

ENVIRONMENTAL LEVELS AND TRENDS

PASSIVE SAMPLING SURVEY OF PBDES AND PCBS IN UK AIR

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Introduction

Persistent organic pollutants (POPs) undergo dynamic exchange between water, soil and vegetation, and the atmosphere. These processes are important in controlling the entry of POPs into food chains, influencing their long-range atmospheric transport (LRAT) potential, and therefore controlling their global cycling and redistribution. It is therefore particularly important to measure/monitor the vapour-phase species in the atmosphere. The capacity of the semi-permeable membrane device (SPMD) is such that it will take anything from 1-2 years to tens of years to reach equilibrium, depending on how effective the compound is at partitioning into the SPMD. Essentially the sampling is undertaken during the linear phase of the uptake, i.e. before it has reached equilibrium, over days, weeks and months. PCBs are perceived to be well mixed in the UK atmosphere. The most widespread air monitoring programmes undertaken in the UK are carried out at about six sites in the UK. A more extensive look at the PCB spatial distributions in the UK should be assessed. It is important to understand the limitations, if any, of looking at just a small number of sites to assess national levels of pollutants. PCB levels in U.K. air are likely to be influenced by several factors, including existing primary emissions and recycling, volatilisation from soil, advective losses from the U.K. atmosphere, reaction in the atmosphere, and soil fate processes such as microbial degradation¹. Several researchers have shown atmospheric concentrations of re-cyclable POPs respond to seasonal or diurnal changes in temperature^{2,3,4}. For this reason it is important to sample over a period long enough to integrate short-term variability when environmental conditions are as stable as possible from site to site.

Methods and Materials

An experimental procedure has previously been described⁵. Therefore only a brief description of the procedure and methods will be given here. For the passive sampling survey, SPMDs were deployed at 40 sites throughout Britain, 1 on the east and 1 on the west coasts of Éire as seen in figure 1. The sampling period was 28 days. The SPMD deployment devices were posted to each site in sealed containers. The SPMDs themselves were housed in a stainless steel container with one face exposed and downward facing, thus protecting the SPMD from direct UV radiation and rain whilst making sure that it was exposed to the wind from all directions. The devices were deployed approximately 1 meter from ground level and away from any direct exhaust fumes where possible. Upon harvesting, the deployment devices were resealed in their containers and posted back to Lancaster, where they were extracted and analysed for PCBs, PBDEs and selected OC pesticides by GCMS using EI mode for PCBs and NCI mode for PBDEs. SPMDs were dialysed in hexane for 48 hours and cleaned using silica/alumina and gel permeation chromatography columns.

Results and Discussion

During the deployment period in Britain there was an outbreak of foot and mouth disease. Consequently large areas of the country had restrictions in place preventing access to the countryside. As a result samplers were not deployed in central and south Wales, the Home Counties and along the

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Figure 1. Passive Sampling Survey Sites

Scottish and English border but the remainder of the country was well covered. Temperature effects were reduced because the temperature was relatively constant over the sampling period averaging 15°C. Amounts sequestered by the sampler are defined as a mass per SPMD e.g. (ng/SPMD). This mass can be converted to an uptake rate (ng/SPMD/day). Using information obtained from field studies the sampling rates determined for PCBs varied between 2–28 m³/day but may vary somewhat with compound and deployment conditions. The data presented in this paper will report sequestered amounts as ng/SPMD/day for the deployment period. Samplers were deployed at agricultural, rural, semi-rural coastal and urban locations. The sum of the PCB sequestered amounts ranged from 0.016–2.3 (ng/SPMD/day) and the sum of the PBDE sequestered amounts ranged from 0.004–1.1 (ng/SPMD/day). In the main, PCBs and PBDEs remained relatively constant within their own class of compound from site to site. In the case of PCBs, the sites that showed elevated levels were Plymouth 0.88 (ng/SPMD/day), Dorset 0.66 (ng/SPMD/day), Norwich 2.3 (ng/SPMD/day), Manchester 1.4 (ng/SPMD/day), Preston 0.75 (ng/SPMD/day), Sunderland 0.9 (ng/SPMD/day) and Paisley 1.5 (ng/SPMD/day). Average sequestered amount for the remaining sites was 0.17 (ng/SPMD/day). PCB levels at Plymouth, Dorset and Norwich coastal sites may have been influenced somewhat by advection from Central and Eastern Europe as well as local re-emissions from soil and aquatic compartments. Manchester, Preston, Sunderland and Paisley are all highly urbanised and industrial locations, and could have been significantly influenced by emissions from local primary and/or secondary sources. The profile of PCB congeners 28, 52, 118, 153, 138, and 180 differs within these sites suggesting that different sources are affecting different sites. From the data collected urban centres would appear to be ongoing sources of pollution. The following PBDE congeners were detected -28, -37, -47, -99, -100, -153, -154. The sum of the PBDEs ranged from 0.004–1.06 (ng/SPMD/day). Derby 0.3 (ng/SPMD/day), Chesterfield 0.8 (ng/SPMD/day), Manchester 1.06 (ng/SPMD/day), Sunderland 0.43 (ng/SPMD/day) and Paisley 0.13

