OCURRENCE OF BROMINATED FLAME RETARDANTS IN SEWAGE SLUDGES FROM SPAIN: HIGHER BROMINATED DIPHENYL ETHERS CONTRIBUTION

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a family of synthetic chemicals widely used in industry to delay, inhibit or even suppress combustion processes in manufactured items. These products are frequently added into plastic, electronic, paint and textile materials and they have been continuously produced and used as flame-retardant additives since 1970s.

According to substitution pattern, 209 isomers are possible, although three major mixtures are employed on industrial scale: Deca-mixture (DecaBDE 209), Octa-mixture (Hepta- and OctaBDEs) and Penta-mixture (PentaBDEs 99 and 100). The widespread application of these mixtures on industry explains the ubiquitous occurrence of PBDEs in the environment. As additives, they are physically mixed into product applications, rather than chemically bound and they have the potential to migrate into environment when conditions are suitable[1].

Their physicochemical structure make them substances of persistent nature, highly lypophylic, bioaccumulative with potential toxic effects observed onto wildlife and humans[2]. Although the acute toxicity is low, there is an increasing concern due to their long term effects on the endocrine system[3] . Owing to the risks to the environment and health of Penta- and Octa BDE commercial mixtures, the European Union has limited their use and commercialisation (2003/11/EEC). Besides, the risk assessment on decaBDE is being performed to clear the uncertainties concerning possible negative effects.

Due to these findings, there is a growing tendency to analyze PBDEs in various environmental and biotic matrices. Concretely, monitoring of PBDEs in sewage sludge is considered very important because of its possible application to agricultural land. Land application of raw or treated sewage sludge can reduce significantly disposal cost component of sewage treatment as well as providing a large part of organic matter supply demanded by many crops. However, this matrix could contain traces of many organic pollutants, such as PBDEs, that should be monitored.

Different European countries have promoted strategies to enlarge the knowledge of PBDE occurrence and levels on sewage sludge. Investigations have pointed out domestic washing of garment/clothes and industrial discharges from plastic and textile manufacture industry as major sources of contamination[4,5].

Considering the number of evaluated facilities is still very limited, this study involves the assessment of selected PBDE congener levels on 21 sewage sludge samples coming from different Spanish locations.

Methods and Materials

Sample collection: Twenty one sewage sludges were sampled in waste-water treatment plants, at different locations throughout Spain. Samples were air-dried (or at 40^{o}C) until constant weight to avoid lack of volatile congeners and poured into sealed amber-glass flasks for preserving from light, humidity and other external factors which might changes its chemical composition. Upon receiving in the laboratory, they were ground to a fine powder, reducing as much as possible the time between collection and analysis.

According to the type of influent stream and the number of inhabitants, the different facilities were divided into several categories shown in Table 1. "Urban" refers to waste-water from highly-populated/low-industrialised sites; "Industrial", to zones with high industrial activity cores and "Mixture", to mixed urban and industrial activities.

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

Category	Type of Influent	Number of inhabitants
U1-	Urban	Lowly populated (< 500.000)
U2-	Urban	Medium populated (500.000 – 1.000.000)
U3-	Urban	Highly populated (> 1.000.000)
M1-	Mixture	Low populated (< 500.000)
M2-	Mixture	Medium populated (500.000 – 1.000.000)
I1-	Industrial	Low populated (< 500.000)

Sample Extraction and Clean up: An amount of 0.5 g of dried sewage sludge was extracted with a mixture of hexane:dicloromethane (1:1) as solvent in an ASE 100 system (Accelerated Solvent Extraction), as published elsewhere[6]. Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to remove organic matter. Clean-up stage was then performed in an automated purification Power PrepTM System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. The extracts obtained were concentrated avoiding dryness, spiked with a known amount of BDE-CVS-EISS standard solution (Wellington Laboratories Inc., Canada) and further analysed by GC/MS. Since Hepta-DecaBDEs were analysed by NCIMS, no spiking with these labelled isomers was needed.

