

Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) in the Abiotic Environment: Surface Water and Precipitation from Ontario, Canada

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Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) have been identified as metabolites of PBDEs, and also as compounds of natural origin in the marine environment; however, there has only been very limited study of their presence in the abiotic environment. In the present study, OH-PBDEs were determined in samples of surface water and precipitation (rain and snow) collected from sites in Ontario, Canada. OH-PBDEs were detected in all the samples analyzed, although half of the observed peaks did not correspond to any of the 18 authentic standards available. Fluxes of Σ OH-PBDEs ranged from 3.5 to 190 pg/m² in snow and from 15 to 170 pg/m²/day in rain, and those were higher at three of the southern Ontario locations relative to a single northern remote site. Concentrations of Σ OH-PBDEs ranged from 2.2 to 70 pg/L in water and from <1 to 420 pg/g in particulate organic carbon (POC), and higher values were found near sewage treatment plant (STP) outfalls in Lake Ontario. Partition coefficients ($\log K_{oc}$) for OH-PBDEs ranged from 4.0 to 5.1. The results in this study suggest that OH-PBDEs are ubiquitous in the abiotic environment and most likely are produced through reaction of PBDEs with atmospheric OH radicals. As well, they may be present in surface waters near STPs due to oxidation of PBDEs and inflows from metabolism by humans and animals.

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in many manufactured items including polyurethane foams, other polymers, and in fabric backing (1–3). While PentaBDE and OctaBDE formulations have been removed from commerce as of 2005 (4), they are nevertheless present in a vast amount of consumer products and may be released to the environment during use and disposal, entering air, sewage treatment systems, and landfills. It has been estimated that approximately 3.9% of PentaBDE present in articles is released through volatilization or dispersed on particle fragments during their assumed service life of 10 years with about 1% emitted to the atmosphere (5). PBDEs have been detected in air (gas phase and particles) from the Great Lakes region (6–9), but the ultimate fate of PBDEs in the atmosphere is unknown. PBDEs have been shown to be debrominated on solid surfaces under sunlight (10), and on SiO₂ aerosols (11). Mono and di-BDEs have been shown to react with OH-radical in the gas phase yielding bromophenols (12). This reaction was postulated to proceed via hydroxylated PBDE (OH-PBDE) intermediates formed by OH-addition (12).

PBDEs are relatively persistent and tetra- to hepta-BDEs are highly bioaccumulative (13). Those have been widely detected in water, sediments, and biota in the Great Lakes (14–19). OH-PBDEs have also been identified in marine organisms (algae, mussel, and fish) (20, 21) as well as human blood (22). In biota of the Great Lakes region, OH-PBDEs have been detected in plasma from benthic-feeding fish in the Detroit River (23). Hydroxylated PBDEs detected in biota include 3-OH-BDE47, 5-OH-BDE47, 4-OH-BDE42, 6-OH-BDE85, and 2-OH-BDE123. The congeners of 6-OH-BDE47, 5-OH-BDE47, 3-OH-BDE47, and 4'-OH-BDE49 have been identified as metabolites in plasma and feces of rodents exposed to PBDEs (24, 25). In addition, several OH-PBDE congeners and related compounds, methoxylated PBDEs (MeO-PBDEs), have also been structurally identified as natural products in marine organisms (20, 21, 26–28).

OH-PBDEs differ in their biological effects compared with their precursor PBDEs. OH-PBDEs are known to bind to transthyretin (29), and have antiestrogenic, antiandrogenic, and antiprogesterone potency (30). In general, concern for wildlife and human exposure to PBDEs is related to developmental neurotoxicity and, at somewhat higher doses, altered thyroid hormone homeostasis (31). The latter effects are suspected to be caused by OH-PBDEs as the metabolites of PBDEs.

There are only very limited measurements of OH-PBDEs in abiotic environmental samples. Hua et al. (32) detected OH-PBDEs with three bromines in a sewage treatment plant (STP) effluent located on the Detroit River and in nearby surface waters. Considering their known toxicity and potential to be retained in blood and blood rich tissues, it is a question if these compounds can exist in abiotic environment and be accumulated by aquatic organisms. Therefore, the full extent of OH-PBDEs contamination in the abiotic environment needs to be elucidated in order to estimate exposure to wildlife and humans. In this study, we extend our previous work on hydroxylated-PCBs (OH-PCBs) (33) in precipitation and surface water samples with the direct measurements of OH-PBDEs in those samples.

