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

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Introduction

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 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 on Persistent Organic Pollutants 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 their successful modelling. 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). 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. The continuous monitoring of these compounds points out the constant decline in their UK air concentrations over the last decades and generally agrees with emission estimates. Additionally, an archive is maintained, which can be used for analysing emerging chemicals, such as alternative flame retardants, pesticides, and further substances of interest as soon as they have been identified.

Materials and methods

In 2012 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

A map showing the 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 continues with samples collected every 2 weeks. This provides sampled air volumes of approximately 700 m^3. Modules, which are prepared just prior to deployment, consist of pre-baked (450 ºC for 24 hours) GF/A filters and two 7.5cm by 5 cm 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.

Details of the analytical procedure are contained in Schuster *et al*. (2012) and Katsoyiannis *et al*. (2010). In summary, 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 soxhlet extraction unit for 18 hours with hexane and 6 hours with toluene.

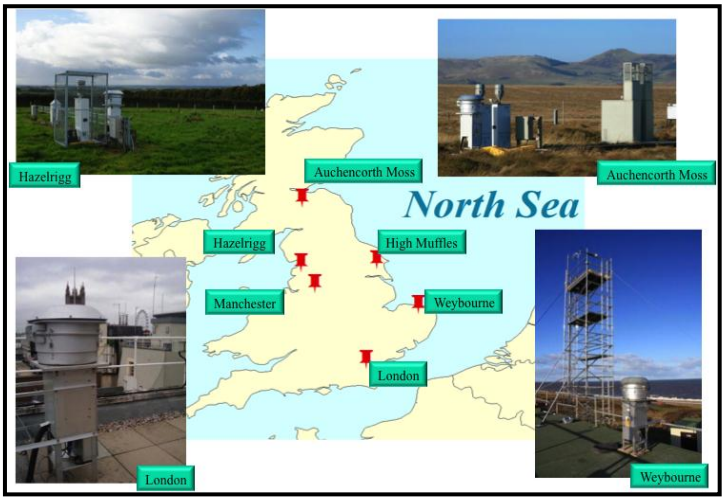

Figure 1. Location of TOMPs sampling points

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. This is followed by acid digestion (H_2SO_4) and a second multicolumn elution. After elution through a gel permeation column the extract is fractionated with a basic alumina column. The PCB and PBDE fractions are analyzed by gas-chromatography mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM). Analysis of the PCDD/Fs, furans and co-planar PCBs is performed on a Micromass Autospec Ultima high resolution-mass spectrometry (HR-MS) operated at a resolution of at least 10,000.

Results and discussion

The main objective of the network is to measure ambient air concentrations for a range of pollutants including PCDD/Fs and PCBs at rural and urban locations in the UK providing long-term trend data. The urban sites in London and Manchester have been running continuously since 1991. A further urban location in Middlesbrough operated from 1993 to 2008. The semi-rural site at Hazelrigg has been running since 1992 and the rural sites at High Muffles and Auchencorth Moss have been operating since 1999 and 2008, respectively. The coastal site at Weybourne has been operating 2008 but this site replaced another location 80km to the south West. ***PCDD*/Fs:** Figure 2 shows the PCDD/F temporal trends for the two rural sites and two of the urban sites from the early 1990s to 2010 (expressed as $pgTEQ_{WHO1998}.m^{-3}$). Applying first-order kinetics to the whole urban time series suggests that concentrations have been decreasing with atmospheric clearance rates in London and Manchester 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 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. Data collected during the winter periods show that concentrations are generally a factor of 2-3 higher than summer concentrations, confirming that diffuse combustion sources continue to be important. These observations taken together suggest that most major readily controllable primary/point sources were reduced by the early/mid-1990s in the UK and that current ambient 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. ***PCBs:*** The annual mean ΣPCB concentrations (sum of congeners PCB 28, 52, 90/101, 118, 138, 153 and 180) across the TOMPs network from the early 1990's are shown in Figure 3. It is clear that the temporal trend data from each site show decreasing concentrations, most demonstrating a statistically significant decrease over time. The recently established sites at Auchencorth and Weybourne, however, have not been running long enough to determine trends.

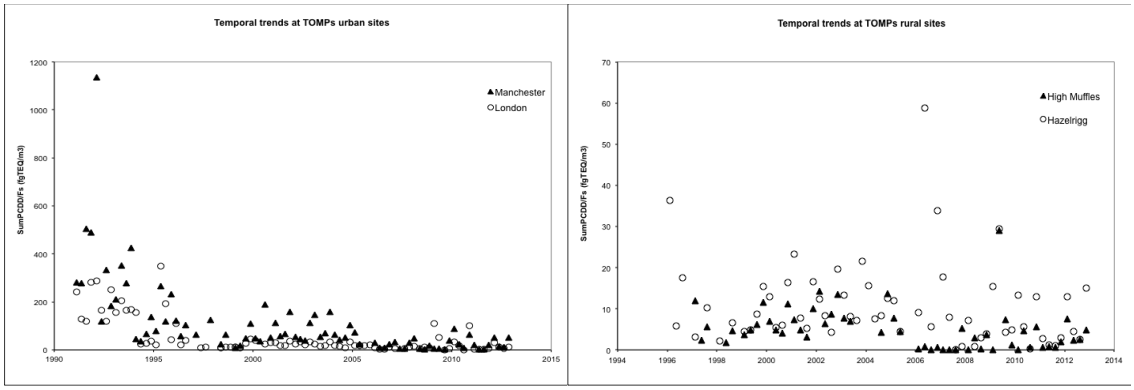

Figure 2 Temporal PCDD/Fs trend data for two urban and two rural TOMPs sites.

