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ScienceDirect
Journal of Environmental Sciences 2012, 24(3) 558–563

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Concentrations and sources of an emerging pollutant, decabromodiphenylethane (DBDPE), in sewage sludge for land application

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Received 12 February 2011; revised 25 March 2011; accepted 28 April 2011

Abstract

The presence of an emerging brominated flame retardant, decabromodiphenylethane (DBDPE), has been confirmed in Spanish sewage sludge. Thirty one samples from different urban wastewater treatment plants (WWTPs) were analyzed for this brominated flame retardant. DBDPE was positively identified and quantified in all samples at lower concentrations (47.0 ± 29.7 ng/g dry weight (dw); mean ± SD) than those obtained for decabromodiphenyl ether (BDE-209) (290 ± 236 ng/g dw; mean ± SD) in a previous study. Influence of the WWTP characteristics in the pollutant levels was evaluated. No significant correlations were obtained between DBDPE concentrations and the population or sewage sludge production rate associated with the plants, neither wastewater treatment method. Sources of DBDPE in the sludge were also evaluated. Data indicate a common origin for DBDPE and BDE-209, which may be related to leaching processes during the use and disposal of consumer products containing these chemicals. Nevertheless, DBDPE contents are not influenced by industrial activities, which suggests that the infusion of DBDPE commercial mixture is not a source of this chemical into the environment, and indicates that the use of DBDPE in the Spanish industry is still low compared to deca-BDE.

Key words: decabromodiphenylethane; polybrominated diphenyl ethers; wastewater treatment plants; sewage sludge

DOI:10.1016/S1001-0742(11)60801-2

Introduction

The European Commission estimates that more than 11 million tons of sewage sludge are produced each year in the 27 EU Member States, of which approximately 48%, almost 5.4 millions tons, are recycled in the agriculture (data predicted for 2010; Milieu Ltd et al., 2010). This proportion varies widely between Member States, the highest was reported for Spain (around 65%) while in other countries like Finland, Belgium or Greece it is less than 5%. Although the sludge is rich in nutrients like nitrogen and phosphorus, suggesting its use as fertilizer in agriculture, it also contains potential contaminants such as heavy metals, pathogens and organic compounds which presence should be evaluated. The current European Sewage Sludge Directive 86/278/EEC, sets limit values for heavy metals (cadmium, chromium, mercury, zinc, lead, nickel, and copper) both in soil and sludge, and addresses pathogen reduction, however, sets no limits for organic contaminants. Some of these compounds have been included in the Working Document on Sludge 3RD Draft (EU, 2000) (dibenzo-*p*-dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs)), but further research is required on emerging organic pollutants, like brominated flame retardants (BFRs), especially polybrominated diphenyl ethers (PBDEs) and its substitutes.

PBDEs are a family of synthetic chemicals widely used in industry to delay, inhibit or even suppress combustion processes (WHO, 1994, 1997). PBDEs have been produced in three commercial mixtures: penta-BDE, octa-BDE, and deca-BDE, related to their different degrees of bromination (Alaee et al., 2003). Nevertheless, their production and use have been restricted when their persistence, bioaccumulation and potential toxicity both in environmental and human samples (de Wit, 2002) have been demonstrated. penta- and octa-BDE comercial mixtures were banned in Europe in 2003 (Directive 2003/11/CE) and have been recently included in the Stockholm Convention (UNEP, 2011). These facts, correlated well with results of our previous study (de la Torre et al., 2011), where we found that PBDE content in sludge was mainly BDE-209, the major congener of deca-BDE technical mixture (La Guardia et al., 2006). However, recent restrictions on the use of deca-BDE, especially in electronics and electrical applications (ECJ, 2008), have forced the industry to move to others unregulated flame retardant.

This study evaluates the presence of decabromodiphenylethane (DBDPE), which has been included in the list of potential flame retardant alternatives to deca-BDE (ECB, 2007), in sewage sludge. Once entering the WWTPs, BDE-209 and DBDPE are almost completely sequestered into the sludge (up to 99%)

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(Ricklund et al., 2008b), and therefore the study of this integrative matrix will be helpfull to elucidate consumer patterns related to the subtitution degree of deca-BDE by DBDPE. The chemical structures of the two compounds are similar (Fig. 1), an hence DBDPE may also become an enrivonmental contaminant of concern (Ricklund et al., 2008a).

