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Polybrominated flame retardants in sewage sludge and sediments (review)

Polibromowane środki obniżające palność w osadach ściekowych i dennych (przegląd)

Abstract

This paper is a wide review of literature concerning the presence of flame retardants in sediments, treated wastewater, sewage sludge and the possibilities of their biodegradation. These compounds are widely applied in, for example, the textile and electronics industries. Flame retardants (FRs) are hydrophobic with very low solubility in water; however, they are released slowly during the washing of clothing, and as a result of the discarding of waste electronic products, etc. FRs show low mobility in the environment and can accumulate in wastewater, sewage sludge, in sediments in the beds of rivers and lakes, and in soil. Total concentrations of polybrominated diphenyl ethers (PBDEs) ranged from 0.59 to 48.000 ng/g d.w and decaBDE (BDE 209) concentrations from 0.4 to 47,400 ng/g d.w. BDE 209 dominated the congener profile.

Keywords: PBDE, FRs, wastewater treatment plant, WWTP, sewage sludge, sediments

Streszczenie

W artykule przedstawiono przegląd literatury dotyczący występowania związków obniżających palność w osadach dennych, ściekach i osadach ściekowych oraz możliwości ich biodegradacji. Związki te są szeroko stosowane, np. w przemyśle tekstylnym i elektronicznym. Środki uniepalniające są substancjami hydrofobowymi o bardzo niskiej rozpuszczalności w wodzie, jednakże są powoli uwalniane podczas prania odzieży lub wymywane ze składowisk odpadów. Wykazują dość niską mobilność w środowisku i mogą kumulować się w osadach ściekowych, osadach dennych rzek i jezior oraz w glebie. Stężenia opisywanych polibromowanych eterów difenylowych (PBDEs) wynosiły od 0,59 do 48,000 ng/g suchej masy, a stężenia decaBDE (BDE 209) wynosiły 0.4–47,400 ng/g s.m. BDE 209 zdominował profil kongenerów.

Słowa kluczowe: PBDE, środki obniżające palność, oczyszczalnia ścieków, osady ściekowe, osady denne

1. Introduction

In recent decades, most of the attention related to persistent organic pollutant (POP) monitoring has focused on the release of these chemicals resulting from production, use and their environmental occurrence. Contemporary studies have shown that wastewater treatment plants (WWTPs), which treat waste primarily from domestic and industrial origins, are sources of POPs and require further investigation with regards to their overall contribution to the contaminant burden on the environment [9, 44]. Widely available consumer products containing these compounds can end up becoming a source of these contaminants. This is the case for flame retardants (FRs) which are chemicals added to an extensive variety of manufactured items in order to inhibit or delay combustion processes [63]. To date, at least seventy-five different brominated flame retardants (BFRs) [2] have been commercially produced. So far, studies have been primarily focused on three groups: polybrominated diphenyl ethers and biphenyls (PBDEs and PBBs); hexabromocyclododecanes (HBCDs); tetrabromobisphenol A (TBBP-A) [9]. The structures of selected organic pollutants are presented in Fig. 1.

