Persistent organic pollutants in ambient air – sources, patterns, and environmental behaviour

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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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Lancaster Environment Centre

This Thesis is dedicated to all those brilliant service engineers out there.

‘When you eat a pastry for the right reasons, it doesn’t
contain any calories,’ said Barney, and Igor nodded.
‘Is that actual science?’
‘More or less.’
‘Decent.’

Douglas Lindsay
Scenes From The Barbershop Floor, Vol.2

Declaration

This thesis has not been submitted in support of an application for another degree at this or any other university. It is the result of my own work and includes nothing that is the outcome of work done in collaboration except where specifically indicated. Many of the ideas in this thesis were the product of discussion with my supervisor Dr Andrew Sweetman.

Lancaster, 28th September 2022

Carola Graf

Excerpts of this thesis have been published in the following publications:

Chapter 2. The TOMPs Ambient Air monitoring Network – continuous data on the UK air quality for 20 years.

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Chapter 6. The UK/Norway SPMD transect

Parts of this chapter have previously been published as part of the 2021 3rd Regional Monitoring Report for Western Europe and Others Group (WEOG) Region to the Global Monitoring Plan for Persistent Organic Pollutants under the Stockholm Convention Article 16 on Effectiveness Evaluation, found under

(WEOG) Region to the Global Monitoring Plan for Persistent Organic Pollutants under the Stockholm Convention Article 16 on Effectiveness Evaluation. March 29, 2021_rev1 ed. http://chm.pops.int/implementation/globalmonitoringplan/monitoringreports/tabid/525/default.aspx

Abstract

Long-term air monitoring datasets are needed for persistent organic pollutants (POPs) to assess the effectiveness of source abatement measures and the factors controlling ambient levels, and to provide governments, regulators, and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation such as the Stockholm Convention and UN/ECE Protocol on POPs. These data can be provided by active or passive air sampling. The UK Toxic Organic Micro Pollutants (TOMPs) Network, using high-volume active air samplers, has demonstrated the constant decline in UK air concentrations for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polybrominated diphenyl ethers (PBDEs) since 1991, in accordance with emission estimates. For a latitudinal passive ambient air sampling transect from the south of England to the north of Norway established in 1994, which had reported several years of decreasing PCB air concentrations previously, increased levels were observed between 2008 and 2016. The reasons for this could include local sources, effects of climate change, and impact of polluted air masses from Eastern Europe. In contrast, PBDE concentrations have decreased since 2000 in line with expectations. Furthermore, seasonal patterns for PCB and PBDE concentrations in UK ambient air are discussed. PCBs generally showed a summer > winter pattern, while ΣPBDE concentrations were distributed over a range of congeners with more uniform concentrations but greater differences in seasonal patterns, thus their overall seasonality was characterized by these contrasting patterns. In addition to long-term trends and regular seasonal variations, short-term emission events like the UK 'Bonfire Night', where increased PBDE concentrations possibly stemming from 'backyard burning' were observed, were shown to impact POPs concentrations in ambient air. In order to overcome some limitations of current air sampling methods, two potential improvements were evaluated and recommended: the

addition of XAD® pods in standard active air samplers, and the addition of monofluorinated PCBs to the range of performance reference compounds for passive air sampling.

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List of Abbreviations and Acronyms

AMAP	Arctic Monitoring and Assessment Programme
Defra	UK Department for Environment, Food and Rural Affairs
EMEP	European Monitoring and Evaluation Programme
EPA	United States Environment Protection Agency
GC-MS	Gas chromatography – Mass spectrometry
GFF	Glass fibre filter
GPC	Gel permeation chromatography
HCB	Hexachlorobenzene
HRGC-HRMS	High-resolution GC – High-resolution MS
NAEI	National Atmospheric Emissions Inventory
NILU	Norwegian Institute for Air Research
LOD	Limit of detection
LOQ	Limit of quantification
OPE	Organophosphate ester
OPFR	Organophosphorus flame retardant
PAH	Polycyclic aromatic hydrocarbon
PAS	Passive air sampler
PBDE	Polybrominated diphenyl ether

PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
POP	Persistent organic pollutant
PRC	Performance reference compound
PUF	Polyurethane foam
SPMD	Semipermeable membrane device
SVOC	Semi-volatile organic compound
TEQ	Toxic equivalency quotient; toxic equivalent
TOMPs	Toxic Organic Micropollutants (network)
UN/ECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
VOC	Volatile organic compound
WHO	World Health Organisation

1 Introduction

1.1 Toxic organic pollutants

Organic pollutants are toxic substances that have been found to be ubiquitous in the global environment. They are often industrial chemicals or by-products from industrial processes. Many organic pollutants have been demonstrated to be persistent, bioaccumulative, and toxic (PBT), which classifies them as persistent organic pollutants (POPs). Lancaster University has been running two long-term air monitoring projects for POPs that are discussed in this thesis. The UK/Norway transect has collected data on polychlorinated biphenyls (PCBs) since 1994, and on polybrominated diphenyl ethers (PBDEs) since 2000. The UK Toxic Organic Micropollutants (TOMPs) network has additionally reported on polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) since its inception in 1991, as well as on PAHs until 2004. While the use of legacy POPs like PCBs and PBDEs has increasingly been restricted over the last few decades, in many areas of application they are now being replaced by new groups of compounds, for example the flame retardants PBDEs by certain organophosphate esters (OPEs). It is therefore important to continuously update environmental monitoring programmes to include not only legacy POPs, but also potentially toxic pollutants they are being replaced by.

1.1.1 Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) enter the environment from various combustion processes and as impurities from the manufacture and use of various chlorinated compounds. Considerable effort has been expended in the UK and elsewhere to try and quantify and rank these sources and their emissions into the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken. PCDD/Fs levels in the environment have been declining since the early seventies and have been the subject of a number of regulations and clean-up actions; however, current exposure levels still remain a concern. PCDDs and PCDFs were added to Annex C of the Stockholm Convention when it entered into force in 2004 (http://www.pops.int/). The NAEI inventory estimates that the emission of PCDD/Fs to the UK atmosphere reduced from 229 g-TEQ in 2010 to 181 g-TEQ in 2019, the majority emitted from combustion processes (Figure 1) (https://naei.beis.gov.uk/reports/).

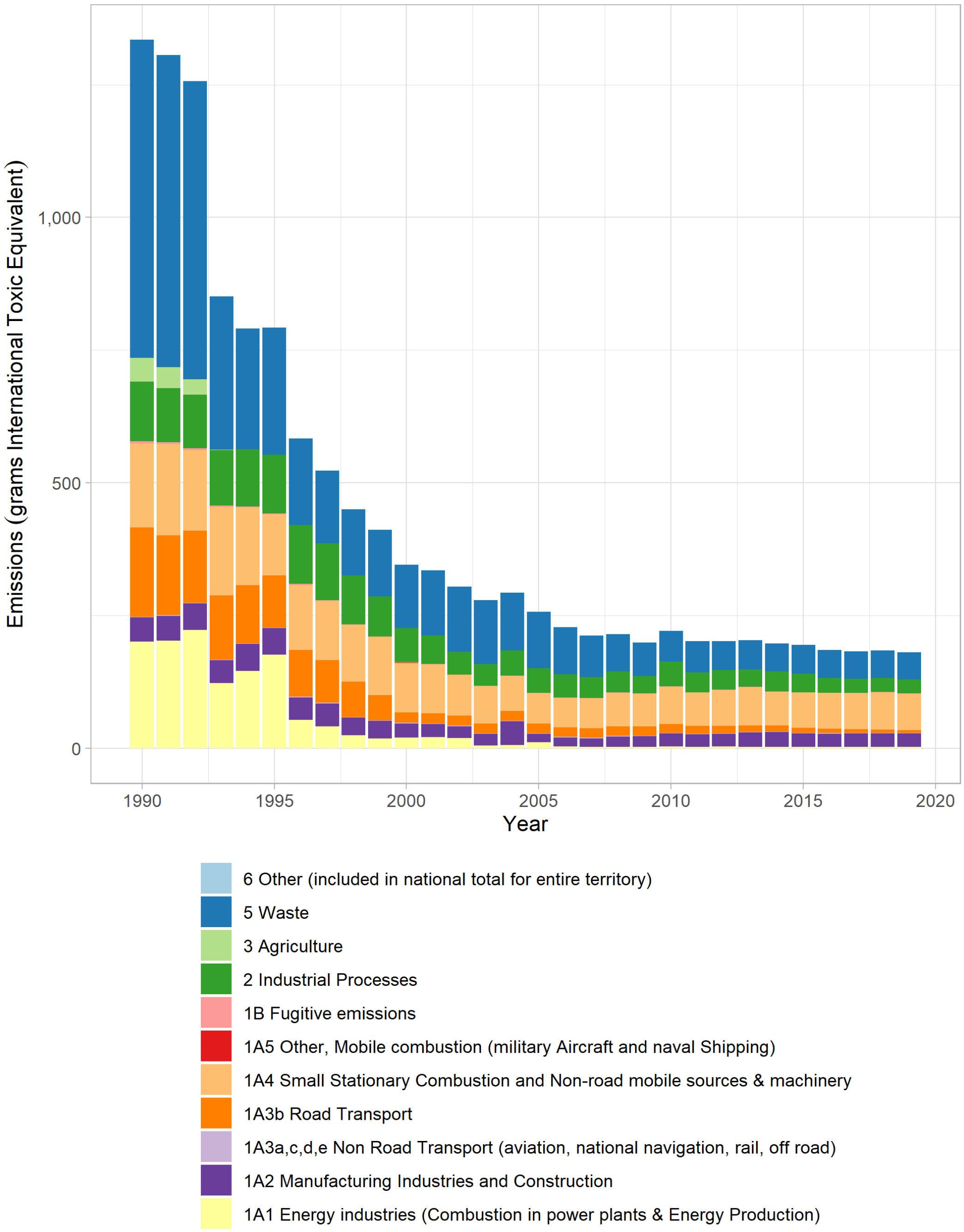

Figure 1. Total UK emissions of Dioxins and Furans for 1990-2019. Figure by Churchill et al. (2021).

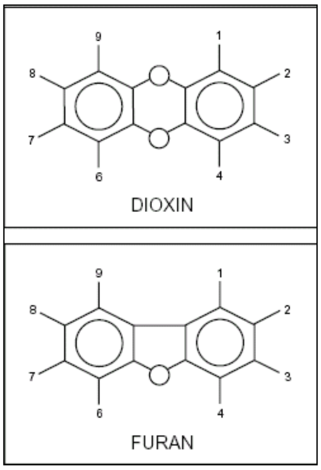

Figure 2. Basic structure of PCDDs ('dioxins') and PCDFs ('furans')

PCDDs and PCDFs are halogenated aromatic hydrocarbons, with PCDDs consisting of two benzene rings connected by a pair of oxygen atoms, and PCDFs of two benzene rings connected by a central furan ring (Figure 2). In all, there are 75 possible PCDDs and 135 possible PCDFs. However, importantly, the compounds containing 0, 1, 2, or 3 chlorine atoms are thought to be of no toxicological significance, and of those containing 4 to 8 chlorine atoms the ones which have chlorine atoms at each of the positions 2, 3, 7, and 8 are the most toxic. Once all four of these positions are occupied by chlorine atoms, the presence of additional chlorine atoms generally progressively reduces the toxicity of the congeners. The relative toxicity of the 17 toxicologically important PCDD and PCDF congeners is defined in a number of toxicity equivalency schemes that can be used to provide an assessment of the relative toxicities of each congener and an estimate of the overall toxicity of a mixture.

The Toxicity Equivalency Factor (TEF) values have been subject to revision and amendment since their inception, but the most widely accepted set of TEF values for the 2,3,7,8-substituted PCDD/Fs is the WHO (WHO-TEQ) system, originally developed in 1990s and last updated in 2005. Another commonly used scheme is the International Toxicity Equivalency Scheme (I-TEQ) which has assigned slightly different TEFs to the WHO schemes. The three TEQ schemes data are contained in Table 1 below.

Table 1. Toxic Equivalency schemes for PCDDs, PCDFs and co-planar PCBs

PCDD/F compound	WHO-1998	WHO-2005	I-TEF	PCBs	WHO-1998	WHO-2005
2,3,7,8-TCDD	1	1	1	**PCB 77**	0.0001	0.0001
1,2,3,7,8-PeCDD	1	1	0.5	**PCB 81**	0.0001	0.0003
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	**PCB 126**	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	**PCB 169**	0.01	0.03
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1			
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01			
OCDD	0.0001	0.0003	0.001			
2,3,7,8-TCDF	0.1	0.1	0.1			
1,2,3,7,8-PeCDF	0.05	0.03	0.05			
2,3,4,7,8-PeCDF	0.5	0.3	0.5			
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1			
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1			
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1			
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1			
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01			
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.001			
OCDF	0.0001	0.0003	0.0001			

1.1.2 Polychlorinated biphenyls (PCBs)

PCBs were first synthesized in 1881 by Schmidt and Schulz, but their commercial production only began in 1929 in the USA (Danse et al., 1997). They were marketed as mixed products under various trade names, depending on the country where they were produced, such as Aroclor (Monsanto, USA), Phenochlor and Clophen (Bayer, EU). Because of high chemical and thermal stability, electrical resistance, and low or no flammability, PCBs had extensive applications. They have been used as dielectric fluids in capacitors and transformers, in plasticisers, adhesives, inks, sealants and surface coatings (de Voogt and Brinkman, 1989; Eduljee, 1988; Harrad et al., 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ (n=1-10) (Figure 3), which leads to 209 possible congeners.

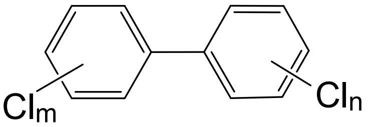

Figure 3. Basic structure of PCBs

The International Council for the Exploration of the Seas (ICES) identified 7 key PCB congeners that are commonly reported in environmental samples. These are PCB 28 (2,4,4’-tri-CB), PCB 52 (2,2’,5,5’-tetra-CB), PCB 101 (2,2’,4,5,5’-penta-CB), PCB 118 (2,3’,4,4’,5-penta-CB), PCB 138 (2,2’,3,4,4’,5-hexa-CB), PCB 153 (2,2’,4,4’,5,5’-hexa-CB), and PCB 180 (2,2’,3,4,4’,5,5’-hepta-CB), although several dozen different congeners can be found in the environment.

Production of PCBs peaked in the 1960s in Europe and USA and terminated in the mid-1970s, when they were ultimately banned in the late 1970s/early 1980s (de Voogt and Brinkman, 1989). The last inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tonnes (Breivik et al., 2002). Approximately 97% of this has been used in the Northern Hemisphere, mostly between 30 °N and 60 °N. Before the ban, PCBs had entered the environment through point and diffusive sources such as landfill sites, accidental releases/spillages via leaking during commercial use of electrical equipment and transformer and capacitor fires, incineration of PCB waste, etc. (Danse et al., 1997; de Voogt and Brinkman, 1989). Current atmospheric levels of PCBs in the environment can be accounted by ongoing primary anthropogenic emissions (e.g. accidental release of products or materials containing PCBs), volatilisation from environmental reservoirs that have previously received PCBs (e.g. oceans and soil) or incidental formation of some congeners during combustion processes (Breivik et al., 2002). The National Atmospheric Emission inventory estimates that the emission of PCBs to the UK atmosphere have decreased from 843 in 2010 to 705 kg in 2022, the majority emitted from electrical equipment such as capacitors and transformers. PCBs were added to Annex A and C of the Stockholm Convention when it entered into force in 2004. There is evidence to suggest that coplanar PCBs (PCBs without chlorine substitution in the ortho position) elicit similar toxic responses to dioxins (Tanabe et al., 1987), based on their binding to an intercellular protein, the Ah-receptor. These selected PCBs ('dioxin-like PCBs', 'dl-PCBs') have therefore also been ascribed TEF values, which have been endorsed by the UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT). These are also listed in Table 1.

1.1.3 Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) were widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. They are referred to as additive flame retardants, because they were simply blended with the product. This makes them more prone to volatilise into the atmosphere during the product lifetime and waste processing/recycling. They reduce fire hazards by interfering with the combustion of the polymeric materials. Their general structure is $C_{12}H_{10-n}Br_nO$ (n=1-10) (Figure 4). Therefore, there are 209 possible PBDE congeners, depending on the position of the bromine atoms on the phenyl rings. Three different types of commercial PBDE formulation have been produced with different degrees of bromination, namely penta-, octa- and deca-BDE products. The penta-BDE product contains a range from tetra to hexa-BDE congeners, the octa-BDE contains a mixture of hexa- to deca-BDE and the deca-BDE contains predominantly the BDE-209 congener and is currently the most widely used PBDE flame retardant product.

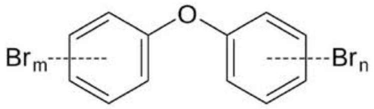

Figure 4. Basic structure of PBDEs

The global demand for PBDEs has previously been very substantial with a peak estimation of 70,000 tonnes for the year 2003 (Hites, 2004). Abbasi et al. (2019) estimated cumulative historical productions of commercial penta-, octa-, and deca-BDE mixtures to be ca. 175, 130, and 1600 kilotonnes, respectively. Of these technical mixtures, the commercial pentabromodiphenyl ether (PeBDE) and commercial octabromodiphenyl ether (OctaBDE) mixtures have been banned in the EU and Japan and were added in 2009 to Annex A of the Stockholm Convention during the 4th Conference of Parties (COP). The addition of deca-BDE followed in 2017.

Congeners BDE 47 and BDE 99 account for approximately 72% of the composition of the penta commercial mixture (PeBDE). In the UK there has been previously relatively high use of PeBDE compared to other European countries as a result of particularly stringent fire retardancy regulations for furniture, although on a worldwide scale the vast majority of PeBDE consumption took place in North America (Abbasi et al., 2019). The PeBDE commercial mixture was added to both flexible and solid polyurethane foams., with flexible foams for example used in car interiors (headrests, ceiling), furniture, carpets, and bedding (Prevedouros et al., 2004). Atmospheric emission estimates for 2012 for the tetra and penta-PBDEs in the UK were 800 kg. Lower brominated PBDEs can also be formed from the degradation (debromination) of higher brominated BDEs, although the environmental importance of this process is still unclear.

1.1.4 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are formed through incomplete combustion of carbon-containing fuels from industrial, commercial, vehicular, and residential sources (Wild and Jones, 1995) as well as forest fires (Campos and

Abrantes, 2021). In addition, previously deposited PAHs held in soil and vegetation compartments may also re-volatilise into the atmosphere (secondary emission) (Becker et al., 2006).

PAHs have been determined to be highly toxic, mutagenic, carcinogenic, teratogenic, and immunotoxicogenic to various life forms (Patel et al., 2020), with benzo[a]pyrene (B[a]P) being the PAH most harmful to human health (Brown et al., 2013). Figure 5 shows the NAEI timeseries of UK emissions of B[a]P (https://naei.beis.gov.uk/reports/). Total emissions have declined substantially from 35 tonnes in 1990, but have levelled out before increasing slightly in recent years to 8 tonnes of total emissions in 2019.

Not all PAHs are considered bioaccumulative, but because of their toxic, persistent, and semi-volatile properties, they were included in the UN/ECE Convention on Long-Range Transboundary Air Pollution 1998 Protocol on Persistent Organic Pollutants (POPs), which entered into force in 2003 (Meijer et al., 2008).

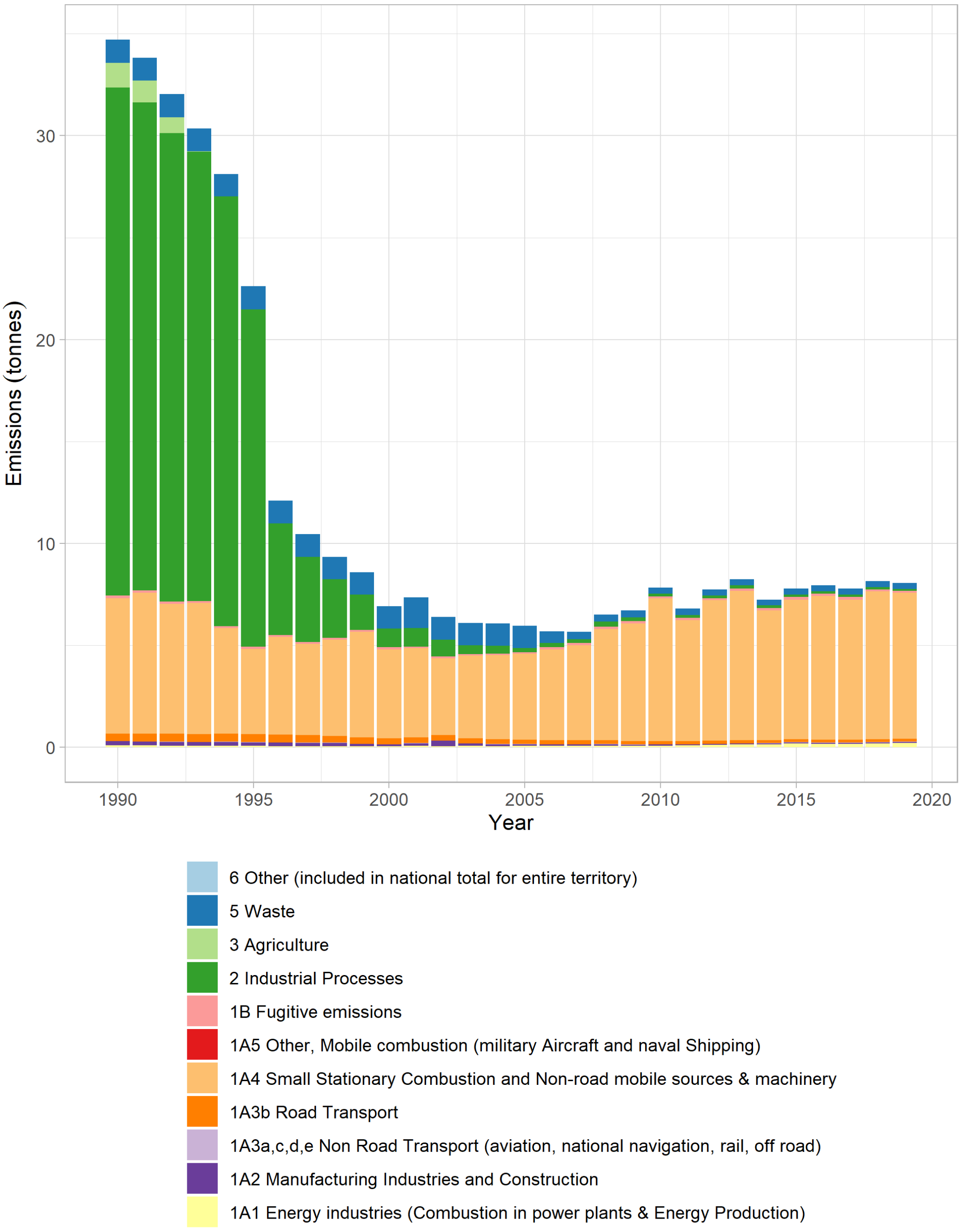

Figure 5. UK emissions of Benzo[a]pyrene (B[a]P). Figure by Churchill et al. (2021).

1.1.5 Organophosphate esters (OPEs)

Organophosphate esters (OPEs) are organic esters of phosphoric acid, containing either alkyl chains or aryl groups, and they may be halogenated or nonhalogenated

(Blum et al., 2019). They are widely used as additive flame retardants (chloralkyl and aryl phosphates) as well as stabilisers, plasticisers and antifoaming agents (alkyl phosphates) (van der Veen and de Boer, 2012; Yang et al., 2019) They are included, for example, in PVC and other plastics, electronic equipment, furniture (especially polyurethane foams), construction materials, textiles, lubricants, hydraulic fluids, and floor polishes. Production and application of OP flame retardants (OPFRs) has increased substantially after the ban and phase-out of penta-, octa, and deca-BDEs, and several OPEs count as high production volume (HPV) chemicals.

Like PBDEs, which they have replaced in recent years, OP flame retardants and plasticisers are generally emitted into the environment by abrasion, leaching, and volatilisation. Since they are semi-volatile organic compounds (SVOCs), high concentrations have been reported in indoor air and dust samples (Greaves and Letcher, 2017). They are also regularly found in water, sediments, soil, ambient air, biota, and human blood and milk, amongst others. Although OPEs were generally not expected to undergo long-range atmospheric transport, their occurrence in samples from remote areas has been reported, which has been attributed to atmospheric transport (Vorkamp et al., 2019).

OPEs are not considered persistent organic pollutants (POPs), as their potential to bioaccumulate through food chains is comparatively low (Du et al., 2019) They are, however, known to be relatively stable and resistant to biodegradation and some OPEs have been classified as carcinogenic and/or toxic or neurotoxic. In 2017, the U.S. Consumer Product Safety Commission (CPSC) accepted a petition to ban furniture, children's products, electronic enclosures, and mattresses containing any member of the class of organohalogen flame retardants (Blum et al., 2019).

1.2 Important international regulations on toxic organic pollutants

1.2.1 The Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention (SC) on Persistent Organic Pollutants (http://www.pops.int/), which was adopted in 2001 and entered into force in 2004, is a global treaty to protect human health and the environment from POPs, and requires parties to adopt and introduce measures to eliminate and/or reduce releases of POPs into the environment (US EPA). with the aim of minimising human and wildlife exposure.

The SC aims to protect human health and the environment from persistent chemicals that have become widely distributed geographically, accumulate in food chains and have demonstrable adverse health effects to humans and the environment. These substances have been connected to serious health effects including certain cancers, and immune and reproductive impairment. Given their ability to undergo long-range transport, either via air, ocean currents, or migrating species, these substances represent a global issue that requires global agreements to ensure exposure to these substances is minimised, as unilateral action is unlikely to be effective for these substances.

On the Convention's inception, a number of substances were selected for inclusion that clearly fulfilled any definition of POPs, i.e. persistent in all environmental compartments, bioaccumulative, toxic, and with the ability to undergo long-range transport and hence contaminate remote environments such as the Arctic. Twelve POPs, the so-called 'Dirty Dozen' were initially listed in the Stockholm Convention under three Annexes. They are aldrin, chlordane, dichlorodiphenyl trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The Annexes relate to the intended method of controlling their release – Elimination (Annex A), Restriction (Annex B), or

Unintentional Production (Annex C). The goal with regard to Annex C chemicals is to continually minimise, and where feasible eliminate, unintentional releases.

Eighteen additional chemicals have since been added to the Annexes of the Convention, including hexabromocyclododecane (HBCDD), lindane, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) and its salts, and polybrominated diphenyl ethers (PBDEs), and new chemicals can be added to the treaty in the future based on a scientific review procedure. POPs listed under the Annexes fall into three broad categories: a) pesticides, b) industrial chemicals such as PCBs (used as coolants and lubricants in transformers, capacitors, and other electrical equipment and in hydraulic fluids) and PBDEs (flame retardants) and c) unintentional by-products of combustion and industrial and non-industrial processes, for example PCDDs and PCDFs (UNEP, 2021).

More recently, substances have been discussed by parties to the SC that are less clearly defined as POPs. A number of ‘emerging’ environmental substances have been detected in the environment, which has raised some concerns as to whether some may be considered as POPs. The detection of such substances in the environment, whilst maybe undesirable, does not necessarily suggest they may be POPs and so a detailed assessment against the defined criteria of persistence, bioaccumulation and toxicity is required.

The SC is governed by the Conference of the Parties (COP), who meet every two years in Geneva, Switzerland. The Persistent Organic Pollutants Review Committee (POPRC) is a subsidiary body to the SC, which was established to review chemicals proposed for inclusion in the Annexes of the Convention. If a substance is deemed to meet the POP criteria, it can be listed in Annex A (elimination), Annex B (restriction), and/or Annex C (unintentional by-products). Candidate POPs can be proposed by any Party by submitting a dossier with specific information about the substance, as described in Annex D of the Convention. Information on chemical identity, environmental persistence, bioaccumulation and the potential for long-range transport and adverse effects are included in the dossier. If the POPRC is satisfied that these screening criteria have been fulfilled, then Parties to the

Convention, along with industry, observers, and NGOs are invited to submit data and information to develop a risk profile. The information requirements are laid out in Annex E of the Convention. The risk profile details information on production, uses, and emissions along with a hazard assessment for affected endpoints, an environmental fate profile, monitoring data if available, and any assessment of exposure occurring as a result of long-range transport. Details of any national or international risk assessments or evaluations can also be included. If the Committee decides that, based on the risk profile, the proposal should proceed, then a risk management evaluation is prepared based on a socio-economic assessment into the potential effects of any production or use restrictions. This procedure is laid out in Annex F. Once the risk profile and risk management evaluation are adopted, then the POPRC can make recommendations to the COP for listing of the chemical in Annexes A, B and/or C.

Article 16 of the Stockholm Convention requires the Conference of the Parties to evaluate periodically whether the Convention is an effective tool in achieving the objective of protecting human health and the environment from persistent organic pollutants. This evaluation is based on comparable and consistent monitoring data on the presence of POPs in the environment and in humans, as well as information from national reports containing information on the measures taken by a Party in implementing the Stockholm Convention, and which provide quantitative information on the effectiveness of such measures in meeting the objectives of the Convention.

As a result of being a Party to the Stockholm Convention, signatories have a number of obligations. These obligations include providing emission inventories, which identify key sources of these substances to the environment, but also can be used to quantify trends in release estimates and the successful control of sources. These emission estimates are multi-media (i.e. air, water and soil) and, along with multi-media environmental fate models, can be used to provide a detailed understanding of the key environmental processes and sinks that may affect the long-term fate of the listed chemicals. Measurement campaigns and long-term monitoring data can also be utilised in conjunction with models to provide additional information on the fate of POPs in the environment. Every five years, signatories to the SC have to submit a National Implementation Plan (NIP), which details the countries' progression and activities for undertaking their obligations. The last UK NIP was submitted in 2017 (Defra, 2017).

Emissions of POPs including PCDD/Fs, PCBs and PBDEs, have been monitored and reported to the Department for Environment, Food and Rural Affairs (Defra) by Lancaster University through the Toxic Organic Micro-Pollutants (TOMPs) air monitoring programme since 1991. The UK recognises that it is important to continue to provide long-term data to ensure that existing controls are sufficient to continue reductions in environmental exposure, but also believes that there is a need to develop strategies to address the 'new' chemicals that are being added to the Convention Annexes. Hence the UK will be developing work around selecting and monitoring some of the recently listed POPs (Defra, 2017).

1.2.2 UN/ECE Protocol on POPs

The Executive Body to the UN/ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) adopted the UN/ECE Protocol on POPs in 1998 in Aarhus, Denmark (UN/ECE Convention on Long-Range Transboundary Air Pollution, 1998). The UN/ECE Protocol on POPs focuses on a list of 16 substances comprising eleven pesticides, two industrial chemicals and three unintentional by-products. The ultimate objective is to eliminate any discharges, emissions and losses of these POP substances.

The UN/ECE Protocol on POPs bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (dichlorodiphenyl-trichloroethane (DDT), heptachlor, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs)). In addition, the UN/ECE Protocol on POPs also severely restricts the use of hexachlorocyclohexane (HCH), including lindane. The Protocol also includes provisions for dealing with the wastes of products that will be banned and it obliges Parties to reduce their emissions of PCDD/Fs, polycyclic aromatic hydrocarbons (PAHs), and HCB below their levels in 1990 (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous, and medical waste, it lays down specific emission limit values.

In 2009, Parties to the Protocol on POPs adopted decisions to amend the Protocol to include seven new substances: hexachlorobutadiene, octabromodiphenyl ether, pentachlorobenzene, pentabromodiphenyl ether, perfluorooctane sulfonic acid (PFOS), its salts and other derivatives, polychlorinated naphthalenes, and short-chain chlorinated paraffins. Furthermore, the Parties revised obligations for DDT, heptachlor, HCB, and PCBs as well as certain emission limit values (ELVs) from waste incineration, sinter plants, and electric arc furnaces for secondary steel production.

1.2.3 European Commission POPs regulation – (Regulation (EC) No 850/2004)

The European Commission ratified the Stockholm Convention in 2004 and adopted the POPs regulation 850/2004 in order to ensure compliance with both the Stockholm Convention as well as the UN/ECE POPs protocol. The Annexes of the Regulation have been updated by Commission Regulations 756/2010/EU and 757/2010/EU. However, in some respects the POPs Regulation goes further than these agreements with the aim to eliminate the production and use of the internationally recognised POPs. For those POPs listed in Annex C (unintentionally produced POPs) the POPs Regulation discusses approaches that can be adopted to, either directly or indirectly, reduce the emission of these substances. These measures are set out in the Directive on industrial emissions 2010/75/EU (IED).

1.2.4 REACH (Regulation (EC) No 1907/2006)

The Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (1907/2006) aims to protect human health and the environment by establishing procedures for collecting and assessing information on the properties and hazards of substances and thus ensuring greater safety in the production and use of all chemical substances. Companies are required to identify and manage the risks linked to the substances they manufacture and sell in the EU, and send this information to the European Chemicals Agency (ECHA) in Helsinki for registration in a database. They must also demonstrate the safe use of the substances, and communicate the risk management measures to users. Unregistered substances may not be manufactured in the EU or imported into the EU, ensuring that industrial chemicals with POP characteristics, i.e. properties of persistence, bioaccumulation and toxicity, are identified and prevented from being produced or imported in the EU (https://echa.europa.eu/regulations/reach/understanding-reach).

1.3 Air sampling

There are two types of air sample collection techniques for toxic organic pollutants in ambient air: active air sampling (AAS), which involves pulling air through a sorbent trap with an electric pump, and passive air sampling (PAS), where analytes are collected on sorbent material mainly by diffusion, without the need for electricity (Hung et al., 2013).

1.3.1 Active air sampling

Active air samplers (AAS) are the most accurate method for POPs ambient air sampling, as they accumulate both gas and particle phase compounds under a controlled flow (Melymuk et al., 2014), resulting in calibrated air sample volumes. Air sampling can be carried out as either high-volume sampling, with typical air flow rates between 15 and 80 $m^3 h^{-1}$, and low-volume sampling with flow rates below 3 $m^3 h^{-1}$ (Melymuk et al., 2014), with the former usually, but not always, resulting in higher total air volumes of several 100 m^3, and the latter of less than 200 m^3, depending on the duration of deployment, which is commonly between hours and a few weeks.

For the projects in this thesis, Tisch Andersen GPS-1 samplers with PM10 heads were used (Figure 6), which exclude any particles larger than 10 µm. Glass fibre filters (GFFs) were used for sampling particle-bound contaminants, and polyurethane foam (PUF) plugs as sorbent for gaseous contaminants. Two PUF plugs were inserted into a glass tube, and both the glass tube and the GFF inserted in a so-called ‘module’, as depicted in Figure 7. The assembled module was mounted on top of the active air sampler, below the sampling head (Figure 8). During sampling, air was pulled in through the sampling head and then through the GFF first and two PUF plugs next, before leaving the sampler at the bottom.

Figure 6. Andersen GPS-1 sampler with PM10 head.

Figure 7. Active air sampling ‘module’ and schematic placement of the sampling media (one GFF and two PUFs). Source of the photo: https://tisch-env.com/product-category/filter-holders-puf-modules-and-cartridges/

Figure 8. The sampling module is mounted on top of the active air sampler, below the sampling head.

1.3.2 Passive air sampling

Because they need no power source and little maintenance, passive air samplers (PAS) provide a cost-effective way of collecting long-term and time-integrated data on air pollution (Gioia et al., 2006) and thus play an important role in fulfilling obligations of international chemicals regulations such as the Stockholm Convention and the UN/ECE Protocol on POPs. Currently, most widespread in use are polyurethane foam (PUF) disks, sorbent-impregnated polyurethane foam (SIP) disks, and semipermeable membrane devices filled with triolein (SPMDs). Deployment periods for PAS are usually between weeks and years.

To utilise passive air samplers for quantitative measurement of the air concentration, the sampling rate R (for linear uptake) or the PAS-air partition coefficient, $K_{PAS\text{-}Air}$, (under equilibrium conditions) have to be established. The sampling rate is specific to the type of sampler (e.g. sorbent, sampler housing) and the environmental conditions (Melymuk et al., 2014). Unlike active air samplers, passive air samplers mainly sample the gaseous fraction of atmospheric pollutants.

In the studies for this thesis, PUF disk passive samplers (PUF-PAS) as well as SPMDs were used. In order to protect the sorbent from environmental conditions, but also to limit their impact on sampling rates, the samplers were deployed in protective housing. For PUF-PAS, this housing consisted of two stainless steel bowls, a wider top one and a smaller bottom one, and the PUF disk was attached to a vertical central rod and positioned in the small gap between the bowls. The assembly was then attached to a pole or rope and deployed at ca. 1-1.5 m height (Figure 9).

Figure 9. Several PUF-PAS are deployed in parallel, protected by their housing made of stainless-steel bowls.

SPMDs were mounted on metal carriers (‘spiders’, Figure 10) and placed inside a protective Stevenson screen housing (Figure 11).

Figure 10. Two SPMDs are mounted onto metal carriers (‘spiders’).

Figure 11. SPMDs are deployed in Stevenson screen housing for protection.

