

# Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands

Jacob de Boer\*, Peter G. Wester, Aschwin van der Horst, Pim E.G. Leonards

*Netherlands Institute for Fisheries Research, PO Box 68, 1970 AB IJmuiden, the Netherlands*

Received 13 February 2002; accepted 28 June 2002

**“Capsule”:** *Suspended particulate matter is an important carrier for higher brominated diphenylethers in the aquatic environment.*

## Abstract

Polybrominated diphenyl ethers (PBDEs) have been determined in 133 samples of suspended particulate matter (SPM), sediments, sewage treatment plant (STP) influents and effluents, fish and mussels from various locations in The Netherlands, as a part of a large Dutch national study on estrogenic contaminants in the aquatic environment (LOES project). Some PBBs were also analysed but not found in any of the samples at detectable levels. PBDEs and PBBs were included in this study because indications of long term effects on the balance of endocrine systems were found in the literature. High concentrations of decaBDE (up to 4600 µg/kg dry weight) were found in SPM from the Western Scheldt. These levels are possibly related to spillage during use of PBDEs in industries upstream the river Scheldt in Belgium. SPM was identified as an important carrier for higher brominated diphenyl ethers in the aquatic environment. DecaBDE was not found at detectable levels in flounder, bream and mussels. The bioaccumulation of decaBDE in these fish and shellfish samples is apparently limited. Lower brominated PBDE congeners (tetra/penta) were also found in the Western Scheldt as well as in the Rhine delta and the river Meuse, but in much lower concentrations than the decaBDE. In contrast with decaBDE, the tetra and pentaBDEs were found in biota. It was concluded that at least a small part of the PBDE can pass STPs.

© 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polybrominated diphenyl ethers; Suspended particulate matter; Sewage treatment plants; Sediment; Fish

## 1. Introduction

Today, 470,000 tons of bromine are produced annually, used in water purification, health care, agriculture, cars and photography (Anon., 2000). However, the most important use of bromine is in flame retardants. Flame retardants are chemicals which, added to materials, inhibit or suppress the combustion process. They are being used in electronic equipment, upholstered furniture, construction materials, and textiles. Thirty-nine percent of all flame retardants are based on bromine (Anon., 2000). Some of the most important brominated flame retardants are: polybrominated diphenyl ethers (PBDEs, composition of various technical mixtures

given in Table 1), hexabromocyclododecane (HBCD), and tetrabromobisphenol-A (TBBP-A).

On 30 January 2001, the European Commission has issued a proposal to ban the production and use of PentaBDE (Dungey, 2001). Polybrominated biphenyls (PBBs) have mainly been used in the USA (de Boer et al., 2000). The production of the main mixture, hexabromobiphenyl (Firemaster BP-6), ceased in 1974, after the Michigan disaster (WHO, 1994). The production in Europe has been limited to decabrominated biphenyl (decaBB), but PBBs have been imported from the USA (Brinkman and de Kok, 1980). The decaBB production, which since 1977 only took place in France, has been terminated a few years ago (de Boer et al., 2000; Spiegelstein, 2000).

PBDEs have been detected in the environment since the late 1970s (Andersson and Blomkvist, 1981; de Boer, 1989; Sellström et al., 1990; Pijnenburg et al.,

\* Corresponding author. Tel.: +31-255-564736; fax: +31-255-56473.

E-mail address: j.deboer@rivo.wag-ur.nl (J. de Boer).

Table 1  
Composition of technical mixes of polybrominated diphenyl ethers (PBDEs)

PBE-mix	Percentage of mixture						
	tetraBDE	pentaBDE	hexaBDE	heptaBDE	octaBDE	nonaBDE	decaBDE
PentaBDE	33.7	54.6	11.7				
OctaBDE			5.5	74.9	3.6	13.9	2.1
DecaBDE						3	97

Source: Spiegelstein, 2000.

1995, Allchin et al., 1999, Rahman et al., 2001; Hale et al., 2001; de Wit, 2002). More recently, more attention is given in the scientific literature to the environmental occurrence of PBDEs. PBDEs were found to be present in sperm whales and a wider range of marine mammal species which is an indication for the presence of these compounds in deeper waters of the ocean (de Boer et al., 1998). PBDEs were also found in relatively high concentrations in marine mammals from the North Sea (de Boer et al., 1998; Lindstrøm et al., 1999). In addition to that, increasing trends of BDE47 and BDE99 concentrations in Swedish human milk were presented (Norén and Meironyté, 1998, 2000), although the most recent data showed that these curves have past the top (Meironyté Guvenius and Norén, 2001) and are declining. The PBDE patterns observed in human milk and in marine mammals and fish mainly consist of 2,4,2',4'-tetra BDE (BDE47) together with smaller amounts of some other tetra, penta and hexa BDEs. PBDEs were also found in several estuaries in Europe, among which those of the rivers Scheldt in The Netherlands and Mersey and Tees in the UK (Allchin et al., 1999; Anon., 1997). In these rivers also relatively high levels (up to mg/kg dry weight) decaBDE were found. Environmental levels of PBBs were reported after the Michigan disaster (WHO, 1994). PBBs have also been reported in fish from German rivers (WHO, 1994) and in North Sea and Baltic fish (Jansson et al., 1993).

The present study was carried out as a part of the Dutch national study on estrogenic contaminants in the aquatic environment (LOES project) (Vethaak et al., 2002). PBDEs and PBBs were included in this study because indications of long term effects on the balance of endocrine systems were found in the literature (de Boer et al., 2000). Other contaminants included in this project were phthalates, alkyl phenols, bisphenol-A and several hormones (Vethaak et al., 2002). The LOES project also included a large biological effect part, focussed on the observation of possible estrogenic effects in fish sampled at the same locations. The objective of this study was to screen the Dutch aquatic environment for concentrations of PBDEs and PBBs. Therefore, fish, mussels, sediment, and suspended particulate matter (SPM) samples of the most important rivers and estuaries were analysed for these compounds.

In addition, SPM samples of a number of sewage treatment plants (STP) influents and effluents were analysed for PBDEs and PBBs to estimate if these compounds were able to pass STPs.

## 2. Methods

The following PBDEs were determined:

47	2,4,2',4'-tetraBDE
85	2,3,4,2',4'-pentaBDE
99	2,4,5,2',4'-pentaBDE
138	2,3,4,2',4',5'-hexaBDE
153	2,4,5,2',4',5'-hexaBDE
209	decaBDE

The BDEs 47 and 99 are the main compounds in the technical Penta-mix. The BDEs 138 and 153 are also present in the Penta-mix, in lower percentages. decaBDE is the main compound (97%) of the technical Deca-mix. BDE 85 was available as a standard, but does not represent a specific technical mixture. Some other important representatives of the technical mixtures such as BDE100 (of the Penta-mix) and BDE183 (of the Octa-mix) were not available at the time of the design of this programme.

SPM samples were obtained from surface waters in the Netherlands and from sewage treatment plant influents and effluents and industrial wastewater by (flow-through) centrifugation (effluent and surface waters) or filtration (influent) of the water samples. Centrifugation took place at 20,000 rpm until 200 g of material was collected. Sediment samples were obtained by pooling nine sub-samples, taken by a Van Veen grab sampler from a square of ca. 100 m<sup>2</sup> 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. The flounder and bream were filleted and the fillets of 25 fishes per location were pooled. Marine mussels (*Mytilus edulis*) and freshwater mussels (*Dreissena polymorpha*) were hanged out in small nets for 6 weeks at

the specific locations, after which they were recollected. Depuration was not applied. The mussels were taken out of the shell and pooled, ca. 100 g mussel flesh per sample. In total 133 samples were analysed. The number of samples per sample type and per location is given in Table 2. The samples were taken during three sampling periods: April, July and September 1999.

