The Lancaster Environment Centre

Annual Report for 2013 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

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Report to the Department for Environment, Food and Rural Affairs, the Northern Ireland Department of Environment, the Scottish Government and the Welsh Assembly

Executive Summary.

This report contains the 2013 quarter 1(Q1), quarter 2 (Q2) quarter 3 (Q3) and quarter 4 (Q4) ambient air concentration data for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polybrominated diphenyl ethers (PBDEs) from the Toxic Organic Micro-pollutants Monitoring Network (TOMPs) which is funded by the Department for Environment, Food and Rural Affairs (Defra) and the devolved administrations.

In 2013, 37 PCBs congeners, 4 co-planar PCB congeners, 22 PBDE congeners, 10 furan congeners and 7 dioxin congeners were measured in each sample. 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).

As in previous years the data summarised in this report shows;

- the seasonal pattern of PCDD/Fs (with higher concentrations in the colder quarters 1 and 4) and the continued decrease in concentrations over time;
- an increase in the 5 year (2008-2012) average concentrations of PCBs compared to the previous 5 year average;
- the continued decrease in PBDEs concentrations which correlates closely with the TOMPs emissions data.

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 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 2010 and will run with a one year extension until September 2014. 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 and PCBs. Polycyclic aromatic hydrocarbons (PAHs) are quantified and reported separately under another monitoring programme currently operated by the National Physical Laboratory.

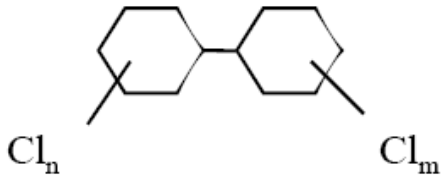
This annual report for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polybrominated diphenyl ethers (PBDEs) includes:

- Information on PCDDs, PCDFs, PCBs, and PBDEs
- 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.
- Review of annual mean and quarterly concentrations.
- Trends in estimated sources of PCBs, PCDDs and PCDFs in the UK

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

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 marked 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).



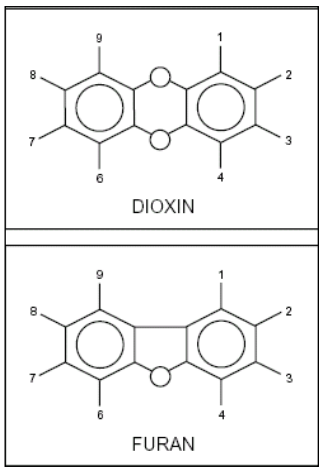
There are 209 different congeners with one to ten chlorines atoms attached. The International Council for the Exploration of the Seas (ICES) 7 PCB congeners generally reported in environmental samples are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB), 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 where 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 was 763kg, 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 federal and state 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 atmospheric was 216 g-TEQ, 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.



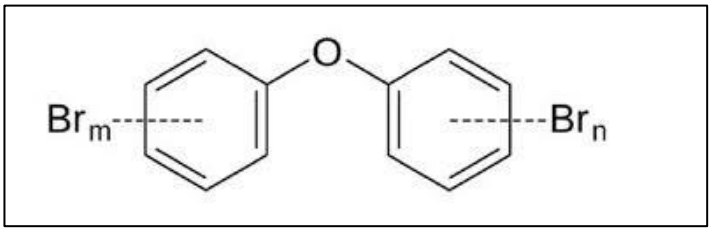
The Toxicity Equivalency Factor (TEF) values have been subject to revision and amendment since their inception but the most widely accepted set of TEF values for the 2,3,7,8-substituted PCDD/Fs is the 'WHO' (WHO-TEF) system, originally developed in 1990s and last updated in 2005. Another commonly used 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	0.0001	0.0001
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	PCB-81	0.0001	0.0003
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	0.0001	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

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 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 PBDE flame retardant product in use.



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 PeBDE 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

account for approximately 72% of the composition of the penta commercial mixture (pentaBDE). Atmospheric emission estimates for 2008 for the tetra and penta PBDEs in the UK were estimated at 2500kg and detailed in the Defra report AEAT/ENV/R2767/WP2 ED47664.

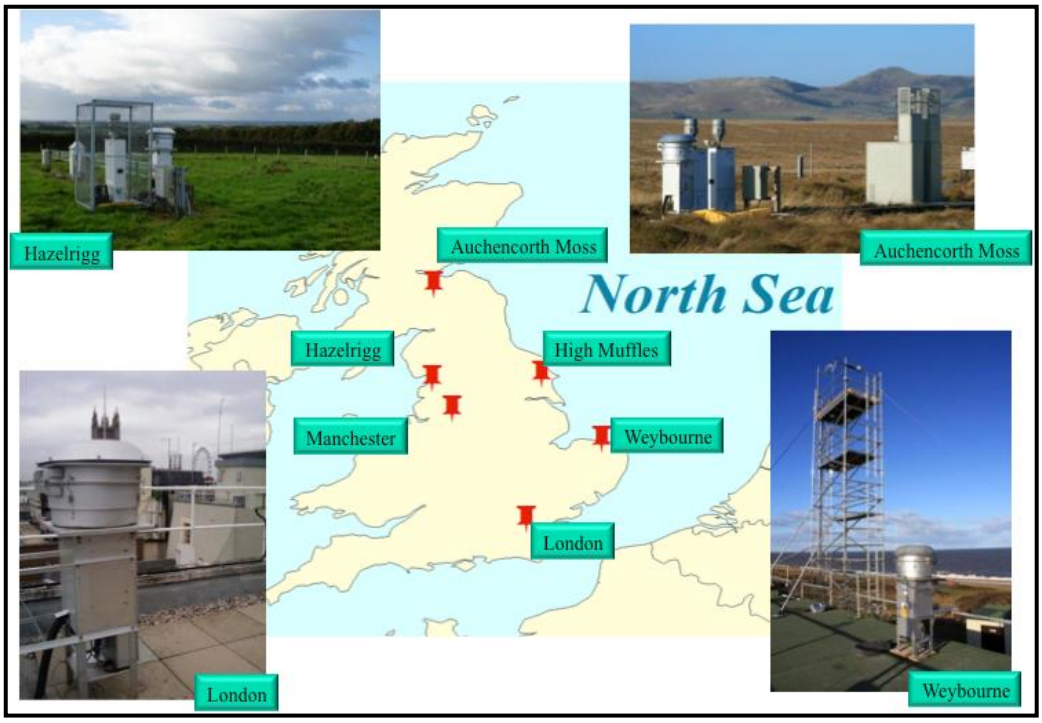
3. TOMPs sites operating in 2013

In 2013 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 ºC 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 (ºC). 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 ºC overnight following established procedures. Each sample (gas + particle) is spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners ($^{13}C_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) and PBDE congeners BDE 51, BDE 128, and BDE 190, and an isotope dilution/recovery standard containing 21 $^{13}C_{12}$-labelled PCDD/Fs and coplanar PCBs. Samples are individually extracted in a Buchi extraction unit for 18 hours with hexane and 6 hours with toluene. PAHs, 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. If necessary this can then be rotary evaporated to 2ml for splitting. 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 m^3 of air. The hexane fraction (topped up to 50 ml with hexane) is then split: 10% (5mL) is used for the PAHs analysis, 40% (20 mL) for the analysis and 50% (25 mL) is archived. The toluene fraction (also topped up to 50 mL using hexane) is also split: 10% (5mL) is discarded, 40% (20 mL) is analyzed and 50% (25 mL) is archived. (The toluene and hexane fractions for archive are combined in the same vials). The same is done for the fractions (40%) that will be analyzed. The 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) followed by two times acid digestion using concentrated H_2SO_4 and a second multicolumn. 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 [$^{13}C_{12}$], PCB 141, [$^{13}C_{12}$] 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 constantly measured in all samples, but only the following congeners are reported: 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 Q4 2010 the following PBDE congeners have been reported; BDE 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 183, 196.

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 10 $^{13}C_{12}$-labelled PCB and PBDE standards, whilst PCDD/F and coplanar PCB data are corrected using 21 $^{13}C_{12}$-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.

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 2013

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 quarters in 2013. 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 3973-5240 m^3.

London, Manchester, High Muffles, Auchencorth and Weyborne and Hazelrigg operated normally with 100% data capture over the year. The sampler at Manchester experienced minor motor/equipment failures in Q1 with an operation efficiency of 85%, although averaging over 96% over the year.

The sites at Hazelrigg, Auchencorth were calibrated in Q3 and the sites at London, Manchester, Weybourne and High Muffles were calibrated in Q4. Quarterly field blanks were also collected from each site.

Table 2. Summary of the bulked air volumes, sample numbers in each quarter in 2013.

