The Lancaster
Environment Centre

Final Report 2010-2016 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

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Report to the Department for Environment, Food
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Department of Environment, the Scottish
Government and the Welsh Assembly

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Executive Summary.

This report covers the reporting period from 2010 quarter 4 to 2016 quarter 3 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), Environment Agency and devolved administrations.

Over this period, 37 PCBs congeners, 4 co-planar PCB congeners, 22 PBDE congeners, 10 furan congeners and 7 dioxin congeners have been continually across the network. The TOMPs network includes sites in London, Manchester, Hazelrigg (Lancashire), High Muffles (North Yorkshire), Auchencorth Moss (Midlothian) and Weybourne (Norfolk). The aim of the TOMPs network, which has operated since 1991, is to provide information on the ambient levels of organic pollutants in the UK through monitoring of air concentrations at six sites. The results and other related scientific work are used to inform policy development on exposure to persistent organic pollutants (POPs).

The specific aims of the TOMPs programme are:

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

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

Further to this, the European Commission ratified the Stockholm Convention in 2004 and adopted the POPs regulation 850/2004 in order to ensure compliance with both the Stockholm Convention as well as the UN/ECE POPs protocol. The provision of long-term environmental monitoring data, such as that provided by TOMPs, is an important component of the UK's obligations under these agreements.

The data presented in this report demonstrates that ambient concentrations in the UK of PCDD/Fs, PCBs and PBDEs are reducing in-line with estimates of atmospheric emissions. As a result of European Union and UK regulations along with international agreements such as the Stockholm Convention, primary sources of these POPs have largely been controlled. On-going diffuse emissions from products still in use and waste processing continue to support ambient concentrations alongside secondary sources from environmental reservoirs such as soils. Ambient concentrations of POPs are generally higher in urban areas although differences between urban and rural locations are reducing. Ambient concentrations of PCDD/Fs and PCBs currently included in the TOMPs network are currently close to limits of quantification, particularly for the rural sites. As it appears that the main sources of PCDD/Fs and PCBs have largely been controlled the network coverage of these substances could justifiably be reduced, which could allow the inclusion of additional substances have been recently added to the Stockholm Convention.

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1. Introduction

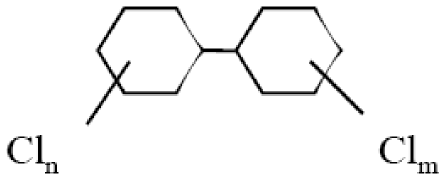
Lancaster University (LU) has been involved in the TOMPs programme since its inception in 1990. LU has managed the programme on behalf of Defra and the devolved administrations since 2004 and operates six air monitoring sites, three urban, two rural and one semi-rural. This contract commenced in October 2010 with annual extensions until September 2016. Atmospheric sampling is carried out at each site, collecting a biweekly sample which is bulked to provide quarterly data. These data are reported to Defra and published on the air quality data website uk-air.defra.gov.uk/. They are also available on the Stockholm Convention Global Monitoring Plan website http://www.pops-gmp.org/. Two sites are currently maintained via sub-contracts; Auchencorth Moss by the Centre for Ecology and Hydrology (CEH) and the Weybourne Observatory by the University of East Anglia. The analytes quantified at Lancaster University are PCDD/Fs ('dioxins and furans'), PBDEs and PCBs. Until 2014 a fraction of the quarterly sample was provided to the polycyclic aromatic hydrocarbons (PAHs) network and the data reported separately.

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

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

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

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

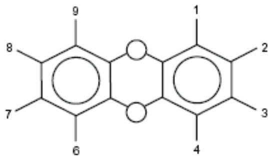


There are 209 possible congeners with one to ten chlorines atoms attached to the biphenyl structure. The International Council for the Exploration of the Seas (ICES) identified 7 key PCB congeners which are commonly reported in environmental samples. These are PCB 28 (2,4,4’-triPCB), PCB 52 (2,2’,5,5’-tetraCB), PCB 101 (2,2’,4,5,5’-pentaCB), PCB 118 (2,3’,4,4’,5-heptaCB), PCB 138 (2,2’,3,4,4’,5-heptaCB), PCB 153 (2,2’,4,4’,5,5’-heptaCB), PCB 180 (2,2’,3,4,4’,5,5’-heptaCB), although several dozen different congeners can be found in the environment.

Production of PCBs peaked in the 1960s in Europe and USA and terminated in the mid 1970s, when they were ultimately banned in the late 1970s/early 1980s (de Voogt and Brinkman, 1989). The last inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tonnes (Breivik *et al.*, 2002). Approximately 97% of this has been used in the Northern Hemisphere, mostly between 30 °N and 60 °N (Breivik *et al.,* 2002). Before the ban, PCBs had entered the environment through point and diffusive sources such as landfill sites, accidental releases/spillages via leaking during commercial use of electrical equipment and transformer and capacitor fires, incineration of PCB waste etc. (de Voogt and Brinkman, 1989; Danse *et al.,* 1997). Current atmospheric levels of PCBs in the environment can be accounted by on-going primary anthropogenic emissions (e.g. accidental release of products or materials containing PCBs), volatilization from environmental reservoirs which have previously received PCBs (e.g. oceans and soil) or incidental formation of some congeners during combustion processes (Breivik *et al.,* 2002). The National Atmospheric Emission inventory estimates that the emission of PCBs to the UK atmospheric have decreased from 843 in 2010 to 733kg in 2014 (latest data), the majority emitted from electrical equipment such as capacitors and transformers. PCBs were added to Annex A and C of the Stockholm Convention when it entered into force in 2004.

PCDD/Fs. Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) enter the environment from various combustion processes and as impurities from the manufacture and use of various chlorinated compounds. Considerable effort has been expended in the UK and elsewhere to try and quantify and rank these sources and their emissions into the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken. Dioxin levels in the environment have been declining since the early seventies and have been the subject of a number of regulations and clean-up actions; however, current exposures levels still remain a concern. PCDDs and PCDFs were added to Annex C of the Stockholm Convention when it entered into force in 2004. The NAEI inventory estimates that the emission of PCDD/Fs to the UK atmosphere reduced from 229 g-TEQ in 2010 to 215 g-TEQ in 2015, the majority emitted from combustion processes.

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



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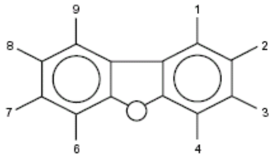

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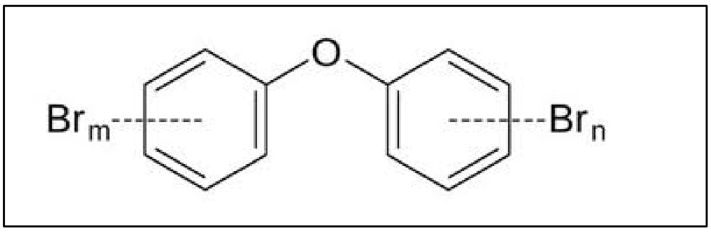
The Toxicity Equivalency Factor (TEF) values have been subject to revision and amendment since their inception but the most widely accepted set of TEF values for the 2,3,7,8-substituted PCDD/Fs is the 'WHO' (WHO-TEF) system, originally developed in 1990s and last updated in 2005. Another commonly used scheme is the International Toxicity Equivalency Scheme (I-TEQ) which has assigned slightly different TEFs to the WHO schemes. The three TEF schemes data are contained in the table below. For consistency the 1998 scheme has been used by the TOMPs network throughout for the assessment of long-term trends, but also converted to I-TEF for comparison with the source inventories. There is evidence to suggest that several of the PCBs elicit similar toxic responses to the dioxins, based on their binding to an intercellular protein, the Ah-receptor. These selected PCBs have therefore also been ascribed TEF values which have been endorsed by the UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT). These are also listed in Table 1.

