The Lancaster
Environment Centre

Annual Report for 2010 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

Dr Rosalinda Gioia

Dr Andy Sweetman

Professor Kevin Jones

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ

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 2010 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) as well as data for polybrominated diphenyl ethers (PBDEs) for Q4 only, 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 2010, 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 www.airquality.co.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.

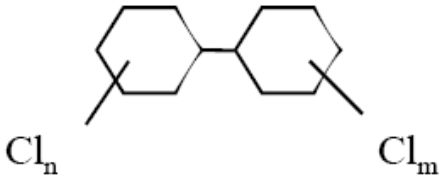
This annual report for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polybrominated diphenyl ethers (PBDEs) (Q4 only) includes:

- 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).

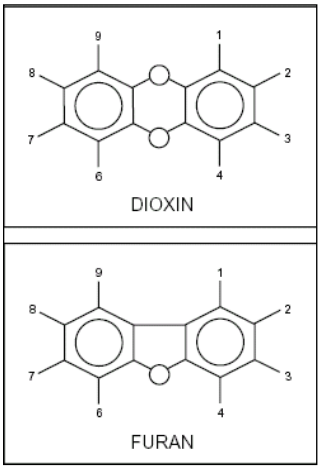


There are 209 different congeners with one to ten chlorines atoms attached. The International Council for the Exploration of the Seas (ICES) 7 PCB congeners generally reported in environmental samples are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB),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

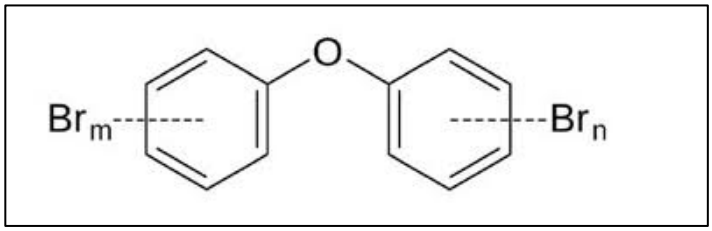
PCBs (e.g. sea and soil) or incidental formation of some congeners during combustion processes (Breivik *et al*., 2002).

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 2008 for the tetra and penta PBDEs in the UK were 2500kg and detailed in a recent Defra report (AEAT/ENV/R2767/WP2 ED47664).

3. TOMPs sites operating in 2010

In 2009 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.

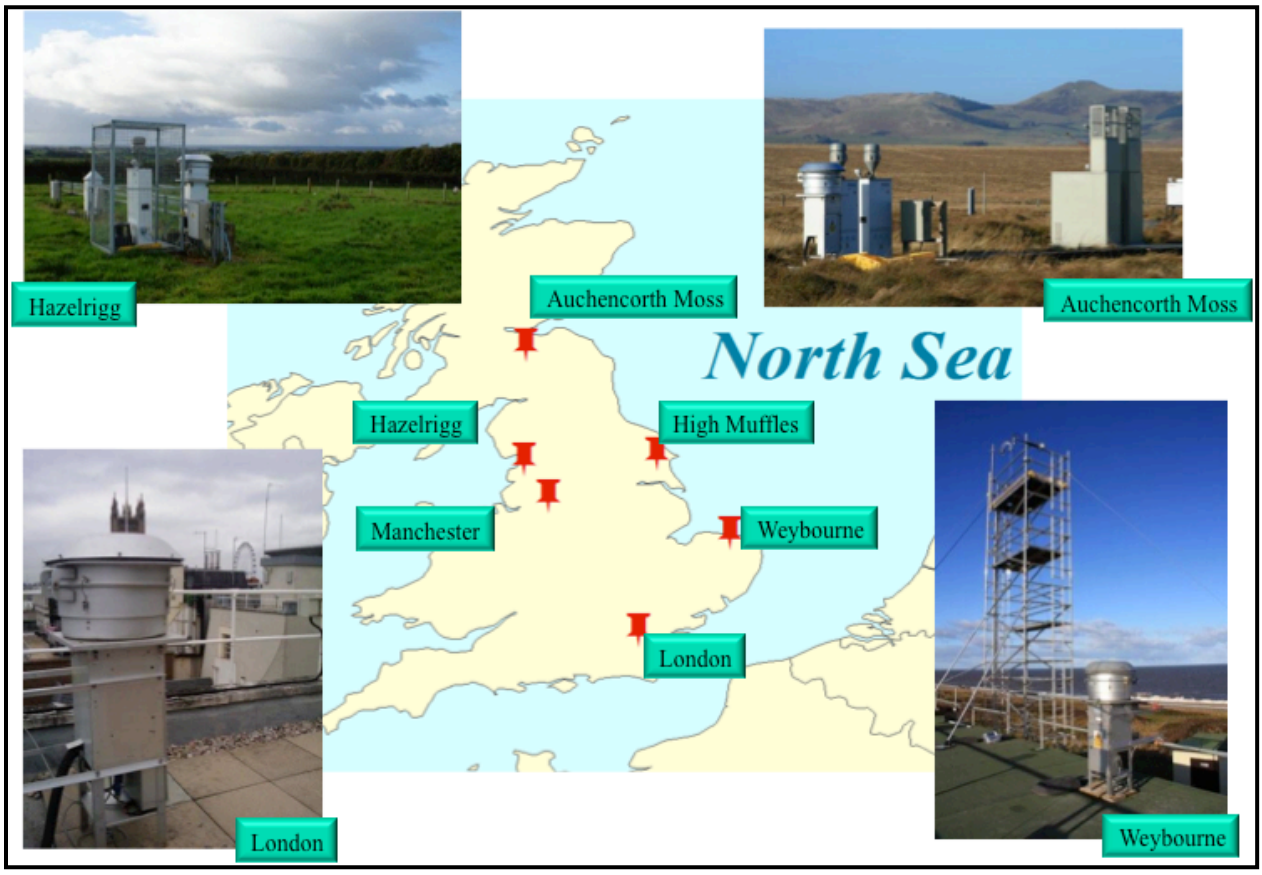


Figure 1. Location map of the current TOMPs sites.

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. More information can be found at:

http://www.lec.lancs.ac.uk/research/chemicals_management/tomps.php

7. RESULTS FOR YEAR 2010

7.1 ***Network Operations***: Table 1 contains information on the bulked air volume (in m^3) and the number of samples bulked for each site and each quarter in 2010. 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). The aim is to obtain an average volume of 500-700m^3 for every two week sampling period to avoid breakthrough of chemicals during sampling, and to ensure the collection of a sufficient level of chemicals within the samples that can be analytically detected. Consequently, the total volume per quarter (bulked volume for 6-7 samples normally collected per each quarter) is approximately 4500-5500 m^3 (see Table 1).

Operational issues during 2010.

The Hi-Volume air samplers at all sites were calibrated during the period April-June 2010 by Lancaster personnel. High Muffles, Manchester and Hazelrigg were calibrated during normal visits for sample collection. Auchencorth Moss and Weybourne were visited by Lancaster personnel for calibration, equipment servicing and sample collection in spring 2010.

The Hazelrigg site has 5 samples for Q1 as a result of the sample collected at the beginning of the quarter being lost due to an electrical failure at the site. The electrical supply was re-established and sampling re-started as normal.

The Manchester site has 5 samples in Q2 as a result of sampler failure leading to an unexposed sample.

The Weybourne site has only 5 samples in Q2 as a result of a longer sample (about 4 weeks) collected at the beginning of the quarter. The last sample of Q3 2010 overlapped with the start of Q4 2010 and so was included in the Q4 sample. This resulted in Q4 consisting of 8 samples instead of the usual 7. The sampler failed during the beginning of the quarter and so Q3 consists of 5 samples.

The High Muffles site in Q3 consists of 6 instead of 7 samples because sample 323 (beginning of Q3) was missing due to motor/electrical failure. The last sample of Q4 was a longer than usual sample with 2130 m^3 collected. The sample started on the 23/11/10 and was collected on the 4/01/11. This resulted from difficulties with site access as a result of the adverse weather conditions over that period.

The Auchencorth site in Q3 has 6 samples instead of 7 as a result of sampler failure.

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2009.

QUARTER 1 (Q1) 2010						
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m^3	**4500**	**4407**	**3914**	**4302**	**4478**	**5194**
Number of samples	7	6	5	6	6	6
QUARTER 2 (Q2) 2010						
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m^3	**4351**	**3512**	**4547**	**4074**	**5119**	**4641**
Number of samples	6	5	6	6	7	5
QUARTER 3 (Q3) 2010						
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m^3	**4648**	**5080**	**5654**	**4287**	**4432**	**3221**
Number of samples	7	7	7	6	6	5
QUARTER 4 (Q4) 2010						
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m^3	**5244**	**4135**	**4814**	**4507**	**5171**	**5138**
Number of samples	6	6	6	4	7	8

In this report data for Q1, Q2, Q3 and Q4 2010 are presented for PCBs, co-planar PCBs and PCDDs and PCDFs and PBDEs.