1.4 Thesis structure

Long-term air monitoring networks provide important spatial information and trend data for a range of historical and emerging environmental contaminants and do not only provide valuable insights into their environmental fate and transport, but also deliver data that can be used to inform the Stockholm Convention and other regulators on the effectiveness of any regulatory measures for these contaminant. Furthermore, they have a potential to give early warning on the increased appearance of chemicals of emerging concern, if the sampling and analytical methods are prepared for them, or to retrospectively determine time trends for these chemicals from archived samples.

With the UK TOMPs ambient air monitoring Network and the UK/Norway SPMD air sampling transect, this thesis presents two of the worldwide longest-running continuous ambient air monitoring programmes. Additional to reporting on trends in legacy POPs concentrations derived from these networks and further projects, and using these data to help a) further our knowledge of environmental behaviour of POPs and b) assess the effectiveness of their regulation, this work also aims to evaluate those programmes themselves and make suggestions to improve their performance for current and future compounds of interest.

One important aspect of long-term monitoring programmes is to guarantee the comparability of the data over the whole duration of the programme to make sure that any time trends visible in the data are not just an artefact of changes in the methodology. This means that any improvements to the methodology must be carefully considered and tested, to make sure that they do not negatively impact other aspects of the dataset. This is especially true for changes to the sampling method, as this is something that cannot be changed or added to retrospectively, unlike new analytical methods, which can be applied to archived samples a long time after they have been taken. On the other side, a change in the sampling method may be necessary when new compounds of interest, like for example lighter PCBs or OPEs, need to be integrated into the monitoring programme. As part of this thesis, two possible improvements to the current networks are being evaluated: 1) the addition of a new sampling medium (XAD® resin) to the existing sampler to expand the range of contaminants that can be sampled in parallel, 2) the introduction of a new group of performance reference compounds (PRCs), added to the sampler before deployment, that would allow for more flexibility in the analytical method and improve the interpretation of the dataset.

The structure of this thesis is as follows:

Chapter 2: The TOMPs Ambient Air monitoring Network – continuous data on the UK air quality for 20 years provides a summary of the long-term time trends for POPs in UK ambient air, which were obtained from the TOMPs Network using high-volume active air sampling, and compares results with recent emission estimates. **Chapter 3: Further insights into regional and seasonal variations in PCB and PBDE concentrations in UK ambient air** adds additional details to Chapter 2. In **Chapter 4: Analysing a wide range of toxic organic pollutants in ambient air using a novel sampling technique**, a variation of the air sampling equipment used in the TOMPs Network is evaluated, with the aim to sample a wider range of compounds with standard high-volume air samplers. These improved samplers have the potential to not only improve sampling efficiency for a number of more volatile chemicals currently included in the Annexes to the Stockholm Convention, but also to easily include future new additions to the Stockholm Convention in the TOMPs Network. **Chapter 5: Short-term variations in POPs in ambient air: The 'Bonfire Project'** describes the impact of short-term events like unsanctioned waste burning on POPs emissions into the UK atmosphere, using the example of the British 'Bonfire Night' festival. **Chapter 6: The UK/Norway SPMD transect** describes another long-term air monitoring project run by Lancaster University, this time using passive air sampling in the UK and Norway. Results of this transect are included in the Regional Monitoring Reports for Western Europe and Others Group (WEOG) Region to the Global Monitoring Plan (GMP) for Persistent Organic Pollutants under the Stockholm Convention. The GMP provides a harmonised organisational framework for the collection of comparable monitoring data on the presence of POPs from all regions, in order to identify changes in their concentrations over time, as well as on regional and global environmental transport. Finally, **Chapter 7: Monofluorinated PCBs (F-PCBs), a new group of potential performance reference compounds for passive air samplers** investigates the suitability of a newly developed group of synthesised chemicals to be used as performance reference compounds (PRCs) in passive air sampling. PRCs have widely been used in passive air sampling networks, including the UK/Norway SPMD transect, for in-situ calibration of the passive sampler sampling rate, and as such have helped to improve the quality of data derived from passive air samplers.

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2 The TOMPs Ambient Air monitoring Network – continuous data on the UK air quality for 20 years

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Abstract

Long-term air monitoring datasets are needed for persistent organic pollutants (POPs) to assess the effectiveness of source abatement measures and the factors controlling ambient levels. The Toxic Organic Micro Pollutants (TOMPs) Network, which has operated since 1991, collects ambient air samples at six sites across England and Scotland, using high-volume active air samplers. The network provides long-term ambient air trend data for a range of POPs at both urban and rural locations. Data from the network provides the UK Government, regulators and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation such as the Stockholm Convention and UN/ECE Protocol on POPs. The target chemicals of TOMPs have been polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and, since 2010, polybrominated diphenyl ethers (PBDEs). The continuous monitoring of these compounds has demonstrated the constant decline in UK air concentrations over the last two decades, with average clearance rates for PCDD/Fs in urban locations of 5.1 years and for PCBs across all sites 6.6 years. No significant declines in rural locations for PCDD/Fs have been observed. There is a strong observable link between the declining ambient air concentrations and the emission reductions estimated in the annually produced National Atmospheric Emission Inventory (NAEI) dataset. These findings clearly demonstrate the unique strengths of long-term consistent datasets for the evaluation of the success of chemicals regulation and control.

Keywords Air monitoring, long-term, POPs, time trends, Stockholm Convention

2.1 Introduction

The Stockholm Convention (SC) on POPs was adopted in 2001 and entered into force in 2004 (UNEP, 2001). The SC aims to protect human health and the environment from persistent chemicals that have become widely distributed geographically, accumulate in food chains and have demonstrable adverse health effects to humans and environment. These substances have been connected to serious health effects including certain cancers, and immune and reproductive impairment. Given their ability to undergo long-range transport, either via air, ocean currents or migrating species, these substances represent a global issue that requires global agreements to ensure exposure to these substances is minimised. Unilateral action is unlikely to be effective for these substances. On the Convention’s inception a number of substances were selected for inclusion that clearly fulfilled any definition of POPs, i.e. persistent in all environmental compartments, bioaccumulative, toxic and with the ability to undergo long-range transport and hence contaminate remote environments such as the Arctic. These included the so-called 'classic' POPs such as the polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT). However, more recently substances have been discussed by parties to the SC that are less clearly defined as POPs. A number of 'emerging' environmental substances have been detected in the environment, which has raised some concerns as to whether some may be considered as POPs. The detection of such substances in the environment, whilst undesirable, does not necessarily suggest they may be POPs and so a detailed assessment against the defined criteria of persistence, long-range transport potential, bioaccumulation toxicity is required.

Parties to these international agreements, including the Stockholm Convention and Aarhus Protocol on POPs under UN/ECE (1998) must take measures to reduce or eliminate releases, to develop an implementation plan and – within their capabilities – encourage and/or undertake appropriate research and monitoring pertaining to POPs. Under the latter category, 'sources and releases into the environment', 'presence, levels and trends in the environment' and 'environmental transport, fate and transformation' are all specifically mentioned. These include robust multi-media source inventories for POPs such as dioxins and PCBs along with long-term air monitoring to ensure that source control measures result in demonstrable reductions in ambient air concentrations, which are central to the fulfilment of signatory parties' international obligations.

The Toxic Organic Micro Pollutants (TOMPs) Network, which has operated since 1991, collects ambient air samples at six sites across England and Scotland, using high-volume active air samplers. The network, which is operated by Lancaster University and funded by the UK Department for Environment, Food and Rural Affairs (Defra), provides long-term ambient air trend data for a range of persistent organic pollutants (POPs) at both urban and rural locations. Data from the network provides Defra and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation. It is also used to demonstrate UK compliance with its obligations under the Stockholm Convention and UN/ECE Long-Range Atmospheric Transport Protocol. Moreover, long-term analysis of air pollutants at trace levels allows detailed studies on atmospheric fate and behaviour processes of persistent chemicals and is the inevitable basis of the successful understanding and modelling of their environmental fate. The target chemicals of TOMPs since its inception have been polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and, since 2010, polybrominated diphenyl ethers (PBDEs). PCBs, PCDDs, PCDFs are listed in Annex A (elimination) and C (unintentional release) of the Stockholm Convention, whilst selected PBDEs are listed in Annex A. This paper explores some of the key outcomes from the TOMPs monitoring network for these compounds and discusses the factors controlling the apparent constant decline in their UK air concentrations. The PAH data collected as part of the TOMPs network, and now incorporated into a larger PAH network, has been reported by Brown et al. (2013) and so will not be discussed in detail in this paper. It is clear that long-term monitoring programmes, such as TOMPs, are key to quantitatively assessing the success of regional and global chemical controls and regulations. However, the ongoing operation of such networks faces many challenges in the future, which are inevitably resource limited, but required to provide data on the long-term ambient air concentrations for an increasing list of substances.

2.2 Materials and methods

2.2.1 TOMPs sites and sampling methodology

Measurements of POPs and PAHs commenced in 1991 when the UK TOMPs network was established with four monitoring stations in urban locations: London, Manchester, Cardiff (University of Cardiff) and Stevenage. The Cardiff and Stevenage stations closed in 1992 and 1993, respectively, and new stations were installed in 1992 at Hazelrigg (a semi-rural location) and Middlesbrough (an urban location). By the start of 1997, the number of monitoring stations had increased to six by the inclusion of two rural stations – Stoke Ferry and High Muffles. At the rural and semirural (Hazelrigg) sites, samplers were located away from major roads, whereas at the urban sites, samplers were located in the city centre on the roof of a building. The site at Stoke Ferry was shut down at the beginning of 2008 and the site at Middlesbrough was phased out to coincide with the redevelopment of the site during 2007. A new TOMPs site was established at Auchencorth Moss, an upland remote peat site close to Edinburgh. This site, operated by CEH (Centre for Ecology and Hydrology) Edinburgh, is part of the Heavy Metal Network and of the European Monitoring and Evaluation Programme (EMEP) network of superstations. These high quality EMEP stations have extended measurement programmes, detailed documentation and trained technical staff. This site is an ideal TOMPs site as it represents a rural/remote location and is likely to be removed from the influence of local sources. Auchencorth Moss started operating in 2008. In order to replace the Stoke Ferry sampler, a new site was established at the University of East Anglia's Weybourne Atmospheric Observatory (WAO), a rural coastal site. This site is approximately 60km to the north east of Stoke Ferry and is an established facility at which fundamental atmospheric research and background air quality monitoring is carried out. Thus, the selection of sites included large urban conurbations, semi-rural locations (rural sites but influenced by nearby towns and transport infrastructure) and rural/remote sites and was believed to be representative of such locations across the UK. However, the undue influence of local sources cannot be completely ruled out.

Currently the TOMPs programme operates 6 sites across England and Scotland (Table 2).

Table 2. Current and discontinued TOMPs air monitoring sites in the UK

Current sites		
London	LON	urban site established in 1991
Manchester	MAN	urban site established in 1991
Hazelrigg (Lancashire)	HR	semi-rural site established in 1992
High Muffles (North Yorkshire)	HM	rural site established in 1997
Auchencorth Moss (Midlothian)	AUCH	rural site established in 2008
Weybourne (Norfolk)	WEY	rural coastal site established at the end of 2008
Discontinued sites		
Stoke Ferry (Norfolk)	SF	rural site established at the end of 1997. Ceased operation in 2007 (transferred to WEY).
Middlesbrough	MID	urban site established at the end of 1993. Ceased operation in 2008.

A map displaying the sampling site locations is shown in Figure 12. Since its inception, the TOMPs network has used Andersen GPS-1 samplers with PM10 size-selective inlets. The samplers are run continuously with samples collected every 2 weeks. This provides sampled air volumes of approximately 700 m^3. Modules, which are prepared just prior to deployment, consist of pre-baked (450 ºC for 4 hours) GF/A glass fibre filters and two 7.5 cm by 5 cm PUF plugs. In addition, sample information and temperature data are recorded, airflows adjusted, data loggers exchanged and preventative maintenance carried out when necessary. The time during which the sampler operates is recorded with a timer, and the flow rate determined using the flow venturi and MagnaHelic gauge. Each sampler is also fitted with a pressure transducer and a data logger that records the pressure drop during the sampling period, so that the sampling rate can be accurately determined. These loggers are monitored remotely to ensure sampling continues with minimal interruption.

Figure 12. Location of TOMPs sampling sites since 1991

2.2.2 Analytical methodology

Details of the analytical procedure are contained in Schuster et al. (2010b) and Katsoyiannis et al. (2010). In summary, each sample is spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners ($^{13}C_{12}$-PCB 28, 52, 101, 138, 153, 180, 209), the PBDE congeners BDE 51, BDE 128, and BDE 190, and 21 $^{13}C_{12}$-labelled PCDD/Fs and coplanar PCBs. Samples are individually extracted in a soxhlet extraction unit for 16 hours with hexane and 6 hours with toluene. PAHs, PCBs, PBDEs, and tri-, tetra- and penta-PCDD/Fs (PCDDs and PCDFs) are extracted in the hexane fraction. The remaining PCDD/Fs are extracted in the toluene fraction. The hexane and toluene fraction are combined for each sample and extracts pooled before purification to obtain three-monthly averaged data. The extracts are then eluted through a multilayer column containing activated silica, basic silica and acid silica. If necessary, this is followed by acid digestion (H_2SO_4) and a second multicolumn elution. After elution through a gel permeation chromatography (GPC) column PCB and PBDE fractions are analysed by gas chromatography - mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM). Afterwards, the extract is fractionated with a basic alumina column. The analysis of the PCDD/Fs and co-planar PCBs is performed on a high-resolution gas chromatography – high-resolution mass spectrometry instrument (HRGC-HRMS), operated at a resolution of at least 10,000.

QA/QC. A number of steps are taken to allow an assessment of the accuracy and reliability of the data. PCB, coplanar PCB, PBDE, and PCDD/F recoveries are monitored in all samples by quantifying $^{13}C_{12}$-labelled PCB, coplanar PCB, and PCDD/F standards and unlabelled PBDE standards. Furthermore, the concentrations of all compounds are corrected using these recoveries. The criteria for the quantification of analytes are: a retention time found within 2s of the standard, isotope ratio found within 20% of the standard, and a signal-to-noise ratio of at least 3. All results are blank-corrected using laboratory and field blanks, which are produced for each site and each quarter, and, together with instrument blanks, are also used to calculate method detection limits (MDLs).

2.3 Results and discussion

The sampling methodology and analytical protocol used in the TOMPs network has been maintained since establishment of the sites, and has provided time-trend data for a range of POPs for over 20 years at some locations. This approach has provided a consistent dataset for dioxins and PCBs allowing the investigation of temporal trends and the assessment of the reduction of sources brought about by the introduction of regulations such as the SC. The TOMPs network provided PAH data from 1991 until 2012, but the sites have now been included in a wider PAH network. As these data over the last twenty years have been reported elsewhere (Brown et al., 2013), they will not be included here.

2.3.1 PCDD/Fs

Summary data for the sum of 17 PCDD/Fs from the six current TOMPs sites, calculated using the WHO 1998 toxic equivalent (TEQ) scheme, show a distinct urban-rural split. All the 17 PCDD/F target congeners were detected in varying concentrations over the sampling period with median concentrations for the urban sites ranging from 58 fgTEQ m^{-3} (MAN) to 20 fgTEQ m^{-3} (LON). The rural and semirural sites have notably lower ΣTEQ values ranging from 8.3 fgTEQ m^{-3} for HAZ, 4.8 fgTEQ m^{-3} for HM, 2.2 fgTEQ m^{-3} for WEY and 1.4 fgTEQ m^{-3} for AUCH. The WEY and AUCH sites have a much shorter time record than the other sites. Figure 13 is a box-and-whisker plot showing the range of concentrations (25th percentile and 75th percentile of the ΣTEQ PCDD/Fs, median and mean values) and outliers (Statistical data provided by StatPlus, AnalystSoft Inc.).

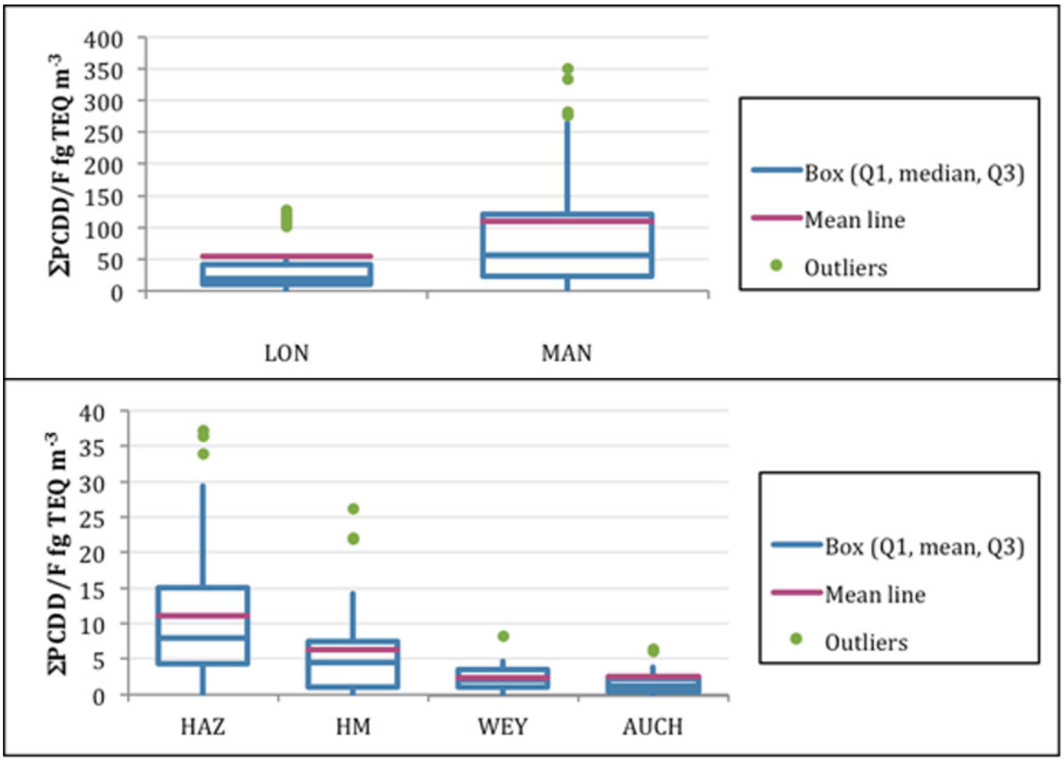

Figure 13. Box-and-Whisker plot of Σ fg TEQ/m3 PCDD/Fs at 2 urban sites (LON, MAN) and 4 rural/semi-rural sites (HAZ, HM, WEY, AUCH) (1990-2012). The purple line indicates the mean values, the blue box covers the lower and upper quartile and median values. Outliers are shown as green dots.

Seasonal variations. Seasonality of PCDD/Fs in ambient air, where winter values exceed summer values, has been widely reported in the literature (e.g. Katsoyiannis et al. (2010)). Increased combustion (i.e., domestic space heating) and seasonal variations in temperature and atmospheric boundary layer height are the likely causes. A subset of the TOMPs dataset (2004-2010) was analysed and seasonal variations were observed, and in some cases the differences between two consecutive quarters were >10-fold. Figure 14 summarizes the seasonal variations in averaged values for all sites. For most sites, the first and fourth quarter had the highest ΣTEQ values. For the urban sites MAN and MID, for example, the concentrations of PCDD/Fs were 2-3 times higher in the first and fourth quarter than during the warmer months. This observation suggests that when ambient concentrations are low (typically in rural areas), emission events such as bonfires or accidental fires (Lee et al., 1999) can exert a measurable influence on the levels and the PCDD/F pattern. Therefore, if an accidental emission event were to occur, the increase in PCDD/F concentrations would be more noticeable at rural sites, where concentrations are typically low during the year, than at urban sites where seasonal differences are more pronounced and dependent on local sources. Within this averaged dataset there are a few notable results. For example, the coastal/rural site at Weybourne produced a relatively high concentration of PCDD/Fs in Q1 2009 of 79 fgTEQ m^{-3}, which is similar to those levels measured in London. It is well known from the monitoring of other atmospheric contaminants (i.e., NO_x http://weybourne.uea.ac.uk/), that this site can receive 'polluted air' from the London area from time to time, and so this could explain the higher levels of pollutants observed at WEY in Q1 which is still evident in the 2004-2010 average. The site at Auchencorth Moss (AUCH) displays relatively low concentrations of PCDD/Fs in the same range to those measured in High Muffles, and occasionally exhibits levels that are even lower than these. Auchencorth Moss is located 20km to the south west of Edinburgh but appears to have very little influence from the city. This can be explained by the dominant wind direction being westerly to south westerly.

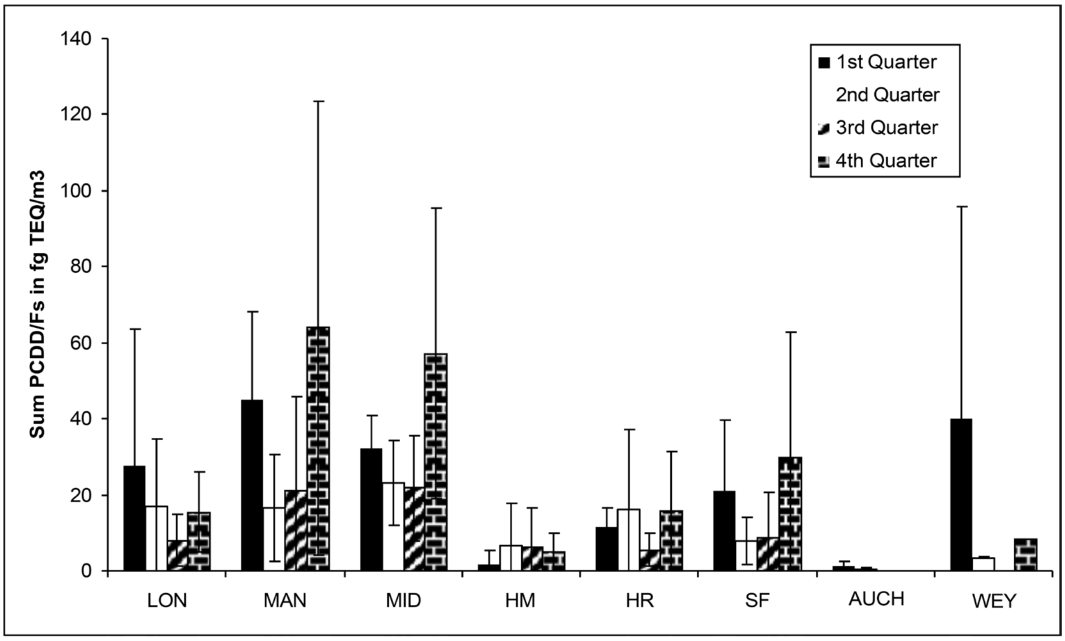

Figure 14. Sum of PCDD/Fs in fg TEQ/m^3 at all sites and quarters over the period 2004-2010. (LON London, MAN Manchester, MID Middlesbrough, HM High Muffles, HR Hazelrigg, SF Stoke Ferry, AUCH Auchencorth Moss, and WEY Weybourne).

Temporal Trends. Figure 15 shows the PCDD/F temporal trends for the combined urban and rural sites from the early 1990s to 2012 (expressed as pgI-TEQ m^{-3}). The data has been converted to the I-TEQ scheme to make a comparison with the emission estimates provided by the National Atmospheric Emissions Inventory (NAEI, https://naei.beis.gov.uk/). Applying first-order kinetics to the whole urban time series suggests that concentrations have been decreasing with atmospheric clearance rates for LON and MAN of 4.9 and 4.8 years, respectively. Estimated annual atmospheric emissions trends from the NAEI can be broadly correlated with the trends in urban ambient air concentrations, suggesting that the inventory has captured the broad mixture of sources, which are mostly from diffuse combustion processes. Rural air concentrations, which are generally much lower than urban concentrations, show no discernible change since 1996.

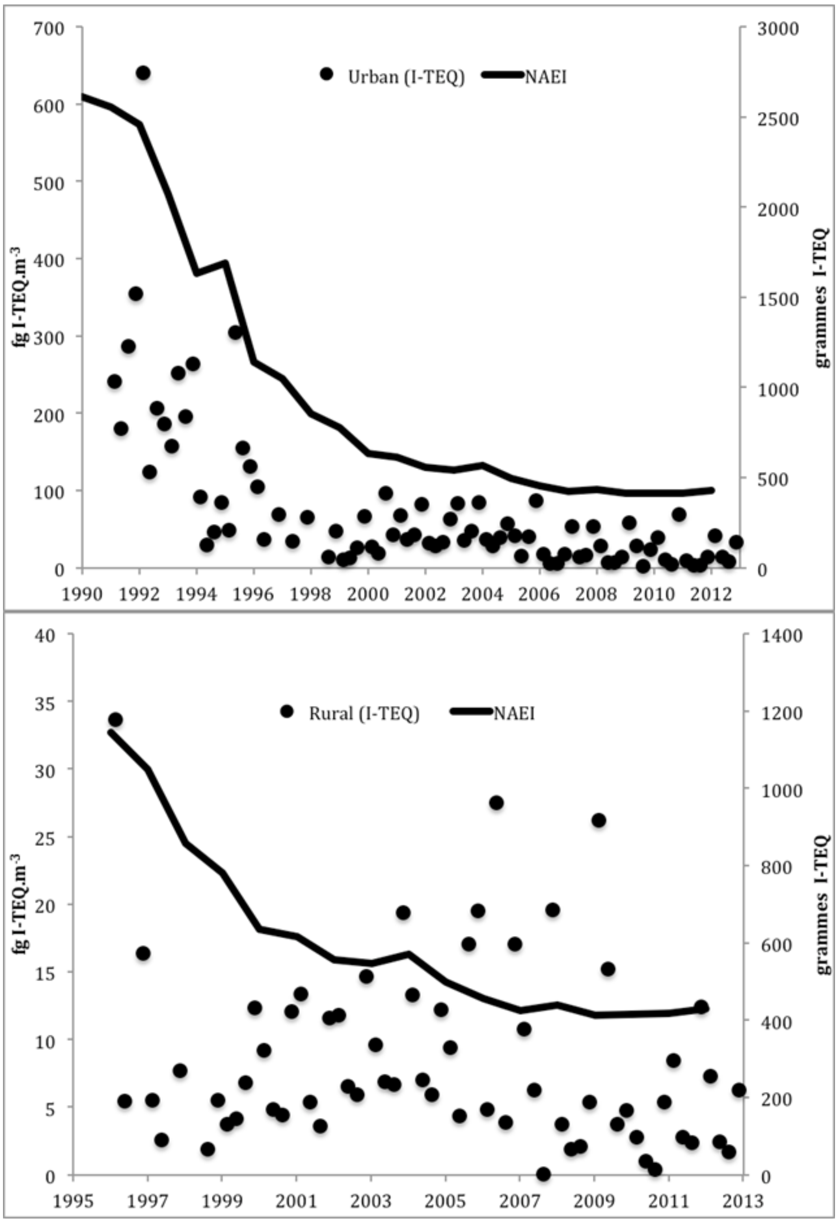

Figure 15. Temporal PCDD/Fs (fgI-TEQ/m^3) trend data for two urban and two rural TOMPs sites. NAEI – National Atmospheric Emission Inventory

The data also suggests that recent urban concentrations are now close to those in rural areas. These trends combined, together with observations of seasonal dependence, suggest that most major readily controllable primary/point sources were reduced by the early/mid-1990s in the UK and that current ambient air levels in both rural and urban areas may remain at broadly similar levels in the foreseeable future, unless there are major changes in energy requirements and generation options, fuel usage, or policy drivers.

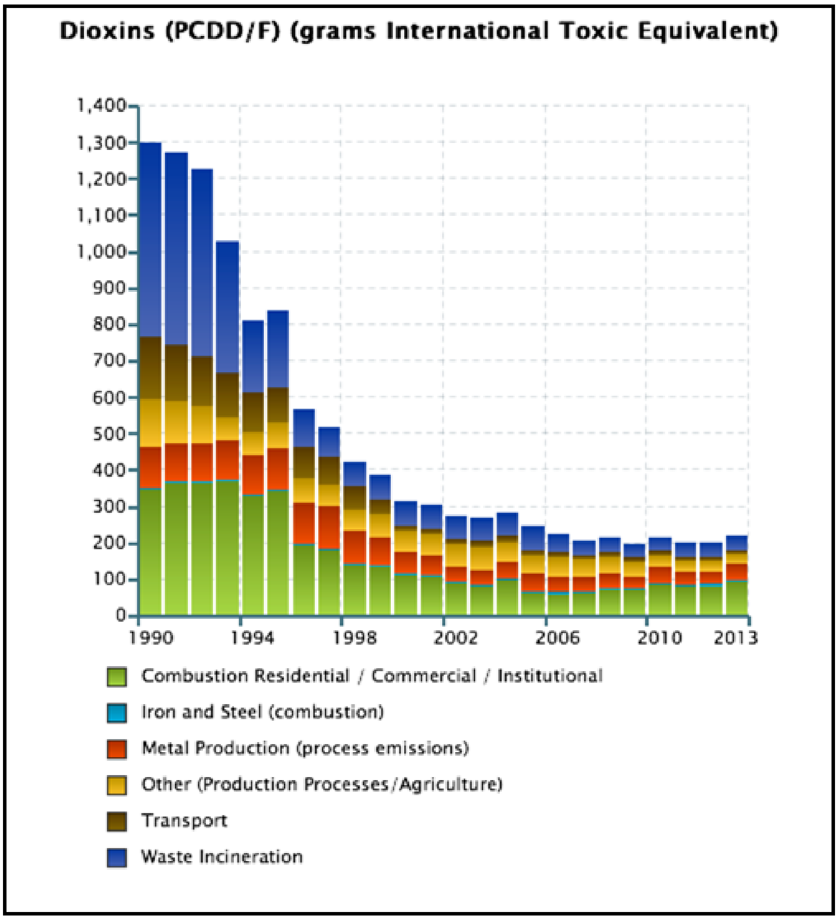

Figure 16. Atmospheric emission estimates for PCDD/Fs for the UK from 1990 to 2013 – National Atmospheric Emissions Inventory.

The NAEI emission estimates for the UK are shown in Figure 16 and clearly demonstrate the decline in UK PCDD/F emissions over the period 1990 to 2013. According to the inventory, PCDD/F emissions were around 1300 gI-TEQ per year in 1990, dropping to 222 gI-TEQ per year in 2013. The main emission reductions have resulted from controls introduced to the iron and steel industry during the 1990s. Katsoyiannis et al. (2010) combined the TOMPs dataset with estimates of

UK ambient air concentrations derived from archive herbage samples with the assumption that the levels found in grass would be reflective of UK ambient at the time the samples were collected. This longer-term perspective (from the early 1900s) provided some interesting insights into the potential controlling factors for PCDD/Fs in UK ambient air. This dataset suggests that ambient concentrations of PCDD/Fs have been steadily declining over the last few decades, with several regulatory measures identified that may have driven emissions down. These could have included the following: the UK Clean Air Act which came into force in 1956; reductions in organochlorine manufacture through the 1960-1980s; reductions in the use of halogenated lead additives in petrol in 1986 and 1992; the introduction of emission controls on municipal and chemical waste incinerators in the mid-1990s, and the general shift away from domestic burning of wood and coal for space heating to the more widespread adoption of electricity and gas. The PCDD/F declines so far indicate that the UN/ECE Protocol (1998) and the Stockholm Convention (2001) appear to have had little additional impact on the already declining ambient PCDD/F levels.

2.3.2 PCBs

Data for the sum of 7 PCB commonly reported congeners PCB 28, 52, 101, 118, 138, 153 and 180 (ΣPCB_7) from the six current TOMPs sites and the urban Middlesbrough site show a distinct urban-rural split. All PCB target congeners were detected in varying concentrations over the sampling period with median concentrations for the urban sites ranging between 141 pg m^{-3} (MAN) and 100 pg m^{-3} (LON). The rural and semi-rural sites have notably lower ΣPCB_7 values ranging from 34 pg m^{-3} for HAZ, 17 pg m^{-3} for HM, 16 pg m^{-3} for WEY to 12 pg m^{-3} for AUCH. The WEY and AUCH sites have a much shorter time record than the other sites. Figure 17 is a box-and-whisker plot showing the range of concentrations (25th percentile and 75th percentile of the ΣPCB_7, median and mean values) and outliers (Statistical data provided by StatPlus, AnalystSoft Inc.).

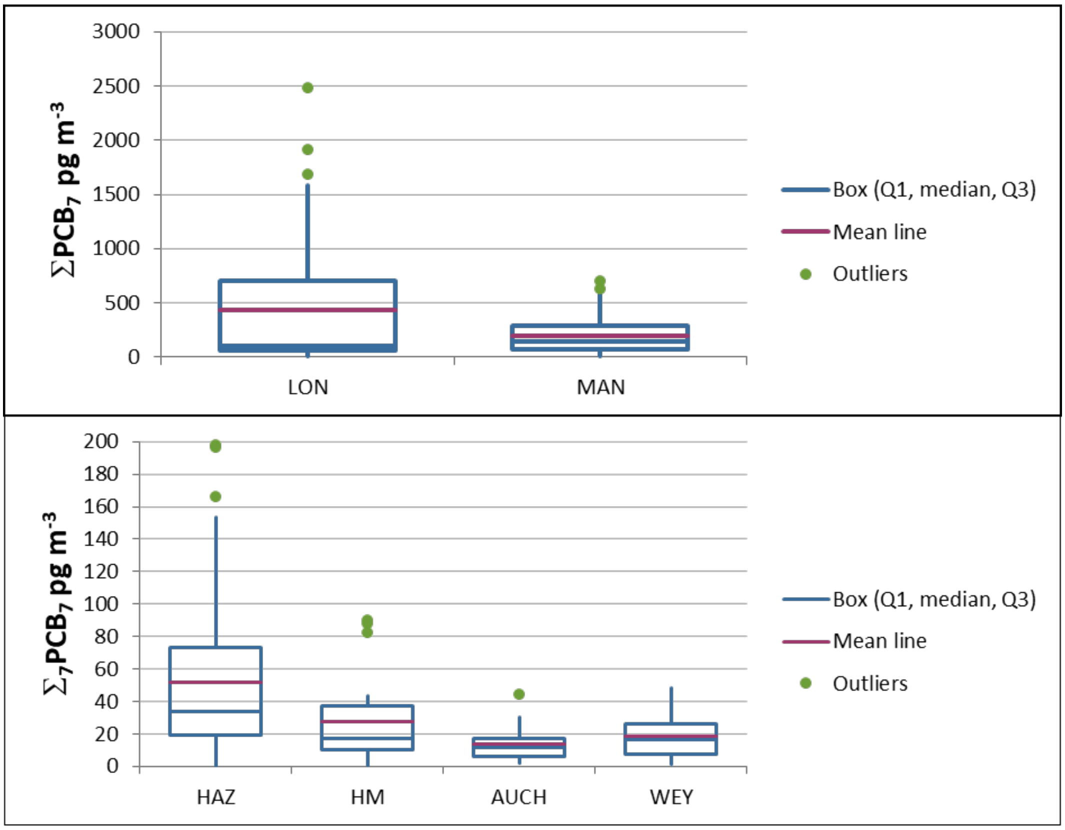

Figure 17. Box-and-Whisker plot of PCB concentrations (sum of congeners PCB 28, 52, 101, 118, 138, 153 and 180) across the TOMPs network showing two urban sites (LON, MAN) and four rural/semi-rural (HAZ, HM, WEY, AUCH) (1990-2012). The purple line indicates the mean values, the blue box covers the lower and upper quartile and median values. Outliers are shown as green dots.

Seasonal Variations. Various studies have reported and discussed strong seasonal trends in PCB air concentrations (Halsall et al., 1995; Melymuk et al., 2012). These observations, where PCB concentrations are generally higher in summer than in winter, can be confirmed by the data from the TOMPs programme. Chapter 3 explores further details on seasonal PCB variations in TOMPs samples. In short, at all sampling sites except for Auchencorth Moss, concentrations are generally highest in summer (Q3, July – September), followed by spring (Q2, April

– June) and autumn (Q4, October – December), with winter (Q1, January – March) showing the lowest concentrations. This pattern is in very good accordance with previous studies.

Temporal Trends. The quarterly ΣPCB_7 concentrations across the TOMPs network from the early 1990s are shown in Figure 18 for the combined urban sites and rural sites. It is clear that the temporal trend data from each site group shows decreasing concentrations, most demonstrating a statistically significant decrease over time. It is important to note that WEY and AUCH have operated over a shorter period of time compared to other sites. Applying first-order kinetics to the urban time series suggests that concentrations have been decreasing with atmospheric clearance rates for MAN, LON and MID of 6.6, 3.9, and 4.9 years, respectively. The rural and semi-rural sites have estimated clearance rates of 5.6 and 7.5 years, respectively. The recently established sites at Auchencorth Moss and Weybourne have not been running for sufficient time to determine trends. Figure 18 also shows the combined estimated annual atmospheric emissions trends from the NAEI. These can be broadly correlated with the trends in ambient concentrations (stronger for urban sites), suggesting that the inventory has probably captured the main ongoing sources. Data from a passive sampler network spanning the UK and Norway has provided similar clearance rates for UK rural sites, which ranged from 5.6 to 15.4 years (Schuster et al., 2010a).