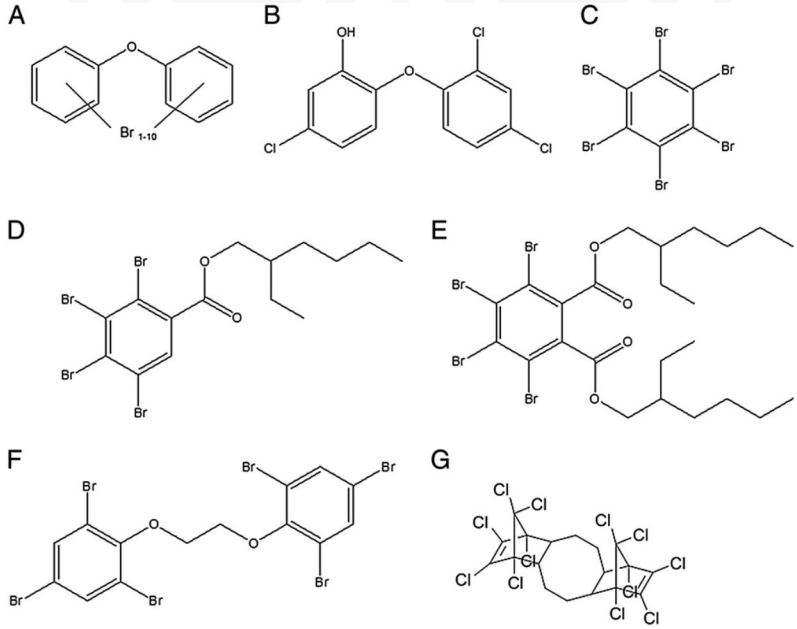

Fig. 1. Structures of (A) PBDEs, (B) triclosan, (C) HBB, (D) TBB, (E) TBPH, (F) BTBPE, and (G) DP [12]

Hexabromocyclododecane (HBCD) is used as a flame retardant mainly in building insulation composed of extruded or expanded polystyrene foam (over 85% of total volume) and some minor uses as backings of upholstery textiles [12]. Since HBCD is used as a flame retardant in several applications, it has the potential for release into the environment from production processes and from the disposal of products containing fire retardants. These

compounds are very hydrophobic and have been reported to be persistent in the environment [3]. With increased regulatory attention directed towards elimination or reduction of discharges, and emissions and losses of organic compounds, it is important that we have a good understanding of the environmental fate and lifetime of HBCD. Moreover, HBCD is listed as a priority substance under the EU Existing Substance Regulations (793/93/EEC) and is currently undergoing a risk assessment in the EU [14]. In the early 1990s, decabromodiphenyl ethane (deBDethane) was introduced as an alternative to its polybrominated diphenyl ether (PBDE) analogue, decabromodiphenyl ether (decaBDE). Over the past twenty years, PBDEs have been shown to be ubiquitously present and persistent in the environment.

2. Biodegradation

Reductive debromination of TBBPA was shown to occur under anaerobic conditions in sediments. In the year 2000, Ronen & Abeliovich observed the degradation of more than 90% of the initially present TBBPA within fifteen days [57]. Voordeckers et al. [65] reported rapid degradation of TBBPA after a duration of sixty days under methanogenic conditions. In both experiments, TBBPA was fully debrominated into bisphenol A (BPA), a well-known estrogenic compound. Depending on the conditions, TBBPA can be biotransformed into BPA (reductive debromination in anaerobic conditions) or TBBPA DME (dimethyl ether) and TBBPA monomethyl ether (O-methylation in aerobic conditions) [41]; however, recent studies have demonstrated a low mineralisation potential for TBBPA in anaerobic digester sludge, soils and freshwater sediments [40]. Mono-, di-, and tri-brominated bisphenol A were identified as intermediate products in an anaerobic batch reactor [4]. The rapid anaerobic degradation of a technical HBCD mixture has also been reported [13, 28]. Products of degradation were not identified and enantioselective degradation of HBCD stereoisomers was not addressed in these studies. No significant degradation of DecaBDE was observed by Schaefer and Flaggs [21] in an anaerobic sediment within thirty-two weeks. Additionally, studies in China have indicated limited bioaccessibility of PBDEs in sewage sludge based on their low desorption rate [43]. In contrast to these findings, Gerecke found that, in fact, DecaBDE slowly degrades under anaerobic condition in sewage sludge [21]. He observed a ecrease of the DecaBDE concentration with a corresponding pseudo-first order degradation rate constant of 1×10^{-3} $d^{-1.}$ Reductive dehalogenation was indicated by the formation of octa- and nona-bromodiphenyl ether congeners. Gerecke et al. [20] suggested that pseudo-first-order degradation rate constants decreased according to the following sequence: TBBPA $\cong$ (±)-γ-HBCD $\cong$ (±)-β-HBCD > (±)-α-HBCD >> DecaBDE. DecaBDE ($\log K_{ow}$ ~10), this is certainly more hydrophobic than the other compounds investigated (HBCD $\log Ko_{w}$ ~ 6, TBBPA $\log K_{ow}$ ~ 6). Therefore, free concentrations of DecaBDE in aqueous environments will be lower than those of TBBPA and HBCD, and this very low free concentration of DecaBDE might be a rate-limiting factor for the biologically mediated transformation of DecaBDE.