DBDPE is a relatively new BFR with similar applications to deca-BDE as an additive flame retardant (Kierkegaard et al., 2004). DBDPE is available on the market since the mid-1980s, under trade name SAYTEX 8010 (Albemarle Corp., USA) and Firemaster 2100 (Great Lakes Chemical Corp., USA). However, it was in the early 90s when DBDPE became commercially important as an alternative to the deca-BDE formulation (Arias, 2001). Although it is not as widely used as deca-BDE due to its higher cost (Eljarrat et al., 2005), it is predicted that DBDPE will become one of the major BFR used by the thermoplastics industry (Konstantinov et al., 2006) following restricted policies focused on deca-BDE and the fact that DBDPE meets the German Dioxin Ordenances because it does not produce polybrominated dibenzo-*p*-dioxins and only minor quantities of of 2,3,7,8-tetrabromodibenzo furan under pyrolysis conditions (Pettigrew, 1993). In agreement with this, Watanabe and Sakai (2003) reported an increasing trend subtitution of deca-BDE for DBDPE in Japan.

First report on DBDPE was published in 2004 (Kierkegaard et al., 2004) and since then, several studies have reported the presence of DBDPE in the environment (Eljarrat et al., 2005; Julander et al., 2005; Law et al., 2006; Zhu and Hites, 2006; Karlsson et al., 2007; Harrad et al., 2008; Qiu and Hites, 2008; Gauthier et al., 2009; Luo et al., 2009; Zhang et al., 2009; Hu et al., 2011). However, the potential sources and environmental behaviours of DBDPE are still not clear (Hu et al., 2011), which emphasizes the need for further research related to this emerging pollutant.

In a previous research we evaluated the presence of PBDEs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in sewage sludge (de la Torre et al., 2011). BDE-209 resulted the major PBDE congener, demostrating the use of deca-BDE comercial mixtures in Spain. Now, the substitution degree of deca-BDE by DBDPE is evaluated. To achive this objective a method to analyse DBDPE using surrogate standards and based on high resolution gas chromatography (HRGC) coupled with mass spectrometry triple quadrupole operating in tandem mode (TQMS/MS) was developed and applied to 31 sewage sludge samples from Spain. Influence of the WWTP characteristics on the obtained DBDPE concentrations was examined.

1 Materials and methods

1.1 Standards and reagents

Three analytical grade solutions: $^{12}C_{14}$-DBDPE (25 μg/mL, in toluene), $^{13}C_{14}$-DBDPE (25 μg/mL, in toluene) and $^{13}C_{12}$-BDE-138 (50 μg/mL, in nonane) were obtained from Wellington Laboratories, Ontario (Canada). A five points calibration curve was prepared; natives ranging from 5 to 2000 ng/mL and labelled at 100 ng/mL. Analyses were carried out with $^{13}C_{14}$-DBDPE as recovery and $^{13}C_{12}$-BDE-138 as injection standards.

Other chemicals including: anhydrous sodium sulphate, copper fine powder, sulfuric acid (95%–97%) and organic trace analysis grade solvents (hexane, dichloromethane, ethyl acetate, and toluene) were purchased from Merck (Darmstadt, Germany).

1.2 Sample collection

Sewage sludge samples were collected between April and June 2006, from thirty one urban wastewater treatment plants (WWTPs) of different sizes and geographically distributed all over Spain (Fig. 2). Samples were poured into sealed amber-glass flasks to protect them from light, humidity and other external factors which might change their chemical composition. Upon receiving in the laboratory, samples were dried at 40°C until constant weight, grounded into a fine powder, and stored at –18°C until

