DISTRIBUTION AND LEVELS OF BROMINATED DIPHENYL ETHERS IN SEWAGE SLUDGE IN ITALY

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Introduction

Brominated flame retardants, in particular brominated diphenyl ethers (BDEs), have become an increasing environmental concern because of their high lipophilicity, persistence, and resistance to degradation. Wastewater treatment plants (WWTP) are one source of BDEs to the environment through their discharge of treated effluent and land application of sewage sludge (Hale et al., 2001). BDEs are not used as individual compounds but rather as mixtures of congeners. The three mixtures used commercially are penta, octa and deca-BDEs (Hale et al., 2003; Hites, 2004). Penta and octa BDE mixtures have been phased out in Europe, but the deca-BDE mixture remains exempt from this regulatory activity (Sissell, 2004), suggesting that the release of its primary component, BDE-209, into the environment may continue at current rates for some years.

During the wastewater treatment, the main removal mechanisms of organic contaminants such as BDEs are sorption on sludge particles, degradation and volatilisation (Fauser et al., 2003). Hydrophobic contaminants such as BDEs, accumulate in sludge. Here we report the distribution and levels of BDEs in sewage sludge of three waste water treatment plants in Italy and compare the range of concentrations with those reported in other parts of the world. To our knowledge, this is the first report on levels of BDEs in sewage sludge in Italy.

Materials and methods

Sewage sludge samples were collected from 3 municipal WWTPs in the Tuscany Region of Italy from July 2007 to January 2008. According to type of influent stream and number of inhabitants, the investigated WWTPs were divided into different categories as shown in Table 1.

Table 1. Type of influent and number of inhabitants related to each facility evaluated.

WWTP	Type of influent	Number of inhabitants
A	Mixture	750000
B	Urban	600000
C	Mixture	160000

Mixture = urban and industrial influent

Sewage sludges were analysed following the method ISO/WD 22032 “Water quality-Determination of Polybrominated Diphenylethers in sediment and sewage sludge by extraction and GC-MS” (2002) with some modifications. Briefly, sludges were freeze dried and homogenized. An aliquot of 5 g of sample was spiked with BDE-77 (Wellington Laboratories) extracted in a Soxhlet extractor for 24 h using an acetone-hexane mixture. After extraction, about 15 g of acidic silica (30% w/w) was added to the extract to remove lipid. Then the extract was filtered through about 5 g of sodium sulphate, and 2 g of activated copper powder was added to the extract to remove elemental sulphur. The extract was rotary evaporated to about 1 ml and then cleaned up by passing through a multilayered silica gel column containing from bottom to top 2 g silica gel, 5 g silica gel /sodium hydroxide, 2 g silica gel, 10 g silica gel /sulphuric acid, 2 g silica gel, 5 g silica gel/silver nitrate, 10 g sodium sulphate. The column was conditioned by passing 50 ml of

dichloromethane and 50 ml of cyclohexane through it prior to the sample extracts. BDE congeners were eluted with cyclohexane and dichloromethane mixture (4:1 v/v). The BDE fractions were concentrated by rotary evaporation followed by evaporation under a gentle stream of purified nitrogen to final volumes of 500 µl. GC-NCI-MS analyses were performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network using selective ion monitoring (SIM), with methane as the reagent gas. The ions m/z 79 and 81 were monitored for for BDEs. An HP-5MS (30 m x 0.25 mm i.d., 0.25 um film thickness) containing 5% phenyl methyl siloxane capillary column was used. The temperature program was 50°C for 1 minute, ramped at 20°C min^{-1} to 130°C, and further ramped at 5°C min^{-1} to 300°C (held for 10 min) and finally ramped at 20°C min^{-1} to 251°C and held for 6 min. BDE-209 was analysed on a 15 m DB-5MS column (0.25 mm i.d. , 0.25 um film thickness) with the following oven program: 90°C for 1 min, ramped at 30°C min^{-1} to 220°C, 10°C min^{-1} to 300 °C, held for 8 min. The ions m/z 484.7 and 486.7 and 488.7 were used for identification of BDE-209. Solvents and reagents used were of analytical grade and tested for purity prior to use. A method blank sample was included in each batch of samples analyzed to monitor the contamination. The results showed all targeted BDEs in blanks were below the detection limit. Mean recoveries of BDE 77 were 79 ±11,2%. The reported concentrations were not corrected for recoveries. The limit of detection (LOD) ranged from 12 to 54 pg/g. For BDE-209 the LOD was 1.5 ng/g.

