The Lancaster
Environment Centre

Annual Report for 2012 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 2012 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 2012, 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).

The TOMPs network provides data to inform the public of air quality, and information to support the development of policy to protect the environment. The specific aims of the TOMPs programme are:

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

There are a number of international instruments aimed at reducing releases into the environment, such as the 1998 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 TOMPs network provides valuable evidence for effectiveness

of such agreements on the concentrations of a range of POPs in UK urban and rural ambient air.

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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 which operates six sites, three urban, two rural and one semi-rural. The current contract commenced in October 2010 and will run until September 2013. 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 http://uk-air.defra.gov.uk. 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.

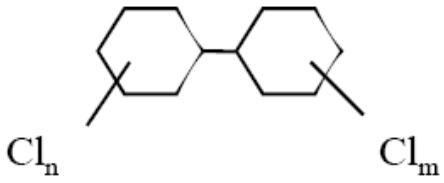
This annual report for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polybrominated diphenyl ethers (PBDEs) (Q4 only) includes:

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

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

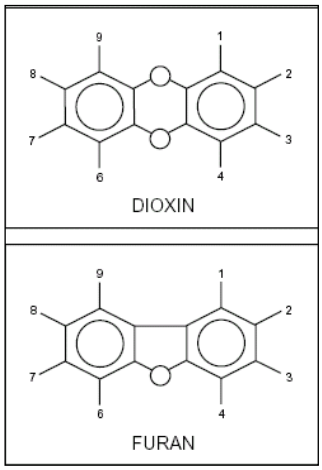
applications. They have been used as dielectric fluids in capacitors and transformers, in plasticizers, adhesives, inks, sealants and surface coatings (*Eduljee,* 1988; *de Voogt and Brinkman*, 1989; *Harrad et al.,* 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents 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.

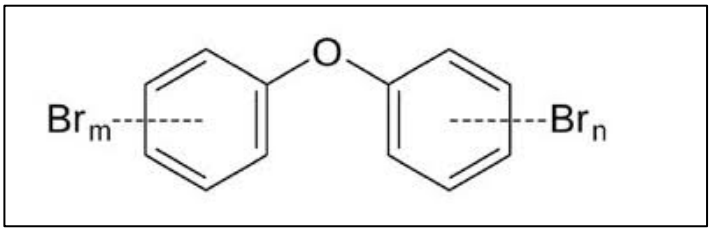
Production of PCBs peaked in the 1960s in Europe and USA and terminated in the mid 1970s, when they where ultimately banned in the late 1970s/early 1980s (de Voogt and Brinkman, 1989). The most recent inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tonnes (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 are 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. sea 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 760kg, the majority emitted from electrical equipment such as capacitors and transformers.

PCDD/Fs. The term Dioxin is commonly used to refer to a family of toxic chemicals that all share a similar chemical structure and a common mechanism of toxic action. This family includes seven of the polychlorinated dibenzo dioxins (PCDDs), ten of the polychlorinated dibenzo furans (PCDFs) and twelve of the polychlorinated biphenyls (PCBs). PCDDs and PCDFs are not commercial chemical products but are trace level unintentional byproducts of most forms of combustion and several industrial chemical processes. PCBs were produced commercially in large quantities until production was stopped in 1977. 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.



Polybrominated Diphenyl Ethers (PBDEs) have been widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. They are referred as additive flame retardants, because they are simply blended with the product. This makes them more prone to volatilize into the atmosphere during the product lifetime. They reduce 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 deca-BDE 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 are currently being phased out in the rest of the world (after being banned in some states of the USA). 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. For the first time a range of PBDE congeners have been included in the TOMPs methodology. The 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 2012 for the tetra and penta PBDEs in the UK were 800kg.

3. TOMPs sites operating in 2012

In 2011 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.

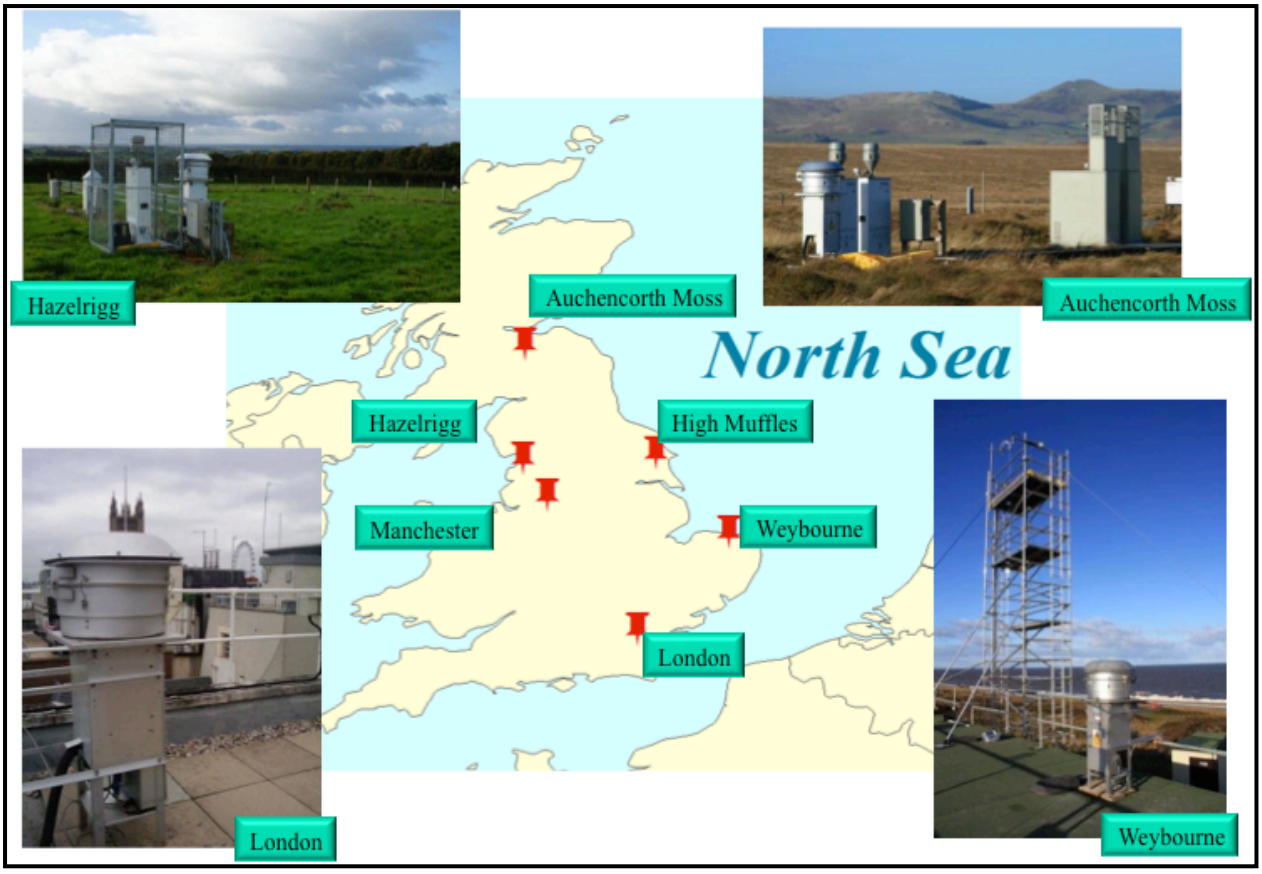


Figure 1. Location map of the current TOMPs sites.

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) 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 and they ranged between 61-101%. PCDD/F and coplanar PCB values 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 UK air quality website (http://uk-air.defra.gov.uk/). Archived samples for each year (50% of the samples) are stored in the freezer in the laboratory at Lancaster University.

7. RESULTS FOR YEAR 2012

7.1 ***Network Operations***: Table 1 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 2012. 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 3490-5240 m^3.

London, Manchester and Hazelrigg operated normally with 100% data capture over the year. The samplers at High Muffles, Auchencorth and Weyborne experienced minor motor/equipment failures with all quarters above an operating efficiency of 90% with averaged collection rates over 97%.

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

In this report data for Q1, Q2, Q3 and Q4 2012 are presented for PCBs, co-planar PCBs and PCDDs and PCDFs and PBDEs.

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2012.