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 2010 ranged from 2.5 to 46 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 46 fg TEQ/m^3 and London 39 fg TEQ/m^3) followed by Hazelrigg (8 fg TEQ/m^3), Auchencorth (5 fg TEQ/m^3), High Muffles (2.8 fg TEQ/m^3) and Weybourne (2.5 fg TEQ/m^3). As with previous years, the two urban sites exhibit higher concentrations of PCDD/Fs than the rural sites by a factor of 10 or greater. 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.

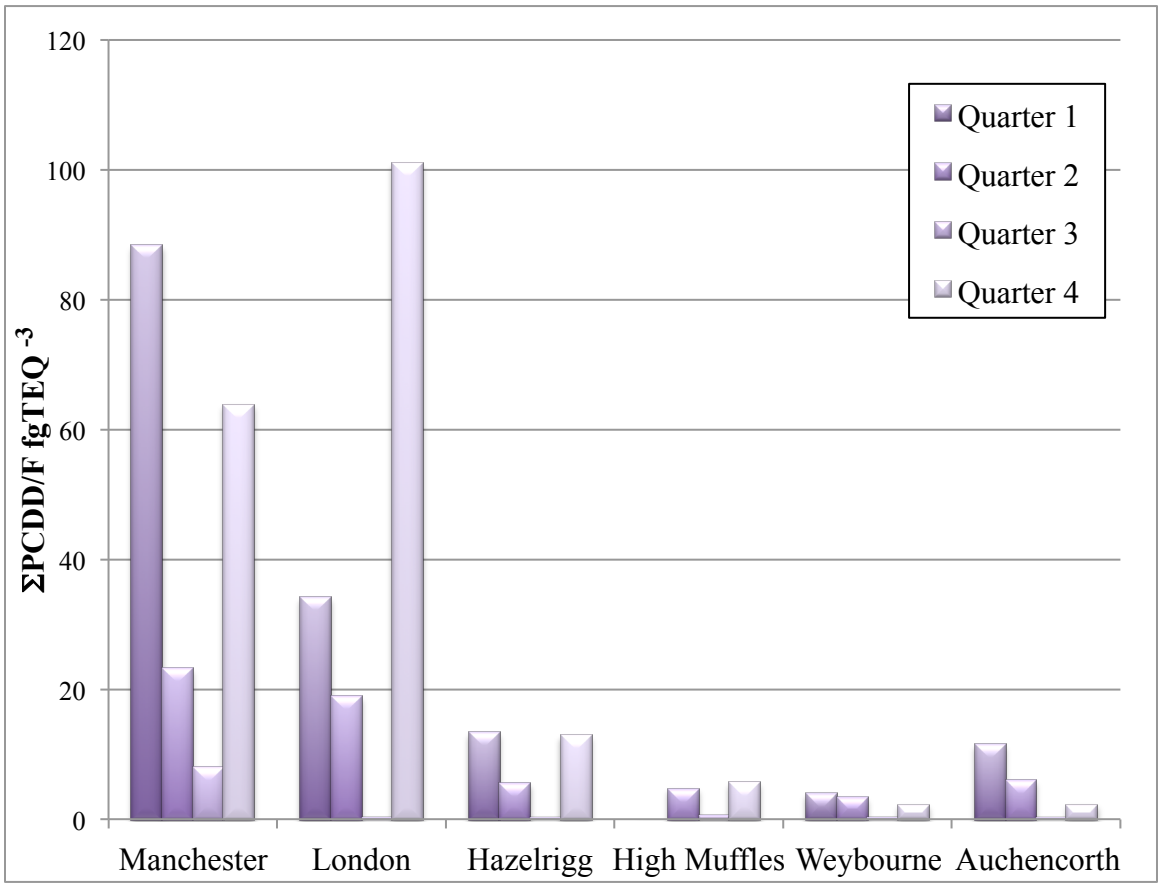
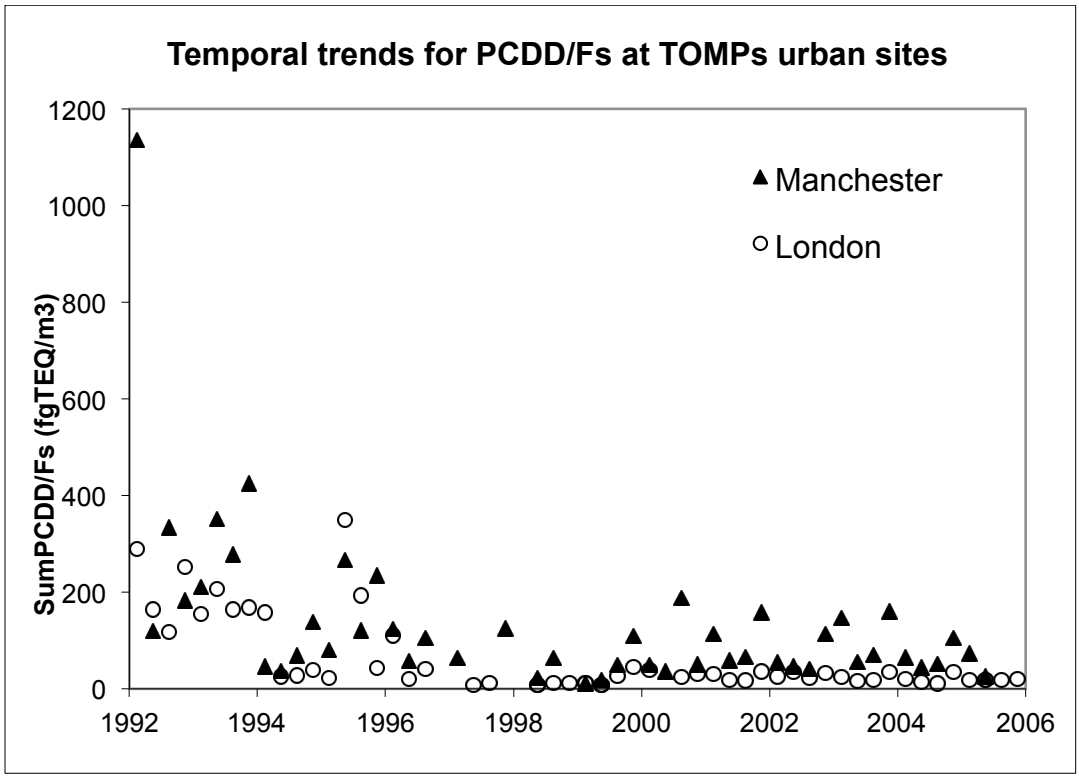


Figure 2. Quarterly PCDD/F data for each TOMPs site in 2010.

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 4.5 and 4.6 years, respectively. The concentration data from Hazelrigg and High Muffles are much lower than the urban sites, but 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 – 2007. During this period PCDD/F emissions reduced from around 1100 g TEQ per year in 1990 to ~225 g TEQ per year in 2000 and further to ~190 g TEQ per year in 2007. The TOMPS program started in the same year (1990) and shows air concentrations generally falling over that period, although there is good evidence that this is actually part of a longer and more systematic decline. Media which are broadly reflective of trends in air – such as herbage and milk – show higher levels in the 1980s than 1990s (Hassanin *et al.,2006* ; Alcock et al., 1996, 1998, Kjeller et al., *1996*), and higher levels still in the 1960s and 1970s. Human dietary intakes of PCDD/Fs are estimated to have declined 4-5 fold between 1982 and 1992 (Van der Gon *et al.,* 2005) and to have declined still further since (UKFSA et al., 2006).



