

Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils

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Abstract

The fate of polybrominated diphenyl ethers (PBDEs) in sewage sludge after agricultural application was analysed. This study was based on the analysis of sewage sludge and sludge amended soil samples collected during 2005. PBDE concentrations in sewage sludge ranged from 197 to 1185 ng/g dry weight (dw), being deca-BDE-209 the predominant congener. PBDE levels in soils ranged between 21 and 690 ng/g dw, being BDE-209 also the predominant congener in all soil samples. Sewage-sludge amendment at the research stations increased concentrations of all BDE congeners 1.2- to 45-fold, with the highest increases for BDE-209. Results obtained evidenced the cumulative effect of the sludge application rates. Moreover, high levels found at soils four years after the last sludge application indicate persistence of PBDEs in soils, including deca-BDE-209.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities for several applications due to their fire retarding properties, including electrical appliances such as television and computers, building materials, and textiles. The similarity in molecular structure of PBDEs with that of environmental toxic pollutants such as PCBs, dioxins, and their resistance to degradative processes, gives rise to concern that they may lead to similar environmental problem. Moreover, for many countries decreasing levels of organochlorine compounds have been reported in human milk (Norén and Meironyté, 2000) while levels for PBDEs increased since 1972 (Meironyté et al., 1999).

In Europe, the agricultural use of sewage sludge is, along with disposal to landfills, the most popular disposal route. Of the total sludge produced in European countries, the percentage of reused sludge reached levels as high as 50% in Germany, 54% in Spain, 65% in France and 71%

in the United Kingdom (Magoarou, 2000). Despite the valuable properties of sewage sludge, such as relatively high levels of organic matter, the widespread application of sewage sludge in agriculture needs to be critically evaluated in view of the concomitant presence of a variety of contaminants that may adversely affect crops and/or soils. In many countries there is a continuous discussion on the significance of sewage sludge fertilization of cultivated land in terms of soil contamination. The recognition that sewage sludge contains organic pollutants, such as PCDDs, PCDFs and PCBs (Pauné et al., 1994; Sewart et al., 1995; Eljarrat et al., 2003) has resulted in studies to identify the possible sources of these contaminants in sewage sludge, and to assess the extent to which they may be transferred through the food chain and ultimately to humans (Eljarrat et al., 1997). As regards PBDEs, first European results from 1988 reveal levels of about 20–30 ng/g dry weight (dw) in sewage sludge collected in Sweden (Hagenmaier et al., 1992). More recently, levels about 200 ng/g dw have been reported in sludge from Sweden and The Netherlands (Sellström et al., 1999; de Boer et al., 2002), and around 500 ng/g dw for samples collected in Denmark (Christensen

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et al., 2003). Higher concentrations were found in USA, with values ranging from 1000 to 2290 ng/g dm for tri- to hexa-BDEs, and from 85 to 4890 ng/g dm for deca-BDE-209, with mean values of about 1600 and 1000 ng/g, respectively (Hale et al., 2003).

Sludge is treated before application to reduce odour and pathogen content and their metal burden is regulated. But attention has focused less on organic pollutants, such persistent organic pollutants including PBDEs. The application of sewage sludge to soils is limited by guideline concentrations of heavy metals in the soil through the EU Directive on the use of sewage sludge in agriculture (COM 86/278). No similar guidelines exist for organic contaminants in sludge or soils at present. The European Union is currently studying the issue and may enact legislation on the application of sewage sludge containing organic pollutants (such as PCBs, NP/NPEO, benzo[*a*]pyrene and PCDDs/Fs) to agricultural land (Gawlik and Bidoglio, 2004).

In contrast to other POPs such as PCBs or PCDDs/Fs, limited work has considered PBDE soil contamination. Very little data are available for PBDE concentrations in soils. Given the huge interest in PBDEs over recent years, it is therefore surprising that only few have been published on their levels and distribution in soils. Thus, the objectives of the present work were: (i) to determine PBDE level of contamination in sewage sludge from Spain; and (ii) to assess the effects of PBDEs in sewage sludge applied to the soil. The work was based on the analysis of sewage sludge and sludge-amended soil samples collected along 2005. To the knowledge of the authors, no current information on PBDE occurrence in these matrices from Spain is available.

