ATMOSPHERIC CONCENTRATIONS OF PBDES IN WESTERN EUROPE

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used and continue to be used extensively in the UK as flame-retardants in a wide range of applications, and have been recognised as ubiquitous environmental pollutants [1]. However there is a lack of atmospheric PBDE concentration data for the UK as a whole. In order to redress this situation, two air sampling campaigns were under taken to assess atmospheric concentrations of PBDEs reaching and within the UK and to investigate factors that control concentrations. The first was based at Mace Head (MH) on the west coast of Ireland (53° 20' N, 9° 54'W) where it was hoped to monitor the background levels in air entering the UK air space from the Atlantic, the site by UK standards would be classed as remote. The second campaign was under taken at two sites in England: Hazelrigg (HR), a field station belonging to Lancaster University and situated on the north west coast of England (54° 2'N, 2° 45'W); and Chilton (CH) a site situated to the south west of Oxford in the south of the UK (51° 40' N, 1° 20'W). The samples were taken simultaneously at the Hazelrigg and Chilton sites to enable air concentrations on a given day to be compared.

Materials and Method

Details of the sampling train, media and artefacts associated with both have been described and discussed in previous studies [2,3].

It was expected that the levels of PBDEs might be low, particularly at the Mace Head site. The sampling strategic therefore concentrated on taking large enough air volumes at each site to enable PBDEs to be detected. At Mace Head this was achieved by using two samplers running continuously and simultaneously for two days for each sample. The sampling media from each sampler were combined and treated as one for each two-day period. The sampling campaign was under taken between 11/07/00 to the 08/09/00, a total of 25 samples were gathered during this period. The sampling regime at the two sites in England was slightly different, again two samplers were used at each site simultaneously to collect two samples over a one-day period, the two samples at each site were combined to create one sample for that sampling period. Sampling took place in two blocks, 23/01/01 to the 27/04/01 and from 31/07/01 to the 04/09/01, during these periods 43 samples were taken at each site. It was not practical nor possible to sample simultaneously at the Mace Head site, hence the different sampling dates.

Samples for all three sites were subject to the same extraction, clean up and quantification procedures. Samples were extracted in DCM for 18 hours, the extract was reduced and passed through a column containing activated silica (2 g) and alumina (1 g) and then through a GPC column, samples were reduced to a final volume of 25 ml. Seven labelled PCB congeners and three PCDD/F congeners were added to the samples prior to extraction and were used to monitor the extraction and clean up procedures, a further two $^{13}C_{12}$ labelled and one $^{12}C_{12}$ PCB congeners were added to the sample prior to injection and were used as internal standards. The samples were analysed on a Finnigan Trace MS

operating in NCI, the following PBDEs were routinely monitored: PBDE 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 120, 138, 153, 154, 166, 181, 190.

Results and Discussion

Table 1 provides a summary of the data from all the sites, in general the ΣPBDEs at all three sites are comparable to levels found in rural air [4], in addition levels at HR and CH correspond to the lower values reported in two other studies [5,6].

Table 1. Air data (pg/m^3) for the three sites.

PBDE	Hazelrigg			Chilton			Mace Head		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
17	0.2	0.5	0.1	0.4	0.8	0.1	0.1	0.1	0.1
28	0.5	1.3	0.1	0.7	1.3	0.2	0.1	0.2	0.1
32	0.2	0.3	0.2	1.0	2.6	0.1	0.1	0.1	0.1
35	0.3	0.4	0.2	0.5	0.9	0.2	2.4	7.0	0.1
37	1.0	3.4	0.2	<DL	<DL	<DL	0.3	0.5	0.1
47	5.2	15	0.8	2.6	7.2	0.7	1.1	1.9	0.2
49	0.4	1.2	0.1	0.5	1.4	0.1	0.1	0.2	0.1
66	0.3	1.2	0.1	0.3	0.7	0.2	1.0	6.6	<DL
71	0.4	3.7	0.1	<DL	<DL	<DL	<DL	<DL	<DL
75	<DL	<DL	<DL	0.4	0.5	0.3	0.1	0.2	0.1
77	0.4	0.4	0.4	<DL	<DL	<DL	<DL	<DL	<DL
85	<DL	<DL	<DL	0.3	0.9	0.2	0.1	0.1	0.1
99	2.7	11	0.5	3.5	15	0.8	0.8	1.9	0.3
100	0.7	2.9	0.2	0.6	2.1	0.2	0.2	0.4	0.1
120	0.2	0.5	0.2	0.2	0.7	0.1	0.1	0.1	0.1
138	<DL	<DL	<DL	<DL	<DL	<DL	0.2	0.2	0.2
153	0.3	0.7	0.1	0.4	1.5	0.1	0.1	0.2	0.1
154	0.2	0.4	0.1	0.3	0.9	0.1	0.1	0.1	0.1
166	<DL	<DL	<DL	<DL	<DL	<DL	0.1	0.1	0.1
181	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
190	<DL	<DL	<DL	0.5	0.7	0.4	<DL	<DL	<DL
PBEB*				30	90	8.9			
ΣPBDE	12	37	2.8	11	33	3.4	3.1	11	0.2

* Pentabromoethylbenzene

Only four or five of the PBDE congeners were routinely detected in all the samples from Mace Head even through the mean total air volume for each bulked sample was >1500 m^3 and the final injection volume 25 ml. The total levels of PBDEs at MH were approximately one third those at the UK sites. Total concentrations of PBDEs at HR and CH did not follow similar trends, levels of PBDEs at Chilton remained relatively constant compared to levels at HR, where levels increased during the summer months.