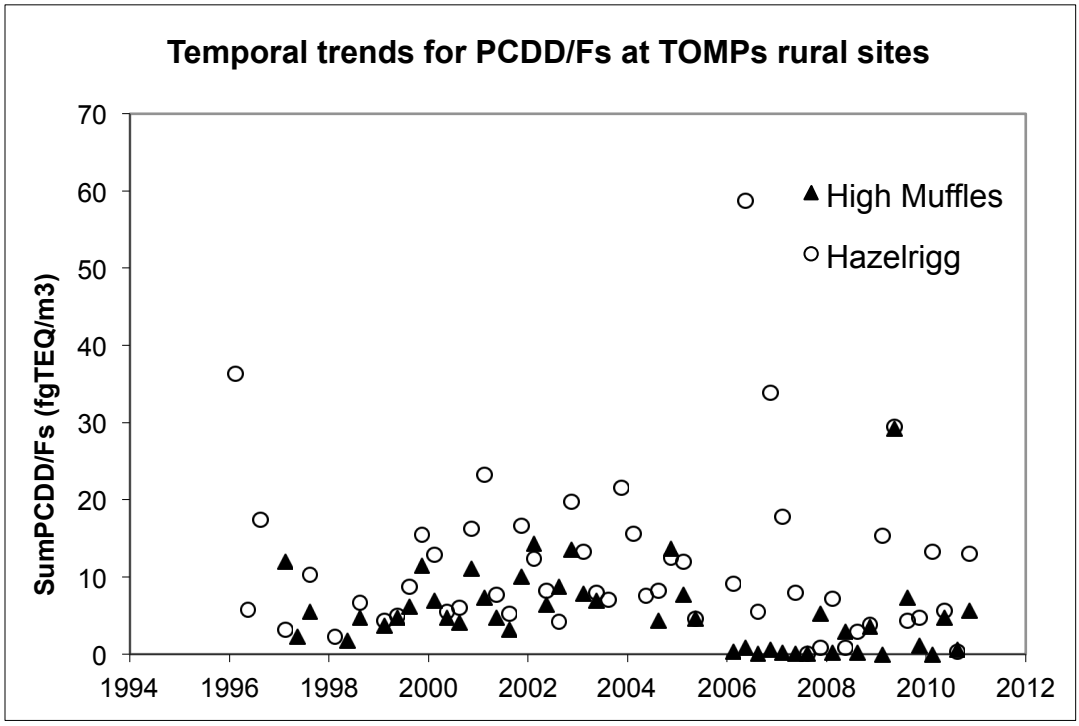


Figure 3. Temporal trends for PCBB/Fs at the urban and rural sites.

7.3 PCBs: Results and discussions

The quarterly PCB concentrations measured at each of the TOMPs sites ranged from 2.6 pg/m^3 to 46 pg/m^3 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, however, both High Muffles and Hazelrigg showed high values in quarter 2, 136 and 96 pg/m^3, respectively. In 2009 the High Muffles dataset contained a similar concentration for quarter 3 (130 pg/m^3) whilst the lowest value was in quarter 1 (1.2 pg/m^3). However, the annual means for 2009 and 2010 were similar 44 and 46 pg/m^3, respectively. The Hazelrigg data in 2009 showed the highest concentration in quarter 3 at 62 pg/m^3 compared to the highest quarter in 2010 occurred in quarter 2 (96 pg/m^3). The annual means, however, were similar for 2009 and 2010 at 29 and 28 pg/m^3, respectively. Given the data represents quarterly averages, it is difficult to determine the reason for High Muffles and Hazelrigg displaying periodic high concentrations given their remote/rural locations; however, these data are from the warmest periods of the year. Therefore, revolatilization of PCBs from surfaces such as soil may be an important process leading to higher concentrations in the atmosphere. However, the elevated concentrations could also be attributed to long-range atmospheric transport from 'source regions' as there are limited local primary sources at these sites.

The urban sites at London and Manchester showed consistent PCB concentrations with previous years and mean values of 16 and 24 pg/m^3, respectively. The ranges for London and Manchester were 6 to 36 pg/m^3 and 11 to 44 pg/m^3, respectively. Concentration data for Weybourne and Auchencorth were the lowest with mean concentrations of 2.6 and 13.3 pg/m^3, respectively. These data are lower than concentrations reported for 2009 which were 34 and 16 pg/m^3 for Weybourne and Auchencorth, respectively.

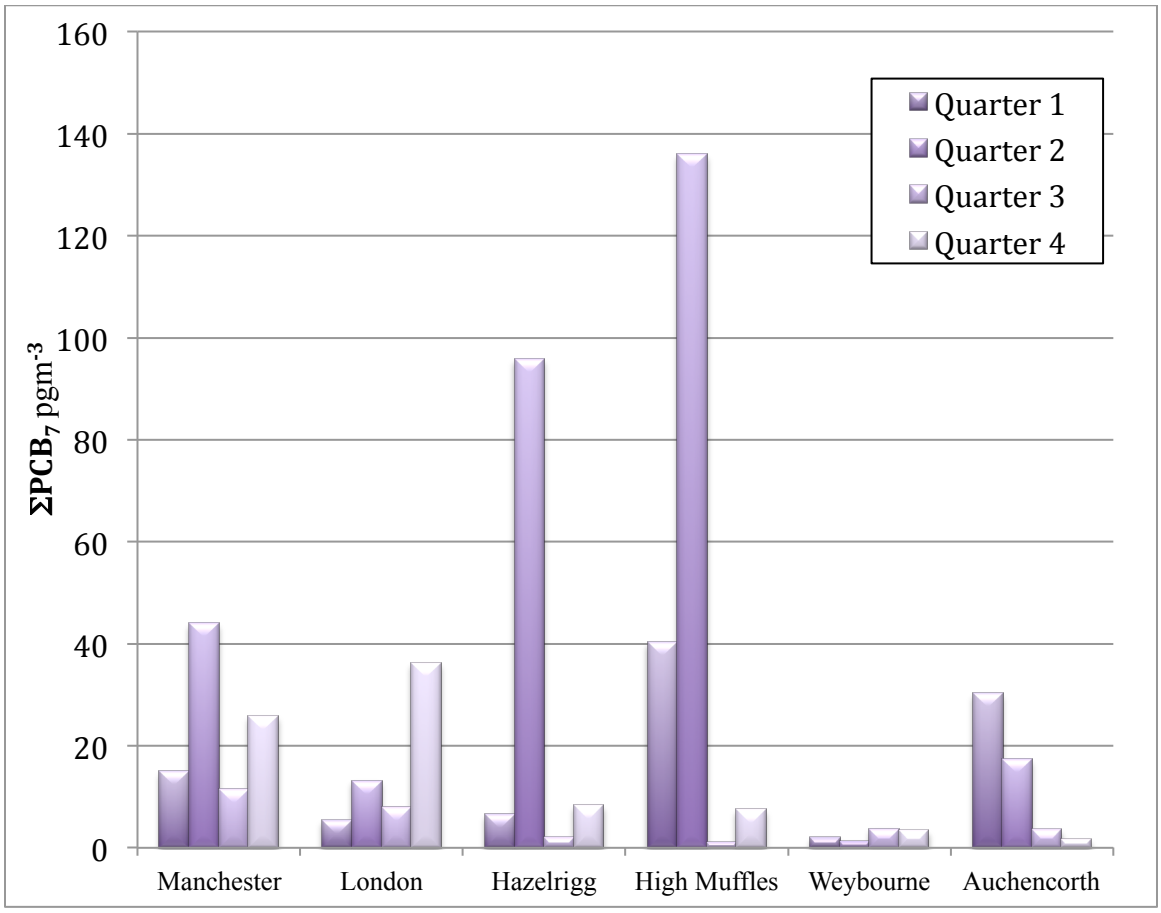


Figure 4. Quarterly ΣPCB_7 data at the TOMPs site for 2010.

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. A key finding of this study from the TOMPs study was that clearance rates (time taken for a 50% decline in concentration) averaged 4.7 ± 1.6 years for all congeners at all sites. These data have only changed slightly with the addition of two further years of data with an average clearance rate of 4.4 ± 1.8 years. Time trend data for individual TOMPs sites for the sum of seven PCBs are presented in Figure 5a-f.