2. Materials and methods

2.1. Chemicals and Materials

23 PBDE congeners, from tri- to deca-BDEs were included in the analytical work: one tri-BDE (BDE-28), three tetra-BDEs (BDE-47, BDE-49, BDE-66), four penta-BDEs (BDE-85, BDE-99, BDE-100, BDE-119), six hexa-BDEs (BDE-138, BDE-139, BDE-140, BDE-153, BDE-154, BDE-155), one hepta-BDE (BDE-183), four octa-BDEs (BDE-194, BDE-196, BDE-197, BDE-203), three nona-BDEs (BDE-206, BDE-207, BDE-208) and the deca-BDE (BDE-209). Tetra-BDE-77, hepta-BDE-181 and ¹³C-deca-BDE-209 were used as quantitative standards. All PBDE standards were purchased from Wellington Labs. (Guelph, Ontario, Canada). All solvents for organic trace analysis were purchased from Merck (Darmstadt, Germany). Alumina cartridges were obtained from IST (Mid Glamorgan, UK) and copper (<63 μm) was obtained from Merck.

2.2. Sample collection

Sewage sludge was sampled in five wastewater treatment plants (WWTPs) during 2005 at different locations

throughout Spain (Barcelona, Burgos, Lleida, Pamplona and Tortosa) (Fig. 1). Table 1 summarizes the characteristics of WWTPs studied.

Soil samples were also collected in 2005 at different selected sites in the province of Barcelona (Catalonia) in the Northeast of Spain. Table 2 presents details of the sampling sites, including amounts of sewage sludge applied. No sludge was applied to the soil sample in Pujalt (P(RS)), which was used as a reference soil. For the rest of sites, used for cultivation of winter crops, sludge had been applied at least once since 1997 when its application began to be controlled and managed by a company adjusting the origin and quantity of sewage sludge for application to the nutrients requirements of the crop to be cultivated in the next growing period. The sludge application was generally carried out in September/October at a rate of between 15 and 25 tonnes dm (dry matter) per hectare. After spreading of the sludge, the soil was ploughed to a depth of between 15 and 20 cm. The soil types were typically calcareous (30% sand, 45% lime and 25% loam, approximately), with pH ~8, and with a low to moderate content of organic carbon (0.9–3.5%). Representative sampling of the topsoil (0–20 cm) was performed with an Auger sampler (Eijkelkamp, Giesbeek, The Netherlands) at a frequency of approximately five subsamples per hectare.

Individual subsamples were transferred to the laboratory at a temperature of 4 °C. Subsamples from the same field were pooled and then frozen at –20 °C before being frozen dried. The lyophilized samples were ground and homogenized by sieving through a stainless steel 2-mm sieve, and stored in sealed containers at –20 °C until analysis.

2.3. Extraction and cleanup

One gram dw of sample was spiked with internal standards (tetra-BDE-77, hepta-BDE-181 and ¹³C-deca-BDE-209). Spiked samples were kept overnight to equilibrate. Then, samples were Soxhlet extracted using 100 ml of a mixture of hexane:dichloromethane (1:1) for 24 h. Two gram copper were added to Soxhlet beaker to remove sulphur interferences. In order to avoid possible combination chemistry at temperature higher than room temperature between halogenated aromatic species present in the crude extract and native copper metal, this one was added in the beaker where the temperature was similar to room temperature. After extraction, the extracts and the rinses of the Soxhlet are combined and then subjected to the cleanup procedure.

Samples extracts were treated with concentrated sulfuric acid (2 × 25 ml) in separatory funnels and subsequently purified with five grams of alumina cartridges. Solid-phase extraction (SPE) cartridges are conditioned with 20 ml hexane. The sample volume loaded are ~1 ml, and the elution step is performed with 30 ml hexane:dichloromethane (1:2). Samples are finally concentrated to incipient dryness and re-dissolved in isooctane (50 μl) containing the recovery



Fig. 1. Map of Spain showing the locations of sewage sludge sampling sites.

