

PBDE AND HBCD LEVELS IN SURFACE SEDIMENTS FROM GERMAN RIVERS

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Introduction

To identify sources and to study the fate and behaviour of chemicals in the environment and their impact on human beings, extensive monitoring in various environmental compartments as well as in human samples is required. Therefore, the German Environmental Specimen Bank (ESB, www.umweltprobenbank.de) was established in 1985 as a permanent facility and comprises archives of representative plant, animal and human specimens collected at various locations representing different ecosystems and different levels of contamination. Specimen types were selected in order to allow pollution load estimation both in time and space. Within a previous study the suitability of sediment cores and solid particulate matter as potential additional matrices for the ESB were investigated¹. For this purpose several sampling techniques were tested and sediment cores were taken at three German rivers and at a reference site. Unfortunately, dating of the river sediment cores was difficult as often no clear stratification was seen. Nevertheless, the surface layers enabled us to get insight in the spacial variation of organic contaminants in the river sediments. Here we report the results of a survey of 10 polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) determined in surface sediments collected at a pristine lake and at 10 locations along the River Rhine, the River Elbe and the River Saar, Germany, using a fully optimised and validated GC-ECNI-MS method.

Material and Methods

In autumn 2002 and 2003, sediment cores from 11 sites were taken along the Rivers Rhine, Elbe, and Saar and at Lake Belau (Fig. 1). Sampling operations are described in detail elsewhere¹. In short, a redesigned freeze-coring device (Shapiro 1958) with liquid nitrogen as the cooling agent was tested and applied to collect unconsolidated sediments except for Lake Belau (B1, Fig. 1) and Blankenese (E5, Fig. 1), where a piston corer had to be used (CO₂ cooling). Sediment cores were cut on site, stored in stainless steel containers, and transported in a nitrogen vapour freezer. Prior to extraction surface sediment samples, which consist of up to 10 cm of the upper sediment horizons, were freeze-dried, sieved (<2mm), and homogenised.

Lake Belau (B1) is situated in the Bornhoeved Lake District in Schleswig-Holstein and served as a reference site. The River Rhine is one of the longest rivers in Europe and at least 50 million people settle along its course to the North Sea, which makes the River Rhine highly vulnerable to contamination by anthropogenic activities. A major river of Central Europe is the River Elbe. Continuous improvements in water quality were achieved since the early 1990s. The River Saar is another major German river running through the Saarland conurbation characterised by coal-, iron- and steel industries, residential districts and traffic systems.

Analysis of PBDEs and HBCD were performed, as described previously², with some modifications. In brief, 1.0 to 8.0 g of sediment were extracted with toluene at 125 °C and 14 MPa using an ASE 200 accelerated solvent extractor (Dionex GmbH, Idstein, Germany) followed by gel permeation chromatography and multi-layer silica gel column chromatography clean-up. The purified extracts were evaporated to a final volume of 100 µl using an automatic evaporation device (flowtherm optocontrol, Barkey GmbH & Co. KG, Leopoldshöhe, Germany). Quantification of BDE 28, BDE 47, BDE 66, BDE 99, BDE 100, BDE 138, BDE 153, BDE 154, BDE 183, BDE 209 and HBCD was performed by high-resolution capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC-ECNI-MS) in the selected ion monitoring mode under the following conditions: GC 6890+ / MSD 5973 (AGILENT, Palo Alto, CA, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Switzerland) and PTV injector CIS 4 plus (GERSTEL, Muelheim/Ruhr, Germany); capillary column: Rtx-CLPesticide (Restek, Bellefonte, PA, U.S.A.), 30 m x 25 mm, film thickness: 0.25 µm; pressure-pulse injection: 50 psi (0.8 min); injection volume: 2 µl; carrier gas: helium; CI ion source reagent gas: methane;

ion source temperature: 200 °C. Under these conditions, PBDEs and HBCD elute from the column between 11 and 35 minutes. While for quantitation of BDE 209 the highly specific ions at $m/z = 484.7$ and $m/z = 486.7$ were monitored, for all other BFRs ions specific to bromine at $m/z = 79$ and $m/z = 81$ were recorded. The monofluorinated brominated diphenyl ethers F-BDE 28, F-BDE 100 and F-BDE 160, BDE 181 and $^{13}\text{C}_{12}$ -labelled BDE 209 were used as internal standards. Quality controls included recovery tests, regular analyses of procedural blanks, blind replicate samples, as well as participation in international interlaboratory studies on the determination of PBDEs. Standards were purchased from Chiron AS (Trondheim, Norway) and Wellington Laboratories Inc. (Guelph, Ontario, Canada).