Materials and Methods

Sample Collection. All the abiotic samples (snow, rain, and water) were collected in 2002–2004 from sites in the Great Lakes basin region in Ontario, Canada. Sampling methodol-

ogy was identical to that for the study on OH-PCBs (33) and details along with a map are provided in the Supporting Information (SI: Materials and Methods; Figure S1). In brief: rain samples were collected using an automated wet only collector equipped with XAD-2 resin without filtration. Large volume water samples were collected using a field centrifuge system and direct pumping through glass fiber filter (GFF) into an XAD-2 column. GFFs were stored for analysis of particulate organic carbon (POC). Large volume snow samples were collected using precleaned aluminum boxes lined with polypropylene autoclave bags, then pumped through an XAD-2 resin column without filtration.

Extraction, Clean Up, and Quantification. Extraction and isolation of OH-PBDEs and PBDEs were based on a method for OH-PCBs previously reported (23, 33, 34) and details are described in the SI. In brief: since ^{13}C -OH-PBDEs were not available when this study was conducted, ^{13}C -4'-OH-PCB120 and PCB166 were employed as internal standards. XAD-2 resin and GFFs were eluted using methanol followed by dichloromethane. The eluate was extracted with 2-propanol and 50% methyl *tert*-butyl ether (MTBE) in hexane mixture after lowering the pH. The pH was then increased to force the OH-PBDEs into aqueous media (phenolic fraction) while the precursor PBDEs remained in the organic phase (neutral/basic fraction). The aqueous phenolic phase was separated and acidified to extract OH-PBDEs into a 50% MTBE in hexane solution. The OH-PBDEs were derivatized to MeO-PBDEs using diazomethane. Both of phenolic and neutral fractions were cleaned up using an acidified silica gel column. The ^{13}C -BDE138 was added to final solution as a performance standard.

The quantification of OH-PBDEs (as MeO-PBDEs) was carried out using gas chromatography (GC: Agilent 6890) coupled with high-resolution mass spectrometry (HRMS: MicroMass Ultima) using a 60 m DB5-MS (0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). Authentic MeO-PBDE standards were synthesized as described previously (35) and those were made available via Stockholm University. Two authentic MeO-PBDE standards were purchased from Accustandard (New Haven, CT). In this study, the peaks which matched retention times and isotopic ratio with authentic MeO-PBDEs were quantified as "identified MeO-PBDEs". Unknown peaks that matched the isotopic ratio were quantified as "unidentified OH-PBDEs" using a average response factor of same homologue group. PBDE congeners were determined based on the method previously reported (36).

Quality Control. Recovery of ^{13}C -OH-PCBs for the analytical procedure (through extraction and cleanup, $n = 47$) averaged $71 \pm 56\%$ for ^{13}C -OH-PCBs with two to four chlorine atoms, and $104 \pm 56\%$ for ^{13}C -OH-PCBs with five to seven chlorine atoms as previously reported (33). Method detection limits (DLs) were defined as three times the standard deviation analytical blank values ($n = 7$). DLs of identified OH-PBDEs ranged from 0.2 to 1 pg/m^2 for snow, 0.5–10 $\text{pg}/\text{m}^2/\text{day}$ for rain, 0.01–0.8 pg/L for water, and 1–60 pg/g for POC samples. Values lower than the DL were treated as zero when means were calculated. Laboratory blanks processed with the samples contained several congeners, e.g., 6-MeO-BDE17, 6-MeO-BDE47, and 6-MeO-BDE90, but contributions of those compounds were <10% of $\Sigma\text{OH-PBDEs}$.

Results and Discussion

Identification and Contamination Status of OH-PBDEs. The mean and range of $\Sigma\text{OH-PBDE}$ and ΣPBDE fluxes (concentrations) in snow, rain and water samples analyzed in this study are summarized in Table 1 and 2 (data on individual samples are available in Supporting Information Tables S1–S7). OH-PBDEs and PBDEs were detected in all of the samples analyzed. The results demonstrate that OH-PBDEs

are ubiquitous in abiotic media such as rain, snow, and water. To our knowledge, this is the first report on the detection and quantification of OH-PBDEs directly in the abiotic environment apart from detection of tribrominated OH-PBDEs in Detroit River water (32).

