Polybrominated Diphenyl Ethers in Sewage Sludge and Effluents of Sewage Plants from a Central Region of Germany

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Introduction

Polybrominated Diphenyl Ethers (PBDEs) belong to the group of bromine-containing flame retardants. They are added to materials such as plastics, resins and textiles in percent concentrations to make them flameproof. While in former times also Penta and OctaBDE formulations were used, today mainly the technical DecaBDE is applied throughout Europe[1, 2].

Meanwhile PBDEs have been found in partly increasing concentrations in a number of aquatic environmental compartments such as river and marine sediments, river water, fishes and mussels[2, 3, 4]. Here, mostly the same PBDE components which are present in the technical mixtures are found in the environment. PBDE emissions can punctually take place during the manufacture or processing of the flame retardants and during the disposal and recycling of flame-retarded materials. This, as a rule, should lead to local contamination but cannot explain the meanwhile wide spread of these flame retardants in the aquatic environment. Therefore, we have to have a closer look at possible further sources.

Examinations of municipal sewage sludges in various European countries have shown that PBDEs can be present in up to the higher ppb concentration level [4, 5, 6]. Here as well, mainly the same Tri to DecaBDE components were found as in technical products. The PBDEs reach the sewage plants via the municipal waste water. Their sources, however, are not clarified. During sewage sludge treatment the PBDEs should remain bound to the sewage sludge due to their physico-chemical properties with increasing tendency from the lower to the higher brominated diphenyl ethers. The sewage sludge should be a PBDE sink in case it is disposed of in a way that destroys (e.g. by combustion) or immobilises (e.g. by waste disposal) the PBDEs. If the sewage sludge is spread on the field as fertiliser in order to improve the soil, the PBDEs will remain available for the environment. Besides, PBDEs can also be released into the aquatic environment via suspended particulate matter from sewage plant effluents. This should be verified in the present examination.

Thus, the sewage sludges and suspended matter from the effluents of 8 municipal sewage treatment plants from a central region of Germany were examined for their PBDE content. The analyses included the quantitation of Tri to DecaBDE under congener-specific determination of components which are typically present in technical PBDE products. This paper reports on the applied method

of analysis and presents the PBDE data for the sewage sludges and the respective sewage plant effluents.

Methods and Materials

All sewage sludge (SS) and suspended particulate matter samples (SPM) from the sewage plant effluents were collected by the Hessian Agency for the Environment and Geology (HLUG) and analysed by the eurofins | GfA. Sewage sludge was taken as random sample from the treatment plants. The suspended particulate matter was collected from the effluents of the plants by means of a centrifuge (Padberg Z61 type) as close as possible to the outlet of the sewage treatment plant.

The sewage sludge was kept cool for short termed storage and transport to the GfA. Suspended particulate matter samples were deeply frozen directly after sampling and transferred to the lab without interruption of the cooling chain. In the GfA lab the samples were defrosted (SPM), homogenized and divided into representative sub portions. For PBDE analysis such portions were freeze-dried and ground by means of a ball mill.

Approximately 5 g each of the dry sample material were Soxhlet extracted with toluene for 12 hours. For PBDE analysis, $^{13}C_{12}$-labelled Tetra, Hexa, Hepta and DecaBDE standards were added to aliquots of the raw extracts as internal standards. After sulphuric acid treatment, liquid/solid chromatography was applied for further clean-up.

The instrumental analysis was performed by means of capillary gas chromatography (HP 6890 gas chromatograph) coupled with a low resolution mass spectrometer (HP MSD 5973). The mass spectrometer was operated in the so-called EI-Mode (Electron Impact Mode) monitoring PBDEmolecular or fragment ions and the different standards. Details of the analytical method can be seen from Table 1. The procedure followed the principle steps which have been applied by GfA for many years for the determination of PBDEs in various matrices [7]. Since neither native nor $^{13}C_{12}$-labelled standards were available for the Octa and NonaBDEs, calibration mixtures were prepared on the basis of technical PBDE products for these components. The PBDEs of these mixtures were identified by means of GC/MS and quantified by GC/FID. For this reason the results for the Octa and NonaBDEs have to be considered rather as semi-quantitative than quantitative. All other PBDEs were determined quantitatively via the internal $^{13}C_{12}$-labelled PBDE standards.

Table 1: Details of the analytical method for the PBDE analysis of sewage sludge and suspended particulate matter from sewage plant effluents.