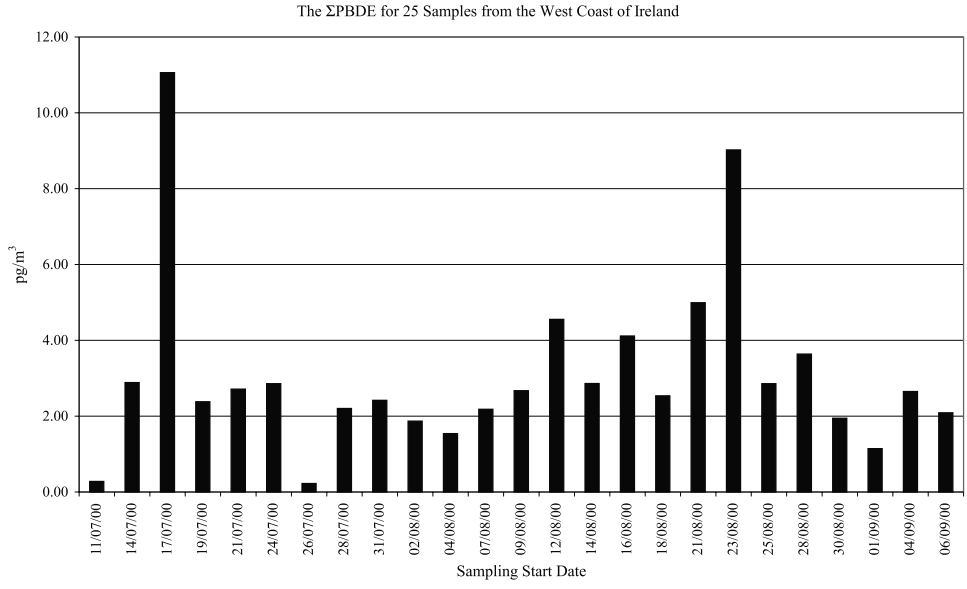

Figure 1. Air Concentrations of PBDEs in 25 samples taken at Mace Head, West Coast of Ireland

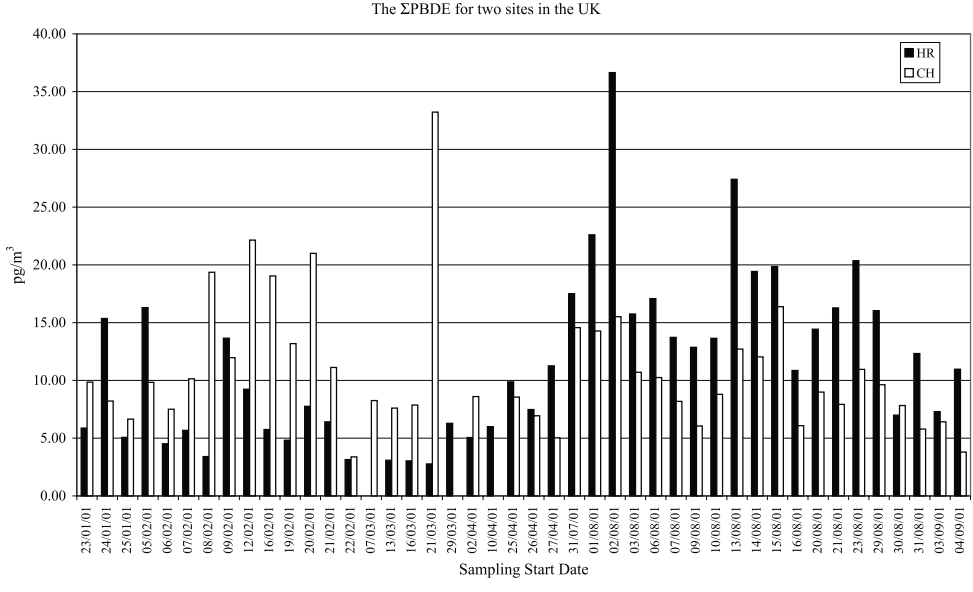

Figure 2. Atmospheric concentrations of PBDEs at two UK sites, Hazelrigg (HR) and Chilton (CH).

During quantification of the CH samples a large unidentified peak was found in all samples, the compound was at high enough levels to be able to analyse using full scan on a GC-MS operating under EI. The compound was found to be pentabromoethylbenzene, a flame retardant only found in the CH samples.

The results suggest that different factors influence the concentrations of PBDEs at the three sites at different times, further work will investigate the relationships between meteorological parameters, advection and concentrations of PBDEs

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