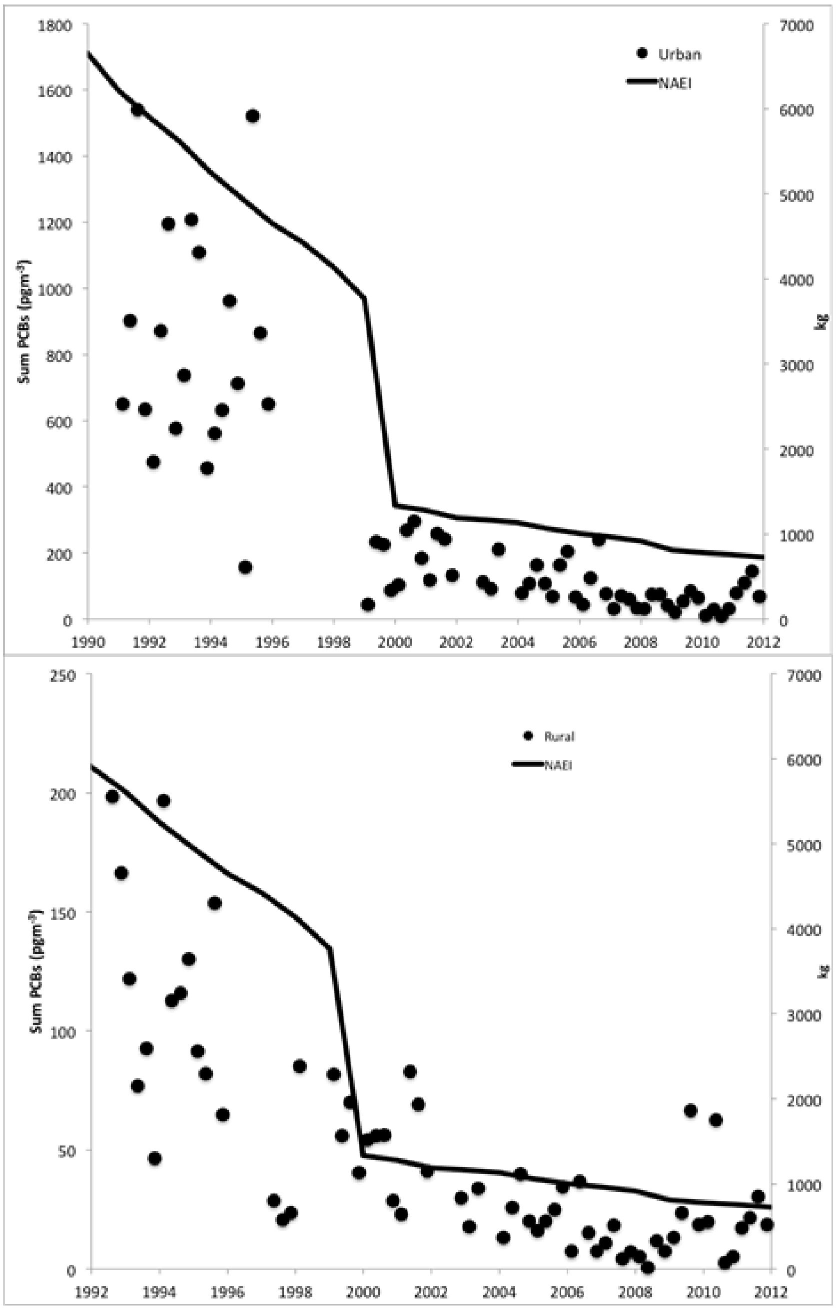

Figure 18. Temporal PCB trend data across urban (upper) and rural (lower) TOMPs sites overlaid with UK PCB emission estimates provided by NAEI. Left y-axis: air concentration ΣPCB_7 pg/m^3, right y-axis: atmospheric emission per year in kg.

A voluntary ban on production of PCBs in the UK was agreed with manufacturers in the late 1960s/early 1970s. Limits on emissions from incinerators, the handling of PCB-containing wastes etc. were applied from the late 1970/80s onwards. Key ongoing primary sources are believed to be the stocks from past use in transformers, capacitors, buildings/sealants etc. which are all potential diffusive primary sources to the atmosphere via volatilisation. The importance of re-emission of previously emitted PCBs from surface soils and sediments is still unclear. However, this represents a potentially important issue which relates to our ability to undertake further source reductions. The NAEI estimated total PCB emissions of 6667 kg in 1990 which reduced to 706 kg in 2013, with the majority of emissions originating from electrical equipment containing dielectric fluids, e.g. transformers. Figure 19 shows the NAEI data for PCBs covering the period 1990 to 2012 and details the main source categories contributing to the UK emissions inventory. It is clear that the main contribution to the total emissions originates from the use of PCBs in dielectric fluids. The notable decrease in the late 1990s in the emission inventory relates to controls placed on electrical equipment mainly used for power distribution.

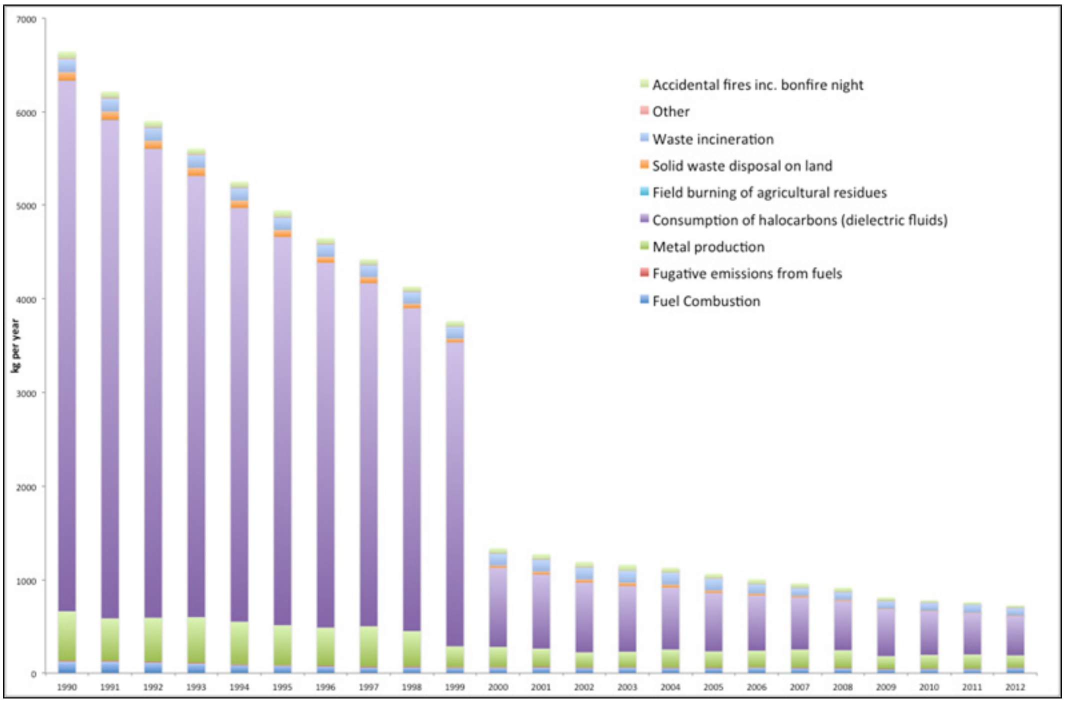

Figure 19. Atmospheric emission estimates for PCBs for the UK from 1990 to 2012 – National Atmospheric Emissions Inventory.

As mentioned above, the temporal trend data from most sites show a decrease in concentrations over time, most of which are statistically significant. The individual trends established at each site and for each of the different congeners measured were found to be not statistically different from each other, suggesting that similar sources have been, and still are, contributing to the measurements. Previous studies by Schuster et al. (2010b), examining the inter-site differences in more detail, established correlations between ambient air concentrations and local population density (i.e., the degree of urbanisation), which suggests that primary emissions on the national scale are still important in controlling ambient levels. Hence the underlying trends of PCBs in the UK atmosphere continue to reflect the controlling influence of diffuse primary sources from the ongoing stock of PCBs, mostly in urban environments. Production and use restrictions came into force in the UK over 40 years ago and trends since monitoring began in the early 1990s should be seen as part of a continuing decline in ambient levels since that time.

Estimates of soil-air fugacity ratios, calculated as $f_{soil}/(f_{soil}+f_{air})$ have increased from 0.04 in 1970 to 0.1 in 2000 and are projected to be 0.2 by 2020. These estimates (based on a methodology by Sweetman and Jones (2000)) demonstrate the net flux of PCBs remains from air to soil, which confirms that primary sources continue to dominate, but the trend suggests that secondary sources will become increasingly important into the future.

Other key long-term monitoring projects for PCBs in the atmosphere are being conducted under the European Monitoring and Evaluation Programme (EMEP) for Europe and the Integrated Atmospheric Deposition Network (IADN) for the Great Lakes area of North America. The Global monitoring plan for POPs in the Western Europe and Others Group (WEOG) (effectiveness evaluation 2nd regional monitoring report) showed that PCBs in air in the WEOG region tend to show generally declining trends at all monitoring stations since the 1990s (UNEP, 2015). Apparent first-order clearance rates for PCBs from other European monitoring networks provide similar declines to the TOMPs dataset. Data collected from Birkenes, Norway, provided clearance rates ranging between 4.5 years and 8.0 years for the seven indicative PCB congeners. The same data from Birkenes showed that all seven congeners followed a similar pattern over the studied period, which probably reflects common sources, as was found within the TOMPs dataset. In all cases, the decline became faster after 2008. Other EMEP stations such as Aspvreten and Rao in Sweden reported slow declines with clearance rates ranging between 11 years (PCB 180) and 20 years (PCB 52) over the period 1995-2012, while for Rao no clear trend was observed over the period 2002-2012. The Integrated Atmospheric Deposition Network (IADN), jointly operated by the US and Canada, reported much longer clearance rates at ambient air monitoring stations around the Great Lakes, ranging from 6.5 to 34 years, with clearance rates being congener-specific.

2.3.3 PBDEs

Polybrominated diphenyl ethers have been widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. They are referred to as additive flame retardants, because they are simply blended with the product. This makes them more prone to volatilise into the atmosphere during the product lifetime. They reduce fire hazards by interfering with the combustion of the polymeric materials. Three different types of commercial PBDE formulation have been produced with different degrees of bromination, namely penta-, octa- and deca-BDE products. The penta-BDE product contains a range from tetra- to hexa-BDE congeners, the octa-BDE contains a mixture of hexa- to deca-BDE, and the deca-BDE contains predominantly the deca-BDE congener and is currently the most widely PBDE flame retardant product in use (ECHA, https.//echa.eu/). Congeners in the commercial mixtures penta-BDE and octa-BDE have already been added to Annex A of the Stockholm Convention in 2009.

The global demand for PBDEs has previously been very substantial with a peak estimation of 70,000 tonnes for the year 2003 (Hites, 2004). In the UK there has been previously high use of penta-BDE as a result of flame retardancy regulations for furniture. Lower brominated PBDEs can also be formed from the degradation of higher brominated BDEs, although the environmental importance of this process is still unclear. In 2010 PBDE congeners were included in the TOMPs methodology. The congeners that have been analysed are: BDE 28 (tri), BDE 47 (tetra), BDE 49 (tetra), BDE 99 (penta), BDE 100 (penta), BDE 153 (hexa), BDE 154 (hexa), BDE 183 (hepta). Congeners BDE 47 and BDE 99 account for approximately 72% of the composition of the penta commercial mixture (penta-BDE). Atmospheric emission estimates for 2012 for the tetra and penta-PBDEs in the UK were 800 kg.

Seasonal Variations. As described and discussed in previous studies (Melymuk et al., 2012; Yang et al., 2013), the seasonal pattern is less uniform for PBDEs than for PCDD/Fs or PCBs. Chapter 3 will provide details on seasonal patterns for PBDE concentrations. Generally, smaller and lighter BDEs like BDE 47 will be prevalent in the warmer months (Q2 and Q3), while larger, heavier BDEs like 183 show elevated concentrations during the colder seasons (Q1, Q4).

Temporal Trends. In order to provide some historical context, the TOMPs air sample archive was used to provide information on the temporal trends of PBDEs in the UK atmosphere (Birgul et al., 2012). The re-analysis of PBDEs in the sample archive focused on four of the six sites over a period ranging from 1999 to 2010. The four sites included were London, Manchester, Hazelrigg and High Muffles. Figure 7 shows the trend data for ΣPBDE (sum of congeners 47, 49, 99, 100, 119, 154, 153, 138, 183) for an average of the four sites with a comparison of atmospheric emission data from Prevedouros et al. (2004). Figure 20 also contains data for 2011 and 2012 from the TOMPs dataset. The emission data, which have been recently updated, are based on a dynamic model of historical estimates of PBDE manufacture, incorporation into products (e.g., polyurethane foams), and subsequent emission from each product type using specific emission factors over their respective life cycles. These time-trend data demonstrate a consistent decrease in concentrations over recent years with the observed decline starting during the period 2001-2003. When examining the site-specific data, the decline is particularly evident in the urban datasets of Manchester and London and at the semi-rural site of Hazelrigg. The calculated ΣPBDE atmospheric clearance rates for these three sites are 3.4, 2.0 and 3.5 years, respectively. Of the individual congeners detected, BDE 47 is the most abundant at all sites and in almost all samples, followed by BDE 99, and both dominated all calculated profiles. Given that these two congeners are the main components of the penta-BDE (PeBDE) technical mixture, with BDE 47 accounting for 38-42% and BDE 99 accounting for 45-49% of the ΣPBDEs, these results likely reflect the extensive use of that specific technical mixture. The strong correlation between the estimated emissions and the measured concentrations ($r^2=0.79$, $p=0.0084$) suggests that ongoing releases from articles containing PeBDE products is likely to be controlling the long-term trends in the UK atmosphere. BDE 183, a congener present in the octa-BDE commercial mixture did not correlate well with congeners present in the penta-BDE mixtures. This suggested that the sources were different, although the concentrations of BDE 183 were generally low or close to the detection limits. Data from a passive sampler network spanning the UK and Norway has provided similar clearance rates for UK rural sites, suggesting a slightly longer value of approximately 6.5 years (Schuster et al., 2010a). However, this estimate was made with a very limited dataset.

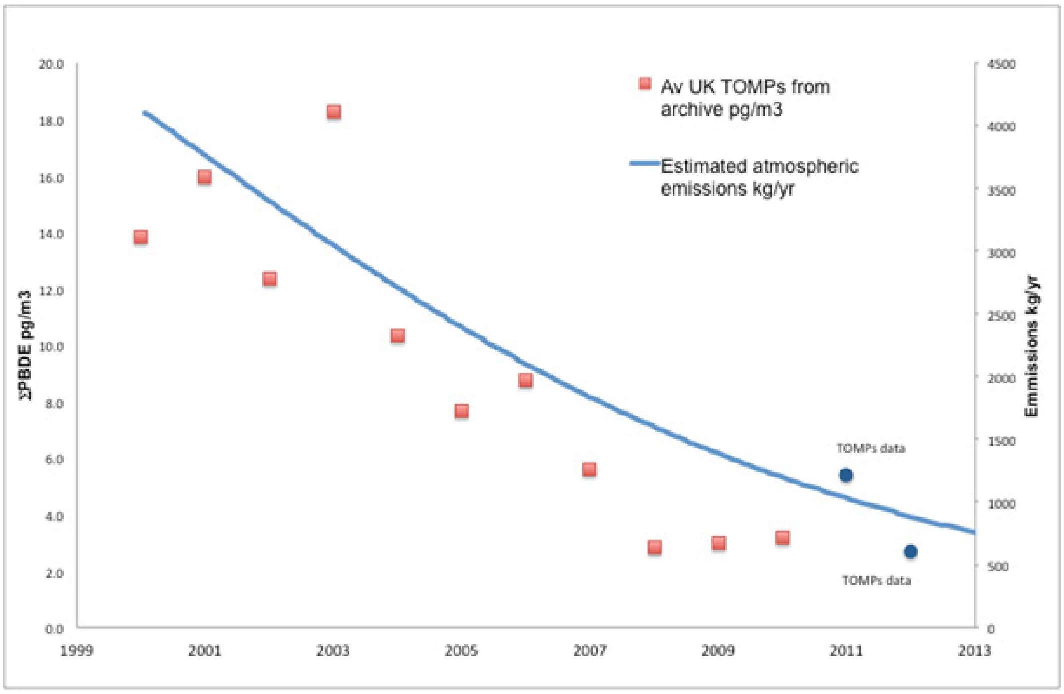

Figure 20. Comparison of estimated annual emissions of PBDEs in the UK in kg (right y-axis) to the average annual concentrations of ΣPBDEs in pg/m^3 provided by the TOMPs network (left y-axis).

2.4 Policy perspective and conclusions

The TOMPs network is responsible for monitoring air quality by providing measurement of the air concentrations of a range of pollutants including PCDD/Fs, PCBs and PBDEs at rural and urban locations in the UK. Monitoring data using a consistent methodology is vital to understanding if the measures taken to reduce POPs emissions into the environment are successful by providing invaluable insights into the long-term trends of POPs in UK air. The UK is a signatory to both the Stockholm Convention on POPs and UN/ECE Protocol on POPs to the Convention on Long-Range Transboundary Air Pollution. Therefore, providing information on past and predicted POPs emissions and concentrations of POPs in the environment can be used to determine if measures taken to control POPs releases into the environment can be shown to be successful.

Assessment of the dataset provided by the TOMPs network over the last 20 years concludes that ambient air concentration data for POPs over the monitoring period show significant decreases across most sites. The exception being for PCDD/Fs measured at the rural/semi-rural sites where no statistically significant trends were observed throughout the whole sampling period. Therefore, it is apparent that ambient air concentrations of PCBs, PCDD/Fs and PBDEs have responded to emission controls and are decreasing or stable at very low levels. Comparison of the temporal trends provided by the atmospheric emission inventories and the decreasing ambient concentrations suggests that the inventories have largely captured the main sources, which remain mainly primary and diffuse. The reconstruction of the historical ambient air trend for PCDD/Fs, however, showed that individual measures to reduce sources of POPs to the environment may not be significant on their own but may contribute to the long-term changes affected by a range of control measures, some of which may not have been directly intended to control POPs. Over the next few years, new 'candidate POPs' and emerging pollutants will be evaluated and a judgment reached as to their environmental significance and regulatory needs. This will create challenges for ambient air monitoring networks such as TOMPs. With finite resources priorities will need to be set to identify those substances that should be targeted for continued monitoring to demonstrate the success of regulation and source control, but to potentially reduce the sampling efforts for those substances that are believed to be sufficiently understood and sources controlled.

2.5 Acknowledgements

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3 Further insights into regional and seasonal variations in PCB and PBDE concentrations in UK ambient air

Abstract

Data from the UK TOMPs network shows that PCB and PBDE congeners in UK ambient air display a seasonal pattern. As ΣPCB air concentrations are dominated by lower-chlorinated lighter congeners, their respective seasonal patterns (summer > winter) were also reflected in ΣPCB patterns. ΣPBDE concentrations are distributed over a range of congeners with more uniform concentrations but greater differences in seasonal patterns, thus their overall seasonality was characterised by these contrasting patterns. In accordance with previous observations, only BDE 47 consistently showed elevated concentrations in the summer compared to the winter months. Whilst no discernible patterns for BDE 99 across all sampling sites were evident, both BDE 153 and BDE 183 concentrations were clearly higher in Q1 (Jan – Mar) and Q4 (Oct – Dec) than in Q2 (Apr – Jun) and Q3 (Jul – Sep), with the highest values occurring in Q4. While continuous emission from primary and secondary sources as well as indoor air ventilation in warmer months seem to be the dominant source of PCBs and PBDEs in recent years, short-term emissions stemming from e.g. demolition of buildings from the mid-20th century, disturbance of contaminated ground by earthworks, or illegal waste burning can have a significant impact on overall concentrations of single samples, especially at remote sites.

3.1 Introduction

Chapter 2 has explored long-term trends in POPs concentrations in the UK atmosphere. However, it is known that in addition to long-term temporal and spatial trends, POPs concentrations in ambient air can also show strong seasonal variations, all of which helps identifying their possible sources, their atmospheric behaviour, and their transport mechanisms. Melymuk et al. (2012) describe seasonal patterns for PAHs, PCBs, and PBDEs in samples collected over the course of a year in the Toronto area, Canada. Degrendele et al. (2020) analysed PCDD/Fs, PAHs, and dioxin-like (dl-)PCBs at a background site in the central Czech Republic between 2011 and 2014. They found that both in PCDD/Fs and PAHs mass concentrations were significantly higher in winter compared to summer, while the opposite was found for dl-PCBs. Baek et al. (2010) measured eight PCBs near an iron and steel-making plant in South Korea. Although the plant was identified as a primary source of PCBs, strong seasonal patterns in PCB concentrations (summer > winter) were found here as well. Cincinelli (2014) analysed PBDEs at an urban and an industrial site in Florence, Italy and reported winter/summer ratios below 0.6 for BDE 28 and BDE 47, but higher and less uniform ratios around 0.8 – 1.0 on average for heavier BDEs. A study including several urban and rural sites in the area of Thessaloniki, Greece (Besis et al., 2016) also showed increased levels of di- and tri-BDEs in the warmer season, and of hexa- and hepta-BDEs in the colder season, with tetra- and penta-BDEs falling in between, which resulted in similar ΣPBDE levels in both seasons on average. Likewise, the ΣPBDE pattern was mixed at nine sampling sites in the rural Shanghai region (Zhu et al., 2017).

The UK TOMPs network provides a unique opportunity to investigate seasonal patterns of POPs over the course of several years in both rural and urban environments. Unlike studies that only run for several months, it is invaluable for the investigation of the different impacts of long-term trends and average seasonal patterns, but also short-term impacts on POPs concentrations that can otherwise interfere with the former and could lead to incorrect conclusions. In this chapter we will therefore use the TOMPs samples collected between 2011 and 2016 to gain further insights into regional and seasonal variations in PCB and PBDE concentrations in UK ambient air.

3.2 Materials and methods

All samples discussed in this chapter are regular TOMPs samples, collected with an Andersen high-volume active air sampler between 2011 and 2016 at the six TOMPs sites London (LON, urban), Manchester (MAN, urban), Hazelrigg near Lancaster (HR, semi-rural), Weybourne on the coast of North Norfolk (WEY, rural), High Muffles in the North York Moors National park (HM, rural), and Auchencorth Moss in the South East of Scotland (AUCH, rural). Thus, all materials and methods are as described in chapter 2.2.

3.3 Results and discussion

3.3.1 Polychlorinated biphenyls (PCBs)

Figure 21 shows the 2011-2016 quarterly ΣPCB_7 concentrations in pg m^{-3} (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180) at the six TOMPs sampling sites. It can be clearly seen that the levels at both urban sites, London and Manchester, were generally three to five times higher than at any semi-rural and rural site (Hazelrigg, Weybourne, High Muffles, Auchencorth Moss), with concentrations in Manchester exceeding those in London between 2011 and 2014, and vice versa in 2015 and 2016.

It seems surprising that PCB concentrations at the very remote site High Muffles occasionally exceeded those of other all other rural and semi-rural sites. However, it is situated in a clearing in a forest plantation (https://uk-air.defra.gov.uk/networks/site-info?site_id=HM), and could thus be impacted by forest management, for example by re-volatilisation of PCBs in nearby soils. Additionally, extensive refurbishment works that might have released PCBs from old building materials have been carried out at a nearby property over the last decade.

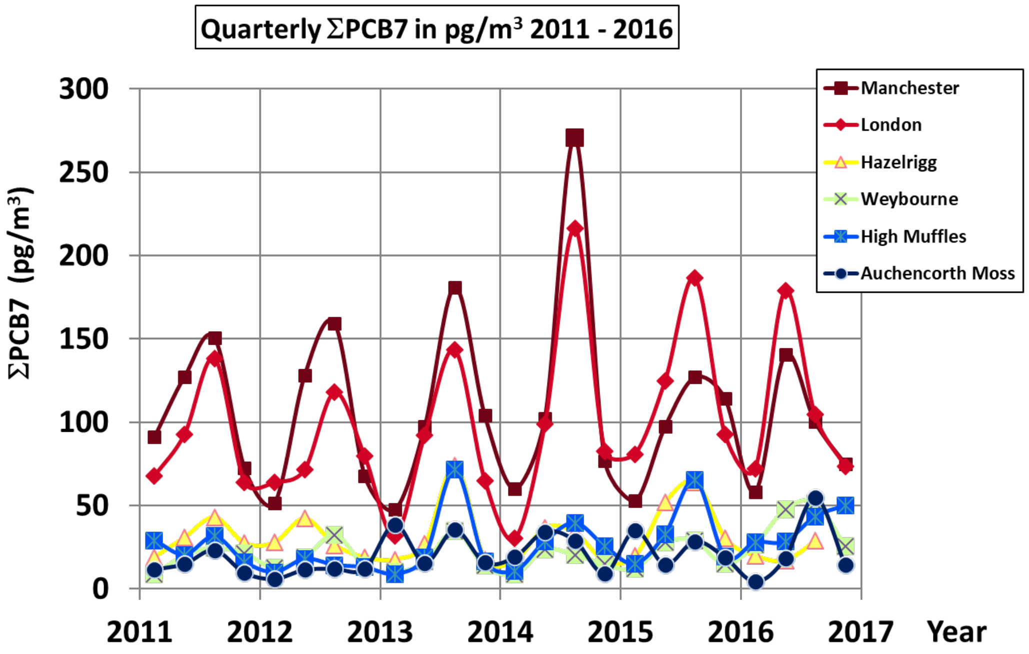

Figure 21. 2011-2016 quarterly ΣPCB$_7$ concentrations in pg/m^3 at two urban (Manchester, London), one semi-rural (Hazelrigg), and three rural (Weybourne, High Muffles, Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

Figure 21 also shows a clear seasonality of PCB levels in MAN and LON, with concentrations usually being higher in the warmer months of quarter 2 and 3 (Q2, Q3) than in the colder months of quarter 1 and 4 (Q1, Q4), while this effect was less clear for the other sites. Thus, 2011–2016 *average* quarterly concentrations were calculated for each site (Figure 22). For all sites except Auchencorth Moss, levels followed the pattern Q3 > Q2 > Q4 > Q1, although unlike Manchester, London, Hazelrigg, and Weybourne, PCB concentrations at High Muffles were only slightly lower in Q4 than in Q2. This could be the impact of the nearby spruce plantation, with its trees being harvested in Q4 to be used as Christmas trees. The seasonal pattern is in accordance with previous reports (Degrendele et al., 2020; Melymuk et al., 2012) and could be caused by the dominance of secondary emissions in this compound group. However, primary emissions would also be expected to rise in warmer months due to increased volatilisation from legacy sources (Bozlaker et al., 2008; Yan et al., 2008; Zhang et al., 1999) as well as increased indoor air ventilation in summer (Currado and Harrad, 2000; Halsall et al., 1995).

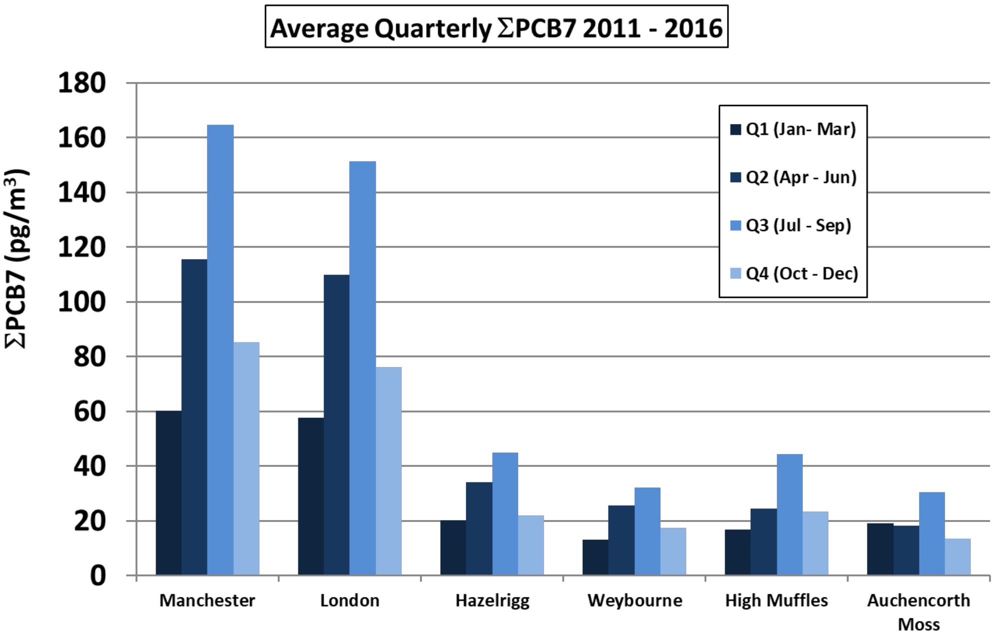

Figure 22. 2011-2016 *average* quarterly ΣPCB$_7$ concentrations in pg/m^3 at two urban (Manchester, London), one semi-rural (Hazelrigg), and three rural (Weybourne, High Muffles, Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

Unlike the other sampling sites, average quarterly concentrations at Auchencorth Moss (AUCH) were Q3 > Q1 > Q2 > Q4, which means that Q1, which usually had the lowest levels, was now the second highest. AUCH is generally the site with the lowest concentrations of all TOMPs sites, so unusual short-term events are likely to have a bigger impact on this site than those with overall higher concentrations. Additionally, this site is situated less than 20 km south of Edinburgh (https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00451), so could occasionally be impacted by more polluted winds from the N/NE direction, and thus the industrial areas to the east of Edinburgh and the Firth of Forth. The wind rose for Edinburg in Figure 23 shows that while the prevailing wind direction in this area is from the south-west, winds from the north-east are also relatively common.

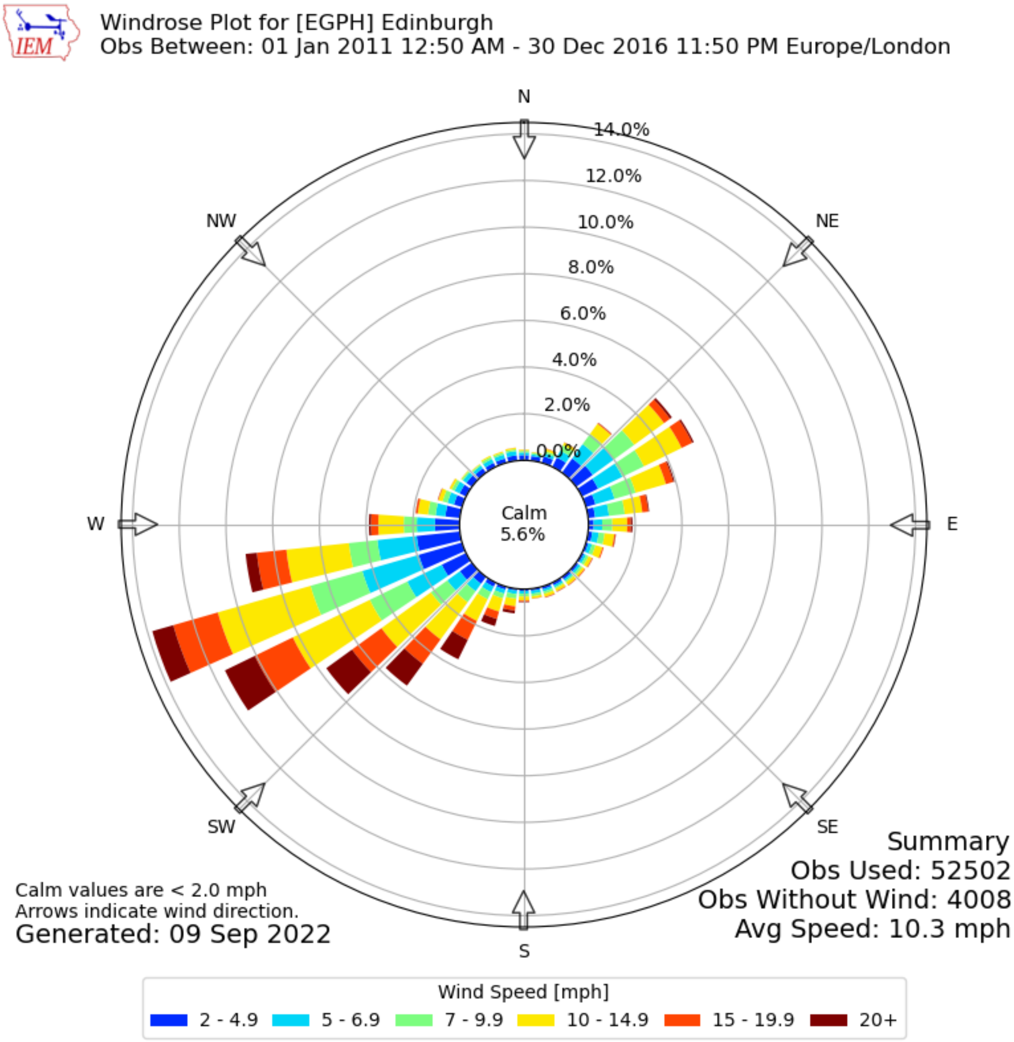

Figure 23. Wind rose for Edinburgh, UK, between January 2011 and December 2016. Source: Iowa Environmental Mesonet (iastate.edu).

PCB concentrations in ambient air are usually dominated by their lower-chlorinated congeners (Schuster et al., 2010). Table 3 and Figure 24 show the 2011-2016 average quarterly concentrations of the single PCB congeners PCB 28 (tri-CB), PCB 52 (tetra-CB), PCB 153 (hexa-CB), and PCB 180 (hepta-CB). Of these, PCB 28 was the dominant congener by far, as expected, followed by PCB 52, PCB 153, and PCB 180. This was true for all sites and all quarters. PCB 28 levels were higher in Q2 and Q3 than in Q1 and Q4 for all sites. With some exceptions, this was also the case for PCB 52 and PCB 153. The picture for PCB 180 is less clear with some elevated concentrations in Q1 or Q4. However, the dominance of tri- and tetra-CBs, which is also obvious in these samples, results in those clear seasonal patterns seen in Figure 21 and Figure 22. Notable here that at Auchencorth Moss the highest PCB 153 and 180 levels were measured in Q1. Melymuk et al. (2012) describe a relatively larger increase of hexa- and hepta-CBs in Toronto air the summer months compared to tri- and tetra-CBs, which is attributed to their greater change in vapour pressure with increasing temperature (18-fold for tri-CBs compared to 35-fold for hexa- and hepta-CBs for the temperature range between -3 °C and 22 °C). This effect could not be seen in this study at all. It is possible that this can be explained by a higher annual temperature range in Toronto (avg. min. T -3°C, avg. max. T. 21°C) compared to the UK (London: avg. min T 5°C, avg. max. T 19°C), as well as other meteorological factors.

Table 3. 2011-2016 average quarterly concentrations in pg/m^3 of four PCB congeners (PCB 28, PCB 52, PCB 153, PCB 180) at two urban (MAN = Manchester, LON = London), one semi-rural (HR = Hazelrigg), and three rural (WEY = Weybourne, HM = High Muffles, AUCH = Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

	AUCH Q1	**AUCH Q2**	**AUCH Q3**	**AUCH Q4**	**HM Q1**	**HM Q2**	**HM Q3**	**HM Q4**
PCB 28	11.62	13.72	24.06	9.57	10.68	19.09	34.73	16.90
PCB 52	2.74	2.62	3.88	2.00	2.53	2.41	5.30	3.37
PCB 153	1.56	0.56	0.81	0.54	1.02	1.18	1.61	1.25
PCB 180	0.26	0.15	0.14	0.11	0.13	0.17	0.26	0.26
	HR Q1	**HR Q2**	**HR Q3**	**HR Q4**	**WEY Q1**	**WEY Q2**	**WEY Q3**	**WEY Q4**
PCB 28	12.05	26.45	34.01	13.78	7.72	18.24	23.10	10.33
PCB 52	3.47	2.94	5.04	3.30	2.52	3.89	3.98	3.01
PCB 153	0.97	1.51	2.10	0.88	1.04	1.15	1.38	1.27
PCB 180	0.25	0.26	0.30	0.22	0.15	0.18	0.22	0.24
	LON Q1	**LON Q2**	**LON Q3**	**LON Q4**	**MAN Q1**	**MAN Q2**	**MAN Q3**	**MAN Q4**
PCB 28	35.55	69.40	93.89	42.82	19.50	39.30	66.51	30.96
PCB 52	9.60	17.02	26.53	12.15	13.81	26.05	34.28	20.26
PCB 153	3.44	6.83	8.28	5.77	5.53	11.15	14.01	6.89
PCB 180	0.66	0.66	1.09	0.95	0.77	0.93	1.06	0.75

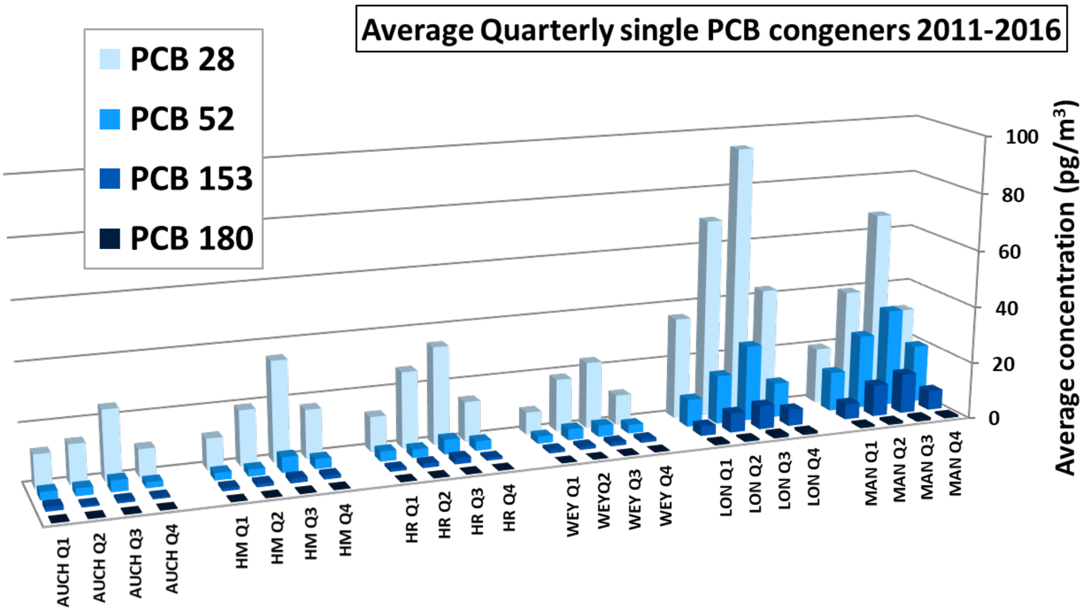

Figure 24. 2011-2016 average quarterly concentrations in pg/m^3 of four PCB congeners (PCB 28, PCB 52, PCB 153, PCB 180) at two urban (MAN = Manchester, LON = London), one semi-rural (HR = Hazelrigg), and three rural (WEY = Weybourne, HM = High Muffles, AUCH = Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

3.3.2 Polybrominated diphenyl ethers (PBDEs)

Figure 25 shows the 2011-2016 quarterly ΣPBDE concentrations at the six TOMPs sites. Their range is much smaller than for PCBs, and the spatial and seasonal patterns significantly less clear than for PCBs, with Manchester, and – to a lesser extend – London only dominating the picture in 2011 and 2012. From 2013 on the semi-rural site at Hazelrigg (HR), and, noticeably, the rural site at Weybourne (WEY), displayed the highest levels for some quarters.

