The TOMPs Ambient Air monitoring Network – continuous data on the UK air quality for 20 years

Carola Graf, Athanasios Katsoyiannis, Kevin C Jones and Andrew J Sweetman

Lancaster Environment Centre, Lancaster University, UK

Abstract

Long-term air monitoring datasets are needed for persistent organic pollutants (POPs) to assess the effectiveness of source abatement measures and the factors controlling ambient levels. The Toxic Organic Micro Pollutants (TOMPs) Network, which has operated since 1991, collects ambient air samples at six sites across England and Scotland, using high-volume active air samplers. The network provides long-term ambient air trend data for a range of POPs at both urban and rural locations. Data from the network provides the UK Government, regulators and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation such as the Stockholm Convention and UN/ECE Protocol on POPs. The target chemicals of TOMPs have been polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and, since 2010, polybrominated diphenyl ethers (PBDEs). The continuous monitoring of these compounds demonstrates the constant decline in UK air concentrations over the last two decades, with average clearance rates for PCDD/Fs in urban locations of 5.1 years and for PCBs across all sites 6.6 years. No significant declines in rural locations for PCDD/Fs have been observed. There is a strong observable link between the declining ambient air concentrations and the emission reductions estimated in the annually produced National Atmospheric Emission Inventory (NAEI) dataset. These findings clearly demonstrate the unique strengths of long-term consistent datasets for the evaluation of the success of chemical regulation and control.

Keywords Air monitoring, long-term, POPs, time trends, Stockholm Convention

Introduction

The Stockholm Convention (SC) on POPs was adopted in 2001 and entered into force in 2004 (UNEP 2001). The SC aims to protect human health and the environment from persistent chemicals that have become widely distributed geographically, accumulate in food chains and have demonstrable adverse health effects to humans and environment. These substances have been connected to serious health effects including certain cancers, and immune and reproductive impairment. Given their ability to undergo long-range transport, either via air, ocean currents or migrating species, these substances represent a global issue that requires global agreements to ensure exposure to these substances is minimized. Unilateral action is unlikely to be effective for these substances. On the Convention's inception a number of substances were selected for inclusion, which clearly fulfilled any definition of POPs, i.e. persistent in all environmental compartments, bioaccumulative, toxic and with the ability to undergo long-range transport and hence contaminate remote environments such as the Arctic. These included the so-called ‘classic’ POPs such as the polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT). However, more recently substances have been discussed by parties to the SC that are less clearly defined as POPs. A number of ‘emerging’ environmental substances have been detected in the environment, which has raised some concerns as to whether some may be considered as POPs. The detection of such substances in the environment, whilst undesirable, does not necessarily suggest they may be POPs and so a detailed assessment against the defined criteria of persistence, long-range transport potential, bioaccumulation toxicity is required.

Parties to these international agreements, including the Stockholm Convention and Aarhus Protocol on POPs under UN/ECE (1998), must take measures to reduce or eliminate releases, to develop an implementation plan and – within their capabilities – encourage and/or undertake appropriate research and monitoring pertaining to POPs. Under the latter category, ‘sources and releases into the environment’, ‘presence, levels and trends in the environment’ and ‘environmental transport, fate and transformation’ are all specifically mentioned. These include robust multi-media source inventories for POPs such as dioxins and PCBs along with long-term air monitoring to ensure that source control measures result in demonstrable reductions in ambient air concentrations, which are central to the fulfilment of signatory parties international obligations.

The Toxic Organic Micro Pollutants (TOMPs) Network, which has operated since 1991, collects ambient air samples at six sites across England and Scotland, using high-volume active air samplers. The network, which is operated by Lancaster University and funded by the UK Department of Environment, Food and Rural Affairs (Defra), provides long-term ambient air trend data for a range of persistent organic pollutants (POPs) at both urban and rural locations. Data from the network provides Defra and researchers with valuable information on emission/source controls and on the effectiveness of international chemicals regulation. It is also used to demonstrate UK compliance with its obligations under the Stockholm Convention and UN/ECE Long-Range Atmospheric Transport Protocol. Moreover, long-term analysis of air pollutants at trace levels allows detailed studies on atmospheric fate and behaviour processes of persistent chemicals and is the inevitable basis of the successful understanding and modelling of their environmental fate. The target chemicals of TOMPs since its inception have been polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and, since 2010, polybrominated diphenyl ethers (PBDEs). PCBs, PCDDs, PCDFs are listed in Annex A (elimination) and C (unintentional release) of the Stockholm Convention, whilst selected PBDEs are listed in Annex A. This paper explores some of the key outcomes from the TOMPs monitoring network for these compounds and discusses the factors controlling the apparent constant decline in their UK air concentrations. The PAH data collected as part of the TOMPs network, and now incorporated into a larger PAH network, has been reported by Brown *et al.* (2013) and so will not be discussed in detail in this paper. It is clear that long-term monitoring programmes, such as TOMPs, are key to quantitatively assessing the success of regional and global chemical controls and regulations. However, the on-going operation of such networks faces many challenges in the future, which are inevitably resource limited, but required to provide data on the long term ambient air concentrations for an increasing list of substances.

Materials and methods

TOMPs sites and sampling methodolgy

Measurements of POPs and PAHs commenced in 1991 when the UK TOMPs network was established with four monitoring stations in urban locations: London, Manchester, Cardiff (University of Cardiff) and Stevenage. The Cardiff and Stevenage stations closed in 1992 and 1993, respectively, and new stations were installed in 1992 at Hazelrigg (a 'semirural' location) and Middlesbrough (an 'urban' location). By the start of 1997, the number of monitoring stations had increased to six by the inclusion of two rural stations – Stoke Ferry and High Muffles. At the rural and semirural (Hazelrigg) sites, samplers were located away from major roads, whereas at the urban sites, samplers were located in the city centre on the roof of a building. The site at Stoke Ferry was shut down at the beginning of 2008 and the site at Middlesbrough was phased out to coincide with the redevelopment of the site during 2007. A new TOMPs site was established at Auchencorth Moss, an upland remote peat site close to Edinburgh. This site, operated by CEH Edinburgh, is part of the Heavy Metal Network and is one of the European Monitoring and Evaluation Program (EMEP) network of superstations. These high quality EMEP stations have extended measurement programs, detailed documentation and trained technical staff. This site is an ideal TOMPs site as it represents a rural/remote location and is likely to be removed from the influence of local sources. Auchencorth Moss started operating in 2008. In order to replace the Stoke Ferry sampler, a new site was established at the University of East Anglia's Weybourne Atmospheric Observatory (WAO), a rural coastal site. This site is approximately 60km to the north east of Stoke Ferry and is an established facility at which fundamental atmospheric research and background air quality monitoring is carried out. Thus the selection of sites included large urban conurbations, semi-rural locations (rural sites but influenced by nearby towns and transport infrastructure) and rural/remote sites and was believed to be representative of such locations across the UK. However, the undue influence of local sources cannot be completely ruled out.