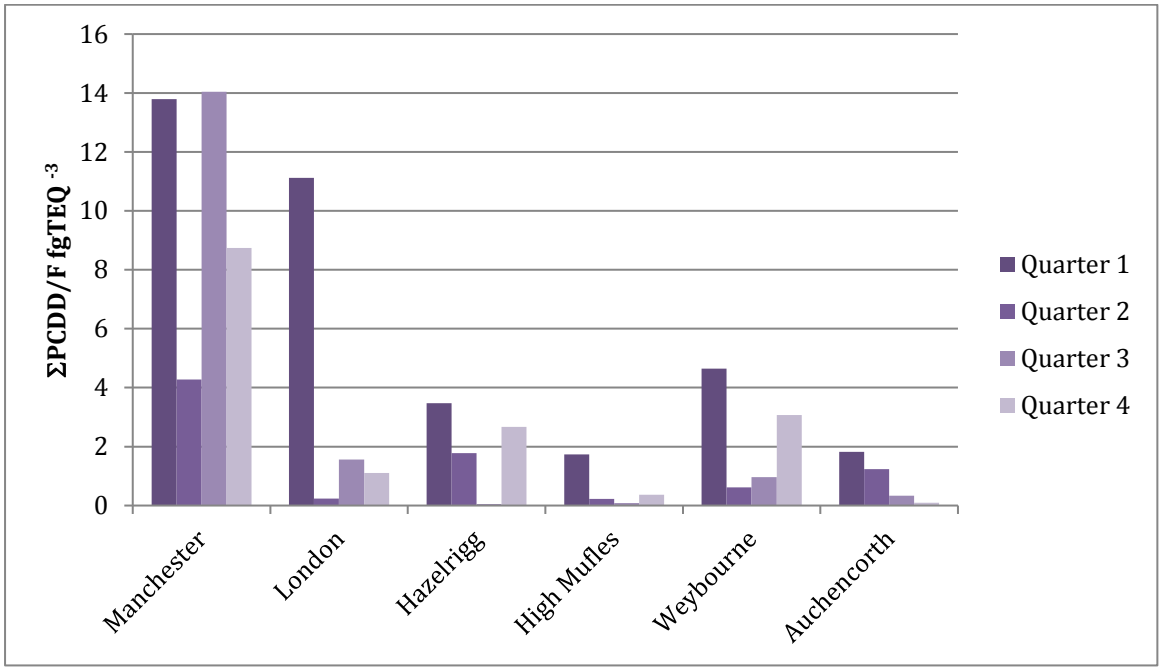
		Start	Time	Finish	Time	% Data capture	Volume m^3
LON	Q1	03/01/13	12:55	27/03/13	12:45	100	4863
	Q2	27/03/13	12:50	05/07/13	11:45	100	4401
	Q3	05/07/13	11:50	02/10/13	12:40	100	4558
	Q4	02/10/13	12:45	27/12/13	16:10	100	4411
MAN	Q1	27/12/13	10:05	04/04/13	11:15	85	3973
	Q2	04/04/13	11:20	27/06/13	14:20	100	4230
	Q3	27/06/13	14:25	03/10/13	10:35	100	4215
	Q4	03/10/13	10:50	09/01/14	10:35	100	4769
HR	Q1	09/01/13	15:15	03/04/13	09:35	100	5042
	Q2	03/04/13	09:40	26/06/13	14:35	100	4437
	Q3	26/06/13	14:40	02/10/13	13:40	100	5084
	Q4	02/10/13	13:45	08/01/14	13:55	100	4333
HM	Q1	27/12/12	12:45	04/04/13	14:15	100	4254
	Q2	04/04/13	14:20	27/06/13	10:10	100	4795
	Q3	27/06/13	10:15	03/10/13	13:30	100	4316
	Q4	03/10/13	13:45	23/12/13	11:25	100	4810

AUCH	Q1	09/01/13	11:10	20/03/13	11:50	100	4439
	Q2	20/03/13	11:50	26/06/13	11:25	100	5240
	Q3	26/06/13	11:56	02/10/13	10:05	100	4486
	Q4	02/10/13	10:05	27/12/13	11:15	100	4494
WEY	Q1	04/01/13	10:45	25/03/13	14:30	100	4713
	Q2	25/03/13	14:30	01/07/13	08:30	100	4252
	Q3	01/07/13	08:30	23/09/13	09:00	100	4255
	Q4	23/09/13	09:00	02/01/14	10:35	100	4452

7.2 PCDD/Fs: Results and discussion

Quarterly PCDD/F data are contained in Appendix 1 and a summary presented in Figure 2. The annual mean PCDD/Fs concentrations measured in 2013 ranged from 0.6 to 10.2 fg TEQ/m^3 and are similar to those we have reported for last 10 years. The highest concentrations were observed at the two urban sites (Manchester 10 fg TEQ/m^3 and London 3.5 fg TEQ/m^3) followed by Weybourne (2.3 fg TEQ/m^3), (Hazelrigg (2.0 fg TEQ/m^3), Auchencorth (0.87 fg TEQ/m^3) and High Muffles (0.6 fg TEQ/m^3). As with previous years, the two urban sites exhibit higher concentrations of PCDD/Fs although the average concentration in London was closer to the sites at Weybourne and Hazelrigg. As with previous years the seasonal pattern, as shown by the quarterly data, shows that the highest concentrations were generally measured in quarters Q1 and 4 with lower values reported for quarters 2 and 3. Although this pattern isn't always clear at the rural sites.

Figure 2. Quarterly PCDD/F data for each TOMPs site in 2013.

