PRESENCE OF POLYBROMINATED DIPHENYL ETHERS IN SPANISH SEWAGE SLUDGES: IMPORTANT CONTRIBUTION OF DECA-BDE

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Introduction

Polybrominated diphenyl ethers (PBDE) are a family of synthetic chemicals widely used in industry to delay, inhibit or even suppress combustion process in manufactured items. Flame retardant products are frequently added into plastic, electronic, paint and textile materials to reduce the risk of ignition. During last years, increasing levels of PBDE have been detected in the environment, suggesting release from the treated surface as main pathway for environmental intake[i]. Their physicochemical structure make them substances of highly lypophylic, bioaccumulative and persistent nature, with potential toxic effects observed onto wildlife and humans [ii].

Some European countries (Switzerland and Sweden) have promoted strategies to enlarge the knowledge of PBDE, in particular their occurrence and levels on sewage sludge. Observations point domestic washing of garment/clothes and industrial discharges from plastic and textile manufacture industry as major sources of contamination. First European results from 1988 revealed levels of about 20-30 µg/kg dw of PBDEs (BDEs 47, 99 and 100) in sludge samples collected in Sweden [iii]. More recently, another Swedish survey conducted on three waste-water treatment facilities pointed levels of PBDE (BDE 47, 99 and 209) of about 200 ng/g dw, along with minor contribution of other contaminants such as TBBPA and HBCD [iv]. Few studies have been carried out in US. Hale et al. [v] compared levels of Tetra-, PentaBDE (BDE 47, BDE 99 and BDE 100) and DecaBDE 209 congeners in sludge from different US locations. Values ranged from 1000 to 2290 µg/kg dw (Tri- to HexaBDE) and from 84 to 4890 µg/kg dw for DecaBDE 209, with mean values of about 1600 and 1000 µg/kg dw, respectively. In general, concentrations of BDE 47, 99, 100 and 209 exceeded those of the major PCB congeners and other halogenated contaminants also found in the sludge.

Following this trend, this work aims a preliminary assessment of selected PBDE congener levels on sewage sludge samples from different waste-water treatment plants in Spain. A qualitative and quantitative characterisation of this matrix is intended, in order to estimate levels of contamination and to identify major congeners.

Materials and Method

Sample collection: Sewage sludge was sampled in six waste-water treatment plants, during 2002 year at different locations throughout Spain. Operating conditions were based on physicochemical treatment of activated sludge, followed by stabilisation and final drying on a belt filter press device.

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

Samples were taken by plant staff, air-dried (or at 40°C) until constant weight to avoid lack of volatile congeners, ground to a fine powder, poured into sealed amber-glass flasks to prevent highly brominated congeners from photodegradation and sent to the laboratory. Upon receiving, they were stored at –20°C reducing as much as possible time between collection and analysis.

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

Sample	Type of influent	Number of inhabitants
M1	Mixture	Low populated (< 500.000)
M2	Mixture	Medium populated (500.000 – 1.000.000)
M3	Mixture	Low populated (< 500.000)
U1	Urban	Low populated (< 500.000)
U2	Urban	Highly populated (> 1.000.000)
I1	Industrial	Low populated (< 500.000)

Sample Extraction and Clean up: A 2.5-gram of dried sludge sample was weighed and fortified with a known amount of $^{13}C_{12}$-labelled, MBDE-MXE quantification standard solution (Wellington Laboratories Inc., Canada). Samples were extracted using a Dionex ASE100 at the conditions listed in Table 2. 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 Prep™ System (FMS, Inc., USA) including acidic silica gel and

basic alumina columns. Different mixtures of hexane:dicloromethane were used to recover target analytes while retaining interfering compounds. 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 Deca-BDE 209 was analysed by NCIMS, no spiking with labelled isomers was needed.