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

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

1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.001
OCDF	0.0001	0.0003	0.0001

PBDEs. Polybrominated diphenyl ethers were widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. They are referred to as additive flame retardants, because they were simply blended with the product. This makes them more prone to volatilize into the atmosphere during the product lifetime and waste processing/recycling. They reduced fire hazards by interfering with the combustion of the polymeric materials (BSEF, 2000; Commission of the European Communities, 2000). Their general structure is $C_{12}H_{10-n}Br_nO$ (n=1-10). Therefore, there are 209 possible PBDE congeners, depending on the position of the bromine atoms on the phenyls rings. Three different types of commercial PBDE formulation have been produced with different degrees of bromination namely penta-, octa- and deca-BDE products. The penta-BDE product contains a range from tetra to hexa-BDE congeners, the octa-BDE contains a mixture of hexa- to deca-BDE and the deca contains predominantly the BDE-209 congener and is currently the most widely used PBDE flame retardant product.



The global demand for PBDEs has previously been very substantial with a peak estimation of 70,000 tonnes for the year 2003 (Hites *et al.*, 2004). Of these technical mixtures, the commercial pentabromodiphenyl ether (PeBDE) and commercial octabromodiphenyl ether (OctaBDE) mixtures have been banned in the EU and Japan and were added in 2009 to Annex A of the Stockholm Convention during the 4th Conference of Parties (COP).

In the UK there has been previously high use of PeBDE as a result of particularly stringent fire retardancy regulations for furniture. Lower brominated PBDEs can also be formed from the degradation of higher brominated BDEs although the environmental importance of this process is still unclear. PBDE congeners were included in the TOMPs methodology from the start of this contract in Q4 2010. The main congeners that have been analysed are: PBDEs 28 (tri), 47 (tetra), 49 (tetra), 99 (penta), 100 (penta), 153 (hexa), 154 (hexa), 183 (hepta). Congeners BDE-

47 and BDE-99 which account for approximately 72% of the composition of the penta commercial mixture (pentaBDE).

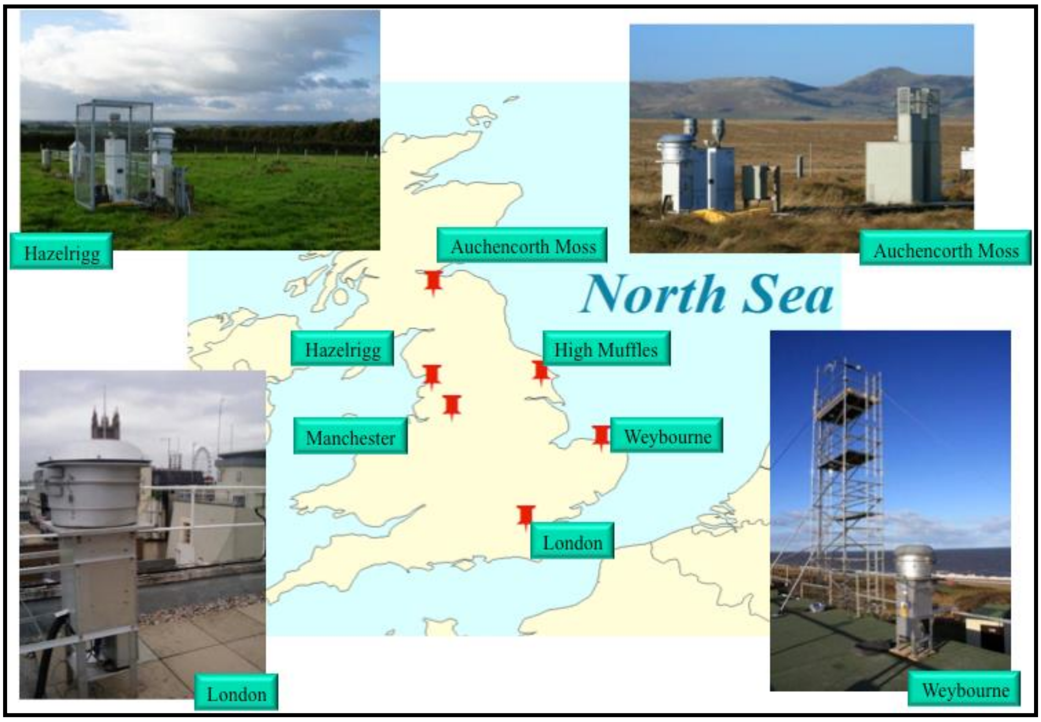
3. TOMPs sites operating from 2010 to 2016

During this contract period 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 Sohxlet extraction unit for 18 hours with hexane and 6 hours with toluene. PCBs, PBDEs and tri, tetra and penta PCDD/Fs are extracted in the hexane fraction. The remaining PCDD/Fs are extracted in the toluene fraction. The extracts are concentrated using rotary-evaporation and nitrogen-evaporation. The hexane and toluene fraction are combined for each sample and extracts pooled before purification to obtain quarterly data (Jan-March (Q1), April-June (Q2), July-Sept (Q3), and Oct-Dec (Q4)). The 6 or 7 hexane fractions (depending on the length of each quarter) of each quarter are then bulked together. The samples are transferred into a 250ml round bottom flask using hexane. 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 measured in all samples, including the seven commonly reported ICES congeners: PCBs 28, 52, 90/101, 118, 138, 153/132 and 180. Some congeners co-elute and are hence reported as a pair, for example, 153/132. Fractions 2 and 3 are solvent exchanged to 15 mL of nonane containing an injection standard of ^{37}Cl-labeled 2,3,7,8-TCDD. Analysis is performed on a Micromass Autospec Ultima high resolution-mass spectrometry (HR-MS) operated at a resolution of at least 10,000. Dioxins, furans and co-planar PCBs are generally found in mixtures containing several kinds of dioxins and dioxin-like compounds, each having its own degree of toxicity. To express the overall toxicity of such a mixture as a single number, the concept of "Toxic Equivalents" (TEQ) has been developed. The concentration of co-planar PCBs and PCDD/Fs are expressed in units of fgTEQm^{-3}. The concentration in fgm^{-3} is multiplied by the WHO Toxic equivalency factors (TEF, 1998) to obtain the final concentration in fgTEQm^{-3}. The WHO TEF scheme used for the data conversion was developed in 1998, and although the scheme was updated in 2005, the original scheme is still used to ensure consistency within the dataset. From Q4 2010 the following PBDE congeners have been reported; BDE 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 183, 196.