		Start	Time	Finish	Time	% Data capture	Volume m^3
LON	Q1	05/01/2012	12:05	27/03/2012	11:45	100	4198
	Q2	27/03/2012	11:50	28/06/2012	12:45	100	4734
	Q3	28/06/2012	12:50	04/10/2012	12:55	100	5019
	Q4	04/10/2012	13:00	03/01/2013	13:00	100	4660
MAN	Q1	29/12/2011	10:40	05/04/2012	10:30	100	4928
	Q2	05/04/2012	10:35	28/06/2012	10:40	100	4224
	Q3	28/06/2012	10:55	04/10/2012	14:20	100	4916
	Q4	04/10/2012	14:25	27/12/2012	10:00	100	4315
HR	Q1	28/12/2011	15:30	04/04/2012	13:55	100	5090
	Q2	04/04/2012	14:00	27/06/2012	14:45	100	4391
	Q3	27/06/2012	14:55	03/10/2012	15:15	100	5058
	Q4	03/10/2012	15:20	27/12/2012	08:00	100	4367
HM	Q1	29/12/2011	13:30	04/04/2012	01:30	98	4857
	Q2	05/04/2012	23:30	28/06/2012	14:40	100	4353
	Q3	28/06/2012	14:50	04/10/2012	11:05	100	4838
	Q4	04/10/2012	11:10	27/12/2012	12:40	100	4232
AUCH	Q1	04/01/2012	10:55	28/03/2012	10:50	100	4493
	Q2	28/03/2012	10:50	04/07/2012	10:10	100	5238
	Q3	04/07/2012	10:10	26/09/2012	10:40	91	4494
	Q4	02/10/2012	11:10	27/12/2012	11:30	100	4599
WEY	Q1	29/12/2011	09:35	02/04/2012	09:25	100	5012
	Q2	02/04/2012	09:25	25/06/2012	09:45	100	3490
	Q3	25/06/2012	09:45	01/10/2012	09:30	93	4483
	Q4	01/10/2012	09:30	04/01/2013	10:45	100	4812

7.2 PCDD/Fs: Results and discussion

Quarterly PCDD/F data are contained in the Appendix 1 and a summary presented in Figure 2. The annual mean PCDD/Fs concentrations measured in 2012 ranged from 0.05 to 12.5 fg TEQ/m^3 and are similar to those we have reported for last 10 years. The highest concentrations were observed in the two urban sites (Manchester 33 fg TEQ/m^3 and London 15 fg TEQ/m^3) followed by Weybourne (9.1 fg TEQ/m^3), (Hazelrigg (8.7 fg TEQ/m^3), High Muffles (4.3 fg TEQ/m^3) and Auchencorth (0.12 fg TEQ/m^3). As with previous years, the two urban sites exhibit higher concentrations of PCDD/Fs and again the average concentration in London was closer to the sites at Weybourne and Hazelrigg. The seasonal pattern as shown by the quarterly data shows that the highest concentrations were measured in quarters Q1 and 4 with lower values reported for quarters 2 and 3.

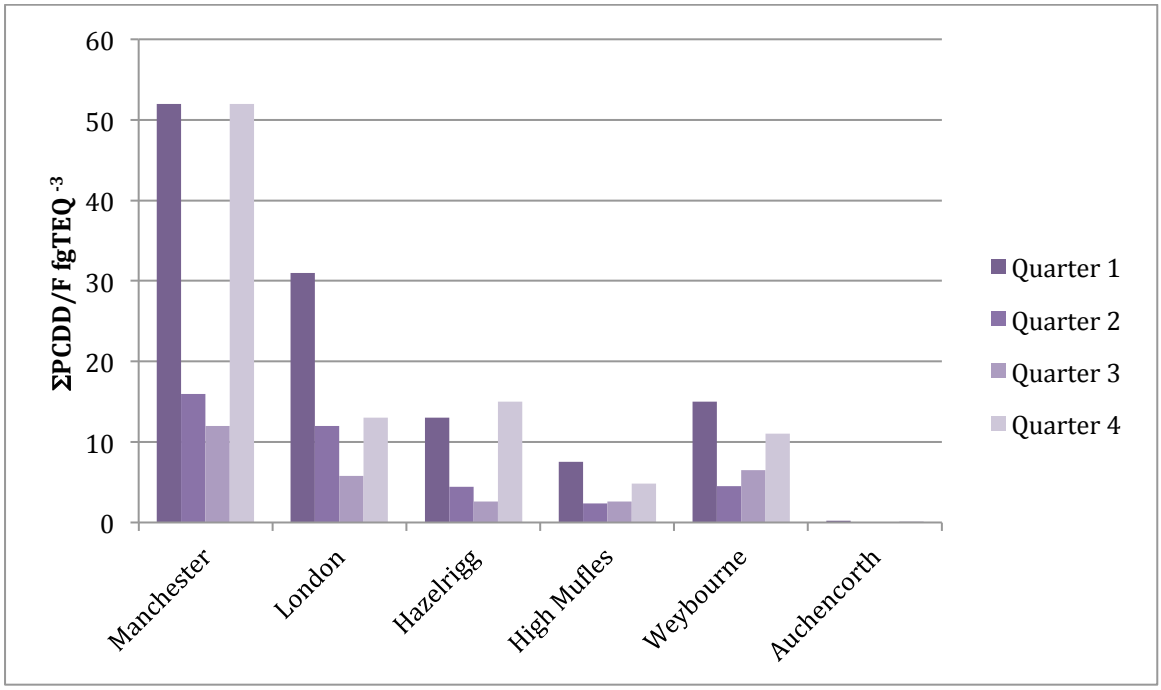
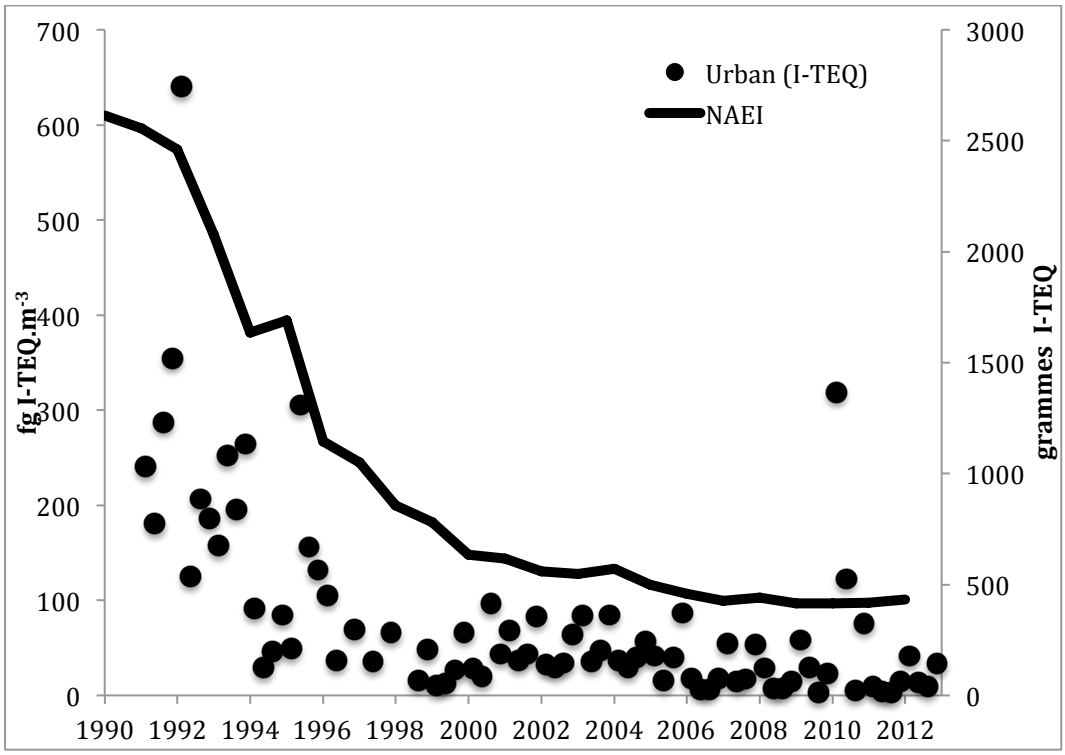


Figure 2. Quarterly PCDD/F data for each TOMPs site in 2012.