The STP influent samples were filtered over Whatman filters (GF/C particle retention 1.2 µm). The filtered volume was 4 l. STP effluent samples could only be taken at a few selected locations, due to the high costs of the required centrifuge, which was used to centrifuge the samples on the spot, and its transport to the various locations. The SPM and STP effluent residues, biota and sediments were mixed with sodium sulphate, allowed to dry for 3 h or overnight (dependent of the volume, < 6 g sample: 3 h) and Soxhlet extracted for 12 h with hexane/acetone (3:1, v/v, 70 °C) (de Boer et al., 2001). All solvents used were nanograde quality, and were obtained from Promochem, Wesel, Germany. The extracts were concentrated on a rotary evaporator and dissolved in 2 ml of dichloromethane. The extracts were cleaned by gel permeation chromatography (GPC) over two Polymer Laboratories (PL) gel columns (300 × 25 mm, pore size 10 µm), using dichloromethane at 10 ml/min. The collected fraction was 18–23 min. The fraction was concentrated under nitrogen, dissolved in iso-octane and further purified by shaking with sulphuric acid. After separation of the iso-octane phase, the sulphuric acid phase is washed twice with pentane to extract all PBEs. Finally, the pentane/iso-octane mixture was concentrated under nitrogen to 2 ml (iso-octane) and eluted over a 1.6 g silica gel column (2% deactivated) with 11 ml iso-octane and 10 ml 20% diethylether in iso-octane. This sequential elution results in both a high recovery and a clean sample. The fractions were combined and concentrated to 1 ml (iso-octane), after addition of a syringe standard (2,3,5,6,3'-penta-chlorobiphenyl (CB112)). An external standard solution of all PBDEs analysed was subjected to the entire method to determine the recoveries. All results reported are corrected for recovery. Amber glassware was used throughout the entire project, while direct sunlight or other UV light entrance in the laboratory was blocked

by installing UV filtering foils at the windows and UV filter plates under the fluorescent lights. This was necessary to prevent possible degradation of decaBDE. The final analysis was carried out by GC/MS, using electron capture negative ionisation (ECNI) as ionisation technique (MSD transferline 290 °C, source temperature 200 °C, quadrupole temperature 106 °C, electron energy 70 eV with methane (3.25 ml/min) as a reagent gas). Initially (period 1), a 25 m CP Sil 8 column [internal diameter (i.d.) 0.25 mm, film thickness 0.25 µm] was used for the determination all PBDEs. However, due to a co-elution of BDE153 with tetrabromobisphenol-A (TBBP-A), BDE153 could not be determined properly in a number of samples taken in period 1. In addition, the decaBDE peak at a 25 m column occasionally varied in shape due to degradation as a consequence of too long exposure to elevated temperatures in the GC oven. Substitution of this 25 m column by a 50 m (i.d. 0.25 mm, film thickness 0.25 µm) CP Sil 8 column enabled the determination of BDE153 and provided a maximum resolution for the determination of all other BB and BDE congeners.

GC conditions: Oven 90 °C, 3 min → 210 °C, 30 °C/min, 20 min 210 °C → 290 °C, 5 °C/min. Injection was pulsed splitless and the carrier gas was helium.

A 15 m (i.d. 0.25 mm, film thickness 0.25 µm) CP Sil 8 column provided good conditions for the determination of decaBDE. The maximum oven temperature during the decaBDE analysis was 300 °C, the injector temperature was 275 °C. The peak identification was based on retention time and the recognition of the Br<sup>-</sup> ion (*m/z* 79/81). For decaBDE, the mass fragments 486.7 and 488.7 were used for additional identification. Detection limits were calculated as three times the noise level of the chromatogram. The limit of determination was set by the lowest concentration of the multi-level (6 point) calibration curve. Further details of the analysis have been reported before (de Boer et al., 2001).

The total lipid contents of the biota samples were determined by a chloroform/methanol extraction according to Bligh and Dyer (1959). Dry weights of sediment and SPM samples were determined after heating at 105 °C for 24 h.

### 3. Results and discussion

The PBDEs 85 and 138 were generally below the detection limits (<1–<0.1 µg/kg dw). An overview of the concentration ranges found for the BDEs 47, 99, 153 and 209 is given in Table 3.

#### 3.1. SPM

All PBDE concentrations in SPM and sediments are expressed on a dry weight basis (Figs. 1–3). Markedly

Table 2  
Sampling scheme

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

Table 3  
Summary of PBDE concentrations in SPM, sediment, biota and waste water residues ( $\mu\text{g}/\text{kg dw}$ )

Sample type	BDE 47	BDE 99	BDE 153	BDE 209
SPM	2.2 (<0.2–9) <sup>a</sup>	2.4 (<0.1–23)	<0.6 (<0.1–9.7)	71 (<9–4600)
Sediment <sup>b</sup>	1.1 (0.3–7.1)	0.6 (<0.2–5.5)	<0.7 (<0.1–5)	22 (<4–510)
Flounder	0.9 (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)
Marine mussels	1.2 (0.9–4.3)	0.5 (0.3–1.6)	<0.1 (<0.1–<0.2)	<4 (<4–<5)
Freshwater mussels	1.8 (0.7–17)	1.4 (0.4–11)	<0.9 (<0.1–1.5)	<23 (<4–<34)
STP influent <sup>c</sup>	2.3 (<0.1–68)	5.2 (0.3–33)	<0.9 (<0.02–<5)	24 (<0.5–330)
STP effluent <sup>d</sup>	22 (11–35)	<1 (<1–<1)	<5 (<0.4–<7)	350 (310–920)
Industrial wastewater	0.4 (<0.1–68)	6.6 (0.3–66)	<1 (<0.02–2.6)	45 (<0.5–200)

<sup>a</sup> Median and range are given for each BDE and each sample type.

<sup>b</sup> <63  $\mu\text{m}$  fraction.

<sup>c</sup> Particulate matter filtered from influent.

<sup>d</sup> Particulate matter centrifuged from effluent.

high concentrations of decaBDE (up to 4600  $\mu\text{g}/\text{kg dw}$ ) were found in SPM from the Western Scheldt (Fig. 3). A clear decreasing trend was observed from the east part of the river near Antwerp (locations 4–9–7) towards sea. The pattern found suggests a relationship between the PBDE concentrations and the textile industry in Antwerp, in which decaBDE is used. The local bromine industry in Terneuzen (location 9), half way the Dutch part of the Western Scheldt, may also have influenced the PBDE levels, but its impact seems to be small compared to the PBDE plume coming from Antwerp. Clear variations in PBDE concentrations in SPM were found between the three sampling periods. It is evident that variations due to variable discharges are rather observed in the SPM than in sediments or biota which both show a more integrative picture. The highest BDE47 and 99 concentrations were found in SPM from the Haringvliet (river Rhine delta, location 1) with 5.2–9 and 4–12  $\mu\text{g}/\text{kg dw}$ , respectively (Figs. 1 and 2). The BDE47 and 99 concentrations at two other locations in the Rhine delta, Nieuwe Waterweg and Rotterdam harbour were also high. Given the extremely low solubility of higher brominated PBDEs in water and the high PBDE concentrations found in these SPM samples, SPM is clearly identified as an important carrier for higher brominated diphenyl ethers in the aquatic environment. This is the first report on PBDEs in SPM, no other data on PBDE concentrations in SPM could be found in the literature. SPM is apparently a good matrix for monitoring the momentary concentration of PBDEs in the aquatic environment. However, both sampling and pre-treatment of SPM samples are rather expensive and laborious.

