PRESENCE OF PBDEs AND DBDPE IN LEACHATE AND COMPOST FROM DIFFERENT SPANISH LANDFILLS

Adrián de la Torre, Paloma Sanz, María Ángeles Martínez

Persistent Organic Pollutant Group, Environmental Department. CIEMAT, Avd. Complutense 22 Madrid, Spain.

Introduction

Management of toxic and hazardous wastes (300,000 Tm/year) and urban wastes (several millions Tm/year) is one of the key environmental problems for the Central Region of Spain. Investment and environmental compromises have been fruitful, but recent research have identified additional concerns, related to some priority pollutants, with may challenge current developments. This is the case of polybrominated diphenyl ethers (PBDEs), which are transfered from consumer products to the environment in the leachate process that occurs in landfills. Leachate is generated by excess rainwater and waste percolating through the waste layer in a landfill. A combination of physical, chemical and microbial processes in the waste, transfers pollutants from the waste material to the percolating water [1]. The leaching processes in landfills are not yet fully understood. In particular, PBDEs are so hydrophobic that they are not readily dissolved and their leachability could be affected by other constituents present in the leachate like dissolve organic matter (DOM)[2].

Only few studies have reported presence of PBDEs in leachates from landfills. Oliaei et al (2002) [3] presented data obtained at five landfills in Minnesota with concentrations of PBDE-47, -99, -100, -153, -154, -207 and -208 ranged widely from non detected to thousands of pg L^{-1}. Osako et al (2004) [4] found levels of PBDEs in leachates from Japan ranged from non detected to 23.1 ng L^{-1}. After, Chiu et al (2006) [5], published levels, from 0.017 to 738.3 ng L^{-1} and , Denon-Schaffer et al (2006) [6] presented levels from 2.8 to 1468.8 ng L^{-1} in Canada. Finally Czerwinski et al (2007) [7], detected levels of the sum of PBDE-47, -100, -99, 153, and -138 varying from non detected to 550 ng L^{-1} in leachates from Poland.

This paper reports preliminary results of on-going research studying municipal landfills as a source of PBDEs in Spain, and it has two main objectives: to show the concentration and composition of PBDEs in leachates and compost from different landfills and to evaluate the presence of a “new” brominated flame retardant, Decabromo diphenyl ethane (DBDPE), in these matrices. Taking into account the major potential environmental impact related to landfill leachate is pollution of ground and surface waters, two samples taken from a stream next to a closed landfill has been included in the survey to evaluate the possible transfer of these compounds from landfills to the environment. To the knowledge of the authors, these are the first published polibrominated diphenyl ethers ,levels for Spanish landfill leachates and the first DBDPE data reported for these matrices.

Materials and Methods

Sample collection:

Liquid samples (Leachate and Water) and solid samples (Compost and Soil) were sampled from five landfills situated in the Central Region of Spain in June - September 2007. Features of samples analysed are described in Table 1. Facility A is a closed landfill; in this case, liquid samples were sampled in a stream next to the landfill, A.1 and A.2 corresponded to the stream influent and the effluent respectively, and the solid sample, A.3, was a soil sample of the closed landfill.

Sample Extraction and Clean up:

Upon receiving in the laboratory, liquid samples were stored into the fridge to preserve from light, humidity and other external factors which might changes its chemical composition. On the other hand, solid samples were dried at 40°C until constant weight to avoid lack of volatile congeners and ground to a fine powder. Prior to extraction all samples were spiked with a known amount of MDBDPE and MBDE-MXE standard solutions (Wellington Laboratories Inc., Canada).