Currently the TOMPs programme operates 6 sites across England and Scotland:

Current sites		
London	LON	urban site established in 1991
Manchester	MAN	urban site established in 1991
Hazelrigg (Lancashire)	HR	semi-rural site established in 1992
High Muffles (North Yorkshire)	HM	rural site established in 1997
Auchencorth Moss (Midlothian)	AUCH	rural site established in 2008
Weybourne (Norfolk)	WEY	rural coastal site established at the end of 2008
Discontinued sites		
Stoke Ferry (Norfolk)	SF	rural site established at the end of 1997. Ceased

		operation in 2007 (transferred to WEY).
Middlesbrough	MID	urban site established at the end of 1993. Ceased operation in 2008.

A map displaying the sampling site locations is shown in Figure 1. Since its inception the TOMPs network has used Andersen GPS-1 samplers with PM10 size selective inlets. The samplers are run continuously with samples collected every 2 weeks. This provides sampled air volumes of approximately 700m^3. Modules, which are prepared just prior to deployment, consist of pre-baked (450 ºC for 4 hours) GF/A filters and two 7.5cm by 5cm PUF plugs. 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. These loggers are monitored remotely to ensure sampling continues with minimal interruption.

Analytical methodology

Details of the analytical procedure are contained in Schuster *et al.* (2012a) and Katsoyiannis *et al.* (2010). In summary, each sample is spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners ($^{13}C_{12}$ PCB 28, 52, 101, 138, 153, 180, 209), the PBDE congeners BDE 51, BDE 128, and BDE 190, and 21 $^{13}C_{12}$-labelled PCDD/Fs and coplanar PCBs. Samples are individually extracted in a Soxhlet extraction unit for 16 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 hexane and toluene fraction are combined for each sample and extracts pooled before purification to obtain three-monthly averaged data. The extracts are then eluted through a multilayer column containing activated silica, basic silica and acid silica. If necessary, this is followed by acid digestion (H_2SO_4) and a second multicolumn elution. After elution through a gel permeation chromatography (GPC) column PCB and PBDE fractions are analyzed by gas chromatography - mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM). Afterwards, the extract is fractionated with a basic alumina column. The analysis of the PCDD/Fs, and co-planar PCBs is performed on a high-resolution gas chromatography – high-resolution mass spectrometry instrument (HRGC-HRMS), operated at a resolution of at least 10,000.

QA/QC. A number of steps are taken to allow an assessment of the accuracy and reliability of the data. PCB, coplanar PCB, PBDE, and PCDD/F recoveries are monitored in all samples by quantifying $^{13}C_{12}$-labelled PCB, coplanar PCB, and PCDD/F standards and unlabelled PBDE standards. Furthermore, the concentrations of all compounds are corrected using these recoveries .The criteria for the quantification of analytes are: a retention time found within 2s of the standard, isotope ratio found within 20% of the standard, and a signal-to-noise ratio of at least 3. All results are blank-corrected using laboratory and field blanks, which are produced for each site and each quarter, and, together with instrument blanks, are also used to calculate method detection limits (MDLs).

Results and discussion

The sampling methodology and analytical protocol used in the TOMPs network has been maintained since establishment of the sites, and has provided time-trend data for a range of POPs for over 20 years at some locations. This approach has provided a consistent dataset for dioxins and PCBs allowing the investigation of temporal trends and the assessment of the reduction of sources brought about by the introduction of regulations such as the SC. The TOMPs network provided PAH data from 1991 until 2012 but the sites have now been included in a wider PAH network. As these data over the last twenty years have been reported elsewhere (Brown *et al*. 2013) they will not be included here.

***PCDD*/Fs:** Summary data for the sum of 17 PCDD/Fs from the six current TOMPs sites, calculated using the WHO 1998 toxic equivalent scheme, show a distinct urban-rural split. All the 17 PCDD/F target congeners were detected in varying concentrations over the sampling period with median concentrations for the urban sites ranging from 58 fgTEQ m^{-3} (MAN) to 20 fgTEQ m^{-3} (LON). The rural and semirural sites have notably lower ΣTEQ values ranging from 8.3 fgTEQ m^{-3} for HAZ, 4.8 fgTEQ m^{-3} for HM, 2.2 fgTEQ m^{-3} for WEY and 1.4 fgTEQ m^{-3} for AUCH. The WEY and AUCH sites have a much shorter time record than the other sites. Figure 2 is a box-and-whisker plot showing the range of concentrations (25th percentile and 75th percentile of the ΣTEQ PCDD/Fs, median and mean values) and outliers (Statistical data provided by StatPlus, AnalystSoft Inc.).

Seasonal variations. Seasonality of PCDD/Fs in ambient air where winter values exceed summer values has been widely reported in the literature (e.g., Katsoyiannis *et al*. 2010). Increased combustion (i.e., domestic space heating) and seasonal variations in temperature and atmospheric boundary layer height are the likely causes. A subset of the TOMPs dataset (2004-2010) was analyzed and seasonal variations were observed, and in some cases the differences between two consecutive quarters were >10-fold. Figure 3 summarizes the seasonal variations averaged values for all sites. For most sites, the first and fourth quarter had the highest ΣTEQ values. For the urban sites MAN and MID, for example, the concentrations of PCDD/Fs were 2-3 times higher in the first and fourth quarter than during the warmer months. This observation suggests that when ambient concentrations are low (typically in rural areas), emission events such as bonfires or accidental fires (Lee *et al.* 1999) can exert a measurable influence on the levels and the PCDD/F pattern. Therefore, if an accidental emission event were to occur, the increase in PCDD/F concentrations would be more noticeable at rural sites, where concentrations are typically low during the year, than at urban sites where seasonal differences are more pronounced and dependent on local sources. Within this averaged dataset there are a few notable results. For example, the coastal/rural site at Weybourne produced a relatively high concentration of PCDD/Fs in Q1 2009 of 79 fgTEQ m^{-3}, which is similar to those levels measured in London. It is well known from the monitoring of other atmospheric contaminants (i.e., NOx http://weybourne.uea.ac.uk/) that this site can receive ‘polluted air’ from the London area from time to time, and so this could explain the higher levels of pollutants observed at WEY in Q1 which is still evident in the 2004-2010 average. The site at Auchencorth Moss (AUCH) displays relatively low concentrations of PCDD/Fs in the same range to those measured in High Muffles, and occasionally exhibits levels that are even lower than these. Auchencorth Moss is located 20km to the south west of Edinburgh but appears to have very little influence from the city. This can be explained by the dominant wind direction being westerly to south westerly.

