

Annual Report for 2017 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

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Report to the Department for Environment, Food
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Executive Summary.

This report contains the quarter 1 (Q1), quarter 2 (Q2) quarter 3 (Q3) and quarter 4 (Q4) ambient air concentration data for polychlorinated biphenyls (PCBs,) polybrominated diphenyl ethers (PBDEs) and HBCDD from the Toxic Organic Micro-Pollutants Monitoring Network (TOMPs) which is funded by the Environment Agency on behalf of the Department for Environment, Food and Rural Affairs (Defra) and the devolved administrations.

In 2017, 37 PCBs congeners, 10 PBDE congeners were measured in each sample. In addition, BDE209 and HBCDD have been added to the analyte list. The TOMPs network includes sites in London, Manchester, Hazelrigg (Lancashire), High Muffles (North Yorkshire), Auchencorth Moss (Midlothian) and Weybourne (Norfolk). The aim of the TOMPs network, which has operated since 1991, is to provide information on the ambient levels of organic pollutants in the UK through monitoring of air concentrations at six sites. The results and other related scientific work are used to inform policy development on exposure to persistent organic pollutants (POPs).

The specific aims of the TOMPs programme are:

- To identify sources of a range of POPs in the UK atmosphere.
- To quantify sources that are regarded as potentially significant.
- To measure concentrations of a range of POPs in ambient air in UK cities and rural locations, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

The ability of certain POPs to undergo long range atmospheric transport (LRAT) has resulted in the negotiation of protocols for their reduction or elimination, and to reduce the risks to regional and global environments. These include the 1998 United Nations Economic Commission for Europe (UN/ECE) Protocol on Persistent Organic Pollutants made under the Convention on Long-Range Transboundary Air Pollution, and the Stockholm Convention (SC) on POPs. The UK is a signatory to both these instruments, and therefore has an on-going requirement to assess the extent of the presence of the listed POPs in the UK environment. Further to this, 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 provision of long-term environmental monitoring data, such as that provided by TOMPs, is an important component of the UK's obligations under these agreements.

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1. Introduction

Lancaster University (LU) has been involved in the TOMPs programme since its inception in 1990. LU currently manages the programme on behalf of the Environment Agency, Defra and the devolved administrations and operates six air monitoring sites, three urban, two rural and one semi-rural. The current contract commenced in October 2016 and will run for a period of three years. Atmospheric sampling is carried out at each site, collecting a biweekly sample which is bulked to provide quarterly data. These data are reported to Defra and published on the air quality data website uk-air.defra.gov.uk/. They are also available on the Stockholm Convention Global Monitoring Plan website <http://www.pops-gmp.org/>. Two sites are currently maintained via sub-contracts; Auchencorth Moss by the Centre for Ecology and Hydrology (CEH) and the Weybourne Observatory by the University of East Anglia. The analytes quantified at Lancaster University are PCDD/Fs ('dioxins and furans'), PBDEs including BDE209 and PCBs. HBCDD is quantified at the University of Birmingham.

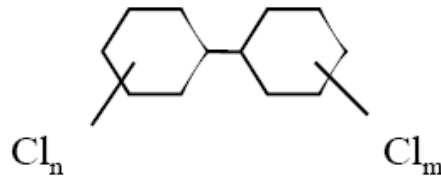
This annual report for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polybrominated diphenyl ethers (PBDEs) includes:

- Information on PCDDs, PCDFs, PCBs, PBDEs and HBCDD.
- A summary of network operations including details of monitoring sites, equipment employed, details of site installations/removals, site calibration visits and equipment servicing and breakdowns
- A summary of the analytical procedure used to detect PCBs, PCDDs/PCDFs and PBDEs and HBCDD.
- Review of annual mean and quarterly concentrations.
- Trends in estimated sources of PCBs, PCDDs and PCDFs and PBDEs in the UK

2. Background to PCBs, PCDDs and PCDFs, PBDEs and HBCDD.

PCBs were first synthesized in 1881 by Schmidt and Schulz but their commercial production only began in 1929 in 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 (Monosanto, USA), Phenochlor and Clophen (Bayer, EU). Because of high chemical and thermal stability, electrical resistance, low or no flammability, PCBs had extensive applications. They have been used as dielectric fluids in capacitors and transformers, in plasticizers, adhesives, inks, sealants and surface coatings (*Eduljee*, 1988; *de Voogt and*

Brinkman, 1989; Harrad *et al.*, 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ ($n=1-10$).



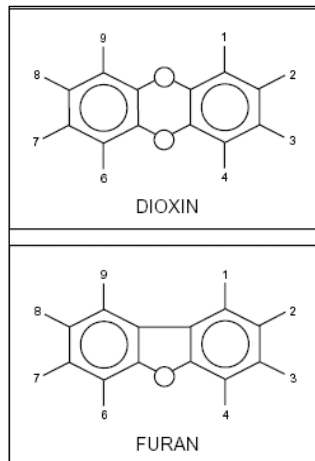
There are 209 possible congeners with one to ten chlorines atoms attached to the biphenyl structure. International Council for the Exploration of the Seas (ICES) identified 7 key PCB congeners which are commonly reported in environmental samples. These are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB), PCB 138 (2,2',3,4,4',5-heptaCB), PCB 153 (2,2',4,4',5,5'-heptaCB), PCB 180 (2,2',3,4,4',5,5'-heptaCB), 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 (Breivik *et al.*, 2002). 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. (de Voogt and Brinkman, 1989; Danse *et al.*, 1997). Current atmospheric levels of PCBs in the environment can be accounted by on-going primary anthropogenic emissions (e.g. accidental release of products or materials containing PCBs), volatilization from environmental reservoirs which 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 atmospheric in 2014 was 733kg, 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.

PCDD/Fs. 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. Dioxin 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 exposures levels still remain a concern. PCDDs and PCDFs were added to Annex C of the Stockholm Convention when it entered into force in 2004. The NAEI inventory estimates that the emission of PCDD/Fs to the UK atmosphere in 2015 was 215 g-TEQ (most recent data), the majority emitted from combustion processes.

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, those that are toxic have chlorine atoms at each of the positions 2, 3, 7 and 8. 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 which can be used to provide an assessment of the relative toxicities of each congener and an estimate of the overall toxicity of a mixture.



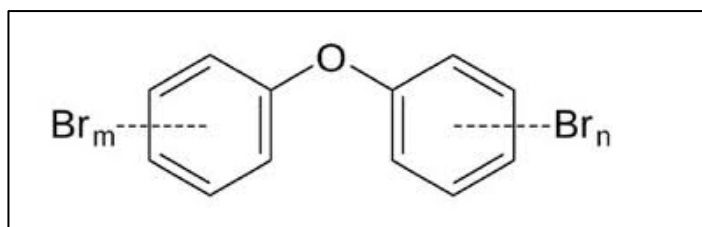
The Toxicity Equivalency Factor (TEF) values have been subject to revision and amendment since their inception but the most widely accepted set of TEF values for the 2,3,7,8-substituted PCDD/Fs is the ‘WHO’ (WHO-TEF) system, originally developed in 1990s and last updated in 2005. Another commonly used scheme is the International Toxicity Equivalency Scheme (I-TEQ) which has assigned slightly different TEFs to the WHO schemes. The three TEF schemes data are contained in the table below. For consistency the 1998 scheme has been used by the TOMPs network throughout for the assessment of long-term trends, but also converted to I-

TEF for comparison with the source inventories. There is evidence to suggest that several of the PCBs elicit similar toxic responses to the dioxins, based on their binding to an intercellular protein, the Ah-receptor. These selected 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.

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			
1,2,3,7,8-PeCDD	1	1	0.5	PCB-77	<0.0201	<0.0201
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	PCB-81	<0.0201	<0.0203
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	PCB-126	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	PCB-169	0.01	0.03
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01			
OCDD	<0.0201	<0.0203	<0.021			
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	<0.021			
OCDF	<0.0201	<0.0203	<0.0201			

PBDEs. Polybrominated diphenyl ethers 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 volatilize into the atmosphere during the product lifetime and waste processing/recycling. They reduced fire hazards by interfering with the combustion of the polymeric materials (BSEF, 2000; Commission of the European Communities, 2000). Their general structure is $C_{12}H_{10-n}Br_nO$ ($n=1-10$). Therefore, there are 209 possible PBDE congeners, depending on the position of the bromine atoms on the phenyls 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 contains predominantly the BDE-209 congener and is currently the most widely used PBDE flame retardant product.



The global demand for PBDEs has previously been very substantial with a peak estimation of 70,000 tonnes for the year 2003 (Hites *et al.*, 2004). 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).

In the UK there has been previously high use of PBDE as a result of particularly stringent fire 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. PBDE congeners have been included in the TOMPs methodology since Q4 2010. The main congeners that have been analysed are: PBDEs 28 (tri), 47 (tetra), 49 (tetra), 99 (penta), 100 (penta), 153 (hexa), 154 (hexa), 183 (hepta). Congeners BDE-47 and BDE-99 which account for approximately 72% of the composition of the penta commercial mixture (pentaBDE).

This report contains the first data for BDE209 (decabromodiphenyl ether) which has been added to the analyte suite. DecaBDE was a high use flame retardant mixture from the polybrominated diphenylether (PBDE) family of chemicals (UNEP 2013). In the UK decaBDE was used primarily in hard plastics (e.g. electrical equipment housings) and flame retardant-backed textiles (most commonly used as curtain fabrics). Examples of historical and current uses of decaBDE include;

- Electric & Electronic (E&E) equipment (e.g. housing s and internal components of TVs, mobile phones, remote controls, scanner components)
- Automobiles/mass transportation (e.g. fabric for head rest and upholstery, reinforced plastics for instrument panel)
- Ships, boats, airplanes, household applications (e.g. electric wiring and cables, audio and video equipment, switches and connectors)
- Textiles and furniture (e.g. upholstery back coating)
- Public, private and industrial buildings/construction (pipes, stadium seats, air ducts for ventilation systems)

BDE209 (decaBDE) was added to Annex A of the Stockholm Convention in 2017. On-going sources to the environment include emissions from products still in use, e.g. pre-treated textiles, high impact polystyrene (HIPS) and thermoplastics. UK emission estimates for 2012 provided by Earnshaw *et al.* (2013) suggest that atmospheric emissions of decaBDE were approximately 180kg per annum, whilst emissions to soil and water are approximately 370kg and 12kg per annum, respectively.