Fluxes of $\Sigma\text{OH-PBDEs}$ in precipitations ranged from 3.5 to 190 pg/m^2 in snow and from 15 to 170 $\text{pg}/\text{m}^2/\text{day}$ in rain (Table 2). Concentrations of $\Sigma\text{OH-PBDEs}$ in water samples ranged from 2.2 to 70 pg/L in dissolved phase and from <1 to 420 pg/g POC in particulate organic carbon. ΣPBDEs fluxes ranged from 30 to 2300 pg/m^2 in snow and from 460 to 2700 $\text{pg}/\text{m}^2/\text{day}$ in rain, while concentrations were ranged from 17 to 250 pg/L in water (Table 2).

Concentrations and fluxes of tentatively "identified" and "un-identified" OH-PBDEs were summarized in Table 2 and individual peaks with relative retention times (RRT) on GC-HRMS chromatogram were summarized in Supporting Information Tables S8–S11. To evaluate the importance of unidentified OH-PBDEs, the identification ratios ($\Sigma_{\text{identified OH-PBDEs}}/\Sigma\text{OH-PBDEs}$) were calculated and summarized in Table 2. The ratio ranged from 0 to 1 for all the media with an average of 0.6. This result suggests that almost half-of $\Sigma\text{OH-PBDEs}$ detected in this study were not identified even with the 18 authentic congener standards available. Quantification of unidentified OH-PBDEs is necessary to understand the full extent of OH-PBDE contamination in the abiotic environment. In addition, it should be considered that both of identified and unidentified OH-PBDEs could be coeluted even those that were identified with 60 m capillary column on GC-HRMS, because there are numerous numbers of theoretical OH-PBDEs isomers (20). Further improvement of analytical technique is required to identify those compounds individually.

Since OH-PBDEs are ionizable compounds, there is a possibility that the scavenging efficiency of these chemicals by rain and snow in atmosphere could vary depending on the pH, as well as the collection efficiency by XAD-2 resin. Malmberg (37) reported the pK_a for 4-OH-BDE42, 3-OH-BDE47, and 6-OH-BDE47 were 8.1, 6.8, and 7.8, respectively. It has been observed that the pH of precipitation has been around 4–5 in the southern Ontario region (38). At this pH, the OH-PBDEs in precipitation would be in their protonated form and thus would likely be efficiently absorbed by XAD-2 resin, similarly to OH-PCBs (33).

Geographical Distribution of OH-PBDEs. Figure 1 shows the geographical distributions of $\Sigma\text{OH-PBDE}$ fluxes and concentrations in snow, rain, and water samples from Ontario, Canada. The distribution of $\Sigma\text{OH-PBDE}$ fluxes in snow samples was relatively uniform and no clear trend was observed. ΣPBDE fluxes in snow samples also showed a similar trend (SI Figure S2). The snow samples represented deposition over the entire winter because the whole snow column was collected toward the end of the season.

Higher $\Sigma\text{OH-PBDE}$ fluxes in rain were found at the three southern sites (R2–R9) than at a northern site (R10) (Figure 1). This is generally consistent with trends for PCBs and PBDEs between the upper and lower Great Lakes (7, 8, 33, 39) and between urban and rural areas (40). The higher $\Sigma\text{OH-PBDE}$ fluxes in southern Ontario are plausibly due to the larger population and greater past use of PBDEs in urban areas in southern Ontario compared to more lightly populated northern areas. However, only one rain sample was available at a remote northern site in Ontario (R10), and therefore, this conclusion is tentative.

Higher $\Sigma\text{OH-PBDE}$ and ΣPBDE concentrations in water samples were found near urban areas on Lake Ontario (sites W5, W6, W8, and W13) compared to sites in Detroit River (sites W1–W4) and in further offshore (sites W7, W11, and W12) (Table 1, Figure 1, and SI Figure S2). The ΣPBDE concentrations in water samples in this study (12 ± 64 pg/L)