Temporal Trends. Figure 4 shows the PCDD/F temporal trends for the combined urban and rural sites from the early 1990s to 2012 (expressed as pgI-TEQ m^{-3}). The data has been converted to the I-TEQ scheme to make a comparison with the emission estimates provided by the NAEI. Applying first-order kinetics to the whole urban time series suggests that concentrations have been decreasing with atmospheric clearance rates for LON and MAN of 4.9 and 4.8 years, respectively. Estimated annual atmospheric emissions trends from the NAEI can be broadly correlated with the trends in urban ambient air concentrations, suggesting that the inventory has captured the broad mixture of sources which are mostly from diffuse combustion processes. Rural air concentrations, which are generally much lower than urban concentrations, show no discernible change since 1996.

The data also suggests that recent urban concentrations are now close to those in rural areas. These trends combined together with observations of seasonal dependence suggest that most major readily controllable primary/point sources were reduced by the early/mid-1990s in the UK and that current ambient air levels in both rural and urban areas may remain at broadly similar levels in the foreseeable future, unless there are major changes in energy requirements and generation options, fuel usage, or policy drivers.

The NAEI emission estimates for the UK are shown in Figure SI1 in the Supplementary Information and clearly demonstrate the decline in UK PCDD/F emissions over the period 1990 to 2013. According to the inventory, PCDD/F emissions were around 1300 gI-TEQ per year in 1990, dropping to 222 gI-TEQ per year in 2013. The main emission reductions have resulted from controls introduced to the iron and steel industry during the 1990s. Katsoyiannis *et al.* (2010) combined the TOMPs dataset with estimates of UK ambient air concentrations derived from archive herbage samples with the assumption that the levels found in grass would be reflective of UK ambient at the time the samples were collected. This longer-term perspective (from the early 1900s) provided some interesting insights into the potential controlling factors for PCDD/Fs in UK ambient air. This dataset suggests that ambient concentrations of PCDD/Fs have been steadily declining over the last few decades, with several regulatory measures identified that may have driven emissions down. These could have included the following: the UK Clean Air Act which came into force in 1956; reductions in organochlorine manufacture through the 1960-1980s; reductions in the use of halogenated lead additives in petrol in 1986 and 1992; the introduction of emission controls on municipal and chemical waste incinerators in the mid-1990s, and the general shift away from domestic burning of wood and coal for space heating to the more widespread adoption of electricity and gas. The PCDD/F declines so far indicate that the UNECE Protocol (1998) and the Stockholm Convention (2001) appear to have had little additional impact on the already declining ambient PCDD/F levels.

PCBs: Data for the sum of 7 PCB commonly reported congeners PCB 28, 52, 90/101, 118, 138, 153 and 180 (ΣPCB_7) from the six current TOMPs sites and the urban Middlesbrough site show a distinct urban-rural split. All PCB target congeners were detected in varying concentrations over the sampling period with median concentrations for the urban sites ranging from 141 pgm^{-3} (MAN), 100 pgm^{-3} (LON) to 57 pgm^{-3} (MID). The rural and semi-rural sites have notably lower ΣPCB_7 values ranging from 34 pgm^{-3} for HAZ, 17 pgm^{-3} for HM, 16 pgm^{-3} for WEY to 12 pgm^{-3} for AUCH. The WEY and AUCH sites have a much shorter time record than the other sites. Figure 5 is a box-and-whisker plot showing the range of concentrations (25th percentile and 75th percentile of the ΣPCB_7, median and mean values) and outliers (Statistical data provided by StatPlus, AnalystSoft Inc.).

Seasonal Variations. Various studies have reported and discussed strong seasonal trends in PCB air concentrations (Halsall *et al.* 1995, Melymuk *et al* . 2012). These observations, where PCB concentrations are generally higher in summer than in winter, can be confirmed by the data from the TOMPs program. Figure SI2 in the Supporting Information shows averaged (2011 – 2013) ΣPCB_7 air concentrations for two rural sites (AUCH and HM) and two urban sites (MAN and LON). For all four sites concentrations are highest in summer (Q3, July – September), followed by spring (Q2, April – June) and autumn (Q4, October – December), with winter (Q1, January – March) showing the lowest concentrations (with the exception of HM, where Q4 was slightly lower than Q3). This pattern is in very good accordance with previous studies.

Temporal Trends. The quarterly ΣPCB_7 concentrations across the TOMPs network from the early 1990s are shown in Figure 6 for the combined urban sites and rural sites. It is clear that the temporal trend data from each site group shows decreasing concentrations, most demonstrating a statistically significant decrease over time. It is important to note that WEY and AUCH have operated over a shorter period of time compared to other sites. Applying first-order kinetics to the urban time series suggests that concentrations have been decreasing with atmospheric clearance rates for MAN, LON and MID of 6.6, 3.9 and 4.9 years, respectively. The rural and semi-rural sites have estimated clearance rates of 5.6 and 7.5 years, respectively. The recently established sites at Auchencorth Moss and Weybourne have not been running for sufficient time to determine trends. Figure 6 also shows the combined estimated annual atmospheric emissions trends from the NAEI. These can be broadly correlated with the trends in ambient concentrations (stronger for urban sites), suggesting that the inventory has probably captured the main on-going sources. Data from a passive sampler network spanning the UK and Norway has provided similar clearance rates for UK rural sites, which ranged from 5.6 to 15.4 years (Schuster *et al.*, 2010b).

A voluntary ban on production of PCBs in the UK was agreed with manufacturers in the late 1960s/early 1970s. Limits on emissions from incinerators, the handling of PCB-containing wastes etc. were applied from the late 1970/80s onwards. Key on-going primary sources are believed to be the stocks from past use in transformers, capacitors, buildings/sealants etc. which are all potential diffusive primary sources to the atmosphere via volatilization. The importance of re-emission of previously emitted PCBs from surface soils and sediments is still unclear. However, this represents a potentially important issue which relates to our ability to undertake further source reductions. The NAEI estimated total PCB emissions of 6667kg in 1990 which reduced to 706 kg in 2013 with the majority of emissions originating from electrical equipment containing dielectric fluids, e.g. transformers. Figure SI3 in the Supporting Information shows the NAEI data for PCBs covering the period 1990 to 2012 and details the main source categories contributing to the UK emissions inventory. It is clear that the main contribution to the total emissions originates from the use of PCBs in dielectric fluids. The notable decrease in the late 1990s in the emission inventory relates to controls placed on electrical equipment mainly used for power distribution.

