mL volumetric flasks, followed by 3 rinses of 2mL of fresh DCM and made up to volume. Two aliquots (10 mL each) were added to UGXR scintillation fluid (10ml) in glass scintillation vials and counted after quenching ceased. The extraction method gave analyte recoveries of 90 ± 4 %.

Effect of wind speed on depuration rate.

Although there are restrictions with the range of wind speeds achievable within the chamber, four wind speeds were studied ranging from 0.01 to 0.32 ms^{-1}. All runs were carried out at laboratory temperature. A summary including flow rates is shown in Table 1 and the results (cumulative amount of activity lost over time) shown Figure 2.

Table 1: Summary of Experiments

Flow Rate (m^3 hr^{-1})	Wind speed over SPMD (m s^{-1})	# Chamber Runs	# Backgrounds
0.73	0.32	4	2
0.32	0.14	4	2
0.07	0.03	2	1
0.03	0.01	4	2

Figure 2 Depuration of phenanthrene from SPMDs at a range of wind speeds

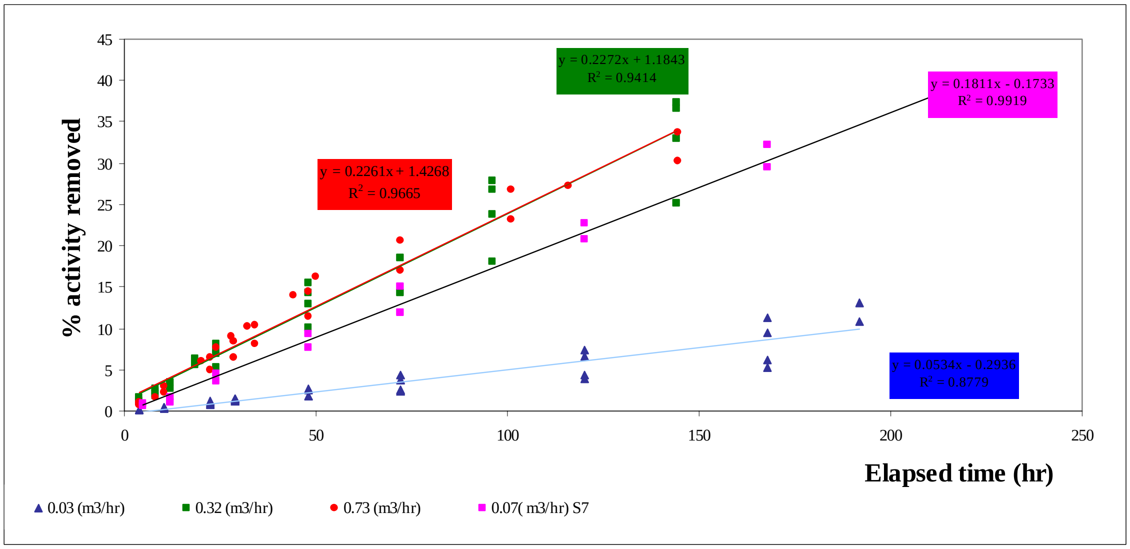


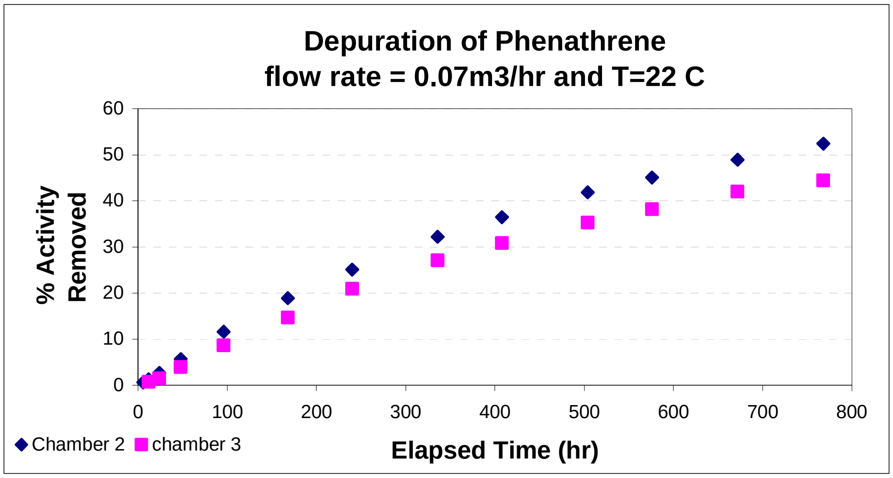
Figure 2 clearly shows that there is a wind effect with the depuration rate increasing with a corresponding increase in air flow. However, the results also suggest that there is a threshold wind speed after which there is no a significant increase in observed depuration rate. By increasing the flow rate by a factor of 2.4, the rate increases by 3.6. However, increasing the flow further by a factor of 4.5 only sees a depuration rate increase of 1.2. And finally at the fastest flow, when the flow rate is increase by a factor of 2.4 this only sees an increase of a factor of 0.1 in the depuration rate. The depuration rate was taken as the slope of the regression lines in Figure 2. (Δ %activity / Δtime). Table 2 contains a summary of these results.