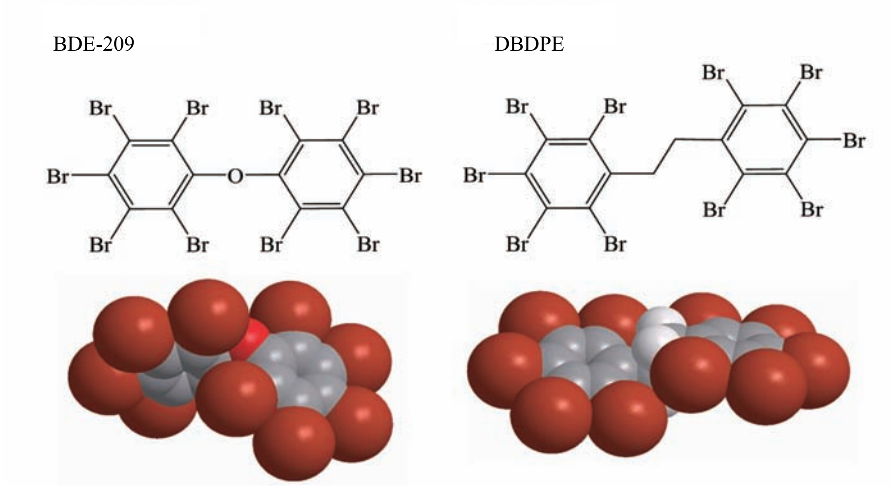

Fig. 1 Chemical structures and Van der Waals surfaces of BDE-209 and DBDPE.

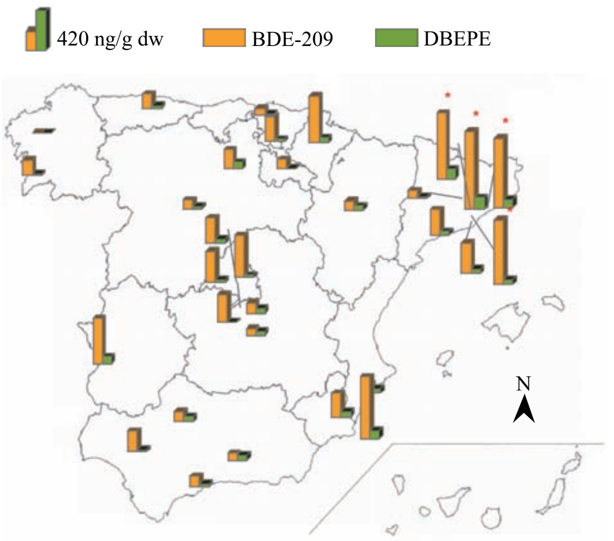

Fig. 2 Concentrations of DBDPE and BDE-209 in ng/g dw (BDE-209 data from de la Torre et al., 2011). Samples labelled with an asterisk corresponded to WWTPs with input of textile industrial effluents.

analysis.

Complete details of the plant characteristics are listed in Table 1. Total population associated with the plants was 13.1 millions, representing around 30% of the Spanish population (INE, 2010). The corresponding sewage sludge production volume of 0.2 millions tons was commensurate with 33% of total Spanish output in 2006 (Milieu Ltd et al., 2010). The 20 of the 31 WWTPs evaluated (65%) apply aerobic sewage treatment, whereas the rest (11 of 31; 35%) are subjected to biological nitrogen (N) and phosphorous (P) elimination in three different digesters: anaerobic, followed by anoxic and finally aerobic. The sludge obtained were mesophilic anaerobically stabilized, subjected to chemical treatment, or no stabilized (84%, 6%, and 9% of the samples analyzed). Although all WWTPs evaluated are classified as urban, 48% of them recognized an industrial effluent input.

1.3 Extraction and clean-up

An Accelerated Solvent Extraction system (ASE 100, Dionex, USA) was used to perform the extraction with a mixture of hexane:dichloromethane (1:1, V/V) as solvent, at 100°C, 10.3 MPa, 90% flush volume and three static cycles (10 min time each). Dried sewage sludge (0.5 g) was spiked with ^{13}C recovery standard (containing 2 ng of $^{13}C_{14}$-DBDPE) and mixed with 2.5 g of anhydrous sodium sulphate and 0.5 g of copper fine powder to remove sulphur interferences. This mixture was introduced into the cell previously loaded by inserting one cellulose filter,

Table 1 Characteristics of the WWTPs and levels of DBDPE and BDE-209 obtained in the samples analyzed