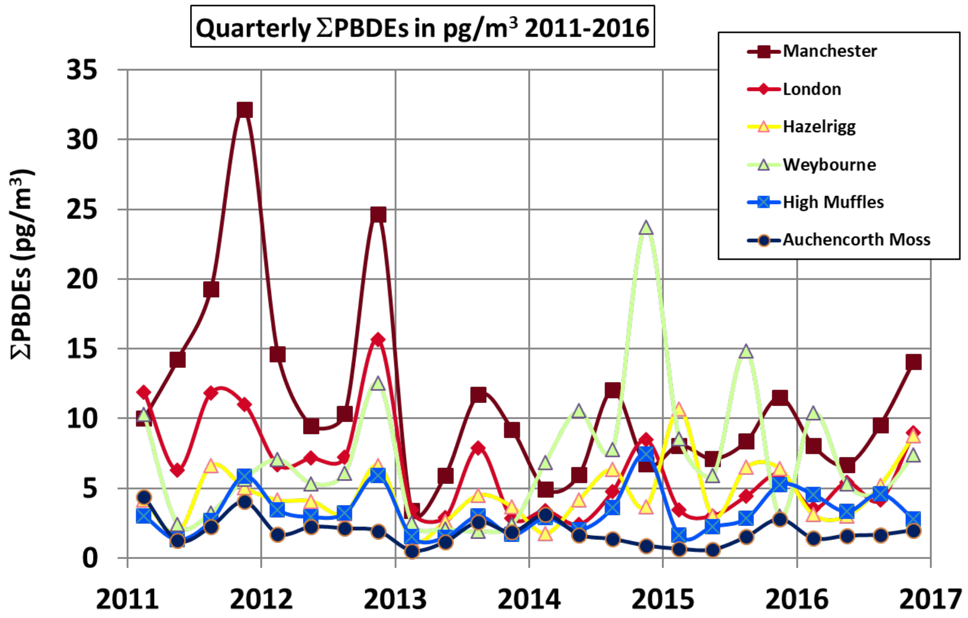

Figure 25. 2011-2016 quarterly ΣPBDE concentrations in pg/m³ at two urban (Manchester, London), one semi-rural (Hazelrigg), and three rural (Weybourne, High Muffles, Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

Likewise, as opposed to PCBs, there was no obvious seasonal pattern for PBDEs (Figure 25). Figure 26 shows 2011-2016 average seasonal concentrations for ΣPBDEs at the six TOMPs sampling sites and here a seasonal pattern can be observed. At all six sites, PBDE levels were highest in quarter 4; followed by quarter 3 for Manchester, London, Hazelrigg, and High Muffles and quarter 1 for Weybourne and Auchencorth Moss. Quarter 2 concentrations were lowest at all sites except Manchester, where it was slightly higher than quarter 1. However, PBDE concentrations fluctuated to a greater extent than PCBs from year to year over the sampling period, so one unusual year can have a large impact on the average.

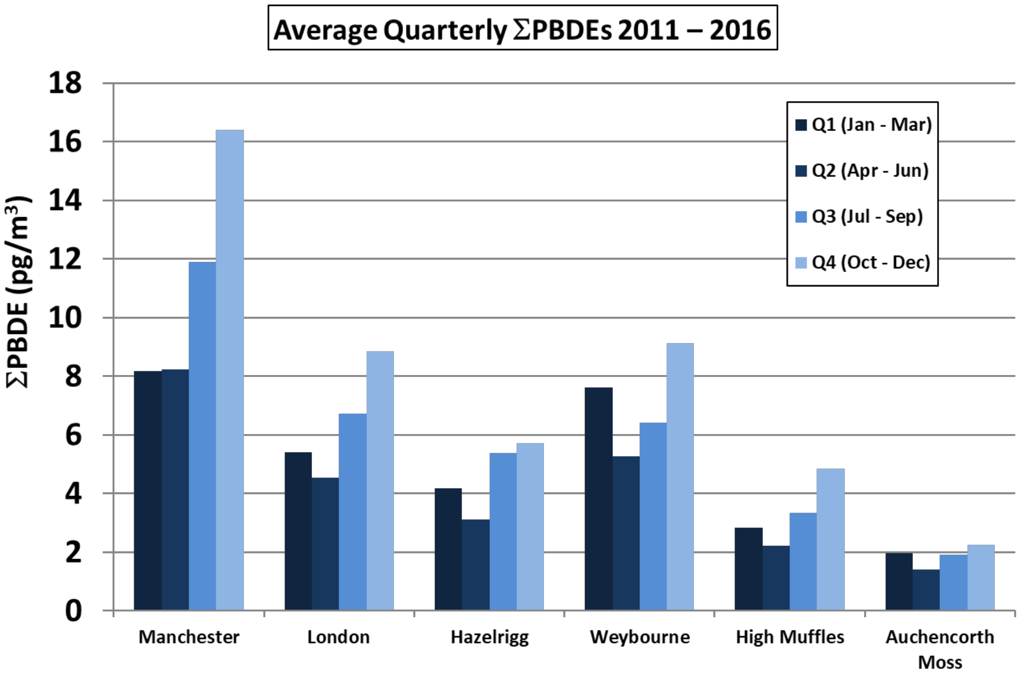

Figure 26. 2011-2016 *average* quarterly ΣPBDE concentrations in pg/m³ at two urban (Manchester, London), one semi-rural (Hazelrigg), and three rural (Weybourne, High Muffles, Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

Compared to PCBs, PBDE levels in ambient air are much less dominated by their lighter congeners (Gouin et al., 2005; Liu et al., 2016). Table 4 and Figure 27 show 2011-2016 average quarterly concentrations of BDE 47 (tetra-BDE), BDE 99 (penta-BDE), BDE 153 (hexa-BDE), and BDE 183 (hepta-BDE). BDE 47, which, like PCBs, is predominantly transported in the gas phase in the atmosphere, also displayed the same seasonal pattern as PCBs and was dominant in Q2 and Q3. BDE 183 on the other side, which is mainly transported in the atmosphere bound to particles (Su et al., 2009), had its highest levels in Q1 and Q4, when particle loadings in the UK ambient air are elevated, for example as a result of domestic heating (Air Quality Expert Group [AQEP], 2012; Harrison, 2020; Laxen, 2010). BDE 99 showed a similar but less pronounced seasonal pattern as BDE 47, with Q2 and Q3 concentrations that were usually higher than those in Q1 and Q4. However, the London site had similar levels all year round, while for Auchencorth Moss highest BDE 99 concentrations were measured in Q1. BDE 153 followed the pattern of BDE 183, but with lower concentrations overall. All in all, these findings are comparable to those of Besis et al. (2016) measured at a site in Thessaloniki, although the differences found between the warmer (avg. T 22 – 26 °C) and the colder (avg. T 10 – 14 °C) season were much smaller for all congeners there.

Table 4. 2011-2016 average quarterly concentrations in pg/m^3 of four BDE congeners (BDE 47, BDE 99, BDE 153, BDE 183) at two urban (MAN = Manchester, LON = London), one semi-rural (HR = Hazelrigg), and three rural (WEY = Weybourne, HM = High Muffles, AUCH = Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

	AUCH Q1	AUCH Q2	AUCH Q3	AUCH Q4	HM Q1	HM Q2	HM Q3	HM Q4
BDE 47	0.58	0.70	0.98	0.69	0.58	0.80	1.36	0.73
BDE 99	0.85	0.36	0.49	0.53	0.47	0.43	0.66	0.80
BDE 153	0.14	0.03	0.02	0.06	0.24	0.08	0.14	0.48
BDE 183	0.48	0.17	0.16	0.24	0.68	0.33	0.35	0.94
	HR Q1	**HR Q2**	**HR Q3**	**HR Q4**	**WEY Q1**	**WEY Q2**	**WEY Q3**	**WEY Q4**
BDE 47	0.46	0.96	1.55	0.74	0.78	1.21	1.58	1.33
BDE 99	0.55	0.62	1.31	0.96	1.30	1.76	2.57	1.94
BDE 153	1.02	0.23	0.22	0.46	0.53	0.38	0.42	0.88
BDE 183	1.04	<LOQ	0.46	1.91	1.80	0.97	0.54	2.89
	LON Q1	**LON Q2**	**LON Q3**	**LON Q4**	**MAN Q1**	**MAN Q2**	**MAN Q3**	**MAN Q4**
BDE 47	1.14	1.65	2.14	1.56	2.04	3.40	5.27	2.83
BDE 99	1.51	1.16	1.52	1.62	1.48	1.61	2.48	1.99
BDE 153	0.35	0.21	0.20	0.63	0.76	0.37	0.47	1.30
BDE 183	0.62	0.22	0.41	1.45	1.53	0.66	0.49	3.51

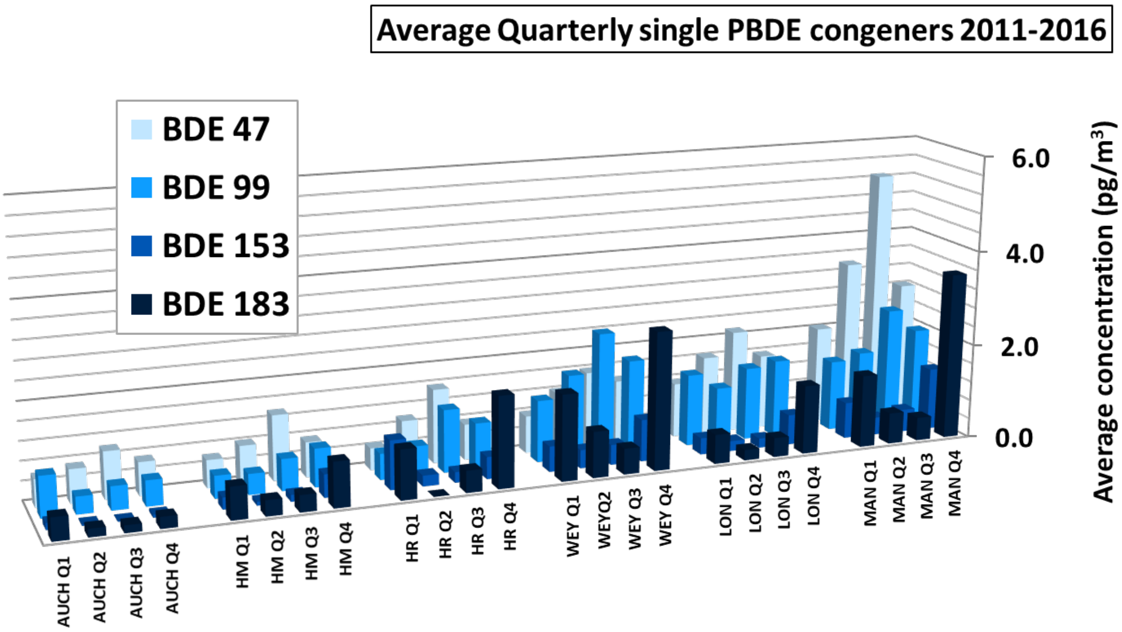

Figure 27. 2011-2016 average quarterly concentrations in pg/m^3 of four BDE congeners (BDE 47, BDE 99, BDE 153, BDE 183) at two urban (MAN = Manchester, LON = London), one semi-rural (HR = Hazelrigg), and three rural (WEY = Weybourne, HM = High Muffles, AUCH = Auchencorth Moss) TOMPs sampling sites. Q1: Jan – Mar, Q2: Apr – Jun, Q3: Jul – Sep, Q4: Oct – Dec.

Higher PBDE concentrations in the winter months could be a result of the seasonal variation of the atmospheric boundary layer ('mixing layer') as described by Coutinho et al. (2007) and Lohmann et al. (2003) for PCDD/Fs. The height of the boundary layer can, dependent on daytime temperatures, vary between ca 1000–2000 m in summer and a few hundred meters or less in winter, which leads to less atmospheric dispersion of emitted pollutants.

As was the case for PCBs, it is likely that non-regular and short-term PBDE emissions will have a large impact on single samples. For example, in Manchester the area around the sampling site has seen a major re-development in the last decade, which has potentially released legacy POPs into the atmosphere, which were then captured by the air sampler. Weybourne, despite being at a remote rural location, is regularly impacted by air masses from industrial areas in Belgium and the Netherlands as well as the Midlands in England. Occasional illegal waste burning has been observed close to the Hazelrigg sampling site in recent years, which could account for some elevated levels there. As the waste burning happens in a location to the north-east of the sampler and only ever lasts one or two days, a signal from this event would mainly be picked up if it coincided with the less common situation of north-easterly winds.

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4 Analysing a wide range of toxic organic pollutants in ambient air using a novel sampling technique

Abstract

Concentrations of semi-volatile organic pollutants in ambient air are usually and most precisely determined using high-volume active air samplers equipped with assemblies containing glass fibre filters (GFFs) - for particle-bound contaminants - as well as polyurethane foam (PUF) plugs for gaseous contaminants. This type of sampler, however, might not be able to effectively collect a range of more volatile pollutants. Including XAD® pods in standard air sampling assemblies is an easy, economical, versatile, and tidy way to sample more volatile compounds with standard high-volume air samplers. With this field-tested method, a wide range of toxic organic pollutants in ambient air, which are individually best sampled with either GFFs, or PUFs, or with XAD®, can be sampled and analysed simultaneously. This increases their range of analytes across the VOC/SVOC spectrum without the need for additional samplers of a different type. Extended sampling periods due to the large surface area and adsorption capacity of XAD® could reduce the number of samples that need to be collected and analysed, saving time and money and improving the environmental impact and relevance of the research project.

4.1 Introduction

A considerable number of man-made and naturally occurring toxic organic pollutants can be detected worldwide in ambient air samples, especially at urban sites, but also in remote regions (He and Balasubramanian, 2010). Among these substances are pesticides, polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs), phthalates (plastic additives), polychlorinated biphenyls (PCBs), and flame retardants like polybrominated diphenyl ethers (PBDEs). Many of these compounds are not only toxic, but have been found to be potentially carcinogenic, mutagenic, and endocrine-disrupting. Long-term air monitoring programmes for toxic organic pollutants have been implemented worldwide (Secretariat of the Stockholm Convention, 2015) to provide data on possible sources, their atmospheric behaviour, and their transport mechanisms. In the UK, this programme has been operated by Lancaster University and funded by the Department of Environment, Food and Rural Affairs (Defra) since 1991 (TOMPs, see chapter 2). Over the last few decades, many of these compounds have been banned or phased out, and/or substituted by replacement compounds, for example PBDEs by organophosphorus flame retardants (OPFR) (Dodson et al., 2012).

Depending on their volatility, a distinction between volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) can be made, with the former being easily released into the atmosphere by volatilisation, and the latter being released only slowly, either by volatilisation or abrasion of the product (Lucattini et al., 2018; Montero-Montoya et al., 2018). While the pollutants monitored in the UK ambient air are generally described as SVOCs, many of the groups mentioned above contain lighter compounds with physical properties that would classify them as VOCs. The United States Environmental Protection Agency [EPA] (2022) and World Health Organisation (WHO) classify VOCs and SVOCs according to their boiling point at a standard atmospheric pressure of 101.3 kPa, with VOCs boiling below 240-260 °C and SVOCs between 240-260 °C and 380-400 °C

As described in chapter 2.2.1, concentrations of organic pollutants in ambient air are often determined using high-volume active air samplers equipped with so-called modules containing either glass fibre filters (GFFs) - for particle-bound contaminants - as well as polyurethane foam (PUF) plugs - for gaseous contaminants, or GFFs only. An illustration of such a module is depicted in Figure 28. This type of sampler, however, might not be able to quantitatively collect the more polar and volatile pollutants, which quickly break through the sampling train, like some PAHs, OPFRs, PFCs, or pesticides. Breakthrough occurs when a chemical is not effectively retained in the sampling sorbent, because the uptake capacity of the sorbent (in this case PUF) is exceeded (Li and Wania, 2021), and depends on factors like the specific surface area of the sampler, sampled air volume, and volatility of the analyte (and thus indirectly on the temperature during the sampling). For example, Melymuk et al. (2016) have found that significant breakthrough in PUF active air samplers occurs at temperatures around 0–10 °C for compounds with vapour pressure >0.5 Pa (3.75E-3 mmHg) at volumes < 700 m^3. In standard active air sampling modules that contain two PUF plugs - a front PUF plug (PUF1) and a backup PUF plug (PUF2) - analyte breakthrough can be judged by the ratio of compounds found in both PUFs, PUF2/PUF1, with acceptable ratios suggested between <0.05 and 0.33 (Bidleman and Tysklind, 2018).

Air samplers with Amberlite XAD® resin have been in use for some time to collect more volatile and lower molecular weight compounds, for example as PUF-XAD®-PUF 'sandwich' active air samplers (Ahrens et al., 2011; Renata and Patricia, 2020), but usually in the form of sorbent-impregnated polyurethane foam (SIP) passive samplers (Abdollahi et al., 2017; Kim and Park, 2014; Koblizkova et al., 2012; Ratola et al., 2017; Rauert et al., 2018; Schuster et al., 2012) or in resin-filled XAD®-tubes (Armstrong et al., 2013), as loose XAD® resin is difficult to handle and loss of resin and contamination are likely. XAD® cartridges have successfully been used in combination with pressurised liquid extraction (PLE) systems. However, these systems are expensive, and sampling can only be carried out with *either* XAD® *or* PUFs. Pre-prepared and pre-cleaned PUF/XAD®-2 'sandwiches' are offered by commercial suppliers but are also expensive and the problems with handling loose XAD® resin during sample processing persist.

Figure 28. High-volume active air sampling assembly. ('module'). Source: https://tisch-env.com/.

Amberlite® XAD® resins have been used for extracting organic compounds from both water as well as air samples (Daignault et al., 1988; Levin et al., 1977; Wania and Shunthirasingham, 2020). Different types of XAD® resins with differing properties are commercially available (DuPont™, 2020). XAD®-2 and XAD®-4, both styrene-divinylbenzene resins, are the ones most commonly used in air sampling. Compared to polyurethane foam, XAD® samplers have a higher surface area, which generally leads to higher sorption capacity and better retention for compounds that would usually suffer from quick breakthrough during the sampling process (Melymuk et al., 2014). Additionally, sorption mechanisms make them more suitable for a number of VOCs/SVOCs like PAHs, pesticides, or PCB congeners (Hayward et al., 2011).

The aim of this project was to develop a way to introduce XAD® into a standard active air sampling module without the problems mentioned above. Therefore, the following criteria had to be fulfilled:

1. The container should have a capacity of several grams of XAD® resin.

2. The final container containing the XAD® should have a diameter similar to that of the PUF plugs, so that it can be inserted into the glass tube together with the PUF plugs, but air cannot bypass the resin.
3. The container material should impact the air flow in the sampler as little as possible.
4. The material containing the XAD® resin has to withstand a thorough pre-cleaning process, preferably with the resin already inside.
5. The resin must be contained safely within the container to avoid spillage during sampler preparation, module assembly and disassembly, and extraction of the XAD®. This means that there must not be gaps in the container.
6. It follows from the previous two points that the material of the container has to be stable under the conditions of hot soxhlet extraction with organic solvents like acetone and hexane. This is also the case for any additional material that might be used to seal the container.
7. The pre-cleaned container must not contain any substances that could negatively impact the extraction, clean-up, and analysis of the target compounds.

The system that was eventually chosen was a so-called 'Mr. Pad®' coffee pod maker. It was commercially available for people using a Philips Senseo® coffee machine that works with pre-filled coffee bags ('pads') that look similar to tea bags (Figure 29).'Mr Pad®' would enable consumers to fill a cellulose filter liner with their own choice of ground coffee and seal it by means of pressure and heat, before using it in the coffee machine.

Figure 29. A Senseo® coffee maker with coffee pod. http://www.friele.no/lage-god-kaffe/senseo/.

This system seemed suitable for a number of reasons:

1. The diameter of the liner/container is 62 mm, which exactly matches the diameter of the glass tube (60mm) for the PUF plugs.
2. Cellulose is a material regularly used in the lab environment and stable against a number of organic solvents.
3. No additional substance is needed to seal the container.
4. Due to its suitability for human food and drink preparation, the material is not expected to contain and leak further substances that could impact the sample.
5. Initial tests showed that one cellulose liner could contain up to 10 g XAD®-4 resin, which is a suitable amount for an active air sampler.

Figure 30 shows a marketing picture of the system that also includes its handling.

Figure 30. 'Mr. Pad®', a commercially available system for preparing coffee pods. http://www.qoqa.fr/fr/offer/2524/.

This chapter describes the development of a modified high-volume air sampling module with the aim of sampling a wider range volatile compounds together with regular SVOCs using standard high-volume air samplers equipped with so-called XAD® pods. It demonstrates the preparation and handling of such modules. Two groups of organic compounds were chosen to test the performance of the sampler due to their wide range of physical-chemical properties: Organophosphate esters (OPEs) and PAHs (Table 5). The K_{OA} values for PAHs range over several orders of magnitude, with naphthalene being present entirely in the gas phase and indeno[1,2,3-*cd*]pyrene being entirely sorbed onto particulates.

Organophosphate esters (OPEs) are widely used as additive flame retardants (chloroalkyl and aryl phosphates) as well as stabilisers, plasticisers and antifoaming agents (alkyl phosphates) (van der Veen and de Boer, 2012; Yang et al., 2019). They are included, for example, in PVC and other plastics, electronic equipment, furniture (especially polyurethane foams), construction materials, textiles, lubricants, hydraulic fluids, and floor polishes. Production and application of OP flame retardants (OPFRs) has increased substantially after the ban and phase-out of penta-, octa, and deca-BDEs, and several OPEs count as high production volume (HPV) chemicals.

Like PBDEs, which they have replaced in recent years, OP flame retardants and plasticisers are generally emitted into the environment by abrasion, leaching, and volatilisation. Since they are semi-volatile organic compounds (SVOCs), high concentrations have been reported in indoor air and dust samples (Greaves and Letcher, 2017). They are also regularly found in water, sediments, soil, ambient air, biota, and human blood and milk, amongst others. Although OPEs were generally not expected to undergo long-range atmospheric transport, their occurrence in samples from remote areas has been reported, which has been attributed to atmospheric transport (Vorkamp et al., 2019).

OP flame retardants are not considered persistent organic pollutants (POPs), as their potential to bioaccumulate through food chains is comparatively low (Du et al., 2019). They are, however, known to be relatively stable and resistant to biodegradation and some OPEs have been classified as carcinogenic and/or toxic or neurotoxic.

Polycyclic aromatic hydrocarbons (PAHs) are formed through incomplete combustion of carbon-containing fuels from industrial, commercial, vehicular and residential sources (Wild and Jones, 1995) as well as forest fires (Campos and Abrantes, 2021). In addition, previously deposited PAHs held in soil and vegetation compartments may also re-volatilise to the atmosphere (secondary emission) (Becker et al., 2006). PAHs have been determined to be highly toxic, mutagenic, carcinogenic, teratogenic, and immunotoxicogenic to various life forms (Patel et al., 2020). Not all PAHs are considered bioaccumulative, but because of their toxic, persistent, and semi-volatile properties, they were included in the UN/ECE Convention on Long-Range Transboundary Air Pollution 1998 Protocol on Persistent Organic Pollutants (POPs) , which entered into force in 2003 (Meijer et al., 2008).

Table 5. Physical-chemical properties of the organophosphate esters and PAHs analysed in this chapter. BP boiling point, MW molecular weight, VP vapour pressure. Properties were obtained from https://www.chemspider.com/.

	BP °C	**MW g/mol**	**VP mmHg**	**logK_{OA}**	**logK_{OW}**
Organophosphate esters (OPEs)					
Triethyl phosphate (TEP)	215	182.15	3.93E-01	5.5	0.80
Tri-*n*-butyl phosphate (TnBP)	289	266.62	2.50E-03	7.7	3.75
Tris(chloroisopropyl) phosphate (TCiPP)	358	327.57	2.02E-05	8.13	2.59
Tris(2-chloroethyl) phosphate (TCEP)	347	285.49	6.13E-02	7.6	1.14
Polycyclic aromatic hydrocarbons (PAHs)					
Naphthalene (NAP)	218	128.17	8.89E-02	5.13	3.37
Acenaphthene (ACE)	279	154.21	3.75E-03	6.52	3.98
Fluorene (FLU)	295	166.22	3.25E-03	6.90	4.18
Phenanthrene (PHE)	340	178.23	6.80E-04	7.68	4.46
Fluoranthene (FLA)	375	202.25	8.13E-06	8.76	4.90
Indeno[1,2,3-*cd*]pyrene (IPR)	536	276.33	1.40E-10	12.55	6.58

4.2 Materials and methods

4.2.1 Materials

The pod-maker ‘Mr. Pad’ and accompanying cellulose liners were bought from household goods suppliers. Polyurethane foams (PUF) plugs (height 50 mm, OD 75 mm) were obtained from Klaus Ziemer GmbH, Germany. Amberlite XAD®-4 resin and 110 mm Whatman GF/A glass microfibre filters were purchased from Scientific Laboratory Supplies, UK. All solvents were HPLC grade or higher and obtained from Fisher Scientific, UK, where also Florisil®, 60-100 mesh, was bought. Merck KGaA, Germany, supplied sodium sulfate anhydrous, 0.63-2.0 mm.

TEP, TnBP, TCEP-d12 were purchased from Sigma-Aldrich, TCEP, TCiPP, TEP-d12, and TnBP-d27 from qmx Laboratories Ltd, UK, and TCPP-d18 from Toronto Reseach Chemicals, USA.

Phenanthrene was bought from Acros Organics, fluorene, acenaphthene, and indeno[1,2,3-*cd*]pyrene from Supelco Inc., naphthalene and fluoranthene from Sigma-Aldrich. d10-phenanthrene, d8-naphthalene, and d10-fluorene came from CDN Isotopes, Canada.

4.2.2 Sampler preparation

The preparation of XAD®-filled pods for this study is depicted in Figure 31 to Figure 33. First, a cellulose liner was inserted in the pod maker and filled with exactly 10 g XAD®-4 resin. The lid was then lowered, pressing the lid of the cellulose liner onto the rim of the lower part of the liner and a seal was created through the application of pressure and heat from the pad maker (Figure 31).

Subsequently, up to five XAD®-filled pads were soxhlet-extracted for 2 x 24 hours with a hexane/acetone 1:1 mixture (Figure 32), and then dried in a desiccator.

Dry pods were wrapped in aluminium foil (baked at 450 °C for 4 hours), labelled, and stored in airtight solvent-rinsed and labelled 500 ml metal tins (Patrico Ltd, UK) in a -20 °C freezer until module preparation.

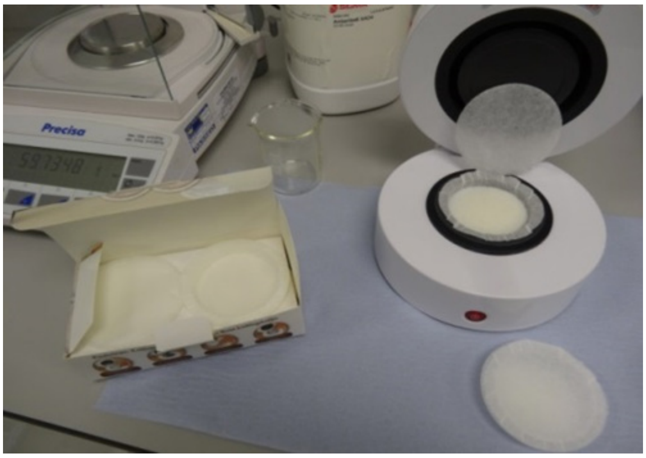

Figure 31. A cellulose liner (commercially available) is filled with an exact amount of dry XAD® resin. The liner can hold up to 10g XAD®-4. The pod is sealed by applying heat to the rim for a few seconds.

Figure 32. The pods can be pre-extracted using the desired method and solvent, for example by soxhlet extraction.

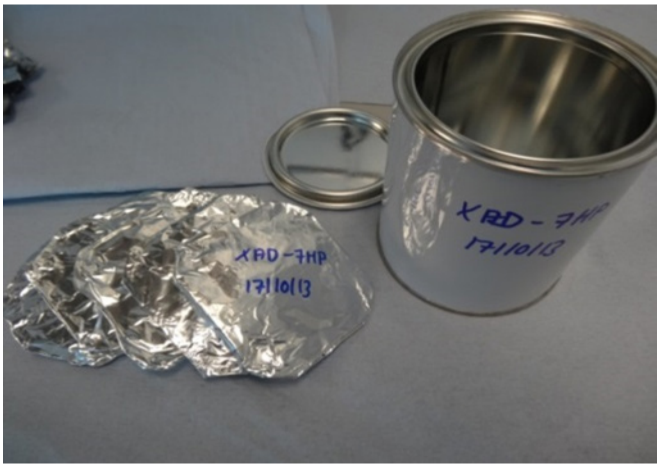

Figure 33. After drying the pods using a desiccator, they are individually wrapped in clean foil and stored in the freezer in an airtight container.

PUF plugs were rinsed with deionised water (Purite Ltd, UK) and dried in a drying oven at 30 °C for a week. The dry plugs were then pre-extracted using a soxhlet apparatus for 2 x 24 hours with a hexane/acetone 1:1 mixture and subsequently dried in a desiccator. They were then wrapped in baked aluminium foil and stored in sealed polyethylene bags for up to two months. Glass fibre filters (GFFs) were baked in a furnace (450 °C, 4 h) and also stored in baked aluminium foil in a sealed polyethylene bag.

Modules with XAD® pods were prepared by first inserting a PUF plug into the glass tube (PUF2), followed by the XAD® pod and another PUF plug (PUF1) (Figure 34). The glass fibre filter was inserted into the head of the module, and all parts of the module assembled. PUFs, XAD® pods, and GFFs were handled with solvent-rinsed tongs or tweezers to minimise contamination. Control modules were prepared at the same time, but without XAD®. Assembled modules were kept in sealed polyethylene bags in a -20 °C freezer until deployment, but for not longer than three days.

Figure 34. The XAD® pod (marked with the blue arrow) can be placed in different positions in the glass jar of the high-volume Sampler, for example between two PUF plugs (upper PUF plug = PUF1, lower PUF plug = PUF2). With 62 mm they exactly match the diameter of the glass tube (60 mm).

4.2.3 Sampler deployment and collection

The modules were installed in pre-calibrated active air samplers at the Hazelrigg field station near Lancaster. The samplers were run in parallel continuously for two weeks, during which around 700 m^3 of ambient air were sampled. After deployment, the samplers were taken to the laboratory, where they were disassembled immediately and each sample stored separately wrapped in clean aluminium foil and stored in a sealed polyethylene bag in a -20 °C freezer until sample extraction.

4.2.4 Extraction, clean-up, and instrumental analysis

All samples were spiked with a mixture of isotope-labelled OPE and PAH standards and extracted separately for 16 hours in 300 ml hexane using soxhlet extraction. The volume of the extracts was then reduced to ca. 0.5 ml with rota-evaporation and nitrogen blow-down and transferred onto a glass column filled with 0.5 g Florisil and a small layer of anhydrous sodium sulfate for clean-up. The column was eluted with 5 ml hexane/acetone 1:1. The eluate was solvent-exchanged to GC vials containing 100 µl toluene and a mixture of internal (syringe) standards.

The extracts were analysed for OPEs on a Thermo Trace GC Ultra / Thermo DSQ II GC/MS system, equipped with a Phenomenex Zebron ZB-1701 analytical column (30 m x 0.25 mm x 0.25 µm) in positive EI-SIM mode. The initial oven temperature was 73 °C (held for 5 min), then increased to 92 °C at a rate of 6 °C min^{-1}, further increased to 190 °C (40 °C min^{-1}), and further to 270 °C (10 °C min^{-1}), where it was held for 10 minutes, and finally to 290 °C (60 °C min^{-1}), where it was held for a final 2 minutes. The GC interface temperature was set to 300 °C, and the MS source temperature to 250 °C. Afterwards, the same extracts were analysed for PAHs on a ThermoQuest Trace Ultra/Finnigan Trace GC/MS equipped with a Phenomenex Zebron ZB-Multiresidue-2 analytical column (30 m x 0.25 mm x 0.20 µm), also in positive EI-SIM mode. The oven programme was as follows: Initial oven temperature 75 °C (held for 5 min), then increased to 290 °C at a rate of 6 °C min^{-1}, and finally to 310 °C (30 °C min^{-1}), held for 8 minutes. Thermo Xcalibur™ software was used for data acquisition and sample processing for all analytes.

4.2.5 QA/QC

Laboratory and field blanks were collected and analysed, and laboratory blank values were subtracted from all other samples. Following this, limits of quantification (LOQs) were calculated for each analyte using the concentration of the highest field blank plus three times its standard deviation, or the instrument limit of detection (LOD) for analytes not found in the field blanks. All values were recovery-corrected using the recoveries of the isotope-labelled standards spiked onto the samples before extraction (recovery standard). The recovery standard itself was quantified to ensure it contained the correct concentrations for all analytes. For each analyte two ions were used for quantification, and usually the lower result of those two was used, unless that ion showed a very weak response and could only be used as qualifying ion.

4.3 Results and discussion

4.3.1 Organophosphate esters

Ambient air concentrations at Hazelrigg for the four organophosphate esters (OPEs) are shown in Table 6 and Figure 35 (page 95). The GFF samples of both modules were dominated by TCiPP, while only traces of TCEP, TnBP, and TEP were found there. TCEP could not be detected in either the PUFs or the XAD® resin. A small amount of TCiPP (less than 10%) was also found in the upper PUF plug (PUF1), but not in the lower PUF plug (PUF2) or XAD®. In the module without XAD®, 13 pg m^{-3} TnBP was measured in PUF1 and 7 pg m^{-3} in PUF2, while the modified module had 21 pg m^{-3} in PUF1, 14 pg m^{-3} in XAD®, and no TnBP in PUF2. Together with 7 pg m^{-3} in the GFF for both modules, this means that ca. 50% more TnBP were found in the module with XAD® compared to the one without (42 vs. 27 pg m^{-3}). However, overall concentrations of TnBP were very low, and the PUF1 sample itself contained 50% more TnBP in the modified module, so it cannot be concluded that higher levels of TnBP would be found in modules with XAD®-4 compared to modules without. TEP, however, shows a different behaviour. In the module without XAD® resin, 24 pg m^{-3} were found in PUF1 and 35 pg m^{-3} in PUF2. This indicates that TEP has suffered from breakthrough in the module during the sampling period, and some amount has been lost. In the modified module, 12 pg m^{-3} were found in PUF1, 70 pg m^{-3} in the XAD®, and only 3 pg m^{-3} in PUF2. This means that there probably was no breakthrough from PUF2 and thus loss of TEP in this module, because most of it has been sequestered by the resin. Overall, TEP concentrations were more than 40% higher when sampled with the XAD® module (93 pg m^{-3}) compared to the module without XAD® (66 pg m^{-3}).