TABLE 1. Sample Information of Snow, Rain, and Water for OH-PBDEs and PBDEs Analysis Collected in Ontario, Canada^a

media	ID	location ^b	date	volume (L)	collected area (m ²)	method ^c	ΣOH-PBDEs	ΣPBDEs ^d	
snow	S1	Grimsby	February 20, 2003	44	8	d	Fluxes (pg/m2)	590	
	S2	Pinery, PP	February 26, 2003	98	5	d	45	530	
	S3	Macgregor, PP	February 27, 2003	113	11	d	17	580	
	S6	Turkey Watershed	March 4, 2003	88	4	d	85	730	
	S7	Evansville	March 5, 2003	89	5	d	89	540	
	S8	Dorset	March 6, 2003	95	6	d	37	420	
	S10	Sibbald, PP	March 7, 2003	95	3	d	95	2300	
	S11	Guelph Lake	March 12, 2003	116	6	d	190	360	
	S13	Pine Valley, GC	March 14, 2003	108	101	d	3.5	30	
	rain	R2	Lake St. Clair	May 3–June 2, 2004	5	0.2	d	81	1400
		R3	Lake St. Clair	June 3–June 30, 2004	2	0.2	d	92	1500
		R4	Grand Bend	April 1–May 4, 2004	7	0.2	d	170	4500
		R5	Grand Bend	May 4–June 3, 2004	5	0.2	d	110	1200
R6		Grand Bend	June 2–June 30, 2004	2	0.2	d	91	460	
R7		Rock Point	Mar. 30–April 30, 2004	4	0.2	d	120	1000	
R8		Rock Point	April 30–June 1, 2004	3	0.2	d	81	590	
R9		Rock Point	June 1–June 29, 2004	5	0.2	d	15	1200	
R10		Turkey Lakes	June 5–July 2, 2004	5	0.2	d	40	na	
water		W1	Detroit River Peche Island	September 1, 2002	80		c	Concentrations (pg/L)	64
	W2	Detroit River Fright Island	September 1, 2002	95		c	6.7	17	
	W3	Detroit River Lake Erie, Detroit River mouth	September 2, 2002	95		c	6.0	64	
	W4	Detroit River Amherst Island	September 2, 2002	95		c	3.0	91	
	W5	Lake Ontario Hamilton Harbour, near STP	September 17, 2002	87		c	56	250	
	W6	Lake Ontario Hamilton Harbour, near steel factory	September 22, 2002	95		c	41	140	
	W7	Lake Ontario Toronto, offshore	October 20, 2002	100		c	15	130	
	W8	Lake Ontario Toronto, near STP	October 20, 2002	97		c	22	95	
	W11	Lake Ontario Toronto, offshore	August 21, 2003	96		c	5.4	100	
	W12	Lake Ontario Hamilton, offshore	October 18, 2004	50		f	5.7	32	
	W13	Lake Ontario Hamilton Harbour, near STP	October 27, 2004	91		f	70	130	
	suspended solid	SS1	Lake Ontario Hamilton, offshore	October 18, 2004	0.95 ^e		f	nd	na
		SS2	Lake Ontario Hamilton Harbour, near STP	October 27, 2004	4.4 ^e		f	420	na

^a nd: Not detected; na: No data available. ^b STP: sewage treatment plant, PP = Provincial Park, GC = golf course. ^c d: direct extraction (no particle removal); c: Centrifuge particle removal before extraction; f: Filtration before extraction (suspended solid on filter was employed for chemical analysis). ^d ΣPBDEs: sum of mono to hepta-BDEs. ^e Concentration of particulate organic carbon (mg POC/L).

TABLE 2. Summary of Fluxes and Concentrations of OH-PBDEs in Snow, Rain, and Water Samples Collected from Southern Ontario, Canada^a