Results and Discussion

With the exception of BDE 138, the analysed congeners were detected in nearly all samples. Concentrations of BDE 28, BDE 66 and BDE 183 were in most cases close to the limit of quantitation (LoQ). In all samples except those taken at the River Saar, BDE 209, representing the technical DecaBDE formulation, or HBCD were the dominant compounds. Table 1 shows the results for individual PBDE congeners and HBCD in surface sediments taken at various locations along the River Rhine, River Elbe and River Saar, as well as at Lake Belau. Concentrations are given on dry weight (dw) basis as concentrations normalised to organic carbon showed the same pattern since there was no significant difference in total organic carbon content of the sediment samples taken from any of the rivers.

Lake Belau

At Lake Belau, BDE 209 and HBCD were found at $0.95 \mu\text{g}/\text{kg dw}$ and $1.89 \mu\text{g}/\text{kg dw}$, respectively. Concentrations of all other congeners were below $0.25 \mu\text{g}/\text{kg dw}$. As this site is not influenced by any industry, atmospheric deposition seems to be the probable source of the low contamination. Similar BDE 209 and HBCD levels had been seen in sediment samples collected in Danish lakes³. Moreover, the measured values correspond to those found in sediments from the nearby German Bight⁴. ΣPBDE (28-209) concentrations in Lake Belau sediments were three times lower than in sediments from Lake Maggiore, Italy⁵. Even the data presented by Zegers *et al.*⁶ for the upper sediment layers of Lake Woserin (Mecklenburg-Western Pomerania, Germany) were two times higher. Therefore, Lake Belau may be considered as a background area for contamination with brominated flame retardants (BFRs).

River Rhine

PBDE concentrations in sediments collected at Weil (R1) and Koblenz (R3) at the River Rhine were in the same order of magnitude and dominated by BDE 209 (Table 1). In sediments from Bimmen (R4), much lower PBDE levels were found. Concentrations of BDE 47 and BDE 99, indicators for the penta-formulation were generally low. HBCD levels ranged from 2.8 to $19.8 \mu\text{g}/\text{kg dw}$ with highest concentration at Koblenz. The fairly high BDE 209 and HBCD concentrations at Koblenz may be due to abandoned industrial sites in the vicinity of the sampling station.

River Elbe

The PBDE congener pattern in sediments from the River Elbe was similar to that in the River Rhine. BDE 209 was the dominating compound with concentrations ranging from 3.3 to $37.9 \mu\text{g}/\text{kg dw}$. Highest concentrations were seen at station Barby (E3), located at the mouth of the River Saale, which passes highly industrialised regions in Saxony-Anhalt and discharges into the River Elbe.