Table 1
Characteristics of WWTPs selected for sludge sample analysis

Location	WWTP	Flow (m ³ /h)	Type of wastewater treated	Primary treatment	Secondary treatment
Barcelona	Piera – Sabadell Riu Sec	2083	Urban	–	Activated sludge
Burgos	Miranda de Ebro	600	Urban	–	No treatment
Lleida	Lleida	2917	Urban	Primary settling	Activated sludge
Pamplona	Arazuri	4313	Urban and industrial	Primary settling	Activated sludge
Tarragona	Tortosa	305	Urban	–	Activated sludge

Table 2
Sample characteristics of soils collected in this study

Code	Site, type of sample	Year of sludge application	Amount of sludge applied (tonnes/ha)	Date of sampling
T	Tornabous, sludge-amended-soil	2003	25	April 29, 2005
		2004	25	
		2005 (January)	33	
H(S)	Hostalet de Pierola, sludge-amended-soil	2003	15	October 25, 2005
		2005 (September)	15	
H(SS)	Piera + Sabadell Riu Sec, sludge applied	–	–	October 25, 2005
P(RS)	Pujalt, reference soil	–	–	October 25, 2005
P(S1)	Pujalt, sludge-amended-soil	1999		October 25, 2005
		2000		
		2001		
P(S2)	Pujalt, sludge-amended-soil	2004		October 25, 2005
P(S3)	Pujalt, sludge-amended-soil	1997–2004	15–20	October 25, 2005
		2005 (August)	15	

standards (PCB-209 and 4'-chloro-2,2',3,3',4,5,5',6,6'-non-abromodiphenyl ether (Cl-BDE-208) (Christiansson et al., 2006)), prior to the analysis by GC–ECNI–MS.

2.4. Instrumental analysis

GC–ECNI–MS analyses were performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network (Agilent Technologies

España, Madrid, Spain). A HP-5 ms (30 m × 0.25 mm i.d., 0.25 μm film thickness) containing 5% phenyl methyl siloxane (model HP 19091S-433) capillary column was used for the determination of congeners from tri- to hepta-BDEs. The temperature program was from 110 °C (held for 1 min) to 180 °C (held for 1 min) at 8 °C/min, then from 180 °C to 240 °C (held for 5 min) at 2 °C/min., and then from 240 °C to 265 °C (held for 6 min) at 2 °C/min, using the splitless injection mode during 1 min, and

injection volume of 2 μ l. The operating conditions were as follows: ion source temperature = 250 °C, ammonia as chemical ionization moderating gas at an ion source pressure of 1.9×10^{-4} torr (Eljarrat et al., 2002). For the determination of octa- to deca-BDEs, a DB-5ms (15 m \times 0.25 mm i.d., 0.1 μ m film thickness) containing 5% phenyl methyl siloxane capillary column was used with helium as the carrier gas at 10 psi. The temperature program was from 140 °C (hold for 1 min) to 325 °C (hold for 1 min) at 10 °C/min (hold for 10 min), using the splitless injection mode during 1 min (Eljarrat et al., 2004a) and injecting 1 μ l (injector temperature = 275 °C). The operating conditions were as follows: ion source temperature = 250 °C, ammonia as chemical ionization moderating gas at an ion source pressure of 2.1×10^{-4} torr. Experiments were carried out monitoring the two most abundant isotope peaks from the mass spectra corresponding to $m/z = 79$ and 81 ($[\text{Br}]^-$) for tri- to octa-BDEs, and to $m/z = 487$ and 489 for nona- and deca-BDEs. Confirmation criteria for the detection and quantification of PBDEs should include the following: (a) all m/z monitored for a given analyte should maximize simultaneously ± 1 s, with signal to noise ratio ≥ 3 for each; (b) the ratio between the two monitored ions should be within 15% of the theoretical. Quantification of tri- to penta-BDEs was carried out by internal standard procedure using tetra-BDE-77 as internal standard, whereas hexa- and hepta-BDEs were quantified using hepta-BDE-181 as internal standard. As regards octa- to deca-BDEs, ^{13}C -BDE-209 was used as internal standard.

