



# Occurrence of Brominated Flame Retardants in Wildlife and the Environment

## Environment

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## Introduction

Brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBB), Hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBPA) have been used extensively over the past two decades as flame retardants in many types of products to reduce flammability. Similarly to other persistent organic pollutants (POPs), these BFRs (except TBBPA) appear to be lipophilic and bioaccumulate in biota and humans. Recent legislation banned certain PBDE congeners. EU directive 2003/11/EC prohibits the use of Penta-BDE and Octa-BDE for the member states of the European community. Therefore, analysis of PBDEs has received increased interest as a result of their known toxicity.

## Materials and Methods

PBDEs, PBBs, HBCD and TBBPA were analyzed in different environmental samples (surface water, river sediments, sewage sludge) and freshwater fish samples from rivers in Germany in 2006. All samples were investigated within the routine analytical service of GALAB Laboratories GmbH. All analyses were performed according standard operation procedures and included addition of isotope labelled internal standards, adequate extraction steps, different column clean-up procedures (GPC, silica gel), sulfuric acid treatment and a derivatization step for TBBPA. The determination of the analytes was carried out using HRGC/HRMS (DFS system, Thermo-Fisher).

n = 155	5 Percentile	25 Percentile	Mean	Median	75 Percentile	95 Percentile
Sum PBDEs	< 0,1	< 0,1	18,5	< 0,1	1,7	80,5
Sum PBBs	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
BC	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
HBB	< 0,1	< 0,1	0,84	< 0,1	< 0,1	< 0,1
HBCD	< 1,0	< 1,0	1,4	< 1,0	< 1,0	< 1,0
TBBPA	< 0,1	< 0,1	11,7	< 0,1	8,1	49,3
Sum BFR	< 1,0	< 1,0	32,6	2,9	13,0	130

Table 1: BFR in surface water samples, values [ng/L]

n = 212	5 Percentile	25 Percentile	Mean	Median	75 Percentile	95 Percentile
Sum PBDEs	< 0,1	< 0,1	70,4	1,9	26,0	309
Sum PBBs	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Bromocyclen	< 0,1	< 0,1	0,19	< 0,1	< 0,1	< 0,1
HBB	< 0,1	< 0,1	0,11	< 0,1	< 0,1	< 0,1
HCBDe	< 1,0	< 1,0	290	< 1,0	5,1	1605
TBBPA	< 0,1	< 0,1	11,9	< 0,1	3,1	19,0
Sum BFR	< 1,0	< 1,0	373	8,2	68,2	1732

Table 2: BFR in sediment samples, values [µg/kg dry weight]

n = 96	5 Percentile	25 Percentile	Mean	Median	75 Percentile	95 Percentile
Sum PBDEs	44,3	107	468	172	276	1769
Sum PBBs	< 0,1	< 0,1	8,2	0,1	9,4	39,8
Bromocyclen	< 0,1	< 0,1	5,2	< 0,1	2,6	24,1
HBB	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
HBCD	< 1,0	< 1,0	37,3	< 1,0	< 1,0	243
TBBPA	< 0,1	12,5	55,2	26,9	53,5	187
Sum BFR	59,7	142	574	193	501	2155

Table 3: BFR in sewage sludge samples, values [µg/kg dry weight]

n = 34	5 Percentile	25 Percentile	Mean	Median	75 Percentile	95 Percentile
Sum PBDEs	5,6	10,1	15,3	15,2	21,0	30,9
Sum PBBs	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Bromocyclen	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	0,24
HBB	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
HCBDe	< 1,0	< 1,0	3,0	< 1,0	< 1,0	19,7
TBBPA	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Sum BFR	5,6	10,1	20,3	17,3	29,7	38,6

Table 4: BFR in fish samples, values [µg/kg fresh weight]

## Results and discussion

Considering their average concentration we focussed on the BFR analytes BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-201, BDE-203, BDE-206, BDE-207, BDE-208, BDE-209, PBB-101, Bromocyclen (BC), HBB (HBB), HBCD, and TBBPA in the samples analyzed.

The analytes BDE-17, BDE-49, BDE-138, BDE-139, BDE-140, BDE-171, BDE-184, BDE-190, BDE-191, PBB-52, and PBB-153 were omitted as their concentration was below the respective determination limit.

### I. Surface Water Samples

The BFR content in surface water samples was determined within a range from below the determination limit to over 130 ng/L with a mean of about 30 ng/L (Table 1). The BFR content of most surface water samples was below the determination limit. The most prominent BFRs in surface water are the PBDEs and TBBPA. BDE-209, BDE-99, BDE-47, and BDE-183 were the most important brominated diphenyl ethers. No centrifugation/filtration step preceded the sample preparation step so the BFRs in surface water are supposed to be bound to suspended organic matter.

### II. Sediment Samples

BFR concentration ranged from below determination limit to above 1700 µg/kg with a mean of about 400 µg/kg dry weight (Table 2). The BFR content of a high percentage of sediment samples was below the determination limit. The most prominent BFRs were PBDEs, HBCD, and TBBPA. Figure 1 gives the BFR distribution pattern. The most prominent analytes were BDE-209, HBCD, and TBBPA. Typical PBDEs present in commercial technical PBDE mixtures can be detected: BDE-47/BDE-99/BDE-100 (Penta-BDE), BDE-183/BDE-197/BDE-196/BDE-203 (Octa-BDE), and BDE-209/BDE-206/BDE-207/BDE-208 (Deca-BDE). It is understood, that the Octa-/Nona-BDE (e.g. BDE-201) are degradation products of BDE-209.