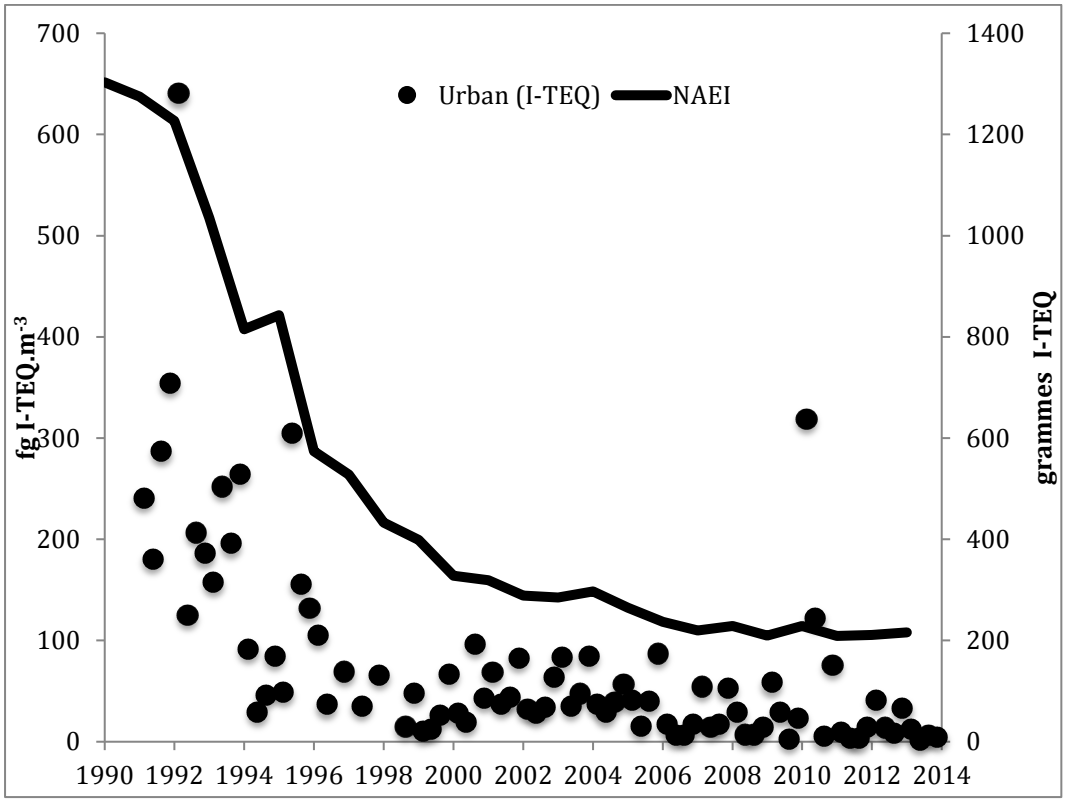


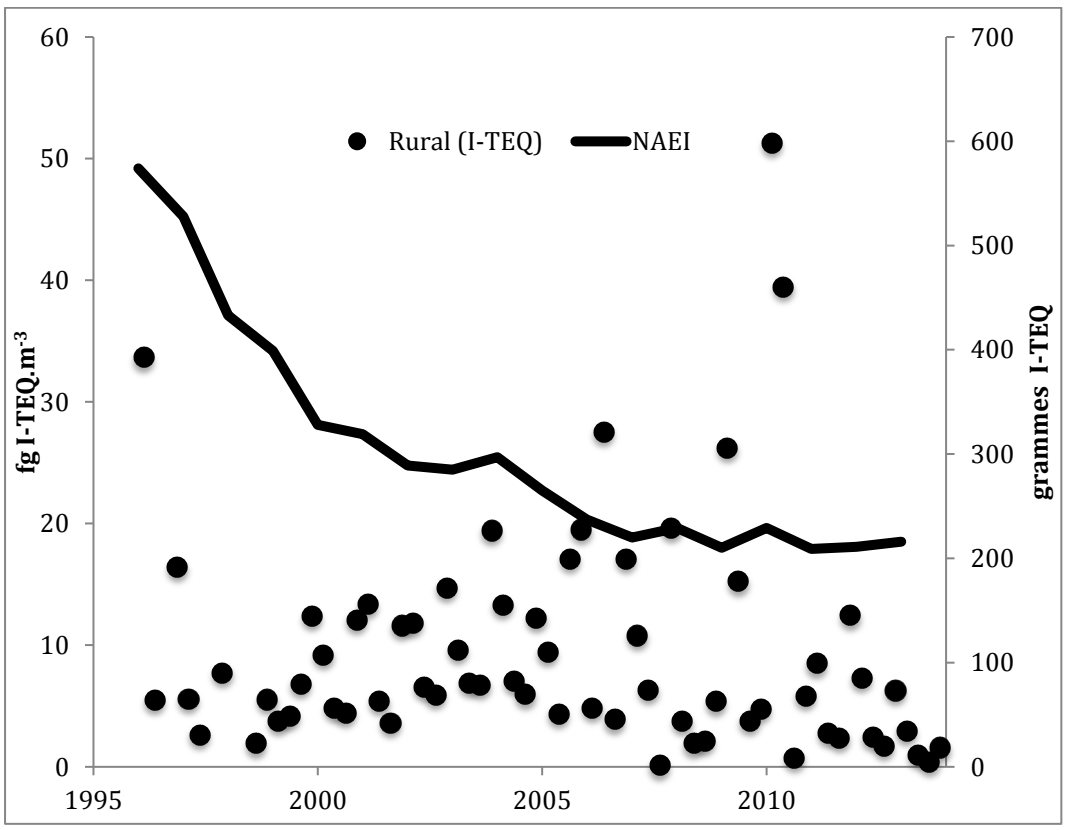
PCDD/Fs constitute two classes of chemicals that are formed unintentionally during combustion (e.g. waste incineration, burning of coal, wood etc.), iron and steel production (also combustion), several metal treatment processes and transport. The contribution from waste incineration has reduced in importance over time. The observed seasonality of PCDD/Fs in air, where winter values exceed summer values, has been seen in the TOMPs dataset and is widely reported in the literature, for example, Coutinho *et al*. (2007) reported average summer/winter ratios of 1:3 for sites in Portugal. Increased combustion (i.e., domestic space heating) and seasonal variations in the atmospheric boundary layer height are the likely causes. The sources of PCDD/Fs to the UK atmosphere are presented in detail by Katsogiannis *et al*., 2010 which discusses the TOMPs programme over a period of 17 years.

The temporal trends for the urban and rural sites are presented in Figure 3, and the estimated atmospheric clearance rates (time taken for a 50% decline in concentration) for London and Manchester are 4.6 and 5.1 years, respectively. The concentration data from Hazelrigg and High Muffles are much lower than the urban sites, and also do not show a significant decrease over time. The Auchencorth Moss and Weybourne data sets are currently too short to determine any temporal trends. Data for UK PCDD/F emissions are provided by the National Atmospheric Emission Inventory over the period 1990 – 2013 (http://www.naei.defra.gov.uk).

During this period PCDD/F emissions reduced from around 1303 g I-TEQ per year in 1990 to 216 g I-TEQ per year in 2013.

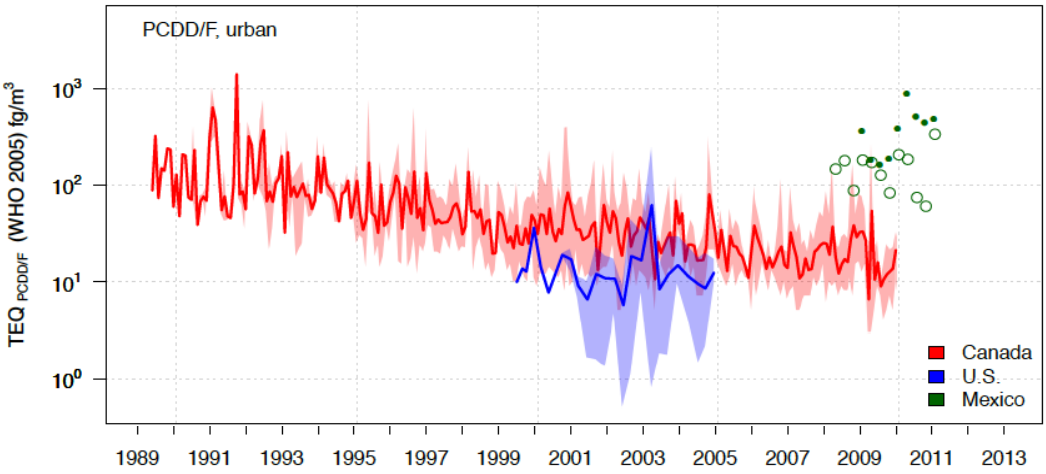
Figure 3. Long-term PCDD/F trend data in fg I-TEQ.m^{-3} from the TOMPs network for the urban (London and Manchester) and the rural (Hazelrigg, High Muffles, Auchencorth and Weybourne) sites. Data are compared to the current NAEI estimates in g I-TEQ per annum.

