Hexabromobenzene and Pentabromophenol in German Sewage Sludge – Indication of Significant Commercial Use

Bertram Kuch[1], Carmen Schneider[1], Jörg Metzger[1], Roland Weber[2]

[1]Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft, University Stuttgart
[2]Pops Environmental Consulting

Introduction

Most studies reporting on environmental burden of brominated flame retardants focus on the three most widely used flame retardants PBDE, TBBPA and HBCD. However, these three flame retardants represented only about 52% of the West European BFR market in 1998[1] and there is a growing number of brominated flame retardants on the market and in use. One important task for environmental analytical chemists is the screening of current pollutants released from industry and society into the environment and especially the recognition and identification of upcoming potential environmental pollutants in an early stage. Sewage sludge is a matrix that reflects current contaminant issues and therefore suitable for screening of contemporary releases of chemicals from industry and society.

The present study reports on the determination of BFR in sewage sludge sampled in 32 waste water treatment plants in South Germany. In addition to the commonly analysed BFR the samples were screened for bromobenzenes and bromophenols. These compound classes include some "chemicals of potential concern" (OSPAR list[2]) like hexabromobenzene (HexaBBz) and pentabromophenol (PentaBP). HexaBBz, the brominated analogue of hexachlorobenzene (included in the POPs list of the Stockholm Convention[3]), was already used in the 70th and early 80th as one major brominated flame retardant e.g. in Japan[4] used for textile fibres (polyester, polypropylene and poly (p-phenylene benzobisthiazole)) and paper'[5]. PentaBP, the brominated analogue of the discontinued PCP, is used as a reactive flame retardant. However, not much information is available on the present application pattern and no attention was paid in recent years on occurrence and concentration of these critical compounds and other bromobenzenes and bromophenols in the environment. The present study indicates that HexaBBz, PentaBP, 1,2,4,5-TetraBBz, and 2,4-DiBP are produced and used as industrial bulk chemicals today and emitted in considerable quantities into the (German) environment.

Materials and methods

The samples were taken from 32 municipal sewage treatment plants with varying impact of industry. All wastewater treatment plants were located in Baden Wuerttemberg (Southwest Germany). Samples (5 to 10 g) were freeze dried before soxhlet extraction (24 h, toluene).

The clean-up procedure for PBDEs and bromobenzenes is described elsewhere[6]. The phenolic compounds were extracted twice by 2N KOH solution and methylated with dimethylsulfate before clean up on a silica column.

Analysis of the samples was carried out by HRGC-LRMS (HP 6890 GC, Agilent 5973 MS, splitless injection) on a non-polar column (DB-5MS; 0.25 mm i.d., length: 30 m, film thickness: 0.25 µm; Agilent, Waldbronn, Germany) using electron impact ionisation (EI). Detection was performed in single ion-monitoring mode (SIM). PCB-209* was used as a standard for quantification.

All concentrations are calculated based on dry matter of the sewage sludge.

Results and discussion

Data obtained from the 32 sewage treatment plants are summarised in Table 1.

1. Concentration of brominated benzenes

Hexabromobenzene was detected in all analysed sludge samples. Concentrations varied significantly among the sewage treatment plants with a median of 55 ug/kg in all samples, but an average concentration of 330 µg/kg and a peak value of 2500 µg/kg (Table 1). With decreasing degree of bromination the concentration of bromobenzenes decreased. However, PentaBBz and TetraBBz were detected in 31 of the 32 samples and TriBBz in 14 samples. In most samples the prevailing tri and tetra isomers were 1,2,4,5-TetraBBz and 1,2,4-TriBBz. Dibromobenzenes were not detected in any of the samples with a detection limit of <0.1 µg/kg dry substance.

The constant ratio of HexaBBz and PentaBBz of ca. 100:14 in all samples (Figure 1) suggests that both contaminants result from the same source and pathway and that PentaBBz is most likely included in this ratio as contaminant of technical grade HexaBBz. In contrast, a weak correlation of HexaBBz/PentaBBz and 1,2,4,5-TetraBBz was observed, indicating that 1,2,4,5-TetraBBz has another source and a different application compared to HexaBBz and PentaBBz.

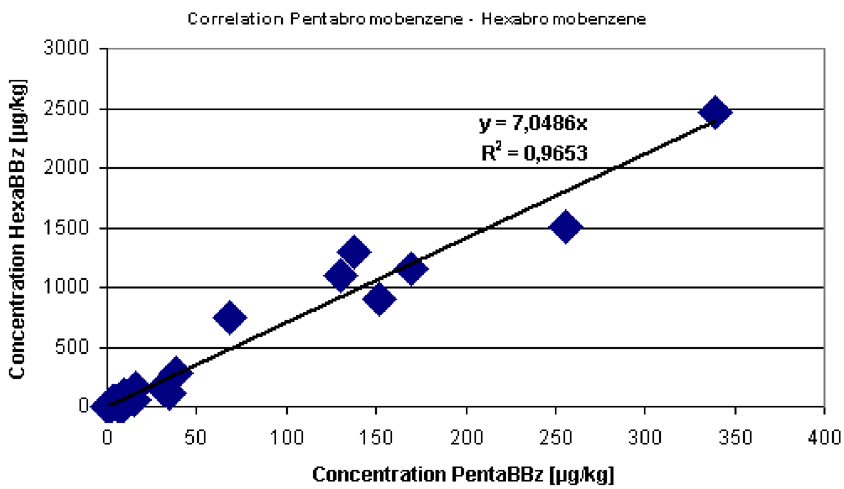

Figure 1: Correlation of PentaBBz and HexaBBz in 32 sewage sludge samples from Baden-Wuerttemberg (Southwest Germany).