Reductive debromination of BDE-209 in the environment could constitute a significant source of lesser-brominated PBDEs to biota. A more recent study [62] showed that BDE-

209 debrominates in sewage sludge and another demonstrated that some halorespiring bacteria will debrominate BDE-209. To determine whether the reductive debromination of BDE-209 occurs in sediments, parallel experiments were conducted using anaerobic sediment microcosms. In the biological system, reductive debromination occurred at rates corresponding to bromine substitution levels with a BDE-209 half-life of only eighteen seconds in comparison with a half-life of almost sixty days for 2,2′,4,4′-tetrabromodiphenyl ether. In sediment, the measured debromination half-life of BDE-209 was well over a decade – this strongly agreed with the predicted value obtained from the biological experiment. Product congeners were predominantly double para-substitute. BDE-209 debrominated in sediment with a corresponding increase in nona-, octa-, hepta-, and hexa-PBDEs. Nine new PBDE congeners appeared in sediment from reductive debromination; furthermore, there is evidence for the debromination of PBDEs that occur in aquatic biota [35].

Less brominated congeners, such as penta- and tetra-BDEs, are more toxic and have higher bioavailability than more highly brominated congeners, such as octa-BDEs [46, 47]. It is therefore important to understand the dominant debromination pathways in order to predict the likely congeners produced from the transformation of environmentally prevalent PBDEs [54]. According to Rodenburg et al. [55], the location of degradation is also very important. If microbial debromination occurs in sediments, then, in the long run, PBDEs will be less persistent and will have a lower tendency to accumulate in sediments. If debromination occurs in sewers, then products of debromination could accumulate more easily in sediments and be problematic in the future – this is consistent with studies conducted by La Guardia et al. [36], who stated that PBDE 47 has a greater biota-sediment accumulation factor than PBDE 209 and could result in greater bioaccumulation of PBDEs in some organisms. Stiborova et al. [60] investigated the potential of autochthonous microflora for the removal of PBDEs and HBCDs in sludge under anaerobic conditions for fifteen months (Table 1). HBCDs were degraded to below detection limits after three months of incubation. The higher brominated congeners were removed faster than those which were lower brominated; however, there was a significant increase in tetra-brominated BDE-49. This implies that degradation of predominant BDE-209 could result in increased concentrations of more toxic lower brominated PBDEs. The initial concentrations of PBDE's and HBCD's are provided in Table 1 [60].

Table 1. The initial concentration of individual PBDE congeners and HBCD and their percentage residues after fifteen months of degradation [60]

Congener	Hradec Kralove		Brno	
	Initial concentration [ng/g d.w.]	PBDEs residue [%]	Initial concentration [ng/g d.w.]	PBDEs residue [%]
Tri-BDE-28	7.9 ± 0.1	Not detected	2.2 ± 0.1	Not detected
Tetra-BDE-47	216.6 ± 1.7	57.9 ± 8.8	54.2 ± 1.6	80.7 ± 14.8
Tetra-BDE-49	18.2 ± 0.5	240.3 ± 35.9	9.6 ± 0.4	249.7 ± 18.2