Using the described methodology, recoveries, standard deviations, detection limits and limits of quantification were calculated upon spiked soil and sludge samples. Recoveries ranged between 61% and 100% (54% for deca-BDE-209); detection limits and limits of quantification were in the range of 0.03–0.4 ng/g dw and 0.09–1.4 ng/g dw, respectively (1.2 and 4.1 ng/g dw for deca-BDE-209). Relative standard deviations of the method were in the range of 3–9% (20% for deca-BDE-209). Moreover, procedure blanks were carried out, showing no presence of analytes of interest.

3. Results and discussion

3.1. Sewage sludge

Concentrations of PBDEs in sludge samples analyzed are listed in Table 3. Results show the occurrence of some BDE congeners in all samples analyzed, independently on the type of influent and number of inhabitants, with concentration levels ranging from 197 to 1185 ng/g dw, and a mean value of 572 ng/g dw. Our PBDE results were consistent with reported data for sewage sludge samples from Denmark (Christensen et al., 2003) with levels around 500 ng/g dw. In another study of PBDE concentrations in sludge from 50 Swedish sewage treatment plants, median concentrations for BDE-47, -99, -100 and -209 were 49, 60, 11 and 120 ng/g dw, respectively (Law et al., 2006). Recent

Table 3

PBDE concentrations (expressed in ng/g dry weight) in sewage sludge samples

	Barcelona	Burgos	Lleida	Pamplona	Tarragona
Tetra-BDE-47	33.1	21.1	17.0	22.9	40.9
Penta-BDE-100	6.29	5.63	5.60	6.50	11.0
Penta-BDE-99	26.9	25.8	25.0	29.3	50.9
Hexa-BDE-154	3.42	3.51	2.47	2.82	4.08
Hexa-BDE-153	3.68	3.55	3.69	3.31	5.70
Hepta-BDE-183	29.6	3.70	4.05	3.66	3.90
Octa-BDE-196	nd	14.9	nq	nq	nq
Nona-BDE-208	nd	1.67	nq	nq	nq
Nona-BDE-207	nd	4.29	nd	1.68	nd
Nona-BDE-206	nd	6.36	nd	nd	nd
Deca-BDE-209	1082	393	508	356	80.6
Total PBDEs	1185	484	566	426	197

nd = below limit of detection; nq = below limit of quantification.

results on PBDEs in sludge from Germany (Knoth et al., 2007) showed levels of tri- to hepta-BDEs ranging from 13 to 288 ng/g dw, and concentrations of deca-BDE-209 between 97 and 2217 ng/g dw. Higher concentrations were found in USA, with values ranging from 1000 to 2290 ng/g dw for tri- to hexa-BDEs, and from 85 to 4890 ng/g dw for deca-BDE-209, with mean values of about 1600 and 1000 ng/g, respectively (Hale et al., 2003).

Of 23 congeners included in the analytical work, 11 different PBDEs were detected, ranging from tetra- to deca-brominated compounds. A characteristic trend is noticed in all cases, with major contribution of deca-brominated congener BDE-209 ranging from 81% to 91% (with the exception of Tarragona sample, with 41%) followed by tetra-BDE-47 and penta-BDE-99. Similar observations have already been reported in the literature (Eljarrat and Barceló, 2004b).

3.2. Sewage sludge amended soils

Concentrations of PBDEs in soil samples analyzed are listed in Table 4. Results show the occurrence of some

Table 4

PBDE concentrations (expressed in ng/g dry weight) in sewage sludge amended soils

	T	H(S)	H(SS) ^a	P(RS)	P(S1)	P(S2)	P(S3)
Tetra-BDE-47	1.23	0.59	33.1	0.69	0.92	1.30	2.04
Penta-BDE-100	0.57	0.60	6.29	1.08	2.15	1.37	1.60
Penta-BDE-99	1.44	0.54	26.9	0.63	1.08	1.28	2.00
Hexa-BDE-154	1.33	0.77	3.42	0.93	1.08	1.15	1.61
Hexa-BDE-153	1.51	nd	3.68	0.94	nd	1.19	1.13
Hepta-BDE-183	3.19	2.89	29.6	1.87	2.73	15.5	8.60
Octa-BDE-196	2.07	nd	nd	nd	nd	nq	nq
Nona-BDE-208	nq	nq	nd	nq	nq	nq	4.54
Nona-BDE-207	1.95	nq	nd	nq	nq	nq	5.96
Nona-BDE-206	3.82	nq	nd	nd	nq	1.99	7.28
Deca-BDE-209	332	24.6	1082	14.6	71.7	161	655
Total PBDEs	349	30.0	1185	20.7	79.6	184	689

(See Table 1 for sampling codes).

nd = below limit of detection; nq = below limit of quantification.