PCDD/Fs constitute two classes of chemicals that are formed unintentionally during combustion (e.g. waste incineration, burning of coal, wood etc.), the refining of petroleum, several metal treatment processes and during the synthesis of certain chlorinated chemicals (e.g. pentachlorophenol). The latter processes have 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. Generally seasonality is less obvious in urban areas than rural, as cities have more constant sources that emit throughout the year. The sources of PCDD/Fs to the UK atmosphere are presented in detail by Katsogiannis *et al*., 2010 which discusses the TOMPs programme over the last 17 years.

The temporal trends for the urban and rural sites are presented in Figure 3, and the estimated atmospheric half lives (assuming first order kinetics) for London and Manchester are 4.8 and 5.2 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 – 2012 (http://www.naei.defra.org). During this period PCDD/F emissions reduced from around 1280 g I-TEQ per year in 1990 to 202 g I-TEQ per year in 2012.



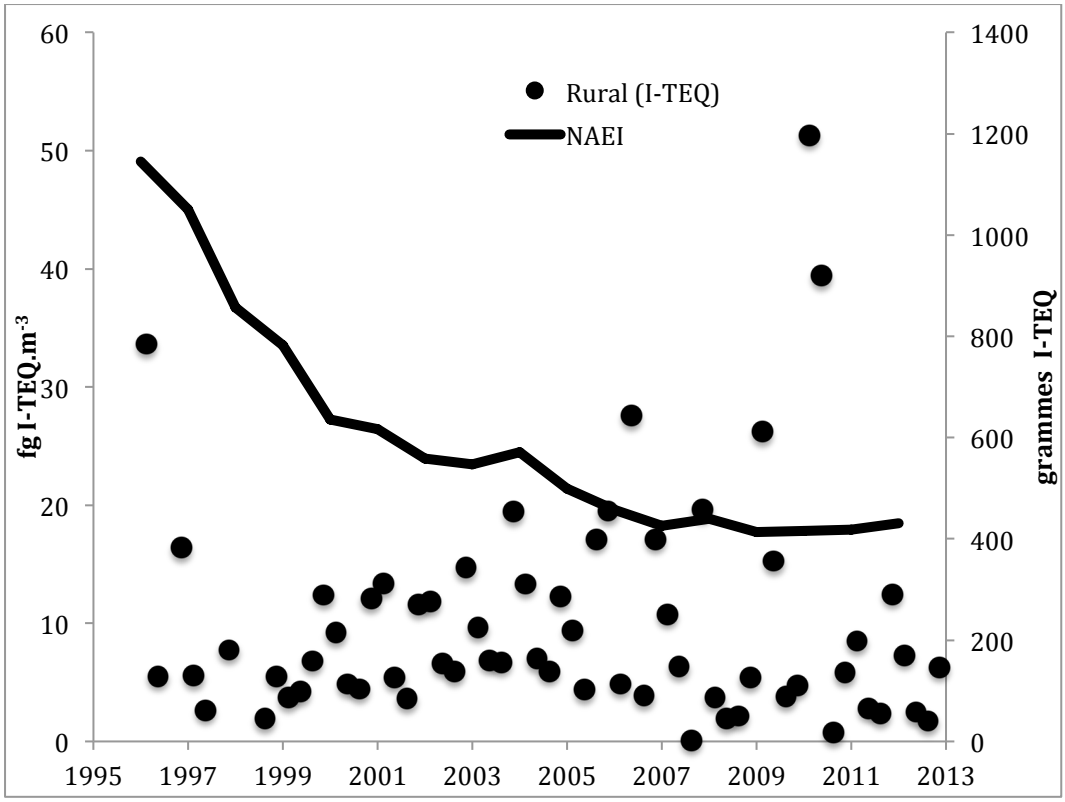


Figure 3. Long-term PCDD/F trend data from the TOMPs network for the urban (London and Manchester) and the rural (Hazelrigg, High Muffles, Auchencorth and Weybourne) sites. Data are presented as averages in fg I-TEQ.m^{-3} and compared to the current NAEI estimates in grammes I-TEQ per annum

The Canadian National Air Pollution Surveillance (NAPS) network provides data on range of ambient air pollutants, including PCDD/Fs, for a range of locations across Canada. NAPs includes 19 sites which are sampled every 24 days using a similar Hi Vol samplers to TOMPs along with Teflon coated glass fibre filters and PUFs as part of the sampling system. Figure 4 shows the temporal trend for ΣPCDD/Fs shows the yearly variation in mean TEQ concentrations using data from all the urban monitoring sites showing a 50% decrease between 1999 and 2007. The concentration data from the NAPS network for urban sites are similar those for London and Manchester over the same period. Over the period 1999 to 2007 ΣPCDD/Fs for the TOMPs urban sites ranged from 11 to 60 fg TEQ m^{-3}, whilst the NAPs data ranged from 18 to 35 fg TEQ m^{-3} over the same period. The NAPS data also showed a decreasing trend over this period, with a slight increase from 2007 to 2008, whilst the TOMPs data showed no discernable trend. The trends shown in Figure 3 only apply when considering the whole dataset.

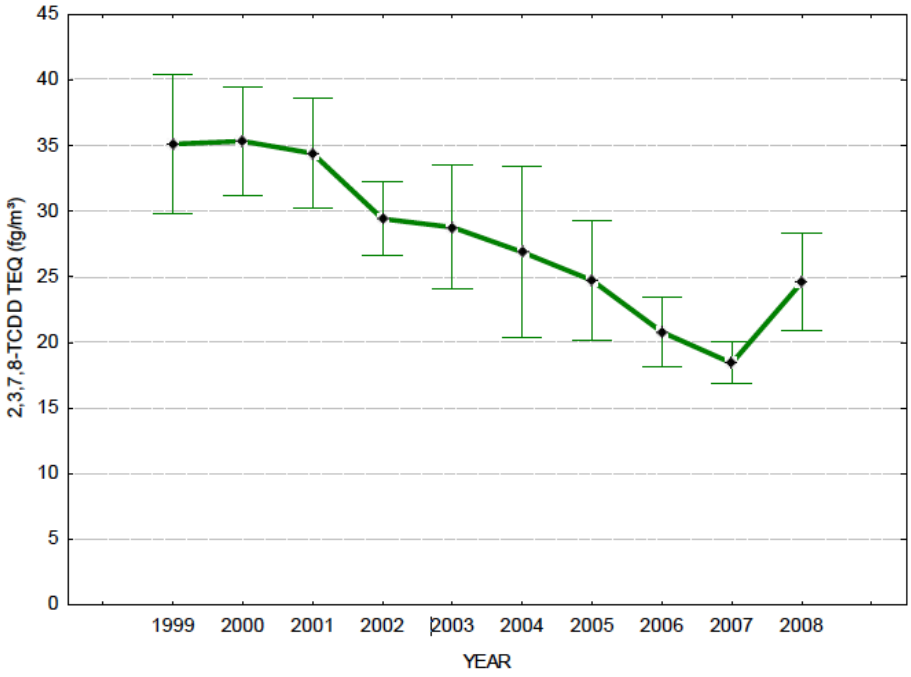


Figure 4. Temporal trend data for the Sum of 2,3,7,8-TCDD toxic equivalent (TEQ) concentrations (fg/m³) at the Canadian National Air Pollution Surveillance Network urban sites (1999–2008). Mean values and 90th percentiles are plotted.

7.3 PCBs: Results and discussions

Quarterly congener PCB data are contained in the Appendix 2 and a summary presented in Figure 5. The quarterly PCB concentrations measured at each of the TOMPs sites ranged from 10 pg/m^3 (Auchencorth) to 102 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 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 (2006-2010) of 60% and 70%, respectively. The annual average concentration for the other sites showed a mixed picture, with Hazelrigg showing a 40% increase, Weybourne a 6% increase, High Muffles a 40% decrease and Auchencorth a 30% decrease over the last five years (Auchencorth 5 year average, Weybourne 4 year average). 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.

