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LEVELS OF PBDE IN VARIOUS ENVIRONMENTAL MATRICES IN AUSTRIA

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Introduction

Polybrominated Diphenylethers are widely used as flame retardents in plastics, textiles and coatings. For the year 1999 the estimated worldwide produced amounts of technical PBDE mixtures were 55.000 t for DecaBDE, 3800 t for OcteBDE and 8500 t for PentaBDE.
DecaBDE is mainly used in plastics, textiles and coatings, OctaBDE in ABS-applications (e.g. computer casings) and PentaBDE in textiles and PU-foames for furniture. During production, use and waste treatment emissions into the environment occure, and because of their chemical stability these substances are regarded as persistant in the environment and they bioaccumulate in humans and wildlife[1,2,3].
Therefore the Environmental Agency Austria started an analytic program to get an overview about the situation of PBDE levels in the Austrian environment.

Methods and Materials

The following matrices were included into the program:

- sewage sludge:
  One dewatered and one activated sludge were taken from a wastewater treatment plant of a leather producing industry and six sludge samples were taken from wastewater treatment plants of textile industries.
- effluents from wastewater treatment facilities:
  24 domestic and industrial wastewater treatment facilities spread throughout Austria were investigated.
- effluents from landfills
  two landfill leachates and four with these leachates contaminated groundwater samples were analysed
- Danube River sediments and suspended particulates
  sediment samples were taken from the River Danube along its way through austria. At two sampling sites suspended particulate matter was also collected.
- feed
  three feed samples of different origin (protein mix, cereals, fish) were analysed

The sample amounts used for analysis were 10 g freezedried solid sample or 0.5 l water sample. The analytic methode, published by W.Knoth et al.[2], includes soxhlet extraction, cleanup by 4 steps of column liquid chromatography and measurement with a GC/HRMS System. The quantification was done by isotope dilution with 7 ^{13}C-labeled standards, which were added prior to extraction. The detection limits are in the range between 0.1 and 2 ng/kg and between 0.001 and 0.1 ng/l respectively

Results and Discussion

PBDEs were detected in nearly all environmental samples. The following tables show the results as minimum and maximum, as well as calculated mean and median for the different matrices.

Table 1. Concentrations of PBDE in effluent water of domestic and industrial wastewater treatment facilities (24 samples)

PBDE	**MIN** ng/l	**MAX** ng/l	**MED** ng/l	**MW** ng/l
# 11	n.d.	0.21	0.0008	0.01
# 17 / 25	0.0084	0.24	0.02	0.037
# 28	n.d.	0.56	0.067	0.11
# 47	0.8	4.6	1.8	2.2
# 49	n.d.	0.22	0.056	0.061
# 77	n.d.	0.31	0.0058	0.022
# 99	0.33	5.4	0.74	1.4
# 100	0.091	0.87	0.19	0.29
# 116	n.d.	0.14	n.d.	0.0089
# 138	n.d.	0.68	0.044	0.085
# 140	n.d.	0.59	0.015	0.041
# 153	0.086	0.91	0.29	0.33
# 154	n.d.	0.3	0.086	0.12
# 155	n.d.	0.13	0.014	0.019
# 166	n.d.	0.054	n.d.	0.0069
# 181	n.d.	0.39	n.d.	0.048
# 183	0.29	6	0.98	1.7

Table 2. Concentrations of PBDE in landfill leachates and groundwater contaminated by landfill leachates (6 samples)

PBDE	MIN ng/l	MAX ng/l	MED ng/l	MW ng/l
# 11	n.d.	0.55	0.0092	0.066
# 17 / 25	0.011	4.1	0.041	0.61
# 28	0.036	4	0.18	0.81
# 47	0.99	72	3.8	14
# 49	0.035	11	0.14	1.4
# 77	n.d.	0.046	0.0056	0.013
# 99	0.37	83	1.3	15
# 100	0.1	15	0.36	2.6
# 116	n.d.	0.2	n.d.	0.044
# 138	n.d.	2.6	0.065	0.55
# 140	0.014	1.9	0.048	0.31
# 153	0.1	13	0.57	2.8
# 154	0.065	6.6	0.45	1.5
# 155	0.013	0.64	0.032	0.15
# 166	n.d.	0.87	n.d.	0.097
# 181	n.d.	64	n.d.	7.7
# 183	0.5	21	0.98	7

Effluent water:

The PBDE concentrations in effluent water samples are relatively low, with maximum concentrations of the most abundant congeners up to 6 ng/l (Table 1.). The concentrations of PBDE in the landfill leachates (Table 2.) are higher than the concentrations in the effluent samples by one order of magnitude, comparing the most abundant congeners (#47, #99, #100, #183). The contaminated groundwater samples show concentrations similar to the effluents from wastewater treatment facilities.

Sewage sludge

The PBDE concentrations in the sewage sludge samples from the leather industry are in the concentration range of river sediment samples, whereas the sewage sludge samples from the textile industry show high concentrations of PBDEs in a range of several thousand ng/kg (Table 3.).

