MEASUREMENT OF PBDES IN LANDFILL LEACHATES

Chiu CH[1], Poole G[1], Thibert B[1], Cooper D[2], Hawke L[2]

[1]Analysis and Air Quality division, Science and Technology Branch, Environment Canada; [2]Science Applications International Corporation, 335 River Road, Ottawa, Ontario, K1A 0H3, Canada

Introduction

Polybrominated diphhenyl ethers (PBDEs) have been used mainly as additive flame retardants in polymer resins and plastics. These synthetic mixtures are normally mixed with polymers rather than chemically bonded. As a result, PBDEs have a great potential for migration and leaching out from the polymeric products.

Environment Canada and Health Canada published the Environmental Screening Assessment Report on PBDEs in early 2004 [1]. This report concluded that tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-BDE, which are found in commercial PeBDE, OBDE and DBDE, are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity and thus satisfy the definition of "toxic" under Paragraph 64(a) of CEPA 1999. As a results, these compounds have been proposed by both ministers to be added to the List of Toxic Substances in Schedule 1 of the Canadian Environmental Protection Act, 1999 (CEPA 1999).

To investigate the amount of PBDEs that could be leached out from landfill waste into other parts of environment, a total of 19 leachate samples were collected from 11 landfill sites and analyzed for target PBDE congeners and homologues. This paper provides information on sampling, levels of PBDEs found in leachate samples and a preliminary analysis of the data.

Sampling

A total of 19 1-liter leachate samples were collected from 11 waste disposal sites (WDS) located within 100 km of Ottawa during the year of 2005. In the first phase of the study, 6 leachate samples (L1-L6) were collected from 6 WDS in February 2005. For the second phase, leachate samples were re-collected from the 6 sites in addition to the 5 new sites during the spring and early summer of 2005. Samples were taken mainly from WDS with two types of leachate collection design. One has engineered liners and a leachate collection system beneath the waste area to collect leachate and prevent off-site migration. Many WDS, however, do not have the leachate collection system. For these landfill sites, samples were collected from their groundwater monitoring wells. Leachate strength of these samples is expected to be lower due to dilution with groundwater. Information with respect to the landfill site operation under which samples were collected is briefly summarized in Table 1. Residential waste is the major source (53-90%) for all landfill sites except for site #5 that contains 52% waste from institutional, commercial and industrial (IC&I) sources. Three sites (#2, 4 & 5) have 9-11% biosolids and only site #2 has 2% hazardous waste.

Sample Extraction and Analysis

About 100 to 300 g of leachate were weighed out into a beaker and spiked with C13 labelled surrogates. The leachate was vacuum filtered through a Gelman A/E filter to separate particulates from the aqueous fraction. The aqueous fraction was extracted in a separatory funnel with dichloromethane while the air dried particulates were extracted overnight in a soxhlet apparatus with toluene. The extracts were combined and exchanged to hexane before passage through a modified silica column with 10 % dichloromethane. The extract was then exchanged to hexane and passed through an activated basic alumina column to separate the PBDE from possible interfering co extractants. The cleaned up extract was concentrated to dryness and made up to a final volume of 20 uL by addition of the recovery standard solution just prior to HRGC/HRMS analysis.

Samples were analyzed using the AutoSpec GC-HRMS system operated in a positive electron impact ionization mode at 10,000 resolution. A 15 meter DB5-HT GC capillary column (15m x 0.25mm x 0.1 um film) was used for separation of PBDEs. A minimum of one labelled BDE was used as a surrogate for each homologue except for octaBDE for which no standard was commercially available at the beginning of this study. A total of 35 target BDE congeners as well as isomers of 9 homologues (di- to deca-BDE) were measured. Most of the target congeners were well separate from their neighbouring isomers except for a few compounds. The co-eluted isomers such as BDE-28/33, 119/120, 138/166 and 171/190 were reported as combined value.

Results and Discussion

It is well known that PBDEs are present in the indoor air of offices and laboratories that are equipped with furniture and computers [2]. To minimize the background level of PBDEs, an effort was made to remove these types of materials as much as possible and practical from the lab where samples were processed. As a result, the levels of PBDEs in blanks were reduced dramatically to an acceptable range.