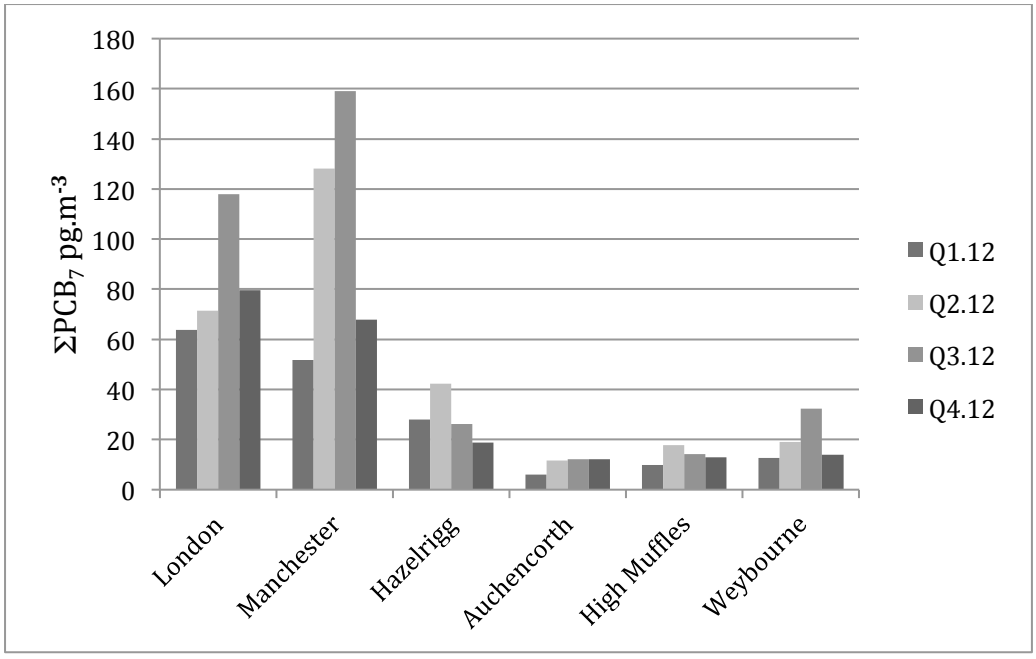


Figure 5. Quarterly ΣPCB_7 data at the TOMPs sites for 2012.

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 in detail by Schuster *et al*., 2010 which discusses the TOMPs programme over the period 1991 to 2008. With the addition of the 2012 data, the clearance rates (time taken for a 50% decline in concentration) provided by the TOMPs network for urban sites averaged 5.3 years and for the rural sites averaged 9 years. Time trend data for the urban sites (London, Manchester) and rural sites (Hazelrigg, High Muffles, Auchencorth and Webourne) are

presented in Figure 5. These data have been plotted against the estimated UK emission data from the NAEI (http://www.naei.defra.org).

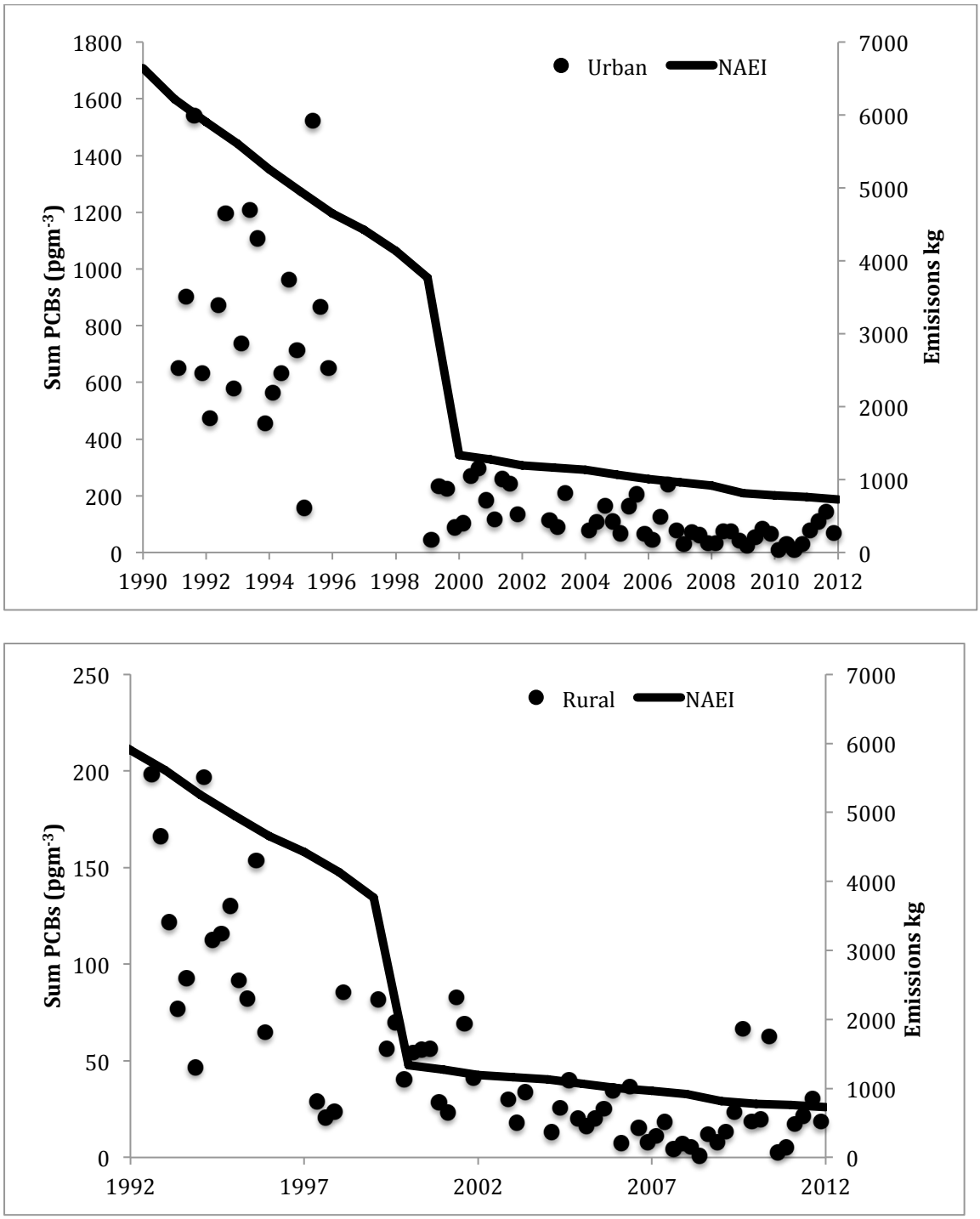


Figure 6. $\sum_7$PCB Long-term PCB trend data from the TOMPs network for the urban (London and Manchester) and the rural (Hazelrigg, High Muffles, Auchencorth and Weybourne) sites. Data are presented as averages in pg m^{-3} and compared to the current NAEI estimates in kg per annum

The NAEI suggests that emissions of PCBs to the UK atmosphere have reduced from 6200 kg in 1992 to 730 kg in 2012. 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 5 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 halving time of PCBs in the vapor phase was 14.9 (± 1.1 years).

7.4 PBDEs: Results and discussions

2012 was the second 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. The most prominent congeners, accounting for between 19% and 74% of the Σ_{22}PBDEs were BDE47 and BDE99 (mean value 43%). These congeners were prominent in the commercial pentaBDE mix, accounting for 72% of the total. London and Manchester showed the highest concentrations of Σ_{22}PBDEs at 9.2 pg/m^3 and 14.8 pg/m^3, respectively. The other sites were lower at 4.5, 2.0, 3.9, and 7.8 pg/m^3 for Hazelrigg, Auchencorth, High Muffles and Weybourne, respectively. A summary of these data are shown in Figure 7.