Table 6. Measured air concentrations of Organophosphate esters in pg/m^3 at the Hazelrigg field station using a traditional module (GFF-PUF1-PUF2, top) and a modified module with XAD® (GFF-PUF1-XAD®-PUF2, bottom). TCEP Tris(2chloroethyl) phosphate, TCiPP Tris(chloroisopropyl) phosphate, TnBP Tri-*n*-butyl phosphate, TEP Triethyl phosphate.

Standard Module				
	TCEP	**TCiPP**	**TnBP**	**TEP**
GFF	7	249	7	7
PUF1	<LOQ	22	13	24
PUF2	<LOQ	<LOQ	7	35
Σ Module	7	271	27	66

Module with XAD-pod				
	TCEP	**TCiPP**	**TnBP**	**TEP**
GFF	7	252	7	8
PUF1	<LOQ	19	21	12
XAD-pod	<LOQ	<LOQ	14	70
PUF2	<LOQ	<LOQ	<LOQ	3
Σ Module	7	271	42	93

4.3.2 PAHs

Ambient air PAH concentrations in pg m^{-3} for both samplers can be found in Table 7 and Figure 35. Indeno[1,2,3-*cd*]pyrene (IPR) could only be detected in the GFF sample of both modules, with 87 pg m^{-3} and 119 pg m^{-3}, respectively. Fluoranthene was found in GFF and PUF1, with levels in the latter five to six times higher compared to the former. Phenanthrene (PHE) was found in all samples, but only in concentrations around 50 pg m^{-3} in the GFF and PUF2 samples, but almost 50 times as much in the PUF1 sample (2402 pg m^{-3} and 2250 pg m^{-3}, respectively). Only very small amounts were measured in the XAD®-4 sample. As PUF2 contained less than 2.5% PHE compared to PUF1, no significant breakthrough had occurred and polyurethane foam can be considered to be a very efficient sampler for phenanthrene. In the sampler without XAD® resin, PUF1 contained 806 pg m^{-3} Fluorene (FLU), and PUF2 470 pg m^{-3}. It seems likely that a significant amount of FLU has been lost in this sample. However, in the other module only 59 pg m^{-3} were measured in XAD®, and 128 pg m^{-3} in the lower PUF plug. This means that while polyurethane foam is not a particularly efficient sampling medium for FLU, XAD®-4 is even less so. Other resins or adsorbents should be tested in place of XAD®-4 to achieve better sampling performance. Acenaphthene (ACE) concentrations in the standard module were 147 pg m^{-3} in PUF1 and 140 pg m^{-3} in PUF2, which again shows significant breakthrough of the compound. Unlike for FLU, however, XAD®-4 is shown to be a suitable sampling material for ACE with 606 pg m^{-3} found in this part of the module, which is more than four times as much as in PUF1 (138 pg m^{-3}), and only 40 pg m^{-3} can be found in the PUF2 sample here. As a result, more than 2.5 times as much ACE can be reported using the modified module (784 pg m^{-3}) compared to the standard one (287 pg m^{-3}). Finally, naphthalene levels in the module without XAD® were 101 pg m^{-3} and 143 pg m^{-3} for PUF1 and PUF2, respectively, and 78 pg m^{-3} (PUF1) and 75 pg m^{-3} (PUF2) in the modified module, but 7174 pg m^{-3} in the XAD®-4 pod. This means that overall the module with XAD® sampled almost exactly thirty times as much naphthalene (7327 pg m^{-3}) as the one without (244 pg m^{-3}). It also means that naphthalene is the dominant compound in the sample using XAD®-4 resin, while a traditional air sampling module would show phenanthrene to be dominant with levels about ten times as high as for naphthalene.

Table 7. Measured PAH air concentrations in pg/m^3 at the Hazelrigg field station using a traditional module (GFF-PUF1-PUF2, top) and a modified module with XAD® (GFF-PUF1-XAD®-PUF2, bottom). IPR Indeno[1,2,3-*cd*]pyrene, FLA Fluoranthene, PHE Phenanthrene, FLU Fluorene, ACE Acenaphthene, NAP Naphthalene.

Standard Module						
	IPR	**FLA**	**PHE**	**FLU**	**ACE**	**NAP**
GFF	87	112	51	<LOQ	<LOQ	<LOQ
PUF1	<LOQ	597	2402	806	147	101
PUF2	<LOQ	<LOQ	49	470	140	143
Σ Module	87	709	2502	1276	287	244

Module with XAD-pod						
	IPR	**FLA**	**PHE**	**FLU**	**ACE**	**NAP**
GFF	119	118	55	8	<LOQ	<LOQ
PUF1	<LOQ	580	2250	649	138	78
XAD-pod	<LOQ	<LOQ	26	59	606	7174
PUF2	<LOQ	<LOQ	51	128	40	75
Σ Module	119	698	2382	844	784	7327

In summary, both compounds in the experiment that would be classified as VOCs, (TEP, boiling point BP 215 °C, logK$_{OA}$ 5.5, and naphthalene, BP 218 °C, log K$_{OA}$ 5.13) showed much better sorption to XAD®-4 than to PUF, and would be difficult to sample quantitatively with traditional high-volume air samplers. Additionally, the fact that TEP concentrations are relatively low despite already high air volumes means that the sampling duration cannot easily be shortened. This is particularly true in cases where other chemicals with low environmental air concentrations are supposed to be collected with the same sampler. XAD®-4 resin also proved particularly efficient for acenaphthene, which, by its boiling point, would be considered an SVOC, (BP 279 °C, logK$_{OA}$ 3.98). Finally, XAD®-4 seems better than PUF at adsorbing TnBP (BP 289 °C, logK$_{OA}$ 7.7). However, for fluorene PUF would be the preferred sampling material, despite a similar BP (295 °C) and even a lower logK$_{OA}$ value (6.90) compared with TnBP. With a logK$_{OW}$ of 4.18 it is slightly more nonpolar than TnBP (logK$_{OW}$ 3.75), but also more nonpolar than TCiPP and TCEP, which shows that the preference for PUF on the one side and XAD® on the other side probably cannot be explained by physical parameters alone, but in addition also by molecule structure and its interaction with the sorbent material (Hayward et al., 2011).

Only low levels of phenanthrene were found in the XAD® sample compared to PUF, while the other compounds were not present in XAD® at all. TCiPP and fluoranthene were found in both PUF1 and GFF, TCEP and indeno[1,2,3-*cd*]pyrene in the GFF, although from this experiment it cannot be ruled out that they could have been sampled by XAD® alone if they had not already been removed by the GFF or PUF before reaching the XAD® pod below.

4.4 Conclusion and outlook

XAD® pods are an easy, economical, and tidy way to sample more volatile compounds, for example the OPE triethyl phosphate and the PAHs naphthalene and acenaphthene, with standard high-volume active air samplers. They are versatile, as the specific adsorber material and pre-cleaning method can be chosen depending on the compounds of interest. For higher air concentrations or longer deployment times, more than one pod could be used. For a wide range of chemicals, different adsorber materials could be mixed. In this experiment, XAD®-4 was used; other options include XAD®-2 or XAD®-7HP.

With this field-tested method, a wide range of toxic organic pollutants in ambient air, which are individually best sampled with either GFFs, or PUFs, or with XAD®, can be sampled and analysed simultaneously. The large surface area and adsorption capacity of XAD® also means that compounds that would normally show breakthrough during high-volume air sampling, because their equilibrium is reached very quickly on polyurethane foam, can now be sampled together with trace organic chemicals that require relatively large air volumes to be collected due to their low environmental concentrations.

Including XAD® pods in existing active air sampling networks, like the UK TOMPs network, would be a simple and cost-effective way to address some of their known limitations. It would increase their range of analytes across the VOC/SVOC spectrum without the need for additional samplers of a different type. Increased specific surface area and thus sampling capacity of XAD® resin compared to PUF could also increase the breakthrough volume of SVOCs that are successfully sampled with current methods and air volumes, but would show breakthrough with increased air sample volumes, for example lower-chlorinated PCBs. Suitability of XAD® for these compounds would need to be tested first, however. If successful, this would mean that air flow rates and/or sampler deployment times could be increased, which would improve the detection of air pollutants with low ambient air concentrations. Extended sampling periods would reduce the number of samples that need to be collected and analysed, saving time and money and improving the environmental impact of the research project. This would be particularly of advantage for large-scale air sampling networks, which often include very remote sampling sites.

4.5 References

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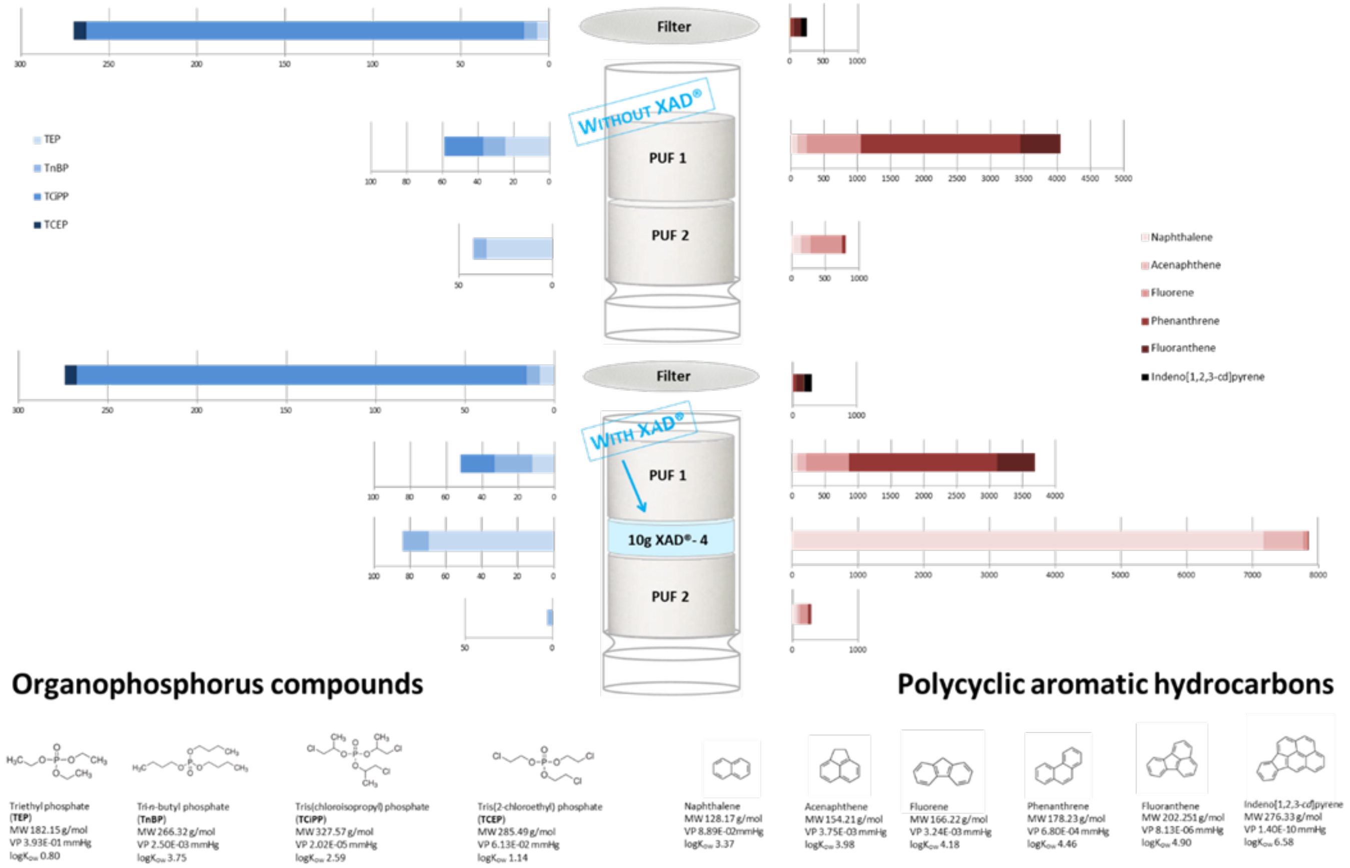

Figure 35. Air concentrations of selected OPs and PAHs in pg/m^3 at Hazelrigg Field Station near Lancaster University using modules without (top) and with (bottom) XAD®-4 pods.

5 Short-term variations in POPs in ambient air: The 'Bonfire Project'

Abstract

Daily ambient air samples were taken over a two-week period before, during, and after the UK 'Bonfire Night' on the 5th of November 2016. Samples between the 4th and 6th of November showed increased polybrominated biphenyl ether (PBDE) concentrations compared to background levels, but no such increases for polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). Elevated levels of BDE 99, BDE 153, BDE 154, and BDE 183 in particular indicate that potentially penta-BDE and octa-BDE-containing old furniture, upholstery, and plastics were illicitly added to some private bonfires. Compared to a similar study carried out in 2000 at the same location, both absolute PBDE air concentrations during the 'Bonfire Night' period, and their relative increase compared to background levels have decreased, reflecting their ban in the EU in 2004 and their addition to Annex A of the Stockholm convention in 2009. The absence of any noticeable increase in HCB levels during 'Bonfire Night' suggests that HCB is no longer used as a colour enhancer in fireworks.

5.1 Introduction

While regular sources of persistent organic pollutants (POPs) in the atmosphere can be considered well-characterised, including long-term trends in emissions, environmental concentrations, and spatial and seasonal patterns, this is much less so for the impact of irregular, short term events with the potential to release large amounts of POPs. This is mainly due to the fact that they are usually unintentional releases, such as wildfires, so no sampling campaign can be planned beforehand to capture them. When these events occur, the emphasis is clearly on ending them as quickly and by all sensible means possible. Thus, possible ambient air pollution can mainly be investigated after the event or if the impact was large enough to significantly show up in air samples collected regularly even at some distance. This will only be the case if the event was substantial enough to a) produce a noticeable spike in pollution levels of samples that are usually integrated over weeks, months, or even years, and b) be noticed by or communicated to the researchers carrying out the air sampling.

This would, for example, be the case for prolonged and expansive forest fire events if the affected vegetation or soil contained substantial levels of the analytes of interest that are then volatilised in high temperatures, for example polychlorinated biphenyls (PCBs) or pesticides, or if the analytes themselves were produced during biomass combustion, for example polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polycyclic aromatic hydrocarbons (PAHs). It would, however, less likely to be the case for small-scale events and events on private property, for instance earthworks and demolition of buildings potentially burdened with legacy POPs at construction sites, house fires, small fires at landfill sites, or unsanctioned small-scale incineration of garden and bulky waste on private properties.

Eckhardt et al. (2007) reported on two biomass burning events that led to greatly increased PCB levels at the remote Arctic Zeppelin research station on Spitsbergen. First, from a boreal forest fire in North America in July 2004 encompassing an area of about 5.8 million hectares, and secondly from agricultural fires in Eastern Europe in spring 2006. Gong and Wang (2021) investigated frequent forest fires in the central Himalaya and state that these are not only important sources of POPs locally, but also contribute ca. 20% more atmospheric POPs and PAHs to the Tibetan Plateau, which would make forest fires an important secondary source of these analytes. Furthermore, Gong et al. (2021) discuss the overall role of forests on POPs cycling and distribution in forests, and the impact of forest fires and deforestation on the ability of forests to sequester POPs.

One opportunity to research relatively unregulated short-term events that could lead to POPs emissions into the atmosphere is the British tradition of Guy Fawkes Night, or 'Bonfire Night' on the 5th of November each year. Although having a political background in the seventeenth century, it is nowadays mainly characterised by a large number of bonfires being lit and fireworks being released, and celebrations organised by small groups of friends and families, by charities and local community groups, and by local councils organising large events with professional firework displays and requiring entry tickets alike.

Dyke et al. (1997) measured PCDD and PCDF air concentrations before, during, and after the 1994 'Bonfire Night' at Oxford in England and Cardiff in Wales and found an increase in PCDD and PCDF concentrations by approximately a factor of four during the period of bonfire night. Farrar et al. (2004) analysed air samples taken in Lancaster, UK in November 2000 and reported a sharp increase in PAH concentrations over the 'Bonfire Night' period as well as an even larger simultaneous increase in PBDE levels, in particular BDE 99, BDE 153, and BDE 154. They hypothesised that products treated with the commercial penta-BDE mixture, such as household furnishing foams and textiles, were subject to unsanctioned burning on private bonfires.

Fireworks are also a potential source of the POP hexachlorobenzene (HCB). Historically, HCB was most commonly used as a pesticide, but was also present as by-product and/or impurity in several chemical processes, such as the manufacture of chlorinated solvents, chlorinated aromatics and pesticides. It was also used in fireworks as a chlorine donor to enhance and brighten the intensity of colours (DAERA, 2012). HCB is included in the 1998 Aarhus Protocol on Persistent Pollutants (UNEP, 2001), and as such its use in fireworks is prohibited. However, Schwarz et al. (2014) analysed firework articles which were already placed on the market, i.e. had already been type- and batch-tested by notified bodies and manufacturers/importers in Europe. They discovered a violation rate of 1.5% in these samples, meaning the limit value for HCB of 50 mg kg^{-1} was exceeded. For a similar EUROPOP project, there was a reported higher violation rate of 10% on average with HCB contamination ranging from 62 mg kg^{-1} up to 127,000 mg kg^{-1}. However, in only a small number of these cases legal action was taken. Given already high atmospheric background levels of HCB (Gioia et al., 2006), it is therefore unlikely but not impossible that noticeable amounts of HCB are released during large firework events like the UK ‘Bonfire Night’, in particular when fireworks for residential use are acquired from sources that cannot guarantee the compliance with official certification requirements.

In this study, the effects of ‘Bonfire Night’ on atmospheric PCB, PBDE, and HCB concentrations near Lancaster, UK were investigated. In addition, a recently developed adaptation to a standard active air sampling assembly using pods filled with XAD® resin was tested, in particular regarding its potential to improve sampling of relatively volatile analytes such as HCB.

5.2 Materials and methods

5.2.1 Materials, sampler preparation, and sampling

Samples were obtained by active air sampling using sampling modules. Three types of modules were prepared, containing either XAD®-4 resin, XAD®-7HP resin, or no XAD® resin. Sampling modules were prepared as described in Chapter 4.2.2. In short, they contained a glass fibre filter (GFF), two pre-cleaned polyurethane (PUF) plugs, and either a pre-cleaned cellulose pod with 10 g XAD®-4 or 2 cellulose pods with 5 g XAD®-7HP resin each between the two PUF plugs, or no pod. XAD®-7HP resin has a lower density than XAD®-4 resin, exceeding the volume fitting in the cellulose liner, which is why two pods containing 5 g were used instead.

Polyurethane foam (PUF) plugs (height 50 mm, OD 75 mm) were obtained from Klaus Ziemer GmbH, Germany. Amberlite XAD®-4, Amberlite XAD®-7HP resin and 110 mm Whatman GF/A glass microfibre filters were purchased from Scientific

Laboratory Supplies, UK. All solvents were HPLC grade or higher and obtained from Fisher Scientific, UK, except for HPLC grade dichloromethane (DCM), which was bought from Rathburn Chemicals Ltd, UK. Merck KGaA, Germany supplied sodium sulfate anhydrous, 0.63-2.0 mm. Bio-Beads S-X3 for gel permeation chromatography (GPC) were from Bio-Rad Laboratories.

An HCB-containing pesticides analytical standard mixture was acquired from Protocol Analytical Supplies Inc., USA, as was the PCB analytical standard mixture, and the ^{13}C-PCB mixture was from CIL standards, USA. A native PBDE standard mixture was bought from Chiron Ltd, UK, a ^{13}C-labelled PBDE mixture and a separate ^{13}C-BDE 209 standard from Wellington Laboratories, Canada. Native BDE 209 was purchased from Cole-Parmer Ltd, UK.

The modules were installed in three pre-calibrated active air samplers at the Hazelrigg field station near Lancaster. The samplers were run in parallel, and every 24 hours, during which around 240 ±20 m^3 of ambient air were sampled, the sampling modules were exchanged around 12pm (midday) for new ones, except for the first sampling period, which lasted 70 hours, corresponding to ca. 600 m^3 air. The first of twelve samples for each sampler type was deployed on the 28th of October 2016 and collected on the 31st of October, the last sample each was deployed from the 10th to the 11th of November. With Bonfire Night being on the 5th of November, this meant that samples were collected during a period spanning roughly one week before and one week after the actual event. The flow rates were determined using a flow venturi and a MagnaHelic gauge. After deployment, the samplers were taken to the laboratory, where they were disassembled immediately and each sample stored separately wrapped in clean aluminium foil and stored in a sealed polyethylene bag in a -20 °C freezer until sample extraction.

5.2.2 Sample extraction, clean-up and instrumental analysis

All samples were spiked with a mixture of isotope-labelled recovery standards and extracted separately for 16 hours in 300 ml hexane using soxhlet extraction. The volume of the extracts was then reduced to ca. 2 ml with rota-evaporation, and split into two identical samples. One of them was archived for future analysis, the other further reduced to 0.5 ml under nitrogen and cleaned up with an 8 g/8 g silica/acid silica column eluted with 150 ml hexane. The eluate was again reduced to ca. 0.5 ml, and a second clean-up step followed using a 6 g gel permeation chromatography (GPC) column eluted with a 1:1 mixture of hexane and DCM, where the first 15 ml of the eluate were discarded and the subsequent 30 ml, containing all analytes, collected for analysis. Finally, the extracts were evaporated to <0.5 ml under a gentle stream of nitrogen, transferred to a GC vial containing 25 µl dodecane with internal (syringe) standards, and further evaporated to a final volume of 25 µl.

The extracts were analysed for BDE 209 on an Agilent 7000A GC-MS/MS system in positive EI-MRM mode with pulsed splitless injection. The analytical column used was 5 m x 0.25 mm x 0.12 µm of an Agilent CP-Sil 8 CB analytical column operated in backflush mode. The initial oven temperature was 110 °C, held for 1.5 min, increased to 320 °C at a rate of 30 °C min $^{-1}$ and then held for another 3.5 min. The MSD transfer line was set to 320 ^{0}C, and the MS source temperature to 230 ^{0}C. Agilent MassHunter® software was used for data acquisition as well as processing.

PCBs and tri- to hepta-BDEs were analysed using a Thermo DSQ II GC-MS system, equipped with an Agilent CP-Sil 8 CB GC column (50 m x 0.25 mm x 0.12 µm). The initial oven temperature was 100 °C (held for 2 min), then increased to 140 °C at a rate of 20 °C min^{-1}, further increased to 200 °C (4 ^{0}C min^{-1}), where it was held for 10 min, and finally to 300 °C (4 °C min^{-1}), held for 25 minutes. The GC interface temperature was set to 300 °C, and the MS source temperature to 250 °C. Thermo Xcalibur™ software was used for both data acquisition and sample processing.

5.2.3 QA/QC

Field blanks for all three types of samplers were collected at the beginning and the end of the sampling period. Laboratory blanks for GFFs, PUFs, XAD®-4 pods, and XAD®-7HP pods were also analysed, and values were subtracted from all other samples. Following this, limits of quantification (LOQs) were calculated for each analyte using the concentration of the highest field blank plus three times its standard deviation, or the instrument limit of detection (LOD) for analytes not found in the field blanks. All values were recovery-corrected using the recoveries of the isotope-labelled standards spiked onto the samples before extraction (recovery standard). The recovery standard itself was quantified to ensure it contained the correct concentrations for all analytes. Calibration standards were run in regular intervals between samples to check the performance of the instruments. For each analyte two ions were used for quantification, and usually the lower result of those two was used, unless that ion showed a very weak response and could only be used as qualifying ion.

5.3 Results and discussion

5.3.1 Polybrominated diphenyl ethers

Daily ambient air concentrations for polybrominated diphenyl ethers (PBDEs) during the study are depicted in Figure 36 and Table 8 (page 116). PBDEs were almost exclusively found on the glass fibre filter (GFF) and in the upper PUF (PUF1), so the differences between the three types of sampler were small and the results are shown as averages over all three samplers and the sum of all samples within one sampler – GFF, PUF1, PUF2, and XAD®, if applicable. The calculated air concentrations of tri- to hepta-BDEs were generally quite low and between 0.5 and 1.6 pg m^{-3}, except for the three days around 'Bonfire Night', where Σ tri- to hepta-BDE concentrations rose to over 10 pg m^{-3} on the 4th of November and then subsided over the course of the next three days. BDE 209 (deca-BDE) was consistently the most abundant of all PBDE congeners analysed, however concentrations fluctuated wildly between the sampling days, ranging between 0.6 and 21 pg m^{-3}, and the relative contribution of BDE 209 to overall PBDE levels was between 40% and over 90%. This compares to air concentrations between 92 ± 130 and 370 ± 520 pg m^{-3} found during a transect study in the UK Midlands between June 2012 and January 2013, which represented 61-92% of ΣPBDE in that study (Drage et al., 2016). These values, however, are higher than BDE 209 concentrations measured in other studies, where levels between <LOQ and 85 pg m^{-3} were detected in urban air in recent years, and between <LOQ and ~50 pg m^{-3} in remote and rural locations (Rauert et al., 2018; Saini et al., 2020). This may be the result of differences in fire regulations between countries and preferences in the flame retardants used, as the 85 pg m^{-3} were also found in a UK sample (London).

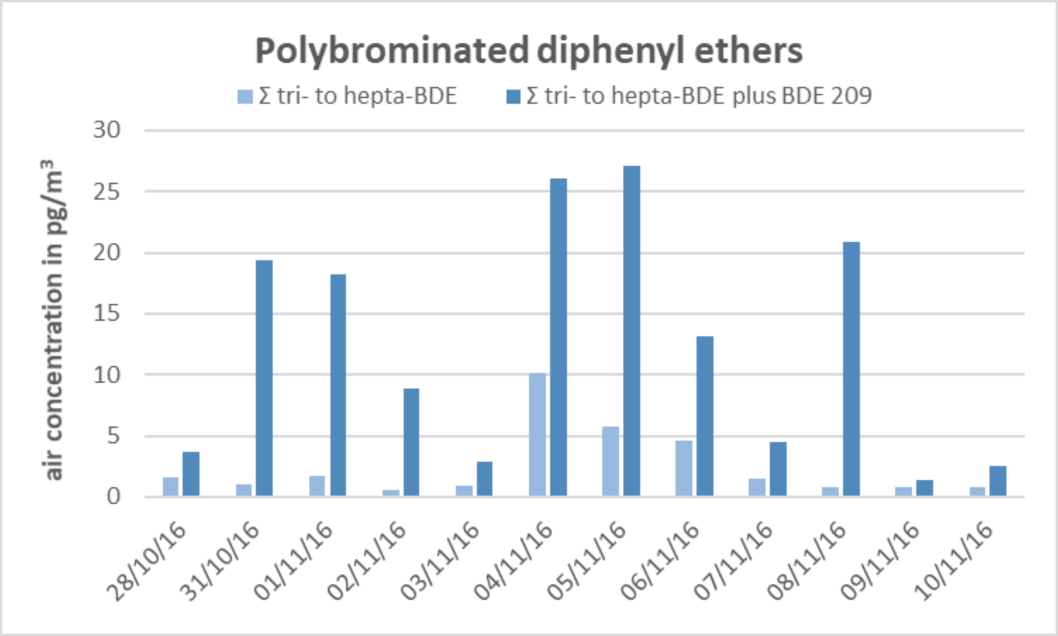

Figure 36. Daily Σ tri- to hepta-BDE (light blue) and Σ tri- to hepta BDE plus BDE 209 (dark blue) air concentrations at Hazelrigg field station.

Figure 37 and Figure 38 show the PBDE congener profiles for each day, Figure 37 including BDE 209 and Figure 38 excluding BDE 209. BDE 183 (hepta-BDE) was present in all samples, and BDE 47 (tetra-BDE) and BDE 154 (hexa-BDE) in most of them. The appearance of BDE 99 (penta-BDE) and BDE 153 (hexa-BDE) on the 4th of November is striking, coinciding with the overall increase in PBDEs on that day. BDE 154 and BDE 183, although present in most or all samples, also have their highest absolute concentrations on the 4th of November, decreasing slowly over the course of the next three days.

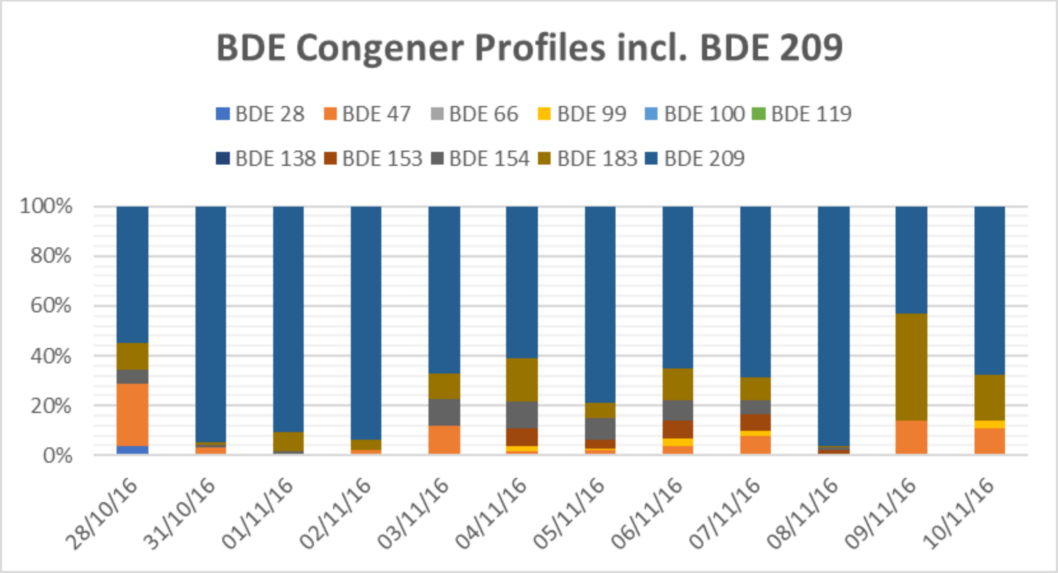

Figure 37. PBDE congener profiles (% contribution of respective congener to ΣPBDE) of daily samples 28/10-11/11/2016.

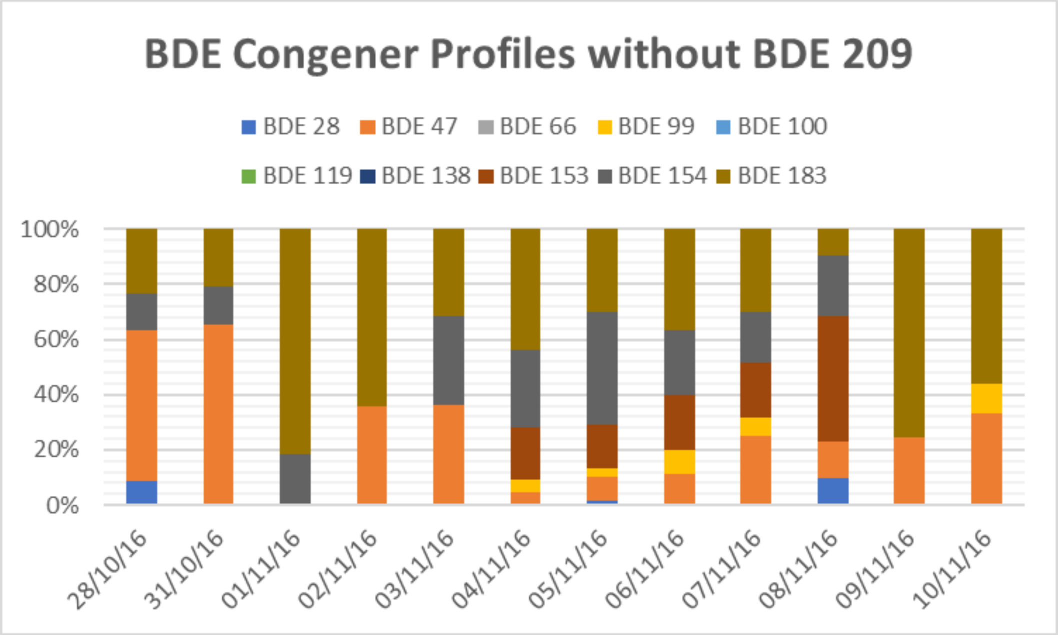

Figure 38. PBDE congener profiles (% contribution of respective congener to ΣPBDE) of daily samples 28/10-11/11/2016, excluding BDE 209.

Figure 39 shows the wind roses for Blackpool, Lancashire (roughly 30 km to the southwest of Hazelrigg field station), and Figure 40 the air temperatures measured directly at the meteorological observation site at the field station for the sampling period. Temperatures are slightly higher at the beginning of the study, which may explain the relatively higher fraction of BDE 47 in the first two samples, but concentrations were generally close to the method LOQ, and small changes can make the difference between the congener being reported or considered <LOQ. The wind roses show no significant difference between days with high and low PBDE concentrations, although north-north-westerly winds over ‘Bonfire night’ would make it more likely that signals from local sources of the nearby populated area (Lancaster City) would be captured.

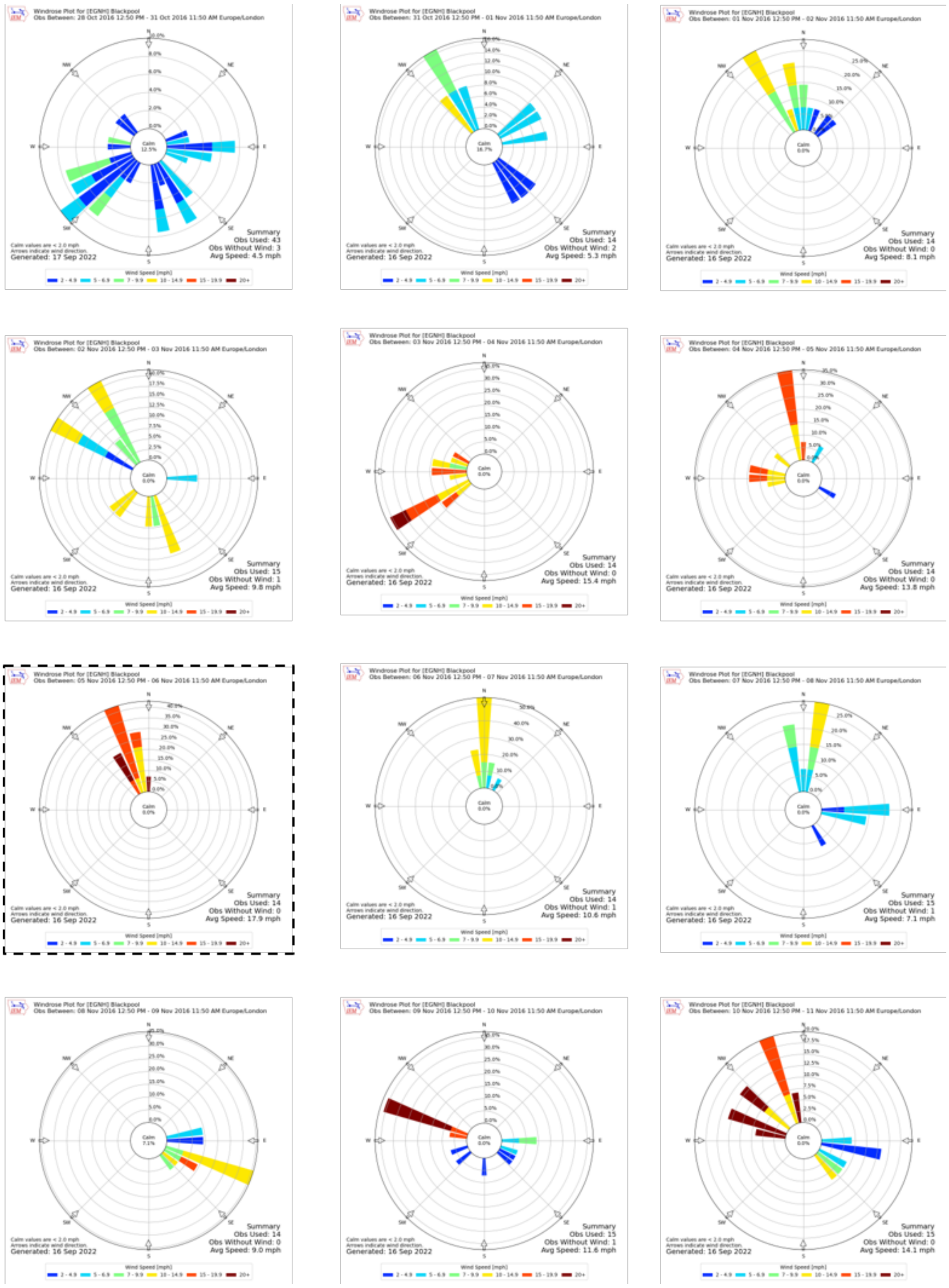

Figure 39. Wind roses for Blackpool, Lancashire, for the sampling period 28/10-11/11/2016. The wind rose containing 'Bonfire Night' is highlighted. Source: Iowa Environmental Mesonet (iastate.edu).

