OCCURRENCE OF PBDEs AND THEIR BROMINATED ALTERNATIVES IN SLUDGE FROM WASTEWATER TREATMENT PLANTS (WWTPs) IN KOREA

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Introduction

Brominated flame retardants (BFRs) are organobromine compounds that are widely used in various commercial applications to reduce the flammability of products. Polybrominated diphenyl ethers (PBDEs) are most widely used BFRs, which have been marketed as three commercial mixtures: pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE) and decabromodiphenyl ether (deca-BDE). Because of environmental and health concerns, the penta- and octa-BDE commercial mixtures were banned in Europe and the United States (US) from 2004[1,2]. PBDEs have not been produced in Korea, but are imported from various countries due to rapid growth of electronic markets. Deca-BDE commercial mixtures have been used as major BFRs[3]. Based on worldwide regulation and industrial demands, alternatives or replacements for PBDEs have been developed in recent years[4,5]. Among non-PBDE brominated flame retardants (NBFRs), decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) are most frequently detected in the environment such as sewage sludge[4,6,7], indoor dust[8], sediment[9] and biota samples[10]. And these chemicals can be released to the environment from consumer products and industrial usage. Sludge is an environmental media to reflect household and industrial usage of various chemicals and a secondary source of toxic substances produced from wastewater treatment plants (WWTPs). In 2011, there are about 500 WWTPs in Korea, the treating capacity of which was approximately 25.0 million tons/day[11]. These WWTPs produced approximately 3.0 million tons of sludge in 2011, which was released to the environment. Sludge can be the secondary sources of various contaminants by ocean dumping, incineration, landfills and bio-solids for agricultural land[12]. The deca-BDE and DBDPE are sequestered into the sludge (up to 99%)[13] due to their physicochemical properties such as high octanol-water partition coefficient (K_{ow}) and total organic carbon-water partition coefficient (K_{TOC})[14]. Therefore, sludge will be good media to elucidate consumer patterns of PBDEs and NBFRs. Although the occurrence of PBDEs and NBFRs is of an emerging concern in the environment, there is only a report on PBDEs in sludge from WWTPs in Korea[16]. In addition, no data is available on the occurrence of NBFRs in Korea. The objectives of this study were to determine the concentrations of PBDEs and NBFRs in sludge from three different types of WWTPs and to grasp consumer patterns of BFRs for Korean industry. To assess the environmental impact of these contaminants, the annual emission fluxes of PBDEs and NBFRs via WWTPs to the environment were estimated.

Materials and methods

Sludge samples were collected from three different types of WWTPs between July to October in 2011. Based on the regions (4 cities and 7 Provinces), watershed (4 rivers and 3 side-seas) and wastewater treating capacity, representative 40 WWTPs were selected. According to inflow rate of industrial wastewater, the WWTPs were divided into three types such as domestic, mixed and industrial types; 0% to 3% for domestic, from 20% to 60% for mixed and higher than 70% for industrial. Table 1 shows detailed information on the WWTPs including the influents sources, wastewater capacity, equivalent habitants and sludge production rate. To obtain a representative sludge sample from each WWTP, sample collection was performed during 3 days for each plant. The collected samples were well-mixed and then were poured into pre-cleaned polypropylene (PP) bottles. The samples were transported to the laboratory and stored in a freezer at –20ºC until extraction. Preparation and instrumental analyses of PBDEs and NBFRs in sludge samples were performed following the methods described elsewhere with some modification[3,4,6,9].

Results and discussion

Concentrations of PBDEs and NBFRs in sludge

The total concentrations of PBDEs (∑PBDE; the sum of 22 PBDE congeners), DBDPE and BTBPE in sludge samples from Korean WWTPs are summarized in Table 1. The concentrations of ∑PBDE ranged from 298 to 48000 ng/g dry weight (dw) with a mean value of 3240 ng/g dw. Among three different types of WWTPs, the highest concentrations of ∑PBDE were found at sludge samples from industrial-WWTPs (I-WWTPs; mean: 6000 ng/g dw), followed by mixed WWTPs (M-WWTPs; 2100 ng/g dw) and domestic-WWTPs (D-WWTPs; 1260 ng/g dw). Our finding indicates that PBDEs are largely using in industrial sector than domestic area. Among individual sludge samples, the highest concentrations of ∑PBDE were found at sludge from I-11 (48000 ng/g dw) and I-8 (21600 ng/g dw), which are located close to textile and paper industries. High levels of BDE 209 in WWTP influents are associated with textile industries[17]. High levels of PBDEs in sewage sludge from Spain are also associated with textile industries[18]. Our result suggests that textile and paper industry could be one of major contamination sources of PBDEs in Korean environment.