The 19 leachate samples were processed in 5 batches along with one de-ionized water blank (method blank) for each batch. The average total BDE in our water blanks was 17 pg/mL or 5 ng per sample. Most of detected compounds were tetra-, penta-, hepta- and octa-BDE isomers with four dominated congeners, BDE-47, 99, 183 and 209 at 2-4 pg/mL or 0.6-1.2 ng/sample. This background level is comparable to another study in which similar compounds were detected in Milli-Q purified water at 1.2-4.5 ng/sample when 18 liters of water was used [3].

Table 2 presents BDE values after blank correction in a decreasing order of total BDE. Zero value represents a concentration of BDE at or below the water blank level. Results of leachate samples shows that total BDE varied considerably from close to a background level (less than 20 pg/mL) to over 700 pg/mL. Leachate L11 from landfill site #2 has the highest total BDE concentration and is 10 times greater than the second highest leachate L1 from site #1. Landfill 2 is a large landfill site that has 29 hectares. The site was in operation between 1960 and 1980 and has since been capped and left to naturally attenuate. It has 2% hazardous waste where all other landfill sites in the study have none. Surrogate recoveries for most of samples are between 40 and 90% except for diBDE that falls in a lower range of 20-70%. Overall, PBDEs in about half of the leachates are not much higher than the background level. More than a dozen of target BDE congeners are detected significantly in half of the leachates. The major congeners in leachate samples such as BDE-47, 99, 100, 153, 154 and 209 are commonly found in other environmental media including soil [4], water [5], sediment [6], indoor and outdoor air [2, 7, 8], vegetation [9] and fish tissues [10]. TetraBDE and pentaBDE appear to be the two dominate groups in addition to decaBDE for all samples.

The level PBDEs in leachates collected from the same site on different dates varied significantly. For example, sample L1 and L10 were collected from landfill site #1 in February and April respectively and their total BDE are different by a factor of two. Also sample L2 and L11 were taken from landfill 2 in winter and spring respectively and differ by a factor of 13. Comparing the six leachates (L1, L2, L3, L4, L5 & L6) collected in winter to the six leachates (L10, L11, L15, L16, L13 & L14) collected in spring two months later from the same landfill sites, there is no trend to indicate that PBDE level is greater in the winter or spring season. Concentrations of PBDEs were confirmed by repeating the analyses of seven selected samples (L2, L6, L9, L10, L11, L12, and L13). It seems that more study is needed if one wants to know how PBDE levels in leachates are affected by the seasonal variation. A recent study on leaching high-impact plastics shows that total PBDEs, particularly octa-, nona- and deca-BDE, were leached out at much higher concentration using leachants (de-ionized water) containing 20% methanol or dissolved humic solution at 1000mg/L based on organic carbon [11].

In order to see if there is any correlation between PBDEs concentration and the amount of suspended particulate and pH in leachates, each filter was weighted before and after the filtration of a leachate sample and an aliquot of the leachate was measured for pH. The mass of particulate in samples varied from 0.04 to 3.29 g while pH values were

almost the same between 7 and 8. Results indicate that no correction between PBDEs and suspended particulate or pH in leachates can be observed.

Conclusion

Significant amount of PBDEs were detected in half of the leachate samples that were collected from 11 landfill sites. A large variation in PBDE concentration in leachate samples collected on difference dates from the same landfill site was observed. This variation may be due to the change in seasonal variation or other factors yet to be determined. The total BDE in leachate can be as high as greater than 700 ppt (pg/mL) after blank correction. The major congeners found in leachates such as BDE-47, 99, 100, 153, 154 and 209 are also commonly found in other environmental media. TetraBDE and pentaBDE are the two most dominate isomer groups in most of the leachate samples.