^a H(SS) corresponded to Barcelona sewage sludge (see Table 2).

BDE congeners in all samples analyzed, with concentration levels ranging from 21 to 690 ng/g dw. As expected, the lowest value was obtained for the reference soil sample (P(RS)), whereas fields that had received sewage sludge had higher PBDE burdens. Of 23 congeners included in the analytical work, 11 different PBDEs were detected, ranging from tetra- to deca-brominated compounds. Similar to previously observed with sludge samples, a characteristic trend is noticed in all cases, with major contribution of deca-brominated congener ranging from 71% to 95%. It is also important to notice the contribution of hepta-BDE-183 congener in all the soil samples. BDE-183 is often taken as indicative of the presence of the octa-BDE formulations (Law et al., 2003). Thus, the presence of BDE-183 could indicate the use of octa-BDE commercial formulations in the studied area. The use of these formulations was also hypothesised when analysing marine sediment samples collected in Catalonia (Northeast of Spain) (De la Cal et al., 2003).

Very little data are available for PBDE concentrations in reference soils. Hassanin et al. (2004) reported the first data on PBDEs in background soils, analysing samples from the United Kingdom and Norway collected in 1998. They observed PBDEs in rural surface soils at concentrations ranging from 1 to 12 ng/g, matching reasonably well with our reference soil value (21 ng/g). Similar data were obtained by Harrad and Hunter (2006) in their study of PBDEs in surface soils taken from 10 locations across the West Midlands, with PBDE concentrations ranging from 0.01 to 5 ng/g dw. Sellström et al. (2005) also reported PBDE levels in reference soil samples, with the lowest reported values (between 0.03 and 0.84 ng/g dw). In general, PBDE concentrations in reference soil are low, and these levels are probably reflective of atmospheric deposition.

As regards sewage sludge-amended soils (Table 4), PBDE levels higher than those obtained in control soil were found, with concentrations ranging from 31 to 690 ng/g dw. Moreover, results obtained for the sludge-amended soils evidenced the cumulative effect of the sludge application rates, with the highest PBDEs concentration of 690 ng/g dw in the soil sample that was been yearly sludge-amended since 1997 (P(S3)). This may indicate a buildup of PBDEs with repeated sewage-sludge application. It is interesting to note that PBDE concentrations in the amended soil P(S1), four years after last sludge application, indicates persistence of PBDEs, including BDE-209 in soils. Thus, the use of sewage sludge as a fertilizer increased concentrations of PBDEs in agricultural soils and these will remain in the soil for a long time. The same finding has been previously observed for PCBs (Harrad et al., 1994). Sellström et al. (2005) also reported high levels of PBDEs, including BDE-209, in soils from a farm 20 years after the last application.

Two other studies have been carried out in order to determine PBDE contamination in agricultural soils. Matscheko et al. (2002) examined PBDEs in sewage sludge-

amended soils from Sweden. PBDE concentrations for tetra- to hepta-BDEs ranged from 0.03 to 0.11 ng/g dw in reference soils and 0.08 to 840 ng/g dw in amended soils, indicating that sewage-sludge amendment contributes much more to soil concentrations than atmospheric deposition. Similar results were obtained by Sellström et al. (2005), who studied the effect of sludge application on concentrations of PBDEs in soil samples collected in Sweden in 2000.