Table 2. Concentrations (ng/g dry weight) of PBDEs and their brominated alternatives in sludge samples from three different types of wastewater treatment plants (WWTPs) from Korea.

	D-WWTPs		M-WWTPs		I-WWTPs		Total	
	Average ± SD	Range	Average ± SD	Range	Average ± SD	Range	Average ± SD	Range
BDE 17	1.32 ± 2.06	<LOQ-7.70	0.22 ± 0.33	<LOQ-0.89	-	<LOQ	0.58 ± 1.43	<LOQ-7.70
BDE 28	1.24 ± 0.63	0.26-2.19	0.68 ± 0.91	<LOQ-2.97	0.17 ± 0.36	<LOQ-1.23	0.71 ± 0.77	<LOQ-2.97
BDE 47	10.2 ± 14.0	0.81-61.8	3.84 ± 1.87	2.45-7.84	2.15 ± .20	<LOQ-16.8	5.74 ± 9.81	<LOQ-61.8
BDE 66	1.05 ± 0.97	<LOQ-3.48	0.41 ± 0.43	<LOQ-1.21	0.53 ± 0.44	<LOQ-1.56	0.71 ± 0.74	<LOQ-3.48
BDE 71	0.68 ± 1.50	<LOQ-4.75	0.62 ± 0.96	<LOQ-2.33	-	<LOQ	0.41 ± 1.08	<LOQ-4.75
BDE 85	0.78 ± 1.76	<LOQ-7.36	0.28 ± 0.19	0.12-0.72	0.06 ± 0.13	<LOQ-0.48	0.40 ± 1.15	<LOQ-7.36
BDE 99	20.0 ± 34.5	1.39-148	9.38 ± 6.95	4.00-25.6	1.92 ± 3.51	<LOQ-13.4	10.8 ± 23.2	<LOQ-148
BDE 100	4.97 ± 10.0	0.28-42.3	1.82 ± 1.37	0.71-5.22	0.33 ± 0.39	<LOQ-1.05	2.52 ± 6.59	<LOQ-42.3
BDE 119	0.54 ± 0.83	<LOQ-3.01	0.04 ± 0.11	<LOQ-0.33	0.17 ± 0.31	<LOQ-0.84	0.29 ± 0.59	<LOQ-3.01
BDE 126	-	<LOQ	-	<LOQ	-	<LOQ	-	<LOQ
BDE 138	0.06 ± 0.24	<LOQ-0.97	-	<LOQ	-	<LOQ	0.02 ± 0.15	<LOQ-0.97
BDE 153	0.70 ± 0.94	0.06-4.15	0.42 ± 0.25	0.21-0.94	0.07 ± 0.10	<LOQ-0.26	0.40 ± 0.66	<LOQ-4.15
BDE 154	1.48 ± 3.11	0.08-13.1	0.63 ± 0.45	0.27-1.65	0.10 ± 0.13	<LOQ-0.36	0.77 ± 2.03	<LOQ-13.1
BDE 183	0.63 ± 0.85	<LOQ-2.56	9.81 ± 13.7	<LOQ-32.6	1.31 ± 3.84	<LOQ-14.9	2.95 ± 7.65	<LOQ-32.6
BDE 184	-	<LOQ	-	<LOQ	0.16 ± 0.62	<LOQ-2.40	0.06 ± 0.38	<LOQ-2.40
BDE 190	0.21 ± 0.58	<LOQ-2.09	-	<LOQ	0.17 ± .65	<LOQ-2.53	0.15 ± 0.54	<LOQ-2.53
BDE 191	-	<LOQ	-	<LOQ	0.06 ± 0.24	<LOQ-0.94	0.02 ± 0.15	<LOQ-0.94
BDE 196	3.49 ± 3.02	<LOQ-8.59	2.02 ± 6.05	<LOQ-18.1	1.88 ± 3.57	<LOQ-12.0	2.55 ± 4.03	<LOQ-18.1
BDE 197	2.60 ± 2.38	<LOQ-7.26	2.21 ± 6.64	<LOQ-19.9	0.91 ± 1.50	<LOQ-4.16	1.88 ± 3.55	<LOQ-19.9
BDE 206	30.1 ± 32.2	<LOQ-142	334 ± 230	98.8-727	70.4 ± 157	<LOQ-537	114 ± 187	<LOQ-727
BDE 207	24.5 ± 28.6	6.43-128	284 ± 142	90.1-498	29.8 ± 59.1	<LOQ-198	84.9 ± 132	<LOQ-498
BDE 209	1154 ± 430	596-2061	1442 ± 1076	782-3930	5931 ± 12640	296-47400	3010 ± 7932	296-47400
ΣPBDE	1259 ± 422	756-2169	2092 ± 1387	1066-5032	6041 ± 12860	298-48171	3240 ± 8048	298-48171
BTBPE	1.07 ± 0.51	0.48-1.98	3.45 ± 6.68	0.38-21.0	0.97 ± 1.61	<LOQ-5.25	1.57 ± 3.35	<LOQ-21.0
DBDPE	20.0 ± 24.8	<LOQ-89.2	29.3 ± 33.6	<LOQ-108	594 ± 865	<LOQ-3145	237 ± 589	<LOQ-3145
DBDPE/BDE209	0.02 ± 0.02	0.00-0.08	0.03 ± 0.04	0.00-0.13	0.45 ± 0.85	0.00-3.26	0.18 ± 0.55	0.00-3.26