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Table 1 Summary of Waste Disposal Sites

Site ID	Sample ID	Sampling Date	Site Age	Operation	Size 1000m^3	Annual Fill Rate, 1000t/y	Waste Sources	Leachate Collection System
Landfill 1	L1 L10 L12	09/02/05 11/04/05 11/04/05	Since 1980	active	7,400	235	78% residential, 12% IC&I, 6% C&D	yes
Landfill 2	L2 L11	09/02/05 11/04/05	1960-1980	closed	>1000	n/a	88% residential, 10% biosolids, 2% hazardous waste	no
Landfill 3	L3 L15	16/02/05 22/04/05	Since 1977	active	40 - 1000	25	60% residential 36% IC&I 4% other	no
Landfill 4	L4 L16	6/02/05 22/04/05	Since 1980	active	150	7	53% residential, 31% IC&I, 11% biosolids	no
Landfill 5	L5 L13	24/02/05 13/04/05	Since 1986	active	1300	45	52% IC&I, 39% residential, 9% biosolids	yes
Landfill 6	L6 L14 L21	24/02/05 13/04/05 28/07/05	Since 1980	active	40 - 1000	15	75% residential, 20% IC&I 5% other	no
Landfill 7	L17	28/04/05	Since 1980	active	<40	n/a	90% residential 10% other	no
Landfill 8	L18	28/04/05	Closed after 1991	closed	40 - 1000	n/a	90% residential 5% IC&I 5% other	no
Landfill 9	L7	19/04/05	Pre-1980	active	<40	n/a	90% residential, 10% other	no
Landfill 10	L8	19/04/05	Pre-1980	active	<40	n/a	90% residential, 10% other	no
Landfill 11	L9	28/07/05	Pre-1980	active	<40	n/a	90% residential 10% other	no
L12 and L21 are the background well samples; IC&I – institutional, commercial and industrial; C&D – construction and demolition								

Table 2 PBDEs in Leachates After Blank Correction

Sample ID	L11	L1	L2	L7	L5	L10	L13	L8	L12	L6
Landfill Site	#2	#1	#2	#9	#5	#1	#5	#8	#1	#6
BDE-7	3.839	0.330	0.289	0.017	0.032	0.181	0.120		0.003	
BDE-15	1.499	2.604	0.104	0.111	0.026	2.504	0.240		0.028	
BDE-17	12.945	0.057	1.094	0.146	-0.055		0.646		0.006	
BDE-28/33	34.229	0.734	2.589	0.538	0.292	1.107	0.318		0.071	
BDE-37	3.943	0.200	0.234		0.178	0.200	0.021			
BDE-47	120.752	1.498	7.701	7.003	5.911	2.040	8.500		0.589	
BDE-49	23.885	1.285	1.685	0.210	1.664	2.486	1.889	0.008	0.016	
BDE-66	27.765	0.213	1.786	0.167	0.174	0.650	0.288	0.011	0.032	
BDE-71	5.865	0.172	0.255	0.031		0.095	0.299		0.004	
BDE-75	1.943	0.537	0.170	0.025		0.157	0.046			
BDE-77	0.441	0.007	0.021	0.044		0.006				
BDE-85	2.610	0.281	0.181	0.125		0.239	0.351			0.001
BDE-99	239.753	10.915	15.499	2.703	15.122	7.265	8.798		0.280	0.154
BDE-100	45.610	2.257	2.697	0.886	2.988	2.227	2.091		0.060	
BDE-119/120	9.082	0.549	0.358		0.315	0.575	0.176	0.013	0.017	0.034
BDE-126		0.011	0.004		0.107	0.014				0.000
BDE-138/166	2.171	0.602	0.226	0.099	0.230	0.212	0.121		0.046	0.056
BDE-139	1.957	0.409	0.152	0.013	0.145	0.242	0.133		0.009	0.027
BDE-153	60.851	4.039	4.031	0.310	2.551	2.842	1.426		0.623	0.293
BDE-154	29.701	3.603	1.767	0.157	1.954	2.347	1.271		0.027	0.078
BDE-155	1.728	0.238	0.080	0.007	0.093	0.118	0.072			0.001
BDE-170	0.664			0.203	0.025			0.017		0.083
BDE-171/190	0.192		0.039	0.420	0.021				0.157	0.054
BDE-180	1.789	0.078	0.286		0.155				0.582	0.344
BDE-183	7.595				0.000				0.808	1.052
BDE-196	5.722	0.673	0.337	0.077	1.637				1.029	0.285
BDE-197	9.032	0.790	0.444	0.372	2.580		0.371		1.001	0.646
BDE-203	2.911	0.836	0.216	0.266	1.059	0.098	0.136		0.653	1.383
BDE-205	0.000									
BDE-206	1.267	1.267	0.303	0.837	0.217	0.282	0.265	0.770	0.206	0.094
BDE-207	3.877	1.925	0.461	1.619	0.516	0.439	0.472	0.299	0.519	0.388
BDE-208	2.212	1.505	0.200	0.820	0.088	0.413	0.181	0.190	0.138	0.009
BDE-209	24.185	29.825	9.456	36.897	5.125	4.638	4.005	26.863	3.934	0.769
Isomer Group										
DiBDE	8.630	4.171	0.616	0.159	0.078	5.261	0.432		0.039	
TriBDE	56.236	2.558	4.383	0.751	0.432	2.812	1.253		0.086	
TetraBDE	198.260	6.166	13.069	7.637	7.653	6.698	11.173		0.531	
PentaBDE	303.490	14.855	19.298	3.670	19.183	10.450	11.417		0.349	0.132
HexaBDE	98.617	9.291	6.329	0.615	5.060	6.060	3.091		0.726	0.521
HeptaBDE	19.134	0.289	0.405	0.003	0.195				1.791	1.725
OctaBDE	22.390	3.016	1.132	0.737	5.506	0.198	0.466		2.807	2.338
NonaBDE	7.351	4.693	0.959	3.273	0.817	1.129	0.914		0.859	0.487
DecaBDE	24.185	29.825	9.456	36.897	5.125	4.638	4.005	26.863	3.934	0.769
Total PBDE	738.308	74.878	55.662	53.758	44.064	36.504	31.678	24.360	11.137	5.182

