Levels and trends of past 20 years of polybrominated diphenylethers in mussels from the Seine estuary, France

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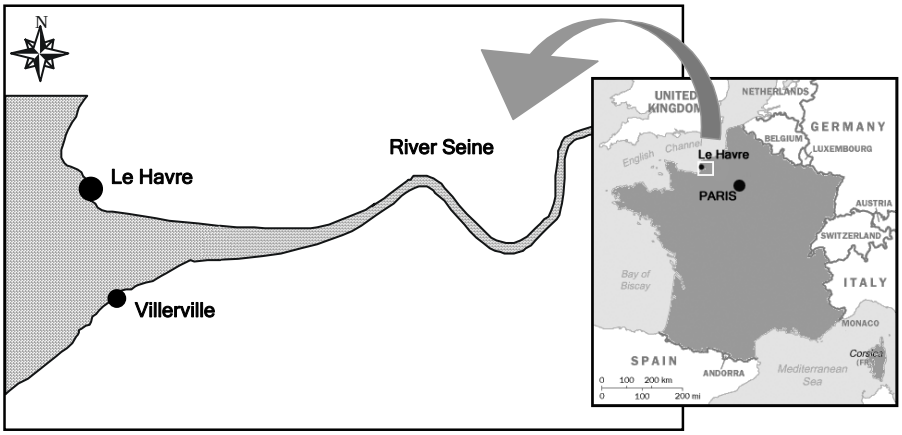
Introduction

Polybrominated diphenylethers (PBDEs) have been used as the chemical flame retardants since 70s. It has also been reported that the production and use (in many plastics, textiles, polyurethane foams and electronic circuits) of these chemicals has increased exponentially since 1980. In parallel to this increase, the environmental levels of these halogenated hydrocarbons have risen very rapidly. A number of published scientific data demonstrate an exponential increase in the concentrations of PBDEs in various biological and sediment samples originating from different areas of the marine environment [1,2,3]. Furthermore, a few recent reports from Sweden [3,4,5] have shown a decline in the last few years of PBDE levels in the environment and human milk and suggested that this reduction may reflect regularatory measures taken in Europe. Nevertheless, the data on the temporal trends in biological samples of the PBDEs are yet relatively rare. These studies require good sample sets of archived samples, and more data is needed to better understand the declining concentrations of PBDEs in the environmental samples. Our study of PBDE levels and trends was done on the archived freeze-dried samples of marine mussels (*Mytilus edulis*) collected over the past 22 years within the French National "Mussel Watch" Network (RNO). Besides that, the bioaccumulation of PBDEs was shown to be high in mussels [6,7] but the literature on PBDE concentrations in mussels is sparse and to the best of our knowledge no study of temporal trends of PBDEs in molluscs have been reported so far. The results presented in this communication were obtained from the first set of mussel samples collected since 1981 to 2003. The sampling site at the mouth of the Seine estuary, France, is known to receive a high input of chemical contaminants.

Figure 1. Location of the sampling site Villerville in the Seine estuary, France.



Materials and methods

Sampling

The sampling site location is shown in Figure 1. The mussel samples selected for the chemical analysis were collected each year during the same period of late November or early December. This avoids possible differences of PBDE concentrations related to the spawning period and/or physiological states of the mussel. Living mussels were depurated, and whole mussels removed from their shells, homogenized and stored at –20°C before freeze-drying. Each sample consists of a pooled sample of about 20 mussels of homogeneous size.

Extraction and clean-up

Approximately five grams (dry weight) of mussel sample were spiked with recovery standards and extracted twice with dichloromethane using accelerated solvent extraction (ASE, Dionex). Each extraction consisted of five static cycles, two minutes long, at a temperature of 100°C and a pressure of 138 bars. Purification of coextracted lipids was done by gel permeation chromatography (GPC) on laboratory prepared column (Bio Beads SX-3 200-400 Mesh). Isooctan was added as a keeper solvent to the organic extracts prior the evaporation. Further fractionation of the concentrated extracts was done on a two layer silica/alumina column. Before analysis, the samples were treated with sulphuric acid to remove remaining lipids.