As mentioned above, the temporal trend data from most sites show a decrease in concentrations over time, most of which are statistically significant. The individual trends established at each site and for each of the different congeners measured were found to be not statistically different from each other suggesting that similar sources have been, and still are, contributing to the measurements. Previous studies by Schuster *et al.* (2010a), whilst examining the inter-site differences in more detail, established correlations between ambient air concentrations and local population density (i.e., the degree of urbanization), which suggests that primary emissions on the national scale are still important in controlling ambient levels. Hence the underlying trends of PCBs in the UK atmosphere continue to reflect the controlling influence of diffuse primary sources from the ongoing stock of PCBs, mostly in urban environments. Production and use restrictions came into force in the UK over 40 years ago and trends since monitoring began in the early 1990s should be seen as part of a continuing decline in ambient levels since that time.

Estimates of soil-air fugacity ratios, calculated as $f_{soil}/(f_{soil}+f_{air})$ have increased from 0.04 in 1970 to 0.1 in 2000 and are projected to be 0.2 by 2020. These estimates (based on a methodology by Sweetman and Jones (2000) demonstrate the net flux of PCBs remains from air to soil which confirms that primary sources continue to dominate, but the trend suggests that secondary sources with become increasing importance into the future.

Other key long-term monitoring projects for PCBs in the atmosphere are being conducted under the European Monitoring and Evaluation Programme (EMEP) for Europe and the Integrated Atmospheric Deposition Network (IADN) for the Great Lakes area of North America. The Global monitoring plan for POPs in the Western Europe and Others Group (WEOG) (effectiveness evaluation 2nd regional monitoring report) showed that PCBs in air in the WEOG region tend to show generally declining trends at all monitoring stations since the 1990s (UNEP, 2015). Apparent first order clearance rates for PCBs from other European monitoring networks provide similar declines to the TOMPs dataset. Data collected from Birkenes, Norway, provided clearance rates ranging between 4.5 years and 8.0 years for the seven indicative PCB congeners. The same data from Birkenes showed that all seven congeners followed a similar pattern over the studied period which probably reflects common sources, as was found within the TOMPs dataset. In all cases, the decline became faster after 2008. Other EMEP stations such as Aspvreten and Rao in Sweden reported slow declines with clearance rates ranging between 11 years (PCB 180) and 20 years (PCB 52) over the period 1995-2012, while for Rao no clear trend was observed over the period 2002-2012. The Integrated Atmospheric Deposition Network (IADN), jointly operated by the US and Canada, reported much longer clearance rates at ambient air monitoring stations around the Great Lakes, ranging from 6.5 to 34 years, with clearance rates being congener-specific.

PBDEs. Polybrominated diphenylethers 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 to 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. 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-BDE contains predominantly the deca-BDE congener and is currently the most widely PBDE flame retardant product in use. The commercial mixtures penta-BDE and octa-BDE have already been added to Annex A of the Stockholm Convention in 2009.

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). In the UK there has been previously high use of penta-BDE as a result of flame 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. In 2010 PBDE congeners were included in the TOMPs methodology. The congeners that have been analysed are: BDE-28 (tri), BDE-47 (tetra), BDE-49 (tetra), BDE-99 (penta), BDE-100 (penta), BDE-153 (hexa), BDE-154 (hexa), BDE-183 (hepta). Congeners BDE-47 and BDE-99 account for approximately 72% of the composition of the penta commercial mixture (pentaBDE). Atmospheric emission estimates for 2012 for the tetra and penta-PBDEs in the UK were 800kg.

Seasonal Variations. As described and discussed in previous studies (Melymuk *et al.* 2012, Yang *et al.* 2013), the seasonal pattern is less uniform for PBDEs than for PCDD/Fs or PCBs. Figure SI4 in the Supporting Information shows seasonal averages (2011 – 2013) for BDE 47 (tetra), BDE 99 (penta), BDE 153 (hexa), and BDE 183 (hepta) at two rural (AUCH and HM) and two urban (LON and MAN) sites. In accordance with the previous observations, only BDE 47 shows elevated concentrations in the summer compared to the winter months across all sites. While there is no discernible pattern for BDE 99, both BDE 153 and BDE 183 concentrations are clearly higher in Q1 and Q4 than in Q2 and Q3, with the highest values in Q4 (October – December).

Temporal Trends. In order to provide some historical context the TOMPs air sample archive was used to provide information on the temporal trends of PBDEs in the UK atmosphere (Birgul *et al.* 2012). The re-analysis of PBDEs in the sample archive focused on four of the six sites over a period ranging from 1999 to 2010. The four sites included were London, Manchester, Hazelrigg and High Muffles. Figure 7 shows the trend data for ΣPBDE (sum of congeners 47, 49, 99, 100, 119, 154, 153, 138, 183) for an average of the four sites with a comparison of atmospheric emission data from Prevedouros *et al.* (2004). Figure 7 also contains data for 2011 and 2012 from the TOMPs dataset. The emission data, which have been recently updated, are based on a dynamic model of historical estimates of PBDE manufacture, incorporation into products (e.g., polyurethane foams) and subsequent emission from each product type using specific emission factors over their respective life cycles. These time-trend data demonstrate a consistent decrease in concentrations over recent years with the observed decline starting during the period 2001-2003. When examining the site-specific data the decline is particularly evident in the urban datasets of Manchester and London and at the semi-rural site of Hazelrigg. The calculated ΣPBDE atmospheric clearance rates for these three sites are 3.4, 2.0 and 3.5 years, respectively. Of the individual congeners detected, BDE-47 is the most abundant at all sites and in almost all samples, followed by BDE-99, and both dominated all calculated profiles. Given that these two congeners are the main components of the penta-BDE (PeBDE) technical mixture, with BDE-47 accounting for 38-42% and BDE-99 accounting for 45-49% of the ΣPBDEs, these results likely reflect the extensive use of that specific technical mixture. The strong correlation between the estimated emissions and the measured concentrations ($r^2=0.79$, $p=0.0084$) suggests that on-going releases from articles containing PeBDE products is likely to be controlling the long-term trends in the UK atmosphere. BDE-183, a congener present in the octa-BDE commercial mixture did not correlate well with congeners present in the penta-BDE mixtures. This suggested that the sources were different, although the concentrations of BDE-183 were generally low or close to the detection limits. Data from a passive sampler network spanning the UK and Norway has provided similar clearance rates for UK rural sites, suggesting a slightly longer value of approximately 6.5 years (Schuster *et al.,* 2010b). However, this estimate was made with a very limited dataset.