Analyses from mono- to hexa-BDE were carried out by GC/MS/MS in a Varian Saturn 2000 workstation equipped with a CP-3800 Gas Chromatograph coupled to a 2000 Ion-Trap Tandem Mass Spectrometer, 1079 Programmable Injector and CP-8200 Autosampler (Varian, Walnut Creck, CA, USA). A high performance fused-silica capillary column Factor Four (30 m., 0,25 mm. of i.d, 0,25 µm film thickness) was used. Complete details of this analytical methodology were published elsewhere [vi]. Deca-BDE 209 was studied by using GC/NCIMS in a Gas Chromatograph Agilent 6890 connected to a Mass Spectrometer Agilent 5973 Network (Agilent Technologies, Madrid, Spain). A DB-5ms capillary column (15 m., 0,25 mm. of i.d., 0,25 µm film thickness) containing 5% phenylmethylsiloxane was used with helium as the carrying gas at a constant pressure of 10 psi. The temperature program was from 140ºC (held for 1 min.) to 325ºC (held for 10 min.) at 10ºC/min., using splitless injection during 1 min. Other operating conditions were 250ºC ion source temperature and ammonia as chemical ionisation moderating gas at an ion source pressure of 1.9 x 10^{-4} Torr [vii].

ASE extraction conditions	
Presure (psi)	1500
Temperature (ºC)	100
Static time (min)	10
Flush volume (%)	90
Purge Time (sec)	120
Number of Static Cycles	3
Solvent	Hexane:DCM (1:1)

Table 2: ASE 100 extraction conditions for samples analysed.

Results and Discussion

Concentrations of Di- (7,15), Tri- (17,28), Tetra- (49, 47, 66), Penta- (100, 119, 99, 85), Hexa- (154, 153) and Deca-BDE 209 in sludge samples analysed are listed in Table 3. Results show the occurrence of some BDE congeners in all samples analysed, independently on the type of influent and number of inhabitants. A characteristic trend is noticed in all cases, with major contribution of Deca-brominated congener (93-99 %), and minor contents of Tetra-BDE 47, Penta-BDEs 99 and 100, and Hexa-BDEs 153 and 154. Similar observations have already been reported in literature [viii]. Recent 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 Hexa-BDE) were seen to be significantly reduced (50%) [ix]. This may suggest a shift on the industrial use of BDE technical products from lower to highly brominated mixtures, which is in connection with such high values of Deca-BDE found in the Spanish sludge. Commercial Deca-mixture composition is 0,3-3 % Nona-BDE and 97-98 % Deca-BDE [x]. Regardless its low water solubility and vapour pressure, present results could indicate Deca-BDE is highly released into the environment.

Table 3: BDE concentrations in ng/g dw of sludge samples analysed.

BDE congener		M1	M2	M3	U1	U2	I1
Di-BDE	7	---	---	---	---	0,2	---
	15	0,4	---	0,2	---	0,5	0,5
Tri-BDE	17	0,7	0,1	0,1	---	0,4	1,0
	28	1,4	0,4	0,5	---	1,0	0,8
Tetra-BDE	49	4,7	0,6	0,9	2,7	1,8	2,1
	47	83,6	21,4	28,3	1,8	49,8	38,5
	66	1,6	0,4	0,5	---	1,0	0,9
Penta-BDE	100	14,0	4,5	5,7	0,2	8,0	7,7
	119	0,1	---	0,1	0,6	---	0,2
	99	64,2	23,4	25,6	---	37,6	34,5
	85	1,6	0,6	0,9	---	1,2	1,2
Hexa-BDE	154	---	4,2	---	---	1,7	10,4
	153	5,0	2,7	7,8	---	---	16,4
∑Tri-Hexa-BDE (% of total)		177,3 (3,2)	58,3 (6,9)	70,6 (5,5)	5,3 (0,2)	103,2 (1,7)	114,2 (0,6)
Deca-BDE209 (% of total)		5430,0 (96,8)	785,7 (93,1)	1203,0 (94,5)	3590,9 (99,8)	5836,6 (98,3)	18032,3 (99,4)
TOTAL:		**5607,3**	**844,0**	**1273,6**	**3596,2**	**5939,8**	**18146,5**