Sample	WWTP						
	Equivalent population	Rate (ton/yr)	Influent[a] (%ind)	Treatment[b]	BDE-209[c] (ng/g dw)	DBDPE (ng/g dw)	DBDPE/BDE-209
1	188610	4149	n.r.	A	5.45	3.25	0.60
2	195000	3000	n.r.	A	331	49.6	0.15
3	400000	4500	n.r.	A	169	23.3	0.14
4	280000	2569	n.r.	A	674	92.6	0.14
5	143324	3838	n.r.	A	491	78.8	0.16
6	288000	50512	n.r.	A	114	54.0	0.47
7	620000	18300	n.r.	A	224	19.8	0.09
8	575000	47450	n.r.	A	111	30.8	0.28
9	562500	7686	n.r.	A	94.6	51.6	0.55
10	950000	12867	n.r.	A	283	50.9	0.18
11	1000000	17949	n.r.	A	300	6.90	0.02
12	1314831	12960	n.r.	A	694	51.5	0.07
13	105851	3910	n.r.	A	79.2	57.5	0.73
14	116000	3709	15	A	271.3	33.9	0.12
15	80000	2510	16	A	92.0	23.3	0.25
16	622673	8708	20	A	207	72.5	0.35
17	228000	4216	20	A	749	87.0	0.12
18	225000	2500	20	A	715	112	0.16
19	320000	3147	35	A	346	32.3	0.09
20	165000	2800	40	A	843	125	0.15
21	700000	16719	n.r.	B	98.4	41.1	0.42
22	570000	8166	n.r.	B	96.2	27.59	0.29
23	590000	32872	n.r.	B	255	56.0	0.22
24	852961	24005	4	B	75.2	17.5	0.23
25	259125	17184	8	B	155	31.5	0.20
26	195323	1560	10	B	76.2	43.7	0.54
27	466560	2680	10	B	99.0	6.02	0.06
28	382249	12184	10	B	109	62.1	0.23
29	350000	6600	20	B	272	26.0	0.05
30	650000	8000	25	B	500	56.4	0.11
31	456304	8639	51	B	452	24.1	0.17
				Mean	290	47.0	0.25
				Range	5.45–843	3.25–125	0.02–0.73

[a] n.r.: no recognised input of industrial effluents.
[b] Type of treatment: A: conventional biological (aerobic digester); B: biological elimination of N and P (anaerobic + anoxic + aerobic digester).
[c] Data from de la Torre et al., 2011.

followed by 2.5 g of anhydrous sodium sulphate. The extract obtained was solvent exchanged with hexane and transferred into a separation funnel where was liquid-extracted with 50 mL of concentrated sulphuric acid.

Following clean-up and fractionation stage was performed in an automated purification Power Prep™ System (FMS Inc., USA) including acidic silica gel, basic alumina and carbon columns. This stage was optimized to analyze various analytes in two separate fractions: Fraction A, containing DBDPE and PCDD/Fs; and Fraction B, containing PBDEs. Data for PCDD/Fs and the rest of PBDEs have been previously published (de la Torre et al., 2011).

The fractions obtained were finally concentrated using a TurboVap® II evaporator (Vertex Technics, Spain) under nitrogen to incipient dryness and re-dissolved in 20 µL of nonane spiked with the injection standard solution (containing 2 ng $^{13}C_{12}$-BDE-138) before being analyzed by HRGC-TQMS/MS.

1.4 Instrumental analysis

Analyses of DBDPE were carried out in a CP-3800 Gas Chromatograph (Varian, USA) fitted with a 15-m J&W Scientific DB-5MS capillary column (0.25 mm i.d. × 0.10 µm film thickness) and connected to a Varian 320-MS-TQ Spectrometer. Pulsed splitless (0.21 MPa) injections were performed on an injector set isothermally at 280°C. The initial oven temperature was set at 140°C with 1 min hold time, and ramped at 20°C/min to 310°C and held for 8 min. Transfer line, ion source and manifold temperatures were 280, 300 and 42°C, respectively. Helium at a constant flow (1 mL/min) was used as carrier gas.