A total of eight BDE congeners were detected in samples and quantified. These are BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183 and BDE-209. Quantification was carried out with the external calibration standard method. Peaks were quantified only if the signal to noise exceeded 3.

Results and Discussion

Data on BDEs in sewage sludge from Italy are scarce. BDE concentrations for sludge samples collected from all three wastewater treatment plants are presented in Table 2.

Table 2. Mean concentrations ± SD of BDEs in sludge at various stages of the wastewater treatment process.

WWTP	Sewage Sludge	n	Concentration (ng/g d.w.)										
			#28	#47	#99	#100	#153	#154	#183	#99:#100	Total #28-183	#209	Total #28-209
A	PS[a]	6	0.8±0.3	23.4±8.8	39.8±9.8	6.8±1.9	9.9±2.1	7.4±2.0	3.3±0.8	85:15	91.4	29581±18119	29764
	SS[a]	4	0.7±0.2	26.8±19.7	38.1±13.8	6.7±2.3	9.2±3.8	7.0±3.1	4.5±2.4	85:15	93.0	21750±7792	21936
	DWSS[a]	3	0.9±0.4	49.4±37.3	47.4±35.7	5.6±3.6	8.9±5.6	7.5±5.4	5.5±2.1	89:11	125.2	3756±1184	4006
B	PS[a]	3	1.1±0.3	84.3±36.8	96.9±58.2	16.9±8.0	16.4±4.3	12.9±5.7	5.2±3.2	85:15	233.7	2477±1089	2944
	SS[a]	3	0.7±0.4	23.3±14.9	39.3±21.1	6.3±2.5	5.4±1.7	5.6±1.6	2.3±0.8	86:14	82.8	540±472	706
C	PS[a]	3	0.8±0.5	53.3±24.5	85.7±33.2	15.4±7.3	15.9±6.8	10.5±5.4	6.5±4.2	85:15	188.1	12457±7665	12833
	DWSS[a]	3	1.0±0.6	36.2±12.6	17.7±9.2	3.1±0.8	2.7±1.3	2.0±1.1	3.5±1.4	85:15	66.2	3801±998	3933

[a] Abbreviations are as follows: primary sludge (PS), secondary (activated) sludge (SS) and dewatered sludge (DWSS)

The Σ_7PBDE concentrations (excluding BDE209) ranged from 91.4 to 233 ng/g dry weight (d.w.). These concentrations are similar to those reported for sewage sludge from Europe, but lower than those for sludge samples collected in the United States (Gevao et al., 2007). In Figure 1 results are summarized as penta, octa and deca-BDE for discussion. Penta-BDE was calculated taking into account BDE 28, 47, 99, 100, 153 and 154, which represent the main congeners in the technical penta-BDE mixture (Bronkal 70-5DE), while octa-BDE according to the amount of BDE-183 in Bronkal 79-8DE as reported by La Guardia et al. (2006). Deca-BDE was assumed to correspond with the amount of BDE-209 which accounts for more that 90% of the compounds in deca technical products (La Guardia, 2006).