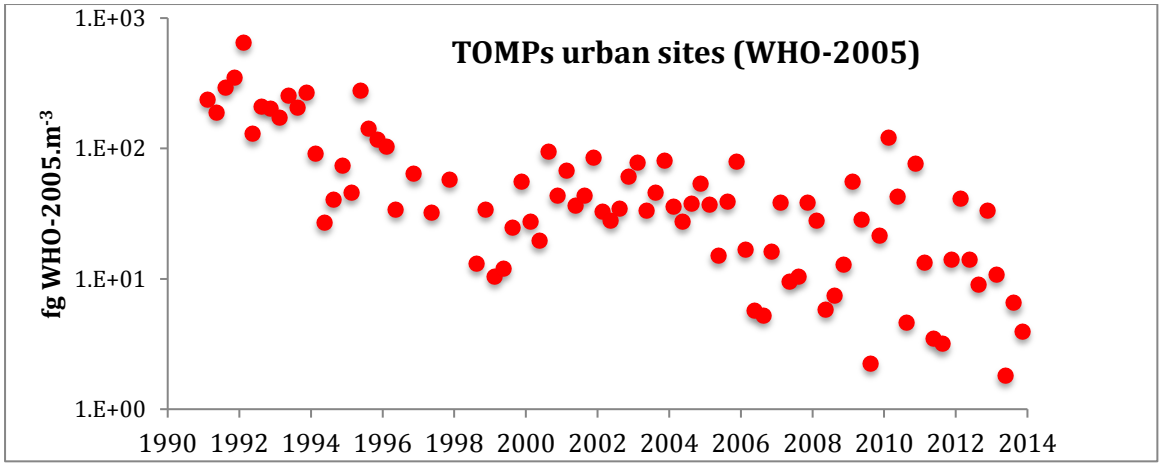


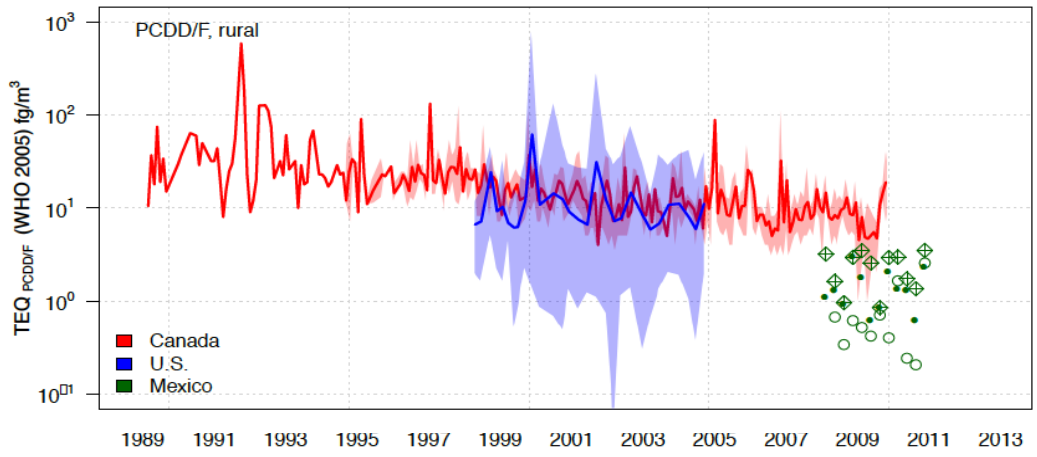


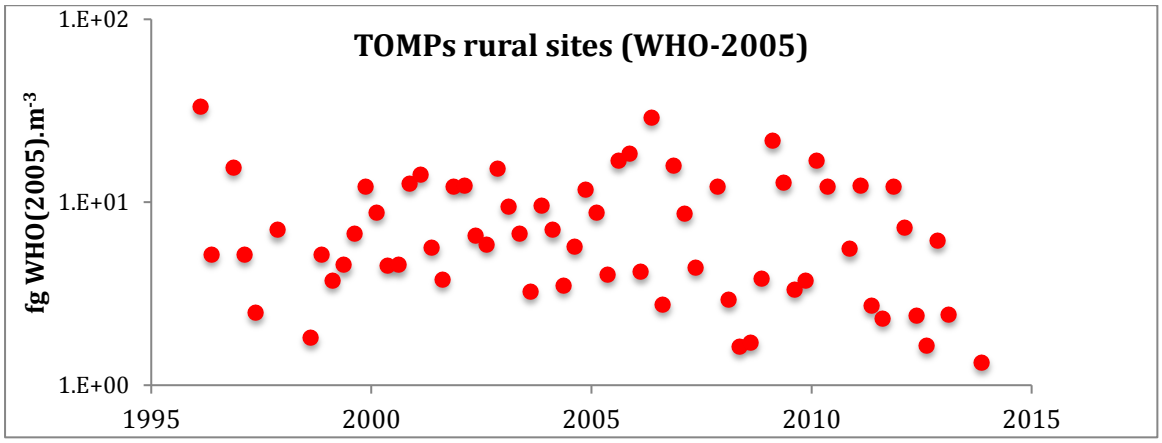
A recent report by the Commission for Environmental Cooperation (CEC, 2014) provides a comparison, for the first time, information on PCDD/F air concentrations from monitoring network activity in Canada, Mexico and the United States. The CEC report combines information from the Canadian National Air Pollution Surveillance (NAPS), the US National Dioxin Air Monitoring Network (NDAMN) and the Mexican Dioxin Air Monitoring Network (MDAMN) to provide data on sources and well as temporal trends for PCDD/Fs. The data are presented in Figure 4 and compared to the TOMPs data split into urban and rural locations. Note the data are presented on a $\log_{10}$ scale.

Figure 4. Long-term PCDD/F trend data from the Canadian National Air Pollution Surveillance (NAPS), the US National Dioxin Air Monitoring Network (NDAMN) and the Mexican Dioxin Air Monitoring Network (MDAMN) compared to TOMPs network for the urban and the rural sites. Data are presented on a log10 scale in fg WHO_TEQ.m^{-3}









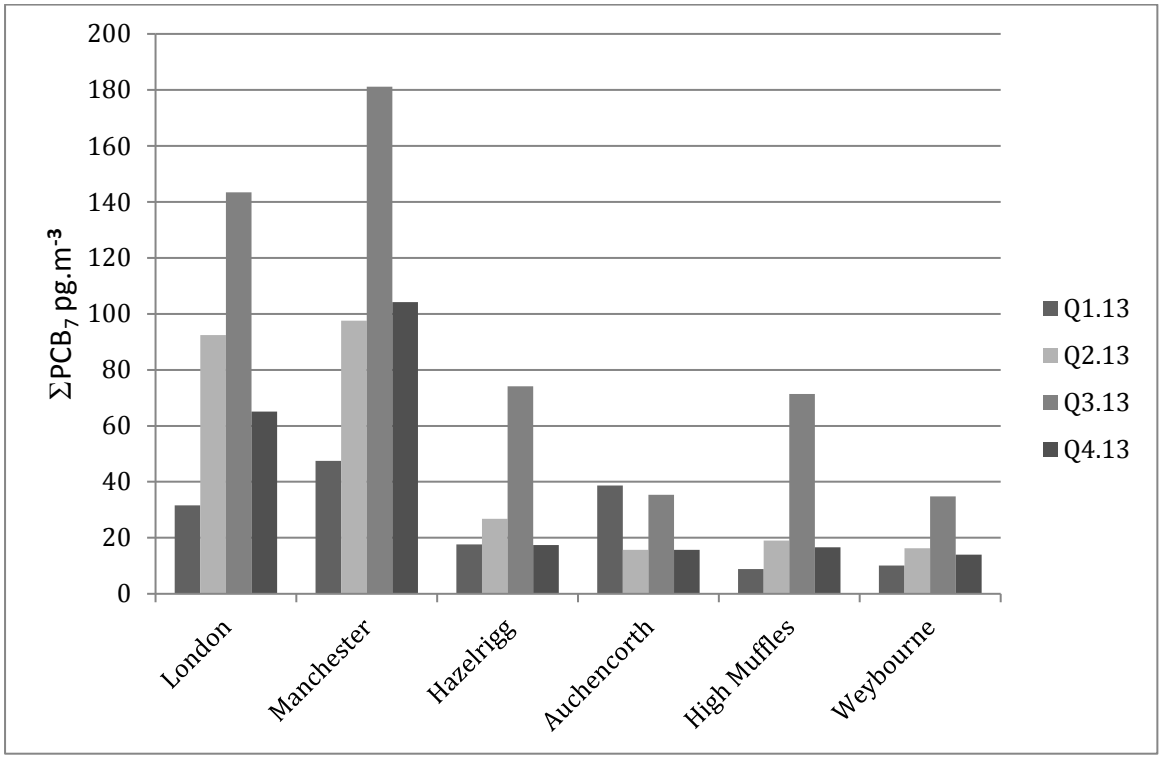
These datasets suggest that similar trends are being observed in the Canadian, US and UK sites in both urban and rural locations (the Mexican dataset is too short for comparison). This suggests that the sources and success of source reduction measures are similar in both regions.

7.3 PCBs: Results and discussions

Quarterly congener PCB data for the 6 TOMPs sites are contained in th Appendix 2 and a summary presented in Figure 5. The annually averaged PCB concentrations measured at each of the TOMPs sites ranged from 19 pg/m^3 (Weybourne) to 108 pg/m^3 (Manchester) 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 the population density surrounding the site i.e. higher for urban sites by a factor of 5. The urban sites at London and Manchester showed an increase in the PCB concentrations compared with previous average values over the last five years (2008-2012) of 38% and 54%, respectively. The annual average concentration for the other sites also showed an increase compared to the previous 5 year average, with Hazelrigg showing a 40% increase, High Muffles a 9% increase and Auchencorth a 80% increase,

although Weybourne showed no change over the last five years. At each site the quarterly data showed a distinct seasonal pattern with higher levels in Q2 and Q3 which are characteristic of temperature driven diffusive sources.