The calculated atmospheric clearance rate averaged across all long-established sites is 4.7 ± 1.6 years, which is a reflection of the estimates of UK emissions from the National Atmospheric Emission Inventory (http://www.naei.defra.gov.uk). The individual trends established at each site and for each of the different congeners were found to be not statistically different from each other suggesting that similar sources have been, and still are, contributing to the measurements. When examining the inter-site differences in more detail, it was established that concentrations could be correlated to 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 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.

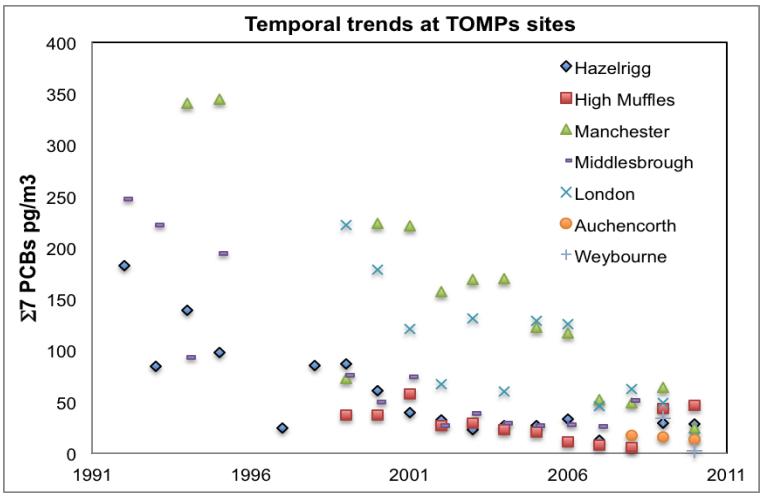

Figure 3. Temporal PCB trend data for all TOMPs sites.

***PBDEs*:** Since 2010 a number of PBDE congeners have been included in the TOMPs network. 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. The re-analysis of PBDEs in the sample archive has focused on four of the six sites over a period ranging from 1999 to 2010. Figure 4 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 4 also contains data for 2011 and 2012 from TOMPs. 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.

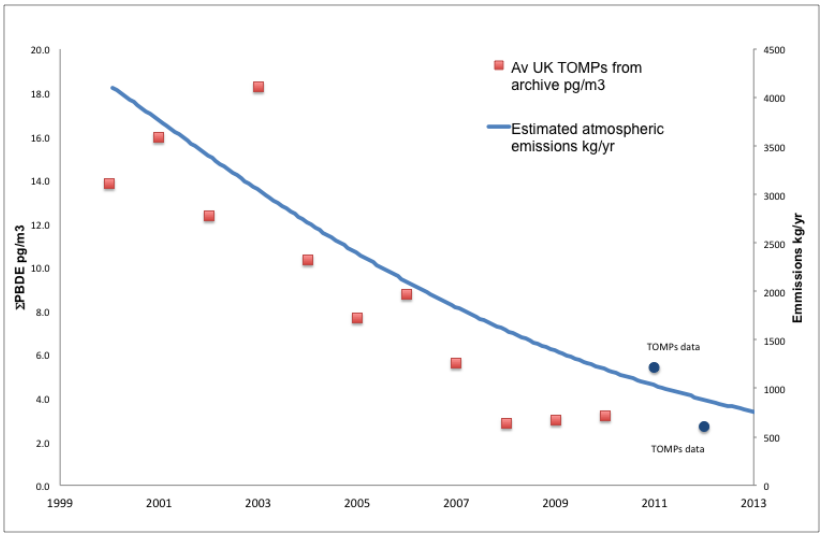

Figure 4 Comparison of estimated annual emissions of PBDE in the UK to the average annual concentrations of ΣPBDEs

The sampling methodology and protocol used in the TOMPs network has been maintained since establishment of the sites, and has successfully provided time-trend data for a range of POP chemicals for nearly 20 years at some locations. This approach has provided a consistent dataset for PCDD/Fs and PCBs allowing the investigation of temporal trends and the assessment of the reduction of sources bought about by the introduction of regulations such the Stockholm Convention. However, International chemical regulatory agreements such as the Stockholm Convention and the UN/ECE POPs protocol are now considering a wider range of contaminants which will need to be considered for inclusion in the network. Whilst it is important to maintain the current valuable time trend data, it is equally important that the network should increase the number of contaminants measured and reported. This demand on networks such as TOMPs, will continue to provide challenges into the future.

Acknowledgements
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