Liquid samples, (1-2 L) were subjected three times to liquid-liquid extraction with 100 ml of dichloromethane, while solid samples (0.5 g d.w.) were extracted with a mixture of hexane:dichloromethane (1:1)100ºC, 1500psi, 90% volume and three static cycles, using an ASE 100 system (Accelerated Solvent Extraction). 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^{TM} System (FMS, Inc., USA) including acidic silica gel, basic alumina and carbon columns. Different mixtures of hexane:dicloromethane and toluene were used to recover target analytes while retaining interfering compounds. The extracts obtained were concentrated to incipient dryness and spiked with the recovery standard BDE-CVS-EISS (Wellington Laboratories Inc., Canada) previously to be analyzed by Gas Chromatography-Low Resolution Mass Spectrometry (GC-LRMS).

Sample Analysis:
Analyses of PBDEs were carried out by GC-qEI-MS in a Agilent 6890 Gas Chromatograph equipped with a 7683 Autosampler, and a temperature programmable injector (PTV) working in pulsed splitless, connected to a LRMS detector, Agilent 5973 MSD Network. Besides, analysis of DBDPE was performed by GC/MS/MS in a Varian 320-MS-TQ Spectrometer equipped with a CP-3800 Gas Chromatograph and a Varian CP-8400 Autosampler. For both analysis, PBDEs and DBDPE, a J&W Scientific DB-5MS (15 m x 0.25 mm x 0.10 µm film thickness) capillary column was used. Complete details about the analysis methods were published elsewhere, both for PBDEs [8] and for DBDPE [9].Identification and quantification was carried out using isotopic dilution, which allows a high accuracy in the calculation of final results.

Results and Discussion

Concentration levels of the samples analysed are listed in Table 2, for liquid samples, and Table 3, for solid samples. Limits of detection, LODs, were defined as the smaller concentration giving a signal with S/N>3. LODs of PBDEs, obtained with the liquid samples ranged from 1 to 600 pg L^{-1} for Tri to Nona PBDEs and from 0.4 to 10.5 ng L^{-1} for Deca-BDE, while for solid samples ranged from 9 to 897 pg g^{-1} d.w. for Tri to Nona PBDEs and from 1.4 to 9.2 ng g^{-1} d.w. for Deca-BDE. Simultaneously, LODs of DBDPE ranged from 10 to 60 pg L^{-1} in the liquid samples and from 0.03 to 1.13 ng g^{-1} d.w. in the solid samples. Recoveries for PBDEs were in the range of 51 to 138 % for solid samples and of 54 to 138 % for liquid samples.

PBDEs:
The total concentration of PBDEs ranged from 24 to 300 ng g^{-1} d.w. in the compost samples and from 0.38 to 45.48 ng L^{-1} in leachates. The highest concentrations were related to PBDE-209, -99, -47 and -183 in compost samples. However, not similar congener profiles were found for leachates samples, presenting each one a different congener distribution. These data are lower than those published by Czerwinski[7] (not detected-550 ng L^{-1}) in Polish leachates and Danon-Schaffer[6] (2.8- 1468.8 ng L^{-1}) in Canadian ones. It is important to notice that the highest levels found in leachate corresponded to those leached from the compost, B.1 > B.2, D.3 > D.1 and D.2, and E.2 > E.1, see Table 2. Consequently, it could be thought that PBDEs leaches easily from the compost to the liquid phase.

In the same way, it can be observed that the fermentation compost B.4 (24.07 ng g^{-1}) presents a lower level of PBDEs than the maturation compost of the same facility, B.3 (42.52 ng g^{-1}). This fact could be due to the evaporation of volatile compounds and consequently concentration of analytes, which takes place during compost process. It is known that fermentation occurs prior to maturation. In Facility E, a leachate from an Osmosis Plant was analysed. Levels decrease in comparison to others obtained in the same facility, E.3 (0.38 ngL^{-1}) <E.2 (15.29 ng L^{-1}) and E.1 (1.79 ng L^{-1}), which suggest that Osmosis treatment could eliminate PBDEs.

On the other hand, analyses carried out in the closed landfill, A, revealed that no significant pollution of BFRs can be observed in the stream. PBDEs in the influent were smaller than those found in the effluent, A1 and A2, 1.07 and 1.2 ng L^{-1} respectively. As the same time, the soil sample presented a low level of PBDEs, 7.7 ng g^{-1} d.w.

