PBDEs AND PBBs IN SUSPENDED PARTICULATE MATTER, SEDIMENTS, SEWAGE TREATMENT PLANT IN- AND EFFLUENTS AND BIOTA FROM THE NETHERLANDS

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Introduction

Polybrominated diphenylethers (PBDEs) and biphenyls (PBBs) were analysed in suspended particulate matter (SPM), sediments, sewage treatment plant (STP) influents and effluents and biota from various locations in The Netherlands, as a part of a large Dutch study on estrogenic contaminants (LOES project)[1]. Other contaminants studied in this project were phthalates, alkyl phenols, bisphenol-A and several hormones. The LOES project also included a large biological part, focussed on the observation of possible estrogenic effects in organisms sampled at the same locations. PBDEs can cause effects on the thyroid function[2], and several congeners can interfere with the aryl hydrocarbon receptor[3]. PBBs and PBDEs are used as flame retardants[4]. Their presence in increasing concentrations in environmental and human samples has been reported recently[4-6]. The production of PBDEs has gradually shifted from pentabrominated mixes towards decabrominated diphenylether.

Methods

SPM samples were obtained by centrifugation from surface waters in the Netherlands. Municipal STP influents and industrial waste water samples were filtered and STP effluents were obtained after centrifugation. Sediment samples were obtained by pooling grab samples per location. All sediment samples were sieved (<63 μm). Flounder (*Platichthys flesus*) samples were taken by beam trawling and bream (*Abramis brama*) samples by small bottom trawls. Marine mussels (*Mytilus edulis*) and freshwater mussels (*Dreissena polymorpha*) were hanged out in small nets for six weeks at the specific locations, after which they were recollected. Depuration was not applied. In total 133 samples were analysed (Table 1). The samples were taken during three sampling periods: April, July and September 1999. The PBDEs and PBBs were determined after Soxhlet extraction with hexane/acetone (3:1, v/v, 12 h), HPLC clean-up over two PL gel columns and further purification by elution over a silica gel column and sulphuric acid treatment. Amber glassware was used throughout the entire project, while direct sunlight or other UV light entrance in the laboratory was blocked, to prevent degradation of the decaBDE. The final analysis was carried out GC/MS, using electron capture negative ionisation (ECNI) as ionisation technique with methane as a reagent gas. Care was taken not to expose decaBDE (and decaBB) unnecessarily long to elevated temperatures by using a 15m CP Sil 8 column. The temperature of the splitless injector was 275°C and the maximum oven temperature 300°C. A 50 m CP Sil 8 column was used for the determination of the other PBDE and PBB congeners to enable a maximum resolution. The peak identification was based on retention time and the recognition of the Br^- ion (m/z 79/81). Chlorobiphenyl (CB) 112 (2,3,5,6,3'-pentaCB) was used as an internal (syringe) standard. The following PBBs and PBDEs were determined: BBs 15, 49, 52, 101, 153, 169 and 209 and BDEs 47, 85, 99,138, 153 and 209. The nomenclature is similar to that of the PCBs[7]. The method was tested with good results in the first international interlaboratory study on PBDEs[8]. The total lipid contents of the biota samples were determined by a chloroform/methanol extraction according to Bligh and Dyer[9]. The dry weights were determined after heating at 105°C for 24 h.

Table 1. Sampling scheme.

Sample type	Number of samples	Number of locations
SPM	44	18
Sediment	22	17
Flounder and bream	35	20
Mussels (freshw. + marine)	16	16
STP influent/effluent	13	9
Industrial wastewater	3	3

Results and Discussion

PBBs were not found above the detection limits in any of the samples. The detection limits for most PBBs were between <1 and <0.1 ng/g dry weight (dw), but between <1 and <10 ng/g dw for decaBB. This result is in agreement with the negligible PBB production in Europe over the past decades, with only some minor production of decaBB which has been terminated recently. The PBDEs 85 and 138 were generally below the detection limts (<1 - <0.1 ng/g dw). BDE 100 was not included in this project but was found in chromatograms of most samples. An overview of the ranges of the BDEs 47, 99, 153 and 209 is given in Table 2.

Table 2. PBDE concentrations in SPM, sediment, biota and waste water (ng/g dw).

Sample type	BDE 47	BDE 99	BDE 153	BDE 209
SPM	2.2(<0.2-9)[1]	2.4(<0.1-23)	<0.6(<0.1-9.7)	71(<9-4600)
Sediment	1.1(0.3-7.1)	0.6(<0.2-5.5)	<0.7(<0.1-5)	22(<4-510)
Flounder	16(0.6-20)	0.2(<0.01-4.6)	0.1(<0.02-<1)	<0.9(<0.2-<6)
Bream	16(0.2-130)	0.1(<0.01-<0.8)	0.9(<0.04-4.1)	<5(<0.03-<21)
Mar. mussels	1.2(0.9-4.3)	0.5(0.3-1.6)	<0.1(<0.1-<0.2)	<4(<4-<5)
Freshw. mussels	1.8(0.7-17)	1.4(0.4-11)	<0.9(<0.1-1.5)	<23(<4-<34)
STP influent[2]	2.3(<0.1-68)	5.2(0.3-33)	<0.9(<0.02-<5)	24(<0.5-330)
STP effluent[3]	22(11-35)	<1(<1-<1)	<5(<0.4-<7)	350(310-920)
Ind. waste water[2]	0.4(<0.1-68)	6.6(0.3-66)	<1(<0.02-2.6)	45(<0.5-200)

[1] Median and range are given for each BDE and each sample type; [2] filtrate; [3] residue.