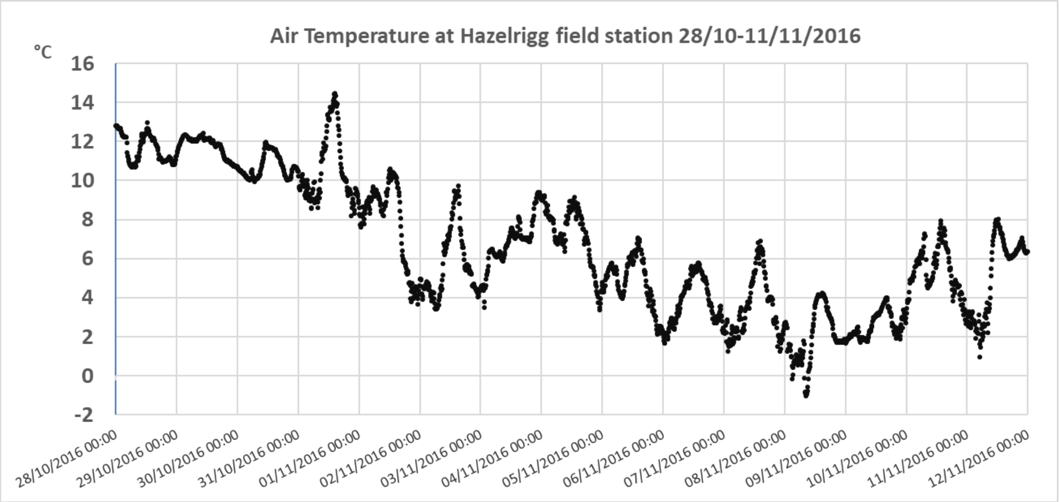

Figure 40. Air temperature in °C at Hazelrigg field station during the sampling period 28/10–11/11/2016.

It is therefore likely that the elevated levels of BDE 99, BDE 153, BDE 154, and BDE 183 resulted from local events around that time, specifically the eponymous bonfires around 'Bonfire Night'. BDE 183 was a main component of the octa-BDE commercial mixture, BDE 99 of the penta-BDE mixture, and BDE 153 and BDE 154 of both. BDE 47, another main component of the penta-BDE technical mixture, was not found at elevated levels during the 'Bonfire' period. Before their ban in the EU in 2004 and their addition to the Stockholm convention in 2009, octa-BDE mixtures were mainly used in plastic housings of electrical and electronical equipment, while the penta-BDE mixture was widely used in textiles and foam furnishings. It is theorised that PBDE-containing household waste was illegally added to some private bonfires. In 2016, 'Bonfire Night' fell on a Saturday, so many popular official events were held on that day exactly, which may have resulted in some smaller, private events to be moved to the days before. This would explain why the peak in PBDE air concentrations was already on Friday, the 4th of November, the day before actual 'Bonfire Night'.

Indeed, the findings here are very similar to those of Farrar et al. (2004), who carried out a similar study in 2000 at a nearby location. They, too, found highly elevated levels of the BDE congeners contained in commercial BDE mixtures. In that study, the increase of BDE concentrations compared to background levels was even higher than in this study, despite already higher background levels in 2000, before the widespread ban of PBDEs, compared to 2016, several years after the ban. This could indicate that in addition to the decrease in PBDE emissions from primary sources during production or intended use of PBDE-containing products, average PBDE levels in obsolete household equipment and furnishings have also started to decline, although it is also likely that a) there were fewer bonfires in the area compared to 2000, b) fewer discarded household items were added to the bonfires and c) the air masses sampled contained a smaller fraction of air impacted by the bonfires. It is possible that there were no apparent increases in BDE 47 (tetra-BDE) concentrations during 'Bonfire night' observed during this study (as opposed to a ca. 4-fold increase in 2000) because over the years since the ban lighter PBDEs have already volatilised. As a result, their atmospheric concentrations are more uniform over the course of the year and mainly influenced by increased volatilisation with increased environmental temperatures from a number of diffuse sources, while higher-brominated congeners are released from their products at sporadic incineration events rather than through volatilisation.

Furthermore, given the relative dominance of the deca-BDE commercial mixture over the penta- and octa-mixtures in the last decades, there is a possibility that the BDE congeners observed are the result of degradation of deca-BDE in consumer products, rather than the emission of penta- or octa-BDE mixtures used in the past themselves. This begs the question why no increase in BDE-209 itself was observed in parallel with the other congeners in this project. Future projects that could help answering this question could include further air sampling campaigns over 'Bonfire Night', and the controlled incineration of old consumer products in specialised large-scale scientific burn facilities and the subsequent analysis of any PBDEs emitted.

5.3.2 Polychlorinated biphenyls

Figure 41 and Table 8 (page 116) show daily polychlorinated biphenyl (PCB) ambient air concentrations during this study, and Figure 42 their congener profiles. PCBs were almost completely found in the top PUF (PUF1), and there was no significant difference between the sampler types, so as for PBDEs results are depicted as the average over all three samplers for one day, and the sum of GFF, PUF1, PUF2, and XAD®, if applicable.

ΣPCB air concentrations in the first two samples (28-31/10 and 31/10-1/11) were elevated compared to the rest of the study, which may be the result of higher air temperatures or prevailing winds from the SW and SE direction (Liverpool-Manchester-conurbation) at the beginning of the study, or a combination of both. Congener profiles were relatively uniform across all samples, however, with no obvious impact of either temperature, wind direction, or ‘Bonfire Night’ visible.

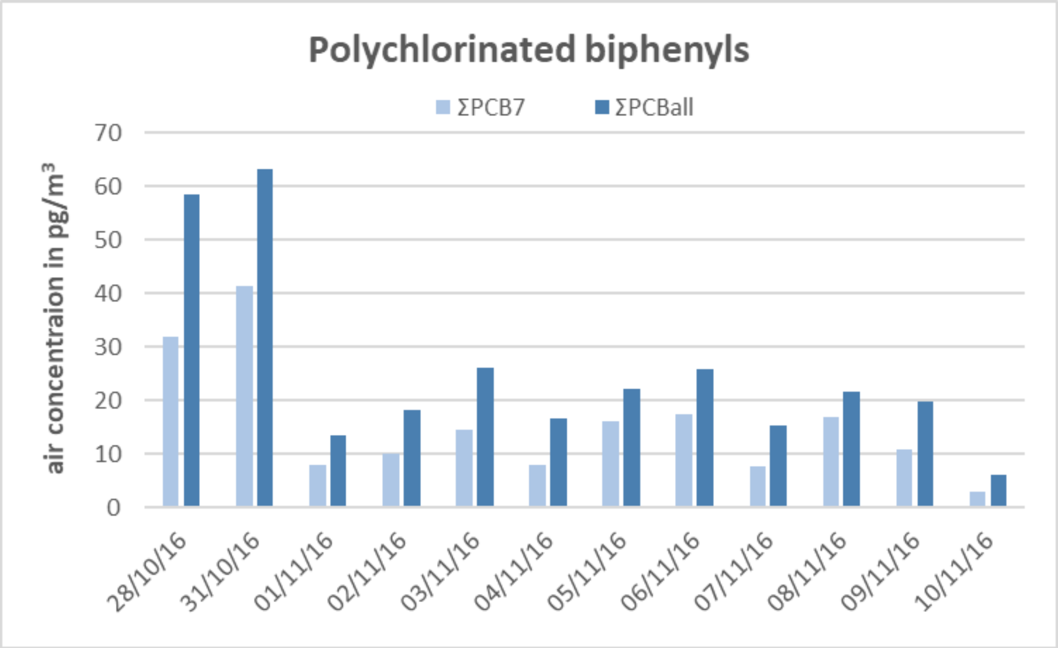

Figure 41. Daily ΣPCB_7 (light blue) and ΣPCB_{all} (dark blue) air concentrations at Hazelrigg field station.

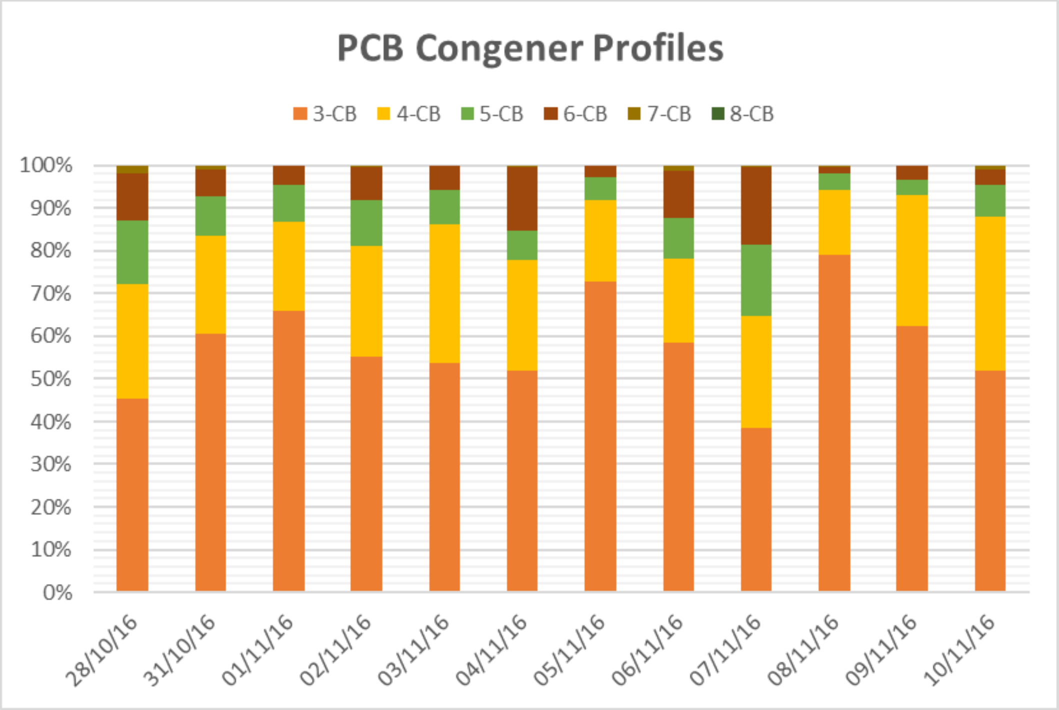

Figure 42. PCB Congener profiles of daily samples 28/10-11/11/2016.

This is in contrast with the results from Farrar et al. (2004), who described a doubling in PCB concentrations during the 'Bonfire Night' period, although this, too, was a less pronounced effect than for PBDEs. It is possible that in 2000, several decades after their widespread restrictions or ban in European countries, the PCB burden of household products illegally added to private bonfires had started to reduce compared to PBDEs, which were still very much in use then, comparable to PBDE burdens in today's waste after the ban. On the other hand, Farrar reports that increases were stronger for lower-chlorinated compounds, which could also be the result of increased PCB volatilisation from soils below and around the bonfire due to the temperature increase, and release of PCBs from firewood (Gullett et al., 2003; Lee et al., 2005).

5.3.3 Hexachlorobenzene

Results for hexachlorobenzene (HCB) are shown in Figure 43 (page 115) and Table 8 (page 116).

The impact of XAD® resin on HCB sampling. Unlike PCBs and PBDEs, a significant fraction of HCB was sampled in the XAD® resin, both XAD®-4 and XAD®-7HP. Figure 43 thus shows daily HCB results separately for each sampler and each compartment of the sampler. For most sampling days, for example the period between the 4th and 9th of November, the main fraction of HCB was adsorbed to the PUF1 sample, and the standard sampler (module) would therefore have been sufficient to accurately report HCB concentrations in ambient air.

In some samples however, notably samples 28-31/10 and 31/10-1/11/16, HCB concentrations were as high in PUF2 as in PUF1 for the sampler without XAD®, and similar (31/10) or even considerably higher (28/10) in the XAD® fraction for samplers including XAD® pods. In these cases, it can be assumed that the HCB sampling capacity of the top PUF plug had been exceeded, and HCB was breaking through to the lower parts of the sampler. However, for the sampler without XAD®, HCB concentrations in the backup PUF (PUF2) were as high as in PUF1, which means that HCB was probably breaking through the backup plug as well and was therefore not quantitatively sampled by these standard modules.

In the samplers with XAD® pods, a similar fraction (31/10) or even greater fraction (28/10) of HCB was retained in the XAD®, with very little breakthrough to the PUF2 sample. In these samplers, HCB would have been sampled quantitatively, and could thus be reported correctly. However, in all samples in this study, HCB levels found in XAD®-4 samples were higher than in XAD®-7HP samples, which may either be due to XAD®-4 being more suitable for HCB sampling, or due to decreased extraction efficiency from XAD®-7HP during soxhlet extraction with hexane. This could potentially be improved with different extraction solvents or longer extraction times, and will have to be tested in future experiments.

HCB ambient air concentrations calculated for the deployment period 28-31/10/16 were 39 pg m^{-3} without XAD®, 84 pg m^{-3} with XAD®-4, and 71 pg m^{-3} with XAD®-7HP. For the deployment period 31/10-1/11/16, calculated concentrations were 30 pg m^{-3}, 46 pg m^{-3}, and 40 pg m^{-3}, respectively.

Both samples for which the inclusion of XAD® in the sampler had a significant impact on the calculated HCB air concentrations were taken at the beginning of the study, when air temperatures were higher than during the rest of the study. Additionally, the first sample was taken over three days with a final air sampling volume of 600 m^3 compared to 240 m^3 otherwise. HCB air concentrations calculated from this sample were also at least twice as high (ca. 80 pg m^{-3}) than the other samples, while the sample taken 31/10-01/11/16 did not show elevated levels.

In conclusion, while including XAD® resin in the samplers made no difference for the sampling of PCBs and PBDEs, it increased calculated air concentrations for HCB by up to 100% depending on sampling conditions. It is therefore suggested to include XAD® resin in samplers for sampling

- of analytes with a volatility higher than that of tri-CBs
- of analytes with high air concentrations
- at higher air temperatures
- for longer periods or at higher air flows.

HCB air concentrations during 'Bonfire Night'. As shown in Figure 43, an increase of HCB concentrations from the fireworks during or around 'Bonfire night' could not be observed. As discussed above, any fireworks used in official displays or purchased from legal sources like supermarkets would now be expected to be free of HCBs, and fireworks from other sources for private displays were either HCB-free as well, or any HCB contained was thermally destroyed at the point of release or not abundant enough to create a signal, especially given relatively high background concentrations in ambient air.

5.4 Conclusions and outlook

Daily air sampling around the 2016 UK 'Bonfire Night' revealed increased PBDE concentrations in ambient air compared to background levels, but no such increases were observed for PCBs and HCB. Elevated concentrations of BDE 99, BDE 153, BDE 154, and BDE 183 in particular indicate that penta-BDE and octa-BDE-containing old furniture, upholstery, and plastics were possibly illicitly added to some residential bonfires ('backyard burning'). Compared to a similar study in 2000, both absolute PBDE air concentrations during the 'Bonfire Night' period, and their relative increase compared to background levels have decreased, reflecting their ban in the EU in 2004. Since their phase-out, PBDEs in consumer goods have been replaced by other flame retardants like organophosphorus flame retardants (OPFRs) and novel brominated flame retardants (NBFRs). Further studies will show if this change is also reflected by increased OPFR and NBFR air concentrations during 'Bonfire Night'.

5.5 References

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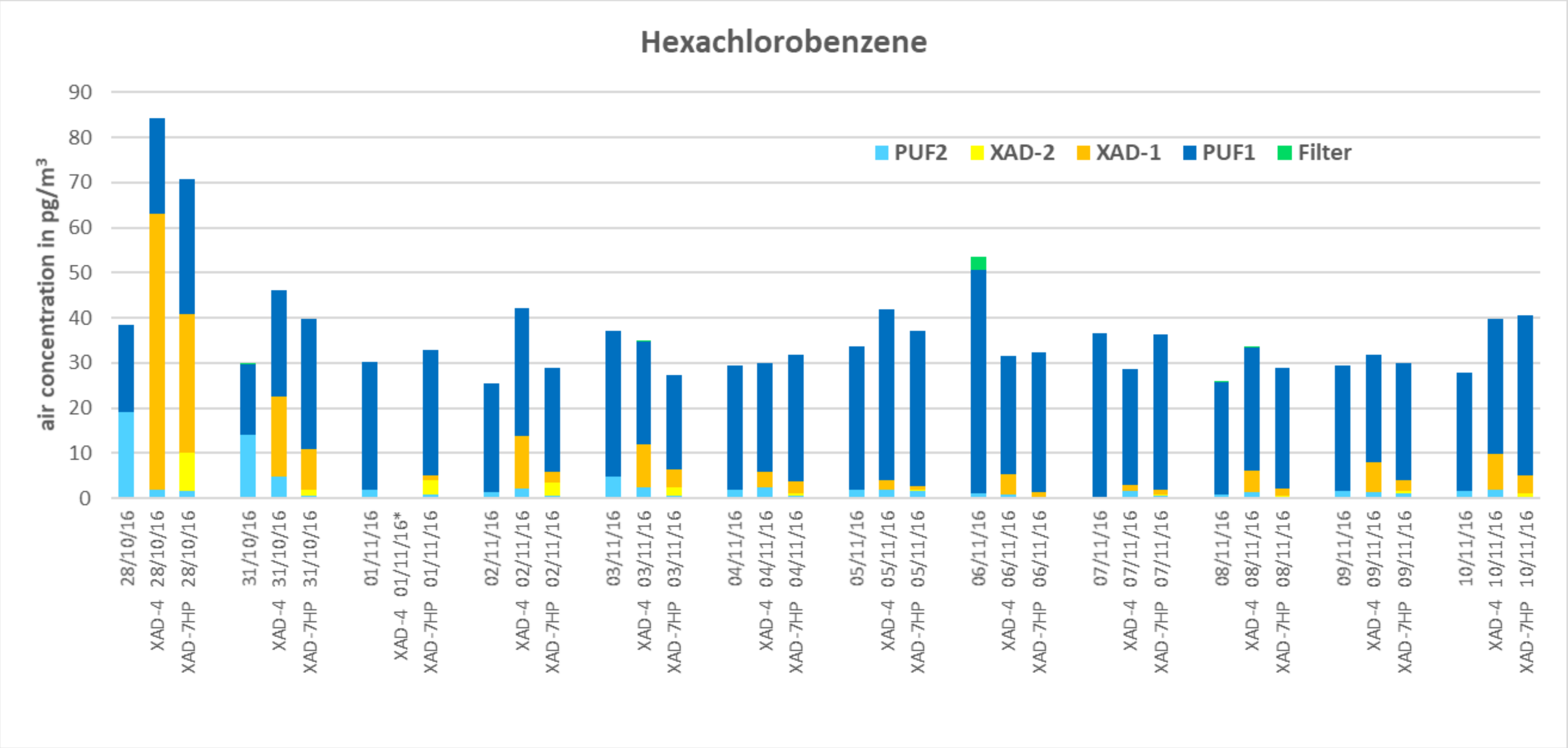


Figure 43. Daily Hexachlorobenzene (HCB) air concentrations in pg/m³ at Hazelrigg field station 28/10-11/11/2016 calculated using samplers with 10 g XAD®-4, 10 g XAD®-7HP, or no XAD® resin. *no XAD®-4 containing sampler 1/11/16.

Table 8. Average measured target compound concentrations in pg/m³ for each sampling day of the ‘Bonfire Project’.

Sampling date (start)	28/10/16	31/10/16	01/11/16	02/11/16	03/11/16	04/11/16	05/11/16 (Bonfire Night)	06/11/16	07/11/16	08/11/16	09/11/16	10/11/16
HCB	61.38	38.58	31.49	32.14	33.17	30.47	35.39	39.11	33.82	29.45	29.77	36.04
PCB 18	1.83	3.05	0.82	1.24	2.33	1.94	1.15	1.51	0.66	0.76	0.59	0.38
PCB 22	4.34	3.31	1.37	1.71	0.82	0.86	0.58	0.00	1.05	0.66	2.34	0.64
PCB 28/31	20.30	31.96	6.62	7.16	10.80	5.87	14.33	13.58	4.13	15.66	9.43	2.09
PCB 41/64	5.21	2.15	0.34	1.11	1.72	0.50	1.05	1.17	1.03	1.32	1.51	0.54
PCB 44	3.54	2.65	0.48	0.73	2.03	1.23	0.87	0.91	1.52	0.47	1.16	0.34
PCB 49	1.06	1.95	0.44	0.49	1.10	0.37	0.47	0.52	0.15	0.27	0.79	0.22
PCB 52	3.90	4.85	0.62	1.21	1.82	0.62	0.59	1.12	0.60	0.53	0.81	0.44
PCB 56/60	1.35	1.07	0.41	0.37	0.67	0.70	0.46	0.42	0.39	0.36	0.70	0.14
PCB 70	0.75	0.99	0.00	0.14	0.11	0.11	0.00	0.35	0.06	0.09	0.00	0.09
PCB 74	0.00	0.96	0.52	0.68	1.01	0.75	0.75	0.61	0.24	0.23	1.12	0.40
PCB 87	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 90/101	2.77	2.21	0.50	0.75	0.85	0.40	0.34	0.98	0.88	0.19	0.18	0.16
PCB 965	2.28	2.23	0.50	0.71	0.84	0.52	0.28	0.82	0.56	0.16	0.38	0.29
PCB 99	0.44	0.05	0.00	0.00	0.00	0.05	0.15	0.10	0.00	0.00	0.00	0.00
PCB 104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 105	0.00	0.09	0.00	0.00	0.05	0.00	0.00	0.00	0.07	0.00	0.00	0.00
PCB 110	1.50	0.54	0.19	0.08	0.05	0.00	0.00	0.25	0.29	0.05	0.00	0.00
PCB 114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 118	1.69	0.58	0.00	0.31	0.33	0.21	0.46	0.23	0.73	0.45	0.12	0.00
PCB 123	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 132/153	2.03	1.26	0.14	0.48	0.51	0.66	0.27	0.97	1.00	0.08	0.33	0.08
PCB 138	1.02	0.56	0.09	0.23	0.28	0.28	0.08	0.47	0.47	0.10	0.08	0.04
PCB 141	0.32	0.16	0.00	0.00	0.00	0.00	0.00	0.13	0.04	0.00	0.00	0.00
PCB 149	2.01	1.42	0.25	0.51	0.56	0.68	0.24	0.92	0.90	0.17	0.25	0.06
PCB 151	1.01	0.73	0.11	0.22	0.12	0.13	0.00	0.40	0.37	0.00	0.00	0.04
PCB 156	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

PCB 157	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 158	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 167	0.00	0.00	0.00	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00
PCB 170	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 174	0.29	0.06	0.00	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00	0.00
PCB 180	0.29	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 183	0.17	0.07	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.05	0.00	0.00
PCB 187	0.38	0.16	0.00	0.06	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
PCB 188	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 189	0.00	0.19	0.00	0.00	0.00	0.04	0.00	0.17	0.00	0.00	0.00	0.06
PCB 194	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 199	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 203	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BDE 28	0.15	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.07	0.00	0.00
BDE 47	0.89	0.67	0.00	0.21	0.34	0.48	0.49	0.50	0.36	0.10	0.19	0.27
BDE 66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BDE 99	0.00	0.00	0.00	0.00	0.00	0.48	0.19	0.41	0.09	0.00	0.00	0.09
BDE 100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BDE 119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BDE 138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BDE 153	0.00	0.00	0.00	0.00	0.00	1.89	0.91	0.92	0.29	0.34	0.00	0.00
BDE 154	0.21	0.14	0.31	0.00	0.30	2.84	2.33	1.07	0.26	0.16	0.00	0.00
BDE 183	0.38	0.21	1.38	0.37	0.30	4.47	1.70	1.67	0.43	0.07	0.58	0.46
BDE 209	2.01	18.36	16.52	8.32	1.91	15.94	21.43	8.58	3.11	20.07	0.59	1.72
3-CB	26.47	38.31	8.81	10.11	13.95	8.68	16.06	15.10	5.84	17.08	12.36	3.11
4-CB	15.80	14.62	2.80	4.73	8.47	4.29	4.19	5.10	3.99	3.26	6.10	2.16
5-CB	8.69	5.73	1.19	1.95	2.13	1.17	1.24	2.39	2.53	0.85	0.68	0.45
6-CB	6.39	4.13	0.59	1.43	1.47	2.48	0.59	2.89	2.78	0.35	0.67	0.22
7-CB	1.14	0.53	0.00	0.06	0.00	0.04	0.00	0.32	0.05	0.05	0.00	0.06
8-CB	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣPCB_{all}	58.48	63.33	13.39	18.28	26.01	16.68	22.08	25.79	15.20	21.59	19.82	5.99
ΣPCB_7	31.99	41.46	7.97	10.14	14.60	8.03	16.07	17.36	7.81	17.01	10.97	2.82
Σ tri- to hepta-BDE + BDE 209	3.64	19.38	18.21	8.90	2.85	26.09	27.13	13.14	4.54	20.82	1.35	2.53
Σ tri- to hepta-BDE	1.64	1.02	1.69	0.58	0.94	10.15	5.70	4.57	1.43	0.75	0.77	0.81

6 The UK/Norway SPMD transect

Abstract

In 1994, a latitudinal ambient air sampling transect from the south of England to the north of Norway (UK/Norway transect) was established with eleven sampling sites, mainly in remote locations, using semi-permeable membrane devices (SPMDs) as passive air samplers. The aim of this transect was to investigate spatial and temporal trends of persistent organic pollutant (POP) concentrations, and in particular to test the hypotheses of global distillation and fractionation. After several years of decreasing PCB air concentrations along the UK/Norway transect sites reported previously, increased levels were observed for the four sampling campaigns between 2008 and 2016. The reasons for this are yet unknown, but could include local sources, effects of climate change, and impact of polluted air masses from Eastern Europe. In contrast, PBDE concentrations have decreased since 2000 in line with expectations following the recent phase-out of PBDEs in Europe, and now also exhibit a clear spatial difference, with an explicit distinction between relatively polluted sites in England and relatively unpolluted sites in the north of Norway. In addition to the latest data in the time series, we also discuss some limitations of the UK/Norway SPMD sampling transect and suggest improvements.

6.1 Introduction

In 1994 a latitudinal ambient air sampling transect from the south of England to the north of Norway (UK-Norway transect) was established with eleven sampling sites, mainly in remote locations, using semipermeable membrane devices

(SPMDs) as passive air samplers (Ockenden et al., 1998). The aim of this transect was to investigate spatial and temporal trends of POPs (persistent organic pollutants) concentrations, and in particular to test the hypotheses of global distillation and fractionation. Over the years, results from this network have been used in several publications investigating sources, fate, environmental behaviour, and long-term trends of POPs such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs).

Ockenden et al. (1998) described relatively uniform distribution of tetra-CBs along the transect. Higher-chlorinated CBs, however, showed a general decrease in atmospheric concentrations with increasing latitude, with the south-north concentration gradient increasing with increasing chlorination, in accordance with the hypothesis of global fractionation. In addition, the calculation of soil/air fugacity quotients using nearby soil samples suggested an air/soil system near equilibrium in the study area, with PCBs 52, 101, 118, and 153 having a slight tendency to outgas from soil into the atmosphere, and PCBs 138 and 180 further accumulating in soil.

Meijer et al. (2003) confirmed the relative importance of lighter PCB congeners with increasing latitude described by Ockenden et al. (1998), and additionally reported generally decreasing PCB concentrations between the sampling periods 1994-96 and 1998-2000, and calculated atmospheric clearance rates between 1.7 and 4 years. This decline was similar for all congeners and all sites, indicating that PCB concentrations in the atmosphere were still mainly controlled by primary emissions, and the decline therefore a result of declining primary emissions.

Gioia et al. (2006) calculated atmospheric clearance rates for all PCBs of 4.1 ± 1.3 years by analysing UK/Norway transect samples collected in the period 2000-2002 and 2002-2004 and comparing them with the results from the previous campaigns. Again, no statistically significant differences between congeners or sites were observed, corroborating the hypothesis that primary emissions were still the main source of PCBs in the atmosphere. Gioia also for the first time reported PBDE concentrations from the transect. They were in the same range as

PCBs for single congeners and dominated by PBDE 47 and 99, and generally declining at the Norwegian sites but increasing at the UK sites when 2000-2002 and 2002-2004 samples were compared.

Schuster et al. (2010) calculated atmospheric clearance rates of 8.4 ± 3.2 years for PCBs between 1994 and 2008, and of 2.2 ± 0.4 years for PBDEs between 2000 and 2008. Temporal trends for PCBs were found to be in accordance with emission estimates by Breivik et al. (2007) and the UK National Atmospheric Emissions Inventory, and correlated well with the emission estimates for individual sampling areas, with areas with higher population densities estimated to also have higher emissions. This correlation further confirmed the ongoing importance of primary emissions for atmospheric PCB levels. However, results also indicated a reduction in the rate of decline for PCBs.

While most studies in have found an overall decrease in air concentrations of POPs over the last few decades (Degrendele et al., 2020; Graf et al., 2016; Kalina et al., 2019; Wong et al., 2021), there have also been some recent signs of a reversal of this trend. For example, Rauert et al. (2018) measured PBDEs in ambient air as part of the Global Atmospheric Passive Sampling (GAPS) network, and found similar concentrations in 2014 compared to samples collected in 2005.

In their review of POPs concentrations in glacial systems in the northern hemisphere, Pawlak et al. (2021) included data on atmospheric concentration ranges in the glacial systems of the Alps, the Arctic, and the Tibetan Plateau. They highlighted the increased re-emission of several POPs from alpine glaciers due to increased temperatures, and predicted ongoing and future accumulation of some POPs in the Arctic.

The three northernmost of the current sampling sites of the UK/Norway transect are located within the Arctic Circle and are included in the Arctic Monitoring and Assessment Programme [AMAP] area of the Arctic. In a recent study, Hung et al. (2022) provided an overview of the potential influence of climate change on the levels and trends of POPs and chemicals of emerging Arctic concern (CEAC) in the

Arctic. They reported increasing air concentrations for some POPs such as PCB 52 and PCB 101 at the Icelandic reseach station Stórhöfði in recent years, attributed to their release and volatilisation from melting ice and diminishing extent of sea ice cover, and discussed the possibility of rising local POPs emissions through increased human activities in the Arctic. The increase in PCB levels at Stórhöfði was also previously reported in the Arctic Monitoring and Assessment Programme [AMAP] Assessment 2015: Temporal Trends in Persistent Organic Pollutants in the Arctic (2016), which also showed that PBDEs in air were declining at the European stations Zeppelin, Stórhöfði and Pallas but not (since the early 2000s) at Alert in Canada.

Furthermore, Hao et al. (2021) analysed 19 PCBs in one-year passive air samples at seven Arctic sites taken in seven consecutive years from August 2011 to August 2018. PCB concentrations were mostly found to be lowest in the 2011/12 and 2016/17 samples and highest in the 2012/13 and 2013/4 samples, with the other years ranging in between. This study also found PCB 11 to be the most prevalent PCB congener, which accounted for 25.0-80.5% of the ΣPCB_{19}. PCB 11 is an unintentional byproduct during the production of modern pigments , and as such a PCB of non-Aroclor (or other commercial PCB mixtures) origin, the importance of which has only become apparent in recent years (Jahnke et al., 2022; Vorkamp, 2016). Sources of non-Aroclor congeners are paint pigments and colorants, adhesives, and sealants. Some PCB congeners can only be attributed to Aroclor/commercial PCB mixtures and others (like PCB 11) only to non-Aroclor sources. However, many congeners can be of both Aroclor and non-Aroclor origin, including the important Aroclor-congeners PCB 28 and PCB 52 and the dioxin-like congener PCB 77, which were all found in high concentrations in yellow pigments (Vorkamp, 2016). While atmospheric concentrations of these congeners still seem to be predominantly the result of legacy PCB sources (Jahnke et al., 2022), with the continuing worldwide removal of their stocks, PCB emissions of non-Aroclor origin can be expected to play an increasingly important role. This has to be taken into account for the interpretation of long-term environmental monitoring programmes and when modelling long-term trends of POPs concentrations in the environment.

According to forecasts, secondary emissions of PCBs accumulated in environmental reservoirs (sediment, water, soil, snow, and ice) are becoming more important than primary sources. Whilst climate change will likely lead to increased emissions relative to current climatic conditions, by the end of the 21st century absolute PCB concentrations are forecast to be several orders of magnitude below present levels due to long-term reductions in primary emissions (Carlsson et al., 2018). Specifically, de Wit et al. (2022) summarised possible impacts of climate change *within* the Arctic on POPs and chemicals of emerging concern as follows: "Increasing temperatures and cryospheric changes have increased the mobility and transfer of POPs between physical environmental compartments of the Arctic through various mechanisms, including enhanced volatilization of contaminants from water, snow and ice, and re-mobilization of contaminants from melting of sea ice (*i.e.* multi-year and first-year ice), glacier ablation, and permafrost thaw, degradation and slumping." They predicted a future decline in primary emissions of POPs, but a slight increase in absolute secondary emissions.

For this chapter, four more sampling campaigns of the UK/Norway SPMD transect, (2008-10, 2010-12, 2012-14, 2014-16) were collected, extracted, and analysed for PCBs and PBDEs. Their results are discussed in the context of overall trends in POPs air concentrations. Furthermore, some aspects of the UK/Norway SPMD transect are critically examined.

6.2 Materials and methods

6.2.1 Sampling sites

The current sampling sites of the UK/Norway transect are listed in Table 9 and displayed on a map in Figure 44. After the addition of the Norwegian sites 6, Birkenes, and 12, Tromsø, the transect now consists of 13 sites.

Table 9. List of current sampling sites of the UK/Norway SPMD transect

Site Name	No. on Map	Latitude	Longitude	Comments
North Wyke	1	50.76853	-3.90368	
Aberystwyth	2	52.43228	-4.02052	
Hazelrigg	3	54.01349	-2.77566	Semi-rural site
Colonsay	4	56.07888	-6.22891	
Ullapool	5	58.03132	-5.07233	
Birkenes	6	58.38842	8.25205	Since 2010
Ualand	7	58.53600	6.37599	
Osen	8	61.24696	11.74191	
Fureneset	9	61.29428	5.04268	
Namsvatnet	10	64.98572	13.58410	
Bodø	11	67.38831	14.66014	
Tromsø	12	69.77518	18.60491	Since 2010
Lakselv	13	69.82961	25.16889	

Figure 44. Location of the UK/Norway SPMD transect. For a description of sites, see Table 9.

6.2.2 Sampling and analytical procedure

Passive air samples were collected using standard triolein-filled SPMDs (semipermeable membrane devices), either bought from Environmental Sampling Technologies (EST), USA (2008-10 and 2010-12) or, for the deployment periods 2012-2014 and 2014-2016, self-prepared with triolein (glyceryl trioleate) purchased from Sigma-Aldrich, using the method described by Bustamante et al. (2013). SPMDs were deployed in Stevenson screens for a period of two years. At each site, two samples and one field blank were collected. Before deployment, all SPMDs including field blanks were spiked with 5 ng of a mix of ^{13}C-labelled PCB congeners (^{13}C-PCB 28, 52, 101, 138, 153, 180, 209) as performance reference compounds.

Further details on the sampling procedure can be found in Gioia et al. (2006) and Schuster et al. (2010), where also most of the analytical procedure is described in detail together with the QA/QC procedures. In short, extraction was carried out by dialytic extraction of the samples, spiked with PCB 54 and PCB 155 (recovery standards), in 100 ml fresh hexane each for two periods of 24 h. The first clean-up step was with an activated silica/acid silica (8 g/8 g) column – this differs from previous years, where either only an activated silica column (1994-1996) or a deactivated silica/deactivated alumina column (1998-2006) was used. This was followed by two subsequent 6 g gel permeation chromatography (GPC) columns. PCBs and PBDEs were analysed together using a Thermo DSQ II GC-MS system equipped with an Agilent CP-Sil 8 CB GC column (50 m x 0.25 mm x 0.12 µm).

6.3 Results and discussion

6.3.1 Polychlorinated Biphenyls (PCBs)

Spatial trends. Figure 45 shows the ΣPCB(90/101/118/132/138/153/180) in ng/sampler for all sampling sites since 1994 (site 6, Birkenes and site 12, Tromsø were only established in 2010), Figure 46 the single congeners in pg/sampler, and Figure 50 (page 144) the respective congener profiles [relative contribution of each congener to ΣPCB(90/101/118/132/138/153/180)]. Overall concentrations decreased from the south of England to the north of Norway. Unlike the other sites, site 3 (Hazelrigg) near Lancaster University can be considered a semi-rural rather than a remote site, and consequently showed the highest PCB levels. In Norway, highest PCB concentrations in this transect were generally found at the Ualand site. Congener profiles were relatively similar, with all congeners present at all sites in most years. The PCB 90/101 fraction usually ranged from ca. 20-25% for the sites in England and Wales to 35-40% in the north of Norway. PCB 118 contributed between 5 and 15% to the total, with no real latitudinal trend visible, and relatively high variations between the samples. PCB 132/153 accounted for around 30% at all sites, and PCB 138 for between 20 and 30%, again without any clear spatial trend. PCB 180 concentrations were generally quite low, with it typically making up just over 5% at most sites, but only between 3 and 4% at the northernmost sites, where it occasionally fell below the LOQ. There was no 2012-2014 sample at Site 4 (Colonsay), as the sampler was located next to a building which burned down in December 2013. The following sample, which was only deployed for one year between 2015 and 2016, had by far the highest concentrations for this sampling site. This sample also showed a very unusual congener profile, with PCB 90/101 only contributing 10% and therefore 2/3 less than usual to ΣPCB(90/101/118/132/138/153/180). PCB 132/153 (35%) and PCB 138 (39%) were elevated as well, and PCB 180 had its highest fraction (12%) in this sample compared to all other sites and years. Both the high overall PCB levels and the congener profile dominated by heavier, less volatile PCB congeners indicate that either the incident itself or subsequent construction and earthworks exposed materials and soil with high legacy PCB concentrations, which now became visible in air samples.