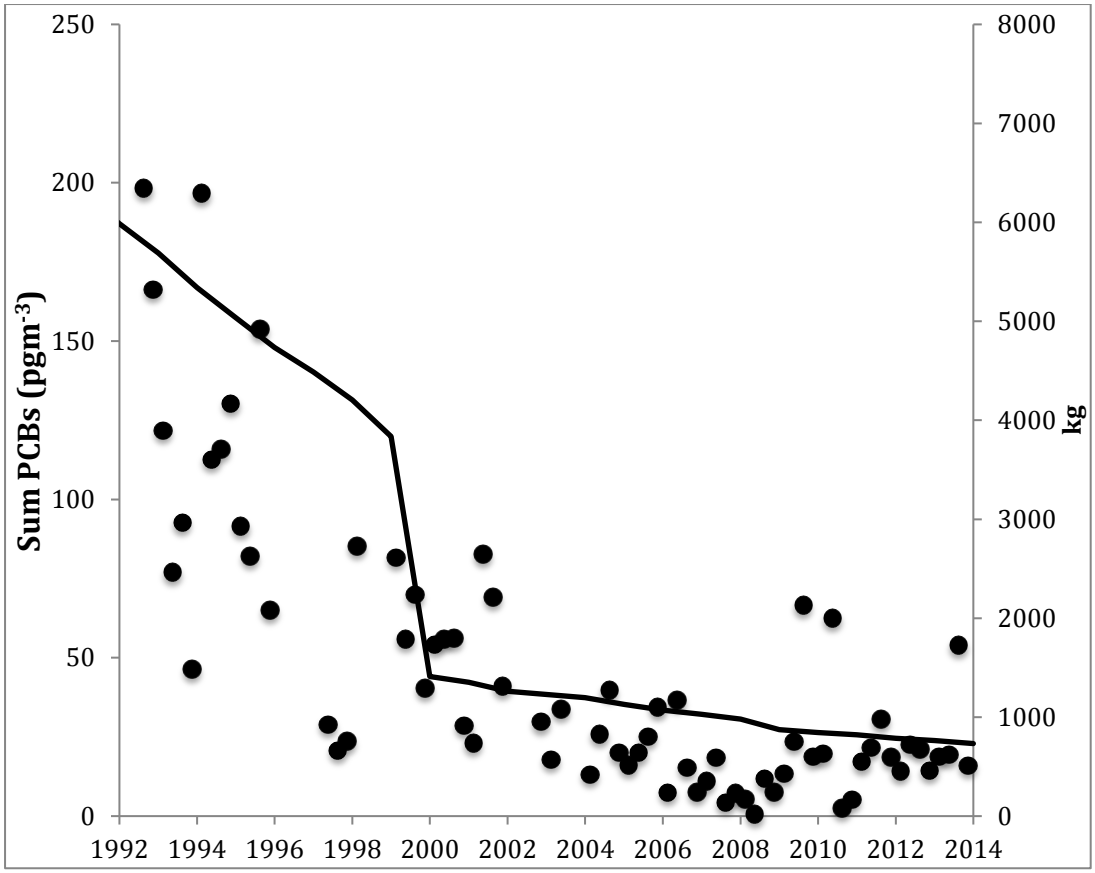
Figure 5. Quarterly ΣPCB_7 data at the TOMPs sites for 2013.



Ambient PCBs 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 by Schuster *et al*., 2010 which discusses the TOMPs programme over the period 1991 to 2008. With the addition of the

2013 data, the clearance rates (time taken for a 50% decline in concentration) provided by the TOMPs network for urban sites averaged 5.7 years and for the rural sites averaged 6.2 years. Time trend data for the urban sites (London, Manchester) and rural sites (Hazelrigg, High Muffles, Auchencorth and Webourne) 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, then only Hazelrigg shows a downward trend with a clearance half life of 11 years. Data for the other sites show either no trend or a slight upward trend. This suggests that the environment has potentially reached a steady state with environmental cycling and secondary sources controlling ambient concentrations.

Figure 6. $\sum_7$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 pg m^{-3} and compared to the current NAEI estimates in kg per annum



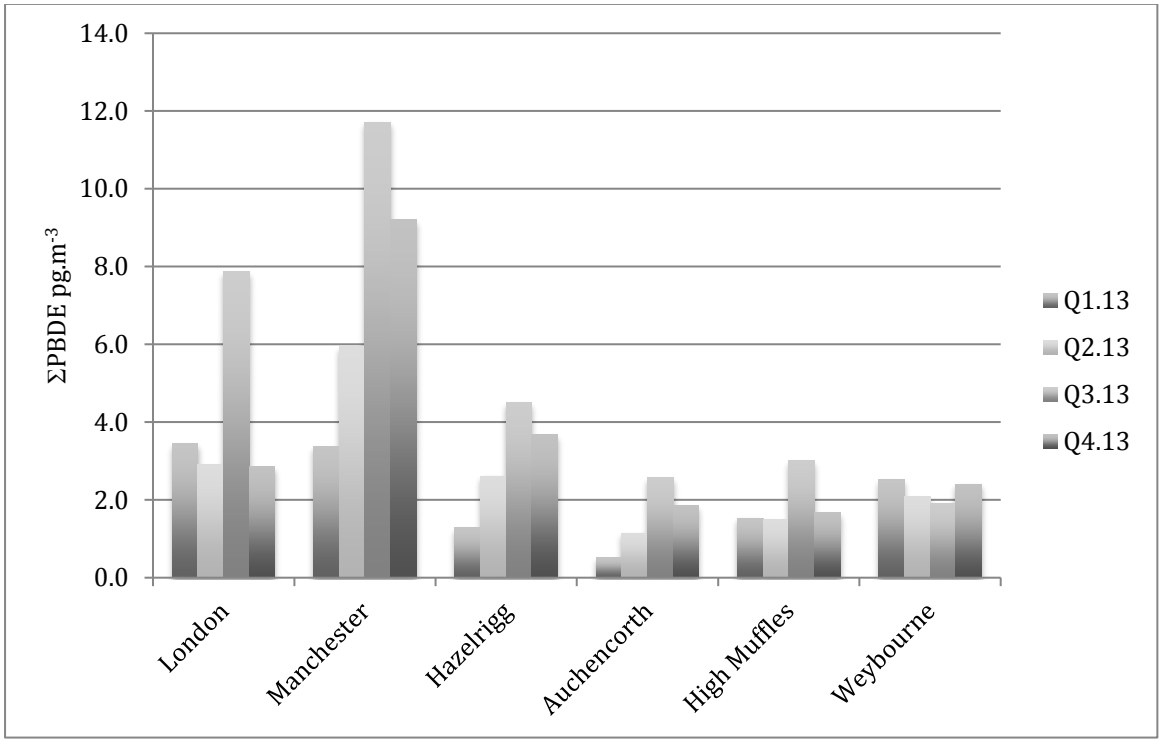
The NAEI suggests that emissions of PCBs to the UK atmosphere have reduced from 6200 kg in 1992 to 730 kg in 2013. Contemporary sources include continued presence of PCBs in dielectric fluids, power generation, small scale waste burning and sewage sludge application to land. The data in Figure 6 shows 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 (± 1.1 years) which is longer than the clearance rates observed for the TOMPs network sites.

7.4 PBDEs: Results and discussions

2013 was the third complete year for the inclusion of PBDEs in the TOMPs network. Twenty two individual congeners have been measured and the data reported in Appendix 3. A summary of the quarterly data is shown in Figure 7. The most prominent congeners, accounting for between 36% and 85% of the Σ□□PBDEs were BDE47 and BDE99 (mean value 64%). These congeners were prominent in the commercial pentaBDE mix, accounting for 72% of the total. London and Manchester showed the highest annual average concentrations for Σ□□PBDEs at 4.3 pg/m^3 and 7.6 pg/m^3, respectively. The other sites were lower at 3.0, 1.5, 1.9, and 2.2 pg/m^3 for Hazelrigg, Auchencorth, High Muffles and Weybourne, respectively. As with PCBs there is some evidence that ambient air concentrations are higher in Q2 and Q3 suggesting temperature driven secondary sources could be important.

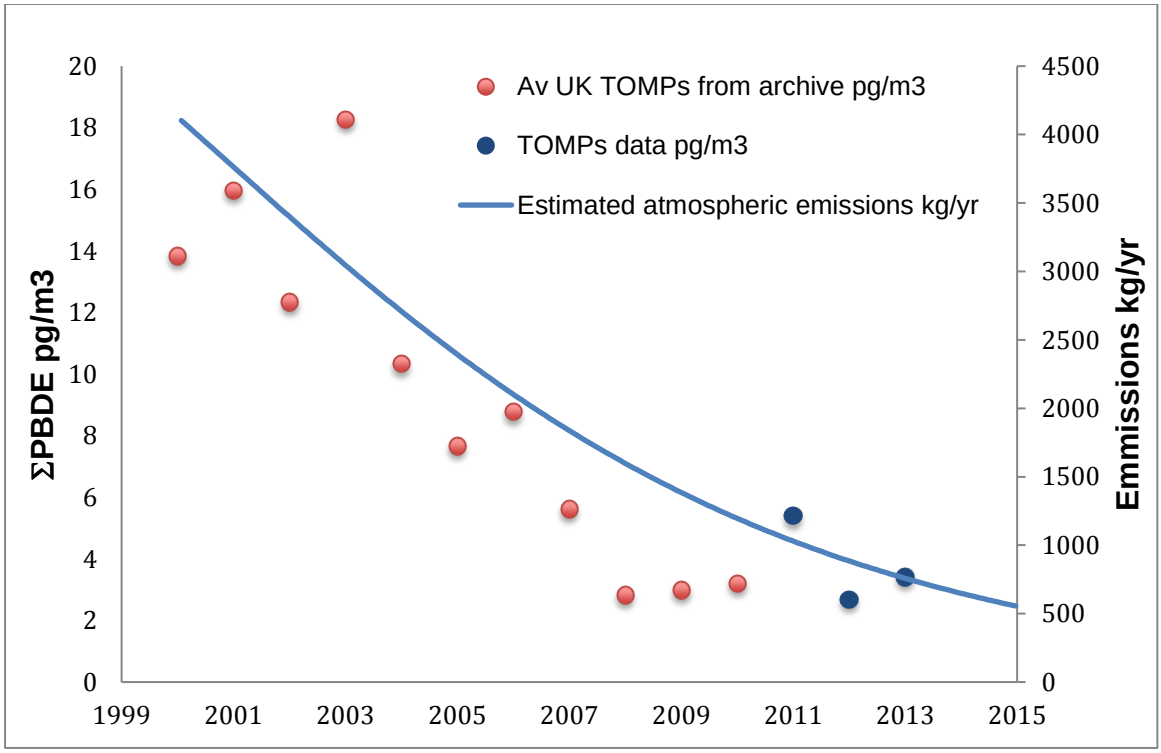
Figure 7. Quarterly ΣPBDE data at the TOMPs sites for 2013.



