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Investigation of PBDEs in Landfill Leachates from Across Canada

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Abstract

Leachates from 27 landfills (e.g. planned disposal area) across southern Canada and 11 dump sites (e.g. unorganized disposal area) in the Canadian North were collected (2006) and analysed (2006-2008) for polybrominated diphenyl ethers (PBDEs). There was wide variability in the results, both in terms of the total PBDE concentrations and in the distribution of congeners. Northern sites tended to have lower concentrations than southern ones, but some northern levels were significant, despite the low population density and lack of industry in the north. The North could potentially act as a sink for PBDE contaminants because many organic compounds get deposited via air or water currents in the North even though they were not manufactured there.

Keywords: landfill leachate, Polybrominated diphenyl ethers (PBDEs), persistent organic pollutants, Canadian North

1. Introduction

Given the health risks of PBDEs and their widespread appearance, including "alarming" levels in marine mammals (Ikonomou et al. 2002b) and in Canada's far northern communities (Ikonomou et al. 2002a), mass balances are needed to indicate the sources, transfer and accumulation of the various congeners in air, water and soil (Macleod et al. 2010). Increasing concentrations in the environment and potential ecological and human health risks also require early implementation of best-management practices to restrain the spread of PBDEs. Studying the leachability of PBDEs from e-wastes (Ma et al. 2012) and examination of landfill sites to determine their fate and transport are logical starting points. Such factors as the nature and extent of PBDE contamination, potential mobility, bio-availability and cumulative amounts in vegetation, soil and drainage water are important. The spatial distribution of PBDE contamination around landfills could assist in determining the sources (Devanathan et al. 2012) and spread of PBDEs.

PBDE levels in the environment are increasing (Ikonomou et al. 2002a; Rayne et al. 2003a; Hites 2004a). Although the EU, Canada and some US states have banned, or are in the process of banning, some PBDEs (European Commission 2005; Peele 2006; Canada Gazette Part II. 2008; Environment Canada 2009), past usage and consumption of PBDEs suggest that even banned congeners will persist in the environment for decades. Moreover, the deca (-209) BDE congener, not yet banned because it is difficult to replace, will continue in production. However, recent developments in the Stockholm Convention reported a proposal to phase out deca-BDE (UNEP-POPS, 2013). PBDEs are also exponentially increasing in Northern Canada, doubling every 4 to 5 years. BDE-47 has been found to be the largest contributor (Ikonomou et al 2002a).

The vast majority of commercial products containing PBDE compounds (electronics, mattresses, polyurethane foam, vehicle interiors, etc.) eventually enter waste streams. Up to 85% of discarded electronic products are ultimately sent to landfills (~80%), with the rest incinerated (Alcock et al. 2003).

The study is intended to assist in filling gaps in mass balance models and in determining the fate and assessing the risk of disposal on land and in landfills. This builds on the results reported in Li et al (2012). The Canadian North was selected because landfills and dumpsites are relatively isolated there. The long term objectives of northern sampling were to investigate how PBDEs are entering and being transferred among landfill (dumpsite) leachates and soils in the Canadian North and in other parts of Canada. A second long term objective was to provide data from locations well removed from population and industries. Another aim was to provide better understanding of the leachability of PBDEs from e-wastes (Ma et al. 2012) and other PBDE-containing products, and the mobility of PBDEs in soils. To the best of our knowledge, this is one of the first Canadian studies to investigate PBDE congener patterns in aqueous media (leachate, effluent and background water). Waste

material at the urban landfill[1] was segregated into different parcels, one for each half-decade (5-year) interval, thus facilitating comparison of leachates from wastes added in different time periods (Danon-Schaffer, et al. 2013a, 2013b).

1.1 Landfills

Landfilling has been the most common way to dispose of municipal solid waste (MSW) in many countries for decades, intended to reduce environmental impacts to a minimum (Francois et al. 2006). Waste is normally landfilled in horizontal layers and then compacted mechanically. The composition of the waste deposited in a landfill is determined by the consumption habits and waste management systems of the community where it is located, as well as changes in product usage (e.g. introduction of plastics in the 1960s) (Sormunen et al. 2008). Daily cover at a landfill normally consists of soil layers and bottom ash from incineration operations, used to minimize transfer as dust into the air. Daily cover may vary and consist of auto-shredder residue and/or shredded upholstery (Petreas et al. 2005). Landfills store heterogeneous materials over time, compacted to a density of 800 to 1,000 kg/m3 (Sormunen et al. 2008). The degree of compaction influences the aerobic decay, temperature, homogeneity and rates of settlement across the landfill site (Campbell 1993).

The final quality of the waste cover is significant to prevent contaminant release to the environment. Environmental management of leachate should include monitoring of leachate quality and quantity, as well as the receiving environment (Campbell 1993). A landfill should be designed to contain leachate collection and treatment, either internally or externally. Some release may occur, no matter how well engineered a landfill is (e.g. with impermeable liners and caps, leachate and gas collection systems).

The behaviour of landfilled PBDE-containing products is poorly understood. Increasing amounts of e-waste continue to enter final disposal streams as faster equipment replaces older devices. Most discarded electronic items enter landfills and/or incinerators for final disposal (RIS International Ltd. 2003; Puckett et al. 2005; UNEP 2005; Grossman 2006; Hileman 2006; US EPA 2007; Wong et al. 2007; US EPA 2008; Ni and Zeng 2009). In recent years (between 2004 and 2013), some provinces in Canada have developed regulations to enforce e-waste recycling and ban them from landfills (Alta. Reg 93/2004; BC 2007, SK, 2007, NS 2008, ON 2009, PEI, 2010, MB 2010, QC 2012). Sediments in the water surrounding landfill and sewage treatment facilities contain nanogram/gram range concentrations of PBDEs (Allchin et al. 1999; de Boer et al. 2003; Chen et al. 2013). Currently, there are few studies (Ma et al. 2012) quantifying the distribution of PBDEs in landfill soils and the mechanism of leaching of PBDEs from such sites.

1.2 Leachate

Leachate is produced from precipitation that falls on the landfill site and percolates through the waste. It can also come from moisture in the waste that is slowly released as more waste or cover is placed on top of the MSW. Compounds contained in the original waste, as well as products resulting from waste degradation, are present in the leachate. Degradation processes

[1] We are unable to identify the landfill because of its confidentiality provisions

are affected by site geometry, waste types and input rates, as well as weather and operational practices (Campbell 1993). In addition to anaerobic processes which affect leachate inside landfills, leachate composition may be influenced by redox reactions, oxygen-demanding biological degradation, volatilization, dilution, sorption, ion exchange and precipitation (Öman and Junestedt 2007).

Proper leachate management is critical for any landfill, given the potential for contamination of aquifers, groundwater and surface water (Campbell 1993). In engineered landfills, geo-membrane liners are typically placed on the bottom of the landfill to prevent leachate migration beyond designated boundaries. Collection pipes commonly carry the leachate out of the landfill to an external collection system for future treatment, to a wastewater treatment plant, or for direct discharge to a body of water (Camobreco et al. 1999; Sormunen et al. 2008).