Among 10 NBFR compounds, DBDPE and BTBPE were only detected in all the sludge samples, suggesting that DBDPE and BTBPE could be leading alternatives for NBFRs in BFR market. The concentrations of DBDPE and BTBPE ranged from <LOQ to 3100 (mean: 237) ng/g dw and from <LOQ to 21.0 (mean: 1.57) ng/g dw, respectively. The concentrations of DBDPE found in Korean sludge were two orders of magnitude higher than the BTBPE concentrations. This result may be related with the BFR market in Korea. The major demand for BFRs in Korea is deca-BDE commercial mixtures, and octa-BDE consumption is negligible. In fact, the mean BTBPE concentration in sludge from M-WWTPs (3.45 ng/g dw) was higher than those found in I-WWTPs (0.99 ng/g dw). Our result implies that BTBPE consumption seems to occupy a minor proportion as alternatives of BFRs in Korea. The highest concentration of DBDPE was found at sludge samples from I-WWTPs (mean: 594 ng/g dw), followed by M-WWTPs (29.3 ng/g dw) and D-WWTPs (20.0 ng/g dw). Although there was no difference in the concentrations of DBDPE in sludge between M- and D-WWPTs, significant differences ($p < 0.05$) were found in the concentrations of DBDPE between I-WWTPs and the other types of WWTPs. Among individual sludge samples, the higher concentrations of DBDPE were found at sludge from I-4 (3150 ng/g dw), I-8 (1360 ng/g dw), I-9 (1160 ng/g dw), I-14 (1100 ng/g dw) and I-5 (1070 ng/g dw). These plants are treating

wastewater influents associated with paper, semiconductor and polymerization industries, suggesting potential sources of DBDPE. Mean concentrations of ∑PBDE (3240 ng/g dw) in sludge measured in our study were similar to those reported for the USA, Italy and China, but were higher than the values reported from European countries such as Sweden, Germany, Switzerland and Spain. Only a Korean study showed higher mean ∑PBDE concentration (6907 ng/g dw) than that found in our study[16], because the samples were collected from WWTPs located in an industrialized region (Ulsan). In fact, the mean ∑PBDE concentration (6000 ng/g dw) from I-WWTPs in our study was similar to that reported in a previous Korean study[16]. Compare to PBDEs, limited studies have reported on the occurrence of NBFRs such as DBDPE and BTBPE in sludge from WWTPs worldwide. The mean BTBPE concentration (1.57 ng/g dw) in sludge from WWTPs in our study was similar to those reported for China[10] and Norway[14]. For comparison of DBDPE, the highest worldwide concentration of DBDPE (1183 ng/g dw) sludge has been reported in sludge from a WWTP near electronic waste (e-waste) in southern China[10]. With an exception of above, the mean DBDPE concentration (240 ng/g dw) measured in our study was 2–60 times higher than the concentrations reported for other countries such as Czech, USA, Spain, Switzerland, New Zealand, Canada, Germany, Singapore, South Africa, China, England and Norway[6,7,14,18]. Higher levels of DBDPE in sludge from Korean WWTPs indicate a widespread use of DBDPE as an alternative of BFRs and could be a great environmental concern. Further studies are needed to investigate environmental distribution of alternatives for BFRs in Korea.

