ENVIRONMENTAL DEBROMINATION OF DECABROMINATED DIPHENYL ETHER

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Introduction

Increasing concentrations of polybrominated diphenyl ethers (PBDEs) in the environment have been recognized as a human and ecological health concern. Nonetheless identification of the major routes of release of PBDEs into the environment is incomplete. To date, the majority of PBDEs detected in biota are congeners containing 6 or less bromines. However, the major commercial product in use is the Deca-formulation, containing >97% decabromodiphenyl ether (BDE209), by weight [1]. Some have explained this paradox by invoking a debromination argument. However, such a degradation route has not been confirmed under realistic environment conditions. Alternatively, PBDE distribution in aquatic biota may be related to differential bioavailability favoring the lower brominated PBDEs. PBDEs have previously been reported to accumulate in wastewater treatment plant (WWTP) sludge[2]. However, an un-retained portion of the PBDE burden has been previously reported entering the environment from the WWTP [3] effluent. Using EPA's Toxic Release Inventory (TRI), a plastics-related facility was identified which, releases significant amounts of Deca- to a WWTP. In an effort to explore the question of potential environmental debromination of Deca- we examined the distribution of tetra- through decaBDE congeners in WWTP influent and effluent, as well as surface waters, sediment and fish from the nearby receiving stream.

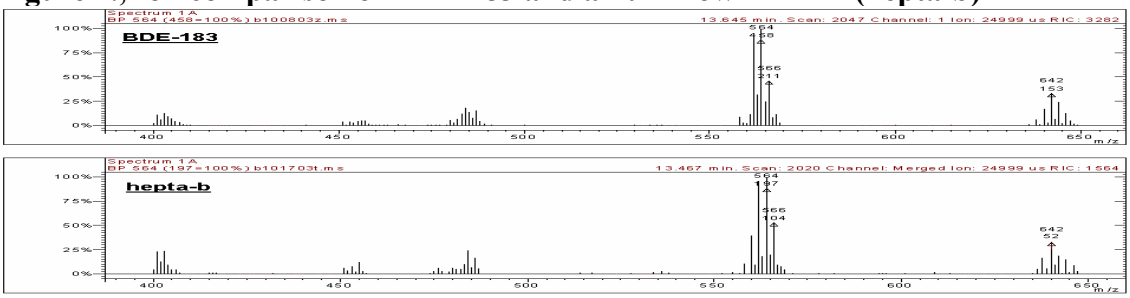
Materials and Method

For PBDE determinations, samples (10-g biota, 20-g sediment, dry wt.) were subjected to enhanced solvent extraction (Dionex ASE 200, Sunnyvale, CA), size exclusion chromatography (Envirosep-ABC®, 350 x 21.1 mm. column; Phenomenex, Torrance, CA) and then further fractionation using 2-g silica glass columns (Isolute, International Sorbent Technology, UK). Liquid samples, (WWTP effluent and receiving stream water, 4-L each) were sequentially extracted in separatory funnels, three times with dichloromethane, exchanged to hexane, and purified, by passage through 2-g silica (SPE) columns. PCB-204 (2,2', 3,4,4', 5,6,6'-octachlorobiphenyl) as a surrogate and decachlorodiphenyl ether as an internal standard were added.

Extracts and PBDEs standards were analyzed by gas chromatography (GC)/ mass spectrometry (MS) (Varian, Saturn 2000 GC/MS, Texas, USA) operated in the electron ionization (EI) mode, scanning from 400 to 650 m/z. From the EI-MS spectra of the standards, two ion clusters were observed with the highest overall intensities. These

clusters are centered on the molecular ion [M^+] and the molecular ion minus two-bromines ([M – 2Br]$^+$). The [M – 2Br]$^+$ ion, which had the highest overall intensity in each of the standards was chosen for quantification of the penta- through octa-BDEs, [M^+] for tetraBDEs. For the nona- and deca-BDEs the [M – 2Br]$^+$ ions exceeded the scan range of our GC/MS. Therefore, the [M – 3Br]$^+$, [M – 4Br]$^+$ and [M – 4Br]$^+$, [M – 5Br]$^+$ ions were chosen, respectively. PBDEs were identified in the samples by comparing relative retention times (RRTs) and ion fragmentation clusters of the analytical standards. The degree of bromination of each unknown was established based on their ion fragmentation compared to the analytical standards (Figure 1.).