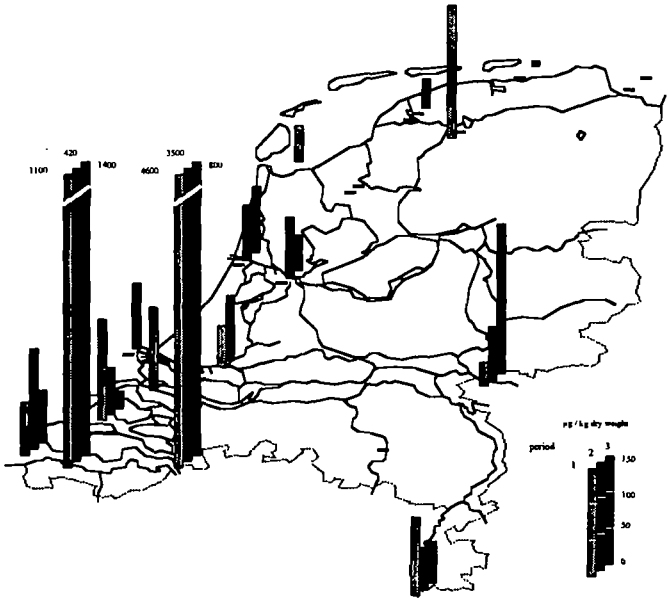

Figure 1. BDE 209 concentrations in suspended particulate matter from The Netherlands

Markedly high concentrations of decaBDE (up to 4600 ng/g dw) were found in SPM from the Western Scheldt (Figure 1). A clear decreasing trend was observed from the east part of the river near Antwerp towards sea. Possibly, this indicates a relationship with the textile industry in Antwerp, in which PBDEs are being used. A similar decaBDE pattern was found in the sediment of the Western Scheldt with higher levels in the east part (up to 510 ng/g dw), decreasing down to 110 ng/g dw at Terneuzen and <4 ng/g dw at Vlisssingen. Clear variations in PBDE concentrations in SPM were found between the three sampling periods, presumably related to variations in PBDE fluxes. The sediment samples were primarily taken in period 3 (September). The decaBDE concentrations in the river Rhine were the second highest after the Western Scheldt, with 84 ng/g dw in sediment from Lobith (German border) and 220 ng/g dw in SPM from Lobith. The highest BDE 47 and 99 concentrations were found in SPM from the Haringvliet (river Rhine delta) with 5.2-9 and 4-12 ng/g dw, respectively.

None of the fish samples contained decaBDE in measurable concentrations (<0.2-<6 ng/g dw). In three marine mussel samples decaBDE was found a level of 5 ng/g dw. However, these mussels had not been depurated after sampling and the concentrations found are very likely due to decaBDE in small particles still present in the mussels. BDE 47 is clearly higher in the fish samples than BDE 99, which is often around the detection limits (ca. <0.1 ng/g dw). Such a selective bioaccumulation of BDE 47 has been reported before[4]. In mussels little difference is found between BDE 47 and BDE 99 concentrations, similarly to the pattern in SPM. This difference in pattern between fish and mussels is most likely related to the lower biotransformation capacity of mussels for BDE 99. Relatively high BDE 47 concentrations were found in bream from the rivers Meuse and Rhine: 110 and 90 ng/g dw (dw ca. 20%).

Finally, relatively high decaBDE concentrations (up to 910 ng/g dw) were found in some STP samples. The differences between BDE concentrations in in- and effluents may be explained by the differences in pre-treatment: filtration (influent) or centrifugation (effluent). In industrial waste

water filtrates up to 200 ng/g dw decaBDE was found. The concentrations of the other BDEs in STP in- and effluents and industrial waste water filtrates were in most cases clearly lower than the decaBDE concentrations (Table 2).
No other data on PBDE concentrations in SPM and STP in-and effluents could be found in the literature. The decaBDE concentrations in sediments belong to the highest reported until now[4]. DecaBDE levels up to 1700 ng/g dw have been reported in the river Mersey (UK)[10].

Conclusions

•High decaBDE concentrations (up to 4600 ng/g dw) were found in suspended particulate matter from the Western Scheldt, possibly related to spillage during use in the textile industry in Antwerp. A similar decaBDE pattern is found in the sediment of the Western Scheldt with high values (up to 510 ng/g dw) close to Antwerp.
•The BDE 47 and 99 concentrations in SPM, sediments and biota from riverine locations indicate a relation with the - possible former – industrial production or use of penta BDE.
•DecaBDE does not accumulate in flounder, bream and mussels.
•Relatively high decaBDE concentrations (up to 920 ng/g dw) were found in some sewage treatment plant influents and effluents.
•DecaBDE and other PBDEs are not effectively removed by sewage treatment plants.
•The presence of decaBDE in suspended particulate matter and sediments demands further studies on the stability and possible degradation of this compound.
•No PBBs were found in Dutch aquatic environment samples above the detection limits.

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