In spite of levels of lower brominated congeners found in the sludge samples (Tri- to Hexa-BDE) constitute a minor fraction in comparison with content of Deca-BDE 209, a close resemblance in pattern is noticed between sludge and the Penta-BDE commercial product Bromkal 70-5DE. The comparison of the BDE congener pattern found in sludge samples and the pattern of a commercial Penta-BDE mixture (Bromkal 70-5DE)[xi] is shown in Figure 1. The notable correlation between both congener profiles could be a consequence of the use of this commercial product. Levels of PBDEs 47, 99 and 100 in Spanish sludge may be explained from the accepted application of this Penta-mixture in polyurethane foams, tapestries and related materials. Considering the use of this commercial product has been recently restricted by European Community [xii], a noticeable reduction of these congeners is expected in the near future.

The variation in total values, ranging from 0,84 to 18,15 µg/g dw, evidences considerable influence of different local sources, having particular operational conditions as type of influent entering the plant and/or the number of inhabitants related to that area. In particular, the highest level, 18,15 µg/g dw, which is mainly due to the Deca-BDE contribution, has been found to be associated to the industrial area with mainly textile manufacture facilities.

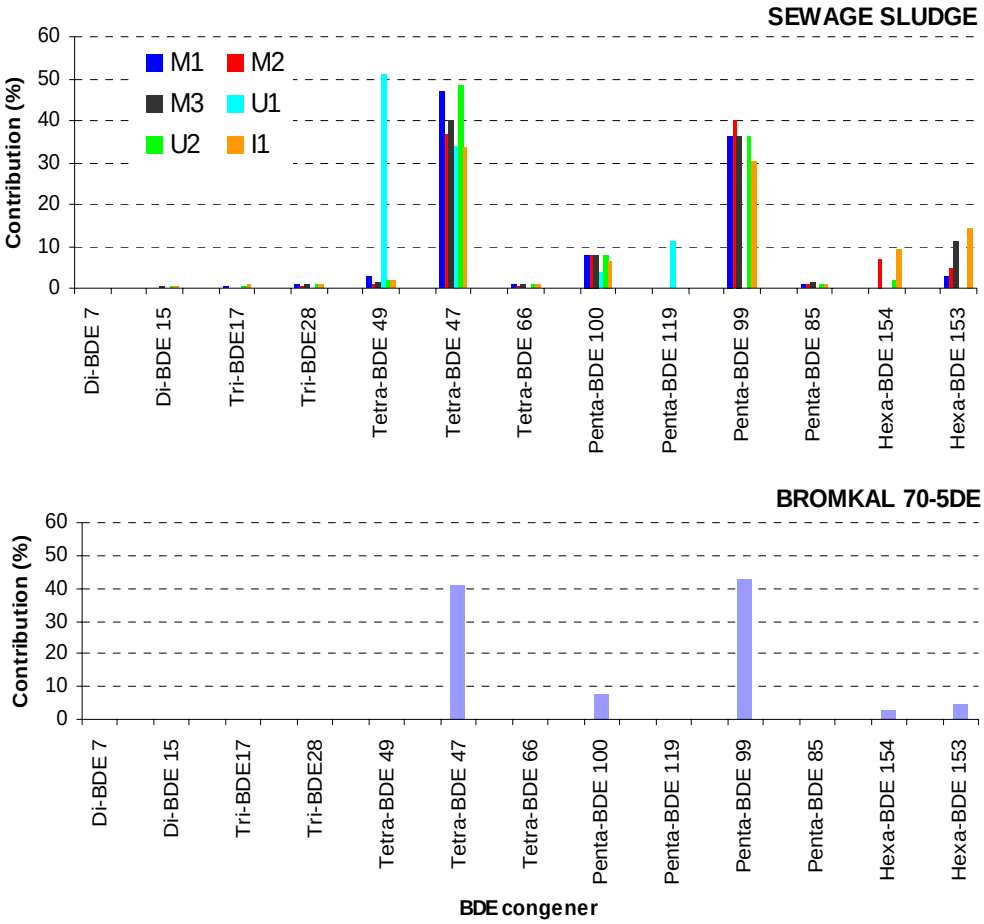

Figure 1: BDE congener pattern in sludge samples and Bromkal 70-5DE.