### 3.2. Sediments

All concentrations shown in Fig. 4 are on a dry weight basis. Sieving of the sediment to <63  $\mu\text{m}$  has caused a certain normalisation, but small differences in

PBDE concentrations due to differences in organic carbon content per location may still occur. The decaBDE pattern in sediment of the Western Scheldt (locations 4–9–7) was similar to that found in SPM: higher levels in the east part (up to 510  $\mu\text{g}/\text{kg dw}$ ), decreasing down to 110  $\mu\text{g}/\text{kg dw}$  at Terneuzen and <2.9  $\mu\text{g}/\text{kg dw}$  (all <63  $\mu\text{m}$  fractions) at Vlissingen (Fig. 4). Again, the input from Antwerp appears to be more important than a supposed contribution from the bromine industry at Terneuzen. Although there is a considerable tidal movement, which could move a possible PBDE plume from Terneuzen to the east, it is unlikely that the higher PBDE levels in the most eastern part of the Western Scheldt would only have been caused by such a tidal influence. The sediment samples were only taken in period 3 (September). The decaBDE concentrations in the river Rhine were the second highest after the Western Scheldt, with 84  $\mu\text{g}/\text{kg dw}$  in sediment from Lobith (German border, location 3) and 220  $\mu\text{g}/\text{kg dw}$  in SPM from Lobith. The highest BDE47 and 99 concentrations in sediment were found at this location (7.1 and 5.5  $\mu\text{g}/\text{kg dw}$ , respectively). The decaBDE concentrations in sediments are among the highest reported until now (de Boer et al., 2000). DecaBDE levels up to 1,700  $\mu\text{g}/\text{kg dw}$  have been reported in the river Mersey, (UK) (Anon., 1997). Much lower decaBDE concentrations were reported in Danish sediments with a maximum level in Copenhagen harbour of 21.5  $\mu\text{g}/\text{kg dry weight}$  (Platz and Christensen, 2001). The decaBDE concentration in North Sea sediment off the Western Scheldt was 32  $\mu\text{g}/\text{kg dry weight}$  (<63  $\mu\text{m}$  fraction) (Klamer et al., 2001), which corresponds with the results of this study. Other decaBDE concentrations in North Sea sediments along the Dutch coast were slightly lower, and decreased further as sampling locations were further away from the coast (Klamer et al., 2001). The BDEs 47, 99 and 153 concentrations in SPM, sediments and biota are not as high as the highest concentrations reported in the literature (de Boer et al., 2000). The high

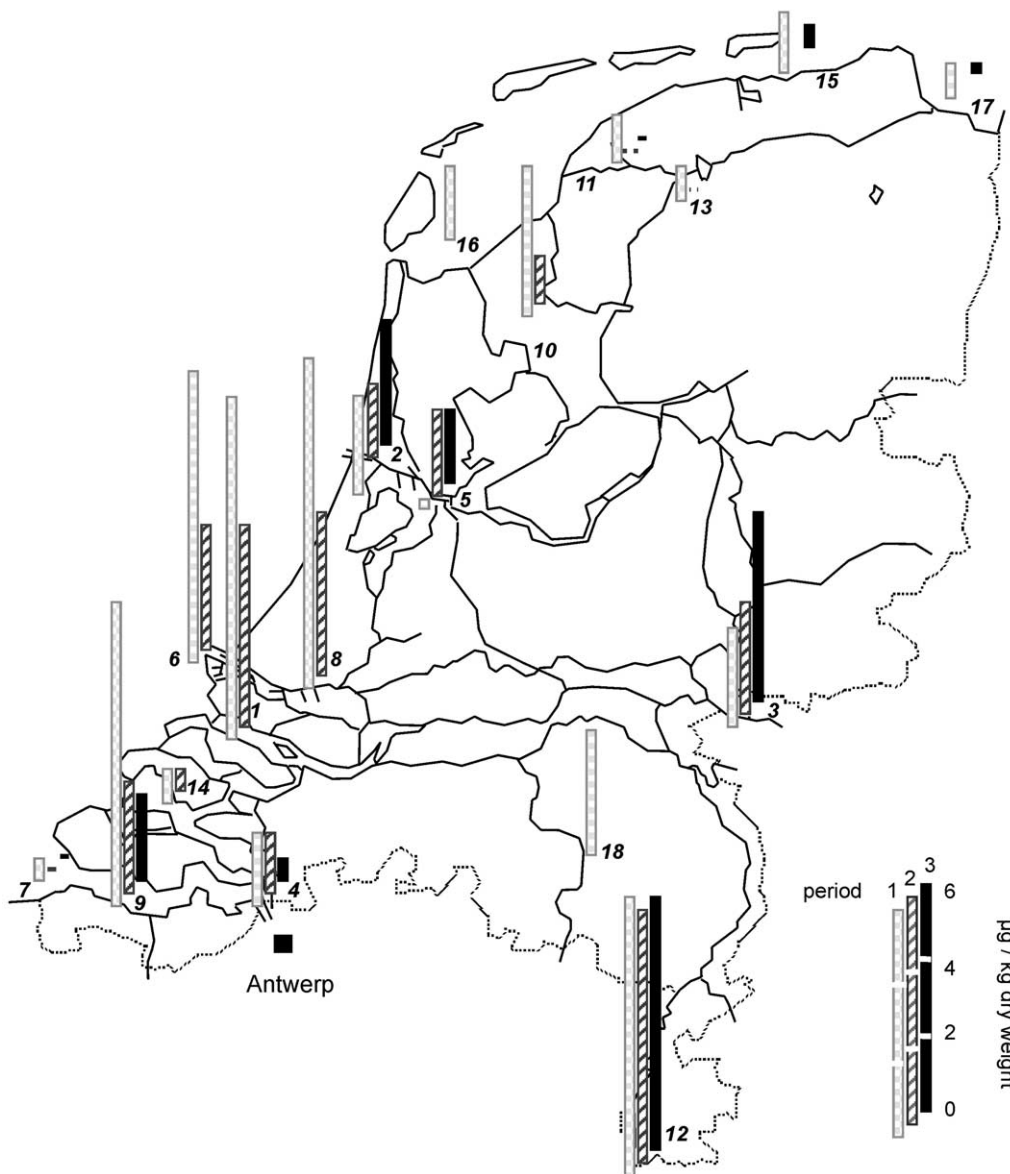


Fig. 1. BDE47 concentrations in suspended particulate matter in  $\mu\text{g}/\text{kg dw}$ ; locations (in The Netherlands): 1. Haringvliet (west), 2. IJmuiden, 3. Rhine (Lobith, border), 4. Western Scheldt (Schaar van Ouden Doel), 5. Amsterdam harbour, 6. Rotterdam harbour (Splitsingsdam), 7. Western Scheldt (Vlissingen), 8. Nieuwe Waterweg (Maassluis), 9. Western Scheldt (Terneuzen), 10. IJssel Lake (Vrouwenzand), 11. Koudevaart (St. Annaparochie), 12. Meuse (Eijsden, border), 13. Bergumer Lake (Bergum), 14. Eastern Scheldt (Hammen), 15. Wadden Sea (Dantzig Gat), 16. Wadden Sea (Den Oever), 17. Ems Dollard (Bocht van Watum), 18. Dommel (near Eindhoven), 19. North Sea (Noordwijk), 20. North Sea (Oestergronden), 21. Meuse (Borgharen), 22. Apeldoorns Canal (Epe), 23. Amsterdam (Westpoort).

decaBDE concentrations in sediment emphasize the need for a thorough understanding of the fate of this compound. Dietary uptake and degradation of decaBDE in fish has been reported to occur in an aquarium experiment (Kierkegaard et al., 1999), but should be confirmed for prevailing conditions in the aquatic environment prior to drawing further conclusions. If a complete absence of degradation of decaBDE would appear from further studies, this should be ensured for the long term, because even the slightest formation of lower brominated diphenylethers from these high levels of decaBDE in the sediment studied could cause serious

environmental damage, even after periods of tens of years.

