

## ATMOSPHERIC PBDEs AND PCNs ACROSS EUROPE: RESULTS OF A PASSIVE SAMPLING PROGRAMME

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### Introduction and context

Atmospheric concentrations of persistent organic pollutants (POPs) are influenced by several factors such as primary emissions, air-surface exchange, reaction in the atmosphere etc. To assess the relative importance of such processes, to assess sources, and validate models, it is desirable to make simultaneous regional measurements of air concentrations. This can only be achieved with the desired resolution with passive air samplers; they are simple to use, cheap and versatile<sup>1</sup>. A range of different passive sampling devices have been utilised. These include polyurethane foam (PUF) disks<sup>2,3</sup> polymer-coated glass slides (POGs)<sup>3</sup> and vegetation<sup>4,5</sup>. PUF disks are a particularly attractive sampler; they are cheap, easy to handle, pre-clean and extract and can be used to sample over periods of several weeks. Information has also been obtained to calibrate them against conventional (active) high-volume air samplers<sup>6</sup>.

Both the PBDE and PCN compound classes are ubiquitous environmental contaminants, which are subject to long-range atmospheric transport. They have been measured in air in remote areas (e.g. the Arctic)<sup>6-9</sup>. They bioaccumulate and there are concerns about the use of these chemicals, with regard to their potential risks to human health and the environment<sup>10,11</sup>. Hence, both PBDEs and PCNs are being considered as potential 'candidate POPs' under the international POPs protocol. Europe is an important global source area for both these compound classes; there are also important differences in the production, usage and hence likely emissions of these compounds in different countries of Europe. However, there is a paucity of information regarding the spatial distribution of these compounds across Europe. PBDEs have been reported in the Irish and English atmosphere, where levels range from 0.2-11 pg/m<sup>3</sup> at background sites to 3.3-33 pg/m<sup>3</sup> in semi-rural/urban sites<sup>13</sup>. Gouin et al. have reported levels exceeding 100 pg/m<sup>3</sup> in Canada<sup>12</sup>.

PCNs and PBDEs enter the environment by different means. PCNs are released to the environment as co-contaminants in commercial PCB formulations, from municipal waste incineration, metallurgical processes and chlorine production<sup>8</sup>. PBDEs have been extensively used in Europe and North America as flame retardants in various products such as plastics, textiles, wire and cable insulation, electrical and electronic connectors, furnishing foam etc. to reduce their fire hazards by interfering with the combustion of the polymeric materials<sup>10,12,13</sup>.

In this study we report the first attempt to monitor the regional distribution of PBDEs and PCNs in the European atmosphere.

### Materials and Methods

The samplers were deployed over a six-week (15<sup>th</sup> June to 30<sup>th</sup> July 2002) period. The sampling devices described previously<sup>2</sup> were adapted so that they could be deployed in sheltered and controlled environments. Samplers were deployed in both remote (background) and urban areas. Remote areas were selected to reflect the general/diffuse atmospheric concentrations. In total 75 samplers were deployed across 22 countries. After the six weeks deployment, the samplers were retrieved and the disks removed and stored in clean bottle jars at -20 °C until extraction.

Samplers were spiked with a range of <sup>13</sup>C<sub>12</sub>-labelled PCB congeners and three PCCD/F congeners to monitor the extraction and cleanup procedures. The samples were extracted for 18 hours with DCM in a Buchi extraction unit. The extract was rotary evaporated and transferred with hexane to a 15 ml amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 ml and cleaned on a 9 mm id chromatography column with 1 g Alumina (BDH neutral Alumina), 2 g silica gel (Merck Silica 60) and 1 cm baked sodium sulphate (all baked at 450 °C overnight) and then passed through gel permeation chromatography (GPC) using 6 g of Biobeads SX 3. The samples were reduced to a final volume of 25 µl.

A further two labelled PCB congeners, <sup>12</sup>C<sub>12</sub> PCB-30 and <sup>13</sup>C<sub>12</sub> PCB-141, were added to the sample prior to injection as internal standards. The samples were analysed for PCNs on a Finnigan Trace MS operated in EI mode; PBDEs were analysed with a GC/MS MD800 operated in NCI mode. The following PBDEs and PCNs routinely detected in >30% of the samples were utilised in the overall elaboration of the data: PBDEs -28, 47, 49, 75, 99, 100, 153 and 154; PCNs - 3-2, 4-10, 4-15, 4-16, 4-18, 5-3, 5-8, 5-9, 5-10 and 5-11.

### Results and Discussion

Typical sampling rates by the PUF disks are ca. 3 m<sup>3</sup> air sampled/day; hence a 6-week deployment yields a sample of ca. 126 m<sup>3</sup> air.

Table 1 presents a summary of the PBDE data. A typical 'working detection limit' for PBDEs in the exposed samples was 0.06 ng/sample. PBDE-47 was detected in 43 of the 71 samples (i.e. 60%) while PBDE 99 was detected in 36 of the 71 samples (i.e. 51%). PBDE 47 and 99 contributed about 77% to the ΣPBDEs. These congeners are the two main components of the Penta-BDE commercial product, used as flame-retardants.

Figure 1 shows the spatial distribution of PBDEs in the European samples. It is difficult in the limited space to highlight all the trends. However, the following observations can be made:

1. Highest loadings were measured in samples from the UK; the UK has a history of PBDE production and has been a major user of PBDE flame retardants, owing to particularly stringent fire regulations;
2. Other high values were detected in urban centres.
3. Non-detectable values were detected in the remote/background sites, especially in Spain, Italy, Sweden and Kazakstan.
4. Values in Eastern Europe were generally low.
5. Differences between the highest and lowest (non-detectable) samples were a factor of ~300.

6. There were differences in the PBDE-47/PBDE-99 ratio between samples. For most samples, the ratio ranged from 0.3-1.6 except for a high case for Italy (2.7). The ratio was ~ 0.5 for most East European countries, Greece and Norway while it was ~ 1.0 for the UK, Czech Republic and Poland.

A typical 'working detection limit' for PCNs in the exposed samples was 0.03 ng/sample. PCNs 3-2, 4-18, 5-3, 5-10 and 5-11 were the most abundant and regularly detected. Figure 1 also shows the spatial distribution of PCNs in the European samples. The following points are noted:

1. PCNs were generally detected in fewer samples and their levels were also lower than PBDEs.
2. Highest levels were detected in the UK, Italy, Poland Russia and Czech Republic and appear to be associated with industrial activities.
3. Only the most abundant lighter PCN (PCN 3-2) was detected further north and south of Central Europe.

**Table 1. Arithmetic mean, range (ng/sample) and average % contribution of individual congeners in the European samples**

	Mean	Range	Average % Contribution
PBDE 28	0.32	0.06-4.5	5
PBDE 47	3.02	0.97-13.5	37
PBDE 49	0.27	0.07-2.0	<2
PBDE 75	0.15	0.07-0.6	<2
PBDE 99	4.00	1.62-20.7	40
PBDE 100	0.73	0.31-3.5	7
PBDE 153	0.37	0.09-2.5	4
PBDE 154	0.30	0.10-1.5	3
PCN 3-2	4.62	1.43-9.2	52
PCN 4-18	0.13	0.03-0.6	3
PCN 5-3	0.42	0.10-1.7	10
PCN 5-10	0.61	0.16-2.0	11
PCN 5-11	1.16	0.28-4.2	24

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**Figure 1**  $\Sigma$ PCN (sum of 12 congeners) and  $\Sigma$ PBDE (9 congeners) (ng/sample)  
PBDE maximum in urban Manchester, UK (44) PCN maximum in urban location in Poland (33)