Figure 1., Ion comparison of BDE-183 and an unknown PBDE (hepta-b)



The GC was equipped with a temperature programmable injector with a 0.5 mm glass injector liner and a DB-5HT (15 m, 0.1 μm film thickness, 0.25 mm ID) (J&W Sci., Folsom, CA) GC column. The injector was initially set at 60 ^oC and after a 1μL injection, held for 30 sec., ramped to 300 ^oC at 180-^oC/minute held for 25 minutes, ramped to 350 ^oC at 100 ^oC/minute held for 5 minutes, column flow 1 ml/min., helium. The GC temperature program: initial column setting 75 ^oC, hold two minutes, ramp at 10 ^oC/min, hold at 350 ^oC for 10 min., total run time 39.5 min. The transfer line set at 320 ^oC, EI ion source temperature 250 ^oC; electron energy was 70 eV and emission current 35 μA. PBDE standards along with unknown PBDEs are listed in elution order in Table 1.

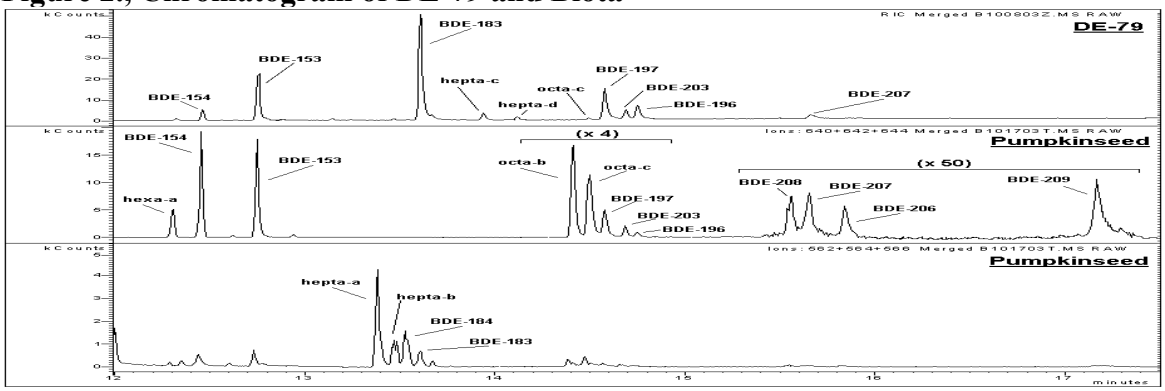
Results and Discussion

A greater than 90% reduction in PBDE concentrations was noted between influents and effluents (data not included). BDE47 and -99 were both detected in the effluent at 8 ng/L (Table 1.). Additional hexa- and nona-BDE congeners were also present. BDE209 was observed at 12,100 ng/L, in the final effluent. Near the outfall, the effluent-dominated receiving stream exhibited similar PBDE concentrations. In addition, BDE203 and -196 were detected at 3 and 2 ng/L, respectively. Sediment collected near the outfall contained BDE154, -153, -47, and -99, ranging from 137 to 1070 ng/kg (dry wt. basis), respectively (Table 1.). BDE209 was also detected in the sediment at 79, 900 ng/kg (dry wt.), along with three nona-BDEs (BDE208, -207 and -206) totaling 13,600-ng/kg (dry wt.). The three nona-BDEs contributed approximately 15% of the assumed total Deca-technical mixture detected in the sediment (Deca-mixture, >97% BDE209 and <3% nona-BDEs [1]). This exceeds the expected nona- contribution for Deca- by 12%, which may be explained

by preferential partitioning of BDE209 out of the waste-stream during the treatment process or debromination of BDE209.

Two fish species (mosquitofish *(Gambusia holbrooki)* and pumpkinseed *(Lepomis gibbosus))* were also collected at the outfall. After a 72-hour depuration period, a composite of each species was made and analyzed. Both fish contained tetra- through nona-BDEs (Table 1.). However, BDE209 was only detected in the pumpkinseed composite (492 µg/kg, % lipid basis, 12% lipid dry weight). In this fish BDE47 and –99 were the dominant congeners. Concentrations were 6530 and 7380 µg/kg (% lipid), respectively. Individual PBDEs concentrations in the pumpkinseed were generally five-fold higher than those in the mosquitofish. Most of the tetra- through hexa-BDEs detected in our fish samples have been previously reported by others [2]. However, by monitoring for ion fragments associated with the higher brominated PBDEs, we were able to establish the presence of additional congeners. These included four hexa-BDEs (BDE-66 and three unidentified hexa-BDEs (hexa-a, -b and -c)), four hepta-BDEs (BDE-183, -184 and two unidentified hepta-BDEs (hepta-a, -b)), and six octa-BDEs (BDE-197, -203, -196 and three unidentified octa-BDEs (octa-a, octa-b and octa-c)) and three nona-BDEs (BDE208, -207, -206). Some of the hepta- and octa-BDEs have been identified in the Octa-mixture (DE-79, Great Lakes, Chemical, USA) (Figure 2.).