Extraction	Soxhlet extraction by means of Toluene for 12 h
Internal BDE Standards	$^{13}C_{12}$-labelled 3,3',4,4'-TetraBDE (BDE 77) $^{13}C_{12}$-labelled 2,2',4,4',5,5'-HexaBDE (BDE-153) $^{13}C_{12}$-labelled 2,2',3,4,4',5',6-HeptaBDE (BDE 183) $^{13}C_{12}$-labelled DecaBDE (BDE 209) (from CIL, Andover, MA, USA via Promochem, Wesel, Germany), added to the raw extract prior to the clean-up
Clean-up of the raw extract	- Liquid/liquid treatment of the extract with H_2SO_4 - Liquid/solid chromatography using basic alumina
GC/MS instrumentation	Capillary gaschromatograph (HRGC) Hewlett Packard/Agilent 6890 coupled with a low resolution mass spectrometer (LRMS) Hewlett Packard/Agilent MSD 5973
Injection	PTV , temperature programmed splitless injection
GC-column	HP-5 capillary column (Hewlett Packard 19091 J-413), 15 m x 0.32 mm inner diameter, film thickness: 0.25 µm
Temperature program	4 min 90 isotherm, at 120 °C/min up to 170 °C, 2 min isotherm, at 7 °C/min up to 320 °C, 8 min isotherm
Ionization	70 eV(EI)
Detection mode	SIM (Selected Ion Monitoring), monitoring of molecular ions and fragment ion masses
Identification	- via relative retention time and elution within the corresponding time window - via masses of molecular or fragment ions - via isotope ratio
Calibration	By means of calibration mixtures containing the four $^{13}C_{12}$-labelled PBDE standards at a constant level and the native BDE standards at different concentrations
Quantification	Via the internal $^{13}C_{12}$-PBDE standards Native Tri- and Tetra BDE via ^{13}C-labelled BDE-77 Native Penta- and HexaBDE via ^{13}C-labelled BDE-153 Native Hepta- to NonaBDE via ^{13}C-labelled BDE-183 Native DecaBDE via ^{13}C-labelled BDE-209
Limits of Quantification (LOQs)	Mean limits of quantification for individual congeners TriBDEs: 0.4 µg/kg HeptaBEDEs : 1 µg/kg TetraBDEs: 0.6 µg/kg OctaBDEs : 4 µg/kg PentaBDEs: 0.8 µg/kg NonaBDEs : 6 µg/kg HexaBDEs: 0.8 µg/kg DecaBDE : 13 µg/kg LOQs refer to the dry matter of the sample material

Results and Discussion

The PBDE data of the sewage sludge samples (SS) from the 8 treatment plants M1 to M8 and of the suspended particulate matter (SPM) from their effluents are presented in Table 2. All data refer to the dry matter of the sample material. PBDEs were detected in all sewage sludge and suspended particulate matter samples. The total Tri to DecaBDE concentrations ranged from 231 µg/kg to 982 µg/kg in case of the sewage sludge (mean of 544 µg/kg) and from 71 µg/kg to 353 µg/kg (mean of 209 µg/kg) for the suspended particulate matter. The concentration ranges and the mean values indicate that the suspended particulate matter of the sewage plant effluents show somewhat lower PBDE concentrations than the sewage sludge samples. When directly comparing the sludge and suspended particulate matter data of the individual sewage treatment plants it can be seen that the differences with respect to the Tri to DecaBDE totals range from a factor of 1.2 to 6.4. However, these differences are strongly influenced by the DecaBDE concentrations.

The homologue patterns of the PBDEs in the sewage sludge samples and in the suspended particulate matter of the effluents are compared in Figure 1. DecaBDE is the main PBDE component in nearly all samples showing proportions of 43 % to 79 % of the Tri- to DecaBDE totals in case of the sludge samples and of 33 % to 58 % for the suspended particulate matter of the effluents. In most samples PentaBDE (mainly BDE-99) and TetraBDE (mainly BDE-47) follow the DecaBDE concentrations. Only in three of the sewage sludge samples NonaBDE show a somewhat higher level than Penta- and TetraBDE. The direct comparison of the PBDE pattern of the sewage sludge and the particulate effluents of the same treatment plant reveals a tendency to different ratios for the lower and higher brominated diphenyl ethers. While for the Tetra and PentaBDEs in the sewage sludge with the exception of M6, the concentrations are often similar or up to a factor of 2.5 higher than in the particulate effluents, Nona and DecaBDEs show mostly larger differences with 2 to 12 times higher concentrations in the sewage sludge. This may reflect that the higher brominated PBDEs have a lower solubility in water and therefore may be stronger bound and retained by the sewage sludge than the lower brominated homologues. The PBDE pattern of the effluents on the other hand may more likely reflect the pattern of the remaining aqueous phase.

The PBDE congeners with the highest concentrations in both, sewage sludge and suspended particulate matter, correspond to the main constituents of the technical PentaBDE and DecaBDE products (BDE-99 and BDE-47 in case of technical PentaBDE and Nona and DecaBDE in case of the technical DecaBDE). BDE-183 and BDE-153, which are the main constituents of technical OctaBDE mixtures were also detected in most samples, however, at a lower concentration level.

