SPATIAL VARIATION IN ATMOSPHERIC LEVELS OF PBDEs IN PASSIVE AIR SAMPLES ON AN URBAN-RURAL TRANSECT

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Introduction

Polybrominated diphenylethers (PBDEs) are found throughout the world as a result of widespread employment as fire retardant agents. Legislation against the chemically similar dioxins and polychlorinated biphenyls (PCBs) has prompted a recent surge in research interest in the PBDEs, in an effort to determine their potential risk as a persistent organic pollutant. Although having a higher preponderance than dioxins and PCBs to partition to particulate matter in the atmosphere[1], it is still important to assess the gas-phase concentrations in our atmosphere, since this is a significant route of long range transportation of PBDEs in the environment, especially the lighter congeners[2], as well as being a potentially significant route of human exposure[3].

Passive air samplers are a cheap and convenient way to sample air at a higher spatial resolution than can be afforded by conventional cumbersome active samplers. An additional advantage is that due to the comparatively long sampling period, final concentrations are integrated over the course of several weeks, thereby removing the influence of short term concentration fluctuations which can be misleading. Several studies have been conducted determining gas-phase PBDE concentrations with passive samplers and yielded encouraging results[4-6].

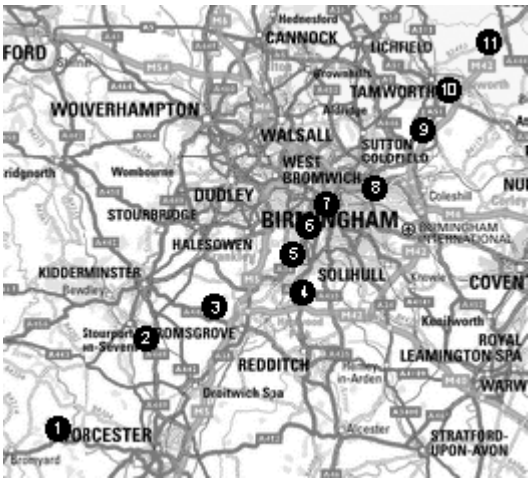
The results given in this manuscript represent the beginning of a 1 year sampling campaign designed to elucidate seasonal and spatial variation in PBDE and PCB concentrations across a large (population c. 2.5 million) conurbation in the generally densely populated UK, where PBDEs have seen widespread use due to the UK fire regulations. It is hoped that through measurements of this kind a

better understanding of the fate and transport of these compounds in and around the urban environment will be obtained. By determining the strength of any urban-rural gradient, and investigating the variation in PBDE concentrations over an annual cycle, we can begin to assess the impact of major urban areas as a potential source of PBDEs to their surrounds, as well the likely fate of these pollutants. This will hopefully lead to informed policy decisions on their usage and environmental remediation.

Methods and Materials

Passive samplers were co-deployed at 11 sites ranging from the rural southwest, across the West Midlands conurbation to the rural northeast, covering a distance of c.80 km (fig.1). They were deployed in the direction of the prevailing wind mass, which generally travels from southwest to northeast in the UK. At each site 4 PUF discs were deployed, to effectively increase the sampling rate fourfold, in stainless steel chambers, as described by other authors[6-7], for a period of one month. Absolute concentrations of PBDE are not given in this paper, since this method of passive sampling requires calibration to determine the air sample volume, which has not been carried out yet for the specific samplers used in this study. During each month sampling period a blank was also collected and final masses corrected accordingly.

Figure 1. Location of 11 sampling sites across the West Midlands, UK, used in this study.



After collection samples were stored at 4^0C until extraction, when the four PUF discs from each individual site were extracted in one Soxhlet extraction flask after being spiked with a surrogate standard solution. Details of the clean-up and instrument parameters for the analysis by GC-MS are given elsewhere[3].