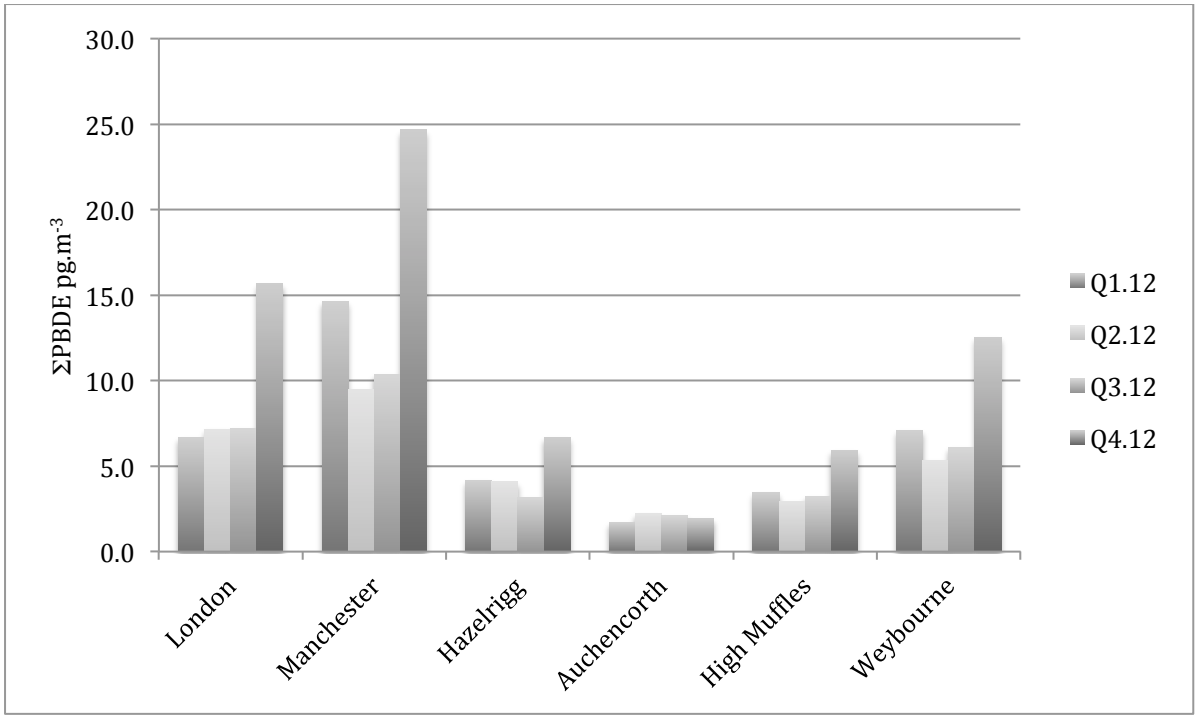


Figure 7. Quarterly ΣPBDE data at the TOMPs sites for 2012

The TOMPs air sample archive has recently been used to provide information the time-trend of pentabrominated diphenylethers in the UK atmosphere. The re-analysis of PBDEs in the sample archive has focused on four of the six sites over a period ranging from 1999 to 2010. These time-trend data demonstrate a consistent decrease in concentration over recent the last 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 half-lives for these three sites were 3.4, 2.0 and 3.5 years, respectively. PBDEs are present in background levels, among the lowest reported in literature. Ma et al. (2013) reported BDE-47 data from the USA/Canadian Integrated Atmospheric Deposition Network (sited around the Great Lakes Region) with halving times of 5−9 years at the urban sites in Chicago and Cleveland. However, at other rural and remote sites they report that concentrations were increasing with doubling times of 7−11 years.

Comparison of concentrations to estimated emissions and employment of PBDE profiles suggest 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 EvnBETR model

and hence these data provide useful information on the effectives of international agreements such as the Stockholm Convention and UN/ECE POPs protocol.

A manuscript covering the temporal trends of PBDEs in the UK environment has been published in Environmental Pollution (Birgul *et al.* 2012).

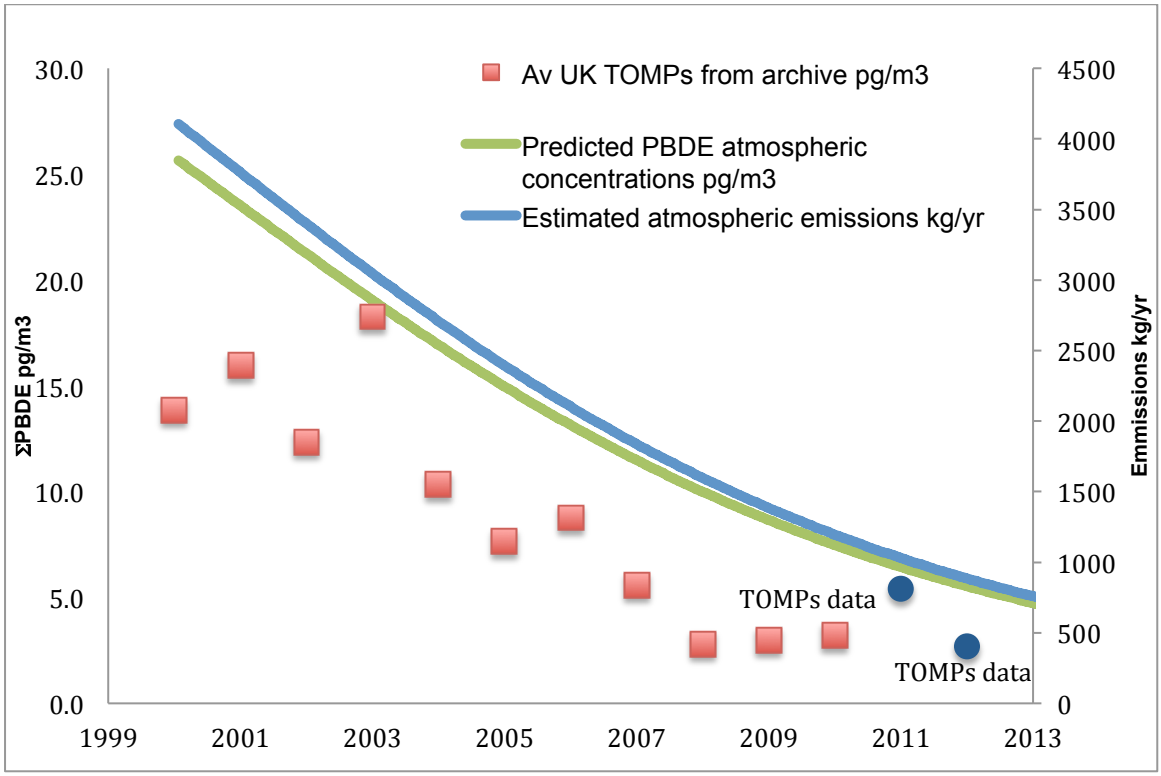


Figure 7. Comparison of estimated emissions, predicted atmospheric concentrations, UK ambient air data derived from the TOMPs archive and contemporary TOMPs data for ΣPBDEs.

8 REFERENCES

1. Alcock, R. E.; Johnston, A. E.; McGrath, S. P.; Berrow, M. L.; Jones, K. C., Long-term changes in the polychlorinated biphenyl content of United-Kingdom soils. Environmental Science & Technology 1993, 27, (9), 1918-1923.
2. Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C. 2002. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach: 2. Emissions. Science of Total Environment 290, 199-224.
3. Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K.C. and Sweetman, A.J. (2012) Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom Original Research Article. Environmental Pollution, 169, Pages 105-111
4. 10 years of data from the National Air Pollution Surveillance (NAPS) network. Data summary from 1999 to 2008. Analysis and Air Quality Section, Air Quality Research Division, Science and Technology Branch, Environment Canada
5. Coutinho, M.; Pereira, M.; Borrego, C. Monitoring of ambient air PCDD/F levels in Portugal. Chemosphere 2007, 67, 1715– 1721.
6. Danse, I. R., Jaeger, R. J., Kava, R., Kroger, M., London, W. M., Lu, F. C., Maickel, R. P., McKetta, J. J., Newwell, G. W., Shindell, S., Stare, F. J., Whelan, E. M. 1997. Position paper of the American Council on Science and Health: Public health concerns about environmental polychlorinated biphenyls (PCBs), Ecotoxicology and Environmental Safety, 38, 71-84.
7. Eduljee, G.H. 1988. PCBs in the environment. Chemistry in Britain, 24, 241-244.
8. Gouin T.; Thomas G. O.; Cousins I.; Barber J.; Mackay D. and Jones K. C. Air-surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. Environ. Sci. Technol., 2002, 38, 1426-1434.
9. Hites, R.A. (2004) Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. Environ. Sci. Technol., 38 (4), 945–956
10. Hassanin, A.; Lee, R. G. M.; Johnston, A. E. and Jones, K. C. Reductions and changing patterns of ambient PCDD/Fs in the UK: Evidence and implications. *Chemosphere* **2006,** *65*, 530-539.
11. Harrad, S. J., Sewart, A. P., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S. R., Jones, K. C. 1994. Polychlorinated biphenyls (PCBs) in the British environment: Sinks, sources and temporal trends. Environmental Pollution, 85, 131-146.
12. Kjeller, L. O.; Jones, K. C.; Johnston, A. E. and Rapper, C. Evidence for a decline in Atmospheric Emissions of PCDD/Fs in the U.K. *Environ. Sci. Technol.* **1996,** *30*, 1398 – 1403.
13. Katsoyiannis, A., Gioia, R., Sweetman, A.J. and Jones, K.C. (2010) Continuous Monitoring of PCDD/Fs in the UK Atmosphere: 1991-2008 Environ. Sci. Technol., 44, 5735–5740
14. Lee, R.G.M., Thomas, G.O. and Jones, K.C. (2004) PBDEs in the Atmosphere of Three Locations in Western Europe. Environ. Sci. Technol., 38 (3), 699–706
15. Ma, Y., Salamova, A. Venier, M. and Hites, R.A. (2013) Has the Phase-Out of PBDEs Affected Their Atmospheric Levels? Trends of PBDEs and Their

