PBDEs in sediments from a polluted area in Europe: The Belgian North Sea, the Western Scheldt Estuary and tributaries

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants to improve fire safety of various consumer products. Of the total worldwide market demand for PBDEs in 2001, which added up to almost 70 000 metric tons, more than 80 % consisted of the fully brominated decabromodiphenyl ether (BDE 209) (BSEF, 2003).

The widespread presence of PBDEs is caused by their broad application area and extremely resistant and lipophilic nature.[1] The water solubility and vapor pressure of PBDEs are also very low.[2] These properties cause residues of these persistent organic pollutants (POPs) to be adsorbed rapidly onto solid particles when released into the environment and to accumulate readily in the organic fraction of soils and sediments. Although sediment is therefore considered as a sink for POPs, they are still bioavailable once adsorbed to the sediment particles.[3,4] Soil and sediment studies can provide valuable information about the pollution load in a certain area and are important steps in mapping possible exposure pathways to various marine and freshwater organisms.

The SE covers a very densely populated and highly industrialized region, resulting in a high pollution level with POPs.[5,6] The area studied covers sediments from the Belgian North Sea (BNS: S1-S6), the Western Scheldt Estuary (SE: S7-S18) and selected freshwater tributaries of the river Scheldt (T1-T14) (Figure 1).

MATERIALS AND METHODS

Based on reported abundance and toxicity, the following PBDE-congeners (IUPAC numbering) were targeted for analysis: 28, 47, 99, 100, 153, 154, 183, and 209.[6,7]

The sediments were dried at room temperature and sieved (180 µm). Between 1 and 5 g sediment was spiked with internal standards and hot Soxhlet extracted for 2.5 h with hexane/acetone (3/1; *v/v*). The extract was cleaned-up using a multi-layer acid and base silica cartridge and analytes were eluted with hexane and dichloromethane. All analyses were performed by GC-MS. PBDE congeners 28, 47, 99, 100, 153, 154, and 183 were analyzed with a 25 m x 0.22 mm x 0.25 µm HT-8 capillary column (SGE). The MS was operated in electron capture negative ionization (ECNI) in the selected ion-monitoring (SIM) mode at the m/z = 79 and 81. For the analysis of BDE 209, a 15 m x 0.18 mm x 0.10 µm AT-5 capillary column (Alltech) was used. The ECNI-MS was operated in SIM mode with m/z = 484.7/486.7 and 494.7/496.7 monitored for BDE 209 and ^{13}C-BDE209, respectively. Details of the method have previously been described by Covaci et al.[7]

Figure 1. Sampling locations.

RESULTS AND DISCUSSION

Only a few congeners could be detected in the BNS sediments; the sum of PBDEs (BDE 28, 47, 99, 100, 153, 154, and 183) was never higher than the calculated LOQ for these locations. BDE 209 however, could be detected in 83 % of samples from the BNS, although at rather low concentrations (1.1 – 24 ng/g dw) (Table 1).

Locations near the industrial harbor of Zeebrugge (locations S4 and S6) were the only locations in the BNS where tri- to hexa-PBDEs could be measured (although near LOQ) and where BDE 209 showed a tenfold higher concentration compared to the other locations in the BNS. Near the harbor of Vlissingen, at the mouth of the SE (locations S7 and S8), slightly elevated BDE 209 levels were seen, while further upstream the SE, levels were low and comparable to the levels found in the BNS until location S15 (near the Dutch-Belgian border). The higher levels found near Zeebrugge and Vlissingen were probably due to the harbors in these cities. Other studies have also found the highest contamination close to populated areas like harbors and urban centers.[8] In the sediment samples from the SE the number of not-detects was lower than in the BNS, but concentrations of PBDEs were low up to location S14. Concentrations of BDE 209 were also relatively low from location S7 to S14 (1.5 – 47 ng/g dw).

At locations S15 to S17, the sum of PBDEs and BDE 209 were approximately 10 to 50 times higher than in the other parts of the SE and ranged from 5.3 to 18 ng/g dw and from 340 to 1200 ng/g dw, respectively. Location S18 however revealed unexpected low levels of both BDE 209 and the lower brominated ones. Although precautions were taken not to sample in areas of the SE that are subjected to dredging, sampling in such an area cannot be ruled out, which would explain this low concentration.

Compared to the BNS samples, the sediments taken from tributaries of the Scheldt displayed relatively high levels (up to 19 ng/g dw for the sum of PBDEs at location

Table 1. Results for individual BDE congeners (ng/g dw) in all samples.