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 has focused on four of the six sites over a period ranging from 1999 to 2010 (Birgul *et al*. 2012). These time-trend data demonstrate 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 and at the semi-rural site of Hazelrigg. The average ΣPBDE clearance

rates 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 EvnBETR environmental fate model. Figure 8 compares the ambient air data from the TOMPs archive and the recent TOMPs data from 2011-13, 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. Quarterly ΣPBDE data at the TOMPs sites for 2013.



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Appendix 1. PCDD/Fs data. (All data in fgTEQ.m^{-3})

MANCHESTER 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	1.22	0.28	0.37	0.47	0.58
1,2,3,7,8-PeCDF	0.28	0.14	0.22	0.19	0.21
2,3,4,7,8-PeCDF	4.01	1.65	4.07	3.56	3.32
1,2,3,4,7,8-HxCDF	1.63	0.40	0.73	0.77	0.88
1,2,3,6,7,8-HxCDF	2.38	0.73	1.71	1.06	1.47
2,3,4,6,7,8-HxCDF	0.63	0.33	1.32	0.94	0.81
1,2,3,7,8,9-HxCDF	<0.44	<0.44	0.09	<0.44	0.09
1,2,3,4,6,7,8-HpCDF	<0.044	0.14	0.30	0.22	0.22
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	0.04	0.07	0.05
OCDF	0.001	0.001	0.001	0.001	0.001
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,7,8-PeCDD	<4.4	<4.4	3.25	<4.4	3.252
1,2,3,4,7,8-HxCDD	0.83	<0.44	0.24	<0.44	0.535
1,2,3,6,7,8-HxCDD	1.19	0.24	0.67	0.47	0.642
1,2,3,4,7,8-HxCDD	0.95	0.14	0.57	0.45	0.526
1,2,3,4,6,7,8-HpCDD	0.66	0.21	0.45	0.53	0.460
OCDD	0.02	0.00	0.00	0.01	0.009
ΣTEQ dioxins and furans	13.8	4.3	14.0	8.7	10.2
3,4,4’5-TetraCB (PCB_81)	0.01	0.02	0.02	0.01	0.015
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

LONDON 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	0.77	<0.44	0.18	0.43	0.46
1,2,3,7,8-PeCDF	0.17	<0.22	<0.22	<0.22	0.17
2,3,4,7,8-PeCDF	3.01	<2.2	1.21	<2.2	2.11
1,2,3,4,7,8-HxCDF	1.09	<0.44	<0.44	<0.44	1.09
1,2,3,6,7,8-HxCDF	2.27	<0.44	<0.44	<0.44	2.27
2,3,4,6,7,8-HxCDF	0.75	<0.44	<0.44	<0.44	0.75
1,2,3,7,8,9-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDF	0.22	<0.044	<0.044	<0.044	0.22
1,2,3,4,7,8,9-HpCDF	0.06	<0.044	<0.044	<0.044	0.06
OCDF	0.001	<0.0004	0.00	<0.0004	0.001
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	0.83
1,2,3,6,7,8-HxCDD	1.11	<0.44	<0.44	<0.44	1.11
1,2,3,4,7,8-HxCDD	1.04	<0.44	<0.44	<0.44	1.04
1,2,3,4,6,7,8-HpCDD	0.63	0.23	0.17	0.66	0.42
OCDD	0.01	0.01	0.00	0.01	0.01
ΣTEQ dioxins and furans	11.1	0.2	1.6	1.1	3.5
3,4,4',5-TetraCB (PCB_81)	0.01	0.02	0.03	0.02	0.02
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

HAZELRIGG 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	0.23	<0.44	<0.44	0.19	0.21
1,2,3,7,8-PeCDF	0.11	<0.22	<0.22	0.06	0.09
2,3,4,7,8-PeCDF	1.96	0.81	<2.2	0.98	1.25
1,2,3,4,7,8-HxCDF	0.41	0.43	<0.44	0.24	0.36
1,2,3,6,7,8-HxCDF	0.35	0.43	<0.44	0.30	0.36
2,3,4,6,7,8-HxCDF	<0.44	<0.44	<0.44	0.35	0.35
1,2,3,7,8,9-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDF	0.13	0.05	<0.044	0.10	0.09
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.044
OCDF	0.001	0.0004	<0.0004	0.0005	0.001
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,6,7,8-HxCDD	<0.44	<0.44	<0.44	0.24	0.24
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDD	0.28	0.07	0.05	0.22	0.15
OCDD	0.01	0.002	0.001	0.005	0.003
ΣTEQ dioxins and furans	3.5	1.8	0.1	2.7	2.0
3,4,4',5-TetraCB (PCB_81)	0.003	0.004	0.006	0.003	0.004
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

AUCHENCORTH 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	0.08	0.06	0.05	<0.44	0.06
1,2,3,7,8-PeCDF	0.04	0.05	<0.22	<0.22	0.05
2,3,4,7,8-PeCDF	0.80	0.35	0.27	<2.2	0.47
1,2,3,4,7,8-HxCDF	0.19	0.15	<0.44	<0.44	0.17
1,2,3,6,7,8-HxCDF	0.29	0.27	<0.44	<0.44	0.28
2,3,4,6,7,8-HxCDF	0.18	0.19	<0.44	<0.44	0.19
1,2,3,7,8,9-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDF	0.07	0.10	<0.044	<0.044	0.09
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.044
OCDF	0.0003	0.0010	<0.0004	<0.0004	0.001
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<4.4
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,6,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDD	0.16	0.06	0.02	0.09	0.08
OCDD	0.004	0.002	0.001	0.001	0.002
ΣTEQ dioxins and furans	1.8	1.2	0.3	0.1	0.9
3,4,4',5-TetraCB (PCB_81)	0.003	0.003	0.004	0.012	0.01
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

HIGH MUFFLES 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	<0.44	0.14	<0.44	<0.44	0.14
1,2,3,7,8-PeCDF	<0.22	<0.22	<0.22	<0.22	<0.22
2,3,4,7,8-PeCDF	<2.2	<2.2	<2.2	<2.2	<2.2
1,2,3,4,7,8-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,6,7,8-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
2,3,4,6,7,8-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,7,8,9-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.044
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.044
OCDF	<0.0004	<0.0004	<0.0004	0.0001	0.0001
2,3,7,8-TCDD	<0.44	0.14	<0.44	<0.44	0.14
1,2,3,7,8-PeCDD	<0.22	<0.22	<0.22	<0.22	<0.22
1,2,3,4,7,8-HxCDD	<2.2	<2.2	<2.2	<2.2	<2.2
1,2,3,6,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDD	<0.44	<0.44	<0.44	<0.44	<0.44
OCDD	<0.44	<0.44	<0.44	<0.44	<0.44
ΣTEQ dioxins and furans	1.7	0.2	0.1	0.4	0.6
3,4,4',5-TetraCB (PCB_81)	0.006	0.005	0.011	0.009	0.01
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

WEYBOURNE 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
2,3,7,8-TCDF	0.21	0.10	0.08	0.15	0.13
1,2,3,7,8-PeCDF	0.10	0.03	0.04	0.08	0.06
2,3,4,7,8-PeCDF	1.87	0.42	0.58	1.17	1.01
1,2,3,4,7,8-HxCDF	0.37	<0.44	<0.44	0.25	0.31
1,2,3,6,7,8-HxCDF	0.47	<0.44	<0.44	0.25	0.36
2,3,4,6,7,8-HxCDF	0.42	<0.44	<0.44	0.23	0.33
1,2,3,7,8,9-HxCDF	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDF	0.14	<0.044	<0.044	0.10	0.12
1,2,3,4,7,8,9-HpCDF	0.02	<0.044	<0.044	0.01	0.02
OCDF	0.001	<0.0004	<0.0004	0.001	0.001
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<0.44
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<0.44
1,2,3,4,7,8-HxCDD	0.16	<0.44	<0.44	<0.44	0.16
1,2,3,6,7,8-HxCDD	0.32	<0.44	<0.44	0.27	0.30
1,2,3,4,7,8-HxCDD	0.19	<0.44	<0.44	0.20	0.19
1,2,3,4,6,7,8-HpCDD	0.35	0.07	0.26	0.33	0.25
OCDD	0.01	0.002	0.01	0.01	0.01
ΣTEQ dioxins and furans	4.6	0.6	1.0	3.1	2.3
3,4,4',5-TetraCB (PCB_81)	0.003	0.002	0.004	0.002	0.003
3,3',4,4'-TetraCB (PCB_77)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	<0.44
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