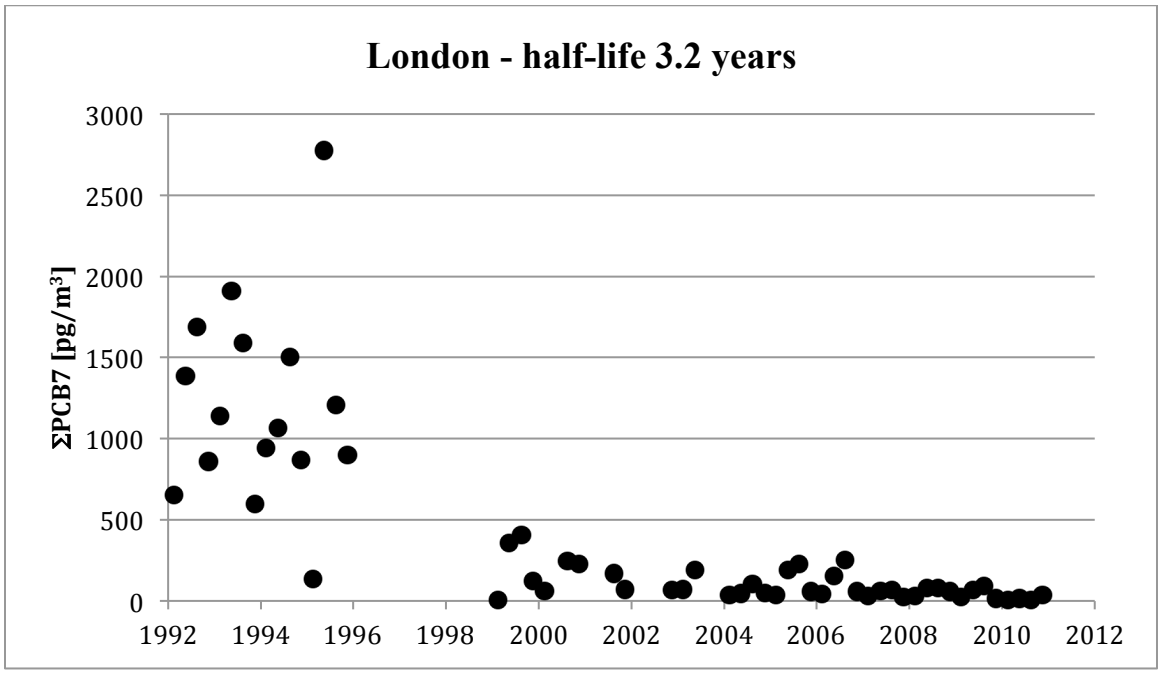


Figure 5a. $\sum_7$PCB temporal trend data for the London TOMPs site.

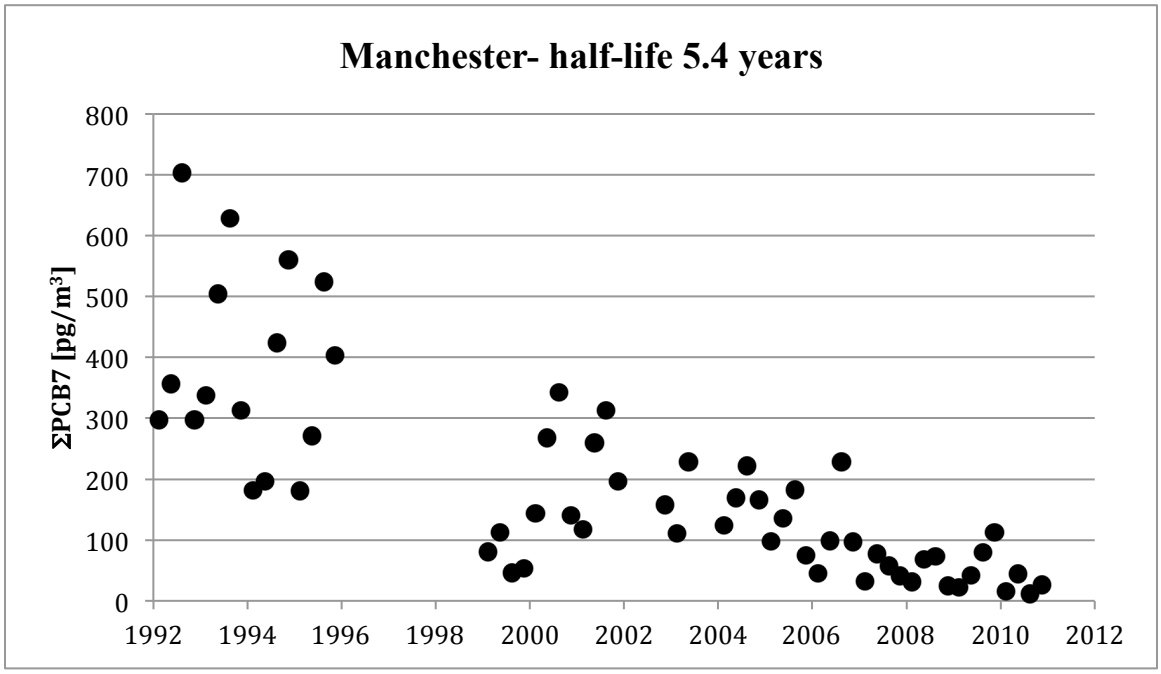


Figure 5b. $\sum_7$PCB temporal trend data for the Manchester TOMPs site.

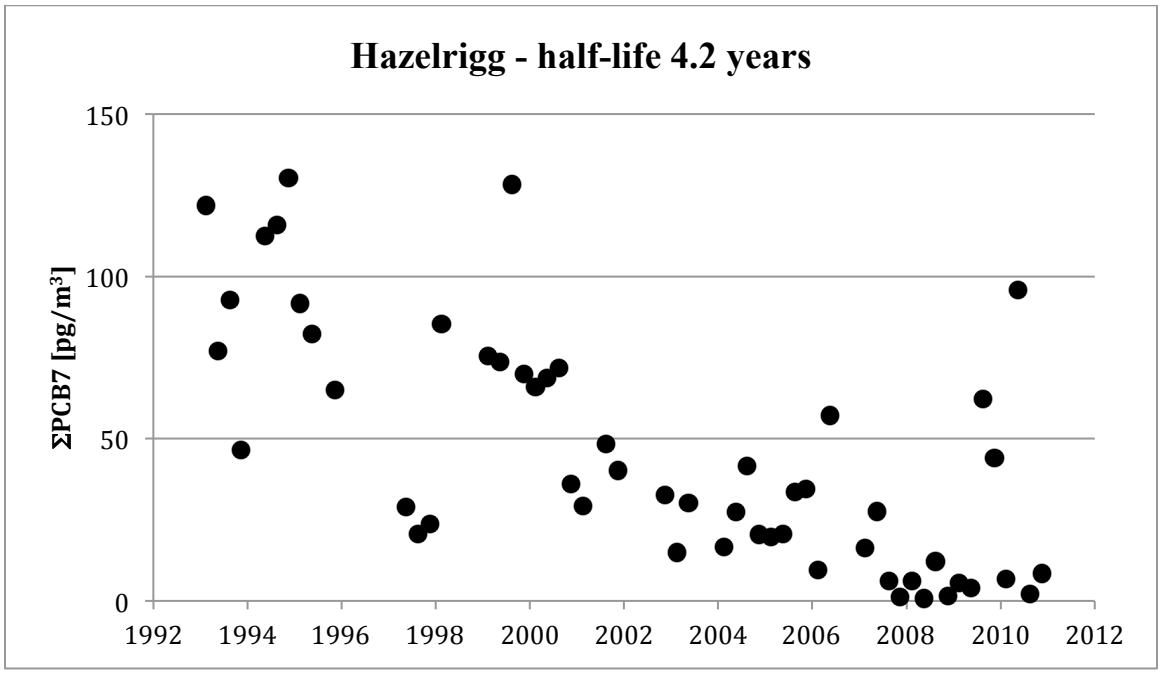


Figure 5c. $\sum_7$PCB temporal trend data for the Hazelrigg TOMPs site.