compounds ^b	fluxes (pg/m ²) snow (n = 9)		fluxes (pg/m ² /day) rain (n = 9)		concentrations (pg/L) water (n = 11)		concentrations (pg/g POC ^c) POC (n = 2)	
	mean	(min-max)	mean	(min-max)	mean	(min-max)	mean	(min-max)
di OH-PBDEs								
3'-OH-PBDE 7 unidentified	nd nd	(<0.2-nd) (<0.2-nd)	nd nd	(<0.5-nd) (<0.5-nd)	nd 1.2	(<0.04-nd) (<0.04-4.4)	nd nd	(<10-nd) (<10-nd)
tri OH-PBDEs								
6'-OH-PBDE 17	nd	(<1-nd)	nd	(<3-nd)	nd	(<0.8-nd)	nd	(<10-nd)
2'-OH-PBDE 28	nd	(<0.2-nd)	nd	(<10-nd)	nd	(<0.8-nd)	nd	(<10-nd)
4'-OH-PBDE 17	nd	(<0.2-nd)	nd	(<3-nd)	nd	(<0.8-1.0)	nd	(<10-nd)
3'-OH-PBDE 28	nd	(<0.2-nd)	nd	(<3-nd)	nd	(<0.8-nd)	nd	(<10-nd)
unidentified	0.33	(<0.2-4.2)	nd	(<3-nd)	9.2	(<0.8-36)	nd	(<10-nd)
tetra OH-PBDEs								
6'-OH-PBDE 49	nd	(<0.2-nd)	nd	(<1-nd)	0.087	(<0.01-0.30)	nd	(<1-nd)
2'-OH-PBDE 68	0.83	(<0.2-6.2)	nd	(<1-1.7)	0.46	(<0.01-1.0)	nd	(<1-nd)
6'-OH-PBDE 47	11	(0.56-34)	12	(2.2-21)	2.7	(0.85-8.2)	60	(<1-120)
3'-OH-PBDE 47	6.9	(0.39-18)	12	(5.0-21)	0.39	(<0.01-1.1)	nd	(<1-nd)
5'-OH-PBDE 47	19	(1.1-57)	23	(<2-43)	1.8	(<0.01-6.7)	31	(<1-63)
4'-OH-PBDE 49	6.5	(<0.2-20)	2.9	(<2-6.5)	1.1	(<0.01-3.9)	45	(<1-90)
4'-OH-PBDE 42	0.80	(<0.2-6.2)	nd	(<3-nd)	0.25	(<0.01-1.0)	nd	(<1-nd)
unidentified	8.1	(<0.2-19)	8.9	(<1-19)	1.2	(<0.01-4.7)	nd	(<1-nd)
hexa OH-PBDEs								
6-OH-PBDE137 unidentified	0.75 nd	(<0.2-6.7) (<0.2-nd)	nd nd	(<7-nd) (<7-nd)	0.12 0.023	(<0.02-1.2) (<0.02-0.30)	nd nd	(<60-nd) (<60-nd)
Σidentified OH-PBDEs	59	(3.1-180)	62	(15-120)	8.4	(1.8-25)	180	(nd-360)
Σunidentified OH-PBDEs	10	(nd-26)	26	(nd-55)	13	(nd-45)	30	(nd-60)
ΣOH-PBDEs	68	(3.5-190)	88	(15-170)	21	(2.2-70)	210	(nd-420)
ΣPBDEs ^d	670	(30-2300)	1200	(460-2700)	100	(17-250)	na	(na-na)
peak number of OH-PBDEs	9	(6-14)	12	(2-15)	27	(2-65)	4	(nd-7)
Σidentified OH-PBDEs/ΣOH-PBDEs ^e	0.9	(0.7-1)	0.7	(0.6-1)	0.6	(0.2-1)	na	(na-0.9)
ΣOH-PBDEs/ΣPBDEs ^f	0.1	(0.03-0.5)	0.1	(0.01-0.2)	0.2	(0.03-0.5)	na	(na-na)
ΣOH-PCBs ^g	43	(nd-100)	28	(nd-44)	22	(0.87-130)	610	(230-990)
ΣPCBs	23000	(1000-54000)	3000	(1500-7300)	590	(190-980)	190000	(95000-290000)
peak number of OH-PCBs	12	(0-19)	35	(0-61)	58	(7-95)	11	(9-12)
Σidentified OH-PCBs/ΣOH-PCBs	0.5	(0.4-0.8)	0.3	(0-1)	0.4	(0.07-1)	0.5	(0.4-0.6)
ΣOH-PCBs/ΣPCBs	0.002	(0-0.004)	0.01	(0-0.02)	0.02	(0.008-0.04)	0.003	(0.002-0.003)

^a nd: not detected; na: no data available. ^b Concentrations of individual congeners and relative retention time for each sample are shown in Supporting Information. ^c POC: particulate organic carbon. ^d Total PBDEs: sum of mono to hepta-BDEs. ^e Σidentified OH-PBDEs/ΣOH-PBDEs: ratio between Σidentified OH-PBDEs to ΣOH-PBDEs. ^f ΣOH-PBDEs/ΣPBDEs: ratio between ΣOH-PBDEs to ΣPBDEs. ^g Data cited from Ueno et al. (33).