The PBDE concentrations and patterns found in the sewage sludge samples from the 8 Hessian municipal sewage treatment plants are similar to those reported for other German regions or for other European countries [3, 4, 5, 6, 8]. Details of the study with more information about the sewage treatment plants will be presented separately [9].

The PBDEs coming into the sewage treatment plants via the urban waste water are mostly bound to the particles and are therefore mainly removed by the sewage sludge. The present study shows, that the effluents of the sewage treatment plants still contain some particle-bound PBDEs which are released into the aquatic environment. The amount of particulate suspended matter of the effluents, however, have to be taken into account in order to assess whether such emissions are of relevance compared to other emissions.

Table 2: PBDE concentrations in municipal sewage sludge (SS) and in the suspended particulate matter (SPM) from the effluents of the sewage plants

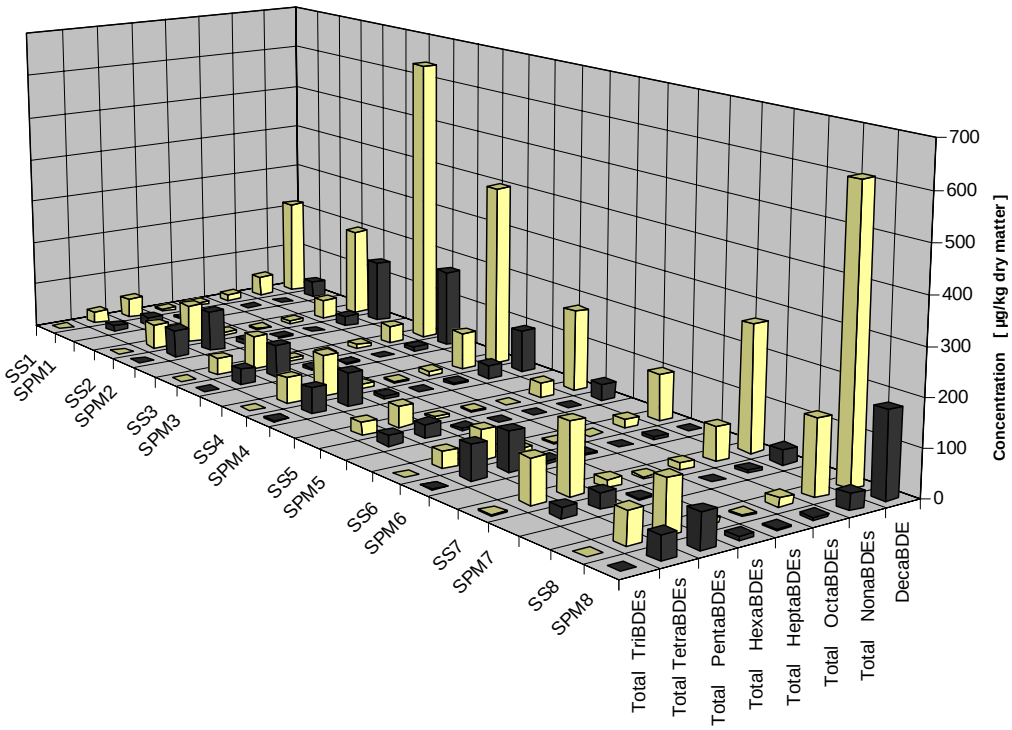
	Concentration [µg/kg $_{dry\ matter}$]															
Municipal sewage plant	**M1**		**M2**		**M3**		**M4**		**M5**		**M6**		**M7**		**M8**	
Sample matrix	SS1	SPM1	SS2	SPM2	SS3	SPM3	SS4	SPM4	SS5	SPM5	SS6	SPM6	SS7	SPM7	SS8	SPM8
2,4,4'-TriBDE (BDE-28)	0.5	< 0.6	0.8	1.0	0.5	0.5	1.1	0.9	< 0.5	< 0.4	0.6	1.4	1.3	< 0.4	0.9	0.9
3,4,4'-TriBDE (BDE-37)	< 0.4	< 0,6	< 0,3	< 0,5	< 0,3	< 0,5	< 0,3	< 0,4	< 0,5	< 0,4	< 0,4	< 0,3	< 0,3	< 0,4	< 0,2	< 0,3
Total TriBDEs	0.5	ND	0.8	1.0	0.5	0,5	1.1	0.9	ND	ND	0.6	1.4	1.3	ND	0.9	0.9
2,4,4',6-TetraBDE (BDE-75)	< 0.6	< 1.0	< 0.5	< 0.8	< 0.4	< 0.9	< 0.5	< 0.6	< 0.9	< 0.6	< 0.6	< 0.5	< 0.5	< 0.6	< 0.4	< 0.5
2,3',4',6-TetraBDE (BDE-71)	0.7	< 1,0	1.6	1.7	1.3	1.6	2.7	1.8	1.0	1.3	1.4	3.4	5.1	1.0	4.6	1.5
2,2',4,4'-TetraBDE (BDE-47)	25.2	12.6	51.7	58.6	35.2	32.4	55.0	53.6	26.7	20.7	35.4	68.9	88.0	22.2	62.7	46.5
2,3',4,4'-TetraBDE (BDE-66)	< 0.6	< 1.0	1.2	1.5	0.8	< 0.9	< 0.5	1.5	< 0.9	< 0.6	< 0.6	1.9	2.1	< 0.6	1.6	1.1
3,3',4,4'-TetraBDE (BDE-77)	< 0.6	< 1.0	< 0.5	< 0.8	< 0.4	< 0.9	< 0.5	< 0.6	< 0.9	< 0.6	< 0.6	< 0.5	< 0.5	< 0.6	< 0.4	< 0.5