QA/QC A number of steps are taken to obtain data that would allow an assessment of the accuracy and reliability of the data. PCB and PBDE recoveries are monitored by quantifying 10 $^{13}C_{12}$-labelled PCB and PBDE standards, whilst PCDD/F and coplanar PCB data are corrected using 21 $^{13}C_{12}$-labelled PCDD/F and coPCB isotope dilution standards, using the injection standard as an internal standard. The criteria for the quantification of analytes are a retention time found within 2s of the standard, isotope ratio found within 20% of standard and a signal to noise ratio of at least 3. Analytical blanks, consisting of solvent are included at a rate of one blank for every 12 samples. The method detection limit was calculated as 3 times the standard deviation of the concentrations found in the analytical blanks. If the concentrations in the blanks are below the instrumental detection limit, then the method detection limit is defined as equal to the instrumental detection limit. All results are blank corrected using the concentration of the field blanks. Field blanks are produced for each site and each quarter and they are used to calculate method detection limits (MDLs). When compounds are not detected in the field blanks, laboratory blanks produced for each quarter are used to estimate MDLs.

6. Data storage.

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

7. Results for covering the period 2010 to 2016

7.1 Network Operations

A summary of the data capture rates and bulked air volumes (in m^3) collected at each site over the contract period are contained in Table 2. 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). Average bulked volume collected at each site under normal operating conditions ranged from 4135 to 5244 m^3 as per Table 2.

The operation of the TOMPs network has improved since the introduction of brushless motors which can run continuously for a period between 2 and 3 years. London, Manchester, High Muffles, Weybourne and Hazelrigg operated normally with data capture rates exceeding 98% over the contract period. The sampler at Auchencorth experienced a power cut and minor motor/equipment failures early in 2016 which reduced the capture rate to 92%, although averaging over 98% for the remainder of the year. All sites were calibrated annually and quarterly field blanks were also collected from each site.

Table 2. Summary of data capture rates and average sample volumes from 2010-2016.

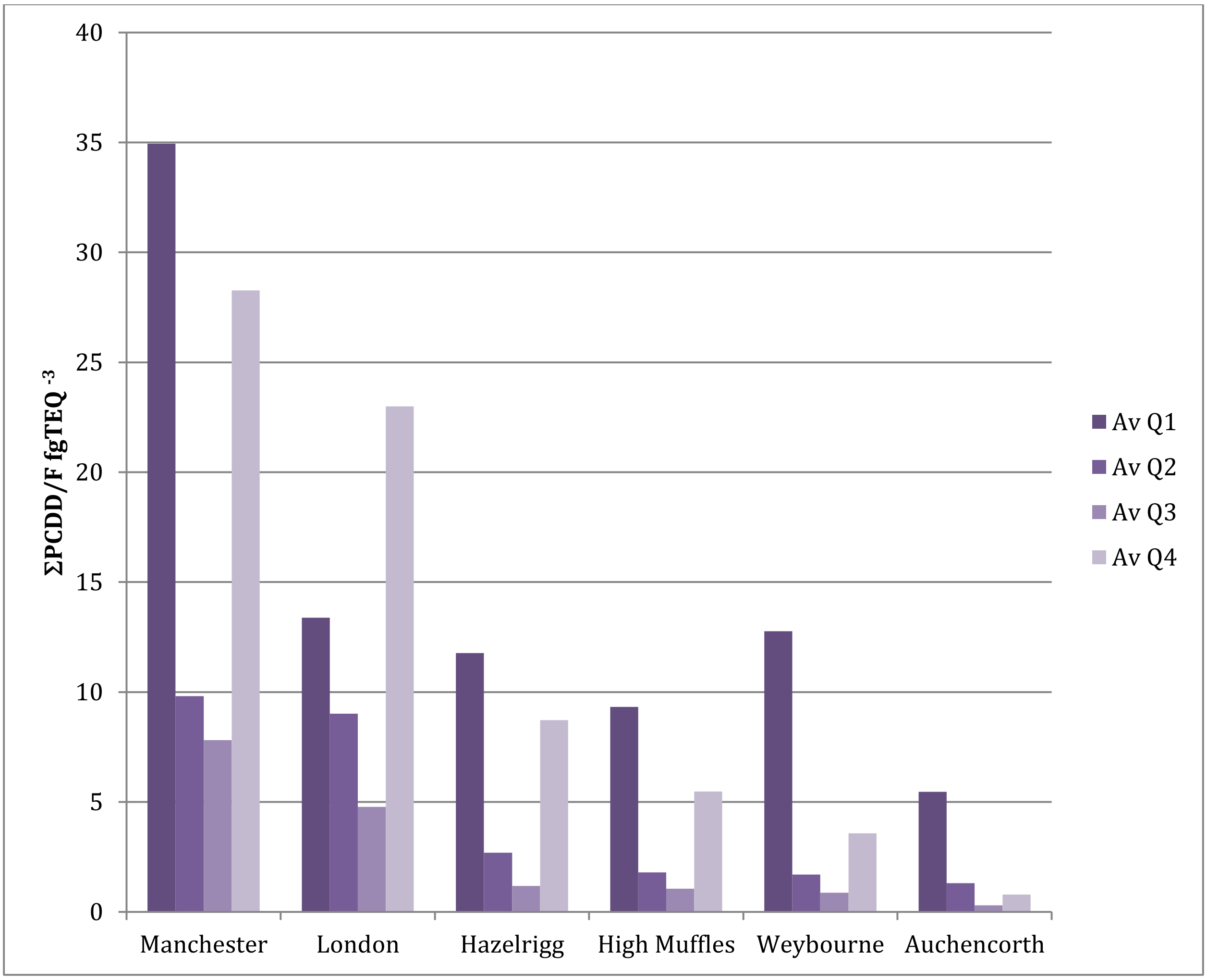
Site	Year	% Average Data capture	Quarterly sample volume m^3
LON	2010 (Q4)	100	5244
	2011	100	4653
	2012	100	4653
	2013	100	4558
	2014	100	4709
	2015	100	4672
	2016 (Q1-Q3)	100	4663
MAN	2010 (Q4)	100	4135
	2011	100	4596
	2012	100	4596
	2013	96	4297
	2014	99	4636
	2015	100	4370
	2016 (Q1-Q3)	100	4745
HR	2010 (Q4)	100	4814
	2011	100	4727
	2012	100	4727
	2013	100	4724
	2014	99	4735
	2015	99	4422
	2016 (Q1-Q3)	100	4848
HM	2010 (Q4)	100	4507
	2011	100	4570
	2012	100	4570
	2013	100	4544
	2014	99	4538
	2015	99	4352
	2016 (Q1-Q3)	100	4753
AUCH	2010 (Q4)	100	5171

	2011	98	4706
	2012	98	4706
	2013	100	4665
	2014	98	5027
	2015	100	4867
	2016 (Q1-Q3)	92	4381
WEY	2010 (Q4)	100	5138
	2011	98	4449
	2012	98	4449
	2013	100	4418
	2014	100	4911
	2015	100	4621
	2016 (Q1-Q3)	100	4709

7.2 PCDD/Fs: Results and discussion

Quarterly PCDD/F data are over the contract period are contained in the annual reports and a summary presented in Figure 2. Generally, concentrations across the sites are very low and getting close to limits of detection. The urban sites in Manchester and London exhibit higher concentrations than the other semi-rural and rural sites by a factor of 4. However, the concentrations at the two urban sites have decreased over the contract period and are becoming increasingly similar to the rural sites. This is particularly true at the site in London. Seasonal patterns, as shown by the quarterly data, shows that the highest concentrations were generally measured in quarters Q1 and Q4 with lower values reported for quarters 2 and 3. This suggests that there is a seasonality to the strength to the sources, which have been associated with increased combustion for heating in the winter.