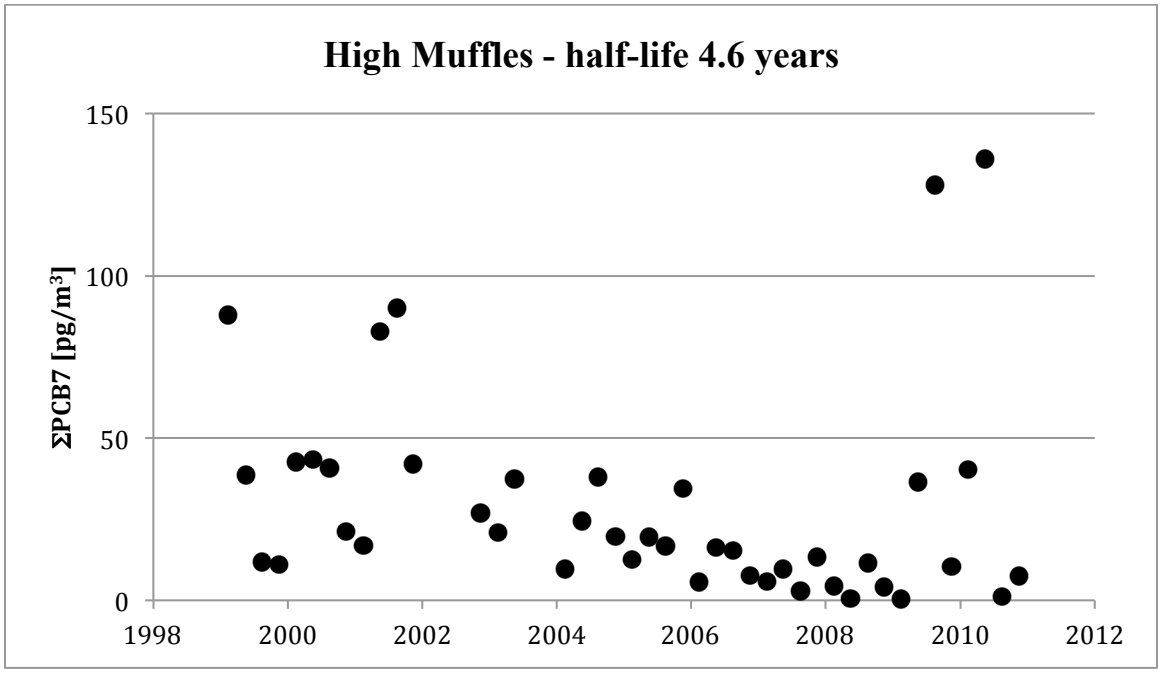


Figure 5d. $\sum_7$PCB temporal trend data for the High Muffles TOMPs site.

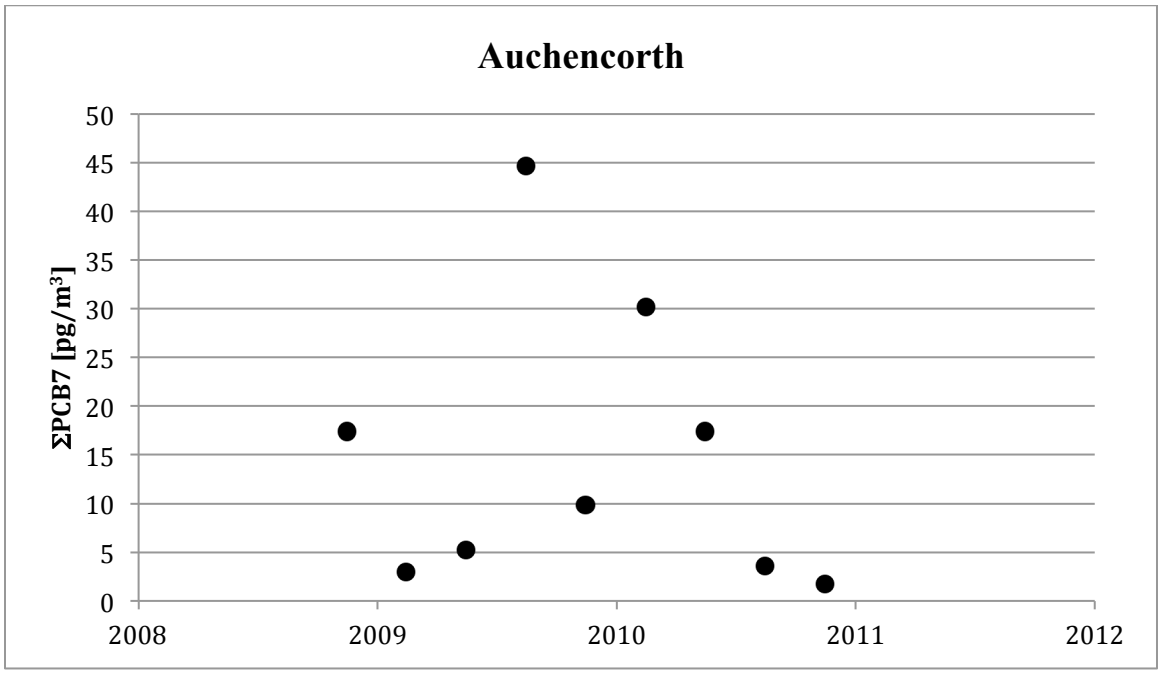


Figure 5e. $\sum_7$PCB temporal trend data for the Auchencorth TOMPs site.

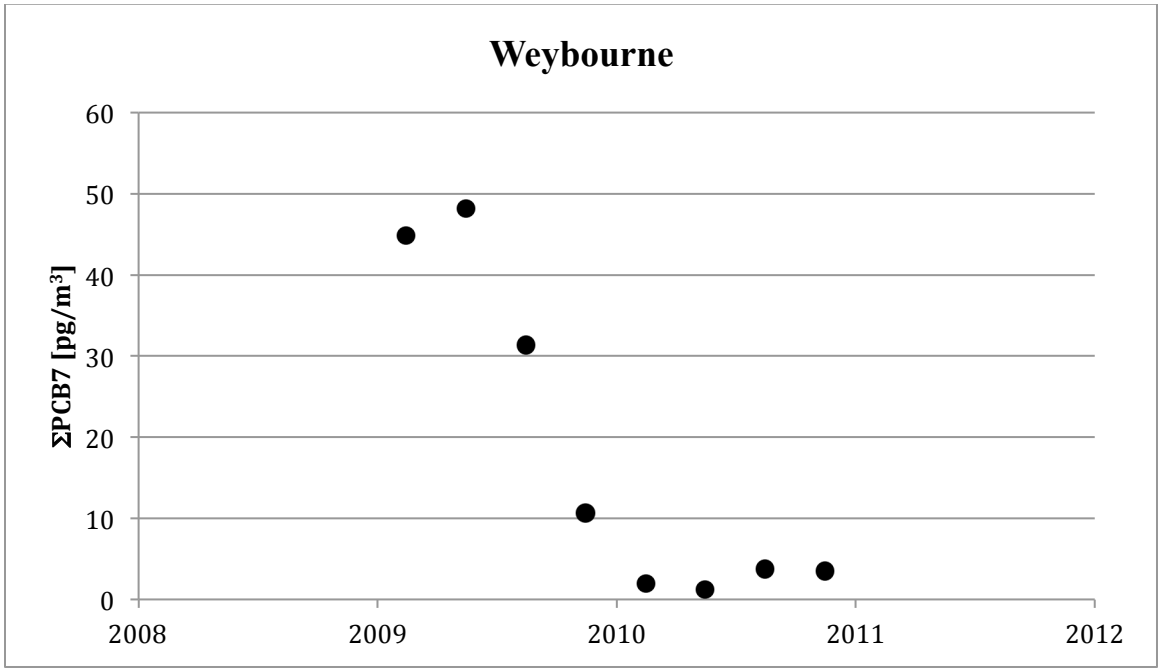


Figure 5f. $\sum_7$PCB temporal trend data for the Weybourne TOMPs site.

7.4 PBDEs: Results and discussions

Quarter 4 2010 is the first time that PBDEs have been included 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 32% and 72% of the Σ_{22}PBDEs were BDE47 and BDE99. These congeners were prominent in the commercial pentaBDE mix, accounting for 72% of the total. London and Manchester showed the highest concentrations of BDE47 plus BDE99 at 9.7 pg/m^3 and 12.1 pg/m^3, respectively. The other sites were lower at 2.6, 0.8, 2.6, 1.6 pg/m^3 for Hazelrigg, Auchencorth, High Muffles and Weybourne, respectively. In 2004 Lee *et al*. carried out an ambient air sampling campaign at Hazelrigg, Chilton (Oxfordshire) and Mace Head (Galway) with 40 samples collected at each site. They reported BDE47 plus BDE99 concentrations ranging from 1.9 pg/m^3 for Mace Head (a European background site) to 6.1 pg/m^3 for Chilton and 7.9 pg/m^3 for Hazelrigg. These data are similar to those measured at the TOMPs sites. Further data and analysis will be presented in the next TOMPs report after the collection of 2011 samples.

