

NOVEL BROMINATED FLAME RETARDANTS AND DECHLORANE PLUS IN SEWAGE SLUDGE IN THE STATE OF BAVARIA, GERMANY

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Introduction

About 25 % of the amount of chemicals used as flame retardants in plastic materials are polybrominated organic compounds. Since most of these substances are used as additives in polymers and thus not chemically bound into the polymer matrix, diffuse release into the environment during product life cycle is possible. Up to now, most studies on levels and fate of brominated flame retardants (BFR) in the environment have focused on polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCD) and tetrabromobisphenol A. Due to persistence and bioaccumulation [1], technical Penta- and OctaBDE were banned in new products in the EU since 15 August 2004 [2]. Further, DecaBDE has been banned in electrical and electronic applications in the EU since 1 July 2008 [3]. This has paved the way for the use of novel BFR as replacement for the banned formulations such as decabromodiphenylethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBB), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and tetrabromo-p-xylylene (p-TBX) [4].

Besides BFR, the chlorinated additive flame retardant Dechlorane Plus (DP) has been produced for nearly 50 years in the USA at the Niagara Falls and can be used in electrical and electronic applications as well as for plastic roofing materials [5] but was only detected in 2006 in the environment close to the production site [6]. Obviously, it is sold and used worldwide including in Europe since DP has been found in tree bark from Germany and Italy [7] and recently in Spanish sewage sludge [8].

In the present study, we analysed these six novel BFR in addition to PBDE and HBCD in sewage sludge from 33 municipal wastewater treatment plants (WWTP) in the state of Bavaria in southern Germany. Further, we determined DP in 12 sludge samples. Sewage sludge is a matrix where a large variety of anthropogenic substances accumulates by different routes of entrance, thus being a suitable screening target for contemporary releases of chemicals into the environment. Additive FR can directly be released into domestic and industrial wastewater by leaching from polymers especially at elevated temperatures and by mechanic abrasion from plastic materials but may also enter WWTP with surface run-off after diffuse release into the air and atmospheric deposition.

Materials and methods

Sampling

In 2008 and 2009, sewage sludge samples from 194 WWTP in different districts of Bavaria were collected for analysis of various groups of (persistent) organic pollutants including PBDE and HBCD. 24 samples from 2008 and 9 samples from 2009 were additionally analysed for the six novel BFR. Samples from 2009 were preferably selected from large WWTP (5 had a capacity of >100,000 population equivalents). DP was determined in 12 sludge samples from 2009 (11 samples were from different plants than those analyzed for BFR).

Analysis of BFR

The determination of the six BFR could successfully be integrated into the analytical method developed for the analysis of PBDE and HBCD in different environmental media [9]. A representative aliquot of the sample was freeze-dried, homogenized and stored in brown glass bottles. 2.0 – 2.5 g of the sample were extracted with a mixture of n-hexane/acetone (1:1, v/v) using pressurized liquid extraction (ASE 200, Dionex) at 80 °C with five static cycles (5 min time each). Before extraction, ¹³C₆-HBB, ¹³C₁₄-DBDPE and ¹³C₁₂-BTBPE as well as ¹³C₁₂-BDE 28, 47, 99, 100, 153, 154, 183, 209 and ¹³C₁₂-γ-HBCD were added as internal standards. The concentrated