Table 3. Concentrations of PBDE in sewage sludge samples from leather and textile industry (8 samples)

PBDE	MIN ng/kg	MAX ng/kg	MED ng/kg	MW ng/kg
# 11	n.d.	0.94	0.26	0.32
# 17 / 25	1.7	1400	330	450
# 28	10	630	290	300
# 47	350	47000	18000	21000
# 49	27	2600	1600	1400
# 77	0.4	21	6.6	7.4
# 99	260	55000	20000	25000
# 100	51	9800	3400	4200
# 116	n.d.	24	n.d.	4.6
# 138	9.9	1300	380	490
# 140	8.1	1300	110	290
# 153	56	6000	2200	2600
# 154	24	5100	1400	1900
# 155	7.2	230	63	90
# 166	n.d.	52	n.d.	6.5
# 181	n.d.	60000	1000	9400
# 183	230	16000	1600	3500

Table 4. Concentrations of PBDE in sediments from River Danube (13 samples)

PBDE	MIN ng/kg	MAX ng/kg	MED ng/kg	MW ng/kg
# 11	n.d.	0.24	n.d.	0.046
# 17 / 25	0.98	44	3.6	6.4
# 28	4.4	110	7	15
# 47	130	3400	200	450
# 49	6	310	16	40
# 77	n.d.	2.4	0.26	0.39
# 99	80	3900	170	460
# 100	19	790	33	93
# 116	n.d.	n.d.	n.d.	n.d.
# 138	1.1	91	4.2	11
# 140	n.d.	29	1.9	4.1
# 153	11	500	29	64
# 154	1.7	350	14	39
# 155	n.d.	17	1.3	2.5
# 166	n.d.	n.d.	n.d.	n.d.
# 181	n.d.	430	22	72
# 183	32	410	84	110

River sediments:

The sediment samples from the River Danube show concentrations of PBDE in a range similar to uncontaminated industrial sewage sludge samples, exept at the sampling site downstream of Vienna the concentrations of the PBDE are much higher (Table 4.). The PBDE levels in the suspended particulate matter of River Danube are similar to those in the sediment samples. (Table 6.).

Feed:

Feed often contains PCDD/F and PCB due to contaminations during the production. Therefore we want to know if there are also PBDEs in feed. We analysed three feed samples of different origin, a protein mix, a cereal based feed and a fatty feed comprising fish. The concentrations of the PBDEs in the fatty feed (most abundand congeners up to 1000 ng/kg) are compareable with concentrations in uncontaminated sewage sludge.

Table 5. Concentrations of PBDE in feed samples of different origin (3 samples)

PBDE	MIN ng/kg	MAX ng/kg	MED ng/kg	MW ng/kg
# 11	n.d.	1.4	0.55	0.54
# 17 / 25	1.4	17	9.2	7.8
# 28	5.7	69	19	26
# 47	100	1200	130	360
# 49	7.7	300	27	78
# 77	0.38	50	7.7	15
# 99	39	310	110	130
# 100	13	210	45	68
# 116	n.d.	49	3.2	14
# 138	1.7	97	21	30
# 140	n.d.	91	12	22
# 153	11	190	36	60
# 154	6.2	120	32	46
# 155	1.5	98	16	26
# 166	n.d.	110	2.6	22
# 181	n.d.	140	21	35
# 183	76	970	110	270

Table 6. Concentrations of PBDE in suspended particulate mater of River Danube (2 samples)

PBDE	MIN ng/kg	MAX ng/kg	MED ng/kg	MW ng/kg
# 11	0.1	0.14	0.12	0.12
# 17 / 25	1.3	1.3	1.3	1.3
# 28	5.9	6.2	6.1	6.1
# 47	120	160	140	140
# 49	6.6	7.4	7	7
# 77	0.26	0.32	0.29	0.29
# 99	97	110	100	100
# 100	21	25	23	23
# 116	n.d.	n.d.	n.d.	n.d.
# 138	3.3	8	5.7	5.7
# 140	2.1	4.8	3.5	3.5
# 153	14	59	37	37
# 154	5.6	15	10	10
# 155	n.d.	1.1	0.55	0.55
# 166	n.d.	n.d.	n.d.	n.d.
# 181	60	150	110	110
# 183	45	580	310	310

Conclusions

PBDEs could be found in nearly all environmental matrices, even though in low concentrations. High concentrations were detected in sewage sludge samples of textile industries, in river sediments downstream of Vienna and in feed comprising fish.

References

1. Bergman, A., Örn, U.; (2001) Organohalogen Compounds, 50, 13.
2. Knoth, W., Mann, W., Meyer, R., Nebhuth, J.; (2002) Organohalogen Compounds, 58, 213.
3. Oliaei, F., King, P., Phillips L.; (2002) Organohalogen Compounds, 58, 185.