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

MANCHESTER 2010	Q1.10	Q2.10	Q3.10	Q4. 10	Average 2010
2,3,7,8-TCDF	5.25	1.71	1.29	13.27	2.15
1,2,3,7,8-PeCDF	1.36	2	<0.22	0.97	1.18
2,3,4,7,8-PeCDF	1.74	1.72	<2.2	15.11	1.76
1,2,3,4,7,8-HxCDF	4.63	1.43	0.9	4.13	1.83
1,2,3,6,7,8-HxCDF	2.12	1.14	1.98	2.72	1.40
2,3,4,6,7,8-HxCDF	3.56	0.86	1.6	3.73	1.60
1,2,3,7,8,9-HxCDF	0.44	0.44	1.2	0.44	0.63
1,2,3,4,6,7,8-HpCDF	14.16	1.15	0.3	0.94	3.91
1,2,3,4,7,8,9-HpCDF	1.44	0.58	0.44	0.11	0.62
OCDF	9.2	3.4	0.02	0.44	3.27
2,3,7,8-TCDD	4.4	<4.4	<4.4	<4.4	4.40
1,2,3,7,8-PeCDD	4.4	<4.4	<4.4	14.16	4.21
1,2,3,4,7,8-HxCDD	0.44	<0.44	<0.44	0.96	0.42
1,2,3,6,7,8-HxCDD	1.07	<0.44	<0.44	2.30	0.58
1,2,3,4,7,8-HxCDD	1.28	0.38	<0.44	3.51	0.62
1,2,3,4,6,7,8-HpCDD	13.22	2.56	0.63	1.54	4.11
OCDD	29.27	6.33	0.12	0.35	8.93
ΣTEQ dioxins and furans	**98.0**	**33.4**	**18.6**	**69.1**	**48.7**
3,4,4'5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.245	0.475	0.042	0.03	0.20
3,3',4,4',5-PentaCB (PCB_126)	0.017	0.022	2.697	3.71	1.61
3,3',4,4',5,5'-HexaCB (PCB_169)	0.021	0.005	0.056	0.08	0.04

LONDON 2010	**Q1.10**	**Q2.10**	**Q3.10**	**Q4. 10**	**Average 2010**
2,3,7,8-TCDF	1.42	0.46	<0.44	6.87	2.30
1,2,3,7,8-PeCDF	0.42	<0.22	<0.22	0.23	0.29
2,3,4,7,8-PeCDF	0.77	0.27	<2.2	23.54	6.70
1,2,3,4,7,8-HxCDF	0.68	0.29	<0.44	7.44	2.21
1,2,3,6,7,8-HxCDF	0.64	<0.44	<0.44	3.62	1.57
2,3,4,6,7,8-HxCDF	0.56	0.29	<0.44	5.41	1.68
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	3.31	0.87	0.1	0.85	1.28
1,2,3,4,7,8,9-HpCDF	0.38	<0.044	<0.044	0.35	0.26
OCDF	1.6	0.89	<0.0004	0.01	0.63
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.40
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	37.41	12.65
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	<0.44	<0.44
1,2,3,6,7,8-HxCDD	0.68	0.27	<0.44	4.74	1.53
1,2,3,4,7,8-HxCDD	0.85	<0.44	<0.44	7.17	2.22
1,2,3,4,6,7,8-HpCDD	6.41	3.73	0.18	2.78	3.27
OCDD	16.39	11.87	0.06	0.59	7.23
ΣTEQ dioxins and furans	**43.4**	**28.6**	**15.1**	**105.8**	**38.60**
3,4,4',5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.306	0.32	0.01	0.06	0.17
3,3',4,4',5-PentaCB (PCB_126)	0.03	0.015	3.00	3.90	1.74
3,3',4,4',5,5'-HexaCB (PCB_169)	0.011	0.003	<0.044	<0.044	0.03

HAZELRIGG 2010	**Q1.10**	**Q2.10**	**Q3.10**	**Q4. 10**	**Average 2010**
2,3,7,8-TCDF	0.69	<0.44	<0.44	2.77	0.47
1,2,3,7,8-PeCDF	nd	<0.22	<0.22	0.24	0.20
2,3,4,7,8-PeCDF	0.63	<2.2	<2.2	2.86	1.65
1,2,3,4,7,8-HxCDF	0.46	<0.44	<0.44	0.69	0.41
1,2,3,6,7,8-HxCDF	<0.44	<0.44	<0.44	0.47	0.41
2,3,4,6,7,8-HxCDF	<0.44	<0.44	<0.44	0.77	0.41
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	1.33	0.48	0.07	0.15	0.48
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	0.03	0.04
OCDF	0.56	1.98	0.0007	0.001	0.63
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.40
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	3.23	4.08
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	0.45	0.41
1,2,3,4,7,8-HxCDD	0.52	0.33	nd	0.83	0.39
1,2,3,4,6,7,8-HpCDD	1.74	<0.044	0.15	0.35	0.49
OCDD	7.4	2.8	0.04	0.10	2.56
ΣTEQ dioxins and furans	**24.6**	**20.0**	**14.6**	**18.2**	**8.0**
3,4,4',5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.08	0.091	0.028	0.01	0.21
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	<0.44	<0.44	1.76
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	0.013	<0.044	<0.044	0.15

AUCHENCORTH 2010	**Q1.10**	**Q2.10**	**Q3.10**	**Q4. 10**	**Average 2010**
2,3,7,8-TCDF	<0.44	0.39	<0.44	0.50	0.44
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	<2.20
1,2,3,4,7,8-HxCDF	<0.44	<0.44	<0.44	1.57	0.72
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	1.33	0.48	0.07	0.06	0.49
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.04
OCDF	0.5562	1.9797	0.0007	<0.0004	0.63
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.40
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<4.40
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	0.52	0.33	<0.044	<0.044	0.23
1,2,3,4,6,7,8-HpCDD	1.74	nd	0.15	0.10	0.66
OCDD	7.4	2.8	0.04	0.03	2.57
ΣTEQ dioxins and furans	**25.9**	**19.9**	**14.6**	**15.8**	**5.01**
3,4,4',5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.08	0.091	0.028	0.002	0.05
3,3',4,4',5-PentaCB (PCB_126)	0.0045	0.01	<0.44	<0.44	0.22
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	0.013	<0.044	<0.044	0.04

HIGH MUFFLES 2010	**Q1.10**	**Q2.10**	**Q3.10**	**Q4. 10**	**Average 2010**
2,3,7,8-TCDF	<0.44	0.45	<0.44	<0.44	<0.44
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	<2.20
1,2,3,4,7,8-HxCDF	<0.44	<0.44	0.53	<0.44	0.46
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	0.05	<0.044	0.05
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	0.14	0.05
OCDF	<0.0004	0.58	<0.0004	<0.0004	0.15
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	4.40
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	4.40
1,2,3,4,7,8-HxCDD	<0.44	<0.44	<0.44	5.48	1.70
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	<0.044	<0.044	0.057	<0.044	0.05
OCDD	<0.004	3.69	0.03	0.04	0.93
ΣTEQ dioxins and furans	**<15**	**19.2**	**15.0**	**20.0**	**2.76**
3,4,4',5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.026	0.143	0.007	0.01	0.05
3,3',4,4',5-PentaCB (PCB_126)	<0.44	<0.44	2.9	<0.44	1.06
3,3',4,4',5,5'-HexaCB (PCB_169)	<0.044	<0.044	<0.044	0.36	0.12

WEYBOURNE 2010	**Q1.10**	**Q2.10**	**Q3.10**	**Q4. 10**	**Average 2010**
2,3,7,8-TCDF	0.3	<0.44	<0.44	0.60	0.45
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	<2.20
1,2,3,4,7,8-HxCDF	<0.44	<0.44	<0.44	0.55	<0.47
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	0.30	0.41
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	0.11	0.06	0.07
1,2,3,4,7,8,9-HpCDF	<0.044	<0.044	<0.044	<0.044	<0.04
OCDF	<0.0004	1.71	0.00065	0.00	0.43
2,3,7,8-TCDD	<4.4	<4.4	<4.4	<4.4	<4.40
1,2,3,7,8-PeCDD	<4.4	<4.4	<4.4	<4.4	<4.40
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	<0.044	<0.044	0.19	0.19	0.12
OCDD	3.67	1.706	0.041	0.06	1.37
ΣTEQ dioxins and furans	**18.4**	**18.3**	**15.1**	**15.2**	**2.49**
3,4,4',5-TetraCB (PCB_81)	<0.004	<0.004	<0.004	<0.004	<0.004
3,3',4,4'-TetraCB (PCB_77)	0.11	0.063	0.018	0.003	0.05
3,3',4,4',5-PentaCB (PCB_126)	0.0072	0.0054	<0.44	<0.44	0.22
3,3',4,4',5,5'-HexaCB (PCB_169)	0.0054	<0.044	<0.044	<0.044	0.03

Appendix 2. TOMPs 2010 PCB data (All data in pg.m^{-3})