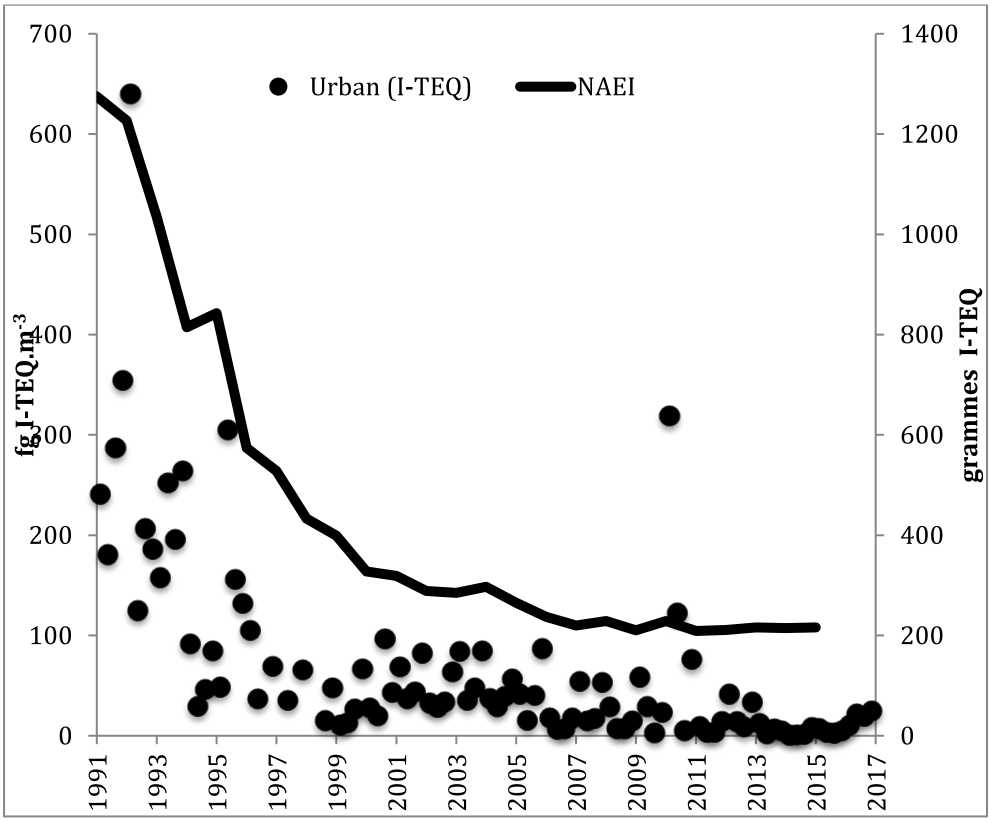
Figure 2. 2010 to 2016 combined average quarterly PCDD/F data for each TOMPs site.

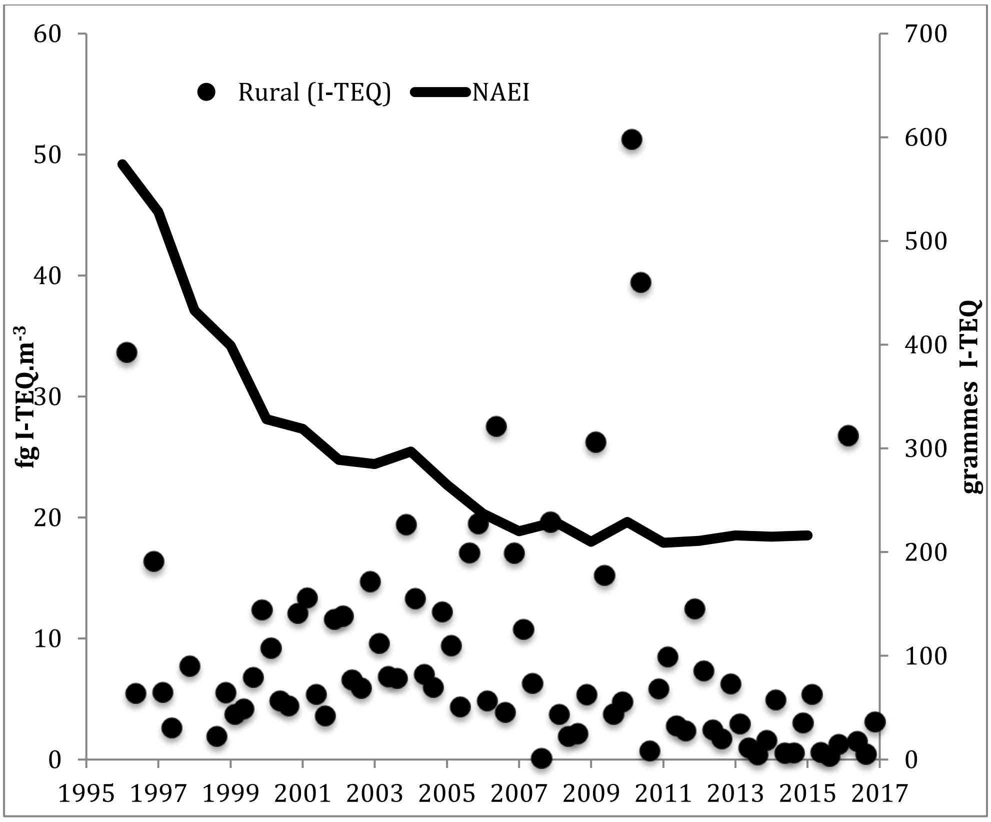


PCDD/Fs constitute two classes of chemicals that are formed unintentionally during combustion (e.g. waste incineration, burning of coal, wood etc.), iron and steel production (also combustion), several metal treatment processes and transport. The contribution from waste incineration has reduced in importance over time. The observed seasonality of PCDD/Fs in air, where winter values exceed summer values, has been seen in the TOMPs dataset and is widely reported in the literature, for example, Coutinho *et al*. (2007) reported average summer/winter ratios of 1:3 for sites in Portugal. Increased combustion (i.e., domestic space heating) and seasonal variations in the atmospheric boundary layer height are the likely causes. The sources of PCDD/Fs to the UK atmosphere are presented in detail by Katsogiannis *et al*., 2010 which discusses the TOMPs programme over a period of 17 years. Further details can also be found in Graf *et al*. (2016).

The temporal trends for the urban and rural sites over the lifetime of the network are presented in Figure 3, with estimated atmospheric clearance rates (time taken for a 50% decline in concentration) for London and Manchester of 5.0 and 5.1 years, respectively. The combined concentration data from the semi-rural site at Hazelrigg and the rural sites at High Muffles Auchencorth Moss and Weybourne data do not show any evidence of a significant downward trend since the mid. 1990s. Data for UK PCDD/F emissions are provided by the National Atmospheric Emission Inventory over the period 1990 – 2015 (http://www.naei.defra.gov.uk). During this period PCDD/F emissions reduced from around 1303 g I-TEQ per year in 1990 to 216 g I-TEQ per year in 2015.