Replacements in the Great Lakes Atmosphere Environ. Sci. Technol., 47, 11457–11464
16. Schuster, J., Gioia, R., Sweetman, A.J. and Jones, K.C. (2010) Temporal Trends and Controlling Factors for Polychlorinated Biphenyls (PCBs) in the UK Atmosphere (1991-2008). Environmental Science and Technology, 44, 8068-8074
17. Thomas, G. O.; Sweetman, A. J.; Parker, C. A.; Kreibich, H.; Jones, K. C. Development and validation of methods for the trace determination of PCBs in biological matrices. Chemosphere, 1998, 36, 2447-2459.
18. Van der Gon, D. H. A. C.; van het Bolscher, M.; Visschedijk, A, J, H.; Zandveld, P. Y. J. TNO report: Study to the effectiveness of the Persistent Organic Pollutants UNECE Protocol and cost of additional measures. Phase I. Estimation of the emission reduction resulting from the implementation of the POPs protocol. 2005.
19. de Voogt, P., Brinkman, U. A. T. 1989. Production, properties and usage of polychlorinated biphenyls. In: Kimbrough R. D., Jensen A A (Eds). Halogenated biphenyls, terphenyls, naphthalenes, debenzodioxins and related products. Elsevier-North, Amsterdam, Holland. Safety, 38, 71-84.
20. UKFSA. Dioxins and Dioxin-Like PCBs in farmed and wild fish and shellfish. Report 0306, 2006**,** at http://www.food.gov.uk/science/surveillance/.

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

MANCHESTER 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
2,3,7,8-TCDF	39	16	12	48	29
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	2.8	<0.44	<0.44	1.4	1
1,2,3,6,7,8-HxCDD	4.2	<0.44	<0.44	2.7	1.7
1,2,3,4,7,8-HxCDD	3.8	<0.44	<0.44	<0.44	0.94
1,2,3,4,6,7,8-HpCDD	1.6	0.5	0.38	2.3	1.2
OCDD	0.021	<0.0274	<0.0246	0.022	0.014
ΣTEQ dioxins and furans	**52**	**16**	**12**	**52**	**33**
3,4,4'5-TetraCB (PCB_81)	0.03	0.061	0.032	0.033	0.039
3,3',4,4'-TetraCB (PCB_77)	<0.0271	0.011	<0.0275	<0.0285	<0.0284
3,3',4,4',5-PentaCB (PCB_126)	2.8	3.2	4.2	4.2	3.6
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

LONDON 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4. 12**	**Average 2012**
2,3,7,8-TCDF	26	11	5.4	11	13
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	1	<0.44	<0.44	<0.44	<0.44
1,2,3,6,7,8-HxCDD	1.8	<0.44	<0.44	<0.44	0.46
1,2,3,4,7,8-HxCDD	1.4	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDD	1.4	0.51	0.37	1.7	0.98
OCDD	0.021	<0.0277	<0.0259	0.026	0.015
ΣTEQ dioxins and furans	**31**	**12**	**5.8**	**13**	**15**
3,4,4',5-TetraCB (PCB_81)	0.029	0.044	0.068	0.029	0.043
3,3',4,4'-TetraCB (PCB_77)	<0.0249	<0.0266	<0.0295	<0.024	<0.0262
3,3',4,4',5-PentaCB (PCB_126)	1.9	2.3	<0.44	1.7	1.5
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	<0.044	<0.044

HAZELRIGG 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4. 12**	**Average 2012**
2,3,7,8-TCDF	13	4.3	2.6	14	8.3
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	0.54	<0.044	<0.044	0.77	0.33
OCDD	0	0.017	<0.024	0.031	0.012
ΣTEQ dioxins and furans	**13**	**4.4**	**2.6**	**15**	**8.7**
3,4,4',5-TetraCB (PCB_81)	0.013	0.013	0.012	<0.0281	0.011
3,3',4,4'-TetraCB (PCB_77)	<0.024	<0.024	<0.024	<0.024	<0.024
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 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4. 12**	**Average 2012**
2,3,7,8-TCDF	3.6	1.4	0.62	1.9	1.9
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	0.33	<0.044	<0.044	0.19	0.13
OCDD	0.03	0.011	0.015	0.012	0.017
ΣTEQ dioxins and furans	**0.24**	**0.086**	**0.037**	**0.13**	**0.12**
3,4,4',5-TetraCB (PCB_81)	<0.024	<0.0254	<0.0269	<0.024	<0.0247
3,3',4,4'-TetraCB (PCB_77)	<0.024	<0.024	<0.024	<0.024	<0.024
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 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4. 12**	**Average 2012**
2,3,7,8-TCDF	7	2.4	2.5	4.8	4.2
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	0.42	<0.044	0.13	0.76	0.33
OCDD	0.02	<0.024	<0.024	0	<0.025
ΣTEQ dioxins and furans	**7.5**	**2.4**	**2.6**	**4.8**	**4.3**
3,4,4',5-TetraCB (PCB_81)	<0.0251	<0.0285	<0.0289	<0.0262	<0.0272
3,3',4,4'-TetraCB (PCB_77)	<0.024	<0.024	<0.024	<0.024	<0.024
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 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4. 12**	**Average 2012**
2,3,7,8-TCDF	12	4.3	6.2	9.8	8.1
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	<0.0204	<0.0204	<0.0204	<0.0204	<0.0204
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	1.4	<0.44	<0.44	<0.44	<0.44
1,2,3,4,6,7,8-HpCDD	0.99	0.18	0.28	0.91	0.59
OCDD	<0.024	0.036	0.014	0.035	0.021
ΣTEQ dioxins and furans	**15**	**4.5**	**6.5**	**11**	**9.1**
3,4,4',5-TetraCB (PCB_81)	<0.0271	<0.0275	0.011	<0.0275	<0.0282
3,3',4,4'-TetraCB (PCB_77)	<0.024	<0.024	<0.024	<0.024	<0.024
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 2010 PCB data (All data in pg.m^{-3})

LONDON 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	22.97	31.84	69.10	27.06	37.74
PCB_22	23.96	32.61	47.74	18.18	30.63
PCB_44	2.28	2.11	1.29	2.01	1.92
PCB_49	3.56	6.05	10.33	5.01	6.24
PCB_52	11.36	14.07	29.61	15.09	17.53
PCB_70	8.26	10.03	19.12	7.83	11.31
PCB_74	2.24	2.61	2.98	1.30	2.28
PCB_87	2.40	4.08	6.11	2.81	3.85
PCB_95	6.99	10.89	13.81	16.01	11.93
PCB_99	1.85	1.14	3.37	2.21	2.14
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.98	2.30	2.70	0.93	1.73
PCB_110	4.96	7.00	9.07	6.68	6.92
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	2.01	2.92	4.21	2.31	2.86
PCB_123	0.34	<0.02	<0.02	1.55	0.47
PCB_138	3.06	3.92	4.53	6.67	4.54
PCB_141	0.68	1.12	1.03	2.13	1.24
PCB_149	3.62	5.29	6.37	14.65	7.48
PCB_151	1.13	1.87	2.29	6.24	2.88
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	<0.02	<0.02	0.21	<0.02	0.05
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.28	0.42	0.52	0.36	0.39
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	0.31	0.47	<0.02	0.19
PCB_174	0.57	0.81	0.97	1.69	1.01
PCB_180	0.75	1.01	1.26	1.86	1.22
PCB_183	0.41	0.53	0.64	1.11	0.67
PCB_187	0.96	1.35	1.56	2.46	1.58
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	0.10	0.20	0.08
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	0.13	0.21	0.28	0.17	0.20
PCB_153+132	3.99	6.05	6.91	11.98	7.23
PCB_31+28	35.21	33.35	58.30	27.57	38.61
PCB_41/64	15.66	27.73	69.00	29.06	35.36
PCB_60/56	2.99	2.92	6.95	2.79	3.91
PCB_90/101	7.45	10.24	13.11	14.01	11.20
PCB_Σ7PCB	**63.8**	**71.6**	**117.9**	**79.5**	**83.2**