Leachate quality depends on the age of the landfill, the stage of waste degradation, and the organic matter, chloride, heavy metals and other organic/inorganic compounds contained in the wastes (Sormunen et al. 2008). The easiest way to characterize leachate is by identifying the main waste decomposition phases in a MSW landfill, these being the acid and methanogenic phases (Spalvins et al. 2008).

1.3 Previous Studies on PBDEs in Leachate

Data on PBDEs in leachates are sparse. Öman and Junestedt (2007) characterized landfill leachates in Sweden for compounds not previously analysed, including PBDEs. Samples were collected adjacent to waste deposit areas to obtain representative samples that would either migrate to surrounding areas or be treated in a sewage treatment plant. Reported PBDE levels were low relative to most reported elsewhere (Li, et al, 2012; Kiddee, et al, 2013).

Oliaei (2005) conducted a leachate study in Minnesota to investigate PBDE contamination in five landfills and sewage treatment plants, finding a range of 24,620-260,420 pg/L total PBDEs in the landfills (Table 1). Osako et al. (2004) analysed leachate from seven municipal and industrial landfills in Japan that contained bulk waste material plus crushed e-waste. The concentrations of PBDEs in leachate varied widely among the seven landfills studied, with relatively high concentrations at landfills that contained large volume of organic material. Due to the hydrophobicity of PBDEs, their levels (<8 to 50,000 pg/L) could have been influenced by dissolved humic substances in the leachate (Osako et al. 2004). The ranges for major congeners analyzed in previous work are compared in Table 1.

Table 1. Summary of previous PBDE concentrations in leachates (pg/L) from the literature.

Reference	This project	Oliaei, 2005	Oman & Junestedt, 2007	Osako et al, 2004	Odusanya, et al, 2008
Location	Canada-wide	Minnesota, USA	Sweden	Japan	South Africa
Type of landfill	municipal	municipal, industrial, demolition	municipal	municipal and industrial	municipal
Extraction method	liquid-liquid	N/A	liquid-liquid	liquid-liquid	liquid-liquid
Type of sample	leachate - grab	leachate	leachate - grab	leachate	leachate - grab
Filtered	yes	N/A	N/A	yes	N/A
Filter size	0.7 µm	N/A	N/A	1 µm	N/A
Solvent	dichloromethane, accelerated solvent extraction (ASE)	N/A	methylene chloride	dichloromethane, Soxhlet with toluene	hexane, dichloromethane, petroleum ether, acetone
BDE-47	BMDL-194,000	180-5,000	1700	<8 - <500	1,470-9,800
BDE-99	BMDL-500,000	230-7,500	NA	<8 - 1,800	440-5,200
BDE-100	BMDL-100,000	50-1,550	1100	<8 - <500	240-2,160
BDE-154	BMDL-81,700	20-870	1	<8 - 1,200	140-2,180
BDE-207	BMDL-21,300	140-1,500	290	NA	NA
BDE-209	BMDL-460,000	24,000-244,000	1100	<800 - < 50,000	NA
Σ total of 6 congeners (range)	BMDL-1,357,000	24,620-260,420	1-1,700	<8-50,000	2,290-19,340
Total PBDEs (background sites)*	56,538	N/A	N/A	N/A	N/A
Total PBDEs (municipal landfills)**	231,713	83,055	838	10,702	22,543

N/A - not available
*Background samples collected in the Canadian North;
** Landfill leachate averages from 20 sites across Canada

In order to facilitate comparison and interpretation, only six congeners common to all jurisdictions are included in this table: BDE-47, -99, -100, -154, -207 and -209.

2. Field Study

2.1 Sampling

A confidential letter was sent to 50 jurisdictions across southern Canada to request leachate samples for PBDE analysis. In the end, 27 of these landfills provided leachate samples from operating landfills and closed landfills still being monitored for groundwater quality. PBDE concentrations were analysed from these 27 samples, and total organic carbon (TOC) values (discussed below in Section 2.4) were obtained from 20 of them. All samples from southern Canada were obtained in September to November 2005 and April to June 2006. Individualized data were provided to all 27 respondents. Variables such as population served by the landfill, age of waste in contact with leachate, type of landfill (municipal, industrial, other), leachate collection method, pH, and conductivity were recorded. Note that each location in southern Canada did its own sampling based on its own sampling protocol, chosen by the landfill operators. Hence, some variability was no doubt introduced by different

sampling procedures, added to variability caused by different waste compositions and different landfilling procedures. Some variability may also be due to weather, such as recent rainfall or prolonged drought, as well as different dates of sampling.

All sampling in the three territories of northern Canada was carried out by the first author, ensuring a uniform sampling methodology, with details on the sampling protocol and procedures described in Li, et al (2012). An initial field trip was made to three northern Canadian locations (Yellowknife, Iqaluit, and Cambridge Bay) during the summer of 2004. A second field trip to eleven landfill sites in the North, including all three locations visited previously, was completed during the summer of 2006. All sampling locations were identified with Global Positioning System (GPS) coordinates. A map indicating sample locations is shown in Figure 1. Leachate, background water and soil samples were collected during both trips to determine the concentrations of measurable PBDE congeners[2]. Sampling sites, types of sample collected, nature of the dumpsites, latitude/longitude and populations of the communities served are specified in the supplemental data. Note that none of these northern dumpsites had liners or covers, and that there was no need to withhold the locations of sampling sites in the north.

Figure 1. Map of Canada.

Large dots indicate communities where samples were collected

[2] Leachate and background data from 2004 are not included in the main analysis due to the limited number of samples collected and the wide variability. Because the 2006 samples could not be collected in precisely the same locations, no comparison is made between the 2004 and 2006 data.

Due to the cost of sampling and analysis, replicate samples were available in only a small number of cases: a) leachate samples from Iqaluit, Hall Beach and Yellowknife, b) sewage effluent samples from Cape Dorset and Pangnirtung, and c) background water samples from Cambridge Bay[3] (Danon-Schaffer, 2010). Raw data are compiled for individual congeners and in groups by bromine number, presented as total BDE groups, i.e. total tri-BDEs, total tetra-BDEs, etc.

All northern leachate samples were collected in 2.5 litre glass amber bottles previously washed with standard laboratory detergent (Alconox; White Plains, NY) and then rinsed in turn with distilled water, technical grade toluene, technical grade hexane, technical grade dichloromethane, and technical grade acetone. Most leachate samples were collected below the top of the groundwater table using Waterra® tubing, with a foot valve fitted at the bottom to dark amber glass bottles of 2.5 L volume. In cases where this was impossible, an amber glass bottle was submerged into leachate collection areas to fill the bottle. Effluent samples were collected at outfall points by placing the amber glass bottle directly under the flow. Samples were then stored at 4 ℃ until analysis.

2.2 Analytical Protocols

Accurate analysis is especially difficult for BDE-209, requiring different clean-up and gas chromatography (GC) analysis than lower brominated congeners (de Boer 2004). All PBDE data presented here were subjected to comprehensive laboratory blank criteria for credibility, TOC, and, where possible, tested for consistency between two major laboratories (Danon-Schaffer, et al, 2013a). Most samples were re-analyzed to confirm PBDE levels and to assess factors affecting reproducibility, in particular to assess sub-sampling due to the lack of homogeneity because of significant loading of particles in the leachate samples. In addition, statistical analyses were performed on the replicate data. BDE-209 tended to have higher standard errors than the other congener groups (Danon-Schaffer 2010).