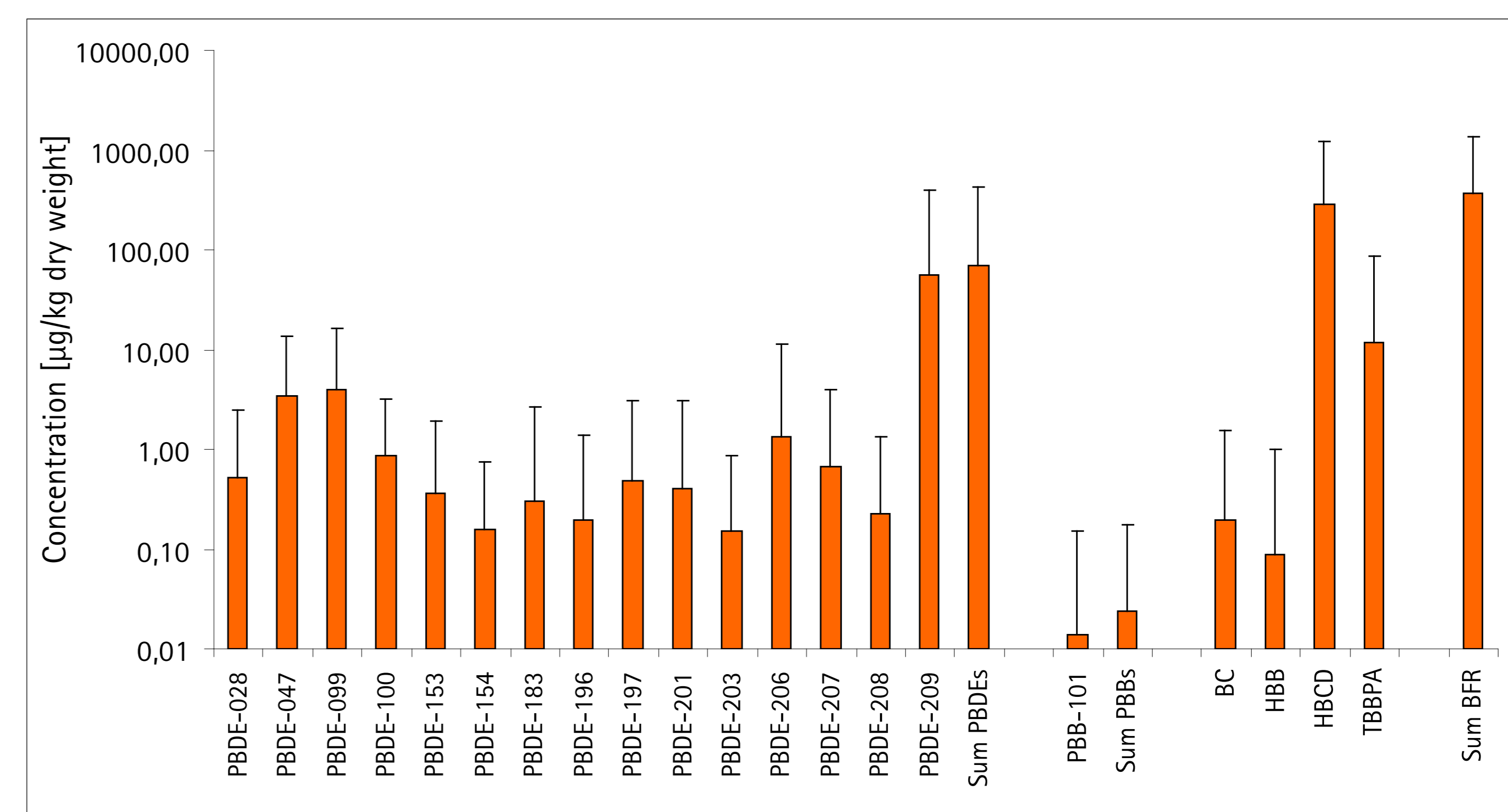


Figure 1: BFR in Sediment Samples; columns represent the mean values of n = 212 samples from Germany (with error bars)

### III. Sewage Sludge Samples

In contrast to sediment samples the BFR contents in all sewage sludge samples analyzed exceeded the determination limits. The levels varied from 50 to over 2000 µg/kg with a mean of about 600 µg/kg dry weight (Table 3). The most prominent BFRs were PBDEs, HBCD, and TBBPA.

### IV. Freshwater Fish Samples

The BFR contamination ranged between 5 µg/kg and 40 µg/kg with a mean of 20 µg/kg fresh weight (Table 4). Only PBDEs and HBCD were detected in freshwater fish. In contrast to the compartments discussed earlier BFR levels in fish are highly regulated by the food chain used by these organism as well as their inherent detoxification mechanisms. So the PBDE distribution pattern is different: BDE-47 and BDE-100 are the most important polybrominated diphenyl ethers, followed by BDE-99 and minor BDEs.

## Conclusions

- GALAB Laboratories GmbH, Geesthacht, Germany offers a reliable service for the state of the art determination of BFR in environmental and food samples
- The coverage of a wide range of different significant parameters combined with the high sensitivity of the HRGC/HRMS DFS system guarantees a high amount of safety for our customers
- Our routined staff has a high expertise in interpreting even unusual or unexpected BFR congener patterns in a wide range of sample types