Policy perspective and conclusions

The TOMPs network is responsible for monitoring air quality by providing measurement of the air concentrations of a range of pollutants including PCDD/Fs, PCBs and PBDEs at rural and urban locations in the UK. Monitoring data using a consistent methodology is vital to understanding if the measures taken to reduce POPs emissions into the environment are successful, by providing invaluable insights into the long-term trends of POPs in UK air. The UK is a signatory to both the Stockholm Convention on POPs and UN/ECE Protocol on POPs to the Convention on Long-Range Transboundary Air Pollution. Therefore, providing information on past and predicted POPs emissions and concentrations of POPs in the environment can be used to determine if measures taken to control POPs releases into the environment can be shown to be successful.

Assessment of the dataset provided by the TOMPs network over the last 20 years concludes that ambient air concentration data for POPs over the monitoring period show significant decreases across most sites. The exception being for PCDD/Fs measured at the rural/semi-rural sites where no statistically significant trends were observed throughout the whole sampling period. Therefore, it is apparent that ambient air concentrations of PCBs, PCDD/Fs and PBDEs have responded to emission controls and are decreasing or stable at very low levels. Comparison of the temporal trends provided by the atmospheric emission inventories and the decreasing ambient concentrations suggests that the inventories have largely captured the main sources, which remain mainly primary and diffuse. The reconstruction of the historical ambient air trend for PCDD/Fs, however, showed that individual measures to reduce sources of POPs to the environment may not be significant on their own but may contribute to the long-term changes affected by a range of control measures, some of which may not have been directly intended to control POPs. Over the next few years, new 'candidate POPs' and emerging pollutants will be evaluated and a judgment reached as to their environmental significance and regulatory needs. This will create challenges for ambient air monitoring networks such as TOMPs. With finite resources priorities will need to be set to identify those substances that should be targeted for continued monitoring to demonstrate the success of regulation and source control, but to potentially reduce the sampling efforts for those substances that are believed to be sufficiently understood and sources controlled.

Acknowledgements

The TOMPs network is funded by the UK Department for Environment, Food and Rural Affairs, the Northern Ireland Department of Environment, the Scottish Government and the Welsh Assembly

References:

Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K.C., and Sweetman, A.J. (2012) Polybrominated diphenyl ethers (PBDEs) in the United Kingdom atmosphere. Environmental Pollution, 169, 105-111

Brown, A.S. Brown, R.J.C., Coleman, P.J. Conolly, C. Sweetman, A.J. Jones, K.C. Butterfield, D.M., Sarantaridis, D., Donovan, B.J. and Roberts I. (2013) Twenty years of measurement of polycyclic aromatic hydrocarbons (PAHs) in UK ambient air by nationwide air quality networks. Environ. Sci.: Processes Impacts, 15 (6), 1199 – 1215

Gioia, R., Sweetman, A. J. and Jones, K. C. (2007). Coupling passive air sampling with emission estimates and chemical fate modeling for persistent organic pollutants: a feasibility study in Northern Europe. Environ. Sci. Technol. 41, 2165-2171.

Halsall, C.J., Lee, R.G.M., Coleman, P.J., Burnett, V., Harding-Jones, P. and Jones, K.C. (1995) PCBs in U.K. Urban Air. Environ Sci. Technol., 29, 2368-2376

Hites, R.A. (2004) Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. Environ. Sci. Technol., 38 (4), 945–956

Katsoyiannis, A., Gioia, R., Sweetman, A.J. and Jones, K.C. (2010) Continuous Monitoring of PCDD/Fs in the UK Atmosphere: 1991-2008. Environmental Science and Technology, 44, 5735–5740.

Lee, R.G.M, Green, N.J.L., Lohmann, R. and Jones, K.C. (1999) Seasonal, Anthropogenic, Air Mass, and Meteorological Influences on the Atmospheric Concentrations of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/Fs): Evidence for the Importance of Diffuse Combustion Sources. Environ. Sci. Technol., 1999, 33 (17), pp 2864–2871

Melymuk, L., Robson, M., Helm, P.A. and Diamond, M.L. (2012) PCBs, PBDEs, and PAHs in Toronto air: Spatial and seasonal trends and implications for contaminant transport. Sci. Total Environ., 429, 272-280

Prevedouros, K., Jones, K.C., and Sweetman, A.J. (2004) Production, Consumption and Emission Estimates for Pentabrominated Diphenyl Ether (PeBDE) in Europe (1970 to 2000). Environmental Science and Technology, 38(12), 3224-3231.

Schuster, J., Gioia, R., Sweetman, A.J. and Jones, K.C. (2010a) Temporal Trends and Controlling Factors for Polychlorinated Biphenyls (PCBs) in the UK Atmosphere (1991-2008). Environmental Science and Technology, 44, 8068-8074

Schuster, J., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M. and Jones, K.C. (2010b) Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs. Environmental Science and Technology, 44(17), 6760-6766.

Sweetman, A.J., and Jones, K.C. (2000) Declining PCB Concentrations in the U.K. Atmosphere: Evidence and Possible Causes. Environmental Science and Technology, 34 (5), pp 863–869

UNECE (1998) Aarhus Protocol on Persistent Organic Pollutants (POPs) www.unece.org

UNEP (2001) The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme (www.pops.int).

UNEP (2015) Global monitoring plan for persistent organic pollutants under the Stockholm Convention Article 16 on effectiveness evaluation. 2nd regional monitoring report Western Europe and others group (WEOG) region.

Yang, M., Qi, H., Jia, H., Ren, N., Ding, Y., Ma, W., Liu, L., Hung, H., Sverko, E. and Li, Y. (2013) Polybrominated Diphenyl Ethers in Air across China: Levels, Compositions, and Gas-Particle Partitioning. Environ Sci. Technol., 47, 8978-8984

Figures:

Figure 1. Location of TOMPs sampling points

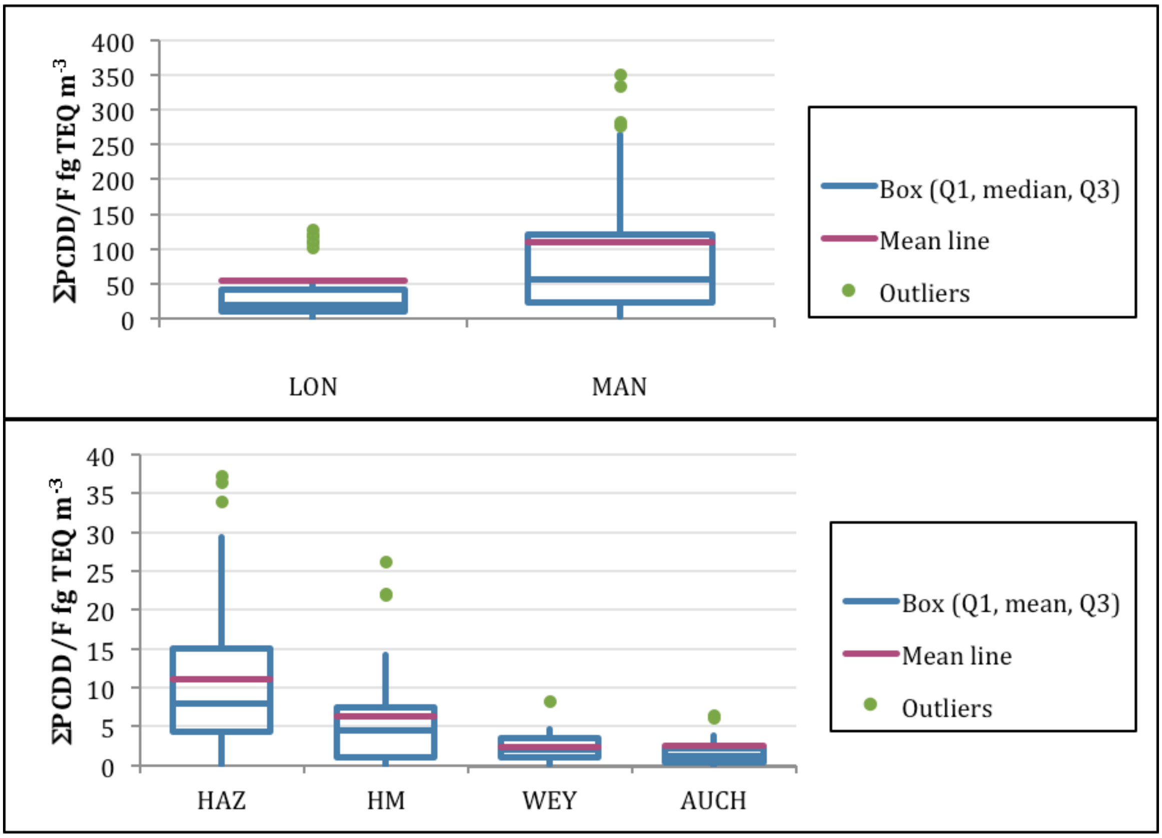

Figure 2. Box and Whisker plot of Σ TEQ PCDD/Fs at 2 urban sites (LON, MAN) and 4 rural/semi-rural (HAZ, HM, WEY, AUCH (1990-2012). The red line indicates the mean values, the blue box covers the lower and upper quartile and median values. Outliers are shown as green dots.

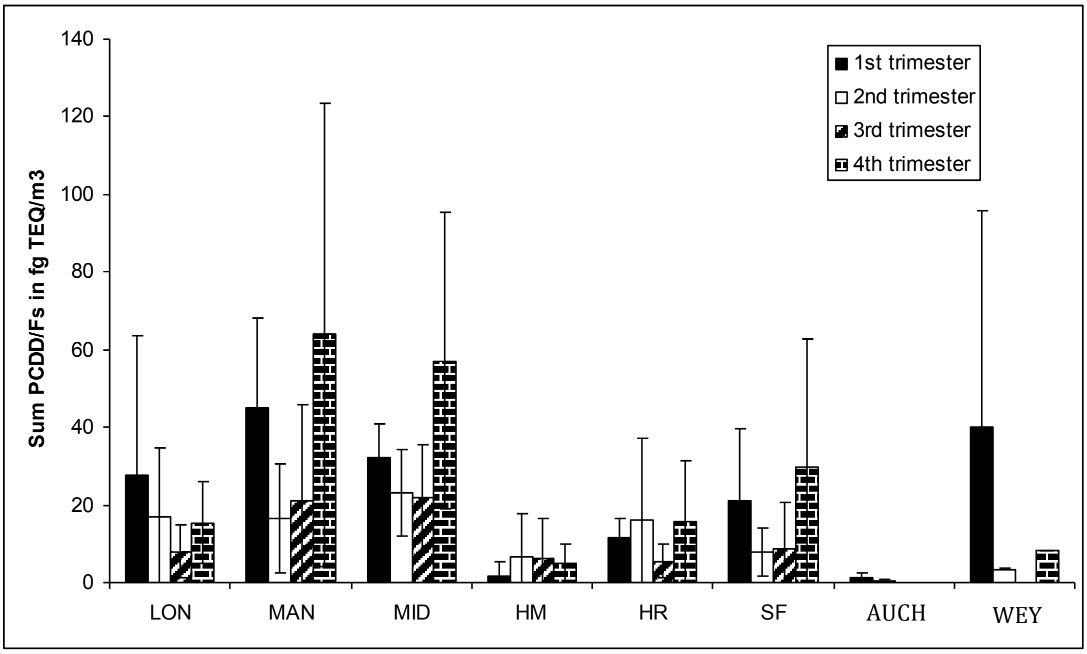

Figure 3. Sum of PCDD/Fs in fg TEQ/m3 at all sites and quarters over the period 2004-2010. (LON London, MAN Manchester, MID Middlesbrough, HM High Muffles, HR Hazelrigg, SF Stoke Ferry, AUCH Auchencorth and WEY Weybourne. 1st trimester Q1, 2nd trimester Q2, 3rd trimester Q3, 4th trimester Q4)

