OCCURRENCE AND FATE OF PBDE IN SEWAGE SLUDGE FROM MUNICIPAL WASTE WATER TREATMENT PLANTS

Wilhelm Knoth[1], Winfried Mann[1], Rita Meyer[1], Judith Nebhuth[1]

[1]Federal Environmental Agency, POP Laboratory, Langen

Introduction

With the rapidly growing use of combustible polymer material, e.g. for IT/TV casings, mattresses, upholstered furniture, the use of flame retardants like polybrominated diphenyl ether (PBDE) has also increased strongly. PBDE are available as three commercial mixtures of BDE congeners named after their principal component: PeBDE , OcBDE and DeBDE. They can release into the environment during their production, use or after disposal and have become ubiquitous.

Because of (exponentially) increasing levels of the main congeners of technical Pe- and OcBDE in human blood and milk in Europe and California, the use and the placing on the market of preparations and articles containing these two flame retardants in concentrations > 0.1% by mass are prohibited from August 15, 2004 in the European Union[4] and in California from the year 2008[1]. The main North American manufacturer of PeBDE flame retardant will voluntarily cease production by the end of 2004[21].

For DeBDE a risk assessment is in progress. Surprising high levels were analysed in blood samples from 155 volunteers in the UK[2] and a debromination to more bioavailable Hx- and HpBDE by juvenile carp (cyprinus carpio) following dietary exposure was observed[20].

The objective of this study is to get more information about the actual levels and time trend of PBDE in sewage sludge in Germany and on a possible degradation of DeBDE by photolytic or reductive debromination during waste water treatment process.

Methods and Materials

Sample Collection. 39 sewage sludge samples from different stages of the waste water treatment process (primary sludge, secondary excess sludge, dewatered digested sludge) were collected from 11 municipal waste water treatment plants of the Rhine-Main area in Germany from March 2002 to June 2003.

Chemical Analysis. The complete sewage sludge sample was sterilized in an autoclave for 20 minutes at 121°C, an aliquot freeze-dried, 2 g spiked with six $^{13}C_{12}$-BDE standards (20 ng BDE 28, 47, 99, 153, 183 and 200 ng BDE 209), one of each degree of bromination and extracted by Soxhlet extraction (Knöfler-Böhm hot extractor) with toluene. The extract was cleaned by a four column

clean-up (SiO_2-$AgNO_3$, H_2SO_4, NaOH, Macro Al_2O_3, Bio-Beads S-X3, Mini Al_2O_3), spiked with the injection standard (20 ng $^{13}C_{12}$-3,3',4,4'-TeBDE (BDE 77)) and reduced to 100 µl. 1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC-EI-LRMS (GC 8000Top-MS Voyager, ThermoQuest) using a DB-5MS (15 m x 0.25 mm, 0.1 µm). The two most intensive mass of the bromine cluster (Tr- and TeBDE: M^+. Te- to DeBDE: M^+-2Br) were measured for each homologue group. The identification of PBDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the $^{13}C_{12}$-labelled internal standards. All congeners except BDE 100 and BDE 154 were quantified based on their corresponding $^{13}C_{12}$-labeled analogues used as internal standards. BDE 100 was quantified using the $^{13}C_{12}$-BDE 99 and BDE 154 using the $^{13}C_{12}$-BDE 153 internal standard[11, 12]. The laboratory took successfully part in the BSEF/QUASIMEME interlaboratory study on brominated flame retardants December 2001 to March 2002. Method blanks were analysed.

Results and Discussion

The total concentration of BDE 28, 47, 99, 100, 153, 154 and 183, the dominating congeners of technical Pe- and OcBDE, ranges from 12.5 to 288 (median 108). With the increasing use of flame retardant polymer material the median level is 13 times higher as reported for Germany in 1992 (total Tri- to HpBDE 0.5 to 17.7 (median 8.4, n=13), not designated which congeners[5]). The concentrations for the Pe- and OcBDE-like congeners are in the same range as analysed in sewage sludge from other European countries like Austria[15], Germany[14], Sweden[16-18], Switzerland[13] and the Netherlands[3] but do not reach the US concentrations[6-9] where a maximum of 2290 (total BDE 47, 99, 100, 153, 154[7]) was detected which is 8 times higher as in Germany (maximum 288).

Levels of BDE 209 varied more between WWTPs, ranging from 97.1 to 2217 (median 256) and reach in two WWTPs (G and K, Table 1) ¼ to ½ of the US maximum 4890[7]. All concentrations in ng/g d.m..

Laboratory studies showed that BDE 209 can undergo photolyse by exposure to daylight[10]. There are however no indications in this study that the bromination pattern of PBDE changes significantly during waste water treatment process (Figure 1 and 2). The ratio of BDE 99 : BDE 100 (86 : 14, Table 1) is nearly the same as reported for technical PeBDE (Bromkal 70-5DE) 84 : 16[19] .

Acknowledgements

We appreciate the good collaboration with the operators of the WWTPs.