As explained by Danon-Schaffer (2010), PBDE concentrations were corrected by subtracting either one or two times the procedural blank values for aqueous samples. Many of the measured concentrations were found to be close to the detection limits (i.e. lab blanks), indicating barely detectable or even undetectable PBDE concentrations. Where BDE data had to be eliminated due to detection limits and blank corrections, these data are counted as zero when calculating totals and for plotting purposes. The PBDE aqueous data were compared with TOC (Danon-Schaffer, 2010) in an effort to better characterize the samples and to see whether there is any correlation between PBDE levels and TOC since PBDE molecules are likely to bind to, and travel with, other carbon-based molecules. In addition, aqueous samples that contained few particles were extracted via a simple liquid/liquid process which required minimum handling. Aqueous samples containing many particles required more extraction steps, beginning with filtration, followed by two different extraction paths. This in turn generated two procedural blanks, followed by centrifugation. The extra handling steps increased the potential for sample contamination as discussed elsewhere (Danon-Schaffer, et al 2013a).

[3] Also known as Ikaluktutiak

Of the 60 congeners measured, only the nine "principal congeners", found in the highest concentrations, are discussed here. The tables in this paper provide data for the nine major congeners (BDE-47, -99, -100, -153, -154, -183, -206, -207, and -209) for each of the media investigated. The sum of these nine congeners constituted more than 90% of the total PBDE measured in most aqueous and soil samples.

The procedure to prepare the background samples for analysis differed from that of the leachate samples. These samples contained few particles, so they were liquid/liquid extracted. The corresponding procedural blanks were treated in the same manner. The potential for lab contamination through this process was greatly reduced due to the few steps involved in the extraction. In addition, consistency in the lab procedural blanks was important in order to provide accurate results, given the low concentrations of PBDEs in the samples.

2.3 Total Organic Carbon (TOC) and Data Normalization

TOC is a measure of the organic carbon in the particulate removed from the leachate samples. The raw PBDE data in the paper, even after procedural blank correction, were extremely variable. TOC is primarily influenced by particle size, analytical extraction efficiency and sampling/sub-sampling. Since particles rich in organic carbon have the greatest potential to bind PBDEs, and since PBDEs preferentially bind to particulates in water (Environment Canada. 2006), we measured the TOC concentration in the samples to examine whether there was any correlation between measured PBDE and TOC levels.

The samples were analysed for TOC on a Control Equipment Corporation (CEC) 240-XA Elemental Analyzer (Leeman Labs, Inc.), with standardization and procedural blank determination using a CAHN Electrobalance (Model 4400) (Knap et al. 1994). TOC content is the sum of the dissolved organic carbon (DOC) and particulate organic carbon (POC).

To determine whether there is a significant relationship between measured PBDE and TOC levels, BDE concentrations were correlated against TOC concentrations for each of the nine principal congeners. BDE-47 was plotted against TOC to illustrate this potential correlation. The Pearson coefficient, R, varied between 0.46 and 0.97, indicating large differences. When all samples are included in the correlation, the degree of correlation decreases in most congeners, as shown by the bottom row of Table 2. There is no apparent difference in the results from the samples that contained particulate and those that did not (Danon-Schaffer, 2010). Table 3 shows a much greater correlation between PBDEs and TOC levels if subsets of the data are taken with the highest measured PBDE concentrations (5, 6, 7 or 11 sites). There is good correlation between PBDE concentrations and TOC levels for most of the "principal" congeners in the samples where the highest PBDE concentrations were found, but the degree of correlation decreases as the degree of bromination increases.

One possible option considered was to normalize all the PBDE concentrations throughout the paper with the corresponding TOC concentration, in order to express the PBDEs as mass fractions of the organic carbon present. However, since the correlation with TOC was weak, except for the locations (Table 2) with the highest PBDE levels, the data are presented here in a dimensional (i.e. not normalized) manner.

Table 2. Pearson correlation coefficients for procedural blank-corrected BDE concentrations and corresponding TOC levels when up to 21 locations are considered at which TOC levels were determined.

# sites	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 207	BDE 206	BDE 209
5	0.971	0.657	0.665	0.690	0.656	-0.092	0.730	-0.323	-0.157
6	0.674	0.685	0.685	0.715	0.691	-0.189	0.268	-0.371	-0.003
11	0.546	0.498	0.500	0.605	0.586	-0.012	0.221	-0.091	0.116
21*	0.466	0.495	0.490	0.490	0.509	0.107	-0.031	-0.178	-0.222

* or as many as survived the procedural blank correction procedure

3. Results and Discussion – Northern Canada

TOC values were evaluated for the 20 leachate samples which survived the procedural blank-correction procedures. Procedural blanks were subtracted from the TOC following analogous procedures to the PBDE analysis procedure (Danon-Schaffer, et al 2013a), leading to a one-times (1x) procedural blank correction for seven of the 20 samples and two times (2×) procedural blank subtraction for the others, depending on the degree of lab contamination at the time of analysis. The results are listed in Table 3 together with the principal congener BDE values and total PBDE concentrations. Figure 2 plots total principal PBDEs (excluding BDE-209) vs. TOC in these samples. Most data indicate a correlation between TOC and PBDE concentration. However, there are four outliers, identified by arrows. Those with similar TOC levels, but different PBDE concentrations, may indicate different point sources. Figure 3 plots the BDE-209 values against TOC. Except for two locations (see Table 2), BDE-209 is the congener that contributes most to the total PBDE concentration. Three outliers are identified in this plot, two with populations >100,000 and the third remote with population <10,000.

Table 3. Procedural blank-corrected sample principal BDE congener concentrations (pg/L) in order of decreasing total organic carbon (TOC) (also in pg/L) content levels from 20 landfill leachates across Canada[4].

