The TOMPs Network

Continuous data on UK air quality for 20 years

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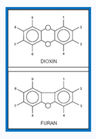
The Toxic Organic Micro Pollutants (TOMPs) Network, which has operated since 1991, currently collects **ambient air samples at six sites across England and Scotland** (Fig. 1). Lancaster University has been operating this UK Department of Environment, Food and Rural Affairs (Defra) funded network from its inception, delivering **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 regulations. It is also used to demonstrate UK compliance with its obligations under the **2001 Stockholm UNEP Convention on Persistent Organic Pollutants** and the **1998 UN/ECE Convention Long-Range Transboundary Air Pollution (LRTAP) Protocol**. Moreover, this research project provides detailed studies on atmospheric fate and behaviour processes that affect persistent chemicals.

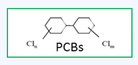
The Target Chemicals

PCDD/Fs



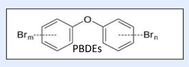
Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are two classes of chemicals which are formed unintentionally during combustion (e.g., waste incineration, burning of coal, wood, etc), the refining of petroleum, metal treatment processes, and during the synthesis of certain chlorinated chemicals. They are classified as POPs under the 1998 UN/ECE LRTAP Protocol and the 2001 Stockholm Convention.

PCBs



Polychlorinated biphenyls (PCBs) were first synthesised in 1881 by Schmidt and Schulz, but their commercial production only began in 1929 in the USA. They were marketed as mixed products under various trade names, depending on the country where they were produced. 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. PCBs are classified as POPs under the 1998 UN/ECE LRTAP Protocol and the 2001 Stockholm Convention. They are therefore subject to international restrictions on production and use and to efforts to identify and reduce ongoing sources. In the UK, a voluntary ban on production was agreed with manufacturers in the late 1960s / early 1970s.

PBDEs



Polybrominated diphenyl ethers (PBDEs) have been widely used as additive flame retardants in products such as furniture, cars, textiles, paints, electronic equipment and plastics to reduce fire risk. They are referred to as additive flame retardants, because they are simply blended with the product. Three different types of commercial PBDE formulation have been produced with different degrees of bromination namely penta-, octa- and deca-BDE products. Of these technical mixtures, the commercial pentabromodiphenyl ether (PeBDE) and commercial octabromodiphenyl ether (OctaBDE) mixtures are classified as POPs under the 2001 Stockholm Convention, have been banned in the EU and Japan, and are currently being phased out in the rest of the world.

PAHs

Polycyclic aromatic hydrocarbons (PAHs) are formed through incomplete combustion of carbon-containing fuels such as wood, coal, fat, tobacco, etc. The major UK sources are currently road transport combustion and domestic combustion. PAHs have been included in the 1998 UN/ECE LRTAP Protocol.

References:
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Gioia, R., Sweetman, A.S., Jones, K.C., 2011. Annual Report for 2010 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network. Unpublished
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The TOMPs sampling sites