### 3.3. Fish and mussels

None of the fish samples contained decaBDE in measurable concentrations ( $<0.2$ – $<21 \mu\text{g}/\text{kg dw}$ ) (Tables 4 and 5). In two marine mussel samples (Western Scheldt, Vlissingen, and Wadden Sea) decaBDE was found at a level of  $5 \mu\text{g}/\text{kg dw}$  (Table 6). However, these mussels had not been depurated after sampling and the concentrations found are very likely due to decaBDE which

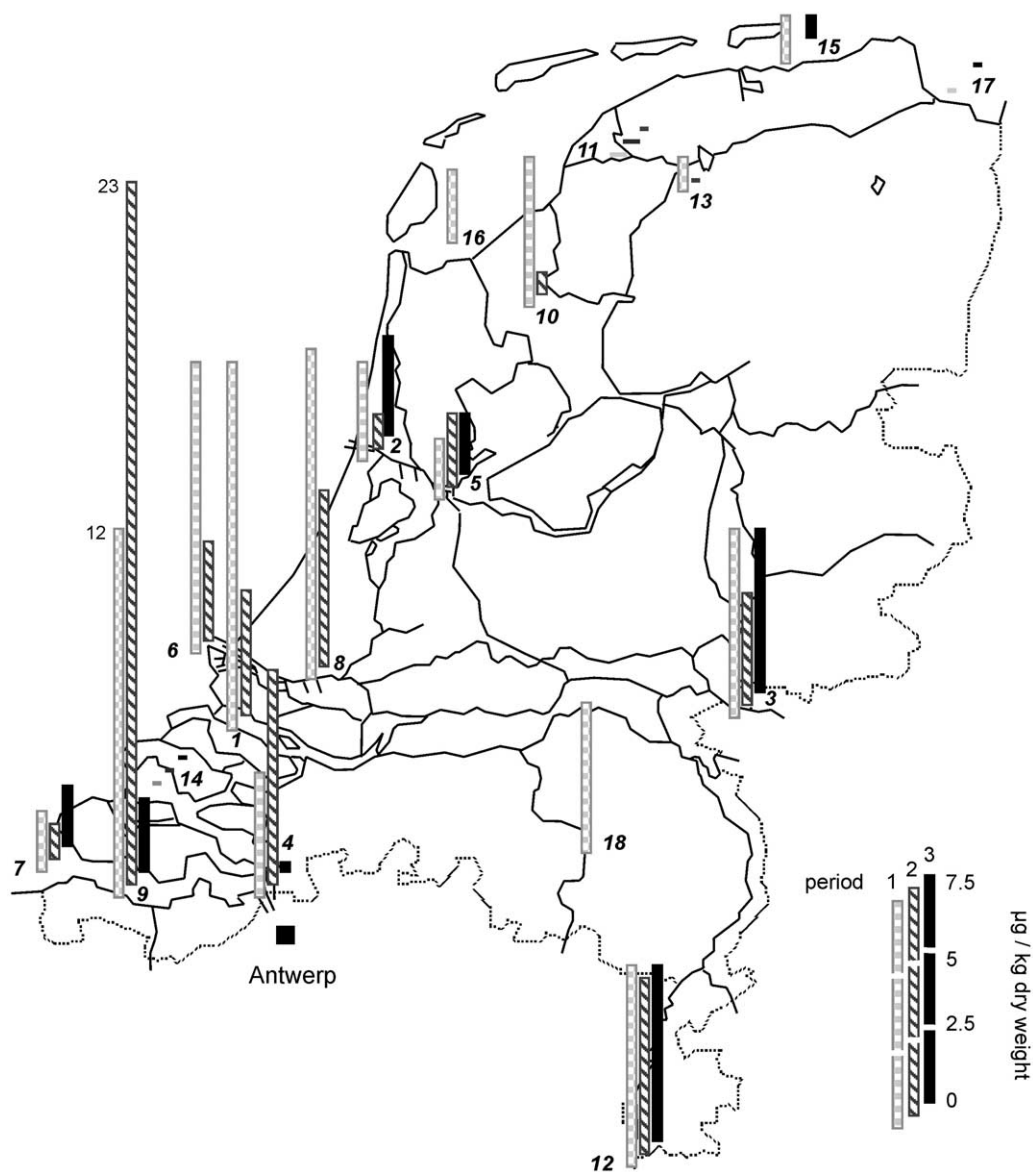


Fig. 2. BDE99 concentrations in suspended particulate matter in  $\mu\text{g}/\text{kg dw}$  (locations see Fig. 1).

is present in small particles in the gut of the mussels (Booij et al., 2000). BDE 47 is clearly higher in the fish samples than BDE99, which is often around the detection limits (ca.  $<0.1 \mu\text{g}/\text{kg dw}$ ). Such a selective bioaccumulation of BDE47 has been reported before (de Boer et al., 2000). In mussels little difference is found between BDE47 and BDE99 concentrations, similarly to the pattern in SPM (Table 7). This difference in pattern between fish and mussels can be explained by a lower biotransformation capacity of mussels for BDE99 or a limited uptake of BDE99 by fish. In sediment and SPM samples BDE47 is normally slightly higher than BDE99. Relatively high BDE47 concentrations were found in bream from the rivers Meuse, Rhine and Dommel (locations 12–3–18):  $110$ ,  $90$  and  $130 \mu\text{g}/\text{kg dw}$ , respectively. A perch sample from south Sweden contained an exceptionally high concentration of  $24,000 \mu\text{g}/$

$\text{kg lipid weight BDE 47}$  (Sellström et al., 1993). Much lower PBDE concentrations were found in herring near Karlskrona and other places along the Swedish coast, with maximum levels of  $18 \mu\text{g}/\text{kg}$  for BDE47,  $7.1 \mu\text{g}/\text{kg}$  for BDE99 and  $3.3 \mu\text{g}/\text{kg}$  for BDE100, all on a lipid weight basis with a mean lipid content of 2% (Nylund et al., 2001). The BDE47 concentrations found in bream from the rivers Meuse (Eijsden), Rhine (Lobith) and Dommel can be considered as relatively high (ca.  $600 \mu\text{g}/\text{kg lipid weight}$ ), when compared to background concentrations such as found at the locations Koudevaart (St. Annaparochie, no 11) and Bergumermeer (location 13) (Table 4). Because of these elevated levels in bream, the median values given in Table 3 for bream are higher than in flounders which originated from the generally more clean marine locations. Clear differences in BDE concentrations in bream are observed between