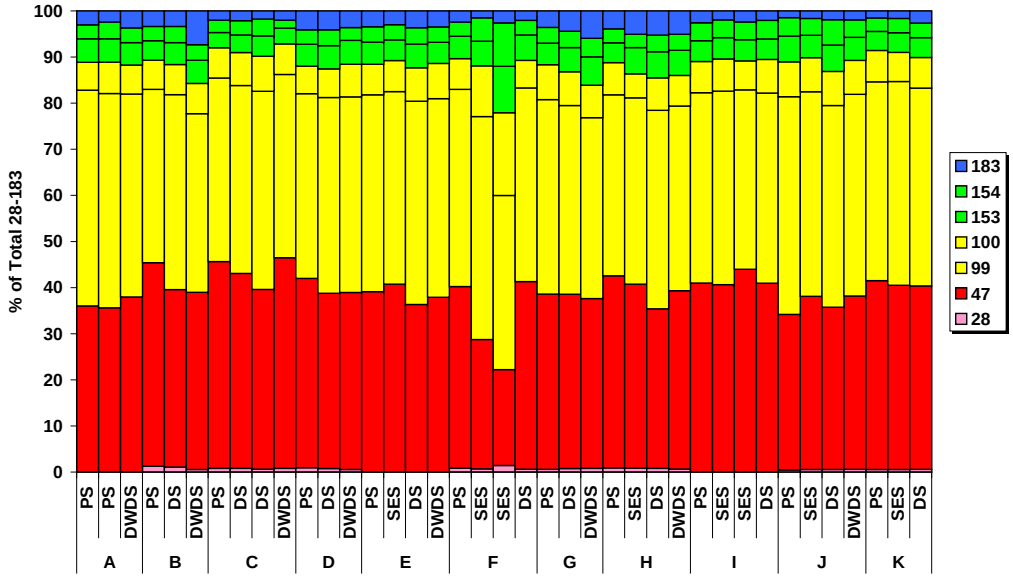

Figure 1: BDE 28-183 profiles in sewage sludge from different stages of the waste water treatment process: Primary sludge (PS), secondary excess sludge (SES), (dewatered) digested sludge (DW)DS of 11 municipal waste water treatment plants (A - K).

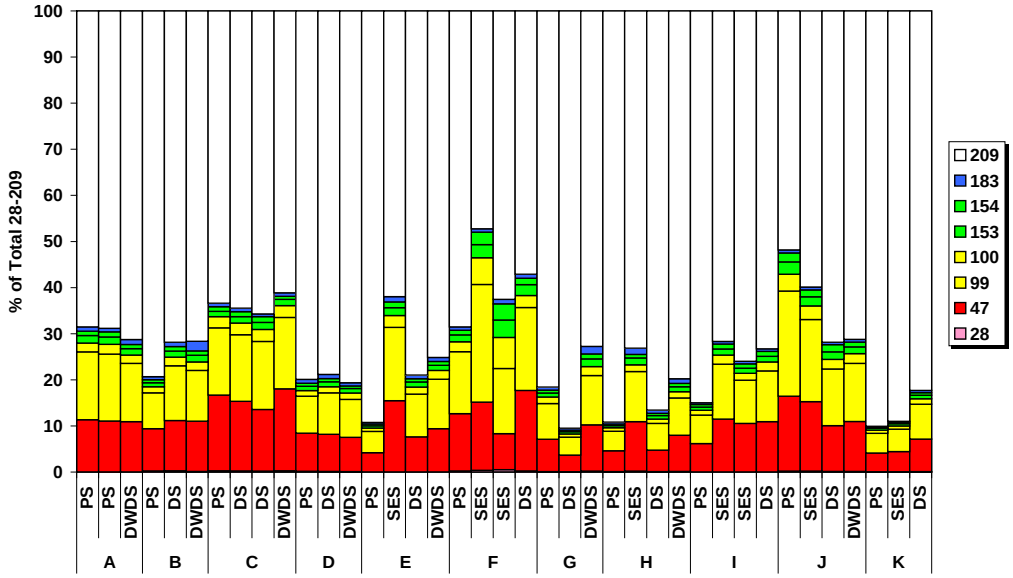

Figure 2: BDE 28-209 profiles in sewage sludge from different stages of the waste water treatment process: Primary sludge (PS), secondary excess sludge (SES), (dewatered) digested sludge (DW)DS of 11 municipal waste water treatment plants (A - K).

Table 1: PBDE in sewage sludge from different stages of the waste water treatment process: Primary sludge (PS), secondary excess sludge (SES), (dewatered) digested sludge (DW)DS of 11 municipal waste water treatment plants (A - K).