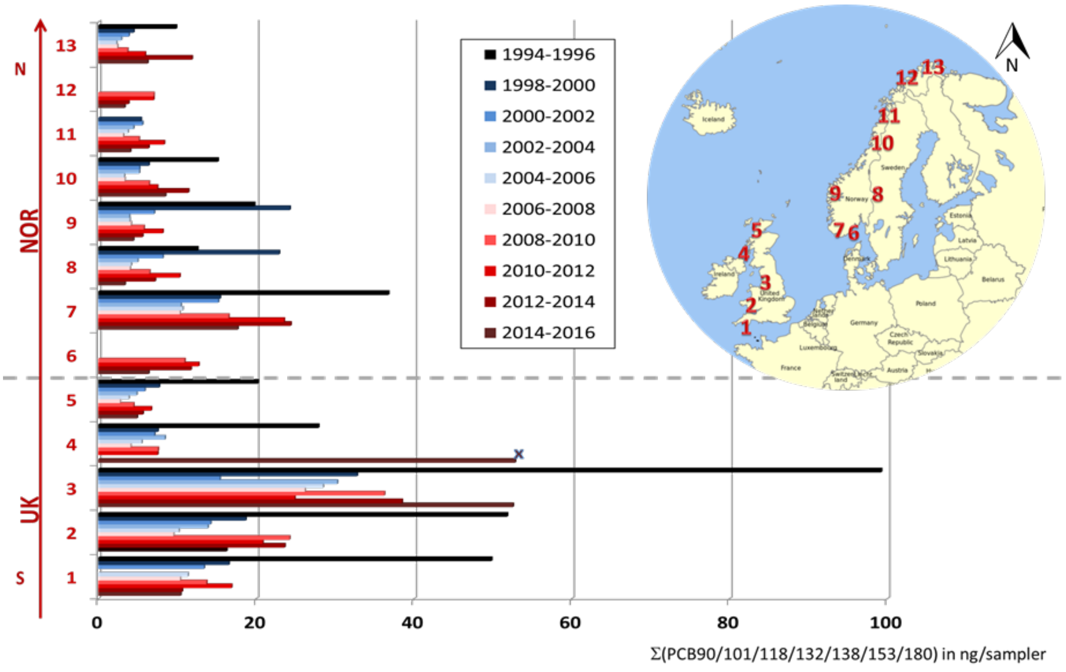
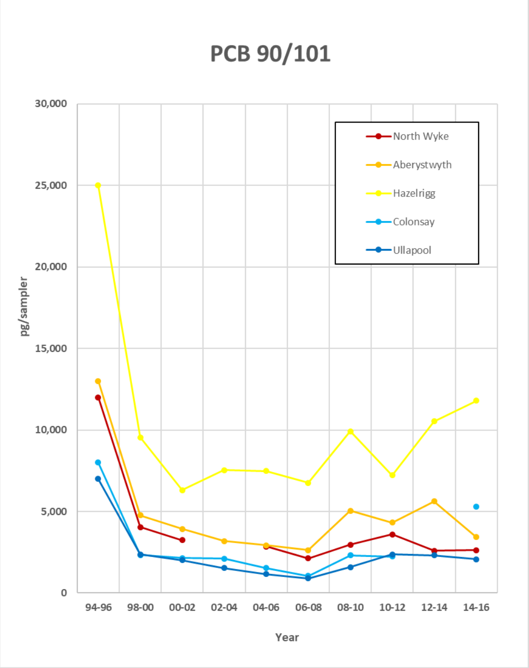
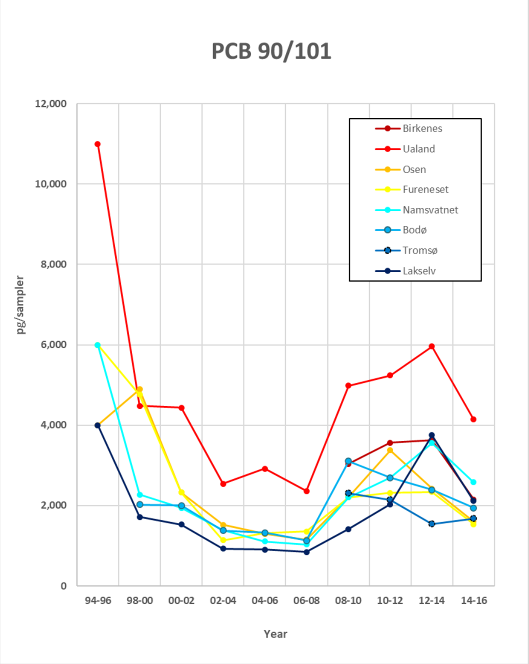
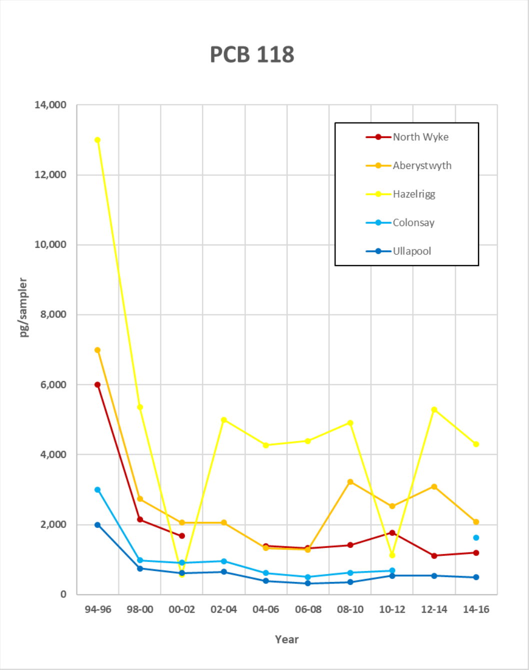
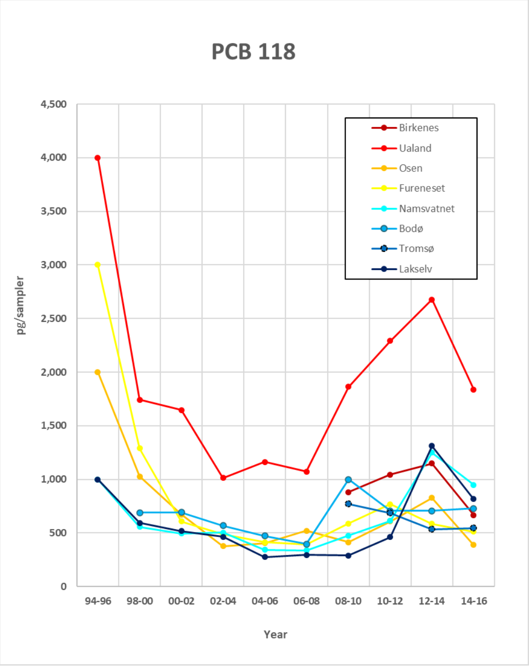


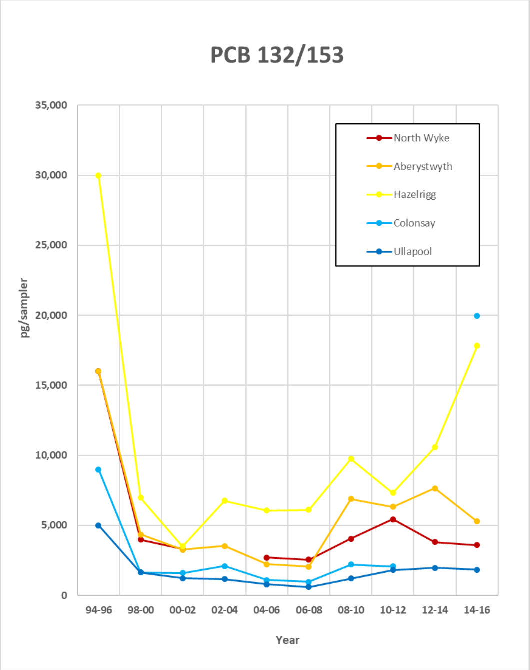
Figure 45. ΣPCB concentrations across the UK/Norway SPMD transect in ng/sampler. 2-year samples between 1994 and 2016 (Birkenes and Tromsø since 2010, no Colonsay sample 2012-2014, ^{x} 1-year sample at Colonsay 2015 – 2016).

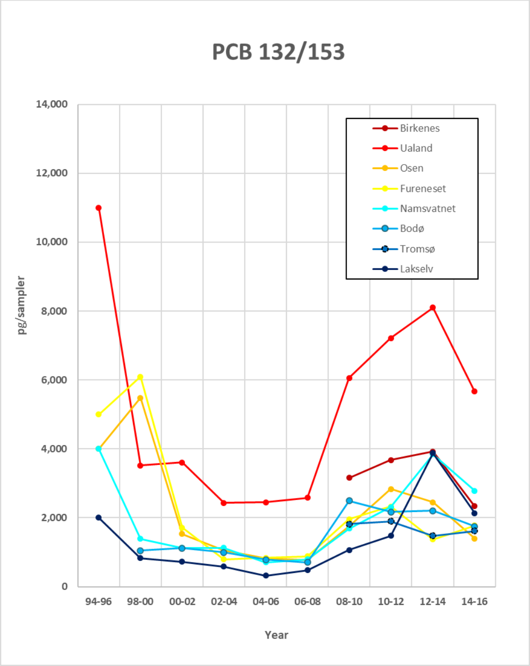

PCB 90/101
pg/sampler
30,000
25,000
20,000
15,000
10,000
5,000
0
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
North Wyke
Aberystwyth
Hazelrigg
Colonsay
Ullapool

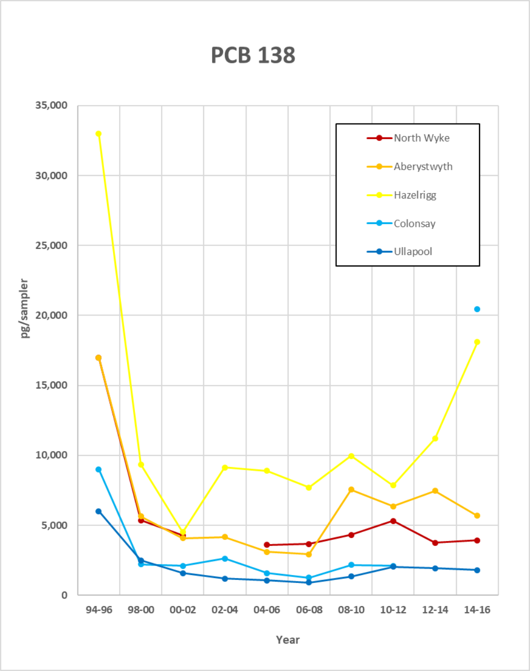

PCB 90/101
pg/sampler
12,000
10,000
8,000
6,000
4,000
2,000
0
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
Birkenes
Ualand
Osen
Fureneset
Namsvatnet
Bodø
Tromsø
Lakselv

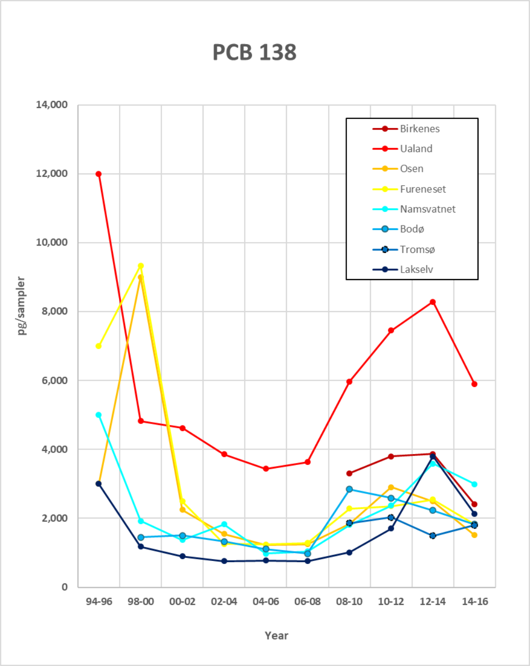

PCB 118
pg/sampler
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
North Wyke
Aberystwyth
Hazelrigg
Colonsay
Ullapool


PCB 118
pg/sampler
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
Birkenes
Ualand
Osen
Fureneset
Namsvatnet
Bodø
Tromsø
Lakselv


PCB 132/153
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
pg/sampler
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
North Wyke
Aberystwyth
Hazelrigg
Colonsay
Ullapool


PCB 132/153
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
pg/sampler
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
Birkenes
Ualand
Osen
Fureneset
Namsvatnet
Bodø
Tromsø
Lakselv


PCB 138
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
pg/sampler
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
North Wyke
Aberystwyth
Hazelrigg
Colonsay
Ullapool


PCB 138
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
pg/sampler
94-96
98-00
00-02
02-04
04-06
06-08
08-10
10-12
12-14
14-16
Year
Birkenes
Ualand
Osen
Fureneset
Namsvatnet
Bodø
Tromsø
Lakselv

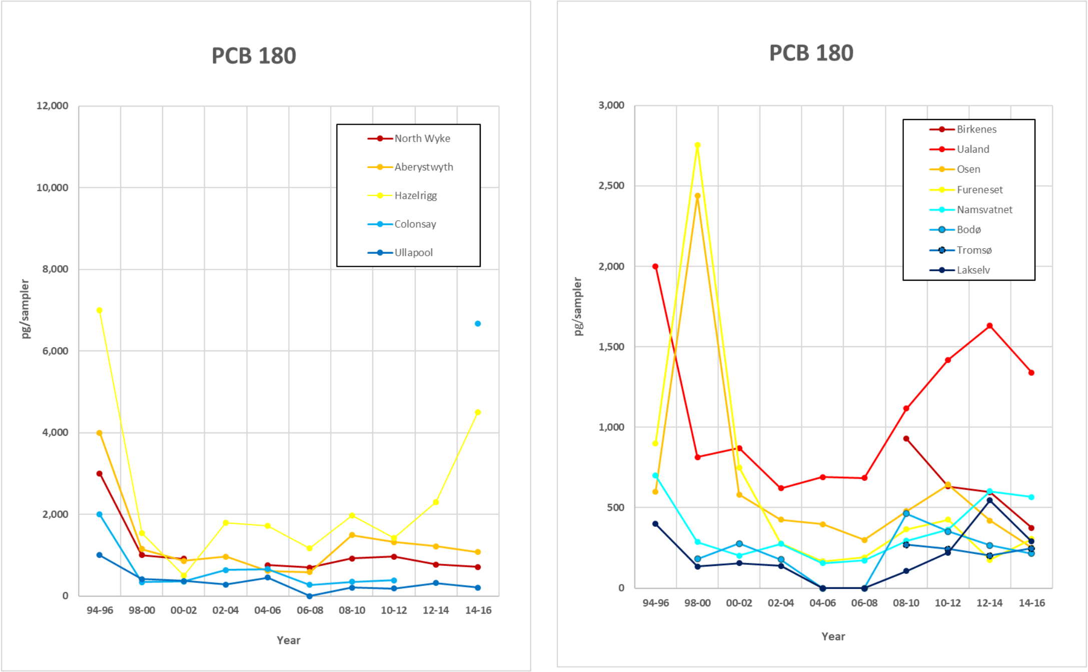
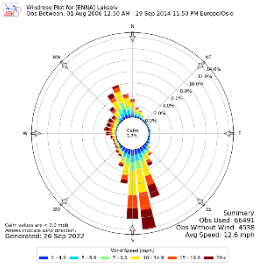


Figure 46. Concentrations of single PCB congeners in pg/sampler. Left: UK sites, right: Norway sites. Previous pages: PCB 90/101, PCB 118, PCB 132/153, PCB 138. This page: PCB 180. Note different scales of the y-axes.

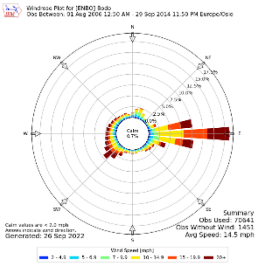
Temporal trends From 1994 until 2008, ΣPCB(90/101/118/132/138/153/180) levels at all transect sites decreased steadily. However, since 2008, no further decrease could be observed. In fact, most sites showed no significant decrease compared to samples around the year 2000 at the same site. This is particularly pronounced at the Norwegian sites, where concentrations increased significantly between the 2006-08 and the 2012-14 at most sites and for most congeners, before going down again. Looking at the congener profile (Figure 50), this cannot be attributed to any specific congener. Only PCB 138 increased in importance relative to previous samples, but this increase alone is not enough to explain the overall increase. Generally, higher ΣPCB(90/101/118/132/138/153/180) concentrations as well as the higher fraction of the less volatile PCB 180 at less remote sites and sites downwind from population centres show that POPs concentrations were still mainly influenced by primary emissions. Although secondary emissions would also be expected to be higher around urban and industrial sites due to increased import into soil etc. in the past, congener profiles would increasingly diverge between industrial/populated sites and remote sites without local primary sources if atmospheric PCB air concentrations at the latter were mainly the result of secondary emissions. In that case, the congener profiles for urban sites would show a slight shift towards heavier congeners over time, and remote sites a clear shift towards lighter congeners. However, such a shift could not be observed.

This uniform levelling-off or increase in PCB concentrations is contrary to the trends generally reported (Hung et al., 2022), and the causes are not yet known. It is possible that mechanisms similar to those leading to an increase in PCB concentrations at the Icelandic research site Stórhöfði also have an impact on the areas covered by the UK/Norway SPMD transect, for example melting sea ice or glaciers for the northernmost sites, or generally increased volatilisation from secondary sources like soils due to increased temperatures. Furthermore, events like the 2006 agricultural fires in Eastern Europe that led to a spike in PCB concentrations at the Arctic Zeppelin research station on Spitsbergen shortly after (Eckhardt et al., 2007) could also have an impact on the sites in this transect through long-range transport either directly or delayed by repeated deposition, re-volatilisation, and atmospheric transport.

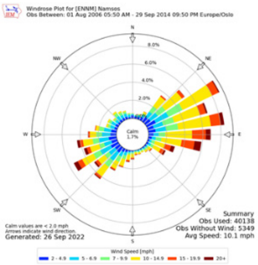
Figure 47 shows wind roses for the Norwegian sites (from north to south) Lakselv, Bodø, Namsos (near Namsvatnet), Oslo, and Kristiansand (near Birkenes). It is clear that in central Norway in particular prevailing winds are from the east. Thus, easterly winds from Eastern Europe have the potential to import substantial amounts of POPs from boreal and agricultural fires into central Norway that could then be further transported to the north and the south of Norway by southerly and northerly winds, respectively. The main PCBs produced in the Russian Federation until 1990 were tetra- and penta-CBs (Sovol, Sovtol-10) and tri-CBs (TCB) (Arctic Monitoring and Assessment Programme [AMAP] (2000)), so an increased contribution of emissions from this direction could lead to a further shift to these lighter PCBs in the congener pattern, an effect that could not be observed in this study (Figure 50). However, this does not take into account all imports, and there are reports of illegal disposals of PCB-containing waste including hexa-CBs (Eco-SPES, 2019), so the extent to which this shift would occur is unclear.



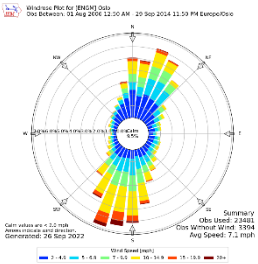
Lakselv



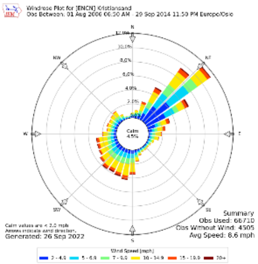
Bodø



Namsos



Oslo



Kristiansand

Figure 47. 2006-14 wind roses for the Norwegian sites (from north to south) Lakselv, Bodø, Namsos (near Namsvatnet), Oslo, and Kristiansand (near Birkenes). Source: Iowa Environmental Mesonet (iastate.edu)

6.3.2 Polybrominated Diphenyl Ethers (PBDE)

Spatial trends. Figure 48 shows the ΣPBDE(28/47/49/99/100/153/154) in ng/sampler for all sampling sites since 2000, when they were included in the UK/Norway SPMD transect (site 6, Birkenes and site 12, Tromsø were only established in 2010, no PBDE data for 2008-2010). In the first samples of 2000 – 2002 and 2002 – 2004, no obvious correlation between PBDE levels and either latitude or remoteness can be observed. Recent samples, however, show a clear pattern of higher levels in England and low levels for the remote Scottish site 5 (Ullapool) and the Norwegian sites. Generally, as with PCBs, distance from populated areas seems to impact PBDE concentrations in ambient air more than latitude. All sites were dominated by BDE 47 and BDE 49, only at Hazelrigg other congeners were regularly found at levels >5 ng/sampler.

Temporal trends. At all sites except site 3 (Hazelrigg), PBDE levels have clearly decreased from the first samples 2000-2002 and 2002-2004. At Hazelrigg, a semi-rural site, there have been construction works and signs of unsanctioned waste burning in the vicinity, which are likely to have influenced the results. Site 4 (Colonsay) shows slightly elevated PBDE values for the sample after the building fire, but not as pronounced as for PCBs.

These declines in PBDE concentrations reflect their ban in the EU in 2004 and their addition to the Stockholm convention in 2009.

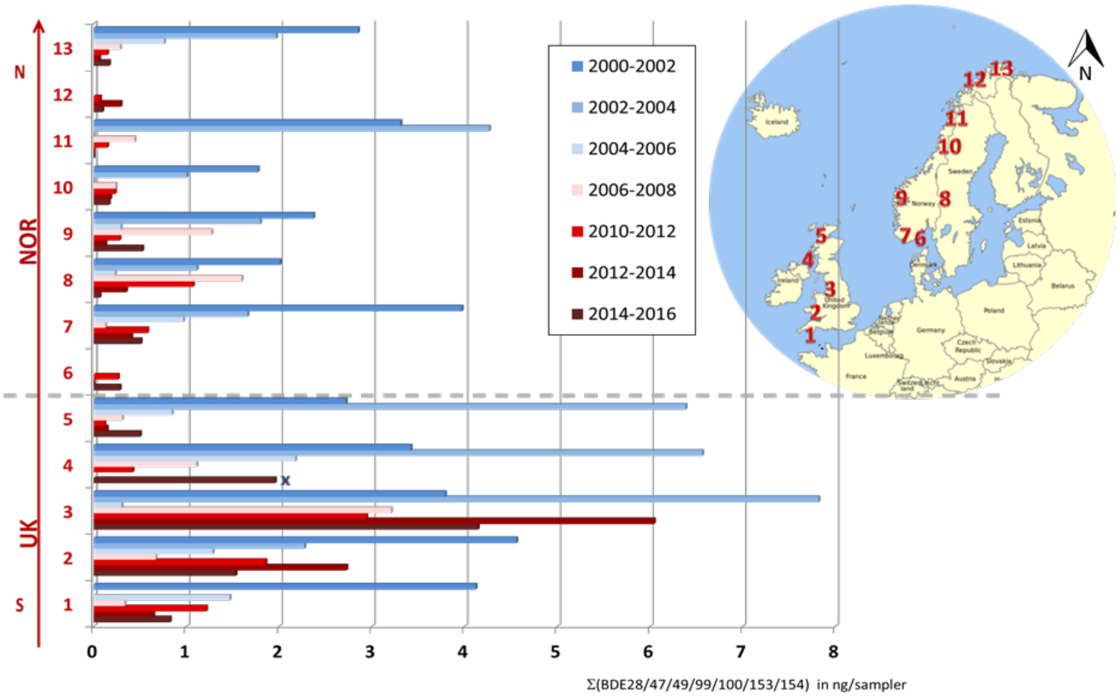


Figure 48. ΣPBDE concentrations across the UK/Norway SPMD transect in ng/sampler. 2-year samples between 2002 and 2016 (Birkenes and Tromsø since 2010, no PBDE results 2008-2010, no Colonsay sample 2012-2014, ˣ 1-year sample at Colonsay 2015 – 2016).

6.3.3 Remarks on the UK/Norway SPMD transect

Long-term research projects in an academic environment. The UK/Norway SPMD transect has been running since 1994, and it is inevitable that projects spanning a period of several decades will involve a large number of different operators carrying out tasks like

- Sampler preparation including the addition of performance reference compounds (PRCs)
- Fieldwork
- Extraction and clean-up
- Instrumental analysis and quantification.

Even with detailed protocols in place, there will be unavoidable changes over time when old instruments have to be replaced by new ones, optimisations lead to changes in extraction, clean-up, and instrument methods, when accessories and supplies are not available anymore and alternatives have to be found, or when new batches of chemicals and analytical standards are used, to name just a few. Especially in an academic environment, where those working on a specific project will often do so only once or twice, different background and training will occasionally lead to different practical approaches. This means it is particularly important to ascertain that differences between sampling campaigns and observed trends do not simply reflect changes in the operator.

In order to ensure comparability of our data with previous results, archived samples were analysed with the current ones. Archived samples are created by splitting the sample after the first clean-up, with 50% of the sample being further processed and analysed and 50% being kept in the freezer as an archive sample. In our case, the results from archived samples were similar to those reported at the time, and gave us confidence that the unexpected increase in PCB levels in the sample were not merely a reflection of a new operator. However, if there had been discrepancies, it would have been difficult to identify the exact reason.

We therefore suggest that the following measures are integral to long-term projects that will be the responsibility of several operators over the course of the project:

- All standard operating procedures (SOPs) need to be extremely detailed, assuming that future operators will routinely work with different laboratory methods than present operators, and will not be familiar with the ones used in the project.
- Ideally, people with main responsibility for the practical work of the project should have been partially involved at least once before.
- A large number of archive samples should be created and routinely analysed with subsequent campaigns if sensible (this would work for POPs, but not for analytes that degrade during storage). Archive samples should

include laboratory blanks, to easily identify issues resulting from differences in sampler handling before deployment, for example pre-cleaning or addition of performance reference compounds (PRCs). They should also include deployed samples before extraction, in order to evaluate this step. It may be useful to collect additional samples at some sampling sites with the purpose of using them as archive samples.

- Archive samples need to be labelled clearly with site details and dates. Codes should be avoided, except for sensitive data. If it is necessary to use codes, future operators need to be informed about their meaning or storage place.
- A person should be appointed to be responsible for the integrity of the archive samples. For example, there should be regular checks that none of the samples have dried out or that labels are starting to come off the sample. This person would also make sure that archive samples are not discarded during freezer clean-outs.
- All data regarding the project should be stored in a central place. This should include raw data after data acquisition, processed data, and any calculations for reports and publications as well as data relating to the samples like temperatures or air volumes, if available.
- Any problems that could have impacted the sample itself or the reported data have to be noted in detail.

Which further factors could impact the results apart from air concentrations? Sampling rates in passive samplers are impacted by meteorological conditions, such as temperature and wind speed (Moeckel et al., 2009; Wania and Shunthirasingham, 2020). The uptake of POPs by SPMDs are air-side controlled, and increasing wind speeds increase the uptake by SPMDs in air. However, as the SPMDs are placed inside Stevenson screens for the UK/Norway transect, varying wind speeds will be buffered and should not have a major impact on sampling rates.

The compound-specific partition coefficient $K_{SPMD-AIR}$ is related to K_{OA} and hence increases with decreasing temperature by a factor of about 2.5–3 for every 10 °C decrease in temperature (Shoeib and Harner, 2002). Higher $K_{SPMD-AIR}$ will result in longer phases of linear uptake before curvilinear or equilibrium partitioning are reached. This means that transect samplers at colder sites can sequester more of an analyte than at warmer sites before equilibrium is reached, despite similar atmospheric concentrations, leading to seemingly higher air concentrations with higher latitudes if only the amount of analyte take-up by the SPMD is taken into account. This phenomenon is well-known for relatively volatile compounds like the pesticide hexachlorobenzene, but also affects tri- and tetra-CBs in cases of long sampler deployment times like for the UK/Norway transect.

Finally, analyte uptake may also come to a partial or complete halt in colder climates. Triolein has a melting/freezing point of around -5 °C, and although uptake by the LDPE membrane will continue, sampling rates will be significantly decreased at the coldest sampling sites in winter (Gioia et al., 2006). Even when temperatures increase, the SPMDs may not be instantly available for sampling. Figure 49 shows a photo taken at the Tromsø sampling site on the 23rd of May 2015. It was reported that the sampler had just begun to emerge from its snow cover. It is clear that atmospheric POPs concentrations derived from air samplers buried by snow for several months of the year will be difficult to compare to those from samplers that are exposed to fresh air masses all year round.

Figure 49. Stevenson screen at Tromsø, Norway starts emerging from the snow on 23/05/2017. Credit: Ingjerd Sunde Krogseth, NILU

With the impact of meteorological conditions such as temperature, wind speed, and precipitation – and especially snow - on sampling duration, sampling rate and equilibrium concentrations, climate change could therefore not only lead to changes in atmospheric POPs concentrations, but could also have an impact on the sampling process itself.

Is the UK/Norway SPMD transect suitable for testing the hypotheses of global distillation and fractionation? The UK/Norway SPMD project was established in order to test the hypotheses of global distillation and fractionation. In the northern hemisphere, this would result in a relative accumulation of lighter POPs in the colder higher latitudes over time, and a relative accumulation of heavier POPs further south, close to their original places of production and main usage. This would be visible in changes in congener profiles over the years, with the lighter congeners contributing increasingly more to the sum of all congeners of a group of compounds at the northernmost sampling sites regardless of changes in absolute concentrations, and the global distribution would reflect the dominance of secondary emissions.

In this study, like the ones before, no changes in congener profiles over time were observed, suggesting that atmospheric PCB and PBDE concentrations still mainly reflect the distribution of primary sources like population centres or local human activity even in remote areas. Additionally, samples in Norway may occasionally be impacted by POPs pollution originating in Eastern Europe. Furthermore, while globally the amount of legacy POPs in the environment is expected to further decrease significantly over the next decades, a multitude of interacting effects of climate change could increase levels locally.

For remote regions, most mechanisms regarding changes in the global distribution of POPs would first and most clearly show up in the lighter congeners like PCB 28 and PCB 52. Unfortunately, this project is not very suitable for both because of long deployment times and relatively low capacities of SPMDs (see above), meaning that tri- and tetra-CBs, unlike higher-chlorinated congeners, reach the stage of curvilinear or equilibrium partitioning (Ockenden et al., 2001; Shoeib and Harner, 2002). This is reflected in the loss of performance reference compounds ^{13}C-PCB 28, which reaches 100% for most samples and most years, and ^{13}C-PCB 52, where losses varied widely between the campaigns, making comparisons difficult. The future inclusion of different types or passive air samplers like sorbent-impregnated PUF disks (‘SIP-disks’) should be considered to better represent a wider range of analytes in the UK/Norway transect. Furthermore, the addition of soil sampling near the transect would allow to determine soil to air fugacity ratios and give further information about current trends in environmental POPs concentrations.

6.4 Conclusions and outlook

After several years of decreasing PCB air concentrations at the UK/Norway SPMD transect sites, increased levels were observed for the four sampling campaigns between 2008 and 2016. The reasons for this are yet unknown, although possible explanations include local sources (as illustrated by the examples of the Hazelrigg and the Colonsay sampling site), effects of climate change and impact of polluted air masses from Eastern Europe. PBDE concentrations on the other hand have decreased since 2000 in line with expectations and following the recent phase-out of PBDEs in Europe, and now also exhibit a clear spatial difference, with an explicit distinction between relatively polluted sites in England and relatively unpolluted sites in the north of Norway. The UK-Norway transect has since continued, with three further two-year samples taken since 2016, and their analysis will show if these trends continue in all cases. Future improvements of the transect could include different types of samplers in order to collect a wider range of analytes, and soil samples to recognise changing patterns of sinks and sources.

6.5 Acknowledgements

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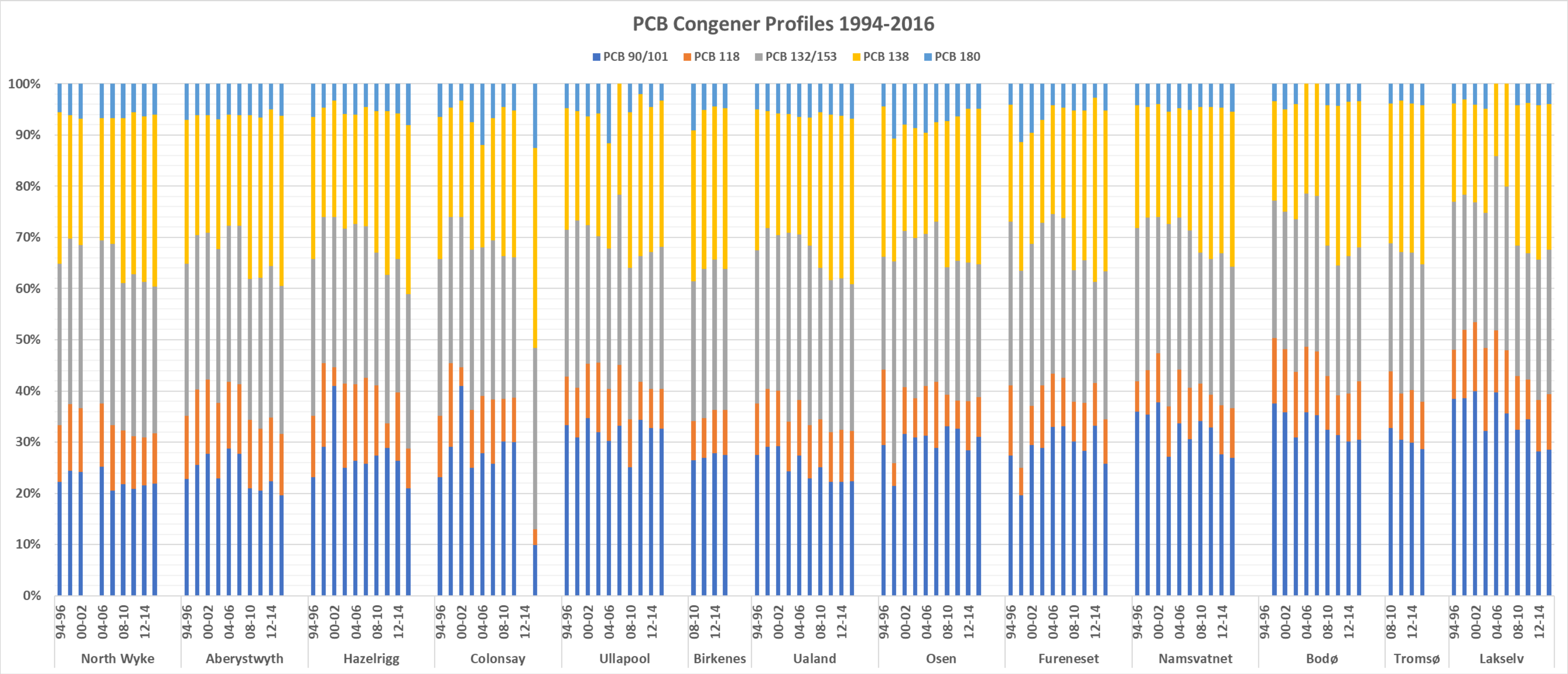

Figure 50. PCB Congener profiles 1994-2016 at all UK/Norway transect sampling sites. % contribution of PCB 90/101, PCB 118, PCB 132/153, PCB138, PCB 180 to ΣPCB(90/101/118/132/153/138/180). No samples for 2002-04 at North Wyke, 2012-14 on Colonsay, 1994-96 in Bodø. 1-year sample 2015-16 on Colonsay. Sampling at Birkenes and Tromsø started in 2008.

7 Monofluorinated PCBs (F-PCBs), a new group of potential performance reference compounds for passive air samplers

Abstract

Performance reference compounds (PRCs), compounds added to passive samplers before their deployment, are regularly used in air or water sampling for in-situ calibration of the passive sampler sampling rate. In this study, monofluorinated PCBs (F-PCBs), added to polyurethane foam passive air samplers (PUF-PAS), were investigated as alternative PRCs to ^{13}C-PCBs, which have widely been used for the sampling of PCBs. F-PCBs were demonstrated to work as PRCs, providing depuration rate constants similar to ^{13}C-PCBs, suggesting their use either instead of ^{13}C-PCBs to allow the utilisation of the latter as recovery or internal standards, or additionally, to increase the number of PRCs within the desired range of depuration, in order to obtain a more reliable and precise representation of the sampling conditions. However, the presence of an impurity co-eluting with PCB 101 might make F-PCBs unsuitable for sampling in areas with low air pollution levels.

7.1 Introduction

Passive air sampling plays an important role in global monitoring of persistent organic pollutants (POPs) and other semi-volatile organic compounds (SVOCs) from small-scale and short-term local studies up to long-term air monitoring programmes. Such programmes may encompass several countries, like the UK/Norway SPMD transect (Gioia et al., 2006; Schuster et al., 2010), continents, like the co-operative programme for monitoring and evaluation of the-long range transmission of air pollutants in Europe ('European Monitoring and Evaluation Programme', EMEP, https://www.emep.int), or even the whole world, like the Global Atmosphere Passive Sampling (GAPS) network (https://gml.noaa.gov/obop/mlo/programs/coop/gaps/gaps.html).

