PBDEs IN WASTE DISPOSAL SITES FROM NORTHERN CANADA

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Introduction

Given the health threats of PBDEs, their widespread appearance, including alarming levels reported in marine mammals and in Canada's far northern communities, mass balances are needed to indicate the sources, transfers and accumulation of the various congeners in air, water and soil. Increasing concentrations of PBDEs in the environment and potential ecological and human health risks also require early implementation of best-management practices to contain PBDEs. Studying the leachability of PBDEs from e-wastes and examination of landfill sites to determine the fate and transport of PBDEs are logical and important starting points. Such factors as the nature and extent of PBDE contamination, their potential mobility, their bio-availability and their cumulative amount in vegetation, soil, and drainage water must be known. The spatial distribution of PBDE contamination around landfill areas could assist in determining the sources and spread of PBDEs.

The vast majority of products containing PBDE compounds are ultimately disposed of in landfills (~80%) and the rest incinerated[1]. It has also been found that sediments in the water surrounding landfill and sewage treatment facilities have ng/g range concentrations of PBDEs[2,3]. At present, there are no reported studies quantifying the distribution of PBDEs in landfill soils and the mechanism of leaching of PBDEs from such sites. In the present study we examine profiles of PBDEs in soil samples collected in impacted sites near three major communities in the Canadian arctic and in background locations. The sites selected were assessed to be impacted by landfill leachate (landfills and dumpsites) and wastewater effluents. The aim was also to identify local sources of PBDEs distinct from long-range atmospheric deposition.

Methods

Sixteen surface soil samples were collected (depths of 0-20 cm below surface) in the summers of 2004 and 2006. The 3 communities sampled were Iqaluit (IQ), Cambridge Bay (CAMBY), and Yellowknife (YELL), see Figure 1. Multiple samples were collected at both the Iqaluit and Yellowknife landfills. The dumpsite in Cambridge Bay in comparison to the other sites was extremely small and only one representative sample was taken. Other samples were drawn from other town locations, including close to wastewater effluent discharge areas. Most sites sampled contained sewage effluent or leachate discharged into the water body nearest each site. Hand trowels were used for soil collection. Samples were refrigerated till analysis. PBDE analysis of all samples was performed using well established GC/HRMS-based analytical methods, details of which are presented elsewhere[4]. Of the 60 congeners measured only those found in the highest concentrations are discussed here: BDE-47, -99, -100, -153, -154, -183, -206, -207 and -209. The sum of these nine congeners constituted more than 90% of the total PBDE measured in most of the soil samples. In the following discussions all data are expressed on a dry weight basis and only samples with concentrations higher than what was observed in the procedural blanks are presented. Typical concentrations measured in procedural blanks are shown in Figure 1.

Results and Discussion

Distribution and Congener Patterns of PBDEs in Impacted sites in the Canadian North

The concentrations of the nine major PBDE congeners measured in the soil samples of the disposal sites selected for this study are reported in Table 1. The total PBDE concentration that resulted from the summation of these nine major PBDE congeners are shown in Figure 1. The overall highest total PBDE concentrations measured in the soil samples from the major landfill sites and vicinity areas were those from Iqaluit (180,695 $\pm$ 331,226 pg/g) followed by samples from Cambridge Bay (154,564 $\pm$ 199,624 pg/g) and Yellowknife (9,098 $\pm$ 13,274 pg/g). These levels were significantly higher than what was measured in corresponding background locations: CAMBY8 = 4,520 pg/g; IQ2 = 1,100 pg/g; and YELL04 = 203 pg/g. The background sample sites were chosen to be representative of clean and undisturbed soils, see descriptions in Table 1. The large difference in concentrations observed between landfill and background soil samples suggest PBDE deposition into these landfills from materials discarded within. The levels measured in background soil samples are assumed to

reflect deposition from atmospheric transport. There were huge variations between the lowest and highest concentration measured in the soil samples within each of the landfills that could be attributed to multiple factors including the historical movement of material within each site and the drainage characteristics of the site. It is important to note however that the major PBDE congener measured in most of the landfill soil samples examined was BDE-209, ranging between 40 and 96% of the total PBDEs (with the exception of CAMBY-3 and -6) and at concentrations reaching up to 597,263 pg/g. Other major congeners detected consistently in the soil samples of all sites were those of the Penta commercial mixture, i.e. BDE-47, -99, 100, 153 and 154. An exception was the soil sample from CAMBY6 which exhibited very high concentrations of BDE-183 which is a major component of the Octa commercial mixture.

Soil samples were collected from various locations within each of the three communities. These samples were gathered with the intent to characterize soils in areas close to known sources of contamination (i.e. landfills, dumps) in Canada's north. Metal dumps are a common occurrence in Northern Canada, however, they are not typically located close to the municipal dumps and can be found inside of the town boundaries or haphazardly situated in remote areas, many times adjacent to a major body of water.