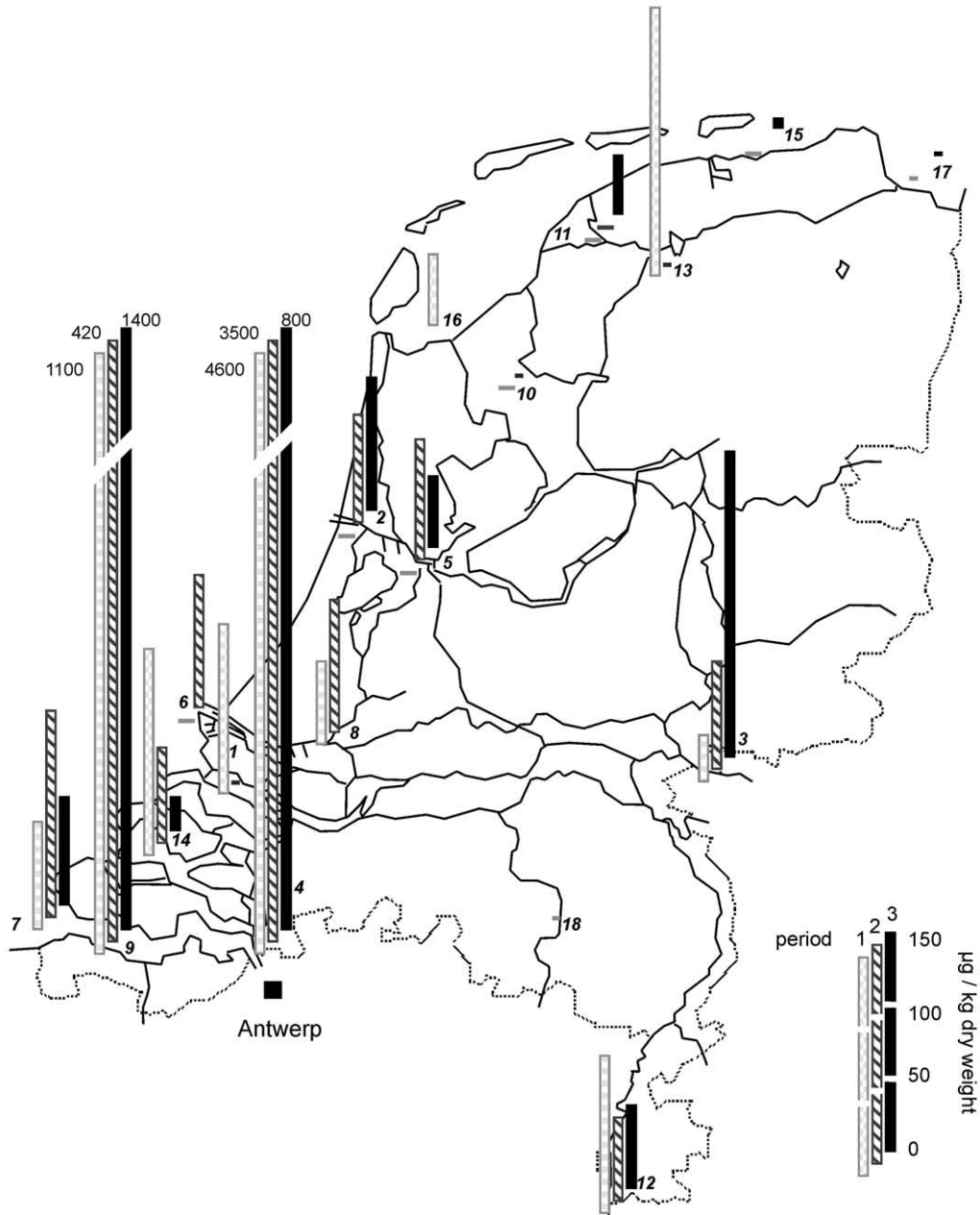


Fig. 3. DecaBDE concentrations in suspended particulate matter in µg/kg/dw (locations see Fig. 1).

the two periods. The higher concentrations were found at the end of the summer (period 3), after which the bream had built up more fat (and thus more contaminants on a dry weight basis, while just after spawning (period 1) the bream is more lean and has lost some of the contaminants during spawning.

### 3.4. STP in- and effluent

Relatively high decabBDE concentrations were found in some STP samples (Table 8). The effluent of the Eindhoven STP contained 920 µg/kg dw decabBDE, whereas the influent contained 72 µg/kg dw. Clearly, decabBDE can pass STPs. The higher concentrations in

the effluent can be explained by a different way of sampling. The influents were delivered at the laboratory as water samples and were filtered over Whatman filters (GF/C, particle size 1.2 µm). The effluents were delivered as particulate matter residues, obtained after centrifugation on the spot, immediately after sampling. Possibly, these centrifugated samples have contained a higher proportion of fine particles, which contained higher concentrations of PBDEs. Large particles could also settle in the STP process, resulting in enrichment of the smaller particles in the effluent. Variation in the PBDE flux through the STP may also have played a role, because the influent and effluent samples were taken at the same moment. The retention time of the

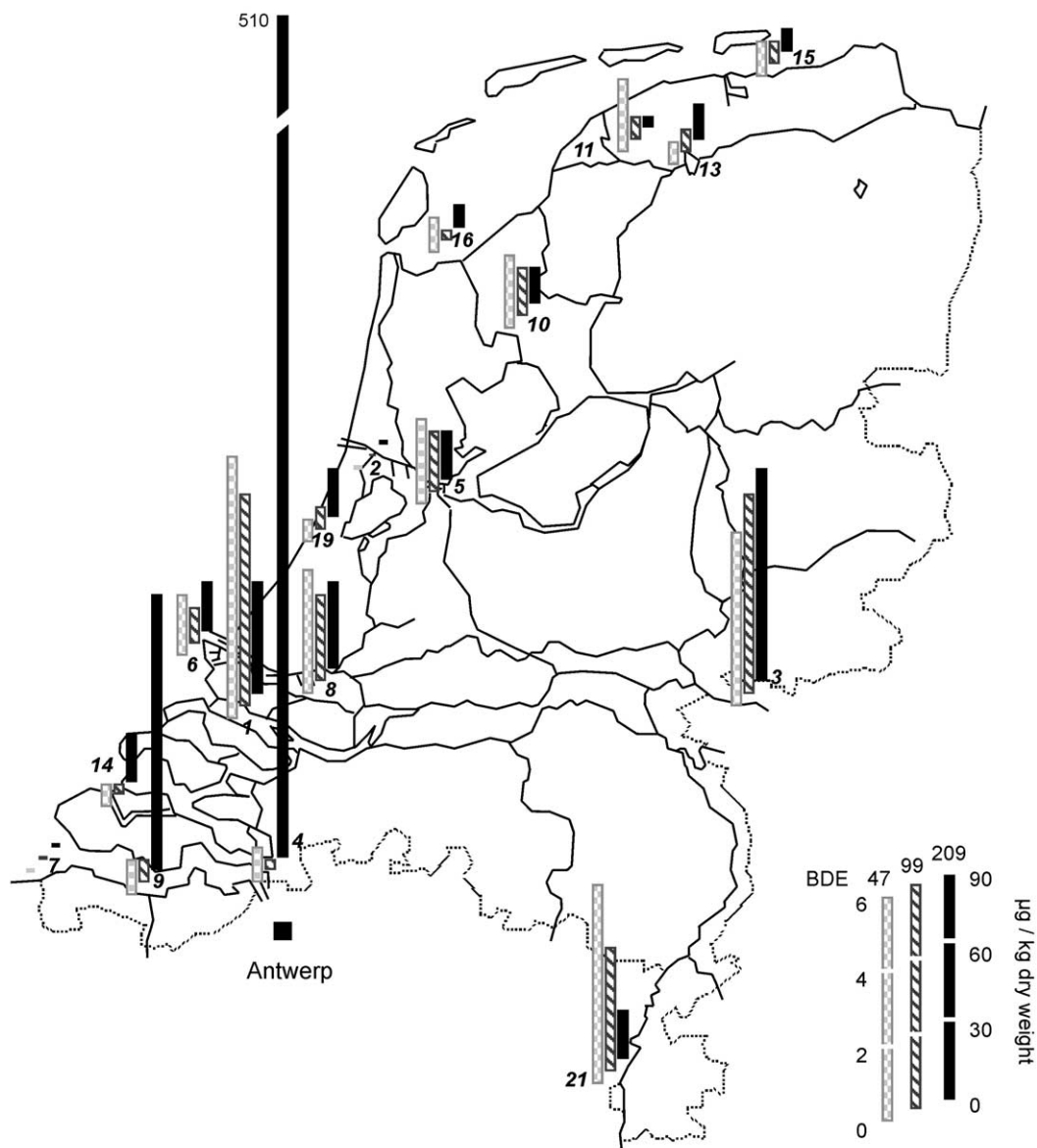


Fig. 4. Concentrations of BDEs 47, 99 and 209 in sediment in  $\mu\text{g}/\text{kg}/\text{dw}$  (locations see Fig. 1).