DBDPE:

The presence of a "new" brominated flame retardant, DBDPE, has been confirmed in these matrices. Decabromodiphenyl ethane was positively identified and quantified in three of the leachates analyzed, with levels ranging from 1.2 to 35 ng L^{-1}.DBDPE in compost varied between 101.20 and 318.20 ng g^{-1}. In samples that present content of DecaBDE and DBDPE simultaneously, DBDPE/DecaBDE ratio was calculated, obtaining values of 0.8 in leachates and 0.7- 21.2 in compost. The high variability of this ratio seems to indicate that the products are used independently. Same behaviour has been published in Spanish sewage sludges [9]. It is important to notice that Facility B have presented higher levels of DBDPE than DecaBDE. This fact could indicate an increase in the replacement of DecaBDE by DBDPE.

Data obtained in this study evidence that leachates could be a potential source of BFRs pollution, demonstrating the importance of landfill leachates collection systems for minimizing release of these pollutants into environment.

These data are preliminary results of an on-going research. As the leachate composition varies significantly among landfills depending on waste composition, waste age and landfill technology, future campaigns are performing in the same facilities to determine time trends, besides including other different facilities.

Acknowledgments

The authors would like to thank Dr. Herráez for providing the samples. This work has been supported in the framework of the Spanish R&D Program (CAM Project: RESIDUOS S-0505/AMB-0352 and MEC Project: TRT2006-00030-00-00).

References

1. Kjelsen P, Barlaz MA, Rooker AP, Baun A, Ledin A, Chiristensen TH. *Critical Reviews in Environmental Science and Technology* 2002; 32:297.
2. Osako M, Kim YJ, Sakai S. *Chemosphere* 2004; 57:1571.
3. Oliaei F, King P, Phillips L. *Organohalogen Compounds* 1992; 58:185.
4. Osako M, Kim YJ, Lee DH. *Chemosphere* 2002; 48:849.
5. Chiu CH, Poole G, Thilbert B, Cooper D, Hawke L. *Organohalogen Compounds* 2006; 68:1753.
6. Dannon-Schaffer MN, Grace JR, Wenning RJ, Ikonomou MG, Luksemburg WJ. *Organohalogen Compounds* 2006; 68:1759.
7. Czerwinski J, Dudzinska MR, Staszowska A, Rault B. *Organohalogen Compounds* 2007; 69:2720.
8. De la Torre A., Martínez MA, Sanz P, Concejero MA. *Fourth International Workshop on Brominated Flame Retardants BFR* 2007.
9. De la Torre A., Concejero MA, Sanz P, Martínez MA. *Organohalogen Comp* 2007; 69:2702.

Table 1: Outline of facilities and samples studied

Facility	Liquid Samples		Solid Samples	
A	**A.1**	Stream Influent	**A.3**	Soil sample
Closed landfill	**A.2**	Stream Effluent		
B	**B.1**	Compost leachate	**B.3**	Maturation compost
	B.2	Landfill leachate	**B.4**	Fermentation compost
C	**C.1**	Landfill leachate		
	C.2	Landfill leachate		
D	**D.1**	Landfill leachate	**D.4**	Maturation compost
	D.2	Landfill leachate	**D.5**	Maturation compost
	D.3	Compost leachate		
E	**E.1**	Landfill leachate	**E.4**	Maturation compost
	E.2	Compost leachate		
	E.3	Osmosis Plant		

Table 2: BFRs concentrations in the pg L^{-1} of liquid samples analysed: S.I. stream influent; S.E. stream effluent; C.L. compost leachate; L.L. landfill leachate.; O.P. osmosis plant.