HBCDD is a brominated flame retardant which has to date been extensively used across the EU within expandable polystyrene (EPS) and extruded polystyrene (XPS) insulation boarding used within roof and cavity wall insulation. HBCDD also has a more limited application (around 1% of total HBCDD use) as a flame retardant for use in high impact polystyrene (HIPS) used for mouldings and housings of electrical goods such as computer monitors, and CRT based televisions. It was first used in the UK in 1975 with a steady increase in use from that time. Although UK production of HBCDD ceased in 2003, imports from the sole producer in Europe continued to supply the increasing demand. Based on VECAP data peak consumption of HBCDD was reached in Europe (including the UK) in 2008 at around 12,000 tonnes of which around 1,670 tonnes were used in the UK (based on extrapolation using GDP). Concerns of human health and environmental effects meant that HBCDD was added to Annex A of the Stockholm Convention in 2013 at the fifth Conference of the Parties with specific exemptions included to make allowances for ongoing processes under the EU REACH regulation. In 2016 a time-limited authorisation was given to 13 companies for two specific applications for use as a flame retardant in expanded polystyrene boarding and use as a flame retardant in the manufacture of expanded polystyrene beads. This Authorisation expired in August 2017 after which no further legal use of HBCDD was permitted in the EU. Data from Broomfield *et al.* (2010) and the REACH Annex XV dossier for HBCDD highlight that principal use (90%) was within insulation boarding with a split of 52% in extruded polystyrene insulation boards (XPS) and 48% in expanded polystyrene insulation boards (EPS). Concentrations of HCBDD were generally low at 0.5-1.0% w/w for XPS and 0.8-2.5% for EPS, although this suggests that there is a potentially large bank of articles containing HBCDD.

3. TOMPs sites operating in 2017

In 2017 the TOMPs programme operated 6 sites:

London (LON)	urban site established in 1991
Manchester (MAN)	urban site established in 1991
Hazelrigg (HR)	semi-rural site established in 1992
High Muffles (North Yorkshire) (HM)	rural site established in 1999
Auchencorth Moss (AC)	rural site established in 2008
Weybourne (WE)	rural coastal site established at the end of 2008

The sites consist of two urban locations in London (LON), Manchester (MAN), three rural sites at High Muffles (HM, North Yorkshire), Auchencorth Moss (AC, Mid Lothian) and Weybourne (Norfolk), one semirural site at Hazelrigg (HR, Lancashire). At the rural and semirural sites, samplers are located away from major roads, whereas at the urban sites samplers are located in the city centre on the roof of a building. The locations of the current samplers in the network are shown in Figure 1.

Figure 1. Location map of the current TOMPs sites.



4. Network sampling operations

The sampling modules for the Andersen GPS-1 sampler are prepared just prior to deployment which involves disassembling, inspecting and cleaning the modules. Modules are stored frozen in sealed bags prior to deployment. All parts of the modules that come into contact with the glass fibre filter (GF/A Whatman) and polyurethane plugs (PUFs, Klaus Ziemer GmbH Langerwehe, Germany) are routinely solvent cleaned between each sample. In addition, the modules are fully disassembled and all parts thoroughly cleaned in solvent. The GF/As are pre-cleaned by baking out in a muffle furnace at 450 °C for 24 hours. They are then transferred to aluminium foil packages (the aluminium foil has also been baked out) and stored sealed until they are used. PUFs and GF/As filters are regularly sent to CEH in Edinburgh who manage the Auchencorth Moss site and University of East Anglia who manage the Weybourne site. The PUFs are prepared for all the sites from the same batches, by a rigorous pre-extraction procedure. This involved a soxhlet extraction in acetone/hexane (1:1), with subsequent solvent removal in a solvent cleaned desiccator, maintained under vacuum. PUFs are also prepared to serve as field and laboratory blanks. The GF/As and PUFs are placed in the sampling modules using solvent cleaned stainless steel tongs and are exposed to the laboratory environment for the minimum amount of time possible.

The modules are changed every 14 days at all sites. 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. Log books are used to record sampling data at each site, but sampling data are also available electronically. The following are recorded routinely for each sample at each of the sites: start time, date, counter reading, MagnaHelic reading; stop time, date, counter reading, MagnaHelic reading; maximum, minimum and actual temperature (°C). Cross-checks are possible between the manually calculated air volume and the electronically calculated air volume. During each visit, the sampler, sampler platform and auxiliary pieces of equipment are checked for corrosion or breakages. A number of spare parts are routinely taken to each site and preventative or remedial maintenance carried out when necessary. Long life brushless motors are used to minimise samples lost through motor failures. A sampler calibration is performed once a year at each site.

5. Extraction and clean-up procedures

Preparation of the samples takes place in a laboratory with restricted access. All glassware is thoroughly solvent cleaned prior to use and where necessary baked out at 450 °C overnight following established procedures. Each sample (gas + particle) is spiked with a recovery standard of $^{13}\text{C}_{12}$ -labeled PCB congeners ($^{13}\text{C}_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) and PBDE congeners BDE 51, BDE 128, BDE 190, BDE209 and an isotope dilution/recovery standard containing 21 $^{13}\text{C}_{12}$ -labelled PCDD/Fs and coplanar PCBs. Samples are individually extracted in a Soxhlet extraction unit for 18 hours with hexane and 6 hours with toluene. PCBs, PBDEs and tri, tetra and penta PCDD/Fs are extracted in the hexane fraction. The remaining PCDD/Fs are extracted in the toluene fraction. The extracts are concentrated using rotary-evaporation and nitrogen-evaporation. The hexane and toluene fraction are combined for each sample and extracts pooled before purification to obtain quarterly data (Jan-March (Q1), April-June (Q2), July-Sept (Q3), and Oct-Dec (Q4)). The 6 or 7 hexane fractions (depending on the length of each quarter) of each quarter are then bulked together. The samples are transferred into a 250ml round bottom flask using hexane. The toluene fractions are then bulked in the same way using hexane. Each quarter will consist of 6-7 two week samples, representing approximately 4500 m³ of air. The hexane and toluene fractions are then combined with 50% of the extract added to a sample archive and the remaining 50% being subjected to clean-up and analysis. These extracts are then eluted through a multilayer 20 mm inner diameter (id) acid silica column containing a small layer of sodium sulphate, 1 g activated silica (Merck Silica 60), 2 g of basic silica (Merck Silica 60), 1 g of activated silica (Merck Silica 60, 4 g of acid silica (Merck Silica 60), 1 g activated silica and a small layer of sodium sulphate (silica and sodium sulphate baked at 450°C overnight). The extracts are eluted through gel permeation columns containing 6 g of Biobeads SX 3 and concentrated to 500 µL. Each sample is then fractionated with a basic alumina column to obtain three fractions. Fraction 1 contains PCBs and PBDEs, Fraction 2 contains co-planar PCBs and Fraction 3 contains PCDD/Fs. Fraction 1 containing PCBs and PBDEs is solvent exchanged to 160 mL of dodecane (for urban site) and 80 mL of dodecane (for the more remote sites) containing PCB 30 [$^{13}\text{C}_{12}$], PCB 141, [$^{13}\text{C}_{12}$] PCB 208, BDE 69, and BDE 181 as internal standards. The PCB and PBDE fractions are analyzed by gas-chromatography mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM). Details of the instruments, temperature programme and monitored ions are given elsewhere (Thomas et al., 1998 and Gouin et al., 2002). Thirty-seven PCB congeners and 22 PBDE congeners are measured in all samples, including the seven commonly reported ICES congeners: PCBs 28, 52, 90/101, 118, 138, 153/132 and 180. Some congeners

co-elute and are hence reported as a pair, for example, 153/132. Fractions 2 and 3 are solvent exchanged to 15 mL of nonane containing an injection standard of ^{37}Cl -labeled 2,3,7,8-TCDD. Analysis is performed on a Micromass Autospec Ultima high resolution-mass spectrometry (HR-MS) operated at a resolution of at least 10,000. Dioxins, furans and co-planar PCBs are generally found in mixtures containing several kinds of dioxins and dioxin-like compounds, each having its own degree of toxicity. To express the overall toxicity of such a mixture as a single number, the concept of “Toxic Equivalents” (TEQ) has been developed. The concentration of co-planar PCBs and PCDD/Fs are expressed in units of fgTEQm^{-3} . The concentration in fgm^{-3} is multiplied by the WHO Toxic equivalency factors (TEF, 1998) to obtain the final concentration in fgTEQm^{-3} . The WHO TEF scheme used for the data conversion was developed in 1998, and although the scheme was updated in 2005, the original scheme is still used to ensure consistency within the dataset. From 2017 decaBDE and HBCDD congeners were added to the suite of analytes. Sample preparation for decaBDE was identical to the method used for other PBDEs but a separate GCMS run was required with 15m column and shorter oven programme. Further details of the HBCDD method are included at the end of this section.

QA/QC A number of steps are taken to obtain data that would allow an assessment of the accuracy and reliability of the data. PCB and PBDE recoveries are monitored by quantifying 11 $^{13}\text{C}_{12}$ -labelled PCB and PBDE standards, whilst PCDD/F and coplanar PCB data are corrected using 21 $^{13}\text{C}_{12}$ -labelled PCDD/F and coPCB isotope dilution standards, using the injection standard as an internal standard. The criteria for the quantification of analytes are a retention time found within 2s of the standard, isotope ratio found within 20% of standard and a signal to noise ratio of at least 3. Analytical blanks, consisting of solvent are included at a rate of one blank for every 12 samples. The method detection limit was calculated as 3 times the standard deviation of the concentrations found in the analytical blanks. If the concentrations in the blanks are below the instrumental detection limit, then the method detection limit is defined as equal to the instrumental detection limit. All results are blank corrected using the concentration of the field blanks. Field blanks are produced for each site and each quarter and they are used to calculate method detection limits (MDLs). When compounds are not detected in the field blanks, laboratory blanks produced for each quarter are used to estimate MDLs.