Location	tetra-BDE	penta-BDE		hexa-BDE		hepta-BDE	nona-BDE		deca-BDE	Sum congeners w/o BDE209 (pg/L)[1]	Sum of 9 congeners (pg/L)[2]	Total PBDEs (pg/L)[3]	% congeners[4]	Total Organic Carbon (TOC) (pg/L)	Total PBDE concentration normalized by TOC	Normalized TOC data
	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-206	BDE-207	BDE-209							
A	150,593	316,891	76,683	62,105	71,744	7,600	6,433	7,142	19,205	699,190	718,395	867,805	83	4.56E+11	2.10E-06	1.90E-06
B	4,485	2,397	696	218	154	428	2,460	1,841	99,621	12,679	112,300	134,182	84	3.95E+11	6.00E-07	3.40E-07
V	19,090	26,047	7,252	7,696	6,642	3,358	2,514	2,213	71,343	74,811	146,154	163,594	89	3.89E+11	2.42E-07	4.20E-07
E	895	2,555	356	482	393	81	1,773	892	27,272	7,427	34,699	36,107	96	3.52E+11	7.07E-08	1.02E-07
F	9,083	4,248	3,160	1,552	1,338	2,509	1,438	1,765	51,235	25,093	76,328	86,916	88	3.33E+11	2.84E-07	2.61E-07
G	5,567	6,025	1,376	810	692	934	3,176	3,770	149,684	22,351	172,035	177,024	97	2.39E+11	7.27E-07	7.41E-07
C	5,489	13,355	11,440	3,299	5,162	17,302	22,476	11,453	279,044	89,975	369,019	400,523	92	2.20E+11	2.32E-06	1.82E-06
D	29,098	32,867	16,699	14,696	15,102	7,587	12,413	10,341	255,028	138,802	393,830	457,050	86	1.88E+11	6.29E-06	2.43E-06
H	6,862	7,958	2,305	4,008	2,966	6,862	95	627	BMDL	31,683	31,683	39,335	81	1.81E+11	2.18E-07	2.18E-07
I	15,491	26,122	7,616	5,677	5,822	1,535	1,902	2,188	45,120	66,353	111,473	127,366	88	1.29E+11	8.37E-07	9.86E-07
J	5,970	4,137	1,076	1,414	1,202	607	680	867	102,208	15,953	118,161	118,161	100	1.04E+11	1.13E-06	1.14E-06
K	14,159	22,470	9,826	2,862	2,315	611	7,720	5,504	230,356	65,468	295,823	308,236	96	1.04E+11	1.39E-06	2.97E-06
L	6,199	1,990	407	277	167	806	934	2,420	103,873	13,200	117,073	117,288	100	6.31E+10	1.86E-06	1.86E-06
M	BMDL	BMDL	BMDL	45	66	406	11,571	12,184	429,294	24,275	453,568	453,565	100	5.86E+10	7.83E-06	7.74E-06
N	5,885	1,814	609	148	120	413	666	1,471	134,754	11,125	145,879	146,607	100	4.01E+10	3.65E-06	3.65E-06
O	788	2,450	560	5,067	1,146	28,350	2,025	10,326	35,012	50,712	85,724	110,428	78	3.53E+10	1.22E-06	3.12E-06
P	BMDL	41	14	50	25	105	802	1,149	59,813	2,187	62,000	62,720	99	2.91E+10	8.12E-06	2.16E-06
Q	4,610	1,507	350	164	128	725	1,799	1,600	181,858	10,884	192,742	193,502	100	2.23E+10	8.66E-06	8.66E-06
R	BMDL	BMDL	BMDL	341	BMDL	628	BMDL	BMDL	BMDL	969	969	969	100	9.45E+09	1.03E-07	1.03E-07
S	6,301	1,748	568	150	90	254	898	1,504	112,085	11,513	123,598	124,076	100	8.11E+09	1.53E-05	1.53E-05

*Average from replicates; BMDL - below method detection limit

1. Sum of congeners = sum of 8 principal congeners w/o BDE-209: BDE-47, -99, -100, -153, -154, -183, -206, -207 (out of a possible 60 congeners identified during lab analysis)
2. Sum of congeners = sum of 9 principal congeners: BDE-47, -99, -100, -153, -154, -183, -206, -207, and -209
3. Total PBDEs = sum of all PBDE congeners analysed, which includes the 9 principal congeners
4. % congeners = sum of the 9 principal congeners divided by the total PBDEs measure and then multiplied by 100

[4] TOC levels were not calculated for Sites T, U, W, X, Y, Z, AA or BB.

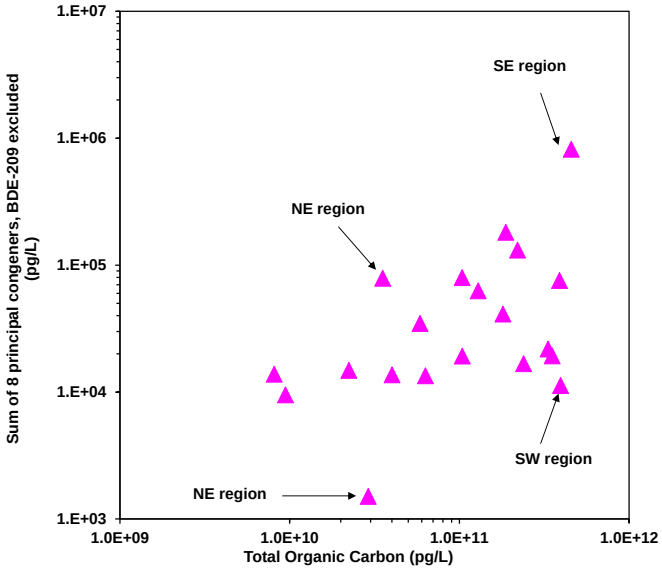

Figure 2. Leachate samples from landfill sites in major cities across Canada in 2005-2006.

Sum of the eight principal congeners (BDE-47, -99, -100, -153, -154, -183, -206, and -207). BDE-209 not included, from Canada-wide aqueous samples vs. total organic carbon (TOC) levels (pg/L). Outliers are indicated by arrows (Lab: DFO-IOS).

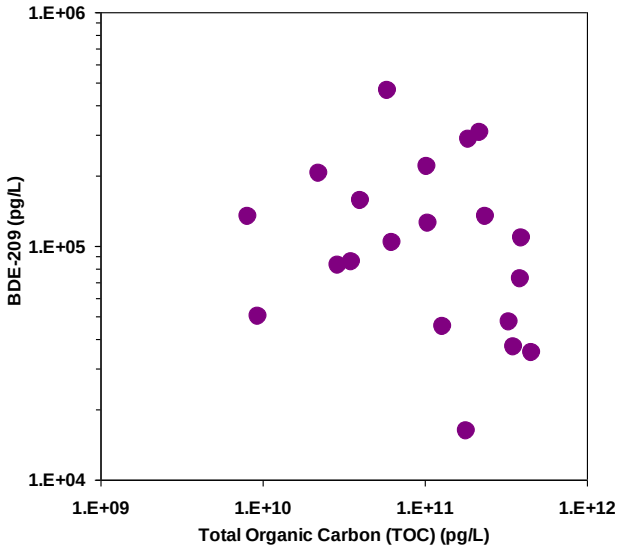

Figure 3. BDE-209 concentrations from Canada-wide aqueous samples vs. total organic carbon levels (TOC) (pg/L) (Lab: DFO-IOS).

Note that there are fewer points than sites analysed due to BMDL (below minimum detection level) concentration values. Arrows indicate samples that behaved differently from the rest because the sources of these samples were very different from one another.

As shown in Table 4, of the three locations (Hall Beach, Cape Dorset and Whitehorse WEP) had measurable concentrations of BDE-47, whereas the remainder were below minimum detection limits (BMDL). All sites had measurable BDE-209 concentrations, although three samples were BMDL for BDE-209. Hence, although analyzing BDE-209 presented particular

challenges of lab contamination and interference, measurable values were obtained. Iqaluit and Hall Beach samples were re-extracted and the new values were averaged with those from the first extraction and are shown in Table 4.