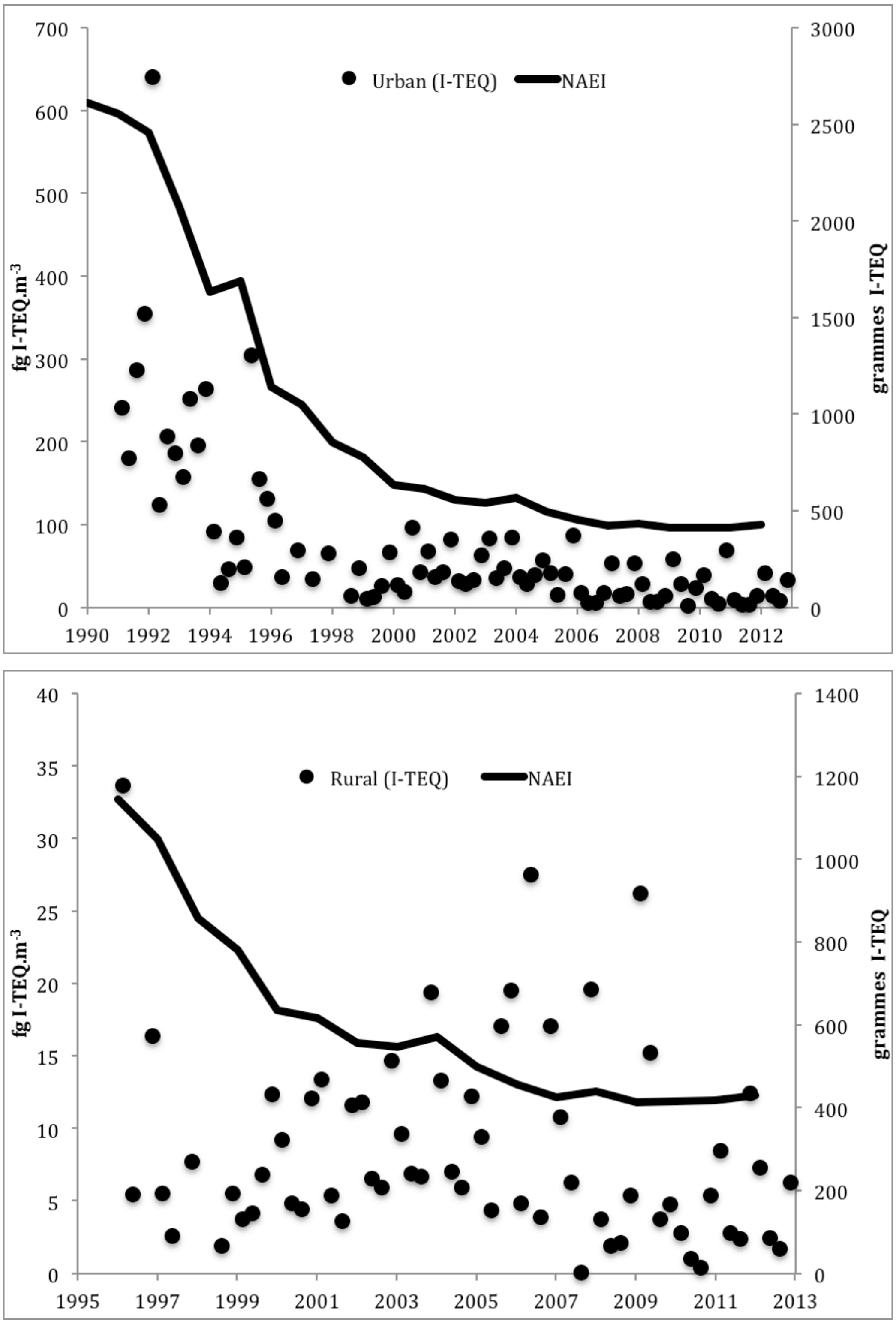

Figure 4. Temporal PCDD/Fs (fgI-TEQ.m^3) trend data for two urban and two rural TOMPs sites. NAEI – National Atmospheric Emission Inventory

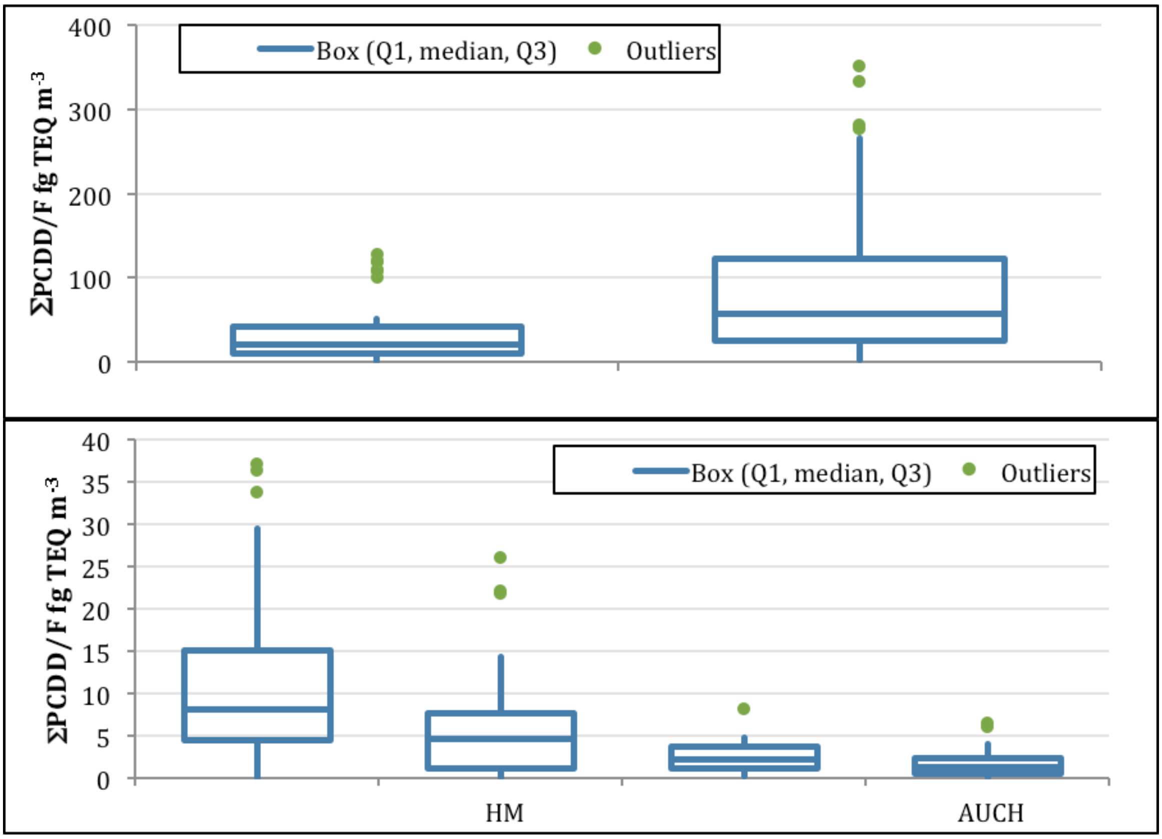

Figure 5. Box and Whisker plot of PCB concentrations (sum of congeners PCB 28, 52, 90/101, 118, 138, 153 and 180) across the TOMPs network showing 3 urban sites (LON, MAN, MID) and 4 rural/semi-rural (HAZ, HM, WEY, AUCH (1990-2012). The red line indicates the mean values, the blue box covers the lower and upper quartile and median values. Outliers are shown as green dots.