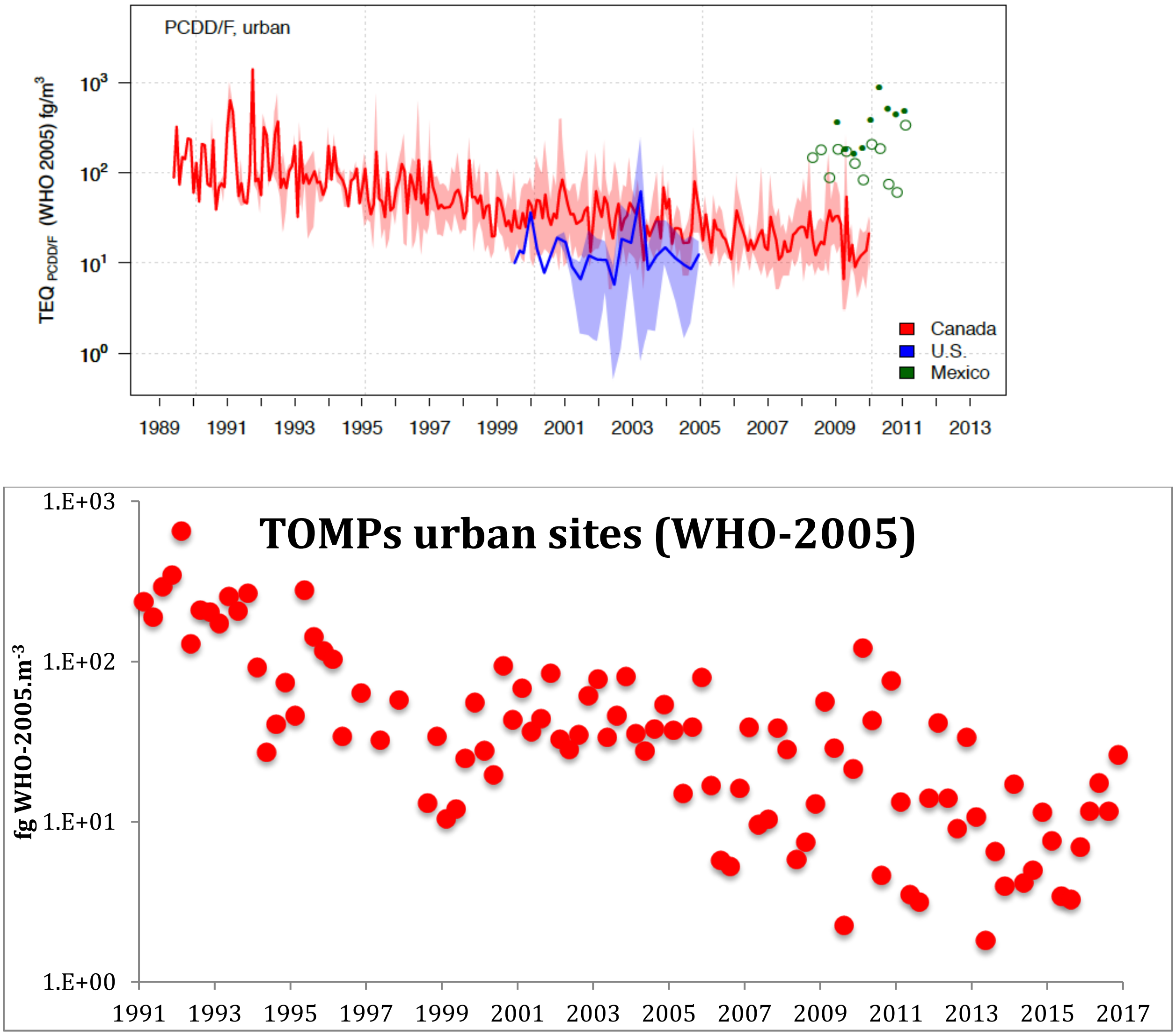
Figure 3. Long-term PCDD/F trend data in fg I-TEQ.m^{-3} from the TOMPs network for the urban (London and Manchester) and the rural (Hazelrigg, High Muffles, Auchencorth and Weybourne) sites. Quarterly data are compared to the current NAEI estimates in g I-TEQ per annum.

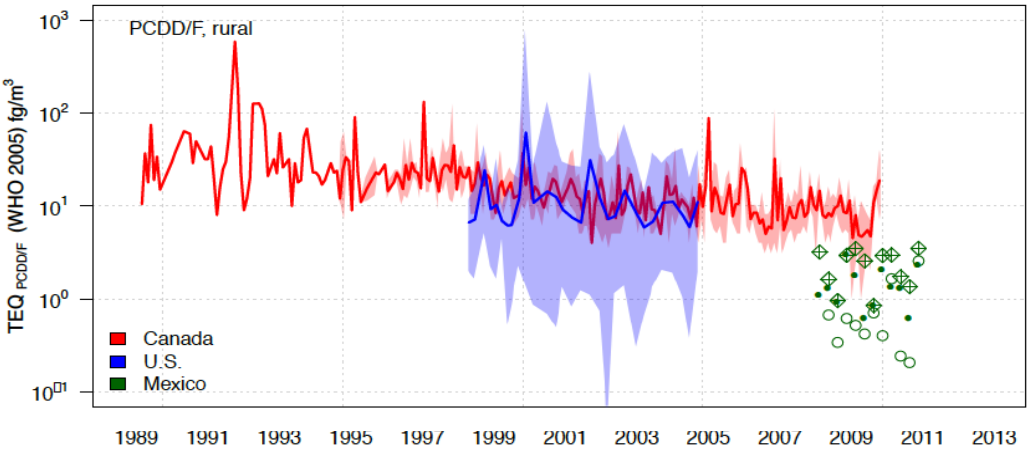


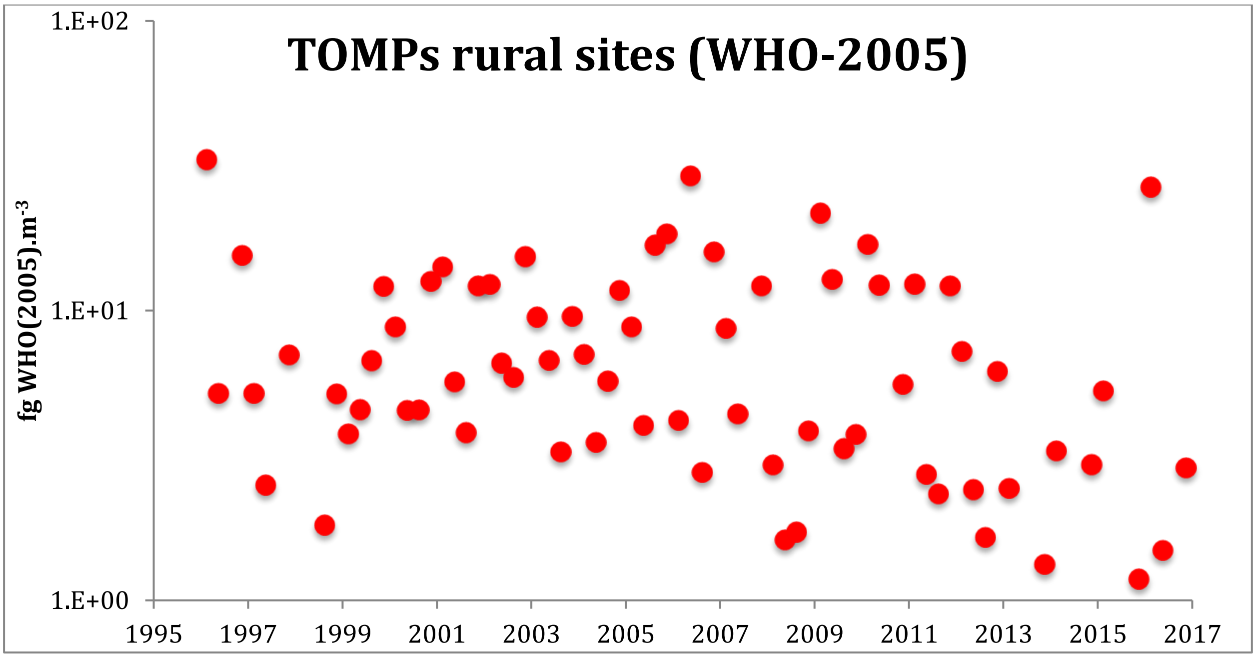


A recent report by the Commission for Environmental Cooperation (CEC, 2014) provides a comparison, for the first time, information on PCDD/F air concentrations from monitoring network activity in Canada, Mexico and the United States. The CEC report combines information from the Canadian National Air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