Yellowknife: Soil samples were collected in three locations (YELL01, 02 and 03) within the landfill, see Table 1 for details. Duplicate samples were taken from YELL01 and 02. The replication obtained from the analyses of the duplicate samples from these two locations was very good, within 25% for most congeners. Two of the locations (YELL02 and 03) had extremely low PBDE concentrations, close to the concentrations measured in background samples. This was unexpected considering the characteristics of the site. The PBDE concentrations measured in the third location, YELL01, were some 10 times higher than what was measured in the other two locations. These findings suggest that site morphology, drainage characteristics, and management of the materials in the landfills play an important role on the amount of PBDEs deposited into the soil of the specific site. The findings also point to the need to collect soil samples underneath the mounts of materials disposed for a more comprehensive site evaluation. In all samples examined from this site BDE-209 was the major congener measured in all three locations.

Iqaluit: Similarly as Yellowknife three locations were sampled within the current landfill in operation at Iqaluit, IQ2W40, IQ3W40, and IQ4W40, and the PBDE concentrations measured are presented in Table 1. Again a huge concentration gradient was observed in the PBDE concentrations among the soil samples from this site. Location IQ4W40 had PBDE levels close to what was observed in background sites. The total PBDE levels detected in the other two locations were orders of magnitude higher, with IQ2W40 = 764,571 pg/g and IQ3W40 = 132,340 pg/g. BDE-209 was the major congener observed in all three soil samples and the relative profiles of the other eight PBDE congeners were very similar among these three samples. The total PBDE concentrations measured in the other two sites: IQ6 (a former dumpsite, a decommissioned military dump) and IQ7 (former metal dump from the 1940s) were close to the levels typically measured in the background sites examined, reflecting atmospheric deposition. It should be pointed out that IQ6 and IQ7 had no linkages to the main landfill of Iqaluit. The materials deposited at these two sites were primarily metal drams etc., not deemed to contain PBDEs as they have been there since the 1940s, i.e. prior to the PBDE era.

Cambridge Bay: Several samples were collected across the Cambridge Bay region in an attempt to characterize the soils for the presence of PBDEs. There was only one municipal dump and one metal dump in the area. The soil samples collected from the municipal dump (CAMBY3) and the metal dump (CAMBY6) had the highest overall PBDE concentrations, 131,478 and 504,548 pg/g respectively, see Table 1. This sample was enriched by the low bromination congeners found in the penta-BDE commercial mixture. The high levels measured in CAMBY6 are not unexpected considering that this dump consists primarily of vehicle wreckages whose upholstery, foam and plastic are known to contain large amounts of PBDEs. The PBDE profiles of CABMY6 were unique among all sixteen samples examined. BDE-183 was the major congener constituting some 45% of the total PBDE levels measured. BDE-209 was not the major constituent in this sample and the profiles of the other eight congeners reflect those of the penta- and octa-BDE commercial mixtures which could originate from the leaching of PBDEs from the vehicle wreckages.

CAMBY7 was a mid-town site, an area thought to be free of PBDE sources. The total PBDE concentration measured at this site was relatively high, 61,838 pg/g with BDE-209 representing 94% of the total PBDEs

measured. The origin of PBDEs at this location is most likely due to particle fallout from the city. The other two sites sampled, CAMBY2 and 5, were in a sewage effluent drainage area with CAMBY5 being downstream from CAMBY2. The total PBDE concentrations measured at the upstream site were twice those measured at the downstream site prior to ocean discharge. This could be due to effluent dilution as it travels downstream. The profiles of the major PBDEs were almost identical between the samples from these two sites. The presence of PBDEs in sewage effluents is well documented. Our findings support those findings but also demonstrate the level of contamination in soil from sewage effluent drainage areas.

Inter-comparison with different jurisdictions

In the present study we identified that substantial concentrations of PBDEs were present in the soil of all potentially impacted sites in the Canadian North. These included sites impacted by landfill leachates, sewage effluents, city fallout and vehicle wreckage facilities. The concentrations measured varied depending on the site characteristics. Here we compare the concentrations of PBDEs measured in soils from this study against PBDE concentrations measured in soils from other countries around the globe. The data compared were divided according to background samples or potential source receptors. Averages of our three background samples and the thirteen impacted sites were constructed and those are presented in Table 2. The data available from other studies are also differentiated between background and impacted and are presented in Table 2 as well. In order to make the data inter-comparable we selected congeners common amongst all of the jurisdictions that reported PBDE concentrations in soil: BDE-47, -99, -100, 153, -154, -183 and -209. The concentrations measured in the background samples from the Canadian North sites were similar to those measured in background samples from north European jurisdictions, see Table 2. As expected the highest PBDE concentrations measured were at sites close to electronic waste facilities, see corresponding data from China in Table 2. The PBDE levels measured at the impacted Canadian North sites were substantial even though they were collected in jurisdictions that are not considered major urban centers. Soil samples from other jurisdictions around the globe from populated areas such as the Pearl River delta and soils near industrial facilities, like the foam plant in the US, had on the average lower levels of PBDEs than what we observed in the soil samples of our study.