Determination of HBCDD in TOMPs extracts

A sub-sample of each quarterly extract (taken from the archive) were eluted with hexane through a multilayer 20 mm inner diameter (id) containing silica (8g) and acid silica(8g). The

extracts were spiked with 50 ng each of $^{13}\text{C}_{12}$ -labelled α -, β - and γ -HBCDD. Samples were concentrated down and exchanged to 200 μL in methanol and transferred to an 300 μL inserted autosampler vial. Determination of concentrations of HBCDD isomers (α -, β - and γ -) was performed on a Sciex Exion UPLC coupled to a Sciex 5600+ Triple TOF MS. Chromatographic separation was achieved with a AccucoreTM RP-MS column (100 \times 2.1 cm, 2.6 μm , Thermo Scientific, Bremen, Germany) using a mobile phase of high purity water (Optima grade, Fisher Scientific (mobile phase A)) and methanol:acetonitrile (3:1, v/v ratio, Optima grade, Fisher Scientific (mobile phase B)). The LC program commenced with 25% B and was ramped to 50% over 1 minute, and increased linearly to 100% B over 5 minutes and held for a further 1 minute. The mobile phase composition was returned to 25% B and held for 1 minute to equilibrate for the next sample. The overall method duration was 8 minutes with a flow rate of 0.3 mL/min. The injection volume was 5 μL and the column oven was maintained at 35 $^{\circ}\text{C}$ throughout. The Triple TOF MS was equipped with a Turbo V ion source, which was operated in negative ion mode using electrospray ionisation at a voltage of -4,500 V. The curtain gas was set at 25 psi, whilst the nebuliser gas (source gas 1) was set at 25 psi and the drying gas (source gas 2) at 35 psi. The CAD gas was set to medium and temperature was 450 $^{\circ}\text{C}$. The instrument was operated in high resolution mode and scanned between 100-1,000 Da. Identification and quantification of target analytes were performed using MultiQuan 2.0 software. Target analytes were identified using a combination of correct retention time and two accurate m/z values. A mass error tolerance of 25 ppm was applied. Native HBCDDs were quantified with m/z 640.6370 and confirmed with 642.6350. A 5-point calibration from 1 pg/ μL to 20 pg/ μL was injected using the instrumental methods above. A linear plot was produced for each HBCDD isomer and an R^2 value of >0.999 was achieved in all cases.

6. Data storage.

The data are reported to Defra and published on the air quality data website uk-air.defra.gov.uk/ and made also available on the Stockholm Convention Global Monitoring Plan website <http://www.pops-gmp.org/>. Archived samples for each year (50% of the samples) are stored in the freezer in the laboratory at Lancaster University.

7. Results for year 2017

7.1 Network Operations

Table 2 contains information on the samples collected, including, bulked air volume (in m^3) and the number of samples bulked for each site for each quarter in 2017. The bulked air volume is obtained by summing the volume (in m^3) obtained from each sample taken during the quarter

(usually 6-7 samples depending on the sampling schedule). Total volume per quarter (bulked volume) under normal operating conditions ranged from 3892-5505 m³.

Manchester, Hazelrigg, High Muffles and Weybourne and operated normally with data capture rates at 100% over the year. In Q4 at the site at London experienced motor failure, as did the site at Auchencorth in Q1, which reduced the operation efficiency at the sites to 96.5% over the year. The power supply failure also required the motor to be replaced.

The samplers were all calibrated once during 2017 with quarterly field blanks collected from each site.

Table 2. Summary of the bulked air volumes, sample numbers in each quarter in 2017.

		Start	Time	Finish	Time	Volume m ³	Data Capture %
LON	Q1	06/01/2017	10:45	31/03/2017	10:50	4302	100
	Q2	31/03/2017	10:50	04/07/2017	11:10	4865	100
	Q3	04/07/2017	11:15	22/09/2017	10:55	4754	100
	Q4	22/09/2017	11:00	03/01/2017	10:45	4065	86
MAN	Q1	05/01/2017	10:50	30/03/2017	13:40	4229	100
	Q2	30/03/2017	13:55	22/06/2017	11:00	4198	100
	Q3	22/06/2017	11:05	28/09/2017	15:10	4936	100
	Q4	28/09/2017	15:15	04/01/2017	13:25	4923	100
HR	Q1	04/01/2017	16:25	29/03/2017	16:30	4371	100
	Q2	29/03/2017	16:30	21/06/2017	14:25	4370	100
	Q3	21/06/2017	14:30	27/09/2017	15:50	5505	100
	Q4	27/09/2017	15:55	02/01/2017	14:35	4938	100
HM	Q1	05/01/2017	13:25	30/03/2017	10:25	4251	100
	Q2	30/03/2017	10:30	22/06/2017	14:30	4266	100
	Q3	22/06/2017	14:35	28/09/2017	11:40	4945	100
	Q4	28/09/2017	11:45	04/01/2017	10:00	4964	100
AUCH	Q1	04/01/2017	10:30	29/03/2017	10:20	3892	86
	Q2	29/03/2017	10:20	21/06/2017	09:20	4490	100
	Q3	21/06/2017	09:20	27/09/2017	09:40	5241	100

	Q4	27/09/2017	09:40	03/01/2017	09:01	5239	100
WEY	Q1	06/01/2017	11:25	27/03/2017	11:15	4048	100
	Q2	27/03/2017	11:15	03/07/2017	10:27	4961	100
	Q3	03/07/2017	10:27	02/10/2017	10:47	4599	100
	Q4	02/10/2017	10:47	04/01/2017	09:30	4756	100

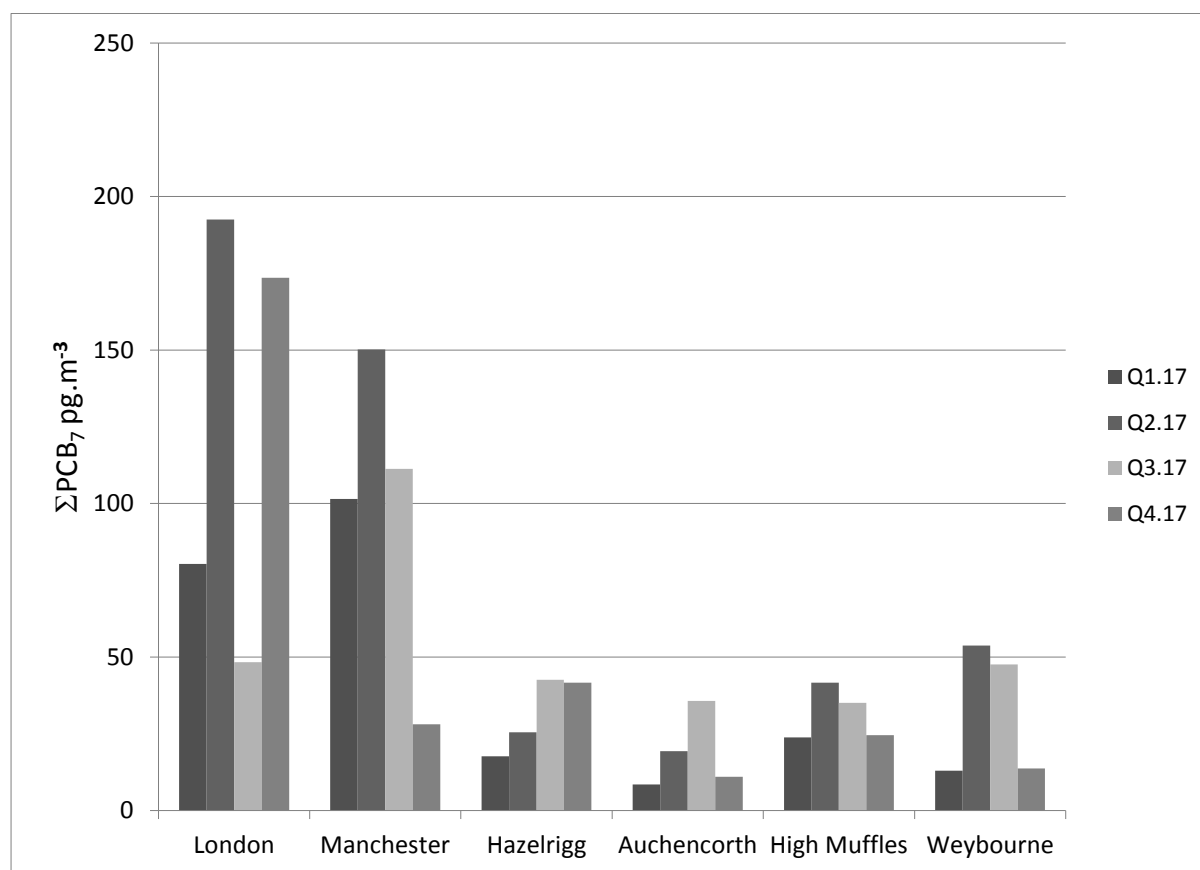
7.2 PCDD/Fs: Results and discussion

The addition of decaBDE and HBCDD to the suite of TOMP analytes has required significant method development and testing. PCDD/F concentrations at all TOMP sites have been declining and so reduced monitoring across the network has been agreed. Although archived samples will remain available for all sites, from 2017 on-wards PCDD/Fs will be reported only at the London and Manchester. The additional method development work has resulted in a delay for PCDD/F reporting at these sites and so data will be published in a future report.

7.3 PCBs: Results and discussions

Quarterly congener PCB data for the 6 TOMP sites are contained in Appendix 1 and a summary presented in Figure 5. The annually averaged PCB concentrations measured at each of the TOMP sites ranged from 124 pg/m³ (London) to 19 pg/m³ (Auchencorth) for the sum of seven indicator PCB congeners (PCBs 28,52,101,118,138,153,180). The data shows, as with previous years, that concentrations are proportional to the population density surrounding the site i.e. higher for urban sites by a factor of 3.9. The urban site at London showed an increase in the PCB concentrations compared with previous average values over the last five years (2011-2016) of 23%, whilst the urban site at Manchester showed a decrease of 7%, over the same period. Weybourne showed a 40% increase, High Muffles a 12% increase compared to their previous 5 year averages. Hazelrigg and Auchencorth showed a 12% and 13% decrease, respectively. It is worth remembering that despite the increase in concentrations at many sites, the concentrations remain low. The quarterly data showed a distinct seasonal pattern with higher levels in Q2 and Q3 which are characteristic of temperature driven diffusive sources. The exception to this was in London which exhibited the lowest concentration in Q3.