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







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

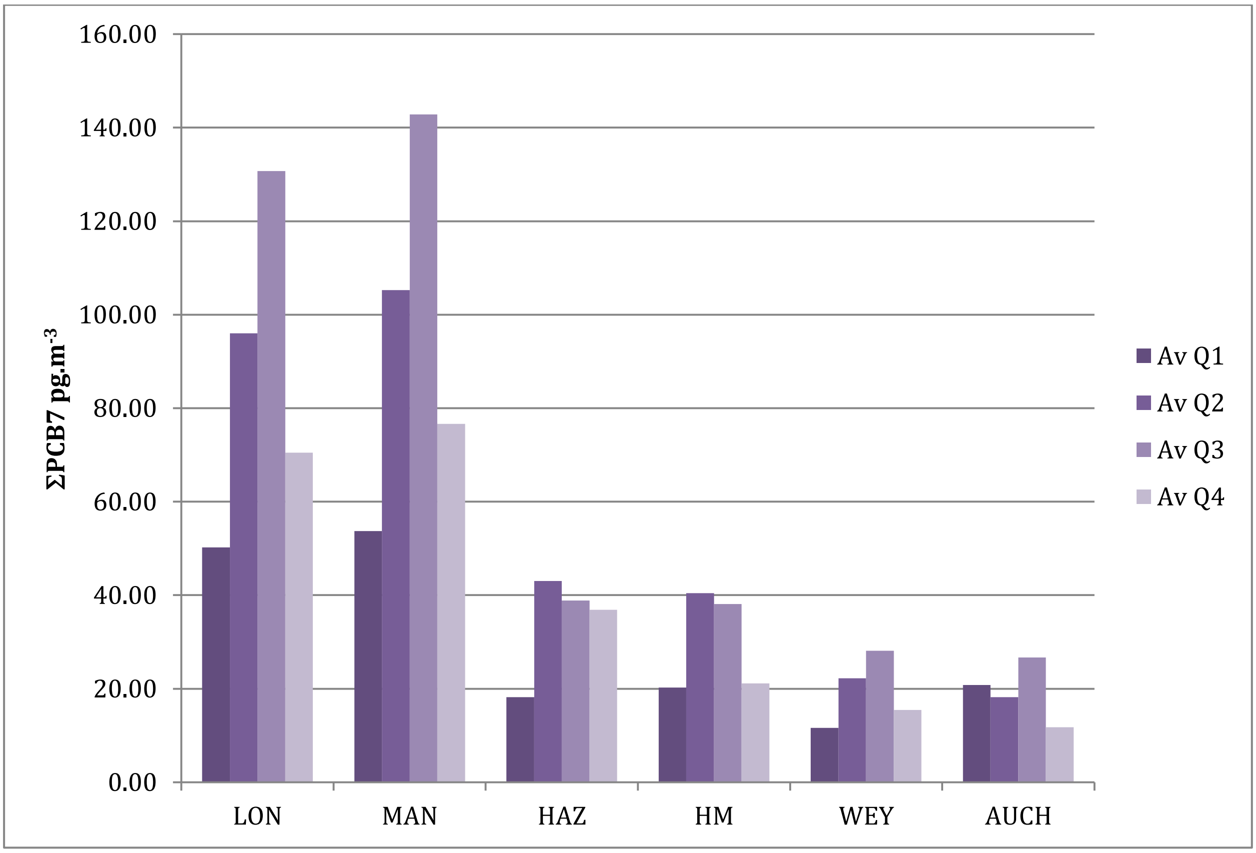
7.3 PCBs: Results and discussions

Quarterly PCB congener data for the 6 TOMPs sites over the contract period are contained in the annual reports and a summary of the quarterly data presented in Figure 5. The annually averaged PCB concentrations measured at each of the TOMPs sites ranged from 16 pg/m^3 (Weybourne) to 94 pg/m^3 (Manchester) for the sum of seven indicator PCB congeners (PCBs 28,52,101,118,138,153,180). The data shows that concentrations are proportional to the population density surrounding the site i.e. higher for urban sites by a factor of approximately

3. The urban sites at London and Manchester showed consistently higher concentrations than the semi-rural and rural sites, although there was no obvious decreasing trend over the period 2010 to 2016. There was no observable trend at the semi-rural and rural sites over this period either.

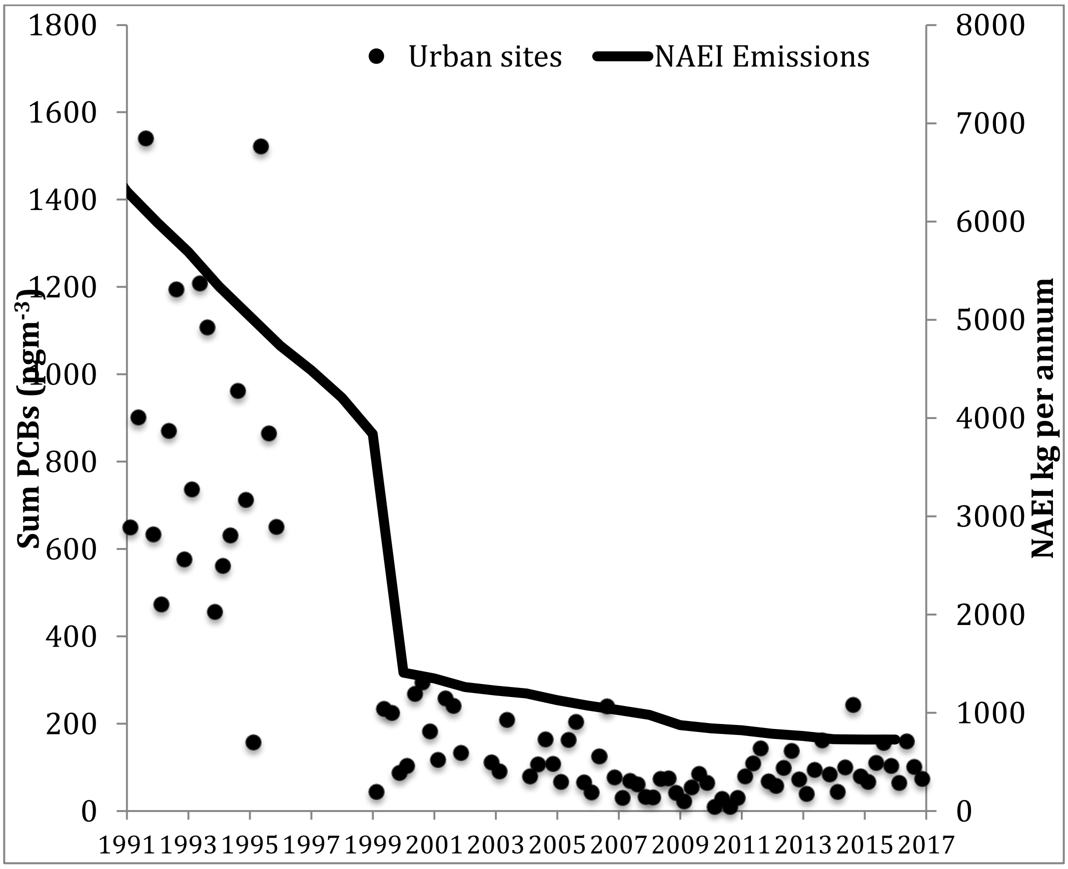
At each site the quarterly data showed a distinct seasonal pattern with higher levels in Q2 and Q3 which are characteristic of temperature driven diffusive sources. This appears to be the case for urban, semi-rural and rural sites. At rural locations this is probably a reflection of temperature driven volatilization from terrestrial surfaces (e.g. soils, vegetation), however, the processes resulting in higher summer concentrations at the urban locations is unclear.