Tetra-BDE-66	11.2 ± 0.1	62.1 ± 6.6	4.8 ± 0.9	58.6 ± 2.0
Penta-BDE-85	17.5 ± 0.2	107.3 ± 23.7	7.5 ± 0.1	138.3 ± 60.2
Penta-BDE-99	208.8 ± 2.1	57.3 ± 4.7	57.0 ± 1.5	60.9 ± 15.9
Penta-BDE-100	55.3 ± 1.0	81.5 ± 6.9	17.2 ± 1.1	47.6 ± 1.9
Hexa-BDE-153	23.3 ± 0.5	54.5 ± 2.1	12.9 ± 0.1	0.9 ± 1.3
Hexa-BDE-154	22.2 ± 0.1	51.6 ± 4.2	12.8 ± 0.1	23.2 ± 2.2
Hepta-BDE-183	24.3 ± 0.7	17.8 ± 2.2	27.1 ± 0.5	17.7 ± 1.2
Deca-BDE-209	685.3 ± 25.7	42.5 ± 8.5	1402.6 ± 44.6	26.5 ± 1.2
Tetra-BDEs	246.0 ± 1.3	73.9 ± 10.7	68.6 ± 0.1	102.8 ± 12.5
Penta-BDEs	281.6 ± 1.9	65.2 ± 7.3	81.7 ± 1.9	65.2 ± 3.1
Hexa+hepta-BDEs	69.8 ± 0.1	40.8 ± 1.6	52.8 ± 0.3	14.9 ± 0.3
Σ10 BDEs	605.3 ± 5.6	64.1 ± 7.4	205.3 ± 2.6	64.1 ± 3.2
Σ11 PBDEs	1290.6 ± 20.1	52.6 ± 8.0	1607.9 ± 47.1	31.3 ± 1.3
HBCD	23.9 ± 0.9	Not detected	19.6 ± 1.2	Not detected

3. Flame retardants in sewage sludge and sediments

While the use of FRs may spare lives and reduce material damage costs incurred during fires, these compounds are able to leach out of products and find their way into the environment, in particular, via WWTPs. Being largely lipophilic, organic FRs are predisposed to binding to lipid-rich sewage sludge once in the WWTP stream. Mass balance calculations of the widely-used flame retardant, polybrominated diphenyl ethers (PBDEs), concluded that 96% are sorbed to sewage sludge [63]. In 2007, Knoth analysed sewage sludge from eleven municipal wastewater treatment plants in Germany. Samples were collected from WWTP of the Rhine-Main in Germany from March 2002 to June 2003. Knoth observed no significant change to the congeners' profile (% of total BDE 28,47,99,153,154 without 209) in sludge sample from different stages of the wastewater treatment process (primary sludge, secondary excess sludge and digested sludge) indicating a degradation of DeBDE for these congeners [33]. The data from this experiment is presented in Table 2.

The highest levels of decaBDE were found in the USA and the United Kingdom, these levels were up to 19,000 and 12.000 ng/g d.w., respectively. Findings in the USA are unsurprising considering that they had the world's highest market demand for decaBDE in 2001 [37]. The per capita market demand for decaBDE in the United Kingdom was suggested to be in line with that of North America due to the UK's history of restrictive fire regulations [25]. It was in samples from the UK that Harrad et al. [25] found the highest ever recorded decaBDE levels in domestic or office dust, these levels were 520.000 and 100.000 ng/g on a dry weight basis. Relatively high decaBDE levels were also found in one sample from New

Zealand and in one sample from China (9500 and 3300 ng/g d.w., respectively). Wang et al. [67] reported decaBDE levels between <LOD and 1108 ng/g d.w. in sludge from thirty-one WWTPs in China. A lot of the Asian production of decaBDE takes place in eastern China [66], this is where both of the Chinese samples in the presented data set originate. In Table 3, the concentrations of FRs in sediments are given.

Table 2. Concentrations of significant PBDE in sewage sludge from different stages of the wastewater treatment process [33]

WWTP/population equivalent	Sludge	Concentration [ng/g d.w.]	
		DeBDE 209	ΣCongeners 28–209
45,000 (3)	**Primary sludge**	169–225	242–281
	Digested sludge	193–354	269–450
	Dewatered digested sludge	135–450	221–558
48,000 (1)	**Primary sludge**	256	494
	Secondary excess sludge	341	569
	Digested sludge	690	960
	Dewatered digested sludge	556	781
50,000 (1)	**Primary sludge**	1895	2104
	Secondary excess sludge	2217	2491
	Digested sludge	1339	1627
63,500 (1)	**Primary sludge**	239	328
	Secondary excess sludge	234	321
	Digested sludge	605	699
	Dewatered digested sludge	417	523
75,000 (2)	**Primary sludge**	169–217	182–266
	Secondary excess sludge	182	294
	Digested sludge	411–1141	520–1261
	Dewatered digested sludge	204–340	280–452
240,000 (1)	**Primary sludge**	199	234
	Secondary excess sludge	334–486	466–640
	Digested sludge	393	537
350,000 (1)	**Primary sludge**	97.1	142
	Secondary excess sludge	206–220	352–437
	Digested sludge	217	266
1,820,000 (1)	**Primary sludge**	209	305
	Secondary excess sludge	182	264
	Dewatered digested sludge	133	186