Table 4. Major BDE congeners in leachate samples from northern Canada (pg/L)

Location sampled	Description	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-206	BDE-207	BDE-209	Σ 9 main congeners	Total BDEs	BDE-209 as % of Total BDEs
Yellowknife (YELL-01)*	Leachate from landfill	BMDL	BMDL	502	214	157	207	BMDL	BMDL	22,152	23,232	26,755	83
Iqaluit (IQ1)*ξ	West 40 landfill (current)	BMDL	BMDL	BMDL	BMDL	40	BMDL	BMDL	1,508	83,137	84,685	84,756	98
Cambridge Bay (CAMBY4)	Leachate and effluent discharge to ocean	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	509	BMDL	13,628	14,137	14,137	96
Hall Beach (HB01)*ξ	Ponded water at municipal dump, edge of town	702	2,461	2,587	3,840	2,398	28,429	4,411	7,310	85,582	137,719	164,235	52
Cape Dorset (CD2)	Runoff from garbage dump	4,117	1,132	483	141	ND	BMDL	1,605	886	49,764	58,128	59,253	84
Whitehorse (SWE-4B)	Current leachate collection at landfill	BMDL	BMDL	BMDL	10	BMDL	BMDL	2,453	1,770	83,420	87,653	88,871	94
Whitehorse (WEP)	War Eagle Pit, historical leachate, 25 m depth	6,199	1,990	407	277	167	806	934	2,420	103,873	117,073	150,090	69
Inuvik (INUVIK2)	Downgradient from dump at Finning Lake	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	NA
Tuktoyaktuk (TUK-2)	Adjacent to main water body, received leachate from dump and discharges directly to ocean	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	ND	ND	ND	BMDL	BMDL	NA
Tuktoyaktuk (TUK-3)	Ponded leachate at dumpsite, subsequently drains to ocean	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	NA

*Average; BMDL - below method detection limit; ND - not detected
ξ These samples were re-extracted. Procedural blank correction for the re-extracted batches corresponds to 2 times procedural blank correction for the first 6 congeners of the table (corresponds to Cluster E described elsewhere, Danon-Schaffer, 2010) and to 1 time procedural blank extraction for the remaining 3 congeners (BDE-206, -207, and -209) (corresponds to Clu elsewhere, Danon-Schaffer 2010). Values presented in this table were averaged with the first extraction.

One-time procedural blank correction, except where noted (corresponds to Clusters D and J described by Danon-Schaffer (2010). (Lab: DFO-IOS)

Compared to all other leachate samples, Hall Beach (HB-01) had a unique concentration profile (Table 4), with higher-brominated congeners having elevated concentrations. One reason may be that this leachate ponded in a low lying area, allowing the molecules to potentially bioaccumulate. The Cape Dorset (CD-2) sample was also collected in a ponded area where the leachate may have been more concentrated. The Whitehorse (WEP) sample was collected from a depth of approximately 25 m. That location is known to contain old leachate (20 years or more), so that high PBDE concentrations are not surprising, given the heavy incorporation of PBDEs as a flame retardant in electronic and other products in the 1980s (Tasaki, et al. 2004; ENVIRON 2003). The volume of leachate in the Iqaluit landfill was much greater than at either Hall Beach or Cape Dorset.

3.1 Distribution and Congener Patterns of PBDEs in Leachate

The highest PBDE concentration in leachate was measured in Hall Beach HB-01 (164,235 pg/L) and Whitehorse, WEP (150,090 pg/L). The major PBDE congener measured in these leachate samples was BDE-209, ranging between 52 and 98% of the total, except for Inuvik (INUVIK2) and Tuktoyaktuk (TUK-2, TUK-3) (see Table 4). The major congeners were present in leachate samples from Hall Beach (HB-01), Cape Dorset (CD-2) and Whitehorse (WEP). Replicate samples were analysed for YELLO1, IQ1 and HB-01: three, six and two duplicates, respectively, increasing the reliability of these results. The highest concentration

of BDE-183, a major component of the Octa-BDE commercial product, was measured in HB-01 (28,429 pg/L). Large variations between the lowest and highest concentrations in these samples are likely due to a combination of factors, including diversity of materials entering the dumpsites, different community characteristics, differences in rainfall and soil permeability and analysis errors, especially when the levels are low.

The HB-01 and WEP samples may have contained all three commercial formulations (Penta, Octa and Deca-BDE), as all 9 principal congeners were present in measurable quantities. For CD-2 and Whitehorse (SWE-4B), the presence of the commercial Deca-BDE product is more apparent, as BDE-207 and -206 patterns are similar, and Deca-BDE is known to contain small amounts of these congeners. However, CD-2 was found to have approximately 7% of BDE-47, one of the more persistent congeners in the Penta-BDE product (typically between 28 and 30% by weight.) This may also indicate a degraded Penta-BDE formulation. Except for HB-01 and WEP, BDE-209 was the major contributor to the BDE concentrations in these leachate samples.

3.2 Background Samples

The background sample sites were chosen because they were likely to be free of contaminants (Iqaluit: IQAX-3 and IQ5W40; Pangnirtung: PANG3; Cape Dorset: CD1; Hall Beach: HB-02; Pond Inlet: PI-1; Cambridge Bay: CAMBY7 and CAMBY8; Inuvik: INUVIK1 and INUVIK2; Tuktoyaktuk: TUK-1; Rankin Inlet; and Whitehorse: WHT-PC). Most are drinking water sources for the communities in which they were drawn. In total, thirteen background water samples were collected. Most of these data (Table 5) were BMDL.

Table 5. Major BDE congeners found in background water samples from the Canadian North (pg/L)

Location sampled	Description	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-206	BDE-207	BDE-209	Σ 9 main congeners	Total BDEs	BDE-209 as % of Total BDEs
Iqaluit (IQAX-3)	Apex Flats	BMDL	BMDL	BMDL	BMDL	ND	BMDL	BMDL	BMDL	62,083	62,083	62,083	100
(Iqaluit (IQ5W40)	Upgradient from W40 landfill (curren	BMDL	BMDL	BMDL	BMDL	ND	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	N/A
Pangnirtung (PANG3)	Upstream river, drinking water sourc	BMDL	BMDL	BMDL	BMDL	ND	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
Cape Dorset (CD1)	Tellik Inlet (Arctic Ocean)	BMDL	BMDL	BMDL	BMDL	ND	BMDL	447	659	32,929	34,035	34,035	97
Hall Beach (HB-02)	Drinking water source for town, lake adjacent to DEW line clean up and close to airport	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	6,391	6,391	6,391	100
Pond Inlet (P1-1)	Primary water source for town, ~ 5km away	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	N/A
Cambridge Bay (CAMBY 7)	Background water	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	N/A
Cambridge Bay (CAMBY 8)*	Towards Mt. Pelly, out of town	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
Inuvik (INUVIK1)	"Road's End" golf course	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	334	15,843	16,177	16,177	98
Inuvik (INUVIK 3)	Boot Lake	BMDL	BMDL	BMDL	ND	ND	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
Tuktoyaktuk (TUK-1)	Former drinking water source for town, "Water Lake"	BMDL	BMDL	BMDL	88	13	848	142	421	BMDL	1,512	1,512	BMDL
Nipissar Lake (Rankin Inlet)	Background source	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	N/A	N/A	N/A	BMDL	BMDL	N/A
Whitehorse (WHT-PC)ξ	Upstream at Porter Creek, prior to entering landfill	4,610	350	1,508	127	165	725	2,849	2,378	204,219	216,929	219,029	93

*Average; BMDL - below method detection limit; ND - not detected; N/A - not available
ξ This sample was subjected to 2 times procedural blank correction for the first 6 congeners of this table (corresponds to Cluster C described elsewhere, Danon-Schaffer 2010) and to 1 time procedural bla extraction for the remaining 3 congeners
(BDE-206, -207, and -209) (corresponds to Cluster G described elsewhere, Danon-Schaffer 2010).