Analysis

Polybrominated diphenylethers were analysed by GC/MS using a Hewlet Packard 6890 gas chromatograph coupled to a Hewlet Packard 5973 low resolution mass spectrometer. The utilized technique of analysis was electron capture negative ionisation mode (ECNI), using methane as the reagent gas. The GC capillary column was a DB1, 15m × 250μm i.d. × 0.10μm film thickness, with a 5m of Siltek-deactivated fused silica guard column. On column injection was used and the injector was programmed to track the oven temperature. The following temperature program was used; start temperature 50°C held for 0.5 minutes followed by an increase to 175°C at 40°C/min, a second increase at 10°C/min to 250°C and a final increase at 50°C/min to 305°C where it was held for 10 minutes. The flow of the helium carrier gas was 1.2 ml/min. The temperature of the interface was 280°C, the MS source was set to 250°C and the quadrupole to 106°C. Ionisation voltage was 165 eV. Spectra were recorded using selected ion monitoring at m/z 79 and 81 for all BDEs except BDE-209, for which the ions 486 and 488 were recorded. The quantification was made using calibration curves in the range 2-200 pg except for BDE-209, which was calculated using a calibration curve in the range 10-200 pg. BDE-190 was used as the internal standard for all BDEs.

Results and discussion

The samples were analysed for BDE-28, BDE-47, BDE-49, BDE-66, BDE-77, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-138, BDE-183 and BDE–209. The concentrations in mussel samples from each year are presented in Table 1. The congeners were only quantified when the S/N ≥5. The relative standard deviation (RSD) for the method (n=5) was less than 10% for all of the compounds analysed, except for BDE-209, for which it was 30%. Blank samples were prepared by extraction of glasspowder. Low levels of BDE-47 and BDE–209 were present in the

blanks with concentrations ≤ 0.06 pg/µl. Therefore, the samples have not been corrected for blanks.

Comparison of temporal trends

The concentrations of the three most prevalent congeners (BDE-47> BDE-99> BDE-100) have increased exponentially in mussels from the Seine estuary between 1981 and 1999/2001. The rate of increase was almost the same for BDE-47 and BDE-99. The concentrations of these congeners was constant between 1999 and 2001, whereas in 2002 and 2003 the concentrations of BDE-47 and BDE-99 decreased significantly. Table 1 shows that the temporal profile of the prevalent BDEs in mussels has a maximum concentration in 1999/2001.

Increasing concentrations of PBDEs during the 1980s have also been observed in other retrospective temporal trend studies. A study of guillemot eggs from the Baltic Sea showed that the concentrations of PBDEs increased from the beginning of the 1970s, but from the mid-1980s, decreased rapidly [5]. The similar trend was also found in a study of PBDEs in pike from Swedish waters, however, the decreasing trend was considerably slower [4]. A decrease of levels has also been observed for BDE-47 and BDE–99 in eel, cod liver and sediment from Dutch rivers, the southern North Sea and Ireland from 1995 to 2001 [8]. Although, in this study, increasing levels were also reported for some UK rivers. For BDE-209 the concentrations in the sediment samples increased by 50% during the same time, indicating a shift to the more intense use of the deca-BDE formulation. In ringed seals from the Canadian Arctic the levels of PBDEs have been reported to increase exponentially since the beginning of the 1980s, and until 2000, no decline of the levels was observed [1].

It appears that temporal profiles show some regional differences. In comparison to some other sites in Europe, in the Seine estuary, the PBDE concentrations in mussels start to decline relatively late. The observed decline of the PBDEs in environmental samples is not yet fully understood. The decline could be related to the decrease in the use of the commercial penta-BDE mixture in Europe [9,10].

Table 1. Concentrations of PBDE congeners in mussels from the Seine estuary, France (ng/g d.w.). nd = not detected or below the detection limit.

	1981	1986	1989	1991	1993	1995	1997	1999	2001	2002	2003
BDE-28	0.19	0.16	0.19	0.21	0.31	0.39	0.34	0.52	0.63	0.40	0.25
BDE-49	1.50	1.46	1.98	2.34	2.46	2.48	2.35	4.19	4.54	2.58	1.88
BDE-47	1.67	1.85	2.86	4.66	5.95	5.55	5.89	9.45	9.96	4.96	4.19
BDE-66	0.17	0.19	0.29	0.54	0.61	0.49	0.55	1.09	0.97	0.62	0.47
BDE-77	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-100	0.30	0.34	0.56	0.97	1.33	1.39	1.13	2.48	2.50	1.38	1.13
BDE-99	0.74	0.79	1.23	2.07	2.61	2.63	2.46	4.34	4.24	2.08	1.56
BDE-85	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-154	0.36	0.41	0.67	0.74	0.56	0.54	0.42	0.70	0.64	0.41	0.30
BDE-153	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-183	0.05	0.12	0.26	0.37	0.25	0.24	0.13	0.24	0.22	0.12	0.08
BDE-209	0.06	0.18	0.14	0.40	0.11	0.05	0.15	0.96	0.31	0.13	0.11