Figure 2., Chromatogram of DE-79 and Biota



BDE183 (the major component of DE-79 (~ 44%, by weight [1])) was detected in the mosquitofish (70 µg/kg, % lipid, 34% lipid), but only a trace concentration (below quantification, < 1 µg/kg, % lipid) was observed in the pumpkinseed. BDE183 was not detected in the influent, effluent, stream or sediment samples. There were individual hepta- and octa-BDEs detected exceeding the –183 concentration in both biota samples. Preferential uptake of these potential trace components of the Octa-mixture cannot be ruled out. However, biological degradation of BDE183 to BDE154 and an unknown hexa-BDE in carp has been previously reported [4], which may partially explain the low levels of –183 detected in our samples.

BDE209 was detected in the effluent, stream, sediment and pumpkinseed samples. Metabolic debromination of -209 has been reported by others, resulting in the

accumulation of BDE155, –154 and five unknown penta- through octa-BDEs in carp [5] and BDE154, -153 and 12 unknown hepta- through nona-BDEs in trout [6], fed BDE209 amended food. Our findings indicate that PBDEs, including BDE209, released to waste streams, have the potential to enter the aquatic environment through WWTP effluent. These results also suggest that BDE209 released from the WWTP is to some extent bioavailable and may undergo metabolic debromination.

Table 1., Retention order and results

IUPAC and ID #s	Compounds	Effluent, ng/L	Stream, ng/L	Sediment, ng/kg (dry wt.)	Mosquitofish, µg/kg (% lipids)	Pumpkinseed, µg/kg (% lipids)
tetra-A	*tetra-BDE*	*nd*	*nd*	*nd*	*nd*	400
BDE-47	2,2', 4,4'-tetra-BDE	8	8	587	1640	6540
BDE-66	2,3', 4,4'-tetra-BDE	*nd*	*nd*	*nd*	40	713
BDE-100	2,2', 4,4', 6 –penta-BDE	*nd*	1	*nd*	427	2340
BDE-99	2,2', 4,4', 5 –penta-BDE	8	12	1070	1660	7380
BDE-85	2,2', 3', 4,4' –penta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
hexa-A	*hexa-BDE*	*nd*	*nd*	*nd*	191	216
BDE-154	2,2', 4,4', 5,6'-hexa-BDE	2	2	137	261	1090
hexa-B	*hexa-BDE*	*nd*	*nd*	*nd*	553	102
BDE-153	2,2', 4,4', 5,5'-hexa-BDE	2	3	213	232	1320
hexa-C	*hexa-BDE*	*nd*	*nd*	*nd*	*nd*	32
BDE-138	2,2', 3,4,4', 5'-hexa-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
hepta-A	*hepta-BDE*	*nd*	*nd*	*nd*	105	256
BDE-184	2,2', 3,4,4', 6,6'-hepta-BDE	*nd*	*nd*	*nd*	36	87
hepta-B	*hepta-BDE*	*nd*	*nd*	*nd*	53	80
BDE-183	2,2', 3,4,4', 5', 6-hepta-BDE	*nd*	*nd*	*nd*	70	*nd*
BDE-185	2,2', 3,4,5,5', 6-hepta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
BDE-192	2,3,3', 4,5,5', 6-hepta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
BDE-191	2,3,3,4,4', 5', 6-hepta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
octa-A	*octa-BDE*	*nd*	*nd*	*nd*	2	*nd*
BDE-181	2,2', 3,4,4', 5,6-hepta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
BDE-190	2,3,3', 4,4', 5,6-hepta-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
octa-B	*octa-BDE*	*nd*	*nd*	*nd*	78	428
octa-C	*octa-BDE*	*nd*	*nd*	*nd*	143	395
BDE-204	2,2', 3,4,4', 5,6,6'-octa-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
BDE-197	2,2', 3,3', 4,4', 6,6'-octa-BDE	*nd*	*nd*	*nd*	25	48
BDE-203	2,2', 3,4,4', 5,5', 6-octa-BDE	*nd*	3	*nd*	12	30
BDE-196	2,2', 3,3', 4,4', 5,6'-octa-BDE	*nd*	2	*nd*	*nd*	7
BDE-205	2,3,3', 4,4', 5,5', 6-octa-BDE	*nd*	*nd*	*nd*	*nd*	*nd*
BDE-208	2,2', 3,3', 4, 5,5', 6,6'-nona-BDE	*nd*	*nd*	402	8	75
BDE-207	2,2', 3,3', 4,4' 5,6,6'-nona-BDE	24	26	707	11	95
BDE-206	2,2', 3,3', 4,4', 5,5', 6-nona-BDE	311	405	12500	*nd*	75
BDE-209	deca-BDE	12100	10200	79900	*nd*	492

nd=not detected

References

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