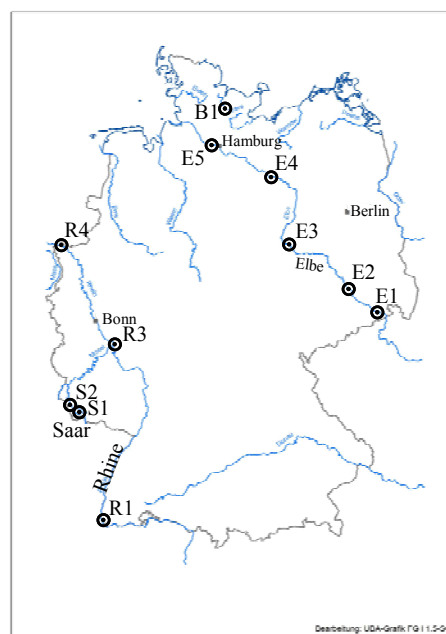


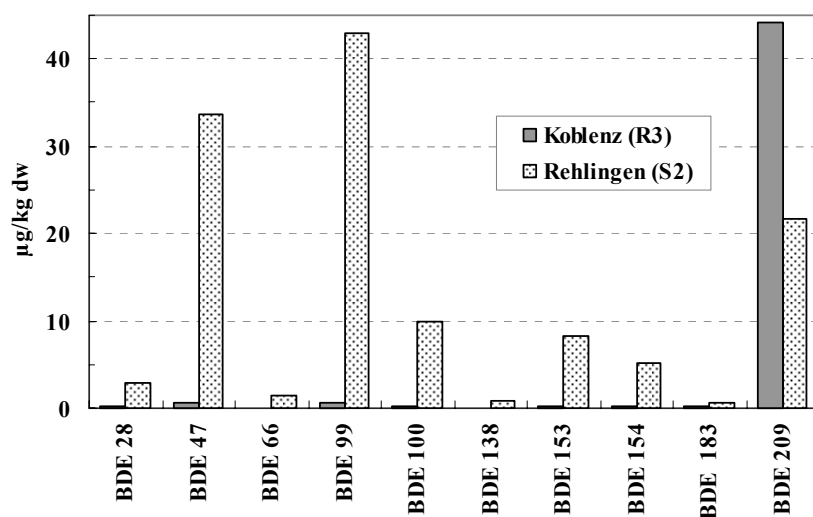
Figure 1: Map of sampling sites: Lake Belau (B1), Weil (R1), Koblenz (R3), Bimmen (R4), Prossen (E1), Zehren (E2), Barby (E3), Cumlosen (E4), Blankenese (E5), GÜdingen (S1) and Rehlingen (S2)

Table 1: Concentrations of PBDE congeners and HBCD in river sediments from Germany [$\mu\text{g}/\text{kg dw}$]

Sampling site	BDE 28	BDE 47	BDE 66	BDE 99	BDE 100	BDE 138	BDE 153	BDE 154	BDE 183	BDE 209	HBCD
Lake Belau (B1)	<LoQ	0.19	0.04	0.22	0.05	n.d.	0.06	0.03	0.06	0.95	1.89
Weil (R1)	0.02	0.56	0.05	0.55	0.12	n.d.	0.06	0.04	0.02	20.69	2.76
Koblenz (R3)	0.12	0.52	<LoQ	0.64	0.20	n.d.	0.18	0.17	0.16	44.17	19.79
Bimmen (R4)	0.05	0.26	n.d.	0.35	0.04	n.d.	0.08	0.05	n.d.	0.45	7.31
Prossen (E1)	n.d.	0.87	n.q.	1.22	0.40	n.d.	0.20	0.13	0.27	9.50	9.93
Zehren (E2)	0.06	1.32	0.04	2.63	0.66	0.01	0.13	0.18	0.03	25.79	0.99
Barby (E3)	0.12	1.15	0.14	1.59	0.38	n.d.	0.28	0.21	0.32	37.88	17.80
Cumlosen (E4)	0.02	0.60	0.03	0.64	0.53	n.d.	0.09	0.03	0.07	24.94	3.28
Blankenese (E5)	0.01	0.11	0.02	0.12	0.04	n.d.	0.02	0.01	0.02	3.34	1.80
Güdingen (S1)	0.30	4.57	0.32	7.30	1.45	0.17	1.19	0.74	0.33	40.54	16.14
Rehlingen (S2)	2.84	33.65	1.39	42.99	9.89	0.88	8.29	5.13	0.69	21.71	8.11

n.d. = not detected; n.q. = not quantified due to interferences; LoQ = limit of quantitation

The lowest BDE 209 level was found at Blankenese (E5), which is consistent with results reported by Stachel *et al.*⁴. The authors explained the low BDE 209 levels at sampling station Blankenese (E5) with its location downstream the dam of Geesthacht, where highest BDE 209 levels were seen in that study. The low flow velocity in front of the dam at Geesthacht is associated with a high sedimentation rate of suspended particulate matter carrying hydrophobic contaminants. Consequently, downstream the dam BDE levels are much lower. At sampling sites Prossen (E1) and Blankenese (E5), BDE 209 levels were lowest although these stations were situated in the vicinity of sewage treatment plants (STPs). This was in contrast to findings by Sellström *et al.*⁷ and Samara *et al.*⁸, who observed significant higher PBDE levels in sediments influenced by STP effluents.