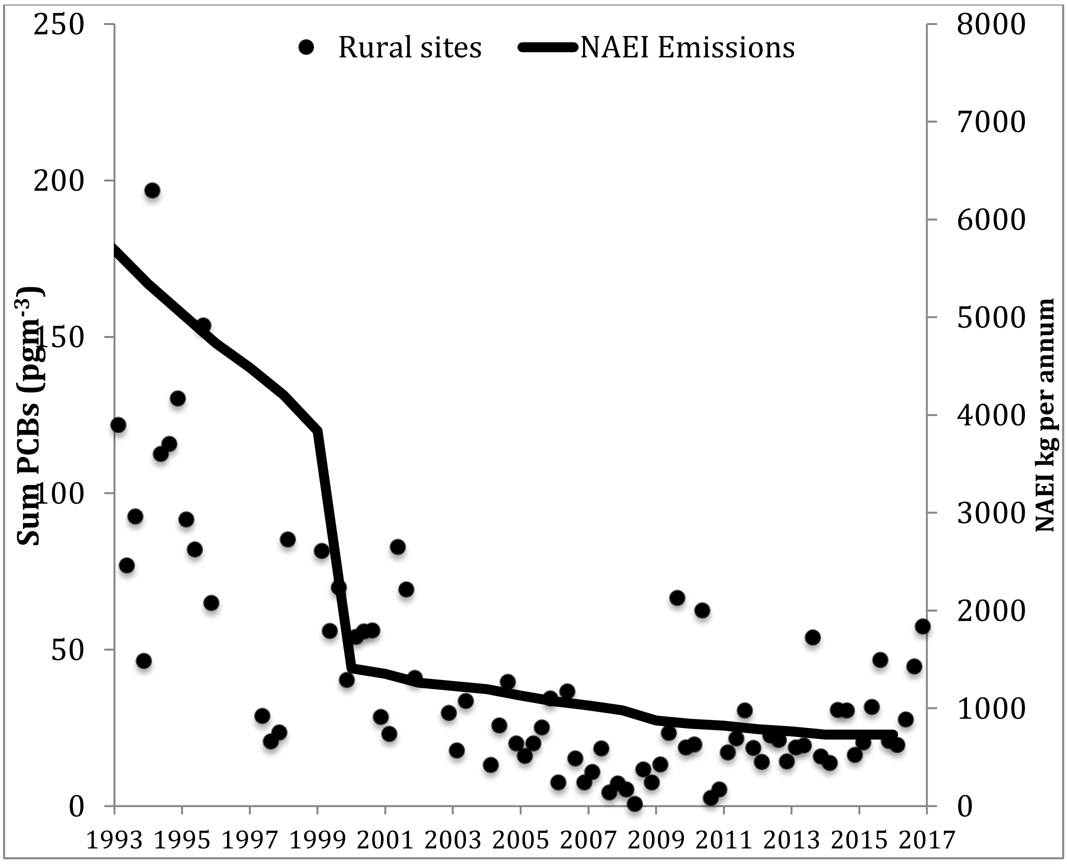
Figure 5. 2010 to 2016 average quarterly ΣPCB$_7$ (congeners 28, 52, 101, 118, 153, 138 and 180) data at the TOMPs sites.



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. Further details can also be found in Graf *et al.* (2016). Over the whole time period that the TOMPs network has been operating the clearance rates (time taken for a 50% decline in concentration) provided by the TOMPs network for Manchester and London were 9.3 and 5.5 years, respectively, and for the Hazelrigg 9.6 years. The datasets for Weybourne and Auchencorth are too short to establish significant trends. No discernable trend was observed for High Muffles. Time trend data for the urban sites (London, Manchester) and rural sites (Hazelrigg, High Muffles, Auchencorth and Weybourne) are presented in Figure 6. These data have been plotted against the estimated UK emission data from the NAEI (http://www.naei.defra.gov.uk). It is interesting to note that when examining the long term trends since 2000 none of the sites shows a downward trend over that period. This suggests that the environment has potentially reached a steady state with environmental cycling and secondary sources controlling ambient concentrations.

Figure 6. $\sum_7$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





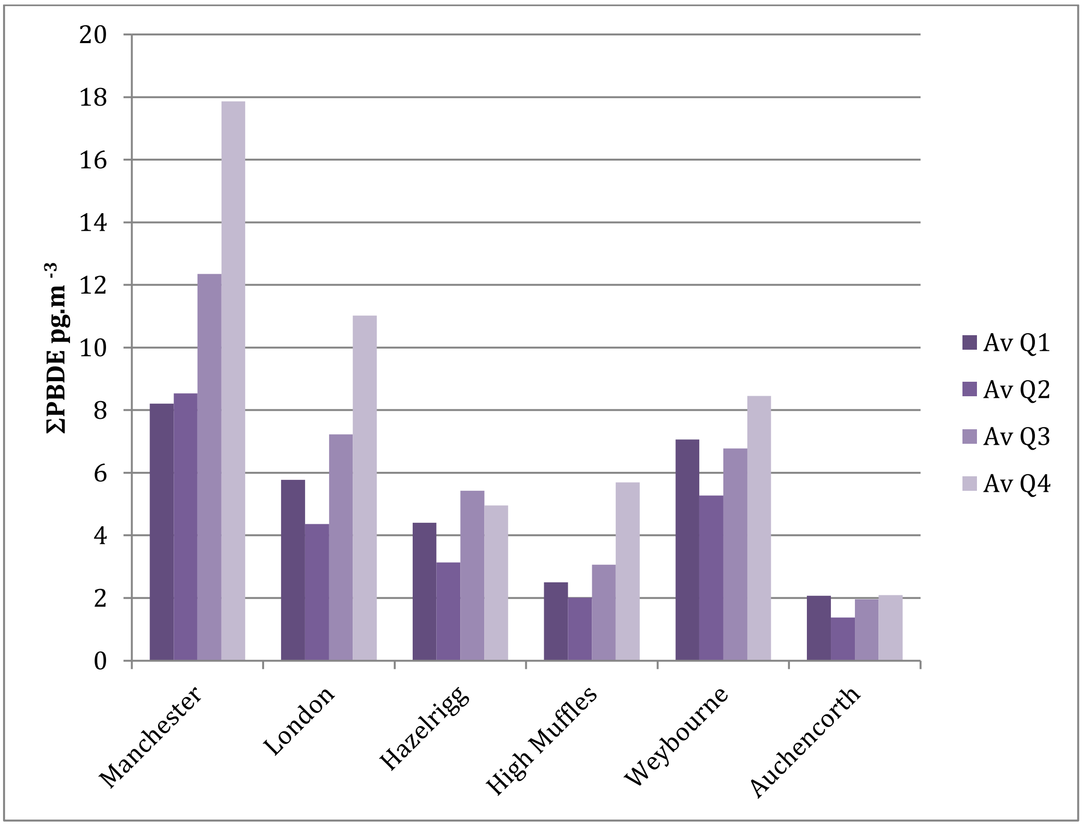
The NAEI suggests that emissions of PCBs to the UK atmosphere have reduced from 6200 kg in 1992 to 730 kg in 2015. Contemporary sources include continued presence of PCBs in dielectric fluids, power generation, small scale waste burning and sewage sludge application to land. The data in Figure 6 shows a sharp decrease in the late 1990's which is attributed to assumed significant reductions in the presence of PCBs in electrical equipment such as capacitors and transformers.