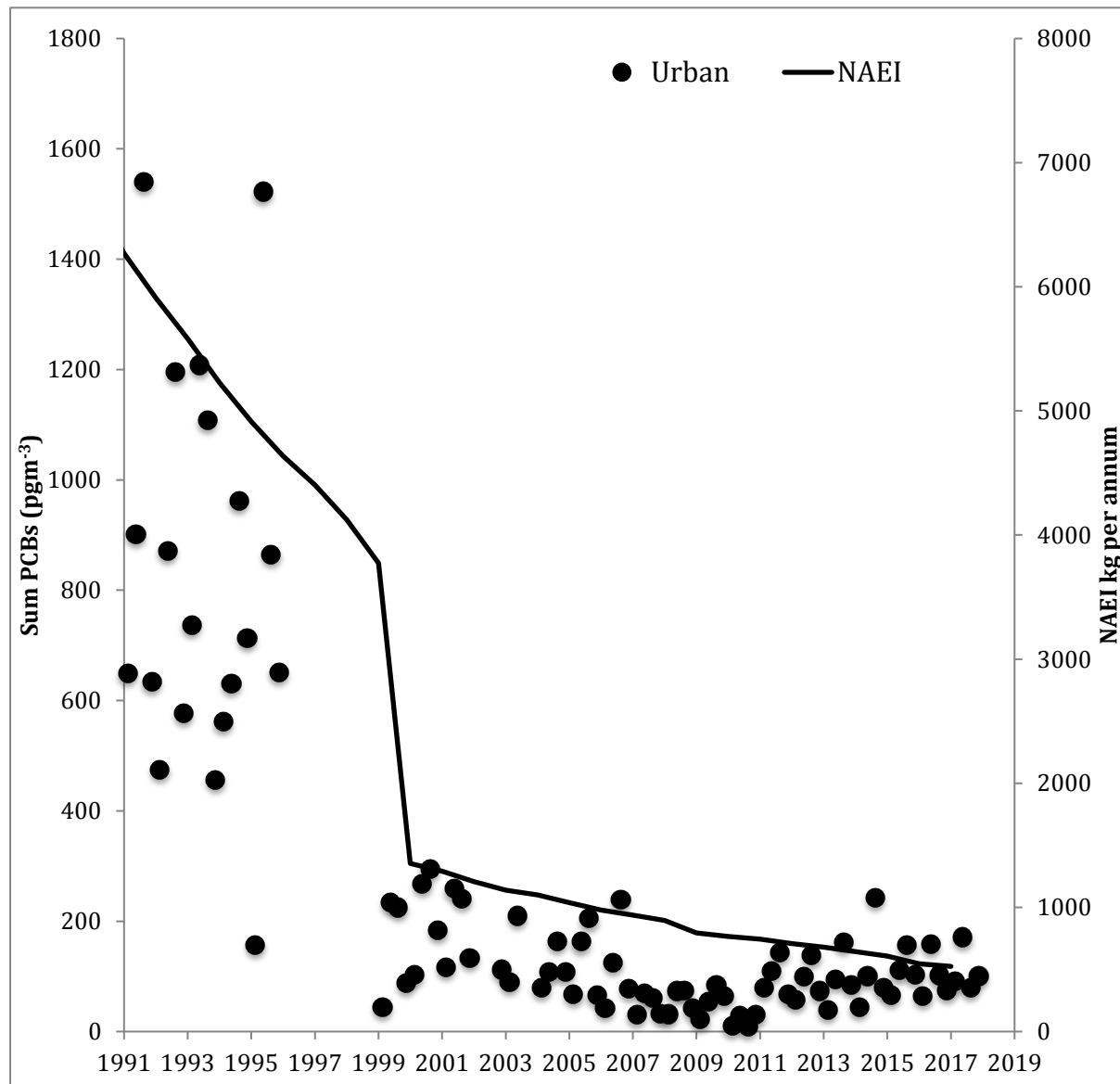
Figure 5. Quarterly ΣPCB_7 (congeners 28, 52, 101, 118, 153, 138 and 180) data at the TOMPs sites for 2017.

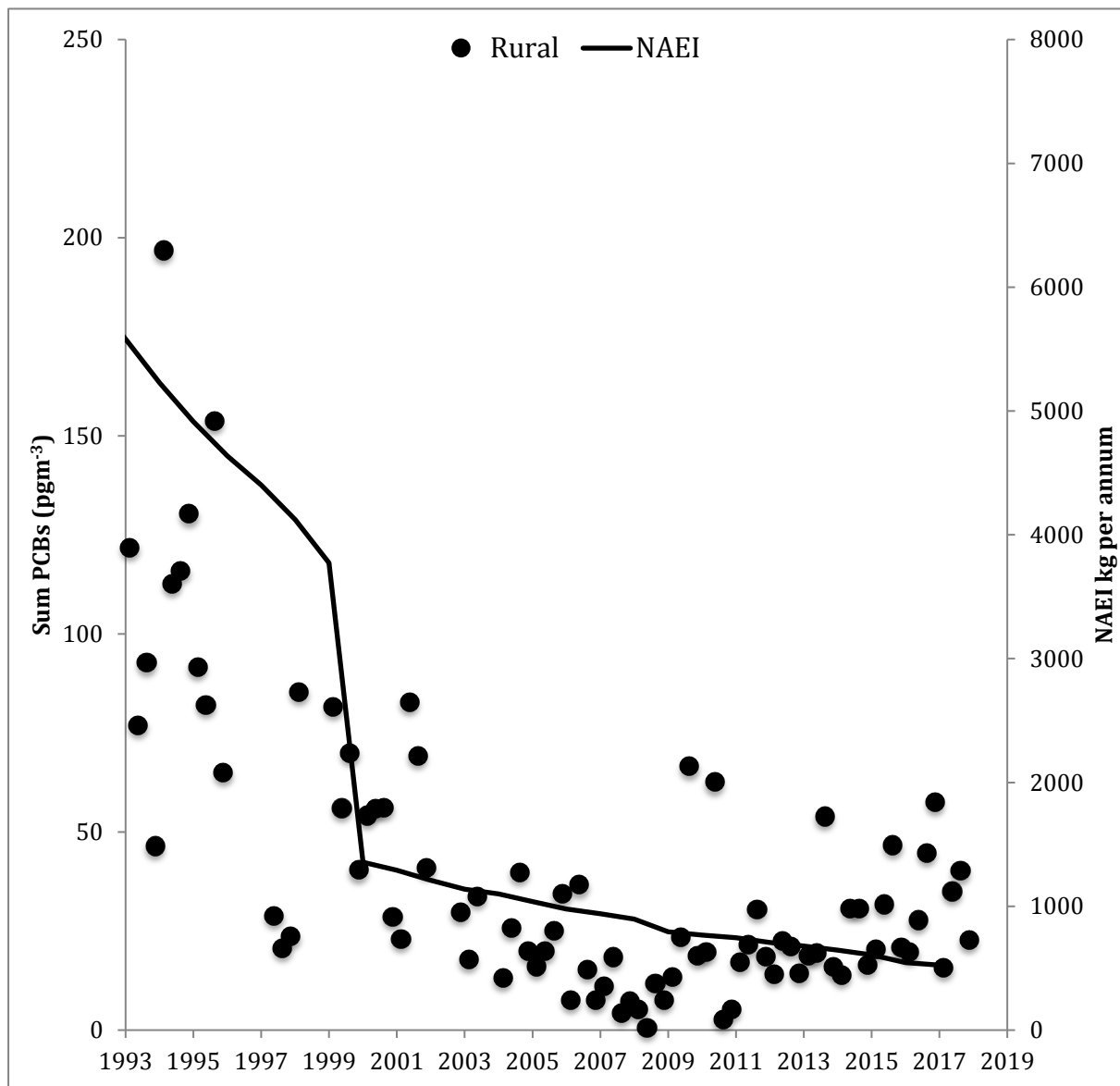


Ambient PCB concentrations are controlled by a range of factors but primarily by proximity of sampling sites to on-going sources. These sources are generally differentiated into primary and secondary sources. Primary sources of PCBs, which are mostly diffuse, include articles or preparations to which they were added, for example, as plasticizers in plastics, sealants, paints and oils. As a result of the application pattern for PCBs in indoor environments, primary sources are mostly found in areas with high population density and hence generally remain higher in urban environments. Emissions from secondary sources describes the process of re-emission or volatilization of PCBs from environmental compartments like soil and sediments which serve as reservoirs for persistent organic chemicals. Generally, the urban sites such as London and Manchester are still influenced by on-going diffuse primary releases of PCBs, whilst more rural sites are influenced by secondary sources and atmospheric transport. A detailed discussion of PCB sources to the UK atmosphere are discussed in detail by Graf *et al.*, 2016 which discusses the TOMPs programme since its inception in 1991. With the addition of the 2017 data, the clearance rates (time taken for a 50% decline in concentration) provided by the TOMPs network for urban sites averaged 15.1 years. For the rural and sites it is difficult to determine a trend with any certainty (r^2 of $\ln(\text{Concentration})$ vs time is less than 0.4). The temporal trends for the urban sites (London, Manchester) and rural sites (Hazelrigg, High

Muffles, Auchencorth and Weybourne) are presented in Figure 6. These data have been plotted against the estimated UK emission data from the NAEI (<http://www.naei.defra.gov.uk>). It is interesting to note that when examining the long term trends since 2000 none of the sites shows a downward trend over that period. This suggests that the environment has potentially reached a steady state with environmental cycling and secondary sources controlling ambient concentrations.

Figure 6. Σ_7 PCB Long-term PCB trend data from the TOMPs network for the urban (London and Manchester) and the rural (Hazelrigg, High Muffles, Auchencorth and Weybourne) sites. Data are presented as averages in pgm^{-3} and compared to the current NAEI estimates in kg per annum





The NAEI suggests that emissions of PCBs to the UK atmosphere have reduced from 6200 kg in 1992 to 525 kg in 2017 (latest data). Contemporary sources include continued presence of PCBs in dielectric fluids, power generation, small scale waste burning and sewage sludge application to land. The data in Figure 6 shows a sharp decrease in the late 1990's which is attributed to assumed significant reductions in the presence of PCBs in electrical equipment such as capacitors and transformers.