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(ng/SPMD/day) showed the highest sequestered amounts relative to the average of the other sites, which was 0.016 (ng/SPMD/day). When detected PBDE-47 was the congener present at highest levels. The most widespread congener was found to be PBDE-37. In general, congener patterns were different from site to site. This was emphasised at Colchester and Ardleigh. Approximately 5 kilometres separates Colchester and Ardleigh. Colchester is a moderately sized town and Ardleigh is a village on the out-skirts of the town. They showed differing congener profiles for PBDEs, although the PCB congener profiles were the same. In general, congener patterns were distinct for each site indicating a possible unique localised source. Comparing PCB and PBDE congeners that have similar K_{OA} values and consequently similar partitioning into an SPMD it can be seen that concentrations of PBDEs are in the same range as PCBs and in some cases greater, as seen in figure 2. In comparison to biota⁸ samples, there is a decrease in the concentration of the hepta and hexa congeners, suggesting that they are more susceptible to degradation in the atmosphere. However they are widely distributed throughout Britain. For both PCBs and PBDEs there was no apparent contamination gradient with latitude. The sequestered amount may vary locally, being influenced by the precise deployment location of the sampler. For example in an urban centre, atmospheric concentrations may vary with proximity to buildings, air vents, localised sources etc. Generalisations are therefore made cautiously. This study demonstrates the feasibility of mapping air concentrations of POPs on a local, regional or national scale, using standardised passive air sampling procedures. It highlights that concentrations are highly variable. PCBs varied by a factor of 144 from the lowest to the highest in this survey of 42 locations, while PBDEs varied by a factor of 246. There are clearly ongoing emissions of PCBs and PBDEs into the UK atmosphere, but the high spatial variability indicates that this is complex. Whilst urban areas are generally higher, this is not always the case and there are clues that local ambient concentrations and the precise deployment locations are strongly influencing the dataset.

Acknowledgements

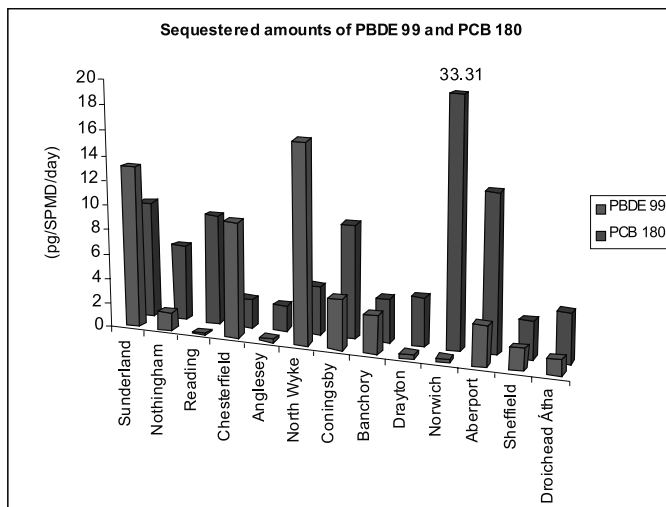


Figure 2. Selected sites showing PBDE 99 (K_{OA} 11.31)⁶ and PCB 180 (K_{OA} 11.43)⁷ (pg/SPMD/day)

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