Ratios between the concentrations in the sludge-treated soils and reference soil at the same site (Pujalt) were calculated using concentrations on a dw basis (*S/R* ratios). Sewage-sludge amendment increased concentrations of all BDE congeners, with the highest increases for deca-BDE-209, followed by hepta-BDE-183. The higher *S/R* ratios for BDE-209 compared to lower brominated BDE congeners are probably due to the higher concentrations of BDE-209 found in sewage sludge (see section 3.1). Fig. 2 illustrates the sludge-amended soil-reference soil (*S/R*) ratios for all BDE congeners detected in both soils. *S/R* ratios ranged from 1.2 to 4.9 for P(S1) amended soil, which was treated during 1999, 2000 and 2001. For P(S2) soil, which was only sludge amended during 2004, *S/R* ratios ranged from 1.2 to 11. And finally, the highest *S/R* values (from 1.5 to 45) were obtained for P(S3) amended soil which has been yearly sludge-amended since 1997.

S/R ratios greater than one was also observed by Matscheko et al. (2002). In their study, PCDD and PCDF concentrations did not increase in the sludge-treated soil, whereas the *S/R* ratios for PBDEs were up to six. Sellström et al. (2005) detected that sewage-sludge amendment increased concentrations of all PBDE congeners 2- to 13-fold, with the highest increases for BDE-209.

It is interesting to note the presence of some nona- and octa-BDEs in sludge- amended soils with the highest PBDE contamination. For P(S3) soil sample, in which BDE-209 was found at 655 ng/g dw, three nona-BDEs (206, 207 and 208) were detected, with the highest value for BDE-206 (7.28 ng/g dw). In the case of T soil sample, in which BDE-209 was found at 332 ng/g dw, octa-BDE-196, nona-BDE-206 and nona-BDE-207 were detected, with the highest value also for nona-BDE-206 (3.82 ng/g dw). The sum of octa- and nona-BDE concentrations represented 2.7% and 2.4% of the deca-BDE-209 amount for P(S3) and T samples, respectively. For the rest of sludge-amended soils, octa- and nona-BDE congeners were below limit of detection or limit of quantification. For these samples, levels of BDE-209 are lower, and then, the expected 2% of BDE-209 concentrations were below the limits of detection and/or quantification.

Deca-BDE-209 was the most contributing PBDE congener in sewage sludge as well as in sludge-amended soils. Debromination of deca-BDE-209 in environmental systems is discussed controversially, leading to the occurrence of lower brominated diphenylethers with known adverse effect for the environment. Watanabe and Tatsukawa (1987) have published that laboratory exposure of BDE-209,