WWTP	Sewage	BDE [ng/g d.m.]										BDE
	Sludge	28	47	99	100	153	154	183	Total 28-183	209	Total 28-209	99 : 100
A	PS	n.a.	34.6	44.9	5.8	4.9	2.9	2.9	96.0	209	305	89 : 11
	PS	n.a.	29.4	38.3	5.6	4.2	3.0	2.0	82.4	182	264	87 : 13
	DWDS	n.a.	20.3	23.6	3.4	2.6	1.7	2.0	53.6	133	186	88 : 12
B	PS	0.6	22.1	18.8	3.2	2.1	1.5	1.7	50.1	192	242	86 : 14
	DS	0.8	29.2	32.1	4.9	3.6	2.6	2.6	75.9	193	269	87 : 13
	DWDS	0.6	37.6	37.9	6.4	5.0	3.3	7.1	97.8	247	345	86 : 14
C	PS	0.8	43.7	38.7	6.4	3.2	2.6	1.9	97.3	169	266	86 : 14
	DS	1.0	54.8	52.7	9.3	4.9	4.0	2.8	129	235	364	85 : 15
	DS	0.9	54.8	60.5	10.7	6.2	5.1	2.5	141	270	410	85 : 15
	DWDS	0.7	39.2	34.1	5.7	2.9	1.5	1.7	85.8	135	221	86 : 14
D	PS	0.5	23.2	22.7	3.4	2.7	1.8	2.3	56.6	225	281	87 : 13
	DS	0.7	36.2	40.4	5.9	4.8	3.3	3.9	95.2	354	450	87 : 13
	DWDS	0.6	41.5	45.8	7.6	5.6	3.1	3.9	108	450	558	86 : 14
E	PS	n.a.	<8	8.7	1.3	1.0	0.7	0.7	12.5	169	182	87 : 13
	SES	n.a.	45.5	46.7	7.5	5.0	3.7	3.4	112	182	294	86 : 14
	DS	n.a.	39.8	48.2	7.9	5.6	3.9	4.0	109	411	520	86 : 14
	DWDS	n.a.	42.7	48.5	8.6	5.1	3.8	3.9	113	340	452	85 : 15
F	PS	0.4	17.6	19.1	3.0	2.2	1.4	1.1	44.6	97.1	142	87 : 13
	SES	1.7	64.6	112	25.4	12.4	11.7	3.4	231	206	437	81 : 19
	SES	1.9	27.4	49.8	23.7	13.3	12.4	3.4	132	220	352	68 : 32
	DS	1.5	92.3	95.3	13.6	12.5	7.2	4.6	227	302	529	88 : 12
G	PS	0.3	18.6	20.6	3.7	2.3	1.7	1.7	49.0	217	266	85 : 15
	DS	0.9	45.3	49.1	8.8	6.3	4.3	5.3	120	1141	1261	85 : 15
	DWDS	0.6	28.1	29.9	5.4	4.7	3.1	4.5	76.3	204	280	85 : 15
H	PS	0.3	14.8	14.0	2.5	1.5	1.1	1.4	35.6	293	328	85 : 15
	SES	0.7	34.4	34.8	4.5	4.9	2.5	4.4	86.2	234	321	88 : 12
	DS	0.8	32.5	40.5	6.6	5.3	3.4	4.9	94.0	605	699	86 : 14
	DWDS	0.7	41.0	42.4	7.0	5.8	3.7	5.4	106	417	523	86 : 14
I	PS	n.a.	14.4	14.5	2.4	1.6	1.4	0.9	35.2	199	234	86 : 14
	SES	n.a.	53.7	55.5	9.2	6.1	5.1	2.5	132	334	466	86 : 14
	SES	n.a.	67.7	59.9	9.7	7.0	6.0	3.7	154	486	640	86 : 14
	DS	n.a.	58.7	59.2	10.4	6.4	5.8	2.9	143	393	537	85 : 15
J	PS	1.1	80.4	113	18.0	13.3	9.6	3.4	238	256	494	86 : 14
	SES	1.3	85.8	101	16.9	11.1	8.4	3.7	228	341	569	86 : 14
	DS	1.5	95.2	118	20.0	15.5	14.8	5.2	270	690	960	86 : 14
	DWDS	1.3	84.5	98.2	16.5	11.2	8.5	4.3	225	556	781	86 : 14
K	PS	1.2	85.6	90.1	14.2	8.7	6.1	3.2	209	1895	2104	86 : 14
	SES	1.5	109	121	17.3	11.6	8.5	4.5	274	2217	2491	87 : 13
	DS	1.8	115	124	19.0	12.4	9.1	7.6	288	1339	1627	87 : 13
	n	28	39	39	39	39	39	39		39		
	Min.	0.3	8.0	8.7	1.3	1.0	0.7	0.7	12.5	97.1	142	
	Max.	1.9	115	124	25.4	15.5	14.8	7.6	288	2217	2491	
	Mean	1.0	47.9	53.9	9.3	6.3	4.7	3.4	126	429	555	86 : 14
	10%	0.5	18.4	19.0	3.1	2.2	1.5	1.6	48.1	169	231	
	50%	0.8	41.0	45.8	7.5	5.1	3.7	3.4	108	256	410	
	90%	1.6	87.1	112	18.2	12.4	9.2	5.2	232	780	1021	
	LOQ	0.2	8	2	0.4	0.1	0.1	0.2	10	6	17	

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