The selection of the masses to monitor was developed in order to avoid the overlap of the base peak related to the loss of 6 bromines of $^{12}C_{14}$-DBDPE fragment $[^{12}C_{14}H_4Br_4]^+$ and the pentabromobenzyl fragment $[^{13}C_7H_2Br_5]^+$ of $^{13}C_{14}$-DBDPE (Konstantinov et al., 2006). Taking into account this problem, a tandem MS/MS method was developed to analyze this compound. First of all, the molecular ions $[M+10]^+$ of $^{12}C_{14}$-DBDPE and $^{13}C_{14}$-DBDPE were isolated in the first quadrupole. Then, after optimizing the collision voltages in the second quadrupole, *m/z* 486.6/484.7 $[^{12}C_7H_2Br_5]^+$ and *m/z* 971.4 $[^{12}M+10]^+$ for $^{12}C_{14}$-DBDPE and *m/z* 493.3/491.1 $[^{13}C_7H_2Br_5]^+$ and *m/z* 985.5 $[^{13}M+10]^+$ for $^{13}C_{14}$-DBDPE were monitored in the third quadrupole. Analyses were performed at 20 eV electron energy. The lowest energy produced less fragmentation of the molecular ion in the source and consequently, more sensitivity was achieved in the second fragmentation, which means lastly, better limit of detection.

1.5 Quality control

Three criteria were used to ensure the correct identification and quantification of DBDPE. First, the retention time must be within ± 1 sec between the analyte and its labelled standard. Second, the ratio of quantifier and qualifier ions must be within ± 15% of the theoretical values. Third, the signal to noise ratio must be greater than 5. Instrumental blanks were injections of nonane run after every sample and were used to monitor contamination between GC injections. Procedural blanks were carried out and analyzed under the same conditions than samples at a rate of one every teen samples on routine basis in the laboratory. DBDPE was at undetectable level in the procedural blanks. Mean recovery for $^{13}C_{14}$-DBDPE was (63% ± 25%; mean ± SD). Mean limits of detection (LODs), defined as the concentration giving a signal to noise ratio greater than 3, was 0.3 pg/g dw. Good linearity was achieved in the linear dynamic range (5–2000 pg) with a correlation coefficient of 0.998.

2 Result and discussion

2.1 DBDPE in sewage sludge

Concentration levels of the samples analyzed are illustrated in Fig. 2 and listed in Table 1. For comparative purpose, levels of BDE-209 in the same samples from de la Torre et al. (2011) have been also included. DBDPE was detected in all samples. Concentrations of DBDPE were lower (47.0 ± 29.7 ng/g dw; mean ± SD) than those obtained for BDE-209 (290 ± 236 ng/g dw; mean ± SD).

DBDPE mean concentration in this study is around two times lower than the one obtained for Europe in an international survey conducted by Ricklund et al. (2008a) (81 ± 62 ng/g dw; mean ± SD). As commented by the authors, this mean is clearly influenced by relative high DBDPE levels found in samples from Germany and Switzerland (8 of the 18 European samples) and could be easily attributed to their commercial ties and the high imports of DBDPE in Germany (Arias, 2001). Spanish samples were not included in that study (Ricklund et al., 2008a). Results for DBDPE in this study (ranging in 3.25–125 ng/g dw) are similar to those reported by Kierkegard et al. (2004) in Swedish samples (from non detected to 100 ng/g dw), and higher than the levels reported in Canadian sludge samples (from 6 to 32 ng/g dw) by Konstantinov et al. (2006) where deca-BDE technical mixture is widely used.

2.2 Effect of WWTP characteristics in DBDPE levels

Correlations between DBDPE, BDE-209, and the WWTP characteristics were evaluated by a Pearson's test, as shown in Table 2.

In agreement with Kierkegaard et al. (2004) and Ricklund et al. (2008a), no significant correlations could be obtained with DBDPE levels and the WWTP characteristics: population and sewage sludge production associated with the plants. Similar results were obtained for PBDEs and PCDD/Fs (de la Torre et al., 2011), indicating that these WWTP characteristics are not indicative of DBDPE concentration.

In our previous study, samples obtained from biological N and P elimination wastewater treatment presented lower PBDE concentrations than those from conventional biological digester. PBDEs could be degradated by microorganism involved in P elimination (de la Torre et al., 2011). However, no statistically significant differences (*p*

Table 2 Pearson correlation matrix for WWTP characteristics and concentrations of BDE-209 and DBDPE obtained

	Equivalent population	Rate (ton/yr)	Influent (%ind)	BDE-209 (ng/g dw)	DBDPE (ng/g dw)	DBDPE/BDE-209 ratio
Equivalent population	1					
Rate (ton/yr)	0.341	1				
Influent (%ind)	–0.102	–0.348	1			
BDE-209 (ng/g dw)	0.007	–0.288	0.620*	1		
DBDPE (ng/g dw)	–0.247	–0.169	0.277	0.704 **	1	
DBDPE/BDE-209 ratio	–0.239	0.111	–0.467	–0.571 **	0.029	1

** Significative correlation at $p < 0.01$; * significative correlation at $p < 0.05$.

< 0.05) were observed in terms of DBDPE concentrations between both types of wastewater treatments.