MANCHESTER 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	11.40	21.46	37.18	19.16	22.30
PCB_22	6.23	9.60	12.42	5.01	8.31
PCB_44	2.20	5.33	1.67	3.36	3.14
PCB_49	1.68	5.23	6.36	4.92	4.55
PCB_52	12.64	30.77	54.98	20.52	29.73
PCB_70	7.47	19.80	23.15	8.77	14.80
PCB_74	2.38	4.37	3.42	2.74	3.23
PCB_87	4.84	15.51	16.01	6.15	10.63
PCB_95	12.29	29.25	33.89	16.80	23.06
PCB_99	3.62	9.87	9.77	3.95	6.80
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	1.51	5.19	5.45	1.92	3.52
PCB_110	8.77	27.03	27.40	11.64	18.71
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	5.04	15.27	14.22	6.37	10.22
PCB_123	0.47	2.05	0.95	0.43	0.97
PCB_138	4.77	12.40	13.70	5.26	9.03
PCB_141	1.02	2.51	2.50	0.78	1.70
PCB_149	5.35	13.44	13.73	6.06	9.64
PCB_151	1.41	3.58	3.73	1.67	2.60
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	0.37	<0.02	0.11	<0.02	0.12
PCB_157	<0.02	<0.02	0.25	0.32	0.14
PCB_158	0.44	1.19	1.25	0.38	0.81
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	0.72	0.51	<0.02	0.31
PCB_174	0.61	1.13	0.92	0.53	0.80
PCB_180	1.03	1.38	1.32	0.84	1.15
PCB_183	0.46	0.75	0.69	0.41	0.58
PCB_187	0.86	1.64	1.55	0.83	1.22
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	0.20	0.16	0.26	0.15
PCB_153+132	5.91	16.63	16.93	6.42	11.47
PCB_31+28	8.94	20.24	24.25	12.48	16.48
PCB_41/64	22.46	30.98	103.96	10.80	42.05
PCB_60/56	2.09	4.84	6.55	1.40	3.72
PCB_90/101	13.33	31.43	33.72	16.06	23.63
PCB_Σ7PCB	**51.7**	**128.1**	**159.1**	**68.0**	**101.7**

HAZELRIGG 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	14.73	47.65	47.80	8.62	29.70
PCB_22	3.95	9.43	12.16	5.28	7.70
PCB_44	<0.02	0.37	0.88	0.56	0.45
PCB_49	0.35	0.92	1.00	1.92	1.05
PCB_52	10.33	11.41	13.07	5.99	10.20
PCB_70	4.86	5.03	7.57	1.06	4.63
PCB_74	4.78	5.16	9.72	3.02	5.67
PCB_87	0.50	<0.02	<0.02	<0.02	0.13
PCB_95	2.39	2.70	2.61	1.85	2.39
PCB_99	0.94	0.81	<0.02	0.43	0.55
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	2.24	4.26	2.60	2.02	2.78
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	<0.02	<0.02	<0.02	1.74	0.43
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	1.01	1.06	0.81	0.44	0.83
PCB_141	0.37	0.85	0.82	0.06	0.52
PCB_149	1.62	1.56	2.22	1.18	1.64
PCB_151	1.27	1.49	1.56	0.56	1.22
PCB_155	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_156	<0.02	<0.02	0.42	<0.02	0.11
PCB_157	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_158	0.43	0.98	0.63	0.32	0.59
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	0.11	<0.02	0.09	0.05
PCB_174	0.30	0.32	0.33	0.18	0.28
PCB_180	0.43	0.44	0.37	0.20	0.36
PCB_183	0.20	0.14	0.13	<0.02	0.12
PCB_187	0.61	0.60	0.70	0.35	0.56
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	0.09	0.12	<0.02	0.05
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	<0.02	0.18	0.11	<0.02	0.07
PCB_153+132	1.25	1.27	1.10	0.57	1.05
PCB_31+28	10.37	22.53	8.00	6.27	11.79
PCB_41/64	47.08	45.29	32.63	15.92	35.23
PCB_60/56	1.85	4.10	4.58	1.10	2.91
PCB_90/101	4.49	5.53	2.84	3.59	4.11
PCB_Σ7PCB	**27.9**	**42.2**	**26.2**	**18.8**	**28.8**

AUCHENCORTH 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	5.43	19.72	11.99	7.43	11.14
PCB_22	1.64	3.69	1.86	6.66	3.46
PCB_44	0.82	0.82	1.06	0.76	0.87
PCB_49	0.46	1.04	0.89	0.89	0.82
PCB_52	2.21	5.86	3.66	2.68	3.60
PCB_70	1.78	3.23	2.90	1.21	2.28
PCB_74	0.51	1.94	1.15	0.33	0.98
PCB_87	<0.02	<0.02	<0.02	0.23	0.06
PCB_95	0.73	1.39	1.81	1.44	1.34
PCB_99	<0.02	0.32	0.33	0.22	0.22
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	0.32	0.46	0.58	0.35	0.43
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	<0.02	<0.02	<0.02	0.25	0.06
PCB_123	0.08	<0.02	<0.02	0.15	0.06
PCB_138	0.39	0.52	0.67	0.62	0.55
PCB_141	0.29	0.48	0.43	0.11	0.33
PCB_149	0.36	0.67	0.85	1.26	0.79
PCB_151	0.13	0.24	0.31	0.52	0.30
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	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	0.09	<0.02	0.14	0.06
PCB_174	0.08	0.13	0.12	0.15	0.12
PCB_180	<0.02	0.21	0.20	0.25	0.17
PCB_183	<0.02	0.08	0.08	0.16	0.08
PCB_187	0.10	0.16	0.18	0.25	0.17
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	0.30	0.67	0.89	1.14	0.75
PCB_31+28	2.73	3.47	5.35	6.10	4.41
PCB_41/64	8.24	17.16	10.82	8.43	11.16
PCB_60/56	<0.02	1.06	0.25	0.18	0.37
PCB_90/101	0.46	0.82	1.32	1.03	0.91
PCB_Σ7PCB	**6.09**	**11.56**	**12.10**	**12.07**	**10.46**

HIGH MUFFLES 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	9.55	14.65	21.81	15.25	15.31
PCB_22	4.46	5.10	6.21	4.26	5.01
PCB_44	0.34	0.46	<0.02	<0.02	0.20
PCB_49	0.71	0.64	2.39	<0.02	0.94
PCB_52	3.46	3.36	5.03	3.95	3.95
PCB_70	2.02	2.16	3.40	0.44	2.01
PCB_74	1.82	<0.02	<0.02	0.89	0.68
PCB_87	0.33	0.17	<0.02	<0.02	0.12
PCB_95	0.91	0.35	1.57	0.59	0.85
PCB_99	0.16	0.19	0.82	0.35	0.38
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.18	0.35	0.42	0.13	0.27
PCB_110	0.65	0.41	1.12	0.01	0.55
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	<0.02	0.45	<0.02	0.11	0.14
PCB_123	0.12	<0.02	<0.02	0.13	0.06
PCB_138	0.61	0.94	1.67	0.38	0.90
PCB_141	0.15	0.17	<0.02	<0.02	0.08
PCB_149	0.63	0.58	1.00	0.57	0.69
PCB_151	0.22	0.08	0.40	0.26	0.24
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	<0.02	<0.02	0.08	<0.02	0.02
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	0.10	<0.02	<0.02	0.02
PCB_174	0.10	0.07	0.19	0.19	0.14
PCB_180	0.15	0.30	0.32	0.24	0.25
PCB_183	0.08	0.14	0.12	0.15	0.12
PCB_187	0.17	0.14	0.36	0.25	0.23
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	0.69	0.87	1.29	0.57	0.85
PCB_31+28	4.42	11.81	5.43	7.17	7.21
PCB_41/64	12.95	24.77	15.96	16.07	17.44
PCB_60/56	0.57	0.33	1.13	0.36	0.60
PCB_90/101	0.65	0.15	0.49	0.44	0.43
PCB_Σ7PCB	**10.0**	**17.9**	**14.2**	**12.9**	**13.7**