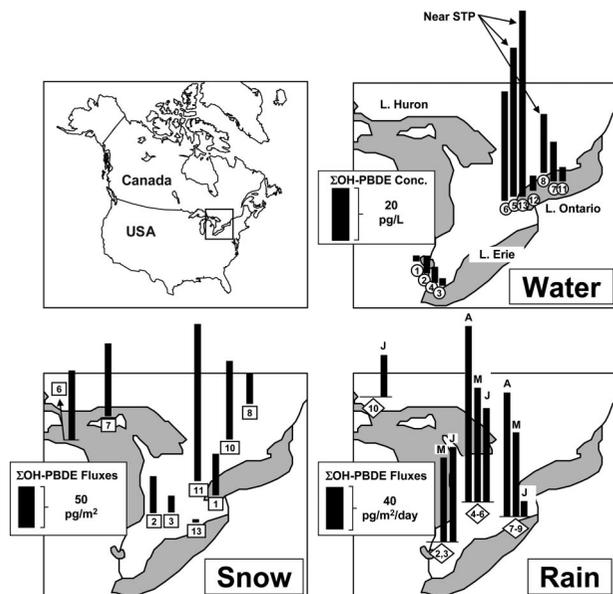


FIGURE 1. Geographical distribution and seasonal variation of total OH-PBDE fluxes and concentrations in rain, snow, and water from Ontario, Canada. STP, A, M, and J indicate sewage treatment plant, April, May, and June, respectively.

were significantly higher than those in filtered surface water samples from Lake Michigan (18 ± 1.8 pg/L) (14) and Lake Ontario (from 4 to 13 pg/L) (15). However, those studies were primarily based on samples from central lake sites while most of the sites in this study were within a few kilometers of STPs, except for W11, which was from the central western basin of Lake Ontario.

Among the Lake Ontario water samples, higher concentrations of Σ OH-PBDEs were found in samples collected within 0.5–2 km from two major STP outfalls in Hamilton Harbour (W5, 6, 13; 41–70 pg/L) and near a large STP in eastern Toronto (W8; 22 pg/L). Hua et al. (32) also detected OH-PBDEs in STP effluents in the Detroit River. OH-PBDEs may be formed in STPs from precursor PBDEs in municipal wastewater through microbial oxidation or reactions with OH radicals if ozone was used for disinfection. Since concentrations of PBDEs in human tissues are higher in North America (3), OH-PBDEs contained in human and animal excretion may also be a source of these compounds in STP outflow.

On the other hand, Σ OH-PBDEs and Σ PBDEs concentrations in water samples from the Detroit River (W1–W4) were generally lower than those from Lake Ontario nearshore waters, even though it is an industrialized and urban region (Figure 1; SI Figure S2). The Detroit samples were collected on the Canadian side of the Detroit River, where PCB and chlorinated dioxins concentrations in sediment were much lower than on the American side (41). Most of the water in this river originates in Lake Huron, where there is less anthropogenic activity compared to Lake Ontario.

Homologue Pattern of OH-PBDEs. The major OH-PBDE components in rain, snow, and water samples were tetra- and penta-brominated diphenyl ether homologues (Figure 2). Small amounts of hexa-brominated homologues were detected in snow and water samples. The homologue patterns in snow and rain samples were similar, and did not vary much among locations or seasonally. In the case of OH-PCBs, a larger proportion of higher chlorinated homologues was detected in rain than snow samples (33), which suggests that higher temperature and larger OH radical concentrations in early summer (rain) than winter (snow) might be responsible for the oxidation of higher chlorinated PCBs congeners. The similarity between OH-PBDE homologue patterns in rain

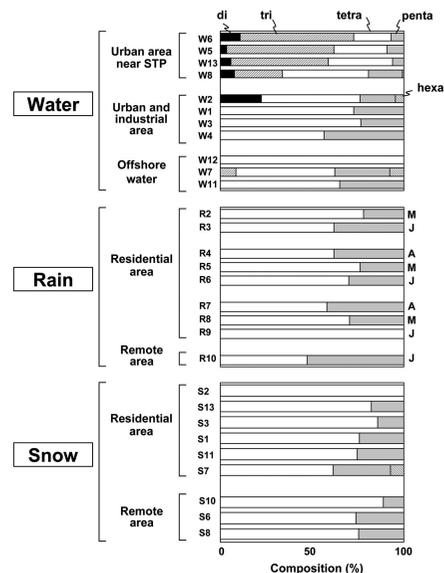


FIGURE 2. Percentage contribution of OH-PBDE homologues detected in snow, rain, and water from Ontario, Canada. STP, A, M, and J indicate sewage treatment plant, April, May, and June, respectively.