Table 3. Concentrations in ng/g of dry weight (min–max or max) of flame retardants in sediments

Compound	Concentration in ng/g d.w.		References	
	Sewage sludge	Sediments	Sewage sludge	Sediments
BDE-17	0.89–42.2	–	[12, 38, 64]	–
BDE-28	0.2–73	–	[12, 34, 38, 49 , 64]	–
BDE-47	0.81–1133	0.031–62.3	[5, 12, 15, 34, 38–39 , 49, 56, 64]	[5, 10 , 11, 29, 50]
BDE-49	0.6–62	0.020–0.053	[34, 64]	[29]
BDE-66	0.2–26.1	–	[12, 34, 38, 64]	–
BDE-85	0.12–57	0.016–0.151	[12 , 34, 38, 64]	[29]
BDE-99	1.17–1510	0.022–59	[5, 12, 15, 34, 38–39, 49, 56, 64]	[5, 10, 11, 29, 50]
BDE-100	0.8–311	0.014–0.241	[5, 12, 15, 34, 38, 39, 49, 64]	[5, 29]
BDE-153	0.06–145	0.01–2.18	[5, 12, 15, 34, 38–39, 49, 64]	[5, 29]
BDE-154	0.08–128	0.016–4.29	[5, 12, 15, 34, 38–39, 49, 64]	[5, 29]
BDE-183	0.3–32.6	0.01–9.14	[12, 34, 38, 39, 56, 64]	[5, 29]
BDE-196	0.2–18.1	0.212–0.549	[38–39]	[29]
BDE-197	0.4–19.9	0.132–0.259	[38–39]	[29]
BDE-203	0.2–59.2	0.153–0.577	[38–39]	[29]
BDE-206	12–1420	0.440–7.93	[12, 38, 64]	[29]
BDE-207	6.43–1430	0.060–1.64	[12, 38, 64]	[29]
BDE-208	7–965	–	[12, 64]	–
BDE-209	0.54–47400	0.03–970	[5, 12, 15, 17, 22, 24, 30, [33 –34, 38, 39, 56, 64]	[5, 10 –11, 29, 30, 50, 71, 72]
Σ PBDEs	0.59–48000	0.36–910	[12, 17, 22, 24, 30, [33, 38, 63]	[5, 7, 11, 30, 32, 50, 72]
TBBPA	0.016–76	0.06–127	[15, 39]	[29, 61]
BPA	262–3590	4.5–100	[23]	[23]
Σ HBCD	0.008–9120	0.005–9.4	[15, 30, 45, 51, 68, 69]	[18, 30, 32, 50, 72]
α-HBCD	0.003–358	0.04–3.9	[30, 39]	[29 –30, 32]
γ-HBCD	0.009–26	0.04–1.95	[30, 39]	[29 –30, 32]
γ-HBCD	0.005–9.3	0.005–38.4	[30, 39]	[29 –30, 32]