WEYBOURNE 2012	Q1.12	Q2.12	Q3.12	Q4. 12	Average 2012
PCB_18	10.65	19.05	22.31	10.77	15.70
PCB_22	5.76	7.28	11.03	4.50	7.14
PCB_44	0.37	0.79	1.30	0.50	0.74
PCB_49	1.04	0.81	2.38	1.24	1.37
PCB_52	3.32	5.42	6.03	3.11	4.47
PCB_70	0.94	1.13	2.70	0.85	1.41
PCB_74	0.35	0.45	0.47	0.47	0.43
PCB_87	0.24	<0.02	0.93	0.31	0.37
PCB_95	1.11	1.55	2.34	1.77	1.69
PCB_99	0.41	0.45	0.44	0.34	0.41
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	0.08	0.14	0.29	<0.02	0.13
PCB_110	0.64	0.87	1.30	0.81	0.91
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	0.50	0.28	0.35	0.32	0.36
PCB_123	0.25	0.15	<0.02	0.16	0.14
PCB_138	0.72	1.02	1.42	1.07	1.06
PCB_141	0.13	0.09	<0.02	0.12	0.09
PCB_149	0.73	0.95	1.34	1.36	1.10
PCB_151	0.20	0.32	0.45	0.53	0.38
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	0.09	<0.02	<0.02	<0.02	0.02
PCB_167	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.16	0.16	0.21	0.18	0.18
PCB_180	0.20	0.16	0.27	0.31	0.23
PCB_183	0.08	0.11	0.16	0.13	0.12
PCB_187	0.25	0.26	0.34	0.29	0.28
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	0.10	0.08	<0.02	0.07	0.06
PCB_153+132	0.97	1.20	1.55	1.46	1.29
PCB_31+28	6.13	9.58	20.68	6.20	10.65
PCB_41/64	5.63	11.00	8.60	5.12	7.59
PCB_60/56	0.44	0.66	0.94	0.34	0.59
PCB_90/101	0.92	1.27	2.15	1.55	1.47
PCB_Σ7PCB	**12.8**	**18.9**	**32.5**	**14.0**	**19.5**

Appendix 3. PBDE data for 2012. (All data in pg.m^{-3})

PBDE LONDON 2012	Q1.12	Q2.12	Q3.12	Q4.12	Average 2012
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	0.39	0.58	0.38	0.45
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	0.35	0.35
BDE_47	1.24	2.03	2.22	3.22	2.18
BDE_49	0.36	0.36	0.39	0.47	0.40
BDE_66	<0.02	<0.02	0.26	0.36	0.31
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	0.32	0.44	0.43	0.37	0.39
BDE_99	0.85	1.24	1.39	2.56	1.51
BDE_100	<0.02	0.33	0.29	0.86	0.49
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	0.65	0.53	0.28	1.24	0.67
BDE_154	0.32	0.19	<0.02	0.63	0.38
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	1.86	0.80	0.81	3.77	1.81
BDE_196	0.55	0.45	<0.02	0.65	0.55
BDE_197	0.53	0.41	0.57	0.79	0.58
BDE 47 + 99	**2.10**	**3.28**	**3.61**	**5.79**	**3.69**

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

PBDE MANCHESTER 2012	Q1.12	Q2.12	Q3.12	Q4.12	Average 2012
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.34	0.38	0.36
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	0.32	0.32
BDE_47	2.83	3.39	3.89	2.94	3.26
BDE_49	0.59	0.51	0.48	0.72	0.57
BDE_66	<0.02	<0.02	0.30	<0.02	0.30
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	0.47	0.48	0.47
BDE_99	1.22	1.30	1.76	2.68	1.74
BDE_100	<0.02	0.46	0.57	0.79	0.60
BDE_119	<0.02	<0.02	<0.02	0.34	0.34
BDE_138	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_153	1.93	0.80	0.47	2.11	1.33
BDE_154	0.78	0.30	0.26	2.21	0.89
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	5.39	1.76	0.99	8.02	4.04
BDE_196	0.93	0.51	0.50	1.71	0.91
BDE_197	0.97	0.44	0.35	1.97	0.93
BDE 47 + 99	4.05	4.69	5.65	5.62	5.00

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

PBDE AUCHENCORTH 2012	Q1.12	Q2.12	Q3.12	Q4.12	Average 2012
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	0.52	0.95	1.03	0.52	0.76
BDE_49	<0.02	0.18	0.19	0.18	0.18
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	0.18	<0.02	0.22	0.20
BDE_99	0.54	0.33	0.53	0.29	0.42
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	0.21	0.18	<0.02	<0.02	0.20
BDE_154	<0.02	<0.02	<0.02	0.11	0.11
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	0.45	0.41	0.37	0.60	0.46
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	**1.06**	**1.27**	**1.56**	**0.82**	**1.18**

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

PBDE HIGH MUFFLES 2012	**Q1.12**	**Q2.12**	**Q3.12**	**Q4.12**	**Average 2012**
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	0.21	<0.02	0.21
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	0.74	1.10	1.40	0.72	0.99
BDE_49	0.25	0.31	0.29	0.29	0.28
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	0.21	0.28	0.27	0.35	0.28
BDE_99	0.34	0.40	0.64	1.07	0.61
BDE_100	<0.02	<0.02	<0.02	0.18	0.18
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	0.23	<0.02	0.58	0.38
BDE_154	0.15	<0.02	<0.02	0.30	0.23
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	0.90	0.63	0.40	1.64	0.89
BDE_196	0.26	<0.02	<0.02	0.42	0.34
BDE_197	0.29	<0.02	<0.02	0.38	0.34
BDE 47 + 99	**1.09**	**1.50**	**2.04**	**1.79**	**1.61**

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

PBDE HAZELRIGG 2012	Q1.12	Q2.12	Q3.12	Q4.12	Average 2012
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	0.20	0.22	0.28	0.17	0.22
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	0.17	0.17
BDE_47	0.78	1.18	0.80	0.70	0.87
BDE_49	0.16	0.21	0.19	0.27	0.21
BDE_66	<0.02	0.14	0.13	0.18	0.15
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	0.18	0.21	0.23	0.20	0.20
BDE_99	0.65	0.58	0.44	0.56	0.56
BDE_100	0.15	0.17	0.19	0.15	0.17
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	0.35	0.23	0.51	0.37
BDE_154	0.20	0.14	0.08	0.34	0.19
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	0.95	0.50	0.43	2.10	1.00
BDE_196	0.25	0.18	<0.02	0.62	0.35
BDE_197	0.22	0.19	0.18	0.68	0.32
BDE 47 + 99	**1.44**	**1.76**	**1.24**	**1.27**	**1.43**

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

PBDE WEYBOURNE 2012	Q1.12	Q2.12	Q3.12	Q4.12	Average 2012
BDE_17	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_28	<0.02	<0.02	<0.02	0.16	0.16
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	0.16	0.16
BDE_47	1.29	1.03	1.41	2.52	1.56
BDE_49	0.19	0.20	0.27	0.35	0.25
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	0.26	0.31	0.38	0.23	0.30
BDE_99	1.71	1.24	1.73	2.12	1.70
BDE_100	0.40	0.26	0.30	0.68	0.41
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	0.66	0.45	0.55	1.04	0.68
BDE_154	0.25	0.15	0.17	0.63	0.30
BDE_166	<0.02	<0.02	<0.02	<0.02	<0.02
BDE_183	1.70	1.08	1.02	3.38	1.80
BDE_196	0.28	0.24	<0.02	0.59	0.37
BDE_197	0.32	0.37	0.26	0.68	0.41
BDE 47 + 99	**3.00**	**2.27**	**3.15**	**4.63**	**3.26**

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