One time procedural blank corrected except where noted (corresponds to Clusters D and J described elsewhere (Danon-Schaffer 2010)). (Lab: DFO-IOS)

No clear pattern emerges from the samples that reported measurable BDE concentrations, except for Cape Dorset (CD1) and Whitehorse (WHT-PCT). A profile similar to the Deca-BDE commercial product is observed for these two samples, with BDE-209, comprising 93-97%, BDE-206 with 1.3%, and BDE-207 ranging from 1.08 to 1.93%. The profile for Tuktoyaktuk (TUK-1) may indicate degradation of Deca-BDE to produce high- and mid-level congeners (i.e. BDE-153, -154, -183, -206, and -207). The concentrations from Pangnirtung, the only community to operate a sewage treatment plant in the northern Canada, were high relative to the other sites. Note that each sample represents a point in space and time and must not be regarded as representative of an entire region.

The total PBDE concentrations from the sum of the nine principal congeners in the background water samples constitute all of the PBDEs measured. Only five of the 13 locations analysed showed measurable concentrations of BDE-209. Its appearance may be related to its greater persistence and being carried north via atmospheric currents and/or by water as fine particulates.

Table 5 indicates that the background water sample from Whitehorse (WHT-PC) was the only sample to show measurable levels of all BDE congeners after procedural blank correction. Given the extremely low solubility of deca-BDE in water, the measured concentrations likely reflect fine particulates in the water, but it is also possible that the solubility could have been increased by humic substances or other components in the water.

4. Results and Discussion – Southern Canada

Complete data from the different jurisdictions where leachate was collected are presented in the supplemental data section. The names of the cities and towns are withheld to comply with the terms of the invitations to participate in the study. Instead, sample locations are identified by an unrelated uppercase letter. The raw data, procedural blank correction and final values are listed in the supplemental data section.

The total PBDE measured concentrations varied substantially from location to location, ranging from 969 pg/L to 867,805 pg/L, as shown in Table 2. BDE-209 was the major congener of those measured. Major congeners detected in the leachate samples of all sites included those prominent in the Penta commercial mixture (BDE-47, -99, -100, -153, and -154), as seen in Figure 4. Thirteen sites (out of a possible 27) indicated BDE-209 values between 60 and 92% of total PBDE concentrations. Five sites not included in Figure 4 are excluded because their congener values were BMDL after procedural blank correction.

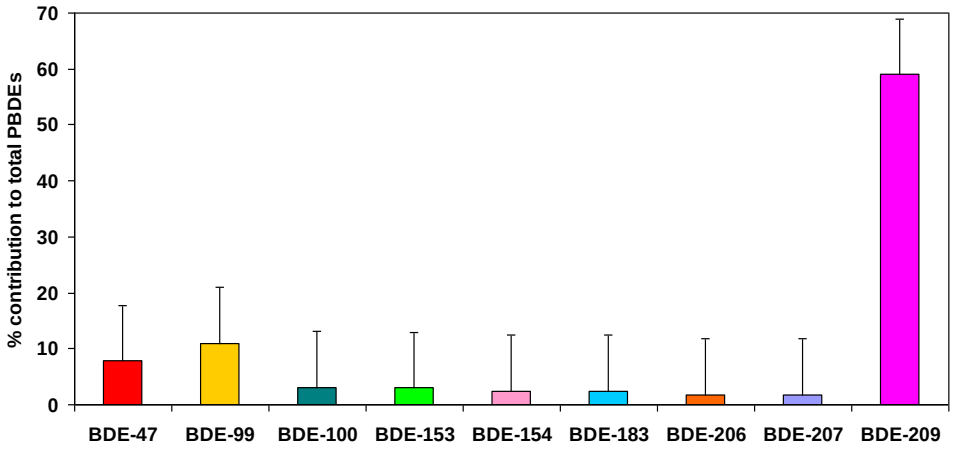

Figure 4. Mean principal BDE congeners in southern Canada leachate relative to total PBDEs. Five sites that fell below method detection limits for all congeners after procedural blank correction are excluded from the averages.

4.1 BDE Ratios Compared with Commercial Product

The dominant BDE congeners in the Penta-BDE commercial product are BDE-47, -99 and -100 (Stapleton et al. 2005). The ratios of concentrations of BDE-47 to BDE-99 and of BDE-47 to BDE-100 are plotted in Figures 5 and 6, respectively, against total PBDE concentrations from leachate in landfills across southern Canada and compared to the corresponding ratios in the Penta-BDE commercial product. As observed in Figure 5, the BDE-47/BDE-99 ratio in the commercial Penta-BDE product DE-71 is 0.6, whereas in Figure 6 the BDE-47/BDE-100 ratio in the commercial Penta-BDE product DE-71 is 3.5. In each case, the same leachate samples collected exhibited ratios close to those of the commercial product shown by the dashed horizontal lines, except for samples with the lowest total PBDE concentrations (which are subject to the greatest uncertainty). This suggests that wastes from which the PBDEs originated contained the Penta-BDE product, discarded recently enough for the congener pattern to still be recognizable.

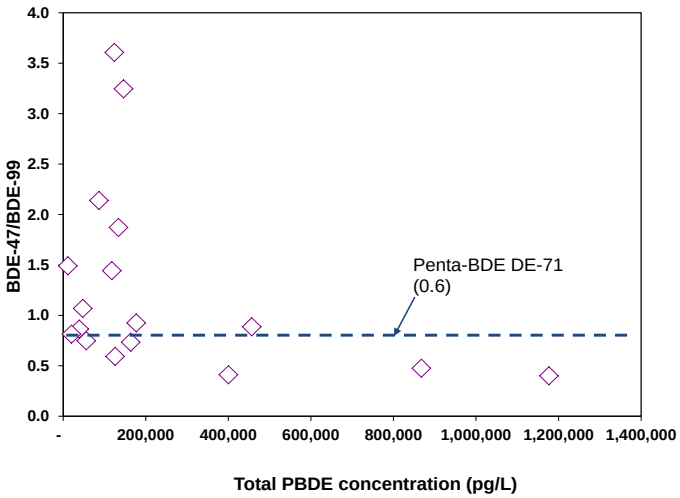

Figure 5. Ratio of BDE-47 to BDE-99 measured in landfill leachates from across southern Canada vs. total PBDE concentration.

Dashed line represents ratio in commercial Penta-BDE product, DE-71 (0.6) (Rayne and Ikonomou 2002). Points represent fifteen of the twenty samples. The other five samples were BMDL after procedural blank correction.