	Location	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	Sum BDEs[$]	BDE 209
BNS	S1	< 0.01	< 0.07	< 0.02	< 0.1	< 0.01	< 0.01	< 0.01	< 0.2	1.1
	S2	< 0.01	< 0.07	< 0.02	< 0.1	< 0.01	< 0.01	< 0.01	< 0.2	1.2
	S3	< 0.01	< 0.07	< 0.02	< 0.1	< 0.01	< 0.01	< 0.01	< 0.2	1.1
	S4	< 0.01	< 0.07	< 0.02	< 0.1	0.03	0.01	< 0.01	< 0.2	24
	S5	< 0.01	< 0.07	< 0.02	< 0.1	< 0.01	< 0.01	< 0.01	< 0.2	2.9
	S6	< 0.01	0.08	0.02	< 0.1	0.03	< 0.01	< 0.01	< 0.2	23
SE	S7	0.01	< 0.07	< 0.02	< 0.1	0.02	< 0.01	< 0.01	< 0.2	17
	S8	0.06	0.24	0.04	< 0.1	0.04	0.03	< 0.01	< 0.2	47
	S9	< 0.01	< 0.07	< 0.02	< 0.1	0.01	< 0.01	< 0.01	< 0.2	1.5
	S10	0.02	0.10	0.03	< 0.1	0.02	0.02	< 0.01	0.41	5.7
	S11	< 0.01	< 0.07	< 0.02	< 0.1	0.01	< 0.01	< 0.01	< 0.2	6.1
	S12	< 0.01	0.09	0.03	0.10	0.02	0.02	< 0.01	0.26	2.8
	S13	0.01	0.07	0.03	0.10	0.02	0.02	< 0.01	0.26	1.9
	S14	0.01	0.09	0.03	0.10	0.02	0.02	< 0.01	0.27	n.a.
	S15	1.1	6.1	1.9	6.1	1.2	1.0	0.15	18	1200
	S16	0.46	3.7	1.00	3.6	0.79	0.72	0.33	11	550
	S17	0.19	1.9	0.53	2.0	0.29	0.28	0.06	5.3	340
	S18	< 0.01	< 0.07	0.04	< 0.1	0.04	0.05	< 0.01	< 0.2	2.7
TRIBUTARIES	T1	0.01	3.9	0.04	0.16	0.03	0.03	0.03	4.2	320
	T2	0.05	0.38	0.09	0.40	0.06	0.07	0.10	1.2	8.1
	T3	0.02	0.09	0.04	0.12	0.03	0.04	0.06	0.38	6.0
	T4	0.01	< 0.07	< 0.02	< 0.1	0.03	0.02	0.04	< 0.2	1.6
	T5	0.02	0.29	0.07	0.37	0.06	0.07	0.08	0.96	10
	T6	0.22	5.6	1.15	7.4	3.0	1.0	0.78	19	24
	T7	0.02	0.19	0.04	0.25	0.04	0.04	0.04	0.63	2.4
	T8	0.02	< 0.07	0.02	< 0.1	0.02	0.02	< 0.01	< 0.2	< 0.1
	T9	0.01	0.11	0.03	0.13	0.13	0.02	0.02	0.44	0.5
	T10	0.01	< 0.07	0.02	< 0.1	0.08	0.02	< 0.01	< 0.2	< 0.1
	T11	0.01	< 0.07	< 0.02	< 0.1	0.02	0.01	< 0.01	< 0.2	0.5
	T12	0.03	0.09	0.04	0.14	0.16	0.04	0.07	0.57	8.2
	T13	0.01	< 0.07	< 0.02	< 0.1	0.03	0.01	< 0.01	< 0.2	0.5
	T14	0.01	< 0.07	< 0.02	< 0.1	0.02	0.02	0.05	< 0.2	120

[$] BDE 209 is not included in the sum of BDEs; n.a. = not available

T6). BDE 209 could be detected in 86 % of the freshwater sediments, with concentrations up to 320 ng/g dw at location T1.

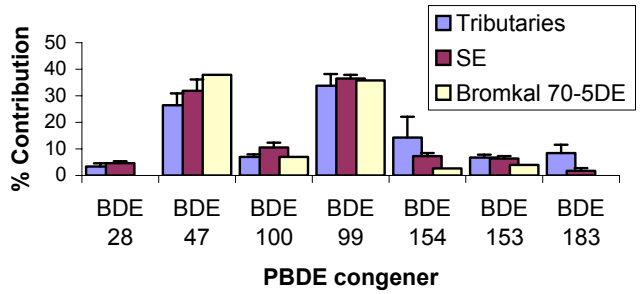
Freshwater sediments seem to be more polluted with PBDEs than marine sediments. This is probably caused by the higher impact of human activity on the inland watercourses and by the heavily industrialized and densely populated country of Belgium. Christensen and Platz[8] also noticed higher PBDE contamination in freshwater than in marine sediments.

PBDE profiles were calculated based only on BDE 28 to 183 (See Figure 2). BDE 209 was not included in the profile to be able to compare with the Bromkal DE70-5 penta technical mixture. Including this congener in the profile would greatly bias the ratios, because the ratio of BDE 209 was 95 ± 3.6 % for the SE samples and varied between 52 % (T9) and 99 % (T1) for the tributaries.

For BNS samples no profile could be established due to the very low PBDE levels. The profile calculated for the SE was very consistent (RSD < 20%, except for BDE 183). The PBDE ratios for the tributaries were less consistent (RSD up to 70%), which can be explained by their geographical distribution. No significant profile differences were found between the SE and the tributaries. Both locations display a virtually similar profile as the Bromkal 70-5DE technical mixture.

When this, or a similar formulation, is a main source, it would imply a high degree of persistence of these compounds to degradation in the sediments.

Figure 2. PBDE ratios of SE and freshwater samples and Bromkal 70-5DE.



Conclusion. PBDE levels in the BNS were low. Levels in the SE, which is considered highly polluted, were low until the Belgian-Dutch border, but were higher more upstream (BDE 209: 1200 ng/g dw). A point source near this location seems very likely. Freshwater samples of tributaries displayed higher levels of PBDEs than the marine and most estuarine locations.

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