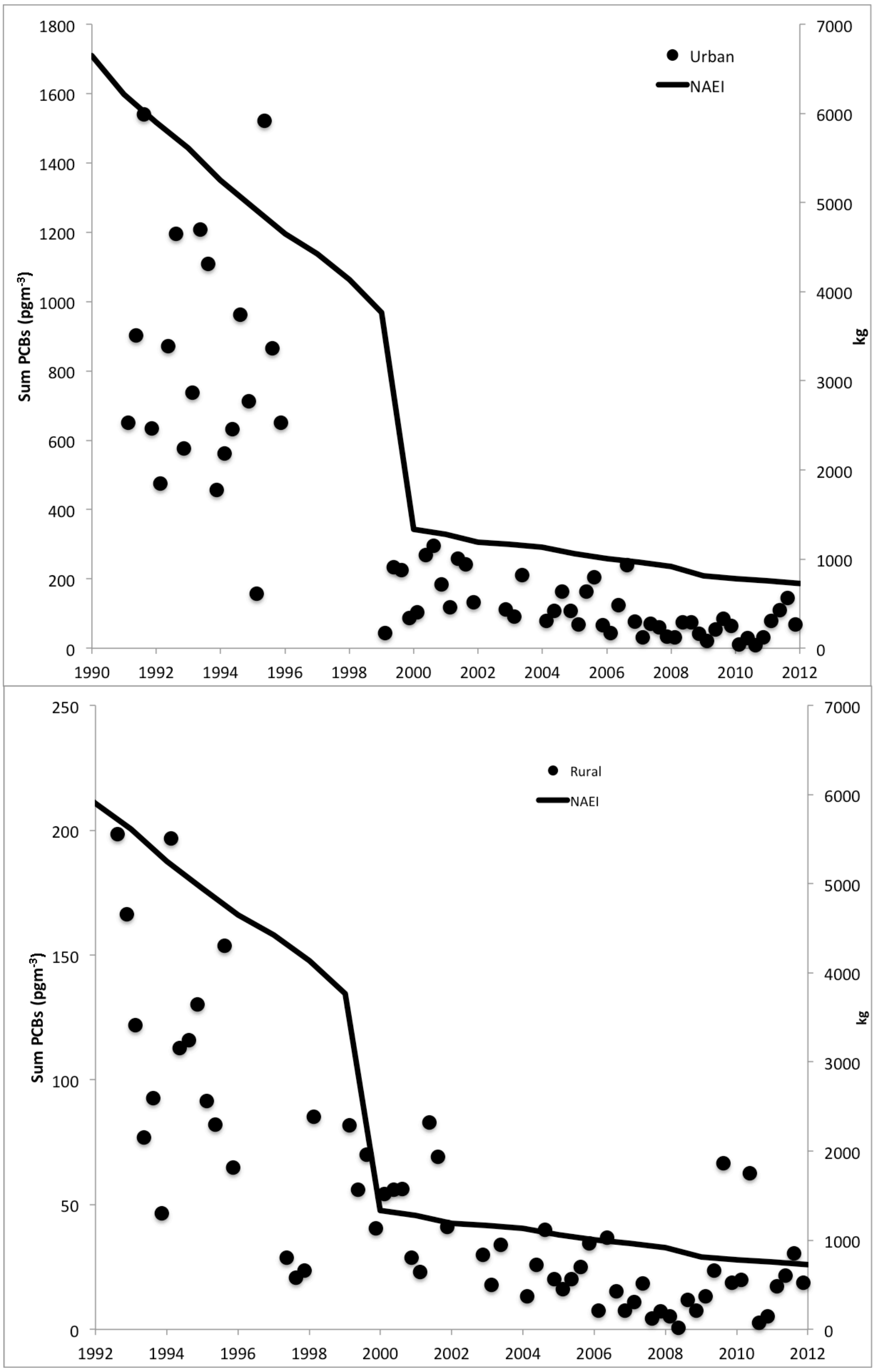

Figure 6. Temporal PCB trend data across urban (upper) and rural (lower) TOMPs sites overlaid with UK PCB emission estimates provided by NAEI. Left x-axis air concentration $\Sigma PCB_7\, pgm^{-3}$, right x-axis atmospheric emission kg per year

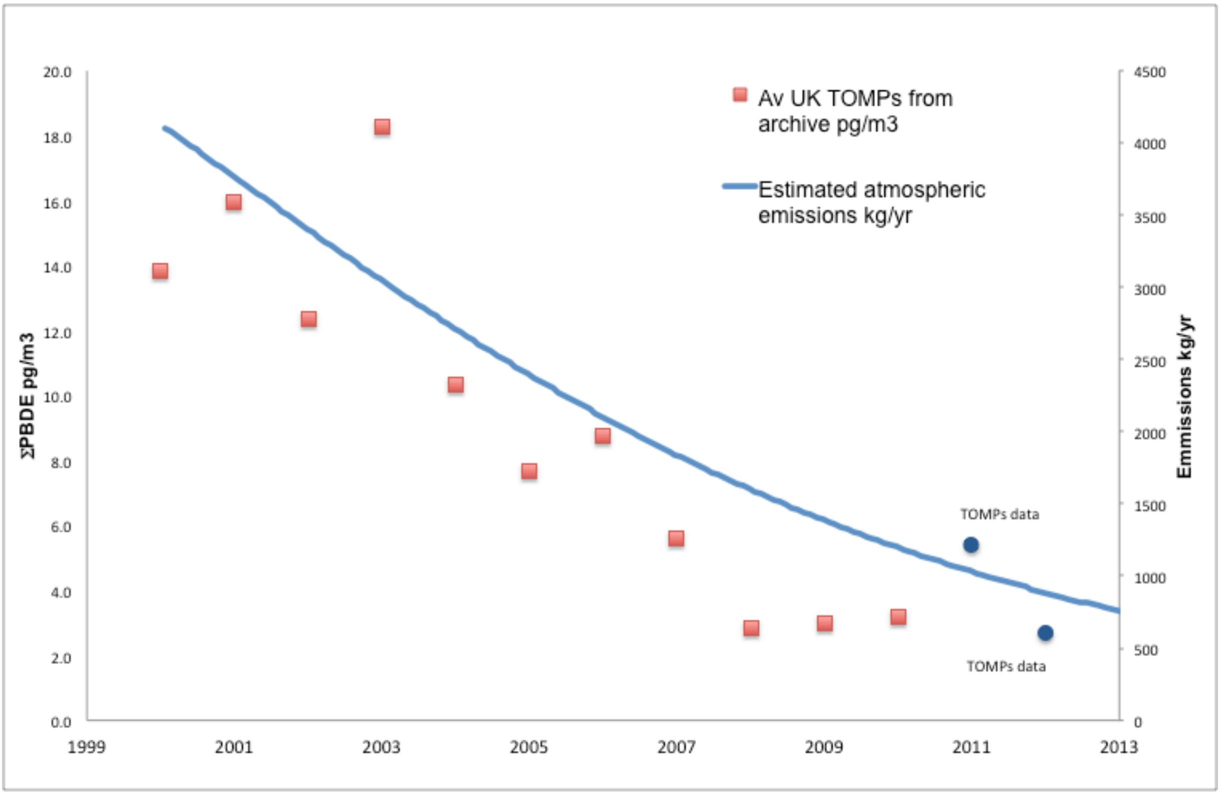

Figure 7. Comparison of estimated annual emissions of PBDE in the UK to the average annual concentrations of ΣPBDEs provided by the TOMPs network.