**Figure 2: Concentrations of selected PBDE congeners in sediments taken from River Rhine and River Saar**

River Saar

In GÜdingen (S1), the ΣPBDE (28-154) was 3 to 15 times higher than at all sampling sites at the River Rhine and the River Elbe, while at the dam Rehlingen (S2) it was even 20 to 100 times higher (Fig. 2). The major congeners were BDE 47 and 99, representing the technical penta-mix. Apparently, there are certain point sources of technical pentaBDEs along the course of the River Saar, in particular in the highly industrialised area of the cities of Saarbrücken, Völklingen and Saarlouis. BDE 209 and HBCD levels were in the same range as those found in sediments from River Rhine and River Elbe (Table 1).

Conclusion

The results indicated a fairly low contamination with BFRs in most of the studied river sediments from Germany, which is in line with previously reported data for the River Elbe⁴. In fact, the levels of the dominating BDE 209 were low in comparison to sediments from sites influenced by point sources, e.g. the River Scheldt, Belgium (up to 8413 µg/kg dw)⁹, the River Vero, Spain (up to 12459 µg/kg dw)¹⁰ and the River Tees, UK (up to 1400 µg/kg dw)¹¹. Hence, diffuse input of BDE 209 appears to be the most important input route.

Sediments from industrialised areas at River Saar were much more highly contaminated with pentaBDE (Table 1) than sediments from the River Rhine and the River Elbe. In view of the fact that a voluntary self-commitment of German plastic and textile additives producers to abandon the use of PBDEs in their products has been in place since 1986, this is quite a surprising result.

HBCD was found in all samples ranging from 1 to 20 µg/kg dw. It is likely that these contaminations originate from diffuse sources as sediments taken downstream of HBCD production sites and of industrial users are much higher contaminated^{7,12,13}.

Acknowledgements

We gratefully acknowledge Margot Muntermann, Federal Environment Agency, for her valuable technical assistance with sample analysis and TOC determination.

References

1. Schulze T., Ricking M., Schröter-Kermani C., Körner A., Denner H.-D., Weinfurtner K., Winkler A. and Pekdeger A. *J Soils Sed* 2007; 7: 361.
2. Lepom P., Karasyova T, Sawal G. *Organohalogen Comp* 2003; 61: 135.
3. Christensen J.H. and Platz J. *J Environ Mon* 2001; 3: 543.
4. Stachel B., Jantzen E., Knoth W., Krüger F., Lepom P., Oetken M., Reincke H., Sawal G., Schwartz R. and Uhlig S. *Journal of Environmental Science and Health* 2005; A40: 265.
5. Vives I., Canuti E., Castro-Jiménez J., Christoph E.H., Eisenreich S.J., Huber T., Mariani G., Mueller A., Skejo H., Umlauf G. and Wollgast J. *J Environ Mon* 2007; 9: 589.
6. Zegers B.N., Lewis W.E., Booiij K., Smittenberg R.H., Boer W., deBoer J. and Boon J.P. *Environ Sci Technol* 2003; 37: 3803.
7. Sellström U., Kierkegaard A., deWit C.A. and Jansson B. *Environ Toxicol Chem* 1998; 17: 1065.
8. Samara F., Tsai C.W. and Aga D.S. *Environ Poll* 2006; 139: 489.
9. Covaci A., Gheorghe A., Voorspoels S., Maervoet J., Steen Redeker E., Blust R. and Schepens P. *Environ Int* 2005; 31: 367.
10. Eljarrat E., Labandeira A., Marsh G., Raldua D. and Barceló D. *Chemosphere* 2007; 69: 1278.
11. Allchin C. and deBoer J. *Organohalogen Comp* 2001; 52: 30.
12. Morris S., Allchin C.R., Zegers, B. N., Hafika, J.J.H, Boon, J.P., Leonards, P.E.G.; van Leeuwen, S.P.J. and deBoer, J. *Environ Sci Technol* 2004; 38: 5497.
13. Eljarrat E., de la Cal A., Raldua D., Duran C. and Barceló D. *Environ Sci Technol* 2004; 38: 2603.