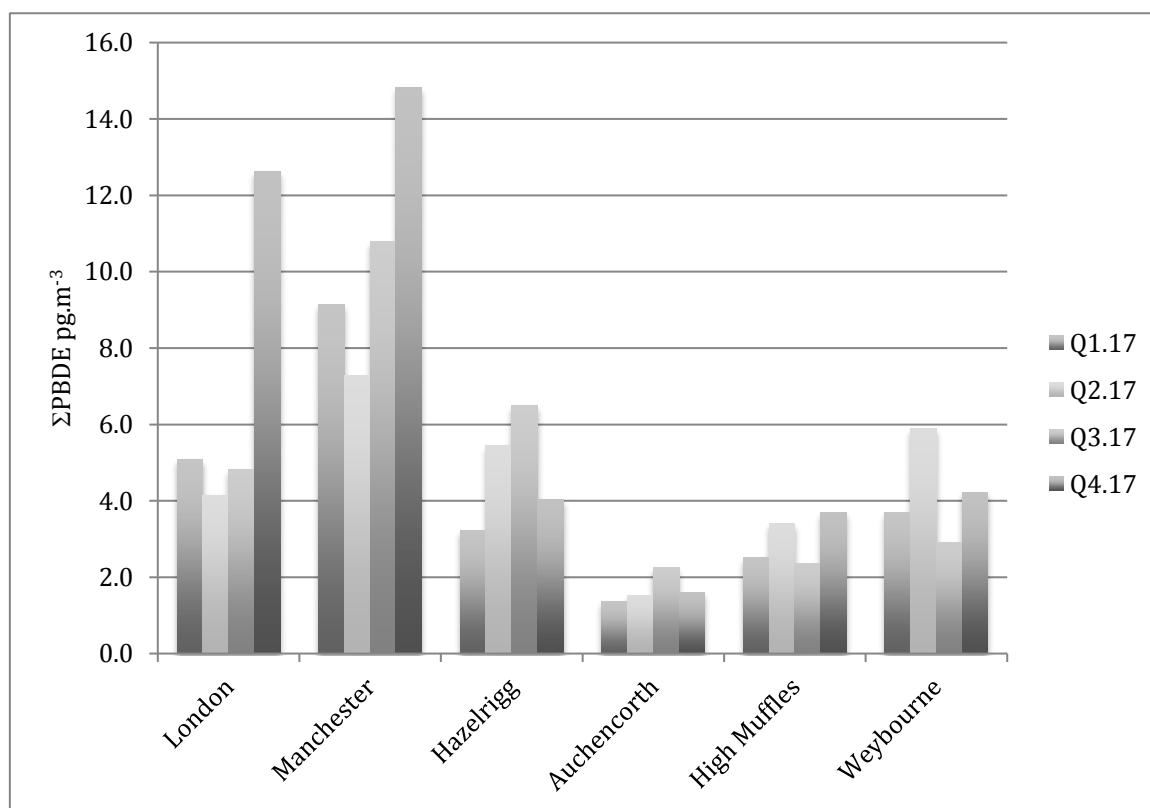
PCBs have been measured as part of the Integrated Atmospheric Deposition Network (IADN) since the early 1990's. IADN is joint project between the U.S. Environmental Protection Agency and Environment Canada which covers 5 ambient air monitoring sites around the Great Lakes. Using similar sampling equipment as TOMPs, the IADN network reports concentration data for 24hr samples collected every 12 days for a range of PCB congeners, organochlorine

pesticides and polycyclic aromatic hydrocarbons (PAHs). PCB concentrations generally showed the slowest rate of decline among all of the chemicals measured by IADN. The clearance rate of PCBs in the vapour phase was 14.9 (\pm 1.1 years) which is longer than the clearance rates observed for the TOMPs network sites.

7.4 PBDEs: Results and discussions

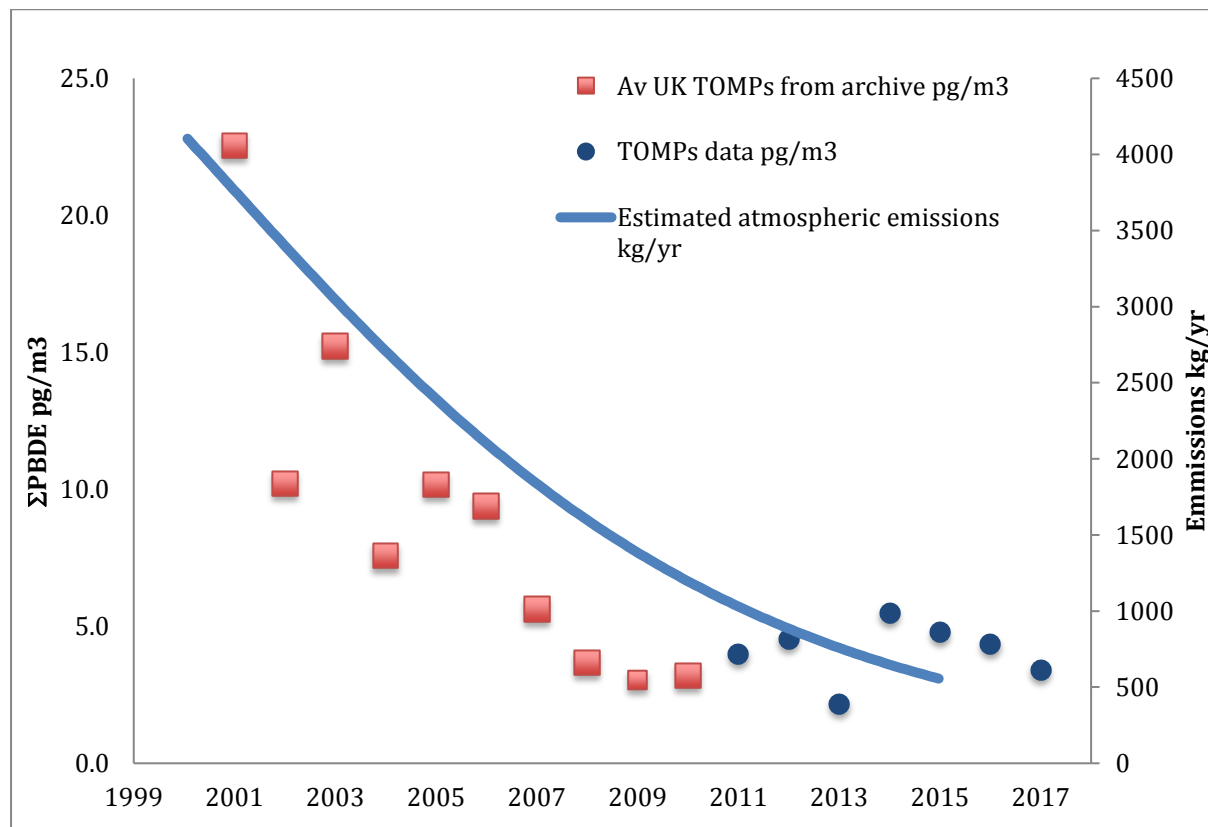
2017 was the seventh complete year for the inclusion of PBDEs in the TOMPs network. Ten individual congeners have been measured and the data reported in Appendix 2. A summary of the quarterly data is shown in Figure 7. The prominent congeners in the commercial pentaBDE mix, accounting for 72% of the total were BDE47 and BDE99. These congeners have dominated the profile in past samples from the TOMPs network and in 2017 accounted for between 59% and 87% across the sampling sites. Manchester, London, Hazelrigg and Weybourne showed the highest annual average concentrations for Σ_{10} PBDEs at 10.5 pg/m^3 , 6.7 pg/m^3 , 4.8 pg/m^3 and 4.2 pg/m^3 , respectively. The sites at High Muffles and Auchencorth were lower at 3.0 and 1.7 pg/m^3 , respectively. However, the difference between urban and rural sites appears to be diminishing. Unlike previous years (although similar to 2015 and 2016) seasonality in ambient air concentrations (i.e. higher in Q2 and Q3 suggesting temperature driven secondary sources could be important) appears to be less clear and varies between the sites.

Figure 7. Quarterly Σ PBDE data at the TOMPs sites for 2017.



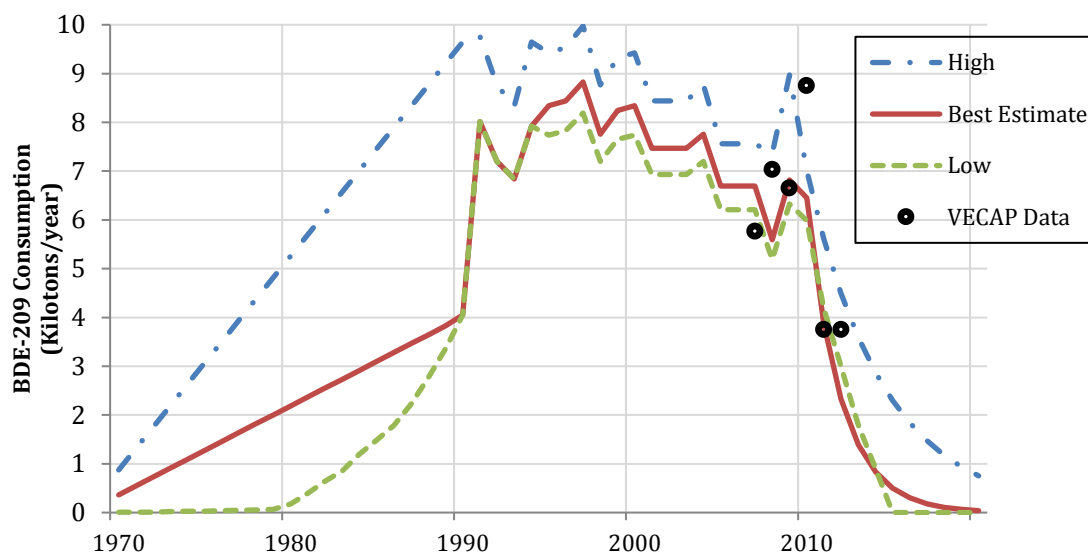
The TOMPs air sample archive has been used to provide information the time-trend of PBDEs in the UK atmosphere. The re-analysis of the sample archive focused on four of the six sites over a period ranging from 1999 to 2010 (Birgul *et al.* 2012). These time-trend data demonstrated a consistent decrease in concentration over recent years with the observed decline starting during the period 2001-2003. This is particularly evident in the urban sites of Manchester and London. The average Σ PBDE clearance rates (time taken for a 50% decline in concentration) for these three sites were 3.4, 2.0 and 3.5 years, respectively. Comparison of concentrations to estimated emissions and use of PBDE congener profiles suggests that PBDEs in the UK atmosphere originate from primary emissions from products that contain mainly the penta-BDE technical mixture. The direct connection with source reduction and UK ambient air concentrations has been established using the Lancaster University EvmBETR environmental fate model. Figure 8 compares the ambient air data from the TOMPs archive and the recent TOMPs data from 2011-17, along with an estimate of emissions to the UK atmosphere. These data show good agreement suggesting that the sources are largely captured in the emission inventory and that ambient air concentrations are declining at a predictable rate.