Results in pg/mL

Table 2 continued

Sample ID Landfill Site	L15 #3	L18 #8	L4 #4	L3 #3	L9 #11	L14 #6	L21 #6	L16 #4	L17 #7
BDE-7	0.004		0.003						
BDE-15	0.010		0.019	0.014					
BDE-17	0.016								
BDE-28/33	0.046		0.040	0.060			0.003		
BDE-37			0.001	0.007					
BDE-47	1.210		0.483			0.508	1.458		
BDE-49	0.292		0.002			0.020	0.046		
BDE-66	0.006						0.061		
BDE-71							0.009		
BDE-75	0.004						0.004		
BDE-77			0.001						
BDE-85	0.018		0.009	0.018	0.026		0.004		
BDE-99	0.535		0.424	0.328	0.057	0.284	0.162		
BDE-100	0.156		0.077	0.019		0.074	0.083		
BDE-119/120			0.017	0.014	0.022		0.035	0.015	0.017
BDE-126									
BDE-138/166				0.002					
BDE-139	0.005	0.005		0.009	0.006				
BDE-153				0.012					
BDE-154	0.047		0.003	0.028	0.017				
BDE-155									
BDE-170								0.018	
BDE-171/190									
BDE-180									
BDE-183									
BDE-196				0.142					
BDE-197		0.033		0.322					
BDE-203				0.088					
BDE-205									
BDE-206	0.005	0.380	0.027		0.064				
BDE-207	0.018	0.463	0.048	0.129	0.096				
BDE-208	0.090	0.265	0.031		0.044	0.032			
BDE-209	6.513	8.262	4.602	1.091	2.133	1.673	0.599		
Isomer Group									
DiBDE	0.024		0.034	0.019					
TriBDE	0.050		0.041	0.043					
TetraBDE	1.367		0.367			0.370			
PentaBDE	0.678		0.503	0.387		0.328			
HexaBDE				0.072					
HeptaBDE									
OctaBDE				0.525					
NonaBDE	0.108	1.105	0.101	0.113	0.199				
DecaBDE	6.513	8.262	4.602	1.091	2.133	1.673	0.599		
Total PBDE	5.079	4.896	3.038	0.210					

Result in pg/mL