waste water in the STP was not taken into account, but more than one sample per day was taken to prepare a composed sample. In an Amsterdam STP  $310 \mu\text{g}/\text{kg dw}$  decaBDE was found in the effluent, whereas  $110 \mu\text{g}/\text{kg dw}$  was found in the influent. It should be taken into account that regularly, ca. each month, the SPM in the influent to which PBDEs are bound, is removed from the STP as the primary sludge, together with the secondary sludge, which is produced during the treatment of the waste water. The fraction of SPM passing the STP is not more than ca. 2.5%. Three sludge samples [Ameland (2x) and St. Annaparochie] showed substantial decaBDE concentrations (up to  $190 \mu\text{g}/\text{kg dry weight}$ ), as well as substantial concentrations of other BDEs (up to  $40 \mu\text{g}/\text{kg dry weight}$  for BDE47) (Table 8b,c). Most of the sewage sludge in the Netherlands is burned in specific sludge

incinerators. In other countries, sewage sludge may be deposited in landfills (Hale et al., 2001). That procedure may cause a delayed input of PBDEs into the environment through contaminated leachate water. Incineration at sufficiently high temperatures under well-controlled conditions will destroy the PBDEs, but less well-controlled incineration may result in the formation of limited quantities of brominated dibenzo-*p*-dioxins and furans and bromochlorodibenzo-*p*-dioxins and furans (Vehlow et al., 2000; Sakai et al., 2001).

Up to  $200 \mu\text{g}/\text{kg dw}$  decaBDE was found in particles filtrated from industrial waste waters. The concentrations of the other PBDEs in STP in- and effluents and industrial waste water residues were in most cases considerably lower than the decaBDE concentrations (Table 2). No other data on PBDEs in STP in- and



Table 4  
PBDEs in fillets of bream

Location	No.	% DW	BDE47	BDE85	BDE99	BDE138	BDE153	decaBDE
<i>(a) Period 1 (<math>\mu\text{g} / \text{kg dry weight}</math>)</i>								
Amsterdam	5	22.7	4.4	0.2	<0.05	<0.02	<0.4	<0.06
Eijsden (Meuse)	12	22.2	9.1	0.2	<0.02	<0.02	<0.4	<0.4
Haringvliet	1	20.1	16	0.2	<0.06	<0.02	<0.7	0.3
Lobith (Rhine)	3	23.7	37	0.2	<0.1	<0.02	1.3	<0.03
Vrouweuzand (IJssel Lake)	10	25.0	13	0.2	<0.03	<0.02	1.0	<0.8
Bergumermeer, Bergum	13	19.7	0.2	0.013	<0.01	<0.02	<0.04	<0.4
Koudevaart, St Annaparochie	11	20.1	0.6	0.02	<0.01	<0.06	0.04	
<i>(b) Period 3 (<math>\mu\text{g} / \text{kg dry weight}</math>)</i>								
Amsterdam	5	24.4	19	<0.08	0.2	<0.2	0.9	<5.5
Eijsden (Meuse)	12	22.8	110	<0.08	<0.1	<0.2	2.9	<5.8
Haringvliet	1	19.4	80	0.07	<0.5	<0.2	<3.2	<5.9
Lobith (Rhine)	3	16.3	90	<0.06	<0.2	<0.2	<2.5	<5.1
Bergumermeer, Bergum	13	19.7	1.9	<0.07	<0.04	<0.2	0.1	<0.8
Vrouweuzand (IJssel lake)	10	20.3	22	<0.1	<0.8	<0.3	<1.6	<8.9
Apeldoorns Canal (Epe)	22	20.5	15	<0.03	<0.09	<0.07	0.4	<21
Dommel, near STP Eindhoven	18	23.5	130	<0.09	<0.6	<0.2	4.1	<6.3

Table 5  
PBDEs in fillets of flounder

Location	No.	% DW	BDE47	BDE85	BDE99	BDE138	BDE153	decaBDE
<i>(a) Period 1 (<math>\mu\text{g} / \text{kg dry weight}</math>)</i>								
Amsterdam (North Sea Canal)	5	19.0	1.0	0.02	<0.2	<0.02	<0.04	<0.4
Schaar v Ouden Doel (Western Scheldt)	4	19.0	0.9	0.04	<0.03	<0.03	<0.06	<0.4
Vrouweuzand (IJssel Lake)	10	18.0	1.0	0.01	<0.1	<0.02	<0.06	<0.4
Noordwijk (North Sea)	19	18.7	0.9	0.04	<0.04	<0.02	<0.05	<0.3
Oestergronden (North Sea)	20	18.7	0.4	0.02	<0.02	<0.02	<0.02	<0.4
Den Oever (Wadden Sea)	16	15.8	2.1	0.03	<0.01	<0.02	0.1	<0.2
Maassluis (Nieuwe Waterweg)	8	15.3	4.3	0.06	<0.08	<0.02	0.1	<0.4
Vlissingen (Western Scheldt)	7	19.5	0.7	0.01	<0.01	<0.02	<0.02	<0.4
<i>(b) Period 3 (<math>\mu\text{g} / \text{kg dry weight}</math>)</i>								
Dantzigat (Wadden Sea)	15	19.3	<1.5	<0.05	0.8	<0.09	<0.1	<5.9
Hammen (Eastern Scheldt)	14	23.3	0.6	<0.1	0.1	<0.2	<0.2	<0.9
Schaar v Ouden Doel (Western Scheldt)	4	18.3	7.5	0.04	0.7	<0.1	0.9	<3.2
Vlissingen (Western Scheldt)	7	38.1	1.0	<0.03	<0.05	<0.08	<0.09	<0.5
Amsterdam Westpoort	23	21.7	5.8	<0.08	0.3	<0.2	<0.3	<0.9
Noordwijk (North Sea)	19	21.7	1.9	<0.06	0.2	<0.2	<0.1	<1.1
Bocht v Watum (Ems Dollard)	17	20.7	0.9	<0.06	0.1	<0.2	0.1	<1.1
Amsterdam	5	16.2	3.6	<0.06	0.3	<0.2	0.2	<1.1
IJmuiden (North Sea Canal)	2	17.5	3.2	<0.09	0.3	<0.2	<0.2	<1.3
Vrouweuzand (IJssel Lake)	10	18.9	1.4	<0.08	0.2	<0.2	<0.1	<1.1
Den Oever (Wadden Sea)	16	20.8	5.2	<0.02	0.8	<0.07	<0.3	<2.3
Maassluis (Nieuwe Waterweg)	8	16.2	20	<0.1	4.6	<0.01	<1.3	<3.6

Table 6  
PBDEs and PBBs in marine mussels, period 3 ( $\mu\text{g} / \text{kg dry weight}$ )