Sample Analysis: Analyses from Tri- to HexaBDE were carried out by GC/MS/MS in a Varian Saturn 2000 workstation equipped with a CP-3800 Gas Chromatograph. A J&W Scientific DB 5MS (40m x 0.18 mm i.d., 0.18 µm film thickness) capillary column was used. Identification and quantification of target species were carried out by following criteria of isotopic dilution technique, allowing high accuracy in the calculation of the final results. Complete details of this analytical methodology were published elsewhere[7]. Hepta- to DecaBDE isomers were studied by GC/NCIMS in a Gas Chromatograph Agilent 6890 connected to a Mass Spectrometer Agilent 5973 Network. A Factor Four VF-5MS (15m x 0.25 mm i.d., 0.1 µm film thickness) containing 95% dimethyl-5% diphenylpolysiloxane capillary column was used for its determination, with helium as the carrying gas at a pressure of 10 psi. The temperature program was from 140ºC (held for 1 min.) to 335 ºC (held for 5 min.) at 20ºC/min, using pulsed splitless injection mode (59 psi pulsed pressure). Injector temperature was from 270 ºC (0.5 min) to 300ºC (15.5 min.) at 700ºC/min. Other operation conditions were 250ºC ion source temperature and ammonia as the chemical ionisation moderating gas at 2.3×10^{-4} Torr ion source pressure. Identification and quantification was carried out using the BDE-MXE solution as external standard. Limits of detection, LODs, were defined as the smaller concentration giving a signal with S/N > 3. LODs ranged from 0.01-0.08 ng/g d.w. (for BDE 17) to 0.22-17.92 ng/g d.w. (for BDE 209).

Results and Discussion

Concentration levels of all samples, presented as ΣTri-HexaBDE (17, 28, 49, 47, 66, 100, 119, 99, 85, 153, 154), ΣHepta-NonaBDE (183, 184, 196, 197, 206, 207) and DecaBDE 209, are listed in Table 2. Results show the presence of some BDE congeners in all samples analysed, with concentrations above the limits of detection. BDE contents found in this study are in the same levels than those reported in other European investigations [8]. Data variation, ranging from 41 to 4150 ng/g dw, evidences the influence of the different local sources, with particular operational conditions like the type of influent entering the plant and/or the number of inhabitants related to that area. In particular, the highest levels (1813 and 4150 ng/g dw), have been associated with industrial areas. No significant differences can be established between urban and mixture areas. However, urban zones with population higher than 1.000.000 inhabitants present similar levels to the majority of industrial locations. Previous studies have corroborated the presence of PBDEs in urban household dust[9], due to the increasing utilisation of different plastic, textile and electric/electronic consumer products. Therefore, the domestic discharges could be responsible of the rise of PBDE levels coming from highly populated zones.

As can be seen in Figure 1, a characteristic trend is noticed in all cases, with major contribution of Deca-brominated congener (56-91 %). Regardless BDE 209 low water solubility and vapour pressure, present results indicate DecaBDE is highly released into the environment. Data from a Swiss survey point increasing concentrations of decabromodiphenyl ether in sewage sludge during the last decade (up to 560%), while levels of lower brominated species (Tri- to HexaBDE) were significantly reduced (50%)[10]. This may suggest a shift on the industrial use of BDE technical products from lower to highly brominated mixtures, which is in connection with DecaBDE high values found in the Spanish sludge. Taking into account the commercial Deca-mixture composition is 0,3-3 % Nona-BDE and 97-98 % Deca-BDE, the NonaBDE contribution (2 -24 %) could be explained both by Deca-mixture use and DecaBDE decomposition [11].

Table 2. BDE concentrations in ng/g dw of sludge samples analysed.

Sample	? Tri-Hexa BDE (ng/g)	? Hepta-Nona BDE (ng/g)	Deca BDE (ng/g)	Total (ng/g)
U1-1	12,0	15,5	13,4	40,8
U1-2	24,4	26,0	103,5	155,7
U1-3	55,6	29,6	213,2	276,6
U1-4	24,6	46,7	245,0	569,9
U1-5	44,2	75,8	484,1	608,1
U2-6	41,9	33,4	305,0	385,5
U2-7	34,4	73,5	462,7	626,3
U2-8	39,1	53,5	766,2	839,3
U3-9	37,5	36,8	323,5	1202,4
U3-10	130,7	160,5	1014,2	1776,3
M1-11	9,3	43,3	68,1	123,4
M1-12	66,3	26,4	162,4	246,6
M1-13	89,5	48,0	314,6	423,1
M1-14	104,5	59,0	614,3	823,7
M1-15	82,1	92,6	1296,8	1562,4
M2-16	23,9	38,4	271,9	345,3
M2-17	53,5	56,5	585,9	664,2
I1-18	61,8	108,9	690,0	958,8
I1-19	38,0	70,9	744,2	1333,1
I1-20	48,8	86,0	1449,9	1813,3
I1-21	87,3	268,0	3553,2	4150,4