Table 2 Summary of wind speed effects on depuration rate

Flow (m^3/hr)	Equation	r^2	Factor increase from lower flow	Factor increase between flows
0.03	y = 0.0534x + 0.2936	0.8779		
0.07	y = 0.1811x - 0.1733	0.9919	2.4	2.4
0.32	y = 0.2272x + 1.1843	0.9414	10.8	4.5
0.73	y = 0.2261x + 1.4268	0.9665	25.0	2.3

These experiments were run over a period of between 6 and 8 days during which the depuration of phenanthrene appears to be linear. In order to investigate the linear range of the depuration process a single run was extended for a total of 32 days. The results of this run suggested that steady state conditions were not achieved over this period – see Figure 3.

Figure 3 Depuration Rate of ^{14}C phenanthrene at flow rate of 0.07 m^3 hr^{-1} and 22° C



Effect of temperature on depuration rate.

The temperature dependence of phenanthrene depuration from a spiked SPMD was studied at three temperatures, namely 10, 22 and 30 °C, all run at a flow rate of 0.03 m s^{-1}. The results show that by increasing the temperature by a factor of 2.2, the depuration rate increases by 2.8 and by increasing it by a factor of 3 increases it by a factor of 12. These results suggest that temperature has an important influence on the depuration rate of phenanthrene. A summary of the results are contained in Table 3 and Figure 4.

Table 3 Summary of wind speed effects on depuration rate

Temp. (°C)	Equation	r^2	Factor increase from lower temp.
10	y = 0.0374x - 0.0739	0.6861	
22	y = 0.1052x - 0.2363	0.9407	2.8
30	y = 0.4439x - 0.4296	0.9976	11.9

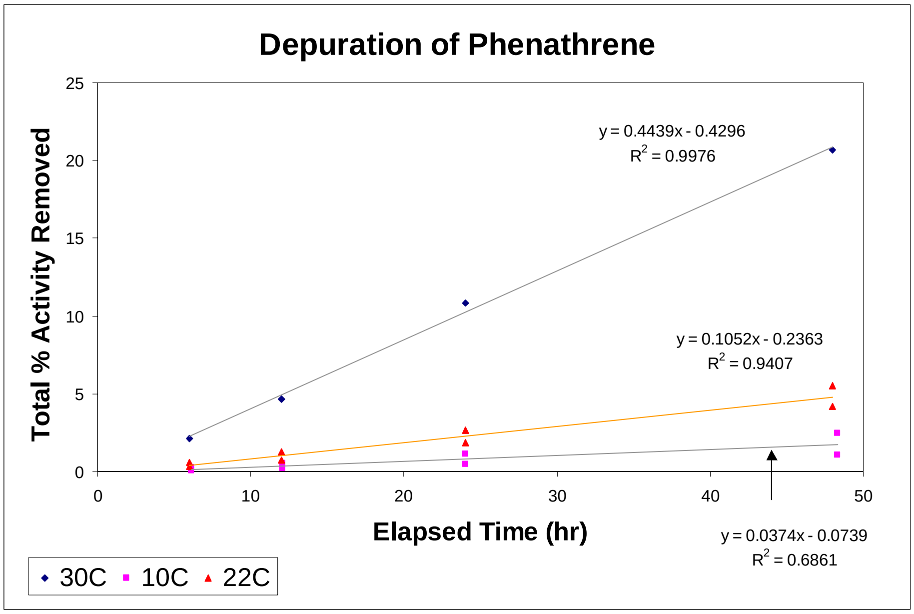


Figure 4 Summary of Phenanthrene Depuration rates over varying temperatures.

Conclusions

It appears from these controlled chamber experiments that both wind speed and temperature exert a effect on the depuration of phenanthrene from SPMDs. The effect of varying the wind speed across the SPMD controls the thickness of the boundary layer and hence the distance through which the phenanthrene has to diffuse. However, this effect appears to be limited to lower wind speeds above which the effect on the boundary layer is minimal. The effect of increasing the depuration rate by increasing temperature could also be related to diffusion through the boundary layer. As the temperature increases so does the molecular diffusion rate although this effect is limited – a 20°C increase in temperature results in a 13% increase in molecular diffusion. Temperature is also likely to control the diffusion rates in the triolein and through the polyethylene which would require further investigation.

Section 10

POP multimedia model inter-comparison study (MSC-E, Moscow)

As a result of the decision of the Executive Body for the Convention on Long-Range Transboundary Air Pollution (ECE/EB.AIR/75, January 2002) and taking into account the discussions on POP model intercomparison by the expert group during the third meeting of the EMEP Task Force on Measurements and Modelling (EB.AIR/GE.1/2002/4, March 2002), MSC-E organised an meeting to dicsuss the intercomparison of POP fate models. The first expert group meeting was held in Moscow in November 2002 to initiate the intercomparison exercise. The following section outlines the aims of the study.