Location	No.	DW%	BDE47	BDE85	BDE99	BDE138	BDE153	decaBDE
Reference (Eastern Scheldt)	14	19.8	0.9	0.2	0.3	<0.1	<0.08*	<3.8
Splitsingsdam (Rotterdam harbour)	6	17.6	4.3	<0.2*	1.6	<0.1	<0.2*	<4.1
Noordwijk (North Sea)	19	16.8	3.6	0.05	1.2	0.1	<0.2*	<4.3
Bocht v Watum (Ems Dollard)	17	17.9	1.2	<0.2*	0.6	<0.1	<0.07*	<3.7
Vlissingen (Western Scheldt)	7	18.9	1.3	<0.2*	0.5	<0.1	<0.2*	4.9
Dantzigat (Wadden Sea)	15	21.9	1.1	<0.1*	0.4	<0.1	<0.08*	4.9

Table 7  
PBDEs in freshwater mussels, period 3 ( $\mu\text{g} / \text{kg}$  dry weight)

Location	No.	% DW	BDE47	BDE85	BDE99	BDE138	BDE153	decaBDE
Reference (IJssel Lake)		4.0	<1.0	<0.4	<0.6	<1.0	<0.3	<5.9
Haringvliet	1	3.4	5.6	<0.1	5.0	<1.0	1.5	<30
Lobith (Rhine)	3	2.9	5.6	<0.5	4.2	<1.1	<0.9	<34
Vrouweuzand (IJssel Lake)	10	4.0	0.7	<0.3	0.5	<0.8	<0.2	<23
Bergumermeer, Bergum	13	4.8	0.8	<0.2	0.4	<0.5	<0.1	<15
Eijsden (Meuse)	12	4.1	7.0	<0.2	5.8	<1.0	1.0	<12
Koudevaart, St Annaparochie	11	5.5	<0.8	<0.3	<0.5	<0.7	<0.7	<4.3
Dommel, near STP Eindhoven	18	3.6	17	<0.5	11	<0.9	<1.1	<30
Amsterdam	5	3.9	1.8	<0.3	1.4	<0.9	1.2	<31

Table 8  
PBDEs in waste water

Location	% DS	BDE47	BDE85	BDE99	BDE138	BDE153	decaBDE
<i>(a) Period 1 (<math>\mu\text{g} / \text{kg}</math> dry weight)</i>							
STP Amsterdam Westpoort effl	9.1	14	<1.0	18	<1.1	<4	310
STP Eindhoven, effl	15.1	25	<1.3	28	<0.3	<7	920
STP Oostermeende, infl	100	2.2	<0.1	5.4	<0.9	<0.08	1.1
Textile factory Nijverdal infl	100	0.4	<0.03	6.6	<0.2	<1	45
Industry Genemuiden, infl	100	<0.1	<0.04	0.3	<0.03	<0.02	<0.5
STP Amsterdam Westpoort infl	100	3.4	<0.2	3.6	<0.2	<0.9	110
STP Ameland, infl	100	1.7	<0.1	2.1	<0.1	<0.1	15
STP St Annaparochie, infl	100	0.9	<0.1	0.9	<0.03	<0.3	<20
Industry Almere, infl	100	68	<0.9	33	<0.3	2.6	200
STP Eindhoven, infl	100	2.3	<0.1	1.7	<0.08	<0.07	24
<i>(b) Period 2 (<math>\mu\text{g} / \text{kg}</math> dry weight)</i>							
STP Ameland, sludge	6.1	9.5	<0.4	11	<2	<2.2	<180
STP St Annaparochie, sludge	12.1	11	<0.7	14	<0.8	<2.6	190
STP St Annaparochie, infl	100	9.3	<0.3	5.2	<1.0	1.0	24
STP Ameland, infl	100	16	<0.6	10	<0.7	<2.1	140
<i>(c) Period 3 (<math>\mu\text{g} / \text{kg}</math> dry weight)</i>							
STP Ameland, sludge	2.6	40	<0.7	38	4.0	4.8	8.6
STP Ameland, infl	6.8	16	<0.4	15	1.5	<1.6	330
STP St Annaparochie, infl		1.3	<0.04	1.1	<0.05	<0.2	7.6
STP Oostermeende, infl		0.7	<0.02	0.5	<0.04	<0.1	2.7
STP Eindhoven, effl	10.2	35	<1.1	29	<2.1	<5.0	350

effluents could be found in the literature. Further research on the PBDE balance in STPs is recommended.

### 3.5. PBBs

The PBBs 15, 49, 52, 101, 153, 169 and 209 were also analysed but not found in any of the samples. The detection limits for most PBBs were between <1 and <0.1  $\mu\text{g}/\text{kg}$  dry weight (dw), but for BB209 the detection limits were generally between <1 and <10  $\mu\text{g}/\text{kg}$  dw. This result is in agreement with the negligible PBB production in Europe over the past decades.

### 3.6. Comparison with other contaminants

During the LOES project other potential endocrine disrupting contaminants have been analysed at the same

locations. Table 9 gives an indicative overview of concentrations of other contaminants found at the same locations in the various matrices. The results show that nonylphenol and ethoxylates are more important in terms of concentration than the PBDEs, although decaBDE concentrations in the Western Scheldt are of the same order of magnitude. Bisphenol-A and the hormones estradiol and ethinylestradiol are present at a much lower level. Bisphenol-A and nonylphenol and ethoxylates are wider distributed over the various environmental compartments including the water phase, whereas the PBDEs are mainly found in SPM, sediments and biota, or, in the case of decaBDE, almost exclusively in SPM and sediments. PCBs were not analysed during the LOES study. However, there is a wealth of PCB data in The Netherlands. Those data suggest that PCBs in fish and sediment are generally

Table 9

Overview of PBDE, nonylphenol and ethoxylates and bisphenol-A concentrations in water, SPM and bream from The Netherlands found during the LOES project

Compound	Surface water(ng/l)	SPM (µg/kg dw)	Bream (µg/kg dw)
ΣBDE <sup>a</sup>	–	0.9–18	4.6–39
DecaBDE	–	9–4,600	0.03–<21
Nonylphenol + ethoxylates	0.7–3	60–4,400	680–2,000
Bisphenol-A	0.012–0.2	12–42	1.9–6

<sup>a</sup> Sum of BDEs 47, 85, 99, 100, 138, 153.

higher than the PBDE concentrations, again with the exception of decaBDE in the Western Scheldt.

#### 4. Conclusions

SPM was found to be an important carrier for higher brominated diphenylethers in the aquatic environment. High decaBDE concentrations (up to 4600 µg/kg dw) were found in SPM from the Western Scheldt, most likely related to spills during the use of decaBDE in the textile industries along the river Scheldt in Antwerp and further upstream. A similar decaBDE pattern is found in the sediment of the Western Scheldt with maximum values up to 510 µg/kg dw. The presence of decaBDE in SPM and sediments calls for further studies on the stability or possible degradation of this compound. DecaBDE was not found in flounder, bream, freshwater and marine mussels, which means that if it would bioconcentrate in these biota, it would only be at marginal levels.

The BDE47 and 99 concentrations in SPM, sediments and biota from various riverine locations such as in the rivers Rhine and Meuse, indicate a relation with the—possibly former—industrial use of pentaBDE, including a possible use in German mining.

Relatively high PBDE concentrations (up to 920 µg decaBDE/kg dw) were found in STP influents and effluents. The removal of decaBDE and other PBDEs by STPs is apparently only partially effective. A more detailed study is required to establish a mass balance for STPs, taking into account that the major part of organic material from the influent is removed through the sewage sludge.

In further studies, the selection of PBDEs should be extended with the congeners 100, 154, 183 and possibly also 28, whereas the congeners 85 and 138 are of little value.

The levels of PBDEs in the Dutch aquatic environment are, apart from decaBDE, generally lower than other contaminants such as PCBs and nonylphenol and ethoxylates.