Figure 8. Σ PBDE data at the TOMPs sites over the period 2011 to 2017 (PBDEs have been included in the TOMPs network since 2010/11, data from 2000 produced from archived samples - Birgul *et al.* 2012).



Although decaBDE was added to the Stockholm Convention in 2017 there have been few attempts to calculate emission data or to provide ambient air monitoring data. Earnshaw *et al.* (2013) carried out a substance flow analysis approach to calculate a European consumption and emission inventory which split major products containing decaBDE into two major categories, polymers, and textiles (respective market shares were 75% and 25%). Both categories were assumed to emit BDE-209 to the atmosphere by volatilisation and particle bound emissions. The treatment of textiles with decaBDE was also assumed to emit to the wastewater system. It is clear that changes in regulation over time have affected the distribution of decaBDE use in products between the major use categories i.e. electrical and electronics, textiles, transport vehicles and building products. For example, in a recent assessment the majority (85%) of deca-BDE used in polymer production was found to be used for flame retarding polystyrene. However, with the restriction of the use in electronics and electrical, its use in other applications such as textiles and building materials have become relatively more important. According to the Industry Voluntary Emission Control Action Plan (VECAP) report in 2012 (which covers 84% of the market), and based on 2011 data, the total volume of decaBDE sold was expected to be between 2,500 and 5,000 metric tonnes. This accounts for approximately 10% of the brominated flame retardant market (EC 2011). VECAP market data also suggested that the importance of use in textile applications has increased from 37% to 52% (2011 data). Earnshaw *et al.* (2013) incorporated these data into an estimate of historical and future European decaBDE consumption covering the period 1970 to 2020, which is summarised in Figure 9. These data can be used to estimate the size of the current market for decaBDE (and hence estimate the challenge for identifying substitutes) and provide estimates of emission of BDE-209 to the environment. Owing to the scarcity of data three consumption scenarios were constructed using a combination of Industry data and assumptions concerning import rates and product types. The most uncertain period was prior to 1990 when fewer data were available describing the production and consumption patterns. Both the ‘best’ and ‘high’ estimates assumed a linear increase in consumption from the start of large-scale production (1969) to 1990 when the first Industry data became available. The ‘low’ estimate tracked bromine production over the same period and related that to brominated flame retardant production. Figure 9 also includes VECAP survey data of annual volumes sold by European Flame Retardants Association (EFRA) member companies.

Figure 9 Three different consumption scenarios for Europe based on a range of assumptions including; inclusion/exclusion of imports, and inclusion/exclusion OctaBDE products – taken from Earnshaw *et al.* (2013).

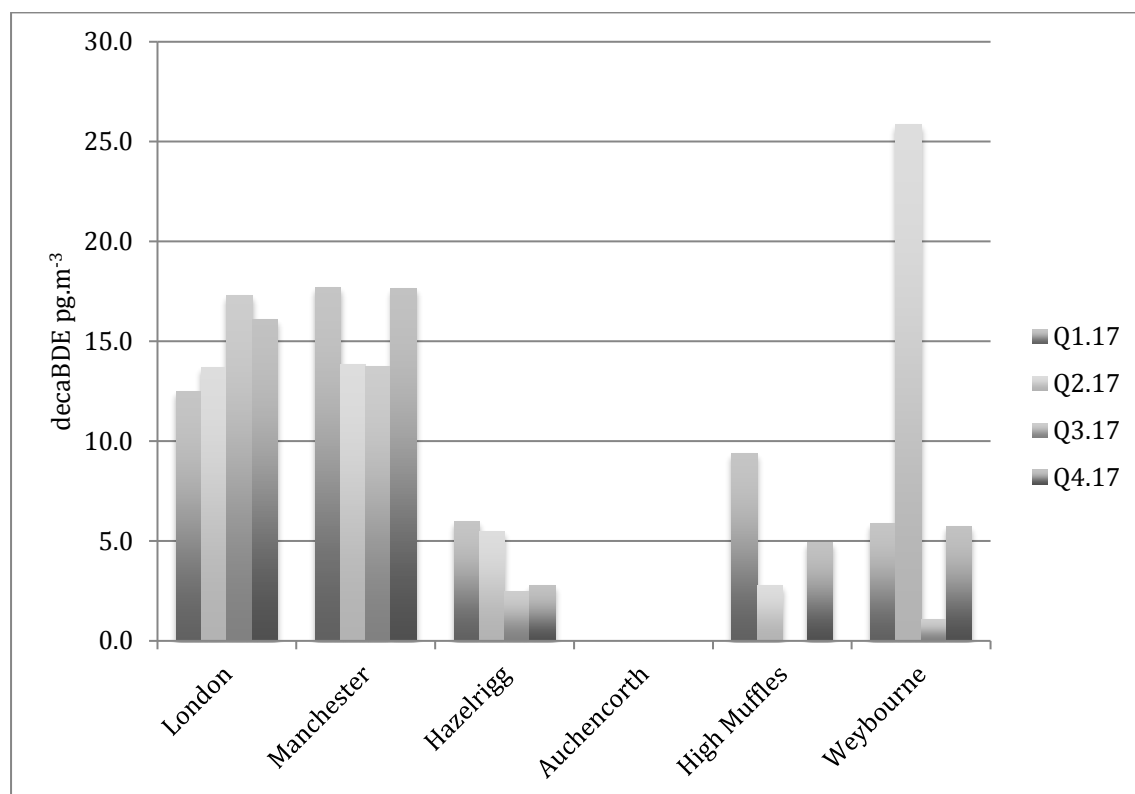


A study by Wilford *et al.* (2008) determined a range of BDEs including BDE-209 in the UK and reported a range of between $<0.5 \text{ pg/m}^3$ to 100 pg/m^3 with a median value of 13 pg/m^3 . BDE209 accounted for 60% of the total BDE fraction associated with the particulate phase. More recent UK data using passive samplers deployed in the West Midlands suggested that mean concentrations across 8 sites ranged from 92 to 370 pg/m^3 Drage *et al.* (2016). Data from a global passive sampling survey of flame-retardant concentrations across 20 megacities/major cities reported decaBDE ranging from 1.7 to 84.8 pg/m^3 with London reporting the highest concentration (Saini *et al.* 2020). Data from the TOMPs sites across the 4 quarters is shown in Figure 10 and Appendix 3.

London and Manchester have the highest concentrations with mean values of 14.9 and 15.7 pg/m^3 , respectively. These values are lower than those reported by Saini *et al.* (2020) for London but are based on active sampling. Direct comparisons between active and passive sampling data for particle bound contaminants should be treated with caution as passive data incorporates uncertainties with sampling rates are difficult to quantify. Data for Auchencorth was below detection limits whilst mean concentrations at Hazelrigg and High Muffles were 4.2 and 4.3 pg/m^3 . The annual average concentration of decaBDE at Weybourne was higher at 9.6 pg/m^3 but this was influence by a single high quarterly value.

If the consumption data provided by Earnshaw *et al.* (2013) are reliable then decaBDE emissions related to consumption should have decreased significantly from 2010 to 2020. A important question, however, is the role of the waste management to provide on-going emissions. Data provided by TOMPs should be able to provide important information on long-term emissions.

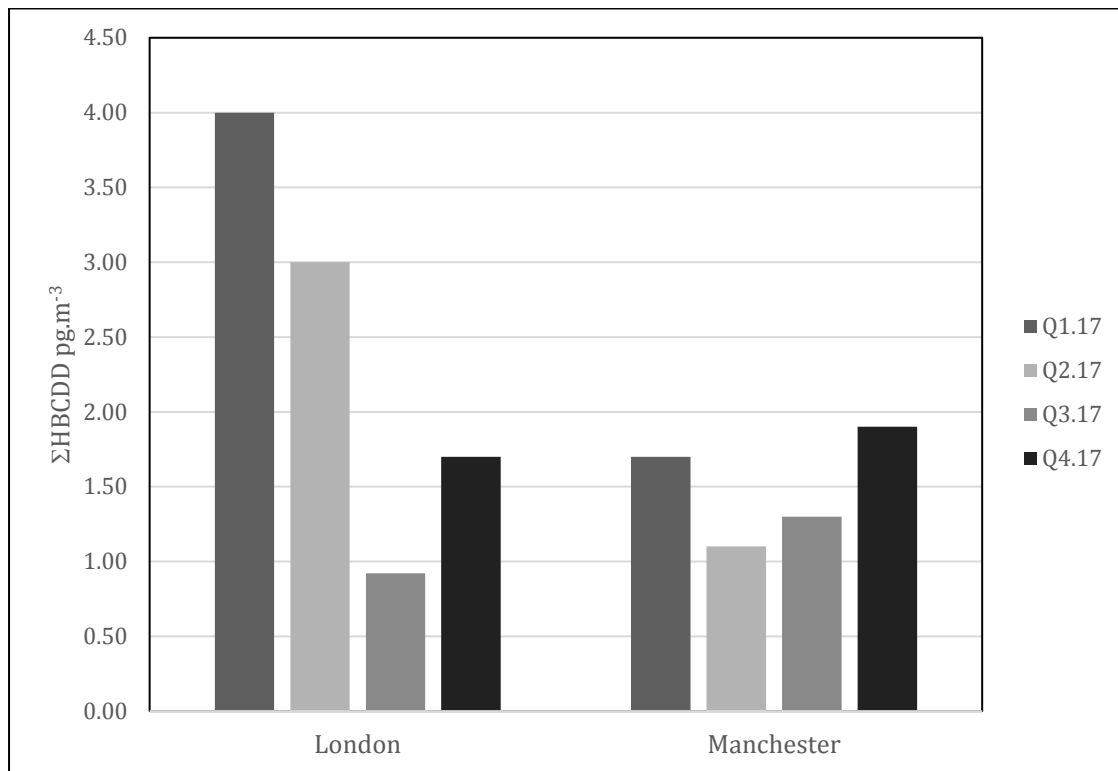
Figure 10. Quarterly decaBDE data at the TOMPs sites for 2017. (detection limit 0.2 pg/m³)