The impact of PBDEs on landfill leachate or landfill impacted soil samples is a largely unexplored area. Our data suggest that substantial concentrations of PBDEs are deposited in soils in and around landfills and they can leach into the aquatic environment via a number of different pathways.

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Table 1 Major BDE congeners found in surface soil samples from the Canadian North (pg/g d.w.)

Location sampled	Description	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-206	BDE-207	BDE-209	Total PBDEs	BDE-209 as % of Total PBDE
YELL01	Old dumping area of landfill; 2 samples averaged**	528	847	175	110	72	101	568	612	20,816	24,412	85.3
YELL02	White goods area of landfill; 2 samples averaged**	132	183	37	27	16	33	43	71	1,322	2,006	65.9
YELL03	Current landfill working area**	160	138	33	10	9	7	13	12	449	877	51.2
YELL04	2km downstream from landfill boundary; background*	99	62	14	5	3	8	ND	ND	ND	203	0.0
IQ2W40	West 40 landfill (current)**	35,448	56,663	11,056	6,608	5,070	4,740	19,764	7,550	597,263	764,571	78.1
IQ3W40	West 40 landfill (current)**	27,743	36,003	7,910	3,755	3,238	999	ND	ND	42,499	132,340	32.1
IQ4W40	West 40 landfill (current)**	55	22	8	2	1	2	ND	ND	2,143	2,237	95.8
IQ6	Former military dump end of old runway**	71	27	8	2	1	6	47	32	2,295	2,526	90.8
IQ7	Former military scrap from 1940s**	191	295	73	34	29	33	34	50	960	1,802	53.3
IQ2	Apex flats, in tidal zone ~400m from shore; backgroun	109	38	11	2	2	4	21	10	890	1,100	80.9
CAMBY2	Sewage effluent drainage area**	5,139	6,359	1,462	1,169	1,023	813	947	1,267	25,901	50,897	50.9
CAMBY3	Municipal dump**	26,648	42,364	8,124	4,858	3,429	1,361	825	1,040	29,063	131,478	22.1
CAMBY5	downstream of CAMBY2, prior to ocean discharge**	2,231	2,495	531	313	297	241	664	571	14,315	24,060	59.5
CAMBY6	Metal dump, auto and other vehicle scrap, etc.**	8,569	15,344	3,332	47,350	11,970	199,344	2,531	32,457	14,275	504,548	2.8
CAMBY7	Mid town**	420	521	121	58	57	61	1,062	588	58,275	61,838	94.2
CAMBY8	Enroute to Mt Pelly 15km NE of town; background*	100	62	16	7	5	33	99	89	4,011	4,520	88.7
Average: sites - impacted (13)		8,256	12,405	2,529	4,946	1,939	15,980	2,038	3,404	62,275	131,046	47.5
Average background (3)		102	54	14	5	4	15	40	33	1,634	1,941	84.2

ND - non detect; * - background; ** - impacted sites

Table 2 Comparison of average PBDE levels in soils from different countries, separated by impacted and background samples (pg/g d.w.). The number of samples averaged is indicated in brackets.

Country	Impacted sites	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Total PBDEs
Canada	Canadian North (13)**	8,256	12,405	2,529	4,946	1,939	15,980	62,275	131,046±234,218
U.S.	foam manufacturing plant (2)[7]	20,000	23,000	2,000	N/A	N/A	N/A	N/A	45,000
China	close to e-waste recycling site (2)[8]	125,000	315,000	46,000	127,000	40,500	420,000	N/A	1,073,500
China	close to e-waste recycling site (6)[9]	177,400	552,000	N/A	62,500	49,000	12,300	N/A	853,200
China	watershed soils (Pearl River Delta) (33)[10]	630	140	30	45	30	35	13,800	14,710
China	close to e-waste recycling site (3)[10]	1,050	1,580	200	850	350	3,700	70,500	78,230
	Background sites								
Canada	Canadian North (3)*	102	54	14	5	4	15	1,634	1,941±2,277
U.K.	grasslands / woodlands (21)[6]	275	590	730	140	60	50	N/A	1,845
Norway	woodlands (24)[6]	250	360	60	50	50	25	N/A	795
Sweden	research stations (5)[5]	35	50	15	10	10	10	480	600

N/A - no available data; * Canadian North background sites and **Canadian North impacted sites, values taken from Table 1

Figure 1. Sampling site locations and PBDE concentrations in surface soil samples for Northern Canada (pg/g)