PBBs were not found in measurable concentrations. Although the toxicity of PBBs may be different from

that of PBDEs, it is unlikely that PBBs will be very important as a contaminant in the Dutch aquatic environment.

#### Acknowledgements

This project was carried out within the framework of the Dutch National Investigation on Estrogenic Compounds (LOES), initiated and financially supported by the Institute for Integrated Inland Water Management and Wastewater Treatment (RIZA), Lelystad, The Netherlands, the National Institute for Coastal and Marine Management, The Hague, The Netherlands, the Netherlands Institute for Public Health and Environment (RIVM), Bilthoven, and Wetterskip Fryslân, and linked to the Dutch part of the EU-COMPREHEND project. The authors thank dr. A.D. Vethaak (RIKZ) and mr. G.B.J. Rijs (RIZA) for their helpful comments, and Mrs. J. van Hesseligen, dr. M. Kotterman and Ms. N. Liesker of RIVO, Mr. J. Jol of RIKZ and the RIZA staff for their skillful assistance.

This paper is dedicated to our colleague and friend Mr. Balte Verboom. Balte Verboom has contributed to this project and to many other research projects at our institute in an invaluable way. While preparing a sampling cruise for a new project, he died suddenly in the laboratory on 10 September 2000 at the age of 59. His skilled assistance and great friendship are painfully missed.

#### References

- Allchin, C.R., Law, R.J., Morris, S., 1999. Polybrominated diphenylethers in sediments and biota downstream of potential sources in the UK. *Environmental Pollution* 105, 197–207.
- Andersson, Ö., Blomkvist, G., 1981. Polybrominated aromatic pollutants found in fish in Sweden. *Chemosphere* 10, 1051–1060.
- Anon, 1997. Report on the One-off Survey DIFFCHEM. Oslo and Paris Commissions. Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME), London, UK.
- Anon, 2000. An Introduction to Brominated Flame Retardants. Bromine Science and Environmental Forum, Brussels, Belgium.
- Bligh, E.G., Dyer, W.J., 1959. A rapid method of total lipid extraction and purification. *Can. J. Biochem. Physiol.* 37, 911–917.
- Booij, K., Zegers, B.N., Boon, J.P., 1989. Levels of some polybrominated diphenylether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (*Mytilus edulis*). *Chemosphere* 46, 683–688.
- Brinkman, U.A.Th., de Kok, A., In: Kimborough, R.D. (Ed.), Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Elsevier, Amsterdam, Oxford, New York, p. 1.
- de Boer, J., 1989. Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (*Gadus morhua*) from the North Sea, 1977–1987. *Chemosphere* 18, 2131–2140.
- de Boer, J., Wester, P.G., Klamer, H.J.C., Lewis, W.E., Boon, J.P., 1998. Do flame retardants threaten ocean life? *Nature* 394, 28–29.
- de Boer, J., de Boer, K., Boon, J.P., 2000. Polybrominated biphenyls

- and diphenylethers. In: Paasivirta J. (Ed.), The Handbook of Environmental Chemistry, vol. 3, part K, pp. 61–95.
- de Boer, J., Allchin, C.R., Law, R., Zegers, B.N., Boon, J.P., 2001. Method for the analysis of polybrominated diphenylethers in sediments and biota. *Trends Anal. Chem* 591–599.
- Dungey, S., 2001. Environmental risk assessment of octa- and decabromodiphenylether. *Proceed. Second International Workshop on Brominated Flame Retardants BFR2001*, Stockholm, Sweden, pp. 37–39.
- Hale, R.C., La Guardia, M.J., Harvey, E.P., Gaylor, M.O., Matteson Mainor, T., Duff, W.H., 2001. Persistent pollutants in land-applied sludges. *Nature* 412, 140–141.
- Lindström, G., Wingfors, H., Dam, M., van Bavel, B., 1999. Identification of 19 PBDEs in long-finned pilot whale (*Globicephala melas*) from the Atlantic. *Arch. Environ. Contam. Toxicol.* 36, 355–363.
- Jansson, B., Andersson, R., Asplund, L., Litzen, K., Sellström, U., Uvemo, U.-B., Wahlberg, C., Wideqvist, U., Odsjö, T., Olsson, M., 1993. Chlorinated and brominated persistent organic compounds in biological samples from the environment. *Environ. Toxicol. Chem.* 12, 1163–1174.
- Kierkegaard, A., Balk, L., Tjärnlund, U., de Wit, C., Jansson, B., 1999. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). *Environ. Sci. Technol.* 33, 1612–1617.
- Klamer, H.J.C., Villerius, L.A., Leonards, P.E.G., Bakker, J.F., 2001. Brominated flame retardants in Dutch North sea surface sediments. *Proceed. Second International Workshop on Brominated Flame Retardants BFR2001*, Stockholm, Sweden, pp. 329–331.
- Meironyté Guvenius, D., Norén, K., 2001. Polybrominated diphenyl ethers in Swedish human milk. The follow-up study. *Proceed. Second International Workshop on Brominated Flame Retardants BFR2001*, Stockholm, Sweden, pp. 303–305.
- Norén, K., Meironyté, D., 1998. Contaminants in Swedish human milk. Decreasing levels of organochlorine and increasing levels of organobromine compounds. *Organohalogen Compounds* 38, 1–4.
- Norén, K., Meironyté, D., 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20–30 years. *Chemosphere* 40, 1111–1123.
- Nylund, K., Kierkegaard, A., Eriksson, U., Asplund, L., Bignert, A., Olsson, M., 2001. Spatial distribution of some polybrominated diphenylethers and hexabromocyclododecane in herring (*Clupea harengus*) along the Swedish coast. *Proceed. Second International Workshop on Brominated Flame Retardants BFR2001*, Stockholm, Sweden, pp. 349–352.
- Platz, J., Christensen, J.H., 2001. Screening of brominated flame retardants in Danish marine and freshwater sediments. *Proceed. Second International Workshop on Brominated Flame Retardants BFR2001*, Stockholm, Sweden, pp. 353–356.
- Pijnenburg, A.M.C.M., Everts, J.W., de Boer, J., Boon, J.P., 1995. Polybrominated biphenyl and diphenylether flame retardants: analysis, toxicity, and environmental occurrence. *Rev. Environ. Contam. Toxicol.* 141, 1–26.
- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenylether (PBDE) flame retardants. *Sci. Total Environ.* 275, 1–17.
- Sakai, S., Watanabe, J., Honda, Y., Takasaki, H., Aoki, I., Futamatsu, M., Shiozaki, K., 2001. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* 42, 519–531.
- Sellström, U., Jansson, B., Jonsson, P., Nylund, K., Odsjö, T., Olsson, M., 1990. Anthropogenic brominated aromatics in the Swedish environment. *Organohalogen Compounds* 2, 357–360.
- Sellström, U., Jansson, B., Kierkegaard, A., de Wit, C., Odsjö, Olsson, M., 1993. Polybrominated diphenylethers in biological samples from the Swedish environment. *Chemosphere* 26, 1703–1718.
- Spiegelstein, M., 2000. Personal Communication, BSEF, Brussels, Belgium.
- Vehlow, J., Bergfeldt, B., Jay, K., Seifert, H., Wanke, T., Mark, F.E., 2000. Thermal treatment of electrical and electronic waste plastics. *Water Manage. Res.* 18, 131–140.
- Vethaak, A.D., Rijs, G., Schrap, M., Ruiter, H., 2002. LOES report 2002.001, ISBN 9036954010. RIZA, Lelystad, RIKZ, The Hague, The Netherlands.
- de Wit, C., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583–624.
- World Health Organisation, 1994. Polybrominated biphenyls, IPCS, (Environmental Health Criteria no. 152). IPCS, Geneva, Switzerland.