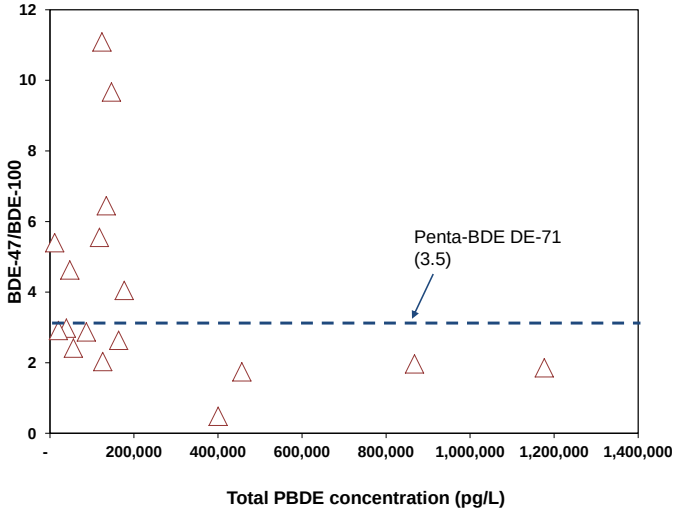

Figure 6. Ratio of BDE-47 to BDE-100 measured in landfill leachates from across southern Canada vs. the total PBDE concentration.

Dashed line represents ratio in commercial Penta-BDE product, DE-71 (3.5) (Rayne and Ikonomou 2002; ENVIRON 2003). Points represent fifteen of the twenty samples listed. The other five samples were BMDL after procedural blank correction.

Some studies have demonstrated that BDE congeners can debrominate as a result of exposure to UV rays (Eriksson et al. 2004; Söderström et al. 2004). However, the decomposition products were not identified in these papers. Stapleton et al. (2005) indicated that BDE-47 could be formed by the removal of a bromine atom from the BDE-99 congener. Note that BDE-47 could diffuse out of the treated product at a faster rate than BDE-99 because BDE-47 has a higher potential for long range transport relative to BDE-99 (Gouin and Harner 2003). Although BDE-100 was not mentioned in the Gouin and Harner (2003) study, its decomposition rate is expected to be comparable to that of BDE-99 given the structural similarity of these two congeners (Stapleton et al. 2005).

4.2 Population as a Determinant of PBDE Concentrations in Landfill Leachate

To create a larger data set, the southern Canada data are combined with the northern Canada data for the rest of this paper. For purposes of data presentation, Canada is divided into four quadrants: northwest, southwest, northeast, and southeast, with the dividing line between east and west taken as the Manitoba-Ontario border, whereas the division between north and south is the 60th parallel (coinciding with the northern boundaries of British Columbia, Alberta, Saskatchewan and Manitoba). Populations are 2006 census values.

In order to show the possible effect of population of the corresponding city/town, both principal congeners and total PBDE concentrations are considered. In addition, if the total PBDE concentrations are broken down into the major congeners discussed throughout this

paper, BDE-209 is the one congener that shows up in the highest concentrations. As expected, there is a strong correlation (R = 0.83) between population served and annual mass flow of wastes sent to the local landfill (tonnes/year). When the correlation of total PBDE concentrations to population is explored, the correlation coefficient is 0.26, as shown in Table 6. This indicates some correlation between PBDEs in landfills and population served, presumably because larger centres tend to be bigger consumers of electronic products and other manufactured goods, as well as being located further south. However, the relationship also depends on how the waste is handled and on the sampling protocols. The small number of sites, variation in sampling procedures and general scatter probably account for the limited correlation with population.

Table 6. Pearson correlation coefficient of total PBDE concentrations *vs*. population and landfill tonnage *vs*. population

Location	Population	Landfill refuse mass flow (tonnes/yr)	Total PBDEs (pg/L)
T	580,000	1,200,000	1,139,532
F	900,000	900,000	69,011
U	1,000,000	740,000	23,719
I	100,000	250,000	108,165
V	120,000	165,000	147,749
S	500,000	163,000	148,244
N	21,000	160,000	170,775
A	380,000	160,000	853,568
H	86,000	156,000	57,237
B	110,000	100,000	119,796
J	48,000	80,000	143,788
G	73,000	67,000	151,082
W	46,000	47,000	25,480
D	28,000	40,000	468,563
X	32,000	40,000	27,755
Y	36,000	38,000	237
Z	25,000	26,000	16,643
L	21,000	25,000	117,288
AA	4,000	12,700	30,848
P	8,000	10,000	84,756
BB	20,000	10,000	26,755
Correlation coefficient of population to total PBDEs: **0.26**			
Correlation coefficient of population to landfill refuse volume: **0.83**			

Approximate population from Statistics Canada 2006 census. Total PBDE concentrations are from our sampling data. Landfill tonnage data reported for each landfill are from 2005-06[5].

Possible correlations were also considered by quadrant and by combinations of quadrants. The mid-to-lower brominated congeners (BDE-47, -99, -100, -153- and -154) correlated best for the south (average R = 0.42) and west regions (average R = 0.40).

Although the PBDE concentrations were generally lower in the northern communities, some northern levels are similar to those of urban centres south of latitude 60. The remaining southern samples were between one and three orders of magnitude higher in total PBDE concentrations than for northern Canada. It is important to put this into perspective. The

[5] Tonnage data was not available for Sites C, E, K, M, O, Q, or R.

landfills examined were not homogeneous in terms of the types of materials disposed, depth, nor in sampling methodologies. These factors undoubtedly contributed to the observed scatter and limited correlations. However, as noted above, some correlation was found within the regions, indicating higher PBDE concentrations with higher refuse volume.

Total PBDEs are plotted against population in Figure 7. The outliers in this figure all correspond to populations less than 50,000. In Figure 8, concentrations of the BDE-47, -99 and -100 congeners are plotted against population, excluding the difficult-to-measure BDE-209. The data again suggest, albeit with considerable scatter, that a larger population tends to result in higher PBDE concentrations in leachate. The correlation appears to be better for BDE-47 than for BDE-99 or -100. Comparison of these two figures provides an indication of how much BDE-209 influences the total PBDE concentration.

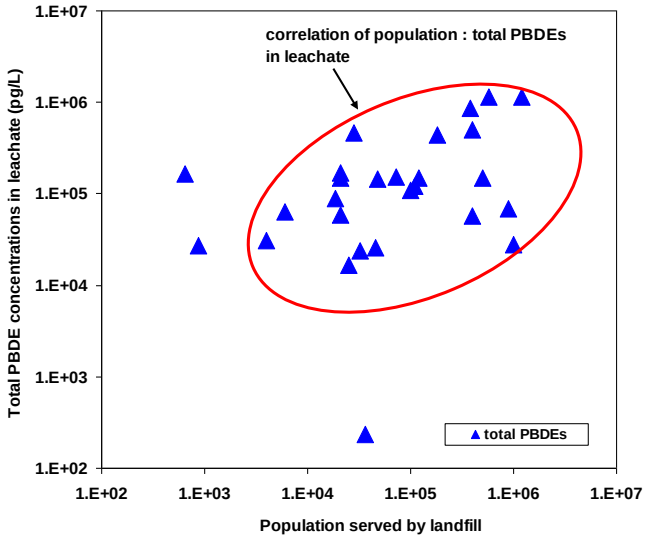

Figure 7. Total PBDE concentrations in leachate as a function of population served by landfill or dumpsite.