7.5 Hexabromocyclododecane (HBCDD)

2017 is the first year for reporting Σ HBCDD in samples from the TOMPs network. For this year the reporting will be restricted to the urban sites in London and Manchester. The average concentration at the London and Manchester sites for Σ HBCDD was 2.21 pg/m³ and 1.7 pg/m³, respectively. Quarters covering winter periods tended to have elevated levels, but this effect was small. The HBCDD technical mixture tended to be dominated by the γ -isomer (~70%) but this dominance was not observed in these samples. There are few data reported for the UK for comparison, although Abdallah et al. (2008) reported an average Σ HCBDD concentration using active air sampling in the West Midlands of 37 pg/m³, whilst passive samplers also deployed in the West Midlands suggested that mean concentrations across 8 sites ranged from 64 to 136 pg/m³ Drage et al. (2016). Data from a global passive sampling survey of flame-retardant concentrations across 6 megacities/major cities across the United Nations Western European and Others Group (WEOG) region reported median Σ HCBDD concentration of 10.8 pg/m³ with London reporting a concentration of 3.8 pg/m³ (Saini et al. 2020).

Figure 11. Quarterly Σ HBCDD data at the LON and MAN TOMPs sites for 2017. (detection limit 0.05 pg/m^3)



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Appendix 1. TOMPs 2017 PCB data (All data in pg.m⁻³)

<u>MANCHESTER 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
PCB_18	38.20	47.18	37.11	32.56	38.76
PCB_22	21.19	49.75	40.41	10.30	30.41
PCB_44	<0.02	10.27	14.36	3.89	7.13
PCB_49	29.39	9.31	4.79	4.24	11.93
PCB_52	6.59	19.95	14.51	5.61	11.66
PCB_70	5.91	9.06	8.38	1.43	6.19
PCB_74	3.68	4.45	8.85	4.65	5.41
PCB_87	3.05	6.13	4.33	0.89	3.60
PCB_95	10.54	15.03	11.52	4.44	10.38
PCB_99	6.09	4.56	4.11	1.34	4.03
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.62	0.52	0.34	0.88	0.59
PCB_110	6.00	10.61	6.95	2.05	6.41
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	4.35	4.51	5.11	1.40	3.84
PCB_123	<0.02	0.62	0.62	<0.02	0.31
PCB_138	1.84	2.00	1.45	0.78	1.52
PCB_141	5.87	10.26	6.86	3.32	6.58
PCB_149	1.84	2.81	1.93	1.04	1.91
PCB_151	5.03	9.05	9.03	2.23	6.34
PCB_156	0.28	0.61	0.35	<0.02	0.31
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.70	0.69	0.29	0.31	0.50
PCB_167	8.23	0.64	1.00	0.74	2.65
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.90	1.02	0.83	0.50	0.81
PCB_180	0.83	1.14	0.81	0.68	0.87
PCB_183	0.52	0.73	0.62	0.35	0.56
PCB_187	0.87	1.41	1.21	0.67	1.04
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	0.32	0.38	<0.02	<0.02	0.18
PCB_194	0.83	<0.02	<0.02	<0.02	0.21
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.44	0.33	0.29	0.36	0.35
PCB_153+132	1.94	4.65	4.46	2.27	3.33
PCB_31+28	77.50	105.42	75.12	13.45	67.87
PCB_41/64	<0.02	14.95	7.56	5.81	7.08
PCB_60/56	3.11	2.30	4.84	1.33	2.89
PCB_90/101	8.49	12.47	9.85	3.92	8.68
Σ7PCB	101.53	150.15	111.30	28.11	97.78

<u>LONDON 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
PCB_18	43.60	57.74	19.25	84.89	51.37
PCB_22	30.02	38.26	20.51	27.98	29.19
PCB_44	7.63	4.71	10.23	16.62	9.80
PCB_49	3.06	5.60	4.78	15.14	7.15
PCB_52	11.57	11.48	7.71	24.65	13.85
PCB_70	1.67	4.00	4.59	6.07	4.08
PCB_74	1.44	3.05	3.52	3.36	2.84
PCB_87	0.93	7.14	1.32	4.36	3.44
PCB_95	6.36	14.41	5.41	15.02	10.30
PCB_99	2.12	7.04	1.73	4.19	3.77
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	1.35	3.68	1.59	5.87	3.12
PCB_110	3.80	10.72	3.78	7.70	6.50
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	2.12	5.12	2.12	4.67	3.51
PCB_123	<0.02	0.86	0.81	1.27	0.74
PCB_138	0.88	2.17	0.84	3.34	1.81
PCB_141	3.43	8.90	3.60	12.31	7.06
PCB_149	1.47	4.47	0.89	4.34	2.79
PCB_151	3.81	12.54	3.96	8.23	7.13
PCB_156	0.44	<0.02	0.11	0.77	0.33
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.28	0.36	<0.02	0.61	0.31
PCB_167	<0.02	0.55	0.20	0.37	0.28
PCB_170	0.53	<0.02	0.21	1.41	0.54
PCB_174	0.73	1.76	0.91	3.43	1.71
PCB_180	1.02	2.73	0.56	2.76	1.77
PCB_183	0.42	1.28	0.29	1.01	0.75
PCB_187	0.97	2.88	1.18	4.01	2.26
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_194	0.15	0.29	<0.02	0.38	0.20
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.40	0.74	0.16	0.90	0.55
PCB_153+132	2.64	6.69	1.94	6.77	4.51
PCB_31+28	55.97	152.68	29.69	113.44	87.94
PCB_41/64	13.04	20.90	2.08	3.10	9.78
PCB_60/56	0.99	1.57	0.74	1.93	1.31
PCB_90/101	6.14	11.60	5.42	17.96	10.28
Σ7PCB	80.35	192.47	48.28	173.59	123.67

<u>HAZELRIGG 2017</u>	<u>Q1.17</u>	<u>Q2.17</u>	<u>Q3.17</u>	<u>Q4.17</u>	<u>Average 2017</u>
PCB_18	6.53	2.36	9.40	7.44	6.43
PCB_22	10.01	23.40	27.54	37.55	24.62
PCB_44	2.32	0.89	3.09	1.03	1.83
PCB_49	2.63	1.16	2.64	1.27	1.92
PCB_52	2.59	2.18	4.36	1.94	2.77
PCB_70	1.70	1.39	1.97	0.97	1.51
PCB_74	1.94	1.58	2.24	1.01	1.69
PCB_87	0.16	0.90	0.81	0.50	0.59
PCB_95	2.36	2.19	2.59	1.18	2.08
PCB_99	2.29	1.10	0.96	0.49	1.21
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.13	0.62	0.08	0.06	0.22
PCB_110	1.02	1.53	1.40	0.83	1.20
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.29	0.47	0.62	0.33	0.43
PCB_123	0.43	0.33	0.22	0.09	0.27
PCB_138	0.34	0.37	0.31	0.22	0.31
PCB_141	1.54	1.32	1.29	0.76	1.23
PCB_149	0.51	0.51	0.44	0.30	0.44
PCB_151	1.68	2.07	1.85	1.10	1.67
PCB_156	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	<0.02	<0.02	0.14	0.08	0.06
PCB_167	<0.02	0.31	<0.02	0.29	0.15
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.47	0.29	0.24	0.19	0.30
PCB_180	0.35	0.32	0.29	0.16	0.28
PCB_183	0.16	0.16	0.13	0.07	0.13
PCB_187	0.41	0.46	0.39	0.28	0.39
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_194	0.09	<0.02	<0.02	<0.02	0.02
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.15	0.11	0.11	0.08	0.11
PCB_153+132	1.02	1.08	0.99	0.63	0.93
PCB_31+28	10.92	19.40	34.09	37.46	25.47
PCB_41/64	4.01	1.52	0.84	6.22	3.15
PCB_60/56	0.23	1.56	0.79	0.94	0.88
PCB_90/101	2.11	1.64	1.98	0.96	1.67
Σ7PCB	17.63	25.46	42.64	41.71	31.86

<u>AUCHENCORTH 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
PCB_18	7.12	10.87	12.93	4.31	8.81
PCB_22	0.93	2.59	1.80	1.91	1.81
PCB_44	1.22	1.29	0.98	0.68	1.04
PCB_49	1.07	1.48	0.63	0.81	1.00
PCB_52	1.27	2.07	2.52	1.39	1.81
PCB_70	0.69	1.16	1.14	0.65	0.91
PCB_74	2.14	2.01	2.97	1.45	2.14
PCB_87	<0.02	<0.02	0.33	<0.02	0.08
PCB_95	0.84	1.84	1.70	0.81	1.30
PCB_99	0.22	0.24	0.28	0.21	0.24
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	0.16	0.21	<0.02	0.09
PCB_110	0.49	0.69	0.53	0.24	0.49
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.17	0.18	0.33	<0.02	0.17
PCB_123	0.09	0.07	0.22	<0.02	0.09
PCB_138	0.14	0.60	0.67	0.14	0.39
PCB_141	0.72	3.60	3.72	0.52	2.14
PCB_149	0.13	2.18	1.84	0.23	1.09
PCB_151	0.64	1.83	2.28	0.58	1.33
PCB_156	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	<0.02	<0.02	0.06	<0.02	0.02
PCB_167	<0.02	<0.02	0.25	<0.02	0.06
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	<0.02	0.27	0.26	0.11	0.16
PCB_180	<0.02	0.12	0.19	0.08	0.10
PCB_183	<0.02	0.14	0.26	0.10	0.12
PCB_187	0.14	0.47	0.84	0.21	0.41
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_194	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_153+132	0.22	0.67	0.89	0.37	0.54
PCB_31+28	5.86	13.80	29.68	8.34	14.42
PCB_41/64	2.00	1.89	3.26	0.86	2.00
PCB_60/56	0.46	0.77	0.56	0.59	0.59
PCB_90/101	0.84	1.86	1.38	0.69	1.19
Σ7PCB	8.49	19.29	35.67	11.01	18.61