Ricklund et al. [52] also detected DBDPE in sewage sludge from all forty-two WWTPs studied in twelve countries worldwide, suggesting that DBDPE is a widespread contaminant, in Europe at least. The highest concentration observed (216 ng/g d.w.) was in a sample from the Ruhr area of Germany. BTBPE, DBDPE and TBBPA-DBPE were determined in sewage sludge samples from southern China [59]. Maximum concentrations of these compounds were 1.7 ng/g, 2000 ng/g and 8950 ng/g d.w., respectively. The high concentrations of DBDPE and TBBPA-DBPE are consistent with their use in the electronics industry in the Pearls' River Delta (PRD) region of China. Primary sludge samples from South Africa contained HBCD (10.69–133.16 ng/g d.w.), TBBPA (19.24 ng/g d.w.) and polybrominated biphenyls – PBB-18, PBB-49 and PBB-101 (14.717, 3.94–15.32 and 14.01–87.96 ng/g d.w., respectively) [8]. Sewage sludge samples collected from the city of Guangzhou in southern China in 2007 had BTBPE concentrations ranging from 0.31 to 1.66 ng/g d.w. with a mean of 0.88 ng/g d.w. [59]. The concentrations of PBDEs in sludge in this study are generally lower than those reported in studies around the world (see Table 3). Hale et al. for example, reported concentrations ranging from 1100 and 2290 μg/kg for samples collected from 11 wastewater treatment plants from four regions in the United States [24]. In another study, North reported similar concentrations with values ranging from 1918 to 2086 μg/kg [48] for sludge samples collected from wastewater treatment plants in Palo Alto, California. In European countries, the levels of PBDEs in sludge from municipal sources are much lower than those in North America by almost one order of magnitude. Sellstrom et al. [58] reported PBDEs in sludge from three sewage treatment plants from Sweden ranging from 140 to 350 μg/kg whereas that reported by Hellstrom [26] were between 8.5 and 275 μg/kg for fourteen wastewater treatment plants also from Sweden. Slightly higher values were reported by Fabrellas et al. [17] in samples collected from six wastewater treatment plants in Spain ranging from 844 to 5939 μg/kg. One of the plants receiving wastewater from an industrial area manufacturing textiles had PBDE sludge concentrations as high as 18146 μg/kg [17].

4. Level of deBDethane

The level of deBDethane found in Germany is at 220 ng/g d.w., the highest so far reported in literature. This is higher than the mean levels for the European samples (81 ng/g d.w.) and the North American samples (31 ng/g d.w.) by factors of 2.7 and 7.0, respectively. The WWTP is located in a highly industrial area (the Ruhr Region) of Germany. According to the sampling protocol, the WWTP receives water from the automobile industry – the automobile industry is a known user of BFRs [19]. There were 3 other samples from the Ruhr Area containing deBDethane levels of 121, 74 and 70 ng/g d.w. Two of these were also among the ten highest in this study. The other eight came from Switzerland, the Czech Republic, China, Singapore, and the USA. There was no information in the sampling protocols suggesting particular industrial sources. However, Germany was reported to account for a majority of the total import of deBDethane into Europe in 2001 [31, 52]. The high levels in sludge from Germany as well as Switzerland and the Czech Republic, which both have close economic

ties to Germany, are consistent with high imports of goods containing FRs'. Unfortunately, more information on the import of deBDethane to the countries studied was not found [52].

Two other studies have reported the presence of deBDethane in sewage sludge. In sludge from eight Spanish WWTPs, deBDethane levels ranged between 0.2 and 15 ng/g d.w. [16], while in ten Canadian sludges, these levels were between 6 and 30 ng/g d.w. [42]. The levels in the Spanish sludge were more than five times lower than the European mean in this study, while the levels from Canada presented by McCrindle et al. [42] were in the same range as the Canadian mean for this study [9].

5. Conclusions

Sewage treatment methods have been evaluated and the results indicate that using the biological N and P elimination treatment method can contribute to the decrease of flame retardant concentrations in sludge. BFR (PBDEs and DP) concentrations correlate with levels of industrial contributions to the wastewater stream. This implies that the release of these compounds is related to industrial activity, likely stemming from the use of the technical product during the manufacture of consumer goods. However, use and disposal of products containing PBDEs could not be dismissed. There is a potential for the bioaccumulation of this class of chemicals from sludge treated soils in food chains, thereby contributing to wildlife and human exposure to these chemicals. Therefore, new methods of bioremediation, such as the usage of spent mushroom compost which shows high TBBPA removal efficiency [70], should be considered.

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