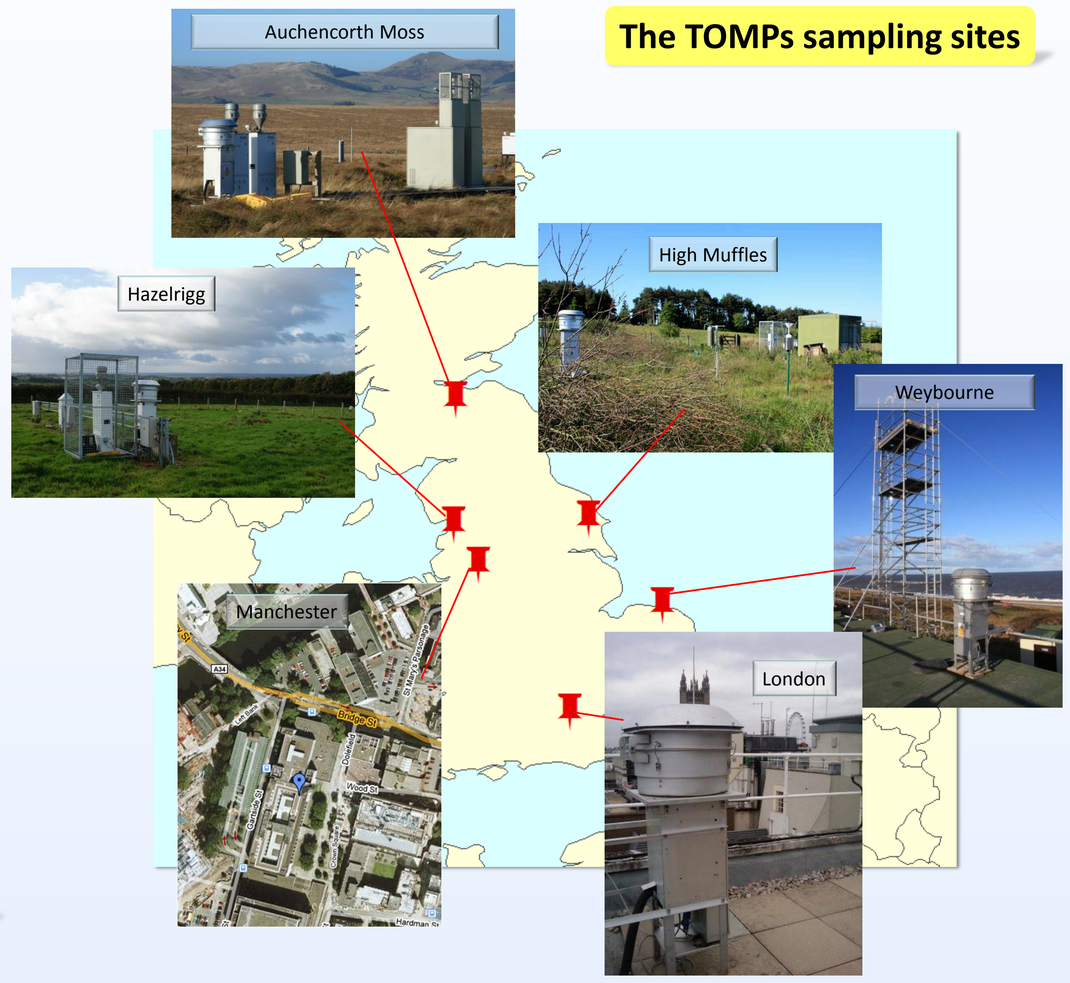

Fig. 1: High-volume air samplers at TOMPs sampling sites

Results

PCDD/Fs

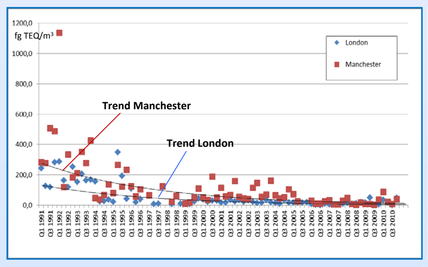

Fig. 7: Time trend for PCDD/Fs at urban sites

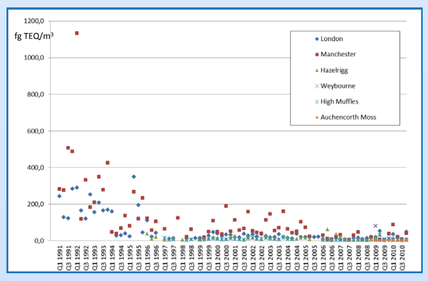

Fig. 8: PCDD/Fs concentrations at all six TOMPs sites

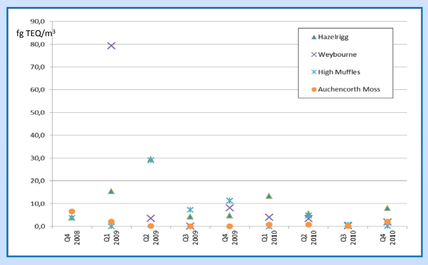

Fig. 9: PCDD/Fs concentrations at semi-rural and rural sites

PCBs

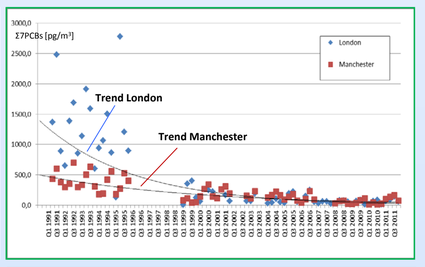

Fig. 10: Time trend for PCBs at urban sites

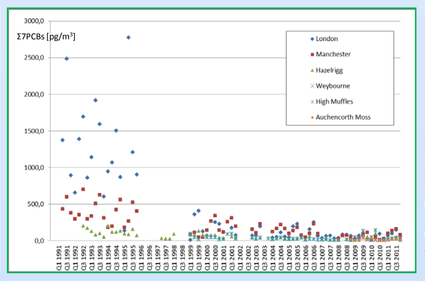

Fig. 11: PCB concentrations at all six TOMPs sites

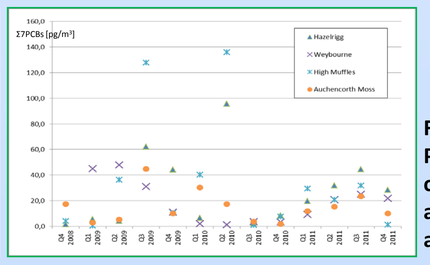

Fig. 12: PCB concentrations at semi-rural and rural sites

The continuous monitoring of POPs for the TOMPs programme has demonstrated the constant decline in their UK air concentrations over the last decades (Fig. 7 – Fig. 12). In the early 1990s, PCB concentrations regularly exceeded 1000 pg/m^3 in London and 500 pg/m^3 in Manchester, while concentrations at these sites have generally stayed below or only slightly above 100 pg/m^3 in recent years. Simultaneously, PCDD/Fs values at these sites have decreased from several hundred fg TEQ (Toxic Equivalents) per m^3 air to usually around 20 fg TEQ/ m^3.