Introduction

Environmental contamination by POP chemicals has been recognised by the international community as a significant problem. As a result, a number of international binding instruments on elimination, restriction, and reduction of POP production, usage, and emissions have been developed. Among these are the LRTAP Convention on POPs and the Stockholm Global Convention on POPs. Many international organizations have included POPs in their work programs (WMO, UNEP, CLRTAP, OECD, HELCOM, AMAP, EUROTRAC, OSPAR, and others). International regulatory activities on POPs include, in particular:

- evaluation of long-range transport, accumulation and deposition of POPs in accordance with existing obligations;
- elaboration of effect-oriented approach for POPs (risk assessment and risk management);
- evaluation of new substances to be included in the regulatory activity.

For the assessment of POP contamination both on regional and global levels a complex monitoring/modelling approach seems to be reasonable. Since there are relatively few measurement data on POP concentrations in various environmental compartments compared to many inorganic species, modelling plays significant role in the assessment of POP contamination.

In designing model tools for contamination assessment one has to take into account that the behaviour of POPs in the environment is characterized, in particular, by their ability to accumulate in different environmental compartments with possible re-volatilisation to the atmosphere. Hence, evaluation of environmental pollution by POPs requires application of multimedia models. At present there exists a range of different types of models describing POP cycling in the environment taking into account intermedia exchange processes. The complexity of such models, in accordance to their purposes, vary from simple box models describing distribution of a pollutant in question between various environmental media to spatially resolved dynamic models taking into account peculiarities of the real environment (such as meteorological and geophysical information).

To obtain comparable results the harmonization of model output is required. The necessity of intercomparison of different types of POP transport models was included in the recommendations of the WMO/UNEP/EMEP Workshop on modelling of atmospheric transport and deposition of POPs and heavy metals held in Geneva, November 1999. Subsequently the work of intercomparison of POP long-range transport models was included in the EMEP work-programme. The recent OECD/UNEP Workshop on the use of multimedia models for estimating overall persistence and long-range transport, Ottawa, October 2001 also identified the necessity of an intercomparison study of POP multimedia models of different complexity.

One of main goals of this intercomparison study is to initiate the work on such a harmonization.

Objectives. The main objectives of the intercomparison study are:

- To strengthen the exchange of scientific experience between different groups working in the field of POP multimedia modelling.
- To increase the transparency of existing models and their results: model concept, parameterisations, time and spatial resolution, output, uncertainties.
- To harmonize the output of POP transport models of different types and complexity for obtaining comparable results at different levels of regulatory activities.

Stages of the intercomparison. The model intercomparison study will be performed in the following stages:

Preliminary Stage. Review of description and parameterisation of models involved into the intrcomparison study.

Stage I. Comparison of process description and parameterization determining POP long-range transport and accumulation in different models.
Stage II. Comparison of calculation results on the level of mass balance (contents of POPs in different environmental compartments: atmosphere, soil/sediments, seawater, vegetation).
Stage III. Comparison of calculation results of participating models with one another and against measurements in various environmental compartments.
Stage IV. Testing model applicability for evaluation of overall environmental persistence and long-range transport potential for new substances.

On the preliminary stage of the intercomparison study the following information on each of participating models will be reviewed:

- Type of the model (box model, spatially resolved models, etc.).
- Description of compartments (boxes) taken into account in the model.
- Description of processes included into the model.
- Model parameterization for chemicals included into the intercomparison study.

This information is required to prepare a detailed program of intercomparison for subsequent stages. At the preliminary stage the list of substances included in the intercomparison study will be determined.

During the first meeting MSC-E suggested that the intercomparison includes Europe (EMEP region) and the Northern Hemisphere as basic regions for investigation and 1990 as a reference year. The following chemicals were proposed for the intercomparison: α-HCH, selected PCB congeners, and B[a]P since these substances cover a wide range of POP physical-chemical properties and are amongst the most widely investigated.

The first stage was designed to compare model descriptions of the main processes determining POP long-range transport (degradation processes in different environmental compartments, processes of intermedia exchange, partitioning between various phases, transport processes in compartments other than atmosphere, etc.).

It is intended that this stage will result in an intermediate report with possible recommendations for parameterization of processes determining the POP environmental transport.

The second stage for comparison will involved a comparison of the mass balance estimates calculated by models (pollutant contents in the environmental compartments, total amounts of a pollutant degraded in different media, etc.). To perform this stage two or three chemicals will be chosen to ensure that a wide range of chemical properties are included. The results of this stage of the intercomparison study will provide the basis of second intermediate report.

The third stage of the intercomparison study is designed to provide a more detailed intercomparison of modelling results with incorporation of the spatial distribution of contamination. Box models with spatially subdivided boxes and spatially resolved transport models will be able to participate. The comparison of modelling results obtained by different models and monitoring data will be carried out. The third intermediate report including model validation against measurements will be the output of this stage.

At the forth stage of the intercomparison study it is supposed to compare model estimates of long-range transport potential and overall environmental persistence. Such testing can be performed for chemicals proposed above as well as for some new chemicals (e. g. PCP). The results of the intercomparison study will be published in the final report including the results of all intercomparison stages, conclusions and recommendations.