LONDON 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	10.7	18.6	<0.02	30.4	14.9
PCB_22	109.9	143.4	<0.02	10.4	65.9
PCB_44	18.9	18.4	10.6	9.9	14.5
PCB_49	36.6	51.8	12.3	41.0	35.4
PCB_52	5	7.2	3	14.1	7.3
PCB_70	<0.02	<0.02	2	0.2	0.6
PCB_74	3.6	3.3	1.8	10.1	4.7
PCB_87	17.8	9.2	2.4	12.9	10.6
PCB_95	0.4	3.1	3.5	8.6	3.9
PCB_99	0.5	6.2	3.8	28.3	9.7
PCB_104	0.7	6	<0.02	15.0	5.4
PCB_105	<0.02	<0.02	<0.02	0.2	0.1
PCB_110	<0.02	<0.02	1.1	1.9	0.8
PCB_114	0.6	5.5	<0.02	16.4	5.6
PCB_118	<0.02	<0.02	<0.02	0.2	0.1
PCB_123	0.24	2.2	<0.02	7.0	2.4
PCB_138	<0.02	<0.02	1.3	0.9	0.6
PCB_141	0.5	3.1	0.7	10.0	3.6
PCB_149	0.2	1	0.1	2.6	1.0
PCB_151	0.4	4.2	0.6	16.9	5.5
PCB_155	0.2	1.8	3.8	7.4	3.3
PCB_156	<0.02	<0.02	<0.02	0.2	0.1
PCB_157	<0.02	<0.02	<0.02	0.2	0.1
PCB_158	<0.02	<0.02	<0.02	0.2	0.1
PCB_167	1	1	<0.02	0.5	0.6
PCB_170	<0.02	<0.02	<0.02	0.2	0.1
PCB_174	<0.02	<0.02	0.12	1.2	0.3
PCB_180	0.06	0.6	0.3	2.0	0.7
PCB_183	0.1	0.8	0.1	3.1	1.0
PCB_187	0	0.4	0.4	1.4	0.6
PCB_188	0.1	1	<0.02	3.1	1.1
PCB_189	<0.02	<0.02	<0.02	0.2	0.1
PCB_194	<0.02	<0.02	<0.02	0.2	0.1
PCB_199	<0.02	<0.02	<0.02	0.5	0.1
PCB_203	<0.02	<0.02	<0.02	0.2	0.1
PCB_153+132	<0.02	<0.02	2.24	0.6	0.7
PCB_31+28	0.43	5.4	<0.02	15.6	5.4
PCB_41/64	17.4	4.2	8.5	124.1	38.6
PCB_60/56	9.2	4.2	0.2	17.2	7.7
PCB_90/101	<0.02	<0.02	1.0	4.8	1.5
PCB_Σ7PCB	5.46	13.15	7.9	36.2	15.7

MANCHESTER 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	0.30	10.50	NQ	27.06	12.62
PCB_22	<0.02	120.40	NQ	10.97	43.80
PCB_44	4.60	25.30	14.80	45.24	22.48
PCB_49	<0.02	33.70	17.40	16.14	16.81
PCB_52	1.20	8.40	1.50	16.83	6.98
PCB_70	1.10	4.40	0.80	0.04	1.59
PCB_74	3.50	24.30	0.90	8.51	9.30
PCB_87	<0.02	2.60	5.20	0.04	1.97
PCB_95	<0.02	8.10	9.80	6.38	6.07
PCB_99	0.90	1.80	6.80	18.59	7.02
PCB_104	<0.02	<0.02	<0.02	4.52	1.14
PCB_105	<0.02	<0.02	<0.02	0.04	<0.02
PCB_110	<0.02	5.07	3.70	2.40	2.80
PCB_114	<0.02	<0.02	<0.02	11.84	2.98
PCB_118	<0.02	3.14	<0.02	0.04	0.81
PCB_123	<0.02	<0.02	<0.02	5.14	1.30
PCB_138	0.20	2.60	3.00	0.41	1.55
PCB_141	0.20	0.50	0.70	5.64	1.76
PCB_149	0.80	3.90	0.60	1.34	1.66
PCB_151	0.90	1.50	1.10	7.95	2.86
PCB_155	8.60	2.90	3.80	3.54	4.71
PCB_156	<0.02	<0.02	<0.02	0.04	<0.02
PCB_157	<0.02	<0.02	<0.02	0.04	<0.02
PCB_158	<0.02	<0.02	<0.02	0.04	<0.02
PCB_167	<0.02	<0.02	<0.02	0.34	0.10
PCB_170	<0.02	<0.02	<0.02	0.04	<0.02
PCB_174	0.15	0.43	0.37	0.57	0.38
PCB_180	0.52	0.20	0.60	0.66	0.49
PCB_183	0.20	0.20	0.30	1.06	0.44
PCB_187	0.50	0.60	0.40	0.43	0.48
PCB_188	<0.02	<0.02	<0.02	0.93	0.25
PCB_189	<0.02	<0.02	<0.02	0.04	<0.02
PCB_194	<0.02	<0.02	<0.02	0.04	<0.02
PCB_199	<0.02	<0.02	<0.02	2.52	0.64
PCB_203	<0.02	<0.02	<0.02	0.05	0.03
PCB_153+132	2.19	3.76	3.99	0.21	2.54
PCB_31+28	4.90	17.50	NQ	8.35	10.25
PCB_41/64	2.00	16.50	5.30	35.84	14.91
PCB_60/56	1.70	<0.02	0.10	0.04	0.47
PCB_90/101	6.00	8.00	2.30	0.04	4.09
PCB_Σ7PCB	15.00	44.00	11.40	25.90	24.08

HAZELRIGG 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	0.2	3.6	NQ	7.09	3.6
PCB_22	<0.02	65.3	NQ	7.55	24.3
PCB_44	9.3	36.8	1.34	<0.02	11.9
PCB_49	<0.02	80.2	0.57	<0.02	20.2
PCB_52	0.8	78.5	0.72	0.86	20.2
PCB_70	0.7	6.8	0.96	<0.02	2.1
PCB_74	5.5	3.1	0.06	1.45	2.5
PCB_87	<0.02	<0.02	<0.02	2.21	0.6
PCB_95	<0.02	<0.02	0.99	2.06	0.8
PCB_99	<0.02	<0.02	1.05	1.96	0.8
PCB_104	<0.02	<0.02	<0.02	1.11	0.3
PCB_105	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_110	<0.02	<0.02	<0.02	0.69	0.2
PCB_114	<0.02	<0.02	<0.02	2.30	0.6
PCB_118	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_123	<0.02	<0.02	<0.02	1.58	0.4
PCB_138	0.08	0.5	0.3	<0.02	0.2
PCB_141	<0.02	<0.02	<0.02	2.81	0.7
PCB_149	<0.02	0.08	<0.02	0.69	0.2
PCB_151	<0.02	<0.02	0.36	2.18	0.6
PCB_155	0.63	2.2	3.24	1.22	1.8
PCB_156	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_157	<0.02	<0.02	<0.02	0.37	0.1
PCB_158	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_167	<0.02	<0.02	<0.02	0.08	0.0
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	<0.02	<0.02	0.03	0.28	0.1
PCB_180	0.13	0.07	0.08	0.23	0.1
PCB_183	<0.02	0.09	0.03	0.42	0.1
PCB_187	0.1	0.09	0.06	0.10	0.1
PCB_188	<0.02	<0.02	<0.02	0.30	0.1
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	0.59	0.76	0.67	0.09	0.5
PCB_31+28	4.91	16.01	NQ	3.06	8.0
PCB_41/64	4.4	13.9	0.5	9.87	7.2
PCB_60/56	1.7	<0.02	0.1	<0.02	0.5
PCB_90/101	0.1	<0.02	0.3	4.23	1.2
PCB_Σ7PCB	6.6	95.8	2.1	8.3	28.2