2.3 Sources of DBDPE and BDE-209 in the sludge

There are two indications in the data obtained that could help to elucidate the potential origins of these compounds in the sludge. First, the good correlation between DBDPE and BDE-209 concentrations ($p < 0.01$; $r = 0.704$), which could indicate a common origin, probably related to leaching processes during use and disposal of products containing these chemicals. Second, the correlation between the recognized industrial percentage in the WWTP influent (Table 2) and the BDE-209 levels ($p < 0.05$; $r = 0.620$), which was not found for DBDPE ($p < 0.05$). These results imply: (1) industrial activities as important sources of deca-BDE in the sludge, and (2) the higher use of deca-BDE formulation in comparison to DBDPE in Spain. The highest values for BDE-209 were found in samples located in Catalonia region, a zone with presence of important textile industries. These samples are labelled with an asterisk in Fig. 2.

Influence of industrial activites in BDE-209 sludge levels was also demonstrated by the good correlation obtained between DBDPE/BDE-209 ratios and BDE-209 levels ($p < 0.01$; $r = –0.571$). DBDPE/BDE-209 ratios increased with decreasing BDE-209 concentrations ($R^2 = 0.3256$), as shown in Fig. 3. Similar fact has been reported by Ricklund et al. (2008a), but in this study DBDPE levels remained almost constant ($R^2 = 0.0008$) when ratio changes, demonstrating that the use of DBDPE in Spain is still low compared to deca-BDE formulation.

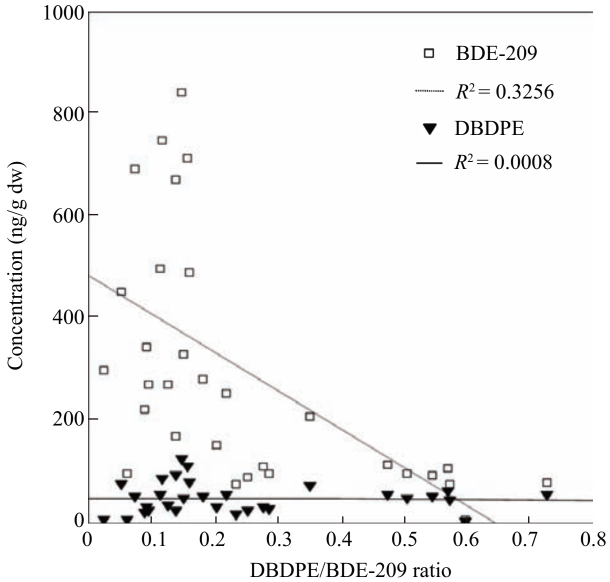

Fig. 3 Regression analyses between BDE-209 and DBDPE concentrations, and DBDPE/BDE-209 ratios for the sewage sludge samples evaluated.

3 Conclusions

DBDPE was positively detected in thirty one sewage sludge samples from different urban WWTPs. Usage and disposal of consumer products resulted the major source for DBDPE in the sludge. Levels of DBDPE are low compared to PBDEs, reflecting a low substitution degree of deca-BDE by DBDPE in Spain. Nevertheless, considering the great importance of the agricultural application as a recycling route for sewage sludge in Europe and especially in Spain, the presence of DBDPE in the sludge could lead to increase its concentration in soils and therefore in the terrestrial food web.

It is expected that as consumption patterns change new pollutants appear in the sewage sludge. For this reason, studies reporting the presence of emerging contaminants in this matrix, should be taken into account when developing or revising the politics about the land application of sewage sludge.

Acknowledgments

This work was supported by the Spanish Minister of Science and Innovation through the Unit of Characterization of the Atmospheric Pollution and Persistent Organic Pollutants, Environment Department, CIEMAT, Spain, and by the Center of Civil Engineering Research (CEDEX) through the 44-403-1-096 project (Research on sludge from wastewater treatment. Directive 86/278/CEE) signed with the Ministry of Environment, Spain.

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