Total TetraBDEs	25.9	12.6	54.5	61.8	37.4	34.0	57.7	56.8	27.7	22.0	36.8	74.2	95.2	23.2	68.9	49.1
2,2',4,4',6-PentaBDE (BDE-100)	5.9	2.4	11.0	11.4	7.0	6.3	12.1	9.6	6.1	3.9	8.5	10.9	19.0	4.2	14.4	8.9
2,3',4,4',6-PentaBDE (BDE-119)	< 0.7	< 1.2	< 0.6	< 0.9	< 0.7	< 2.0	< 0.6	< 0.8	< 1.0	< 0.8	< 0.7	< 0.6	< 0.6	< 0.8	< 0.5	< 0.6
2,2',4,4',5-PentaBDE (BDE-99)	37	16	72.2	76.5	59.3	64.6	76.9	62.8	39.0	25.3	54.2	70.9	126.6	27.8	94.2	61.3
2,2',3,4,4'-PentaBDE (BDE-85)	1.2	< 1.2	2.6	2.8	1.9	1.0	2.9	2.0	1.4	< 0.8	1.9	1.8	4.7	0.9	3.2	2.1
Total PentaBDEs	44.1	18.4	85.8	90.7	72.7	71.9	91.9	74.4	46.5	29.2	64.8	83.6	150.3	32.9	111.8	72.3
2,2',4,4',5,6'-HexaBDE (BDE-154)	1.9	< 1.2	3.5	3.6	2.6	2.3	3.8	2.9	2.3	1.4	2.7	2.3	6.8	1.5	4.9	2.9
2,2',4,4',5,5'-HexaBDE (BDE-153)	3.2	1.4	5.4	5.2	4.2	3.0	6.2	3.8	3.2	1.9	3.8	3.7	9.7	2.2	6.8	4.5
Total HexaBDEs	5.1	1.4	8.9	8.8	6.8	5.3	10.0	6.7	5.5	3.3	6.5	6.0	16.5	3.7	11.7	7.4
2,2',3',4,4',5,6'-HeptaBDE (BDE-183)	5.9	< 1.6	2.5	2.5	4.3	2.4	3.4	2.2	3.2	1.2	2.7	1.6	4.7	< 1.0	3.1	2.3
2,3,3',4,4',5,6-HeptaBDE (BDE-190)	< 1.0	< 1.6	< 0.7	< 1.2	< 0.7	< 1.4	< 0.8	< 1.0	< 1.4	< 1.0	< 1.0	< 0.9	< 0.8	< 1.0	< 0.7	< 0.8
Total HeptaBDEs	5.9	ND	2.5	2.5	4.3	2.4	3.4	2.2	3.2	1.2	2.7	1.6	4.7	ND	3.1	2.3
Total OctaBDEs [a]	13.6	< 6.0	6.5	< 4.5	9.3	< 5.4	10.4	5.2	< 5.2	< 3.8	< 3.6	< 3.2	14.2	< 3.8	18.8	6.4
Total NonaBDEs [a]	44.9	< 8.0	43.5	22.7	39.0	9.3	81.8	30.1	32.5	< 5.1	20.0	4.3	72.8	6.1	158.2	33.7
DecaBDE (BDE-209)	217	38	198	140	639	172	400	93	177	35	100	< 11	268	32	609	181
Total Tri to DecaBDE [b]	357	71	400	327	809	296	656	269	292	91	231	167	623	98	982	353

a Totals of Octa and NonaBDEs have to be considered as semi-quantitative due to the lack of individual native and $^{13}C_{12}$-labelled standards

b Not detected congeners are not included in calculation of the total

ND No congener detected

Figure 1: PBDE concentration profiles in municipal sewage sludge (SS) and in suspended particulate matter (SPM) from the effluents of the sewage treatment plants



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