Facility	A		B		C		D			E		
Sample	A.1	A.2	B.1	B.2	C.1	C.2	D.1	D.2	D.3	E.1	E.2	E.3
	S.I.	S.E.	C.L	L.L.	L.L	L.L	L.L	L.L	C.L	L.L	C.L.	O.P.
Tri-BDE 17	-	-	-	-	-	-	-	-	62	-	121	-
Tri-BDE 28	-	-	67	29	-	-	13	10	236	-	124	-
Tetra-BDE 47	-	-	-	-	-	-	559	438	2284	644	3739	-
Tetra-BDE 66	-	-	-	-	-	-	324	224	1132	422	-	-
Tetra-BDE 77	-	-	-	-	-	-	-	-	-	-	-	-
Penta-BDE 100	-	-	283	164	-	128	47	26	653		-	-
Penta-BDE 119	52	-	-	-	-	-	29	-	-	-	-	-
Penta-BDE 99	53	18	1204	280	-	-	177	82	3827	166	6608	-
Penta-BDE 85	-	-	-	-	-	-	-	-	-	-	-	-
Hexa-BDE 154	-	-	104	-	-	-	20	11	303	49	-	-
Hexa-BDE 153	-	-	186	43	-	-	33	16	961	82	-	42
Hexa-BDE 138	-	-	-	-	-	-	-	-	-	-	-	-
Hexa-BDE 156	-	-	-	-	-	-	-	-	-	-	-	-
Hepta-BDE 184	152	172	327	158	181	327	-	-	160	159	-	160
Hepta-BDE 183	815	1017	1342	971	726	880	41	21	1549	269	1909	178
Hepta-BDE 191	-	-	-	-	-	-	22	-	-	-	-	-
Octa-BDE 197	-	-	174	-	-	-	-	-	795	-	1349	-
Octa-BDE 196	-	-	-	-	-	-	-	-	-	-	-	-
Nona-BDE-207	-	-	624	-	-	-	-	-	1717	-	1436	-
Nona-BDE-206	-	-	546	-	-	-	-	-	2105	-	-	-
Deca-BDE 209	-	-	19754	-	-	-	856	996	29694	-	-	-
? PBDEs	1073	1206	24612	1645	907	1335	2120	1825	45478	1789	15285	380
DBDPE	-	-	-	-	-	-	-	-	35780	1260	68460	-

- = No detected.

Table 3: BFRs concentrations in pg g^{-1} d.w. of solid samples analysed: S soil; M maturation compost; and F: fermentation compost.

Facility	A	B		D		E
Sample	A.3	B.3	B.4	D.4	D.5	E.4
	S	M	F	M	M	M
Tri-BDE 17	-	-	-	208	265	285
Tri-BDE 28	44	258	200	1365	1821	2222
Tetra-BDE 47	-	2400	-	10183	20224	8946
Tetra-BDE 66	796	-	1045	3839	4563	6754
Tetra-BDE 77	-	-	-	-	-	-
Penta-BDE 100	90	542	401	2682	4589	1.227
Penta-BDE 119	-	255		667	1261	975
Penta-BDE 99	134	3292	2.520	17010	29054	9.383
Penta-BDE 85	-	-	-	-		
Hexa-BDE 154	56	286	250	1.557	3801	794
Hexa-BDE 153	62	710	411	4.948	7613	2816
Hexa-BDE 138	69	-	-	-	-	-
Hexa-BDE 156	-	-	-	-	-	-
Hepta-BDE 184	408	692	761	-	-	-
Hepta-BDE 183	1878	3465	2263	7699	7853	4492
Hepta-BDE 191	-	-	-	-	-	-
Octa-BDE 197	527	709	-	8852	4096	3071
Octa-BDE 196	-	407	-	-	-	-
Nona-BDE-207	-	1872	666	10096	7427	5261
Nona-BDE-206	-	1492	532	-	7743	7672
Deca-BDE 209	3623	26136	15026	231668	169523	117653
? PBDEs	7686	42518	24075	300775	269833	171551
DBDPE	-	221300	318200	269900	113000	101200
Ratio DBDPE/Deca 209	-	8.5	21.2	1.2	0.7	0.9

- = No detected