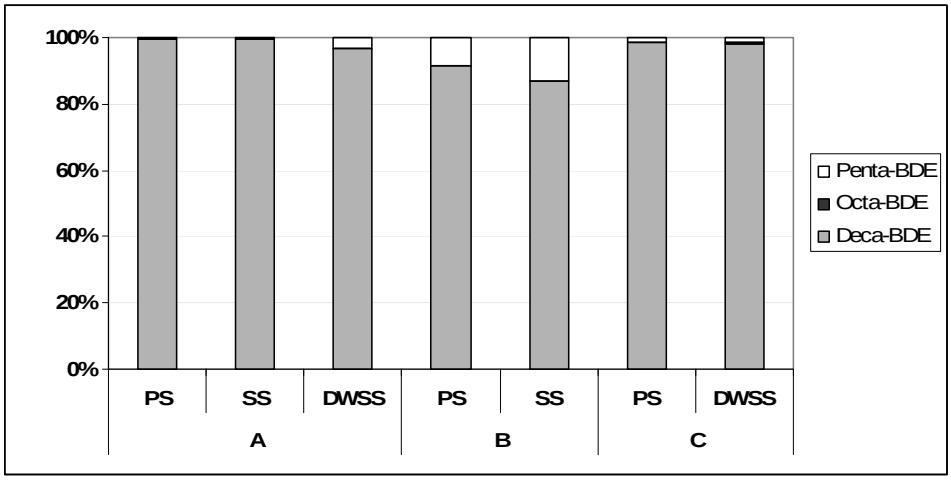

Figure 1. Contribution of commercial mixtures to the Σ_8BDE concentration measured in sewage sludge from different stages of three WWTPs in Italy. Abbreviations see Table 2.

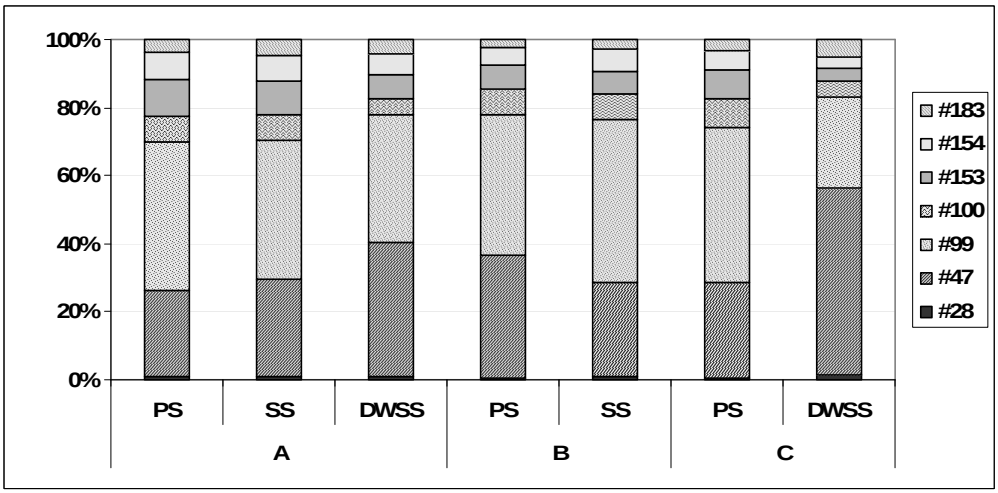

Figure 2. BDE 28-183 congener profile in sewage sludge from different stages of the waste water treatment process. Same data set as in Figure 1 without BDE 209. Abbreviations see Table 2.

BDE-209 was the dominant congener in all samples (see Figure 1), contributing between 86% and 99% of the total BDE. There were significant differences in BDE-209 concentrations between the investigated WWTPs. This result suggested that deca-BDE is the dominant technical formulation present in the various catchments areas from where the wastewater was collected. Different concentrations were observed in the investigated plants, reflecting not only the different lifestyle of inhabitants related to those areas, but also the type of influents. The highest concentrations of BDE-209 were found in plants A and C, mean values 3756 and 3801 ng/g, respectively, which treated predominantly industrial influents. These concentrations are similar to those found by Fabrellas et al (2004) in sludge collected from WWTPs from Spain ranging from 786 to 5837 ng/g dw receiving wastewater from urban and mixture areas.

Excluding BDE-209, the congener contribution as the percentage the remaining congeners (28, 47, 99, 100, 153, 154 and 183) (Figure 2) indicates that the penta mixture is a significant source of BDEs in sludge, reflecting the use of BDEs in consumer products present in the home and thus the lifestyle of the residents.

In all samples, BDE-47 and BDE-99 were the dominate congeners of penta-BDE.

An important scientific issue is whether deca-BDE debrominates in the environment to BDE congeners with fewer bromine atoms that may be more toxic than deca-BDE itself. No significant change of the congener profile (% of total BDE without BDE-209) was observed in sludge samples from different stages in the waste treatment process was observed, so degradation of deca-BDE can not be suggested. This is confirmed by the ratio of BDE99:BDE100 (mean 86:14) (Table 2), which remains constant during the waste water treatment process and is nearly the same as reported for technical Penta-BDE (Bromkal 70-5DE) by La Guardia (2006).

Further monitoring of waster water effluent is needed considering that the occurrence of BDEs, in particular BDE-209, is an ongoing problem and the use of sludge for land application.

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