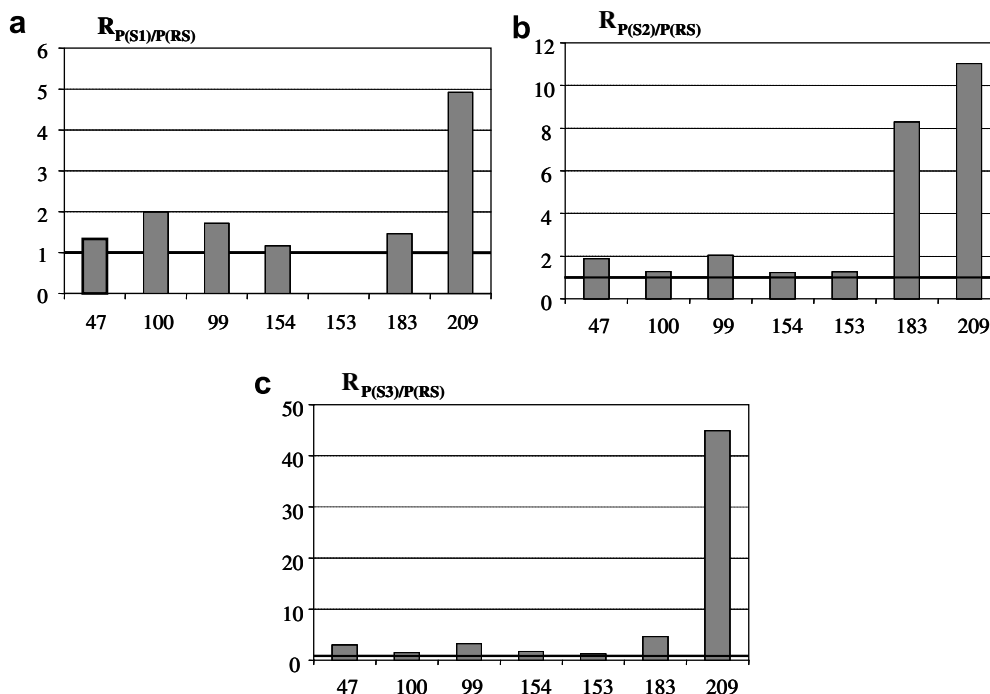


Fig. 2. Sludge-amended soil to reference soil (S/R) ratios for dry weight concentrations of single PBDE congeners, for samples collected in Pujalt area. The ratio showing no difference ($S/R = 1$) is indicated as a darker horizontal line. Note the different scales for a, b and c. (see Table 1 for sampling codes.)

solved in hexane, to UV light promote the formation of a complex mixture of less brominated dibenzofurans and diphenylethers. Hence, BDE-209 in sewage sludge-amended agricultural land could be debrominated by sunlight to lower brominated PBDEs which are more toxic and bioaccumulative. On the contrary, Hale et al. (2002) and de Boer et al. (2000) 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.

3.3. Estimate of sewage sludge contribution to the PBDE concentration in soil

The concentration of PBDEs in soils after the application of sludge could be calculated by the following equation (Jackson and Eduljee, 1994):

$$C_{\text{soil}(t+1)} = C_{\text{soil}(t)} + \frac{C_{\text{sludge}} \times \text{AR}_y}{D \times S_z \times \text{CF}}$$

where: $C_{\text{soil}(t)}$ = soil concentration at time t (ng/kg dw) = 10×10^3 ng/kg dw, C_{sludge} = sludge concentration (ng/kg dw) = 500×10^3 ng/kg dw, AR_y = application rate (kg/ha) = 20×10^3 kg/ha, S_z = soil depth (cm) = 20 cm, D = soil density (kg/cm^3) = 1.5×10^{-3} kg/cm^3 , CF = conversion factor (cm^2/ha) = 1×10^8 cm^2/ha .

$C_{\text{soil}(t)}$ and C_{sludge} values were estimated based on our results as well as published data (see 3.1 and 3.2 sections). AR_y value was set at the mean value of amounts applied in our study (see Table 1), and S_z and D values were set at the default data. Using these values, PBDE loads to soils after the fertilization derived to sludge-amended soil concentration around 15 ng/g dw. This concentration level is lower than those found in sludge-amended soil samples analyzed in this study (Table 3). But, it should be pointed that calculated value estimated only one sludge application, whereas samples studied corresponded to soils in which successive applications were carried out, and a cumulative effect was observed. It is important also to take into account that in these calculations no estimate of PBDE degradation in soil has been included.

4. Conclusions

Sewage sludge samples contained PBDE concentrations in the ng/g level, being deca-BDE-209 the predominant congener. These PBDEs are dispersed in the environment by the spread of the sludge. This was evident from the comparisons of levels found in control soil and sludge-amended soils, where the S/R ratios were between 1.2 and 45, being the higher S/R ratios for BDE-209. Thus, sewage-sludge amendment contributes to significant increases in soil BDE-209 burdens.

There is some discussion of how bioavailable and bioaccumulative BDE-209 is. Moreover, there is still a concern that BDE-209 may debrominate in the environment to

form less-brominated BDE congeners which are more bioavailable than BDE-209 itself. A recent study (Mueller et al., 2006) indicated that interspecific plant interactions may enhance PBDE bioavailability in soil. Thus, although abiotic sorption may limit the potential for human exposure to PBDEs in soil, plants may increase the exposure risk by taking up and translocating PBDEs into aboveground tissues and by enhancing bioavailability in soil.

There are few standards regarding PBDE-contaminated land. The US EPA standard for penta-BDE in residential soil warranting preliminary remediation is 120 mg/kg, and for deca-BDE the standard is 610 mg/kg (US EPA, 2004), however these do not consider potential human health effects. Standards or guidelines for PBDEs which are specific to different land uses (agricultural, playgrounds, commercial) are needed to protect human health.

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