extract was first purified and fractionated on a column filled with 8.5 g active neutral silica and 25 g silica/ 44 % conc. sulfuric acid. The first fraction (270 ml n-heptane) contained DBDPE, HBB, PBT, PBEB and p-TBX together with the PBDE. BTBPE was eluted together with HBCD in the second fraction with 140 ml n-heptane/dichloromethane (1:1, v/v). The DBDPE fraction was further purified on 5 g water-free Alumina B, while the BTBPE fraction was purified on 4 g Florisil, activated for 1 h at 130 °C. From both columns the target compounds eluted in the second fraction with 50 ml n-heptane/dichloromethane (1:1, v/v). Both fractions were concentrated to 50 µl and ¹³C₁₂-BDE 138 was added as recovery standard. Analysis was performed by capillary gas chromatography with PTV injection in the solvent split mode [10] on a non-polar DB-5ms column (l = 15 m, i.d. = 0.25 mm, film thickness = 0.10 µm) coupled to a quadrupole mass spectrometer using electron impact ionisation (TraceGC and TraceDSQ MS, ThermoFisher Scientific). The two most intensive ions of the molecule ion cluster of native compound and corresponding internal ¹³C-standard were used for identification and quantification. ¹³C₆-HBB was used as internal standard for quantification of p-TBX, PBEB and PBT. Response factors were determined with a three-point calibration. Limit of quantification (LOQ) was defined as signal-to-noise ratio of 10:1 of the quan mass trace, limit of detection (LOD) as signal-to-noise ratio of 3:1. In case of a quantifiable blank value in the corresponding laboratory blank sample (silica), the blank value was the LOQ. Concentrations were blank corrected if necessary.

Analysis of DP

The extraction and clean-up/fractionating process as well as the GC-MS method developed for the BFR could successfully be applied to DP. ¹³C₁₀-labelled anti-DP was added as internal standard. DP eluted in the same fractions as DBDPE and PBDE. ¹³C₁₂-BDE 138 was used as recovery standard.

Results and discussion

An overview of the concentrations of the six novel BFR in sewage sludge is given in table 1. All results are calculated based on dry matter (dm) of the sludge samples.

Table 1. Concentrations (in µg/kg dm) of six novel BFR in sewage sludge samples from Bavaria collected in 2008 and 2009

2008 (n = 24)	n > LOQ	Minimum	Maximum	Median	Arithmetic Mean*
BTBPE	20	<0.133 ²	16.5	2.81	3.92
DBDPE	20	n.d. (0.312) ³	77.4	38.2	36.1
HBB	13	<0.005	0.194	0.026	0.034
PBEB	8	n.d. (0.002)	0.052	-	0.022
PBT	15	n.d. (0.002)	0.488	0.057	0.123
p-TBX	9	n.d. (0.003)	0.729	-	0.275
2009 (n = 9)					
BTBPE	6	n.q.**	7.27	2.94	3.50
DBDPE	9	16.7	196	42.8	58.2
HBB	5	<0.047	0.329	0.070	0.124
PBEB	2	n.d. (0.002)	0.248	-	0.043
PBT	6	<0.016	0.544	0.123	0.158
p-TBX	8	n.d. (0.003)	2.73	0.536	0.786

* For the calculation ½ LOQ was used in case of concentrations <LOQ, levels <LOD were set = 0

² LOQ

³ n.d. = not detectable, LOD in parenthesis

** Not quantifiable in two samples, excluded for calculation of the mean value

In most of the 24 samples from 2008 considerable levels of DBDPE between <0.31 and 77.4 µg/kg (Median: 38.2 µg/kg) and of BTBPE from <0.13 to 16.5 µg/kg (Median: 2.81 µg/kg) were found. Only low concentrations of HBB, PBEB, PBT and p-TBX could be detected with maximum values of 0.19, 0.052, 0.49 and 0.73 µg/kg,

respectively. In the nine sewage sludge samples from 2009 the levels of BFR were similar to those found in 2008.

Figure 1 shows the levels of the six novel BFR in the nine sludge samples from 2009 together with those of PBDE and HBCD. DBDPE concentrations were similar to HBCD levels but yet lower than those of DecaBDE (BDE 209). Since DBDPE is used as a substitute for DecaBDE and due to the very similar structure and physical-chemical properties it is likely that diffuse release of DBDPE from flame retarded plastic products into the environment will continue in near future causing increasing concentrations in sewage sludge and other environmental media. Thus, under the criteria of prospective environmental and health protection DBDPE seems not to be a better alternative to DecaBDE.