2. Concentration of chlorinated benzenes

Penta- and hexachlorobenzene were measured for comparison. Both substances are not produced for commercial purpose to date. HexaCBz was industrially produced and commercially used as bulk chemical e.g. as fungicide, wood preservative and for military pyrotechnic smoke[8] and remains in the environment due to its persistency. In addition, both substances are still emitted from industrial sources and combustion sources as unintentionally formed products.

The concentration of these chlorobenzenes in the sewage samples analysed for this study can be described as homogeneous background concentration below 10 µg/kg without peak values (Table 1).

3. Concentration of phenolic flame retardants

The prime phenolic flame retardant TBBPA was detected in all samples with an average concentration of 16.2 µg/kg and a maximum concentration of 62.2 µg/kg.

Pentabromophenol was detected in 20 of the 32 samples with an average concentration of 35.6 µg/kg and a peak value of 870 µg/kg. The significant variation in the concentration and the distinct peak value suggests their origin from point sources in industrial application (e.g. end capping of certain polymers).

2,4-DiBP, an endocrine disrupting substance with estrogenic potential[7], was detected in 27 of the 32 samples with several distinct peak values in some of the samples and a maximum concentration of 2700 µg/kg (Table 1).

4. Concentration of brominated diphenylethers (PBDE)

The sewage sludge samples were also analysed for polybrominated diphenylethers (tri to hepta). All 32 samples contained measurable amounts of PBDE in the range of 44.6 and 461.4 µg/kg with an average value of 133 µg/kg and a median concentration of 112 µg/kg (table 1). Therefore, the average concentration of sum of bromobenzenes was 4 times higher compared to the sum of PBDEs. Also, the average concentration of the sum of PBP or 2,4-DBP were higher compared to the average total PBDE concentration. This indicates the relevance of the contemporary use and release of these monoaromatic BFR into the (German) environment.

Conclusions

Brominated benzenes and brominated phenols were detectable in sewage sludge samples in Germany. The peak values of HexaBBz (2470 µg/kg), PentaBP (870 µg/kg) and 2,4-DiBP (2700 µg/kg) in some municipal sewage sludge plants receiving also sewage from industries suggests that point sources from industry exist for these substances. The study indicates that HexaBBz and 2,4-DiBP (and with a lower emphasize PentaBP) are produced and used as industrial bulk chemical today and emitted in large scale into the environment. The presence of HexaBBz in all 32 sewage sludge samples implies additionally a diffuse background contamination.

It has to be emphasized that the average concentration of HexaBBz was ca. 30 times higher (median concentration 7 times higher) compared to the chlorinated analogue HexaCBz, which is listed as priority substance in the water frame guideline of the European Union[8] and included in the POPs list of the Stockholm convention[4]. HexaBBz and PentaBP are already included in the OSPAR list of substances of possible concern (assigned high bio concentration factors and data raising concern in respect to their toxicological potential)[2]. It would be reasonable that the brominated analogues of banned chlorinated organics, which are used and emitted in bulk concentrations, need a prompt evaluation regarding their persistent, bioaccumulating and toxic potential providing a base for sustainable decisions regarding production and use.

References

1) Danish Environmental Protection Agency, (1999). Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives. Kopenhagen, Denmark.

2) OSPAR Convention (1992). Convention for the Protection of the Marine Environment of the North-East Atlantic, http://www.ospar.org/eng/html/welcome.html, access 05 May 2005.

3) Stockholm Convention on Persistent Organic Pollutants (2001). http://www.pops.int/. Access 05 May 2005.

4) Yamaguchi Y., Kawano M., Tatsukawa, Moriwaki S. (1988) Chemosphere 17: 703-707.

5) International programme on chemical savety (IPCS) (1997) Environmental Health Criteria**(**EHC) 192: Flame Retardants: A General Introduction, World Health Organisation, Geneva, Switzerland **. http://www.inchem.org/documents/ehc/ehc/ehc192.htm.**

6) Hagenmaier H., She J. (1992) Chemosphere 25: 1457-1462.

7) Umweltbundesamt (Ed.) (1997): Substanzen mit endokriner Wirkung in Oberflächengewässern. UBA-Texte 46/97, Berlin, Germany.

8) Bailey R. E. (2001) Chemosphere 43: 167-182.

9**) European Parliament (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000.**http://europa.eu.int/comm/environment/water/water-framework/priority_substances.htm access 05 May 2005.

Table 1: Concentrations of PBBz, PCBz, PBDE and some phenolic flame retardants in 32 sewage sludge samples from Baden Wuerttemberg (Southwest Germany).

(µg/kg dry matter; n.d.: not detected).

Substance group	Substance	Positive samples	Median	Average	Minimum	Maximum
PBDE	Sum PBDE (tri to hepta)	32/32	112.0	133.0	44.7	461.4
Bromobenzene	Tribromobenzene	14/32	-	4.0	n.d.	61.3
	Tetrabromobenzene	31/32	2.6	28.2	n.d.	189.2
	Pentabromobenzene	31/32	7.4	46.1	n.d.	339.0
	Hexabromobenzene	32/32	54.6	329.4	4.5	2468.4
Chlorobenzene	Pentachlorobenzene	30/32	0.8	1.1	n.d.	5.1
	Hexachlorobenzene	31/32	7.9	9.3	n.d.	38.6
Phenolic flame retardants	2,4-Dibromophenol	27/32	70	365.2	n.d.	2700
	Pentabromophenol	20/32	5.6	35.6	n.d.	870.0
	Tetrabromobisphenol A	32/32	6.7	16.2	0.6	62.2