Correlations between chemicals and WWTP characteristics

In this study, there were no significant correlations among the concentrations of ∑PBDE, DBDPE and BTBPE in sludge samples. However, significant correlations were found within lower brominated compounds such as BDEs 47, 99, 100, 153 and 154 (r = 0.966–0.998, $p < 0.001$) and higher brominated compounds such as BDEs 183, 206 and 207 (r = 0.660–0.937, $p < 0.001$). Deca-BDE was not correlated with any congeners of PBDEs and their alternatives. Interestingly, BTBPE was significantly correlated with BDEs 183, 206 and 207 (r = .492–0.605, $p < 0.05$), which are characterized by major congeners of octa-BDE technical mixtures such as DE-79 and Bromkal 79-5DE[20]. This result suggests that octa-BDE commercial mixtures and BTBPE have a similar source and/or behavior during WWTP processes. No significant correlations were found between PBDEs/NBFRs and WWTP characteristics such as capacity, equivalent habitants and inflow rate of industrial wastewater in sludge, with an exception for between ∑PBDE concentrations and inflow rate of industrial wastewater from D- and M-WWTPs (r = 0.453, p <0.05). Our results suggest that WWTP characteristics could not be indicative of the concentrations of PBDEs and NBFRs in sludge. Previous studies reported that concentrations of PBDEs and DBDPE in sludge were not correlated with WWTP characteristics[4,6,18,19].

Congener profiles and potential sources of PBDEs and NBFRs

The relative contributions of the 22 PBDE congeners to the total PBDE concentrations in sludge from WWTPs in Korea are presented in Figure 1. BDE 209 accounted for 89 ± 13% (mean ± standard deviation) of the total PBDE concentrations in all sludge samples. The next contributors were BDEs 206 and 207, which collectively accounted for 9.0 ± 10% of total PBDE concentrations. This profile is similar to the results for air, dust, water and sediment from Korea[3,15] and for sludge from other studies[16,19]. Our results confirmed that use of deca-BDE commercial mixture is a major source of PBDE contamination in Korea.

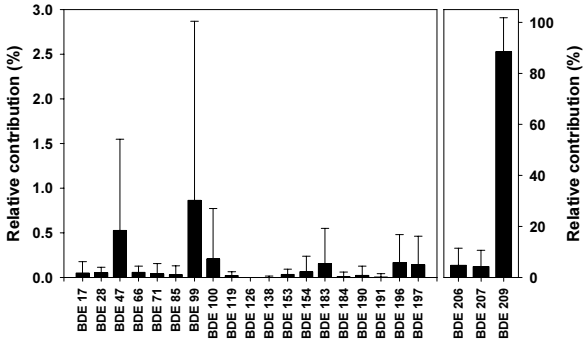

Figure 1. Average normalized congener profiles of PBDEs in sludge samples from wastewater treatment plants (WWTPs) in Korea. Whiskers on the bars represent standard deviations for each PBDE congeners.

The DBDPE/BDE 209 ratio has been used to assess the relative usage pattern for two BFRs[4,6], because the increase in use of DBDPE in BFR market will be resulted in decrease in deca-BDE commercial mixtures. The ratios of DBDPE/BDE 209 in all sludge samples for WWTPs in Korea were calculated to be 0.18 ± 0.55, reflecting still continuing use of deca-BDE commercial mixture. The DBDPE/BDE 209 ratios in sludge from I-WWTPs (on average 0.45) were about 10–20 times higher values than those calculated for M-WWTPs (0.03) and D-WWTPs (0.02). Our finding indicates industrial activities are major contamination source of DBDPE. In fact, higher values > 1 of DBDPE/BDE 209 were found in sludge from I-5 (3.26) and I-9 (1.26), which are located close to semiconductor and polymerization factories. This result is clear evidence for shift of usage pattern from deca-BDE mixture to DBDPE in BFR market of Korea.

Emission fluxes of PBDEs and NBFRs via WWTP sludge to the environment

To evaluate the environmental impact of PBDEs and NBFRs in Korea, the nationwide annual emission fluxes of PBDEs, DBDPE and BTBPE were calculated using total sludge production estimated in 2011. According to the report of Ministry of Environment of Korea, sludge produced from WWTPs in Korea was estimated to be approximately 3.0 million tonnes[11]. The estimated emission fluxes were 7400, 480, and 3.7 kg/year for ∑PBDE, DBDPE and BTBPE, respectively. The annual fluxes of PBDEs and DBDPE to the EU environment were estimated to be 16000 and 680 kg/year for PBDEs and DBDPE, respectively[6]. Gorga et al. (2013)[7] reported that the annual emission fluxes of PBDEs and DBDPE in sludge produced in Catalonia of Spain are estimated to be 57.8 and 6.76 kg/year, respectively. Considering the high levels of PBDEs and DBDPE in sludge from the present study, sludge could be acted as secondary source of PBDEs and NBFRs in the environment. Therefore, systematic monitoring and risk assessment programs for these contaminants should be instituted to protect the health of wildlife and humans in Korea.

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