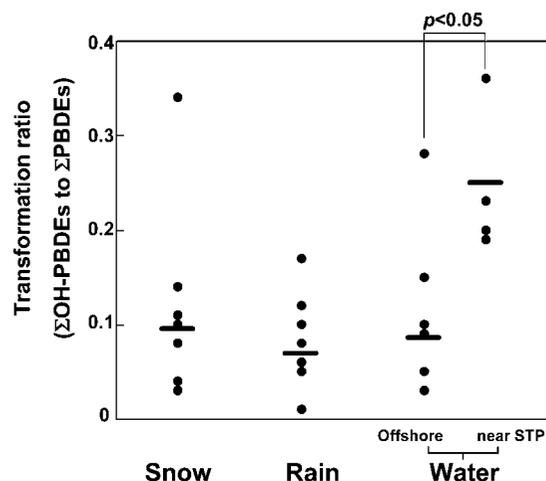


FIGURE 3. Transformation ratios (percentage contribution of total OH-PBDEs to total PBDEs) in snow, rain and water from Ontario, Canada. STP indicates sewage treatment plant.

and snow samples may be due to faster transformation of precursor PBDEs and lower stability of OH-PBDEs as compared to OH-PCBs.

Clear differences in homologue patterns were found among water samples (Figure 2). Higher percentages of OH-PBDEs with two and three bromines were found in samples near STPs. Hua et al. (32) also observed tribrominated OH-PBDEs in water samples collected near STP outflow. On the other hand, other water samples from offshore regions showed mainly tetra- and penta-brominated homologues, and those patterns were similar to those in rain and snow samples. This result suggests that the deposition of OH-PBDEs in rain and snow, as well as gas exchange, may play a greater role than chemical transformation of these compounds in the offshore water environment.

Transformation Efficiency of OH-PBDEs. To evaluate the transformation efficiency from precursor PBDEs to OH-PBDEs, the transformation ratios (Σ OH-PBDEs/ Σ PBDEs) were calculated (Table 2 and Figure 3). These values ranged from 0.01 to 0.3 in snow, from 0.01 to 0.2 in rain, and from 0.03 to 0.4 in water samples (Figure 3). Numbers of detected OH-PBDE peaks on the GC-HRMS chromatograms of those

samples ranged from 6 to 14 in snow, from 2 to 15 in rain, and from 2 to 65 in water samples (Table 2).

Average transformation ratios of rain and snow precipitation samples were similar, and no clear difference was observed among sampling locations (Figure 3). There was also no clear seasonal trend in transformation ratios of rain samples (Table 3). However, a clear seasonal variation was observed in Σ OH-PBDE and Σ PBDE fluxes of rain samples (Figure 1 and SI Figure S2), which were higher in "April" (end of winter) than "May–June" (early summer). This result suggests that both PBDEs and OH-PBDEs may be decomposed in the same manner to additional transformation products such as di-OH-PBDEs by the large amount of OH radicals present in the atmosphere in June compared to April. Raff and Hites (12) detected OH-PBDEs as minor products in their studies of OH radical reactions with mono and dibrominated diphenyl ethers. They noted that the relatively high OH radical concentrations in their experiments likely resulted in the OH-PBDE being consumed by secondary reactions with OH radicals as soon as they were produced.

Of all the abiotic media analyzed, the highest transformation ratio (0.4) and the largest peak numbers (65 peaks) of OH-PBDEs were found in water samples collected near STPs in Hamilton Harbour (W13) (Figure 3 and Table 2). The input of OH-PBDEs as a result of human excretion, combined with oxidation of PBDEs during processing in the STP may explain the higher transformation ratios and larger number of OH-PBDE peaks. Offshore water samples had lower transformation ratios (around 0.1) than those from near STPs (up to 0.4), and the values were similar to snow and rain samples (Figure 3). Similar transformation ratios among offshore water, rain, and snow samples suggests offshore water samples are less influenced by STP sources than OH-PBDE deposition in rain and snow, and/or gas exchange.