Appendix 2. TOMPs 2013 PCB data (All data in pg.m^{-3})

LONDON 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	16.18	20.93	26.54	13.54	19.30
PCB_22	4.34	14.80	17.04	13.43	12.40
PCB_44	4.53	25.93	23.02	6.04	14.88
PCB_49	14.91	60.31	27.19	13.60	29.00
PCB_52	5.93	10.69	19.31	11.67	11.90
PCB_70	1.70	8.84	10.37	5.46	6.59
PCB_74	1.93	4.96	4.83	3.51	3.81
PCB_87	0.94	3.96	6.57	2.37	3.46
PCB_95	3.18	8.85	18.76	6.60	9.35
PCB_99	1.04	2.20	4.73	1.81	2.44
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.54	<0.02	2.95	0.37	1.28
PCB_110	2.11	7.77	16.77	6.29	8.24
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	1.32	2.44	5.16	1.72	2.66
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	1.39	3.57	6.72	2.35	3.51
PCB_141	0.34	0.74	1.63	0.43	0.79
PCB_149	1.93	4.90	9.64	3.09	4.89
PCB_151	0.76	2.65	5.38	1.60	2.60
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	<0.02	0.10	0.41	0.11	0.21
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.10	0.34	0.75	0.18	0.34
PCB_167	<0.02	0.32	0.54	<0.02	0.43
PCB_170	0.13	0.26	0.55	0.22	0.29
PCB_174	0.34	0.53	1.24	0.44	0.64
PCB_180	0.46	0.84	1.65	0.65	0.90
PCB_183	0.20	0.39	0.81	0.29	0.42
PCB_187	0.43	0.90	2.02	0.74	1.02
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	0.15	0.10	0.13
PCB_199	<0.02	<0.02	0.08	<0.02	0.08
PCB_203	0.08	0.12	0.31	0.15	0.17
PCB_153+132	2.33	4.80	10.36	3.62	5.28
PCB_31+28	16.79	61.07	84.71	38.35	50.23
PCB_41/64	7.34	22.01	18.32	8.72	14.10
PCB_60/56	1.15	3.66	3.19	3.18	2.79
PCB_90/101	3.36	8.98	15.47	6.69	8.63
PCB_Σ7PCB	63.8	71.6	117.9	79.5	83.20

MANCHESTER 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	7.58	8.86	19.11	9.97	11.38
PCB_22	3.38	5.24	3.85	5.22	4.42
PCB_44	2.71	2.09	20.67	13.56	9.76
PCB_49	14.62	18.24	48.55	49.86	32.82
PCB_52	11.50	21.13	40.08	25.61	24.58
PCB_70	4.54	10.71	23.16	13.17	12.89
PCB_74	1.43	3.19	7.93	5.35	4.47
PCB_87	3.13	8.91	15.25	8.98	9.07
PCB_95	9.15	21.05	35.01	20.45	21.41
PCB_99	3.07	7.30	10.10	6.74	6.80
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.94	2.77	4.66	1.53	2.47
PCB_110	7.58	20.18	33.89	20.02	20.42
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	3.34	8.97	14.78	7.95	8.76
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	3.00	7.07	12.75	6.73	7.39
PCB_141	0.56	1.30	2.20	1.11	1.29
PCB_149	3.80	8.87	15.18	8.10	8.99
PCB_151	1.30	3.34	5.46	3.30	3.35
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	0.18	0.30	0.61	0.31	0.35
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.22	0.71	1.34	0.68	0.74
PCB_167	0.16	0.23	0.37	0.33	0.27
PCB_170	0.21	0.38	0.55	0.38	0.38
PCB_174	0.40	0.74	1.20	0.60	0.73
PCB_180	0.51	0.79	1.58	1.05	0.98
PCB_183	0.24	0.49	0.72	0.43	0.47
PCB_187	0.52	1.04	1.60	0.97	1.03
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	0.09	<0.02	0.09
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	<0.02	0.20	0.24	0.10	0.18
PCB_153+132	4.28	10.38	17.74	9.56	10.49
PCB_31+28	15.28	25.77	58.16	30.94	32.54
PCB_41/64	6.44	7.37	17.51	18.60	12.48
PCB_60/56	1.26	2.72	2.28	3.15	2.35
PCB_90/101	9.62	23.39	36.01	22.31	22.83
PCB_Σ7PCB	51.7	128.1	159.1	68.0	101.72

HAZELRIGG 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	6.15	10.84	32.18	4.67	13.46
PCB_22	0.41	1.85	3.66	7.42	3.34
PCB_44	0.63	5.85	0.33	7.97	3.70
PCB_49	1.23	17.15	43.75	11.97	18.52
PCB_52	2.24	1.58	0.88	0.34	1.26
PCB_70	0.84	<0.02	0.93	0.41	0.73
PCB_74	0.90	4.04	1.15	<0.02	2.03
PCB_87	<0.02	<0.02	<0.02	1.19	1.19
PCB_95	1.35	2.64	2.44	0.48	1.73
PCB_99	0.42	<0.02	<0.02	0.58	0.50
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	<0.02	<0.02	<0.02	0.94
PCB_110	0.75	3.82	2.92	2.78	2.57
PCB_114	0.88	4.56	4.41	<0.02	3.28
PCB_118	<0.02	<0.02	0.33	1.51	0.92
PCB_123	0.22	0.62	<0.02	<0.02	0.42
PCB_138	0.43	0.50	0.75	0.97	0.66
PCB_141	<0.02	<0.02	<0.02	0.20	0.20
PCB_149	0.73	0.55	0.96	1.38	0.90
PCB_151	0.61	1.26	1.47	1.68	1.26
PCB_155	<0.02	<0.02	0.20	<0.02	0.20
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	0.21	0.62	1.55	0.11	0.62
PCB_167	0.04	<0.02	0.58	<0.02	0.31
PCB_170	0.08	<0.02	<0.02	<0.02	0.08
PCB_174	0.10	0.26	0.32	0.24	0.23
PCB_180	0.15	0.24	0.32	0.22	0.23
PCB_183	0.06	<0.02	0.12	0.06	0.08
PCB_187	0.17	0.48	<0.02	0.35	0.33
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	0.05	<0.02	0.10	<0.02	0.07
PCB_153+132	0.62	1.19	2.69	0.84	1.33
PCB_31+28	12.23	22.39	68.30	10.12	28.26
PCB_41/64	1.04	5.08	4.34	3.13	3.40
PCB_60/56	0.40	<0.02	<0.02	<0.02	0.40
PCB_90/101	1.97	0.89	0.83	3.42	1.78
PCB_Σ7PCB	27.9	42.2	26.2	18.8	28.78

AUCHENCORTH 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	10.72	2.73	6.25	2.61	5.58
PCB_22	<0.02	0.89	0.57	0.70	0.72
PCB_44	6.57	2.27	10.72	5.58	6.28
PCB_49	43.77	11.78	31.25	25.70	28.12
PCB_52	4.52	1.93	5.29	1.77	3.38
PCB_70	0.57	0.78	2.26	0.94	1.14
PCB_74	0.05	0.48	1.73	1.01	0.82
PCB_87	0.11	<0.02	<0.02	<0.02	0.11
PCB_95	7.29	1.00	1.26	0.91	2.62
PCB_99	0.12	0.10	0.15	0.13	0.13
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_110	1.55	0.32	<0.02	<0.02	0.93
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	1.29	0.10	<0.02	0.19	0.53
PCB_123	1.19	<0.02	<0.02	<0.02	1.19
PCB_138	2.91	0.31	0.47	0.39	1.02
PCB_141	1.15	0.10	0.11	0.11	0.37
PCB_149	7.93	0.52	0.73	0.57	2.44
PCB_151	4.03	0.20	0.23	0.11	1.14
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
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	0.15	<0.02	<0.02	<0.02	0.15
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	0.36	<0.02	<0.02	<0.02	0.36
PCB_174	0.80	0.11	0.15	0.10	0.29
PCB_180	0.93	0.15	0.08	0.13	0.32
PCB_183	0.63	0.06	0.05	0.07	0.20
PCB_187	1.36	0.15	0.17	0.14	0.45
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	0.46	<0.02	<0.02	<0.02	0.46
PCB_203	0.09	<0.02	<0.02	<0.02	0.09
PCB_153+132	6.26	0.64	0.79	0.63	2.08
PCB_31+28	16.86	11.80	27.88	11.97	17.13
PCB_41/64	0.70	4.24	14.62	7.47	6.76
PCB_60/56	<0.02	0.21	<0.02	0.47	0.34
PCB_90/101	5.94	0.80	0.91	0.66	2.08
PCB_Σ7PCB	6.1	11.6	12.1	12.1	10.46