Although levels of lower brominated congeners found in the sludge samples (Tri- to HexaBDE) constitute a minor fraction in comparison with DecaBDE 209 content, a close resemblance in pattern is noticed between sludges and the Penta-BDE commercial product Bromkal 70-5DE. Figure 2 shows the comparison of the averaged BDE congener pattern found in urban, mixture and industrial sludge samples, and the pattern of a commercial Penta-BDE mixture (Bromkal 70-5DE). The composition of this product has been previously characterised, comprising primary contributions of TeBDE 47 and PeBDE 99 and less contributions of PeBDE 100 and HxBDE 154 and 153[12]. Levels of PBDEs 47, 99 and 100 in Spanish sludges may be explained from the accepted application of this Penta-mixture in polyurethane foams, tapestries and related materials, despite its use has been recently restricted by European Community. Consequently, the notable correlation between both congener profiles could be a consequence of the use of this commercial product.

Taking into account the possible use of sewage sludge as a fertilizer, the high PBDE content existing in all samples analysed, could lead to increase PBDE concentrations in soils and, therefore, in the terrestrial food web. C. DE Wit et al.[13,14] have reported that sewage sludge adds directly to load of Tri-DecaBDE to soil and this is more pronounced than for PCBs and PCDD/Fs.

Present results need to be confirmed by enlarging number of samples, establishing time trends and analysing the effect of the different post-treatments in order to provide more detailed information, which may be useful for making-decision support systems at both National and International regulatory scale.

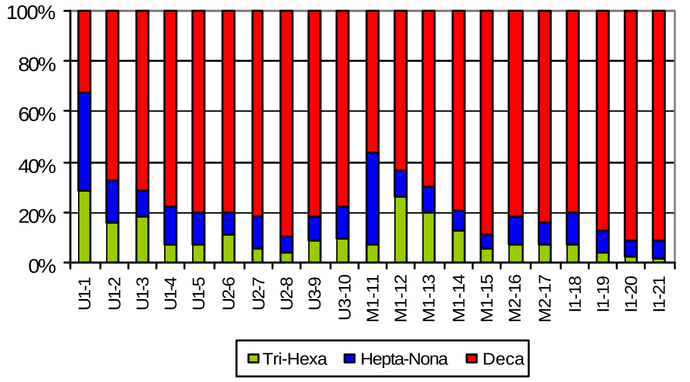

Figure 1. Contribution of Σ Tri-HexaBDE, Σ Hepta-NonaBDE and DecaBDE to the total PBDE content in sewage sludges.

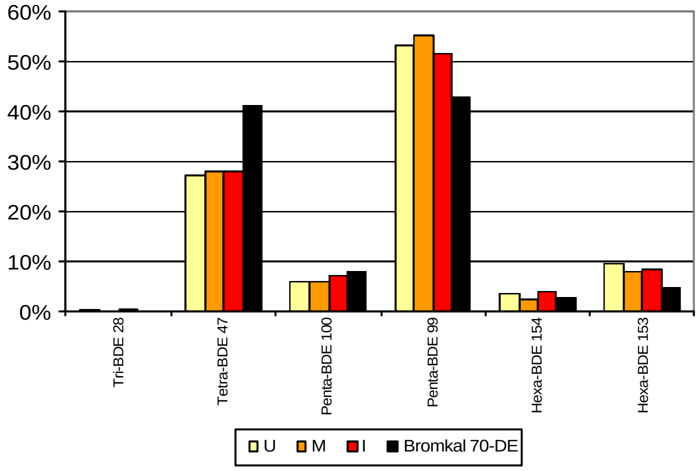

Figure 2. Averaged BDE congener pattern for urban, mixture and industrial sludge samples and Bromkal 70-5DE.

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