Comparison of levels

The highest level in the mussels from the Seine estuary was determined for BDE-47 at the concentration of 10.0 ng/g dry weight (d.w.). The highest concentrations for BDE-

99 and BDE-100 were 4.3 and 2.5 ng/g (d.w.) respectively. In comparison, the concentrations of BDE-47 and BDE-99 in mussels from the Netherlands in 1999 ranged, respectively, from 0.9 to 4.3 ng/g (d.w.) and from 0.3 to 1.60 ng/g (d.w.) [2]. Very high concentrations of the same PBDE congeners were found in mussels from Boston Harbor and New Jersey [11]. The concentration of BDE-47 in the sample from Boston Harbor was 39 ng/g (d.w.). In our set of samples high levels were also found for a compound tentatively identified as BDE-49. Since this compound is present only at very low concentrations in the commercial penta-mixture [1], its high concentrations in all of our samples are surprising. The confirmation of the retention time for this congener was made on two different GC columns. Futhermore, the temporal profile for this congener is similar to the predominant BDE congeners in our samples. However, the exact source of this compound in the Seine estuary mussels is not known. The presence of this congener has also been reported in sewage sludge [12], dungenest crab, English sole and ringed seal [1]. BDE-209 was also quantified in the mussels from the Seine estuary, although at very low levels. Since the mussels had been depurated before preparation of the samples, the presence of BDE-209 should not be attributed to the ingestion of particles which otherwise is known to affect the levels of BDE-209 [8].

Conclusion

The contamination and levels over a 20-year period of time of 13 polybrominated diphenyl ethers in blue mussel from the Seine estuary, France, is to our knowledge reported here for the first time. The levels of BDE-47 and BDE-99 in our samples are comparable to the levels observed in mussels from the Netherlands. The temporal trend is similar to the increase of PBDE levels reported for some other environmental samples in Europe. However, in the mussels from the Seine estuary the decrease of PBDE levels appear only in 2001. This indicates that the decrease in consumption of brominated flame retardants in Europe can now be observed in the declining levels of PBDEs in biota. The identification of BDE-49 at relatively high concentrations in our samples is yet to be confirmed.

References

1 Ikonomou M., Rayne S., Addison R., Environ. Sci. Technol., 2002, 36, 1886-1892.
2 De Boer J., van der Horst A., Wester P. , Organohalogen Compounds, 2000, 47, 85-88.
3 Law R.J., Alaee M., Allchin C.R., Boon J.P., Lebeuf M., Lepom P., Stern G.A., 2003, Environ. Int. 29, 757-770.
4 Kirkegaard A., Bignert A., Sellström U., Olsson M., Asplund L., Jansson B., de Wit C., Environ. Pol. 2004, In press.
5 Sellström U., Bignert A., Kirkegaard A., Häggberg L., de Wit C., Olsson M., Jansson B., Environ. Sci. Technol., 2003 , 37, 5496-5501.
6 Gustafsson K., Björk M., Burreau S., Gilek M., Environ. Toxicol. Chem. 1999, 18, 1218-1224.
7 Booij K., Zegers B., Boon J., Chemosphere, 2002, 683-688.
8 De Boer J., Allchin C., Organohalogen Compounds, 2001, 52, 13-17.
9 Danish Environmental Protection Agency, Brominated Flame Retardants –Flow Analysis and Substitution Feasibility Study, 1999, 240p.
10 Renner R., Environ. Sci. Technol., 2000, 34, 223A-226A.
11 Zhu L., Hites R., Anal. Chem., 2003, 75, 6696-6700.
12 National Environmental Research Institute, Ministry of the Environment, Denmark, NERI Technical Report, 2003, No. 481, 28p.