Long-Term Temporal and Seasonal Trends for PBDEs in the UK Ambient Air

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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.

Polybrominated diphenyl ethers have been widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. 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 fully brominated BDE-209 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, whilst the commercial deca-BDE product has been proposed for inclusion and will be discussed at COP 8 later in 2017.

The global demand for PBDEs has previously been very substantial with a peak estimation of 70,000 tonnes for the year 2003 (Hites, 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, BDE 47, BDE 49, BDE 99, BDE 100, BDE 153, BDE 154, and BDE 183. Congeners BDE 47 and BDE 99 account for approximately 72% of the composition of the penta commercial mixture. Atmospheric emission estimates for 2012 for the tetra and penta-PBDEs in the UK were 800kg.

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 consist of GF/A filters and two 7.5cm by 5cm PUF plugs.

Before extraction, each sample is spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners and BDE 51, BDE 128, and BDE 190. Samples are individually extracted in a Soxhlet extraction unit for 16h with hexane, and the extracts are pooled before purification to obtain three-monthly averaged data. They are then eluted through a multilayer column containing activated silica, basic silica and acid silica. After elution through a gel permeation chromatography (GPC) column PBDEs are analysed on a Thermo Scientific DSQ gas chromatography - mass spectrometry (GC-MS) system fitted with an Agilent CP-Sil 8CB GC column, (50m x 0.25mm, 0.12µm) and operating in EI+ and selected ion mode (SIM).

Previous studies have observed seasonal variations in ambient air concentrations (Melymuk et al., 2012 and Yang et al., 2013), although the seasonal pattern is less uniform for PBDEs than for other compounds like PCDD/Fs or PCBs. This study has investigated seasonal averages for BDE 47, BDE 99, BDE 153, and BDE 183

at two rural and two urban 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 was 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).

In order to provide some historical context the TOMPs air sample archive was used to reconstruct 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. This study provided the trend data for ΣPBDE for an average of the four sites with a comparison of atmospheric emission data from Prevedouros et al. (2004). It also contains data for 2011–2015 from the TOMPs dataset. These time-trend data demonstrate a consistent decrease in concentrations over recent years with the observed decline starting during the period 2001–2003. Of the individual congeners detected, BDE 47 was 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 are likely to be controlling the long-term trends in the UK atmosphere.

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