AUCHENCORTH 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	3.1	5.7	<0.02	<0.02	2.2
PCB_22	6.9	10.6	<0.02	<0.02	4.4
PCB_44	3.7	2	<0.02	<0.02	1.4
PCB_49	18.2	7.6	4.1	<0.02	7.5
PCB_52	18.5	8.6	0.8	1.55	7.4
PCB_70	1.1	1.1	0.6	<0.02	0.7
PCB_74	0.5	0.7	0.7	<0.02	0.5
PCB_87	0.2	0.1	<0.02	<0.02	0.1
PCB_95	0.5	0.68	0.5	<0.02	0.4
PCB_99	0.1	0.11	0.9	<0.02	0.3
PCB_104	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_105	<0.02	<0.02	1.7	<0.02	0.4
PCB_110	0.4	0.3	0.8	0.03	0.4
PCB_114	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_118	<0.02	<0.02	0.3	<0.02	0.1
PCB_123	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_138	0.3	0.3	0.6	<0.02	0.3
PCB_141	<0.02	0.1	0.2	<0.02	0.1
PCB_149	0.5	0.5	0.5	<0.02	0.4
PCB_151	0.1	0.2	0.3	<0.02	0.2
PCB_155	4.7	3.6	<0.02	0.00	2.1
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	0.07	<0.02	0.0
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.05	0.05	0.09	<0.02	0.1
PCB_180	<0.02	<0.02	0.2	<0.02	0.1
PCB_183	<0.02	<0.02	0.1	0.01	0.0
PCB_187	0.1	0.1	0.2	<0.02	0.1
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	1.7	<0.02	0.4
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	<0.02	<0.02	0.1	<0.02	0.0
PCB_153+132	0.49	0.43	0.28	<0.02	0.3
PCB_31+28	10.25	7.5	<0.02	<0.02	4.4
PCB_41/64	0.5	0.1	3	3.30	1.7
PCB_60/56	<0.02	<0.02	0.2	3.06	0.8
PCB_90/101	0.6	0.5	1.4	<0.02	0.6
PCB_Σ7PCB	30.2	17.4	3.6	1.8	13.3

HIGH MUFFLES 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	6.2	16.9	<0.02	13.25	9.1
PCB_22	3.1	56.8	<0.02	8.52	17.1
PCB_44	4.4	27.5	1.62	2.69	9.1
PCB_49	20.6	101.4	1.16	2.54	31.4
PCB_52	21.8	104.2	0.44	3.78	32.6
PCB_70	2.6	1.7	0.77	0.16	1.3
PCB_74	0.84	5.9	0.1	1.61	2.1
PCB_87	0.3	<0.02	0.81	0.40	0.4
PCB_95	1.28	0.905	0.44	0.64	0.8
PCB_99	0.2	0.69	<0.02	2.50	0.9
PCB_104	<0.02	<0.02	<0.02	0.86	0.2
PCB_105	<0.02	<0.02	<0.02	0.16	0.1
PCB_110	0.6	0.9	<0.02	0.21	0.4
PCB_114	<0.02	<0.02	<0.02	1.54	0.4
PCB_118	<0.02	<0.02	<0.02	0.16	0.1
PCB_123	<0.02	<0.02	<0.02	0.80	0.2
PCB_138	0.46	0.64	0.24	0.16	0.4
PCB_141	0.08	0.34	<0.02	5.12	1.4
PCB_149	0.88	1.02	0.14	0.24	0.6
PCB_151	0.42	0.5	<0.02	1.66	0.6
PCB_155	5.19	3.7	1.51	0.69	2.8
PCB_156	<0.02	<0.02	<0.02	0.16	0.1
PCB_157	<0.02	<0.02	<0.02	0.46	0.1
PCB_158	<0.02	<0.02	<0.02	0.16	0.1
PCB_167	<0.02	<0.02	<0.02	0.34	0.1
PCB_170	<0.02	<0.02	<0.02	0.20	0.1
PCB_174	0.06	0.12	0.034	0.21	0.1
PCB_180	<0.02	0.15	<0.02	0.28	0.1
PCB_183	<0.02	0.07	0.019	0.31	0.1
PCB_187	0.1	0.16	0.0507	0.17	0.1
PCB_188	<0.02	<0.02	<0.02	0.31	0.1
PCB_189	<0.02	<0.02	<0.02	0.16	0.1
PCB_194	<0.02	<0.02	<0.02	0.16	0.1
PCB_199	<0.02	<0.02	<0.02	0.15	0.1
PCB_203	<0.02	<0.02	<0.02	0.16	0.1
PCB_153+132	0.68	1.2	0.47	0.72	0.8
PCB_31+28	16.1	29.44	NQ	2.23	15.9
PCB_41/64	0.6	19.3	0.43	19.81	10.0
PCB_60/56	<0.02	<0.02	0.01	3.09	0.8
PCB_90/101	1.16	0.8	<0.02	0.45	0.6
PCB_Σ7PCB	40.3	136.0	1.2	7.5	46.2

WEYBOURNE 2010	Q1.10	Q2.10	Q3.10	Q4.10	Average 2010
PCB_18	<0.02	<0.02	NQ	6.58	2.2
PCB_22	<0.02	<0.02	NQ	4.12	1.4
PCB_44	1.3	1.1	<0.02	<0.02	0.6
PCB_49	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_52	0.2	0.2	0.87	1.87	0.8
PCB_70	0.4	<0.02	1.56	<0.02	0.5
PCB_74	0.77	0.5	0.38	0.72	0.6
PCB_87	<0.02	1.4	<0.02	0.63	0.5
PCB_95	<0.02	0.6	1.21	0.28	0.5
PCB_99	<0.02	1.55	0.42	1.31	0.8
PCB_104	<0.02	1.53	<0.02	0.38	0.5
PCB_105	<0.02	<0.02	1.22	<0.02	0.3
PCB_110	<0.02	<0.02	0.85	<0.02	0.2
PCB_114	<0.02	1.09	<0.02	0.75	0.5
PCB_118	<0.02	<0.02	0.77	<0.02	0.2
PCB_123	<0.02	0.34	<0.02	0.34	0.2
PCB_138	<0.02	<0.02	0.8	<0.02	0.2
PCB_141	<0.02	0.87	0.49	0.71	0.5
PCB_149	<0.02	0.4	0.67	0.29	0.3
PCB_151	<0.02	0.8	0.25	0.84	0.5
PCB_155	0.51	0.35	<0.02	0.30	0.3
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	1.96	0.08	<0.02	0.5
PCB_170	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_174	0.03	<0.02	0.08	<0.02	0.0
PCB_180	0.1	0.12	0.19	0.12	0.1
PCB_183	<0.02	0.17	0.03	0.17	0.1
PCB_187	0.08	0.06	0.16	0.08	0.1
PCB_188	<0.02	0.18	<0.02	0.18	0.1
PCB_189	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_194	<0.02	<0.02	13.83	<0.02	3.5
PCB_199	<0.02	<0.02	<0.02	<0.02	<0.02
PCB_203	<0.02	<0.02	0.11	<0.02	0.0
PCB_153+132	0.39	<0.02	0.39	0.04	0.2
PCB_31+28	1.3	0.9	NQ	1.10	1.1
PCB_41/64	0.3	1.15	<0.02	7.99	2.4
PCB_60/56	0.42	2.05	0.24	1.79	1.1
PCB_90/101	0	<0.02	1.63	0.44	0.5
PCB_Σ7PCB	2.0	1.3	3.8	3.5	2.6

Appendix 3. PBDE data for Q4 2010. (All data in pg.m^{-3})

PBDE Q4 2010	MAN Q4 10	LON Q4 10	HR Q4 10	AUCH Q4 10	HM Q4 10	WEY Q4 10
BDE_17	<0.02	0.18	<0.02	<0.02	0.15	0.01
BDE_28	0.34	0.59	0.06	0.04	0.12	0.03
BDE_32	<0.02	0.15	<0.02	<0.02	0.11	<0.02
BDE_35	0.15	0.31	<0.02	<0.02	0.08	0.04
BDE_37	0.11	0.28	<0.02	<0.02	1.12	0.03
BDE_47	5.20	6.98	1.28	0.74	1.16	0.68
BDE_49	0.80	1.07	0.10	0.10	0.32	0.12
BDE_66	0.31	0.51	0.05	0.03	0.19	0.09
BDE_71	0.18	0.11	<0.02	<0.02	0.07	<0.02
BDE_75	<0.02	0.10	<0.02	<0.02	0.08	<0.02
BDE_77	0.12	0.29	<0.02	<0.02	0.17	<0.02
BDE_85	0.38	0.37	0.12	0.15	0.63	0.09
BDE_99	4.50	5.10	1.27	<0.02	1.44	0.96
BDE_100	0.63	1.34	0.21	<0.02	0.29	0.12
BDE_119	<0.02	0.11	<0.02	<0.02	0.06	<0.02
BDE_138	<0.02	0.08	<0.02	<0.02	0.08	<0.02
BDE_153	1.39	1.26	0.31	<0.02	0.49	0.22
BDE_154	1.89	1.06	0.27	<0.02	0.56	0.25
BDE_166	<0.02	0.08	<0.02	<0.02	0.08	0.11
BDE_183	4.05	1.95	0.61	<0.02	0.65	0.61
BDE_196	2.85	0.19	<0.02	<0.02	0.08	<0.02
BDE_196	2.85	0.19	<0.02	<0.02	0.08	<0.02
BDE 47 + 99	**9.69**	**12.09**	**2.55**	**0.76**	**2.60**	**1.64**

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