Because they need no power source and little maintenance, passive air samplers (PAS) provide a cost-effective way of collecting long-term and time-integrated data on air pollution (Gioia et al., 2006) and thus play an important role in fulfilling obligations of international chemicals regulations such as the Stockholm Convention (UNEP, 2001) and the UN/ECE Protocol on POPs (UN/ECE Convention on Long-Range Transboundary Air Pollution, 1998).

Wania and Shunthirasingham (2020) provide an extensive review of passive air samplers currently in use and their respective advantages and disadvantages. Generally, most widespread in use are polyurethane foam (PUF) disks, sorbent-impregnated polyurethane foam (SIP) disks, and semipermeable membrane devices filled with triolein (SPMDs).

Triolein-containing SPMDs were first designed by the U.S. Geological Survey for the passive sampling of dissolved fractions of persistent organic pollutants from water (Ockenden et al., 2001; Soderstrom and Bergqvist, 2004). To use SPMDs or any other passive air sampler for quantitative measurement of the air concentration, the sampling rate, R, or the PAS-air partition coefficient, $K_{PAS\text{-}Air}$, has to be known. When SPMDs are used for water sampling, $R_{SPMD\text{-}Water}$ is generally pre-calibrated in the laboratory at given temperatures (Huckins et al., 2002). For air sampling, a range of calibration data and partitioning coefficients have been reported for example by Ockenden et al. (2001); (1998), Li and Wania (2021), and the research group led by Tom Harner at Environment and Climate Change Canada (e.g. Abdollahi et al. (2017); Harner et al. (2013); Herkert et al. (2018); Parnis et al. (2016); Saini et al. (2019)).

However, field sampling conditions such as temperature, wind speed, or hydrodynamics (for water samples) can be difficult to replicate and maintain over extended periods. One of the advantages of passive air samplers is that they can be deployed in remote areas, where exact meteorological data are not always available, for example due to the lack of meteorological observation sites nearby, difficulties to run equipment without power supply and in extreme weather conditions, and visits to the sampling site that may be months or even years apart because of their remoteness, which can also be too long for the use of battery-powered data loggers.

Therefore, Huckins et al. (2002) proposed the use of performance reference compounds (PRCs) to calibrate the SPMD sampling rate in water in situ (Soderstrom and Bergqvist, 2004). PRCs are analytically non-interfering organic compounds that exhibit moderate to relatively high affinities to the passive sampler, but cannot be found in the environment (Moeckel et al., 2009; Soderstrom and Bergqvist, 2004). They are added to the sampler before its deployment and will volatilise into the air or dissipate into the water during the deployment period. The amount lost will depend on their physico-chemical properties, exposure time, and wind speed or hydrodynamics (Moeckel et al., 2009).

When isotope-labelled chemicals are used as PRCs, their volatilisation or dissipation rates are related to the uptake rates of the native compounds sampled and well-correlated to their octanol-air partition coefficients K_{OA} (Pozo et al., 2006). K_{OA}, in turn, increases with decreasing temperature by about a factor of 2.5-3 for every 10 °C decrease (Shoeib and Harner, 2002). Ideally, isotope-labelled equivalents of the target compounds are used, for instance ^{13}C-labelled PCBs for the sampling of native PCBs (polychlorinated biphenyls). For passive air samplers, the loss of PRCs from the sampler and uptake of target compounds in the atmospheric gas phase are predominantly air-side controlled (Moeckel et al., 2009; Shoeib and Harner, 2002), and inversely proportional to the thickness of the boundary layer surrounding the sampler. This means that higher wind speeds increase PRC loss and target compound uptake (mass transfer) to the same extent. The depuration rate can therefore be used to calculate the uptake rate of the target compounds and consequently their air concentration C_{AIR}.

Because the total loss of individual PRCs at the end of the sampling period will depend on their $K_{PAS\text{-}Air}$ (related to K_{OA}) and length of deployment, these properties need to be taken into account when choosing the mixture and amount of PRCs spiked before the deployment. Long exposure times and high temperatures can often mean complete or near-complete loss of a compound, which makes it unavailable for internal calibration of the sampler (although it will still provide qualitative information on sampling conditions and their possible impact on target compounds). On the other hand, if the amount of PRC remaining on the sampler is close to the added amount, small errors during the spiking process or variations inherent in the analytical method will have a large impact on the calculated depuration rate and as a consequence the calculation of the target compound air concentrations. Soderstrom and Bergqvist (2004) also noted that “When the released PRC amount is approximately ≥60% of the initial PRC amount in the SPMD, the uptake of compounds with similar or lower SPMD affinity is nonlinear or at equilibrium. In these cases, the use of [the equation for linear and integrative uptake] will underestimate the C_A [air concentration], and instead an exponential or equilibrium model should be used”.

Suggestions regarding the ideal loss of PRC range between 20 – 80% (Gioia et al., 2006; Moeckel et al., 2009; Soderstrom and Bergqvist, 2004), and >60% (Pozo et al., 2006).

Conventionally, a mixture of ^{13}C-labelled PCBs has been used as PRCs for the sampling of PCBs in passive samplers (Soderstrom and Bergqvist, 2004), due to their physico-chemical properties being nearly identical to those of their respective native compound. However, this has a number of drawbacks. For example, these labelled compounds might already be integrated in the analytical method, for example as internal or recovery standards. The preparation of new analytical standards, and the development of new instrument methods can be expensive and time-consuming when internal standards have to be replaced. They are also not 100% chemically pure (a very small amount in the standard will be the respective unlabelled compound), which means that if high amounts of performance reference compound remain on the sampler after deployment, but only small amounts of native compound were sampled because of low air concentrations, the share of native compound from the PRC could be high compared to the total amount. While this can be compensated for by using PRC-spiked laboratory and field blanks, this could increase the method LOQ (limit of quantification) to a value higher than the amount sampled from the air. Furthermore, when detection methods other than mass spectrometry are used, such as an electron capture detector (ECD), isotope-labelled standards cannot be used because they cannot be differentiated from the native target compound. Finally, for some methods with low method recoveries, the use of the isotope-labelled standards most similar to the target compounds may be necessary to guarantee the quality of the results, and suitable replacements may be difficult to find.

In this study, we have tested the use of monofluorinated PCBs (F-PCBs) as alternative performance reference compounds for the sampling of PCBs. Monofluorinated PCBs have one hydrogen atom in their molecule replaced by one fluorine atom. Like isotope-labelled PCBs, F-PCBs have similar physico-chemical properties to their corresponding PCBs, with F-containing aromatic compounds showing similar characteristics in many aspects to those of the corresponding non-fluorinated parent compounds. (Luthe et al., 2009; Sott et al., 2008). Polyurethane foam passive air samplers (PUF-PAS), spiked with (a) ^{13}C-labelled PCBs or (b) F-PCBs as PRCs and (c) without PRCs were deployed for up to half a year, and subsequently their loss of PRCs and uptake of PCBs were determined. In this chapter we will present the results of this study and give possible advantages and downsides for the use of F-PCBs compared to ^{13}C-labelled PCBs as performance reference compounds.

7.2 Materials and methods

7.2.1 Materials

Polyurethane foams (PUF) disks (thickness 13.5 mm, outside diameter 140 mm) were obtained from (Klaus Ziemer GmbH, Germany). Acetone (HPLC grade) and hexane (HPLC grade) for sampler pre-extraction and sample extraction and clean-up were bought from Fisher Scientific, UK. Disks were spiked with a ^{13}C-PCB mixture (CIL standards, USA) or, alternatively, with a 'Dutch Seven F-PCB®' mixture from Chiron UK Ltd. Details about the F-PCB standard can be found in Table 10. Activated silica/acid silica columns for clean-up were prepared using silica gel 60 (0.060-0.2 mm, 70-230 mesh, Alfa Aesar, UK), sulfuric acid (96% extra pure, Acros Organics, UK), and sodium sulfate anhydrous (0.63-2.0 mm coarse granules, Merck KGaA, Germany). Gel permeation chromatography columns were each filled with 6 g Bio-Beads S-X3 from Bio-Rad Laboratories, UK.

Table 10. F-PCBs used in the study with their respective homologue group and IUPAC Number.

Hom. group	IUPAC No.	Compound
Trichloro-	3’-F-CB-28	3’-Fluoro-2,4,4’trichlorobiphenyl
Tetrachloro-	3-F-CB-52	3-Fluoro-2,2’,5,5’-tetrachlorobiphenyl
Pentachloro-	3’-F-CB-101	3'-Fluoro-2,2',4,5,5'-pentachlorobiphenyl
	5’-F-CB-118	5’-Fluoro-2,3’,4,4’,5-pentachlorobiphenyl
Hexachloro-	5’-F-CB-156	5’-Fluoro-2,3,3’,4,4’,5-hexachlorobiphenyl
	3’-F-CB-166	3’-Fluoro-2,3,4,4’,5,6-hexachlorobiphenyl
Heptachloro-	5’-F-CB-190	5’-Fluoro-2,3,3’,4,4’,5,6-heptachlorobiphenyl

http://www.chiron.no/GetFile.ashx?id=161

7.2.2 Sampler preparation

PUF disks were rinsed with deionised water (Purite Ltd, UK) and dried in a drying oven at 30 °C for a week. The dry disks were then pre-extracted using a soxhlet apparatus for 2 x 24 hours with a hexane/acetone 1:1 mixture and subsequently dried in a desiccator. The dry disks were spiked with either 5 ng of the ^{13}C-PCB mixture, 5 ng of the F-PCB mixture, or not spiked at all. All disks were stored in solvent-rinsed amber glass jars in a freezer for clean samples at temperatures below -20 °C until deployment.

7.2.3 Sampler assembly, deployment and collection

Deployment. Sampling was carried out between the 5th of September 2019 and the 4th of March 2020 (181 days) at the Hazelrigg Field Station near Lancaster

University, UK. In order to protect the PUF samplers from adverse weather conditions, they were deployed in labelled stainless steel assemblies described by Melymuk et al. (2021), which were assembled on site (Figure 51). Of each sampler type, (with ^{13}C-PCBs, with F-PCBs, without PRCs) eight samplers were deployed, two of which would be collected after 2, 4, 13, and 26 weeks, respectively. Additionally, two samplers of each type were prepared but not deployed, to become '0 weeks' samples. To avoid contamination, clean nitrile gloves were worn throughout the assembly and deployment process and changed between samplers. The average air temperatures at the Hazelrigg field station for each month of the deployment period are shown in Table 11.

Figure 51. PUF-PAS were deployed in labelled stainless steel assemblies at the Hazelrigg field station near Lancaster University, UK.

Table 11. Average air temperatures in °C at the Hazelrigg field station for each month of the deployment period September 2019 – March 2020, and average for the whole deployment period (DP).

Sep 19	Oct 19	Nov 19	Dec 19	Jan 20	Feb 20	Mar 20	Ø DP
13.25	9.33	6.20	5.95	6.19	5.76	6.40	7.56

Collection. Exposed PUF samplers were removed after 2, 4, 13, and 26 weeks, respectively. The metal assembly was taken apart on site and each PUF disk transferred to a separate solvent-rinsed amber glass jar with lid. A fresh, clean pair of nitrile gloves was worn for every sample. The jars with the samples were immediately transported to the laboratory, where they were stored in a freezer for exposed samples at below -20 °C until extraction. On the day of the 4-weeks sample collection, field blanks were taken. An amber glass jar with one unexposed PUF disk of each type was transported from the laboratory clean sample freezer to the sampling site, and the lids removed for the duration of the collection without removing the disks. Then the lids were put back on, and the field blank moved to the exposed samples laboratory freezer, together with the other exposed disks.

7.2.4 Sample extraction and clean-up

Each PUF disk was spiked with 625 pg recovery standard (25 µl of a 25 pg/µl PCB 55 and PCB 154 solution in iso-octane). The disk was transferred into a soxhlet apparatus and soxhlet-extracted with 300 ml hexane for 16 hours. The extract was then rotary-evaporated to ca. 2 ml, transferred to a 7 ml vial, and further reduced to ca. 0.5 ml under a gentle stream of nitrogen.

The first clean-up step was a silica (8 g) – acid silica (8 g; silica:sulfuric acid 2:1) column, which was eluted with 150 ml hexane. This extract was again rota-evaporated and then reduced to ca. 0.5 ml, which was used for a second, and final, clean up step, a gel permeation chromatography column (GPC, 6 g). First, the sample extract was added to the GPC column, followed by a hexane/DCM 1:1 mixture. The first 15 ml of the eluate were discarded, and the subsequent 30 ml collected. Finally, the collected eluate was again evaporated to almost dryness under a gentle stream of nitrogen and transferred to a GC vial which contained 25 µl dodecane spiked with 25 pg/µl ^{13}C-PCB 141 as internal (syringe) standard.

7.2.5 Analytical instrument setup

The samples were analysed using a Thermo DSQ II GC-MS system, equipped with an Agilent CP-Sil 8 CB GC column (50 m x 0.25 mm x 0.12 µm). The initial oven temperature was 100 °C (held for 2 min), then increased to 140 °C at a rate of 20 °C min^{-1}, further increased to 200 °C (4 °C min^{-1}), held for 10 min, then 300 °C (4 °C min^{-1}), held for 6 min, and finally to 320 °C (10 °C min^{-1}), where it was held for 5 minutes. The GC interface temperature was set to 300 °C, and the MS source temperature to 250 °C. Thermo Xcalibur™ software was used for both data acquisition and sample processing.

7.2.6 QA/QC

One laboratory blank each was analysed for all sampler types. Apart from PCB 101, which will be discussed in the following paragraph, only PCB 49 was detected in some laboratory and field blanks above the instrument limit of detection, but in concentrations far lower than in the exposed samples. Part of the aim of this study was to assess impurities and other impacts on quantifying target analytes when adding relatively high amounts of ^{13}C-PCBs or F-PCBs to the sampler. As a result, no blank-correction was carried out. Unfortunately, the ^{13}C-PCB spiked laboratory blank was lost during the clean-up process, but given that the other two laboratory blanks and three field blanks showed almost no contamination, it was concluded that this would likely have been the case for the lost blank as well. All values were recovery-corrected using the recovery standards PCB 54 and PCB 155. The recovery standard and the PRC spiking standards themselves were quantified to ensure they contained the correct concentrations for all analytes and no evidence of contamination. Calibration standards were included at regular intervals between samples to check the performance of the instruments. For each analyte two ions were used for quantification, and usually the lower result of those two was used, unless that ion showed a very weak response and could only be used as qualifying ion.

7.3 Results and discussion

Performance Reference Compounds. Figure 52 shows the remaining amount of performance reference compounds (PRCs) (^{13}C-PCBs or F-PCBs) on the PUF disks after their respective deployment period. The values are the average of the duplicate samples, and given in pg/sampler. In summary, F-PCBs showed a similar but slightly elevated depuration behaviour compared to ^{13}C-PCBs of the same homologue group. Assuming an exact amount of 5000 pg of each compound had been added to the sampler before deployment, after six months 48% of F-PCB 28 was lost, compared to 36% ^{13}C-PCB 28. F-PCB 52 loss was even higher with 53% after six months, and twice as high as for ^{13}C-PCB 52 (25%). However, this compound showed slightly reduced concentrations even in the F-PCB spiked laboratory blank and the t=0 weeks / field blank sample, so this very low value may reflect an analytical problem in this study rather than its environmental behaviour. Of F-PCB 101 and ^{13}C-PCB 101, 29% and 17% were lost, respectively, but only 11% of F-PCB 118, which also belongs to the penta-chlorinated group. Fluorinated hexa-CBs showed very little depuration (6% for F-PCB 156, 2% for F-PCB 166), which, due to analytical measurement uncertainties, may well mean that almost no fluorinated hexa-CBs were lost within the six-month deployment period at all. Likewise, for the isotope-labelled hexa-CBs ^{13}C-PCB 138 and ^{13}C-PCB 153, the amounts measured on the samplers at the end of the maximum deployment period were actually higher than the 5000 pg originally added. A relatively constant loss between 15% and 29% for F-PCB 190 and between 14% and 18% for ^{13}C-PCB 180 would also seem to be method-related rather than genuine volatilisation, given that this apparent loss can already be observed after a deployment period of only two weeks. With a logK_{OA} of 10.7 (Shoeib and Harner, 2002), PCB 180, like other hepta-CBs, would be unlikely to show significant volatilisation and therefore a reduction after only a few weeks of deployment.

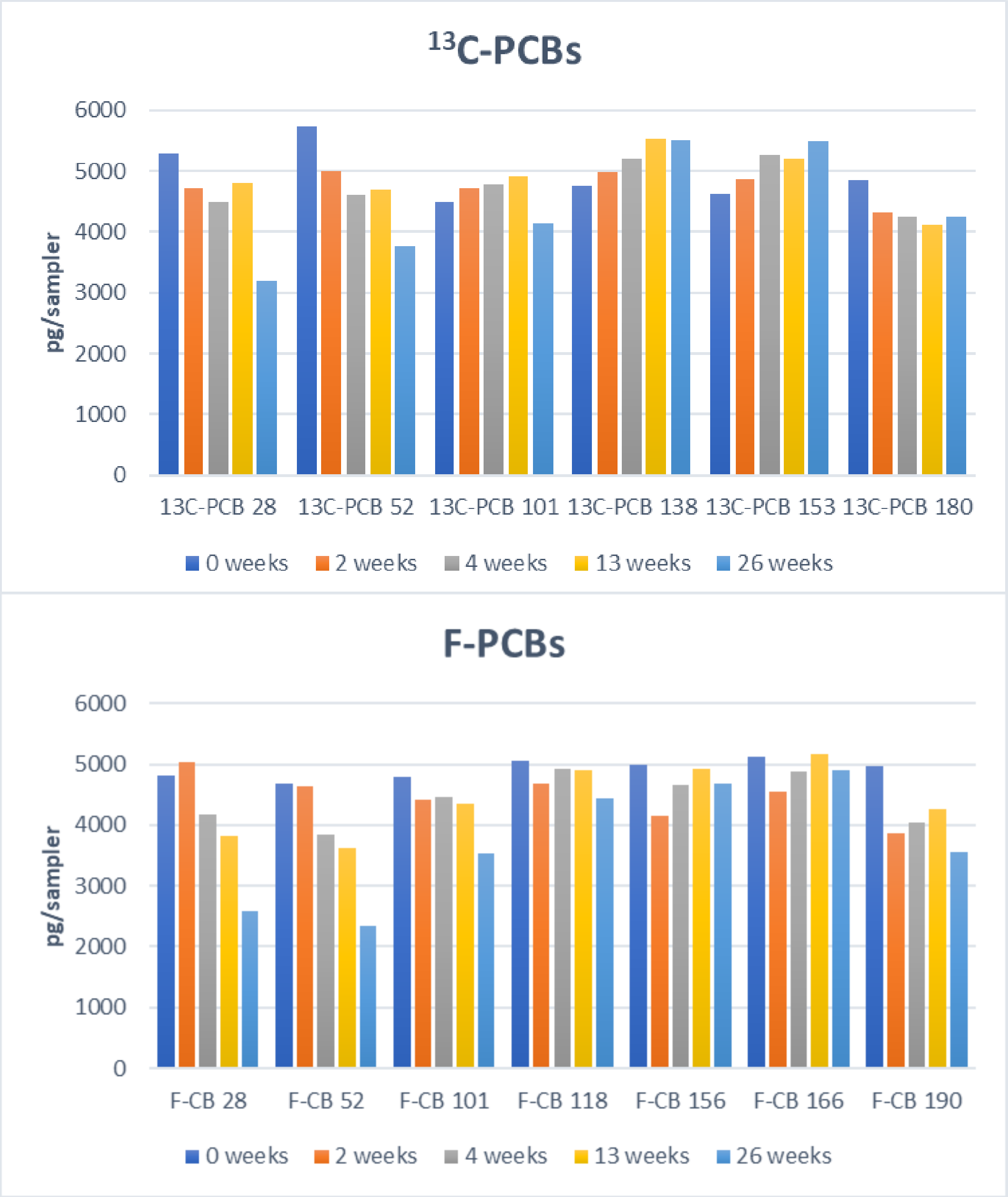

Figure 52. Amount in pg/sampler of the performance reference compounds ^{13}C-PCBs and F-PCBs remaining on the sampler at the start of the study (0 weeks) and after a deployment period of 2, 4, 8, 13, and 26 weeks.

Using the mass $N_{PRC,0}$ of each performance reference compound spiked onto the sampler, the deployment time t, and the mass of PRC measured in the sampler after deployment, $N_{PRC,t}$, a depuration rate constant k_{dep} can be calculated according to Equation 1 (Ockenden et al., 2001).

$$N_{PRC,t} = N_{PRC,0}*\exp(-k_{dep}*t) \qquad (1)$$

k_{dep} = depuration rate constant

$N_{PRC,t}$ = amount of PRC remaining in the SPMD at time t

$N_{PRC,0}$ = amount of PRC added to the SPMD at time zero

Assuming an initial mass of exactly 5000 pg of each PRC (in reality this will be slightly less or more for each sampler), depuration constants have been calculated for each PRC congener after deployment of 28 days, 90 days (3-month samples), and 181 days (6-month samples). The results are shown in Table 12 for F-PCBs and Table 13 for ^{13}C-PCBs. In constant environmental conditions, k_{dep} should also be constant over the whole deployment period. Higher k_{dep} calculated for a 4-week deployment can be explained by higher average air temperatures at the beginning of the study (Table 11), and fit well with a theoretical increase of K_{OA} with decreasing temperature by about a factor of 2.5-3 for every 10 °C decrease, especially for the F-PCBs 28, 52, and 101 as well as the ^{13}C-PCBs 28, 52, and 101. However, analytical uncertainty, exacerbated by only low levels of depuration do not allow for such conclusions for the higher-chlorinated congeners in this study.

It can also be seen from the calculated k_{dep} values that the depuration behaviour of F-PCBs seems to be similar to that of their equivalent ^{13}C-PCBs, with the former displaying slightly higher depuration rates in this study.

Table 12. Amount of F-PCBs remaining ($N_{PRC,t}$) on the sampler after a deployment period of t=28, 90, 181 days and the corresponding depuration rate constant k, calculated using $N_{PRC,0}$ = 5000pg. N/A*: no k_{dep} calculated, as $N_{PRC,t} > N_{PRC,0}$.

Hom. group	IUPAC No.	$N_{PRC,28}$ in pg	$k_{dep(28)}$	$N_{PRC,90}$ in pg	$k_{dep(90)}$	$N_{PRC,181}$ in pg	$k_{dep(181)}$
Trichloro-	3’-F-CB-28	4183	0.00637	3826	0.00297	2581	0.00365
Tetrachloro-	3-F-CB-52	3844	0.00939	3617	0.00360	2331	0.00422
Pentachloro-	3’-F-CB-101	4451	0.00415	4358	0.00153	3543	0.00190
	5’-F-CB-118	4920	0.00058	4897	0.00023	4440	0.00066
Hexachloro-	5’-F-CB-156	4668	0.00245	4919	0.00018	4678	0.00037
	3’-F-CB-166	4880	0.00087	5167	N/A*	4913	0.00010
Heptachloro-	5’-F-CB-190	4043	0.00759	4258	0.00178	3562	0.00187

Table 13. Amount of ^{13}C-PCBs remaining ($N_{PRC,t}$) on the sampler after a deployment period of t=28, 90, 181 days and the corresponding depuration rate constant k, calculated using $N_{PRC,0}$ = 5000pg. N/A*: no k_{dep} calculated, as $N_{PRC,t} > N_{PRC,0}$.

Hom. group	IUPAC No.	$N_{PRC,28}$ in pg	$k_{dep(28)}$	$N_{PRC,90}$ in pg	$k_{dep(90)}$	$N_{PRC,181}$ in pg	$k_{dep(181)}$
Trichloro-	^{13}C-PCB 28	4495	0.00380	4815	0.00042	3194	0.00248
Tetrachloro-	^{13}C-PCB-52	4612	0.00288	4692	0.00070	3766	0.00157
Pentachloro-	^{13}C-PCB-101	4771	0.00167	4926	0.00017	4137	0.00105
Hexachloro-	^{13}C-PCB-138	5193	N/A*	5527	N/A*	5509	N/A*
	^{13}C-PCB-153	5258	N/A*	5193	N/A*	5493	N/A*
Heptachloro-	^{13}C-PCB-180	4255	0.00576	4118	0.00216	4255	0.00089

Uptake of native PCBs. In order to investigate the possible impact of different PRCs on the sampling of native target PCBs, a range of PCBs were analysed in all samples. The results, in pg per sampler (average of two identical samplers), can be seen in Figure 53. Plots on the left-hand side show the sums of all congeners within a homologue group measured, while plots on the right-hand side show those congeners within the homologue group that are the native equivalents of the ^{13}C-PCBs added.

Generally, PCB levels and uptake rates were very similar for all three types of samplers (with F-PCBs, with ^{13}C-PCBs, without PRCs added), as expected, possibly with slightly higher amounts of tetra-, penta-, and hexa-PCBs found in the samplers without PRCs. In addition to the somewhat higher depuration rates at the beginning of the study mentioned above, probably due to higher temperatures, small increases in PCB levels during the first four weeks could be observed here, which can be attributed to higher PCB air concentrations as a result of their increased volatilisation from primary and secondary sources with increasing temperatures. Hepta-CB concentrations including PCB 180 were only slightly above their LOQs in the first weeks and their concentrations should be viewed with this in mind.

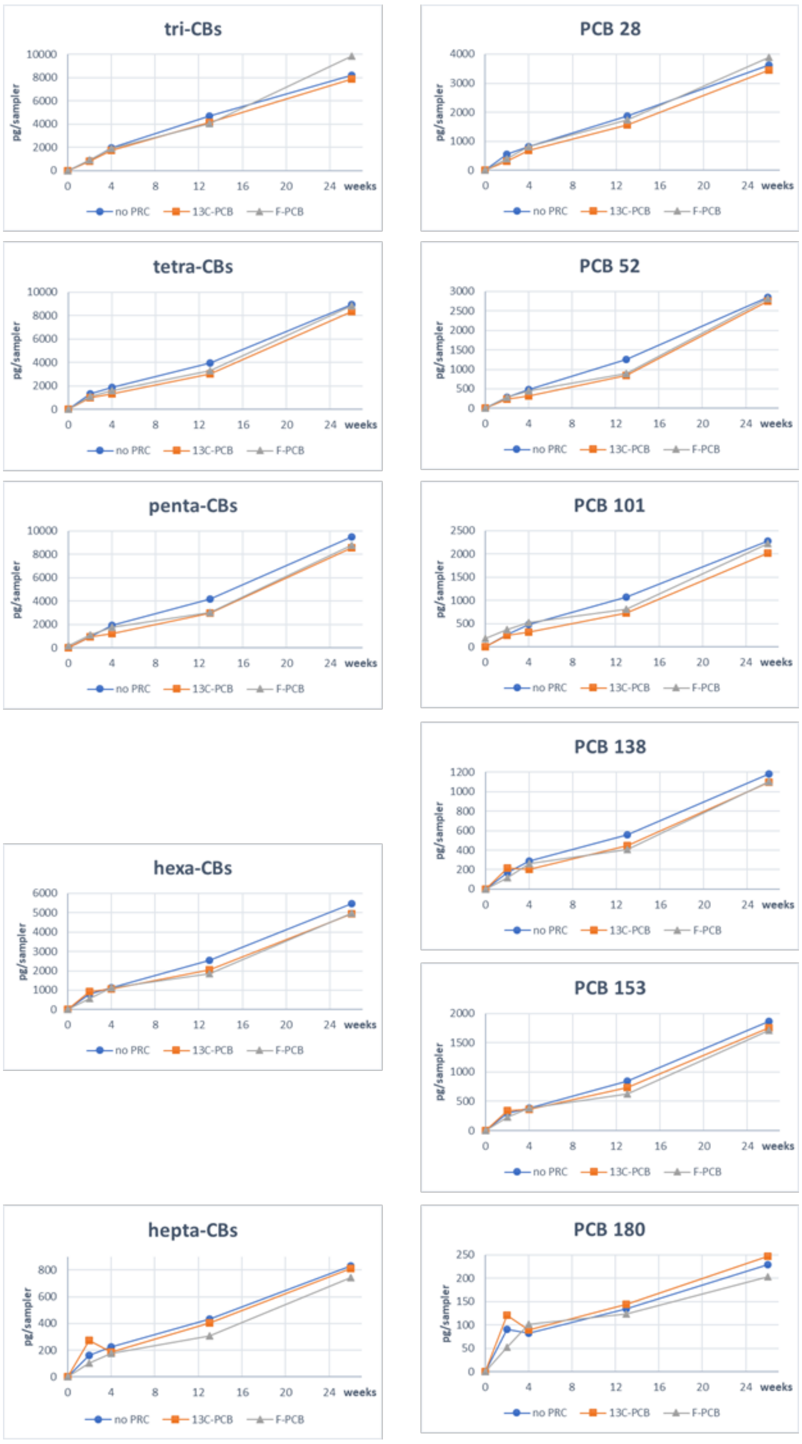

Figure 53. PCB concentrations in PUF-PAS in pg/sampler over the duration of the study. Left: homologue group, right: PRC-^{13}C-PCB-equivalent PCB congener(s) in each homologue group. Deployment time of each sampler in weeks.

One notable issue observed in this study was the presence of an impurity that co-eluted with PCB 101 in all samplers spiked with F-PCBs, including the associated laboratory blank and field blank, and also in the F-PCB spiking solution itself. It has not yet been determined if this impurity is PCB 101 itself - possibly a ~4% impurity of F-PCB 101 - or if it is a different compound showing the same behaviour as PCB 101 during the GC/MS analysis. This impurity amounts to ca. 200 pg/sampler, which is around 10% of the overall PCB 101 sampled after six months in this study. For comparable sampling sites with medium-to-high PCB concentrations in the air, this can easily be compensated for by subtracting the laboratory blank value from all samples. However, as high blanks will also increase the limit of quantification (LOQ) calculated for each compound, for remote sampling sites with very low air pollution levels this could mean that the PCB 101 concentrations measured fall below the LOQ and it would therefore not be possible to report data for this congener. In any case, it would currently be advisable for every laboratory planning to use F-PCBs as part of their PCB method to run tests beforehand to rule out possible problems.

7.4 Conclusions and outlook

F-PCBs have been demonstrated to work as PRCs, providing depuration rate constants similar to ^{13}C-PCBs, as expected. F-PCBs can be used instead of ^{13}C-PCBs to allow the utilisation of the latter as recovery or internal standards, or additionally, to increase the number of PRCs within the desired range of depuration, in order to obtain a more reliable and precise representation of the sampling conditions. Further detailed and robust studies to determine exact $K_{PAS\text{-}Air}$ depending on meteorological conditions and sampler parameters will be helpful as an addition to currently existing datasets for a wide range of SVOCs.

However, before F-PCBs are integrated into any sampling or analytical method, possible impacts need to be assessed beforehand by each analytical group. In this study, only one batch of F-PCBs was used, so it is not clear if and to which extend the PCB-101 impurity is present in every standard solution purchased.

Additional to the data presented here, a second study investigating the use of F-PCBs as performance reference compounds in SPMDs is currently underway with the aim of using F-PCBs as PRCs in the UK/Norway SPMD transect.

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8 Overall conclusions, outlook, and recommendations

Long-term air monitoring datasets are needed for persistent organic pollutants (POPs) to assess the effectiveness of source abatement measures and the factors controlling ambient levels, and to provide governments, regulators, and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation such as the Stockholm Convention and UN/ECE Protocol on POPs. These data can be provided by active or passive air sampling. With the UK TOMPs Ambient Air monitoring Network and the UK/Norway SPMD air sampling transect, this thesis presents two of the worldwide longest-running ambient air monitoring programmes of continuous data on atmospheric POPs concentrations.

The UK Toxic Organic Micro Pollutants (TOMPs) Network, using high-volume active air samplers, has demonstrated the constant decline in UK air concentrations for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polybrominated diphenyl ethers (PBDEs) since 1991, in accordance with emission estimates. Furthermore, PCBs generally showed a summer > winter pattern, while ΣPBDE concentrations are distributed over a range of congeners with more uniform concentrations but greater differences in seasonal patterns, thus their overall seasonality is characterized by these contrasting patterns

Since the inception of the TOMPs network, a range of new POPs have been added to the Stockholm convention, and emerging pollutants are constantly being evaluated as to their environmental significance and regulatory needs. Examples mentioned in this thesis are the di-CB PCB 11 and organophosphate esters. These emerging contaminants are often more volatile than the originally identified POPs, and as such present a challenge to traditional POPs air sampling methods. Including XAD® pods in the standard air sampling assemblies of the TOMPs network would provide an easy, economical, and versatile way to sample more volatile compounds with standard high-volume air samplers without compromising the comparability between old and new datasets, as the sampling of traditional POPs on the glass fibre filter and polyurethane foam plugs in the assembly is not impacted by the inclusion of an XAD® pod. Furthermore, extended sampling periods due to the large surface area and adsorption capacity of XAD® could reduce the number of samples that need to be collected and analysed, saving time and money and improving the environmental impact of the TOMPs network. However, the exact impact of longer sampling periods on the original set of POPs would first need to be evaluated.

At the UK/Norway SPMD transect, a latitudinal passive ambient air sampling transect from the south of England to the north of Norway established in 1994, which had reported several years of decreasing PCB air concentrations previously, increased levels were observed between 2008 and 2016. The reasons for this could include local sources, effects of climate change, and impact of polluted air masses from Eastern Europe. In contrast, PBDE concentrations have decreased since 2000 in line with expectations following the recent phase-out of PBDEs in Europe, and now also exhibit a clear spatial difference, with an explicit distinction between relatively polluted sites in England and relatively unpolluted sites in the north of Norway. A continuation of this project would be important to observe if these differences in temporal trends between PBDEs and PCBs persist further or if they were a short-term phenomenon. In the first case, this would provide important information for estimating and modelling future trends of POPs in the atmosphere.

The transect was originally set up to observe the long-range atmospheric transport (LRAT) of POPs into remote locations and test the hypotheses of global distillation and fractionation. Unfortunately, a two-year deployment of SPMDs has shown to be unsuitable for the sampling of lighter organic pollutants like PCB 28 and PCB 52, which are generally the most likely to undergo LRAT. Therefore, the inclusion of a second sampler suitable for more volatile pollutants into the network should be considered, for example SIP-disks (XAD®-sorbent-impregnated PUF disks). Additionally, the use of monofluorinated PCBs as performance reference compounds could improve the analytical methodology of this project, although a problem with a possible PCB 101 impurity will need to be solved first.

Finally, a range of suggestions were made in Chapter 6.3.3 that should be observed when running long-term projects like the UK/Norway SPMD transect, and these would also be applicable to the UK TOMPs network. These suggestions are:

- All standard operating procedures (SOPs) need to be extremely detailed, assuming that future operators will routinely work with different laboratory methods than present operators, and will not be familiar with the ones used in the project.
- Ideally, people with main responsibility for the practical work of the project should have been partially involved at least once before.
- A large number of archive samples should be created and routinely analysed with subsequent campaigns if sensible (this would work for POPs, but not for analytes that degrade during storage). Archive samples should include laboratory blanks, to easily identify issues resulting from differences in sampler handling before deployment, for example pre-cleaning or addition of performance reference compounds (PRCs). They should also include deployed samples before extraction, in order to evaluate this step. It may be useful to collect additional samples at some sampling sites with the purpose of using them as archive samples.
- Archive samples need to be labelled clearly with site details and dates. Codes should be avoided, except for sensitive data. If it is necessary to use

codes, future operators need to be informed about their meaning or storage place.

- A person should be appointed to be responsible for the integrity of the archive samples. For example, there should be regular checks that none of the samples have dried out or that labels are starting to come off the sample. This person would also make sure that archive samples are not discarded during freezer clean-outs.
- All data regarding the project should be stored in a central place. This should include raw data after data acquisition, processed data, and any calculations for reports and publications as well as data relating to the samples like temperatures or air volumes, if available.
- Any problems that could have impacted the sample itself or the reported data have to be noted in detail.

In addition to long-term trends and regular seasonal variations, short-term emission events like the UK 'Bonfire Night', where increased PBDE concentrations possibly stemming from 'backyard burning' were observed, were shown to impact POPs concentrations in ambient air. Compared to a similar study in 2000, both absolute PBDE air concentrations during the 'Bonfire Night' period, and their relative increase compared to background levels have decreased, reflecting their ban in the EU in 2004. However, the lack of a clear BDE-209 signal at the same time as the other congeners was surprising given the dominance of the deca-BDE commercial mixture over the penta- and octa-mixtures in recent decades, and requires additional investigation, for example by the controlled incineration of old consumer products in specialised large-scale scientific burn facilities and the subsequent analysis of any PBDEs emitted, or by carrying out further air sampling campaigns over 'Bonfire Night'. Since their phase-out, PBDEs in consumer goods have been replaced by other flame retardants like organophosphorus flame retardants (OPFRs) and novel brominated flame retardants (NBFRs). Further studies will also show if this change is reflected by increased OPFR and NBFR air concentrations during 'Bonfire Night'.

Appendix A. Publications authored and co-authored or contributed to

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