Results and Discussion

Figure 2 shows the distribution of the various PBDE congener masses extracted from the samples, normalised to uptake per day, for the month of October, 2003 at each site. Figure 3 shows the spatially corrected distribution of BDE-47, -99 and ∑BDE for this month. ∑BDE concentrations range from ~20 pg/d at the forested rural site 2 to ~106 pg/d at the heavily urbanised city centre site 7, a five-fold increase, and a clear increase in concentrations is visible along the rural-urban gradient, both entering the city from the southwest, and leaving it to the northeast. This is to be expected, as the main source of PBDEs to the atmosphere is considered to be venting of indoor air[2], which will clearly be higher in built-up areas. Other authors have shown an opposite trend in gradient, but this occurred in samples taken during Spring in a colder climate than these samples, and attributed this to a "pulse" of previously-entrained PBDEs re-volatilising from soil and vegetation in rural environments[8]. It will be interesting to see whether such a process occurs in a more moderate climate such as the UK, where temperature means typically vary by only 11^0C ($5\text{-}16^0$) over the course of a year. BDE-47 is

the most prevalent congener at all sites, with uptakes by the samplers ranging from 7.5 pg/day at site 2 to 60.5 pg/day at site 7, with BDE-99 at almost the same levels, ranging from 5 pg/day at site 3 to 46 pg/day at site 7. BDE-28 is found at 2-7.5 pg/day, BDE-100 at 1.5-5, and BDE-153 and 154 generally less than 5 pg/day, where above the instrument detection limit. Using air sampling rates calculated elsewhere[6], air concentrations can be estimated, and are shown in Table 1. They generally agree with previous data for PBDE concentrations. Concentrations for ∑BDE along an urban-rural transect have been measured ranging from 3-8 pg/m^3 in Ontario, Canada[4], while concentrations of the most prevalent BDE congener (-47) in Ireland and the UK were between 0.16 and 1.1 pg/m^3 at Mace Head and 0.72 and 7.2 pg/m^3 at Chilton using Hi-Vol active samplers[9]. Concentrations are generally lower outside the city boundary on the southwest side of the city (Sites 1, 2 and 3) than the northeast (Sites 9, 10 and 11) suggesting that the rural northeast may be subject to a stronger influence from the city as a source of atmospheric PBDEs than the southwest. This observation is possibly attributable to the bulk of advection moving with the typical prevailing wind direction, i.e. SW-NE. This also highlights the possibility that the city is acting as a source of PBDEs to its surrounding rural environment, though more data must be obtained to gain a better idea of the strength of this source.

In summary, the results presented here represent the beginning of a sampling campaign designed to look at the variation of PBDE and PCB concentrations in various environmental media over a major UK conurbation. PBDE masses obtained through passive air sampling are presented for the month of October 2003, and show a clear increase and subsequent decrease in masses as the sampling sites proceed northeast through the city and beyond back to rural locations. Congener profiles and estimated atmospheric concentrations agree well with data published from studies conducted in the UK and Canada. This campaign will yield a greater insight into the transport and fate of PBDEs in a large temperate city and its surrounds.

Figure 2. Uptake of BDEs (pg/day) at 11 sites by passive air samplers during October 2003 along an rural-urban-rural transect of the West Midlands, UK.