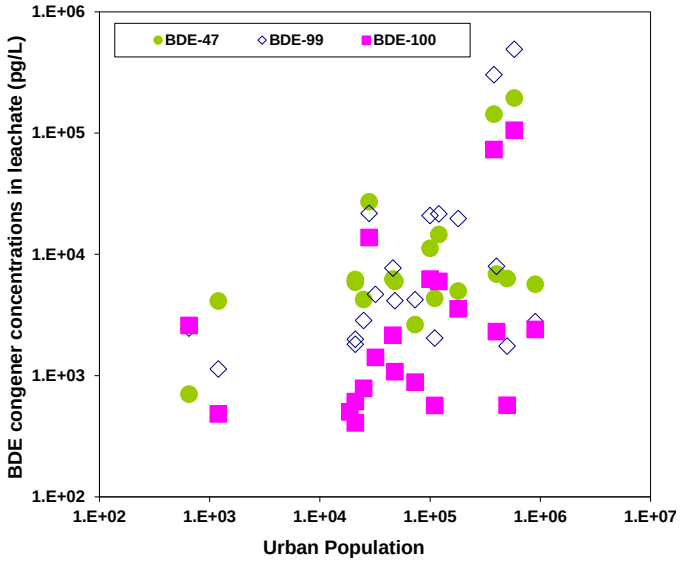

Figure 8. BDE-47, -99 and -100 congener concentrations as a function of population.

4.3 Latitude as a Possible Determinant of PBDE Concentrations in Landfill Leachate

Average and range of total PBDE concentrations are plotted for landfill leachate samples from southern and northern Canada in Figure 9. It is seen that the concentrations tend to be smaller for northern sites. As expected, there is a strong negative correlation between population and latitude, so that at least part of the north-vs.-south effect is due to the population effect discussed above. However, it is likely that lower concentrations in northern Canada than in southern Canada also reflect, to some extent, greater use of plastics and electronic products in the south, and limited north-south atmospheric and water-based dispersion. When data are considered by quadrant, northeast is somewhat higher than northwest, and southwest higher than southeast.

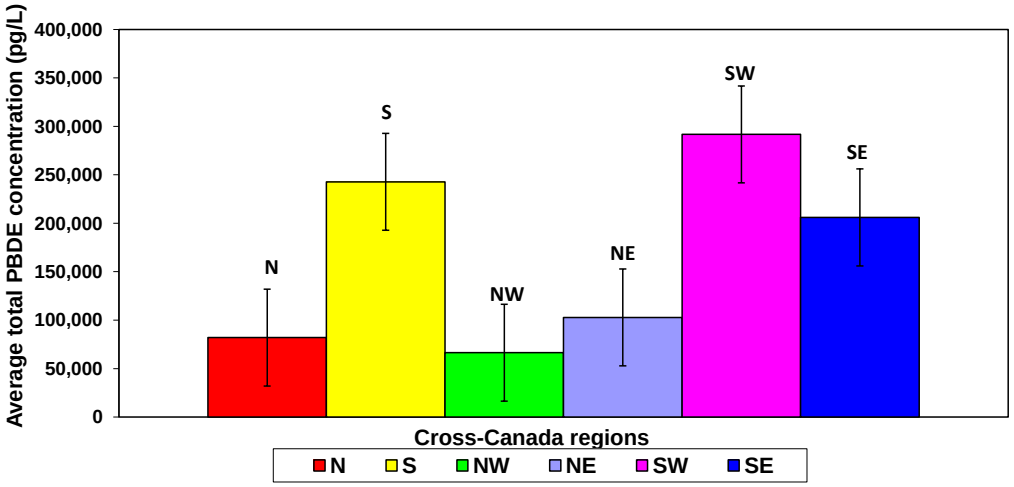

Figure 9. Total PBDE concentrations vs. location in Canada.

4.4 Consequence of PBDEs Leaching into the Aquatic Environment

Leachate containing PBDEs may enter water bodies from landfills (Ma et al. 2012), sewage treatment plants (STP), migration from groundwater, and atmospheric deposition (Meyer et al. 2011; Tian et al. 2011; Ma et al. 2012). PBDEs entering the aquatic environment may also depend on whether or not the leachate is treated prior to discharge. In some cases, PBDEs enter the water table without any STP treatment and/or with negligible removal by STPs (Danon-Schaffer, 2010). To illustrate this, an annual estimate of PBDE levels entering the receiving environment from one relatively large jurisdiction is calculated. A constant volumetric flow rate of 1.8 x 106 m^3/year is assigned[6]. The total PBDE loading from this landfill is ~2.0 kg/year, estimated from the mass flow for the landfill, the total PBDE concentration in the leachate for the landfill in question and the leachate produced per tonne of solid waste.

5. Conclusions

PBDE concentrations were measured in leachate, effluent, and background water samples from across southern and northern Canada. For the leachate samples, PBDE concentrations

[6] Obtained from this urban sewage treatment plant. The identity of the STP is confidential. 2006 data.

were primarily determined to be the BDE-209 congener. A similar pattern emerged for the background water samples, with BDE-209 as the major contributor. The concentrations were surprisingly high from the only community in the northern Canada that operates a secondary sewage treatment plant, indicating that the wastewater treatment plant did not efficiently remove PBDEs. More monitoring and duplicate sampling are needed to augment the data set and to study potential temporal trends and other variables. Given this and the analytical uncertainties described previously, it is impossible at this stage to fully define the sources of PBDEs in the northern dumpsites or to be able to interpret them in more detail.

The total PBDE concentrations in samples from landfills in southern Canada varied substantially, from below method detection limit to 867,805 pg/L. The principal congeners BDE-47, -99, -100, -153 -154, -183, -206, -207 excluding BDE-209, contributed less than 40% of the total PBDEs, while BDE-209 contributed 60 to 92% of the total for the nine principal BDEs. The large variability in data from different locations presented challenges in interpreting the data. Reproducibility was no doubt affected by different sampling procedures, variable weather, different waste dumping regulations and procedures, different types of waste material disposed at the various sites, and inconsistencies in sub-sampling.

Despite all of the possible factors that influence leachate in a landfill, the variability of the PBDE data, and the non-homogeneous samples containing high amounts of particles, some correlations were found. When the total PBDE concentration was correlated against urban population served by the landfill, there was an overall Pearson coefficient, R, of 0.26. Not surprisingly, there was a clear tendency for landfills in northern Canada to have lower PBDE concentrations than those in southern Canada.

TOC was determined for 21 sites, and 20 sites survived after application of procedural blank correction criteria. Total PBDE and TOC values correlated well only when the samples were restricted to subsets of locations with the highest PBDE levels.

Leachates from Canadian landfills on average show considerably higher PBDE concentrations in leachate than reported in the small number of previous landfill studies published in the open literature, from the U.S., Japan, Sweden, and South Africa.

The data suggest that measurable amounts of PBDEs appear in leachate from landfills, whether in southern or northern Canada. Landfill leachate could therefore provide one source of PBDEs in the environment at large. More work is needed to obtain more accurate data and to determine the processes which lead to leaching, degradation and spread of PBDEs from landfills.

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