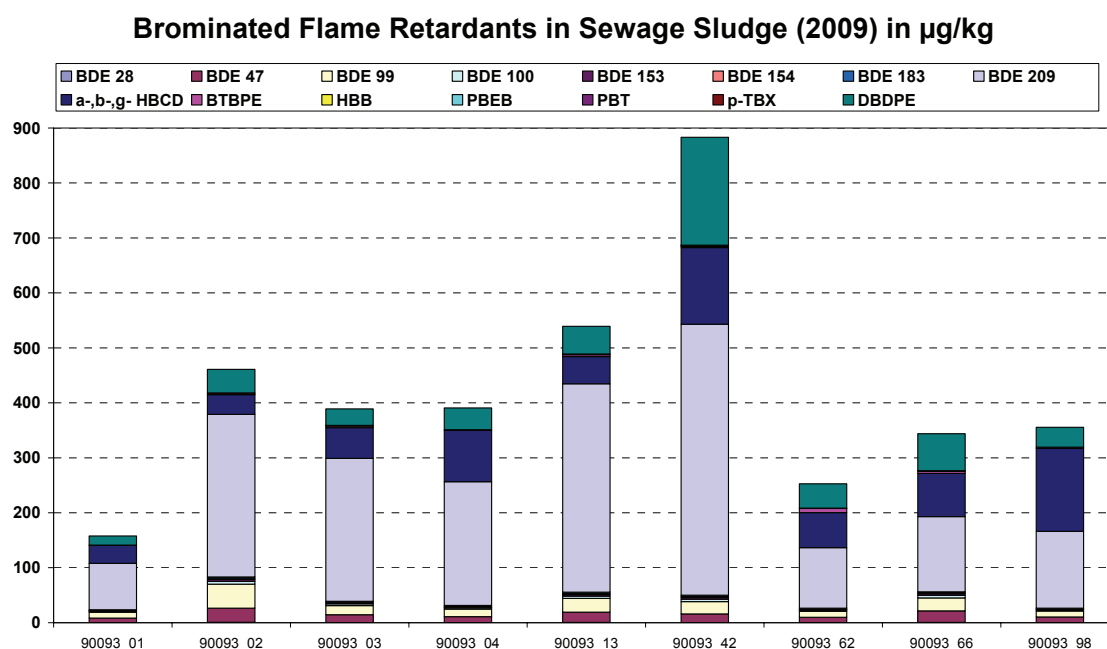


Figure 1. Concentrations of novel BFR and of PBDE and HBCD in 9 sewage sludge samples from Bavaria, southern Germany, from 2009 in $\mu\text{g}/\text{kg}$ dm (x-axis represents sample no.)

HBB was quantifiable in 18 of the 33 samples at low concentrations with a maximum of $0.33 \mu\text{g}/\text{kg}$. This result is in contrast to a study reporting high HBB levels between 4.5 and $2468 \mu\text{g}/\text{kg}$ in all 32 sewage sludge samples collected in the state of Baden-Württemberg in southwestern Germany in 2001 [3]. A possible reason for that unexpected difference could have been that usage of HBB and thus release into the environment might substantially have decreased in Germany during the last decade. Therefore, we analyzed BFR in residue sewage sludge samples from three national interlaboratory comparison studies on dioxins/ furans and PCB from the years 2000 and 2002. However, HBB levels were between 0.061 and $0.12 \mu\text{g}/\text{kg}$ dm and thus as low as in the sludge samples from 2008/09. In addition, we analyzed litter, humus layer and top mineral soil collected in 2008 from an alpine forest region in southern Bavaria. HBB concentrations in the samples did not exceed the low ng/kg range and were one to two orders of magnitude lower than those of the major PBDE congeners thereby indicating that atmospheric deposition of HBB has obviously been of minor importance in southern Germany in the past. This result is in accordance with the low HBB concentrations found in sewage sludge.

The syn- and anti-isomers of DP were found in all 12 analyzed sludge samples. Total DP levels ranged from 6.9 to $72.8 \mu\text{g}/\text{kg}$ dm with a mean value of $22.0 \mu\text{g}/\text{kg}$. A similar concentration range of $2.45 - 93.8 \mu\text{g}/\text{kg}$ with an average of $32.5 \mu\text{g}/\text{kg}$ has been found in sewage sludge from 31 Spanish WWTR very recently [12].

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