PCBs have been measured as part of the Integrated Atmospheric Deposition Network (IADN) since the early 1990's. IADN is joint project between the U.S. Environmental Protection Agency and Environment Canada which covers 5 ambient air monitoring sites around the Great Lakes. Using similar sampling equipment as TOMPs, the IADN network reports concentration data for 24hr samples collected every 12 days for a range of PCB congeners, organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs). PCB concentrations generally showed the slowest rate of decline among all of the chemicals measured by IADN. The clearance rate of PCBs in the vapour phase was 14.9 (± 1.1 years) which is longer than the clearance rates observed for the TOMPs network sites.

7.4 PBDEs: Results and discussions

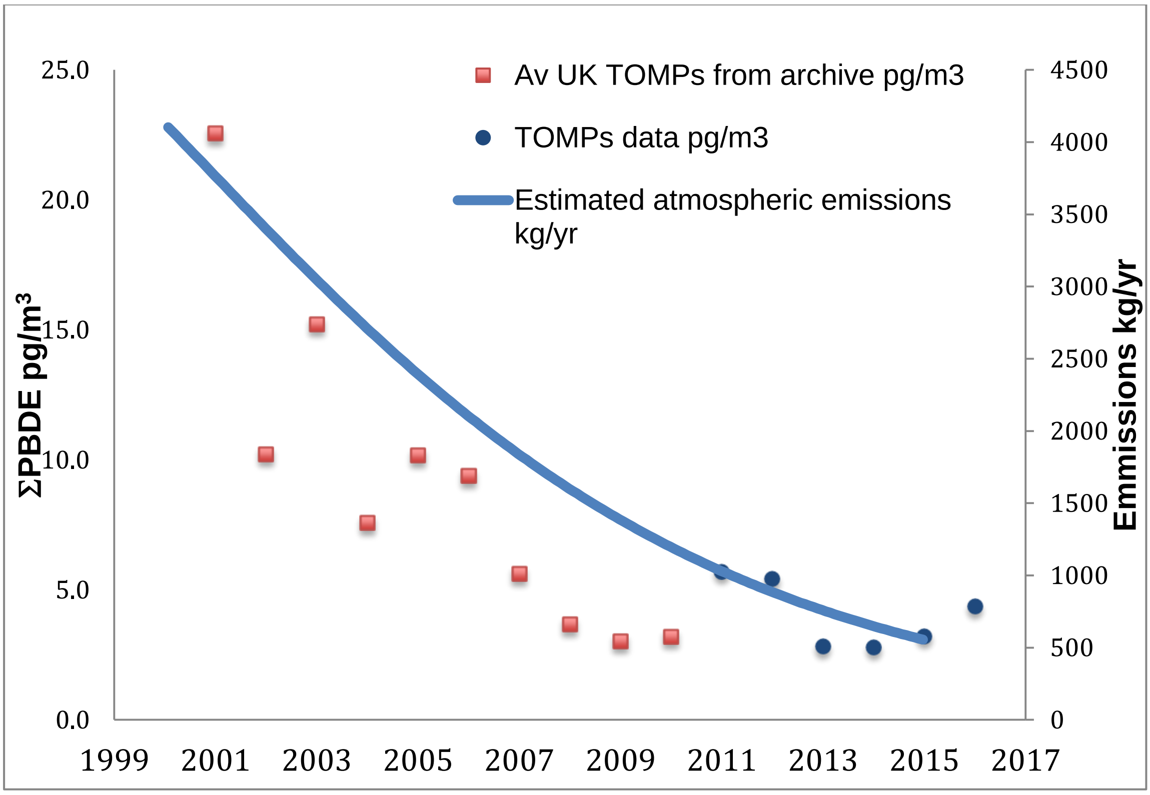
PBDEs were introduced into the TOMPs network during Q4 2010. Twenty-two individual congeners have been measured and the data contained in the annual reports. A summary of the averaged quarterly data over this period are shown in Figure 7. Manchester and London showed the highest annual average concentrations for Σ_{22}PBDEs at 11.4 pg/m^3 and 7.1 pg/m^3, respectively, followed by Weybourne and Hazelrigg at 6.9 pg/m^3 and 4.5 pg/m^3, respectively. High Muffles and Auchencorth exhibited the lowest average concentrations at 3.3 pg/m^3 and 1.9 pg/m^3, respectively. The averaged quarterly data suggests that there is some seasonality in ambient air concentrations, but the patterns are less clear. This could suggest that ambient air concentrations are being affected by on-going primary sources as well as secondary re-cycling in the environment.

Figure 7. 2010 to 2016 combined average quarterly ΣPBDE data at the TOMPs sites.



The TOMPs air sample archive has been used to provide information the time-trend of PBDEs in the UK atmosphere. The re-analysis of the sample archive has focused on four of the six sites over a period ranging from 2000 to 2010 (Birgul *et al*. 2012). These time-trend data demonstrate a consistent decrease in concentration over recent years with the observed decline starting during the period 2001-2003. This is particularly evident in the urban sites of Manchester and London and at the semi-rural site of Hazelrigg. The average ΣPBDE clearance rates (time taken for a 50% decline in concentration) for these three sites were 3.4, 2.0 and 3.5 years, respectively. Comparison of concentrations to estimated emissions and use of PBDE congener profiles suggests that PBDEs in the UK atmosphere originate from primary emissions from products that contain mainly the penta-BDE technical mixture. The direct connection with source reduction and UK ambient air concentrations has been established using the Lancaster University EvnBETR environmental fate model. Figure 8 compares the ambient air data from the TOMPs archive and the recent TOMPs data from 2011-16, along with an estimate of emissions to the UK atmosphere. These data show good agreement suggesting that the sources are largely captured in the emission inventory and that ambient air concentrations are declining at a predictable rate.

Figure 8. ΣPBDE data at the TOMPs sites over the period 2011 to 2016 (PBDEs have been included in the TOMPs network since 2011, data from 2000 produced from archived samples - Birgul *et al*. 2012).



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