The concentrations of all compounds are generally significantly higher at urban (London, Manchester) compared to semi-rural (Hazelrigg near Lancaster) and rural (Weybourne, High Muffles in the North York Moors, Auchencorth Moss) sites. 7 PCB congeners are generally reported in environmental samples : 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) (Fig. 10 – Fig. 12). Estimated clearance rates („Half-Lives") are between 2 and 9 years for PCBs at all sites (Schuster et al., 2010), The PCB fingerprint (relative concentrations) in TOMPs samples has not changed over time, as there are no significant differences in clearance rates for all sites and compounds. This indicates that primary diffusive sources in urban areas are still dominant and the controlling factor of trends in the UK ambient air PCB concentrations.

Estimated clearance rates for PCDDs and PCDFs are between 4 and 5 years at urban sites (Katsoyiannis et al., 2010), and 2 to 4 years for PBDEs at urban and semi-rural sites (data not shown) (Birgul et al., 2012). Semi-rural and rural sites showed no significant decline in their (albeit low) concentrations. Furthermore, no significant change in PCDD/Fs profiles has been observed over the last two decades.

All these data are in good agreement with other European and worldwide long-term air monitoring programmes and emission estimates.

Methodology

Fig. 2: Module for high-volume air sampler

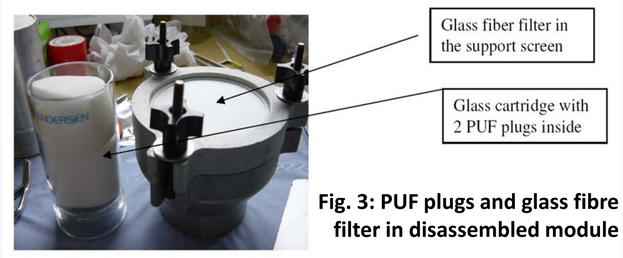

Fig. 3: PUF plugs and glass fibre filter in disassembled module

Fig. 4: GPC, one of the clean-up steps

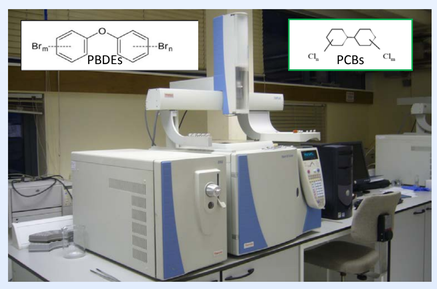

Fig. 5: GC-MS (TRACE GC Ultra / DSQ, Thermo) for the analysis of PCBs and PBDEs

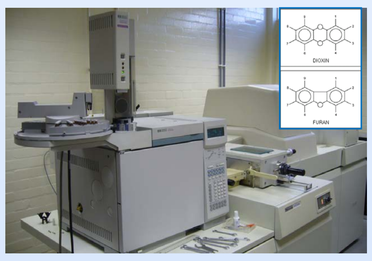

Fig. 6: HRGC-HRMS (HP 6890 Series / Autospec Ultima, Micromass) for the analysis of PCDD/Fs

The analytes currently quantified at Lancaster University for the TOMPs network are PCDD/Fs (polychlorinated-p-dioxins and polychlorinated dibenzofurans) PCBs (polychlorinated biphenyls) and, since 2010, PBDEs (polybrominated diphenyl ethers). Atmospheric sampling is carried out using **high-volume air samplers** (Fig. 1) collecting biweekly samples at each site, which are bulked to provide **quarterly data**. The samplers are equipped with modules (Fig. 2) containing glass fibre filters and polyurethane foam (PUF) plugs (Fig. 3). Sample extracts are obtained using Soxhlet extraction of filters and plugs, followed by diverse clean-up steps (Fig. 4). PCBs and PBDEs are analysed by gas chromatography - mass spectrometry (GC-MS) (Fig. 5), PCDD/Fs are analysed by high resolution GC - high resolution mass spectrometry (HRGC-HRMS) (Fig. 6).

What happens with the data?

All data are reported to Defra and published on the air quality data website **http://uk-air.defra.gov.uk/**.

They provide Defra with valuable information on emission/source controls and on the effectiveness of international chemical regulations.

They are also used to demonstrate UK compliance with its obligations under the 2001 UNEP Stockholm Convention on Persistent Organic Pollutants and the 1998 UN/ECE LRTAP 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.

Additionally, an archive is maintained, which can be used for analysing emerging chemicals, such as pesticedes, alternative flame retardants, and further substances of interest as soon as they have been identified.

The Lancaster Environment Centre

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