On the other hand, it is important to remark that, although the lowest value corresponds with a mixture influent, sample M2, no significant differences can be established between urban and mixture areas. Nevertheless, when comparing plants from urban locations (samples U1 and U2), with no supply from industrial origin, larger DecaBDE levels are found in highly populated sites (sample U2), perhaps as a consequence of the prominent use of thermoplastics, as housing for televisions and computers, or textile stuffs.

Debromination of Deca-BDE in environmental systems is discussed controversially, leading to the occurrence of lower brominated diphenylethers with known adverse effect for the environment. Watanabe et al. [xiii] have published that laboratory exposure of BDE209, solved in hexane, to UV light promotes the formation of a complex mixture of less brominated dibenzofurans and diphenylethers. On the contrary, Hale et al. [xiv] and de Boer et al. [xv] detected little evidence for extensive BDE-209 debromination. Therefore, clarifying this effect as well as assessing features such as half-life and bioavailability is desirable, particularly when sewage sludge is intended for

land application under high sun radiation conditions, as in most Mediterranean countries. This may promote decomposition and subsequent formation of more accessible and bioavailable congeners.

From the view of these results it may be concluded that a better knowledge of these compounds in sewage sludge for land application would be desired. Type of influent as well as likely influence and environmental fate of these substances in the soil should be assessed. Current data only constitute a first approach. Observations need to be confirmed by enlarging number of samples and facilities evaluated, in order to provide more information, which may be useful for making-decision support systems at both national and international regulatory scale.

References

[i] Betts K.S. (2002) Environ. Sci. Technol. 36, 50A-52A.

[ii] 1997 WHO, Environmental Health Criteria 192. Flame retardants: A general introduction. Geneva, Switzerland: International Program on Chemical Safety, WHO.

[iii] Hagenmaier H., She J., Benz T., Dawidowsky N., Düsterhöft L and, Lindig C. (1992) Chemosphere 25, 1457–1462.

[iv] Sellström U., Kierkegaard A., Alsberg T., Jonsson P., Wahlberg C.and de Wit C. (1999) Organohalogen Comp. 40, 383–386.

[v] Hale R.C., Alaee M., Manchester-Neesvig J.B., Stapleton H.M. and Ikonomou M.G. (2003) Environ. Intern. 29, 771-779.

[vi] Larrazábal D., Martínez M.A. and Fabrellas B. (2003) Organohalogen Compounds 61, 57-60.

[vii] Eljarrat E., de la Cal A. , Larrazabal D., Fabrellas B., Barceló D. Submitted to Env. Tox. and Chem.

[viii] Kolic T.M., MacPherson K.A., Reiner E.J., Ho T., Kleywegt S., Payne M and Alaee, M, (2003) The Fifth Annual Workshop on Brominated Flame Retardants in the Environment, Boston, 39-42.

[ix] Kohler M., Zennegg M., Gerecke A.C., Schmid P.and Heeb N. (2003) The Fifth Annual Workshop on Brominated Flame Retardants in the Environment, Boston, 35-38.

[x] Keml (1994) Risk Assessment of Polybrominated Diphenyl Ethers. Stockholm, The Swiedish National Chemicals Inspectorate: 54.

[xi] Sjödin A., Jakobsson E., Kierkegaar A, Marsh G. and Sellström, U. (1998) J. Chromatrogr. A 822, 83.

[xii] EU Directive 2003/11/EC of the European Parlament and of the Council of 6 February 2003 amending for the 24 time Council Directive 76/769/ECC relating to restrictions on the marketing and use of certain dangerous substances and preparations. Official Journal of the European Journal L 42 45-46.

[xiii] Watanabe I. and Tatsukawa R. (1987) Bull. Environ. Contam. Toxicol. 39, 953-959.

[xiv] Hale R.C., La Guardia M.J., Harvey E. and Mainor T.M. (2002) Chemosphere 46, 729-735.

[xv] de Boer J., de Boer K. and Boon J.P. (2000) The Handbook of Environmental Chemistry, In: Paasivirta, J. Ed., Vol. 3. Springer, Berlin, 61-95.