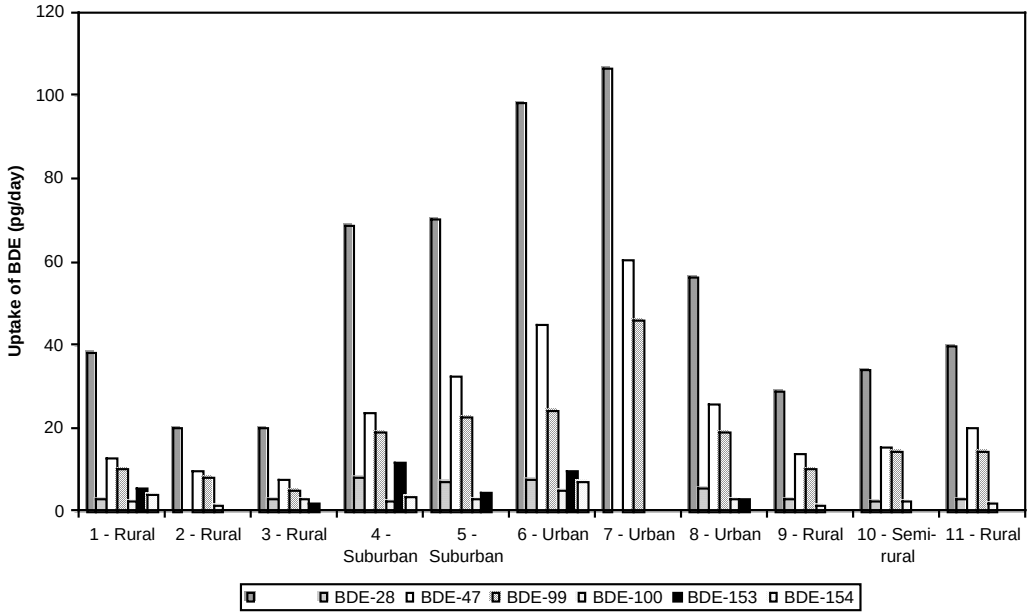


Figure 3. Uptake (pg/day) of ∑BDE, -47 and-99 collected by passive air samplers corrected for distance from Site 7 (City Centre) during October 2003.

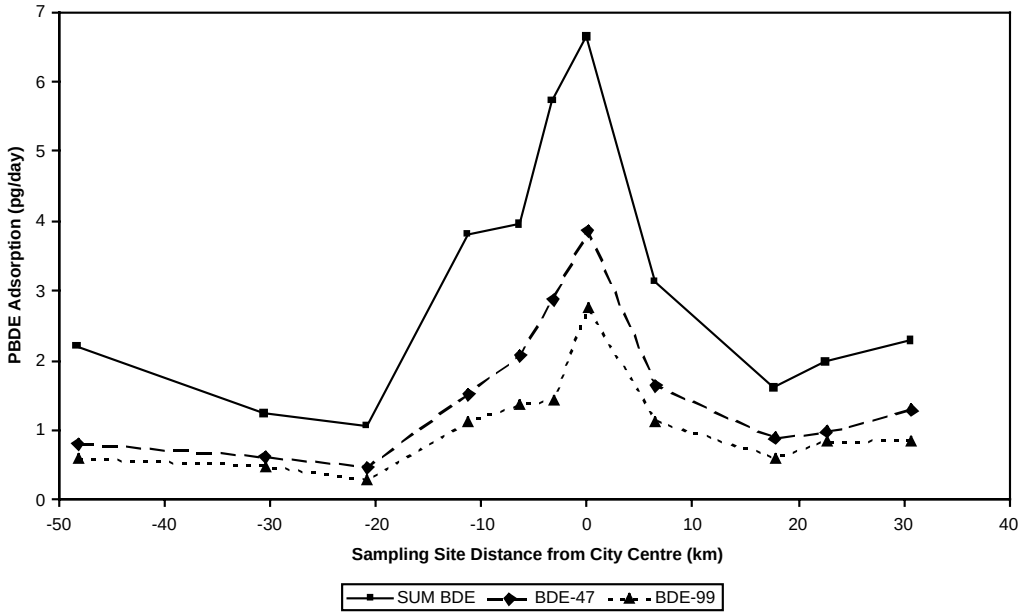


Table 1. Mass range and estimated atmospheric concentration of BDEs in samplers taken 10/03 across the West Midlands, UK.

BDE-	28	47	99	100	153	154	∑BDE
Mass Range (pg/day)	2.4-8.2	7.5-60.6	5.0-46.2	1.4-5.2	1.7-11.8	0.1-6.9	19.8-106.7
Atmospheric Concentration (pg/m^3)	0.2-0.6	0.5-3.9	0.3-2.8	0.1-0.3	0.1-0.8	0.1-0.5	1.3-6.7

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