HIGH MUFFLES 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	2.88	3.64	14.15	5.19	6.47
PCB_22	2.58	1.60	1.97	2.03	2.04
PCB_44	1.32	10.00	19.80	13.62	11.18
PCB_49	2.19	31.64	88.69	34.99	39.38
PCB_52	1.08	1.51	4.96	1.83	2.35
PCB_70	0.62	1.34	2.70	1.51	1.54
PCB_74	0.38	0.98	1.03	0.79	0.80
PCB_87	0.12	<0.02	<0.02	<0.02	0.12
PCB_95	0.74	1.05	1.57	1.16	1.13
PCB_99	0.23	0.19	0.34	0.22	0.25
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_110	0.30	1.08	1.32	0.85	0.89
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.21	<0.02	<0.02	<0.02	0.21
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	0.29	0.53	1.04	0.43	0.57
PCB_141	<0.02	<0.02	<0.02	0.08	0.08
PCB_149	0.47	0.73	1.12	0.65	0.74
PCB_151	0.12	0.39	0.59	0.30	0.35
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	<0.02	0.12	0.51	0.11	0.24
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	<0.02	0.06	0.08	<0.02	0.07
PCB_167	<0.02	<0.02	<0.02	0.14	0.14
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.08	0.07	0.15	0.06	0.09
PCB_180	0.10	0.07	0.32	0.14	0.16
PCB_183	0.05	0.05	0.10	0.07	0.07
PCB_187	0.13	0.18	0.25	0.16	0.18
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	0.03	0.05	<0.02	0.04
PCB_153+132	0.43	0.81	1.28	0.65	0.79
PCB_31+28	6.04	15.25	62.58	12.69	24.14
PCB_41/64	1.89	9.72	25.08	13.06	12.44
PCB_60/56	0.20	0.63	1.76	0.60	0.80
PCB_90/101	0.73	0.87	1.27	0.90	0.94
PCB_Σ7PCB	10.0	17.9	14.2	12.9	13.74

WEYBOURNE 2013	Q1.13	Q2.13	Q3.13	Q4. 13	Average 2013
PCB_18	2.92	4.75	7.76	2.08	4.38
PCB_22	1.18	2.52	3.78	1.10	2.15
PCB_44	2.60	4.56	11.38	3.30	5.46
PCB_49	9.37	17.41	33.07	10.90	17.69
PCB_52	2.01	3.03	5.16	2.80	3.25
PCB_70	0.51	0.70	2.00	1.10	1.08
PCB_74	0.40	0.53	<0.02	0.64	0.52
PCB_87	0.15	0.17	0.17	0.16	0.16
PCB_95	1.24	1.23	2.15	1.26	1.47
PCB_99	0.28	0.29	0.61	0.33	0.38
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_110	0.65	0.67	1.35	0.87	0.89
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.14	0.09	0.40	0.47	0.28
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	0.45	0.46	1.06	0.60	0.64
PCB_141	<0.02	<0.02	0.08	<0.02	0.08
PCB_149	0.78	0.75	1.35	0.89	0.94
PCB_151	0.34	0.27	0.51	0.34	0.36
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	<0.02	<0.02	<0.02	0.08	0.08
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	0.05	<0.02	0.12	<0.02	0.08
PCB_174	0.11	0.11	<0.02	0.10	0.11
PCB_180	0.17	0.13	<0.02	0.08	0.13
PCB_183	0.07	0.07	0.07	0.06	0.06
PCB_187	0.20	0.16	0.29	0.22	0.22
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	0.71	0.70	1.51	0.84	0.94
PCB_31+28	5.51	10.68	24.74	7.95	12.22
PCB_41/64	2.77	5.38	10.44	3.80	5.60
PCB_60/56	0.12	0.24	<0.02	0.19	0.18
PCB_90/101	1.09	1.13	1.89	1.24	1.34
PCB_Σ7PCB	12.8	18.9	32.4	14.0	19.54

Appendix 3. PBDE data for 2013. (All data in $pg.m^{-3}$)

PBDE LONDON 2013	Q1.13	Q2.12	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.46	<0.02	0.46
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	0.88	1.42	2.37	0.99	1.41
BDE_49	<0.02	<0.02	0.39	0.21	0.30
BDE_66	<0.02	<0.02	0.34	<0.02	0.34
BDE_71	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_99	0.90	0.76	1.41	0.69	0.94
BDE_100	0.26	0.24	0.40	0.22	0.28
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	0.40	0.25	0.46	0.41	0.38
BDE_154	0.32	0.23	0.53	0.34	0.35
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	<0.02	<0.02	0.47	<0.02	0.47
BDE_196	0.69	<0.02	1.03	<0.02	0.86
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	1.77	2.17	3.78	1.68	2.35

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

PBDE MANCHESTER 2013	Q1.13	Q2.13	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.34	<0.02	0.34
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	1.16	2.73	6.28	3.17	3.33
BDE_49	<0.02	0.30	0.49	0.40	0.39
BDE_66	<0.02	<0.02	0.33	0.30	0.32
BDE_71	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_99	1.07	1.72	2.66	1.87	1.83
BDE_100	0.26	0.37	0.65	0.47	0.44
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	0.41	0.30	0.46	0.86	0.51
BDE_154	0.49	0.51	0.51	0.85	0.59
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	<0.02	<0.02	<0.02	0.52	0.52
BDE_196	<0.02	<0.02	<0.02	0.77	0.77
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	2.23	4.45	8.94	5.04	5.16

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

PBDE AUCHENCORTH 2013	Q1.13	Q2.13	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	0.30	0.55	1.33	0.96	0.79
BDE_49	<0.02	<0.02	0.14	<0.02	0.14
BDE_66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_71	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_99	0.22	0.38	0.69	0.61	0.48
BDE_100	<0.02	0.09	0.19	0.13	0.14
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	0.10	<0.02	0.10
BDE_154	<0.02	0.12	0.15	0.15	0.14
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_196	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	0.52	0.94	2.01	1.57	1.26

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

PBDE HIGH MUFFLES 2013	Q1.13	Q2.13	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.12	<0.02	0.12
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	0.40	0.64	1.52	0.58	0.78
BDE_49	<0.02	0.10	0.19	0.11	0.13
BDE_66	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_71	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_99	0.55	0.41	0.69	0.52	0.54
BDE_100	0.11	0.11	0.18	0.11	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	0.19	0.10	0.15	0.17	0.15
BDE_154	0.28	0.13	0.14	0.19	0.19
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	<0.02	<0.02	<0.02	<0.02	0.26
BDE_196	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	0.95	1.05	2.21	1.10	1.33

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

PBDE HAZELRIGG 2013	Q1.13	Q2.13	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.26	<0.02	0.26
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	0.33	1.44	2.26	0.76	1.20
BDE_49	<0.02	<0.02	0.31	0.23	0.27
BDE_66	<0.02	<0.02	<0.02	0.19	0.19
BDE_71	<0.02	<0.02	<0.02	0.26	0.26
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	0.07	<0.02	0.07
BDE_99	0.36	0.70	0.93	0.82	0.70
BDE_100	0.09	<0.02	0.38	0.25	0.24
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	0.15	<0.02	0.19	0.39	0.24
BDE_154	0.08	<0.02	0.10	0.50	0.23
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	<0.02	<0.02	<0.02	0.28	0.28
BDE_196	0.27	0.47	<0.02	<0.02	0.37
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	0.69	2.14	3.19	1.58	1.90

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

PBDE WEYBOURNE 2013	Q1.13	Q2.13	Q3.13	Q4.13	Average 2013
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_32	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_35	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_37	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_47	0.56	0.68	0.72	0.62	0.65
BDE_49	<0.02	<0.02	<0.02	0.14	0.14
BDE_66	<0.02	<0.02	<0.02	0.12	0.12
BDE_71	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_75	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_77	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_85	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_99	0.80	0.62	0.41	0.23	0.52
BDE_100	0.15	0.14	<0.02	0.15	0.14
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	0.32	0.21	0.30	0.48	0.33
BDE_154	0.37	0.20	0.12	0.17	0.21
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	0.32	0.26	0.35	0.49	0.35
BDE_196	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_197	<0.02	<0.02	<0.02	<0.02	<0.02
BDE 47 + 99	1.36	1.30	1.13	0.85	1.16

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