<u>HIGH MUFFLES 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
PCB_18	4.31	32.98	18.39	10.77	16.61
PCB_22	1.91	46.35	15.70	12.80	19.19
PCB_44	0.46	0.65	<0.02	3.04	1.04
PCB_49	7.25	3.12	2.03	3.26	3.92
PCB_52	1.13	0.97	8.23	0.78	2.78
PCB_70	0.92	3.92	7.11	2.35	3.57
PCB_74	1.15	4.29	0.56	1.11	1.78
PCB_87	0.31	0.39	0.27	0.18	0.29
PCB_95	1.30	1.40	0.85	1.12	1.17
PCB_99	2.31	0.61	1.52	0.20	1.16
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	0.24	<0.02	<0.02	0.06
PCB_110	0.58	0.73	1.23	0.56	0.77
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.28	<0.02	1.44	<0.02	0.43
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	0.28	0.30	0.36	0.28	0.31
PCB_141	1.23	0.88	1.30	0.74	1.04
PCB_149	0.47	0.51	1.36	0.25	0.65
PCB_151	1.21	1.78	1.26	1.69	1.48
PCB_156	<0.02	0.23	0.99	<0.02	0.30
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	<0.02	0.09	<0.02	<0.02	0.02
PCB_167	0.13	0.23	<0.02	0.71	0.27
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.18	0.19	0.19	0.16	0.18
PCB_180	0.35	0.30	0.34	0.15	0.28
PCB_183	0.13	0.16	0.18	0.10	0.14
PCB_187	0.35	0.34	0.36	0.27	0.33
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	0.06	<0.02	<0.02	<0.02	0.01
PCB_194	0.06	0.07	0.11	0.14	0.10
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.14	0.13	0.11	<0.02	0.10
PCB_153+132	0.64	0.74	3.30	0.51	1.30
PCB_31+28	19.29	38.16	21.13	22.60	25.30
PCB_41/64	2.09	2.01	2.23	6.53	3.21
PCB_60/56	0.50	4.47	5.64	<0.02	2.65
PCB_90/101	1.87	1.15	0.29	0.26	0.89
Σ7PCB	23.83	41.62	35.09	24.58	31.28

<u>WEYBOURNE 2017</u>	<u>Q1.17</u>	<u>Q2.17</u>	<u>Q3.17</u>	<u>Q4.17</u>	<u>Average 2017</u>
PCB_18	7.92	23.25	19.48	6.63	14.32
PCB_22	11.21	32.11	33.89	11.29	22.12
PCB_44	1.98	2.45	3.83	1.61	2.47
PCB_49	1.20	2.30	2.82	0.78	1.77
PCB_52	1.89	4.93	3.10	1.59	2.88
PCB_70	0.29	2.11	1.36	0.38	1.04
PCB_74	0.73	1.65	1.68	0.45	1.13
PCB_87	0.28	0.38	0.42	0.13	0.31
PCB_95	1.97	2.49	2.13	1.31	1.98
PCB_99	0.63	0.70	0.87	0.36	0.64
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.10	<0.02	0.55	0.12	0.19
PCB_110	1.05	1.18	0.90	0.58	0.93
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.51	0.38	0.58	0.41	0.47
PCB_123	<0.02	0.21	0.34	<0.02	0.14
PCB_138	0.29	0.37	0.36	0.16	0.29
PCB_141	1.00	1.41	1.41	0.53	1.09
PCB_149	0.38	0.43	0.38	0.19	0.35
PCB_151	1.55	1.53	1.70	1.20	1.50
PCB_156	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.09	0.09	<0.02	<0.02	0.05
PCB_167	<0.02	0.54	0.35	<0.02	0.22
PCB_170	0.09	<0.02	<0.02	0.09	0.04
PCB_174	0.19	0.27	0.25	0.12	0.21
PCB_180	0.43	0.37	0.31	0.16	0.32
PCB_183	0.13	0.17	0.13	0.08	0.13
PCB_187	0.33	0.35	0.36	0.19	0.31
PCB_188	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_189	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_194	0.16	0.24	<0.02	<0.02	0.10
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.20	0.14	0.10	<0.02	0.11
PCB_153+132	0.63	1.16	0.91	0.58	0.82
PCB_31+28	7.52	44.90	40.80	9.73	25.74
PCB_41/64	1.37	4.05	2.66	1.14	2.31
PCB_60/56	<0.02	0.85	0.83	0.51	0.55
PCB_90/101	1.72	1.63	1.50	1.08	1.48
Σ7PCB	13.00	53.73	47.56	13.71	32.00

Appendix 2. PBDE data for 2017. (All data in pg.m⁻³)

<u>PBDE LONDON 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	<0.02	0.37	<0.02	0.91	0.32
BDE 47	1.87	2.25	1.61	5.68	2.85
BDE 66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 99	1.09	1.02	1.62	3.47	1.80
BDE 100	<0.02	<0.02	<0.02	1.04	0.26
BDE 119	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 138	<0.02	<0.02	0.51	<0.02	0.13
BDE 153	0.62	<0.02	0.55	<0.02	0.29
BDE 154	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 183	1.52	0.51	0.54	1.53	1.02
BDE 47 + 99	2.96	3.27	3.23	9.15	4.65
BDE 209	5.09	4.15	4.83	12.63	6.67

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

<u>PBDE MANCHESTER 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	0.24	0.25	0.30	<0.02	0.20
BDE 47	2.54	6.05	5.43	1.87	3.97
BDE 66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 99	2.45	1.63	2.32	1.09	1.87
BDE 100	0.78	0.89	1.23	<0.02	0.72
BDE 119	<0.02	0.35	0.29	<0.02	0.16
BDE 138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 153	<0.02	0.47	0.73	0.62	0.45
BDE 154	<0.02	0.53	1.49	<0.02	0.50
BDE 183	1.29	0.62	3.02	1.52	1.61
BDE 47 + 99	4.99	7.68	7.75	2.96	5.85
BDE 209	13.82	13.72	17.64	12.49	14.42

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

<u>PBDE AUCHENCORTH</u> <u>2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47	0.77	1.10	1.58	0.77	1.05
BDE 66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 99	0.38	0.43	0.53	0.31	0.41
BDE 100	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 119	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 153	<0.02	<0.02	0.15	0.17	0.08
BDE 154	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 183	0.22	<0.02	<0.02	0.36	0.15
BDE 47 + 99	1.15	1.53	2.11	1.08	1.46
BDE 209	<0.02	<0.02	<0.02	<0.02	<0.02

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

<u>PBDE HIGH MUFFLES</u> <u>2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	<0.02	0.16	<0.02	<0.02	0.04
BDE 47	0.84	1.97	1.35	0.92	1.27
BDE 66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 99	0.65	0.88	0.48	0.68	0.67
BDE 100	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 119	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 153	0.25	<0.02	0.23	0.33	0.20
BDE 154	<0.02	<0.02	<0.02	0.19	0.05
BDE 183	0.78	0.38	0.31	1.58	0.76
BDE 47 + 99	1.49	2.85	1.83	1.60	1.94
BDE 209	9.36	2.77	<0.02	4.94	4.27

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

<u>PBDE HAZELRIGG 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	<0.02	0.22	0.27	<0.02	0.12
BDE 47	1.21	2.02	2.87	1.43	1.88
BDE 66	<0.02	0.28	0.29	<0.02	0.14
BDE 99	1.00	2.10	1.82	1.28	1.55
BDE 100	0.20	0.36	0.44	0.27	0.32
BDE 119	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 153	0.21	<0.02	0.22	0.18	0.15
BDE 154	<0.02	0.20	0.26	0.29	0.19
BDE 183	0.60	0.26	0.33	0.60	0.45
BDE 47 + 99	2.21	4.12	4.69	2.71	3.43
BDE 209	5.97	5.47	2.47	2.77	4.17

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

<u>PBDE WEYBOURNE 2017</u>	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
BDE 28	<0.02	0.21	<0.02	<0.02	0.05
BDE 47	0.95	2.16	1.31	0.88	1.33
BDE 66	<0.02	0.33	<0.02	<0.02	0.08
BDE 99	1.34	2.15	0.93	0.89	1.32
BDE 100	<0.02	0.32	<0.02	0.21	0.13
BDE 119	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 153	0.35	0.17	0.23	0.39	0.28
BDE 154	<0.02	<0.02	<0.02	0.29	0.07
BDE 183	1.05	0.55	0.45	1.57	0.90
BDE 47 + 99	2.29	4.31	2.24	1.77	2.65
BDE 209	5.86	25.84	1.07	5.74	9.62

BDE 47 and 99 are key components in the commercial penta-BDE mixture.

Appendix 3. HBCDD data for 2017. (All data in pg.m^{-3})

HBCDD <u>LONDON</u> 2017	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
α -HBCDD	2.1	1.6	0.53	0.44	1.17
β -HBCDD	0.65	0.91	0.16	0.13	0.46
γ -HBCDD	1.2	0.49	0.23	0.36	0.57
Σ HBCDD	4	3	0.92	0.93	2.21

HBCDD <u>MANCHESTER</u> 2017	Q1.17	Q2.17	Q3.17	Q4.17	Average 2017
α -HBCDD	0.92	0.88	0.75	1.3	0.96
β -HBCDD	0.35	<0.05	0.21	0.28	0.28
γ -HBCDD	0.42	0.21	0.3	0.28	1.5
Σ HBCDD	1.7	1.1	1.3	1.9	1.7