To compare the transformation properties of OH-PBDEs and OH-PCBs, those values for Σ OH-PCBs reported previously (33) were also summarized (Table 2). Transformation ratios (degradation ratio) for OH-PCBs (up to 0.02) were 10–100 times lower than those of OH-PBDEs (up to 0.4). This result suggests that transformation of PBDEs to OH-PBDEs is more rapid than PCBs to OH-PCBs in the abiotic environment. In addition, peak numbers for OH-PCBs (up to 95) were larger than those of OH-PBDEs (up to 65) (Table 2). The predominance of tetra- and penta-BDE congeners (BDE47, 99, and 100) in atmospheric samples (6–9) suggests fewer relevant precursor PBDEs are responsible for the smaller numbers of OH-PBDE congeners compared to the much broader array of PCB and OH-PCB congeners in Great Lakes air (42).

Another transformation may be the photolytic debromination of these compounds (10, 11). Since both debromination and hydroxylation of PBDEs may occur in the atmosphere, further research is required to evaluate the relative importance of these processes.

Source Estimation of OH-PBDEs. Rain and water fluxes (concentrations) of OH-PBDEs and PBDEs in this study seem to be associated with the distances from urban areas (Figure 1 and SI Figure S2). The major OH-PBDE congeners detected were 6-OH-BDE47, 5-OH-BDE47, 3-OH-BDE47, and 4'-OH-BDE49 which were identified as metabolites in plasma and feces of rodents exposed to PBDEs (24, 25). The rodent results support the suggestion that OH-PBDEs detected in this study near STPs could be human and animal metabolites as well as oxidation products of PBDEs in STPs.

On the other hand, OH-PBDEs have been identified as compounds of natural origin (20, 21, 26–28). The congeners suggested as having natural origin 6'-OH-BDE90, 2'-OH-BDE68, and 6-OH-BDE137 were detected in this study (Table 2), and 2'-OH-BDE68 was also found in fish plasma collected from Detroit River (23). Kierkegaard et al. (43) reported that

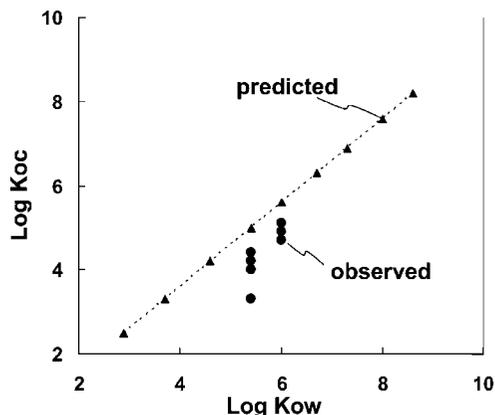


FIGURE 4. Comparison between observed and predicted values of partition coefficient (K_{oc}) for OH-PBDEs in the water sample from Hamilton Harbour, Lake Ontario. Circles and triangles indicate observed and predicted, respectively.

2'-MeO-BDE68 (OH-PBDEs were not analyzed) was detected in fish from remote lake in Sweden. Those reports suggested that those congeners could be of natural origin because the congeners detected lack relevant precursor PBDEs (20, 21, 43, 44). However, OH-PBDEs of natural origin have been isolated only from marine organisms. It is unlikely that freshwater algae would generate significant amounts of brominated compounds in the low bromine environment of lake water. As an additional possibility, some natural origin OH-PBDEs (e.g., 6'-OH-BDE90, 2'-OH-BDE68, and 6-OH-BDE137) detected in this study could have been atmospherically transported from a marine environment. Vetter et al. reported that natural origin aromatic compounds identified in marine organisms were detected in Antarctic air samples (45), and this result suggests certain natural compounds could be transported long distances through atmosphere. Further research is needed to evaluate the contribution and impact of natural origin OH-PBDEs and MeO-PBDEs in inland environment.

Water and Particulate Organic Carbon Partition Coefficient (K_{oc}) of OH-PBDEs. OH-PBDE partition coefficients between particulate organic carbon (POC) and water (K_{oc}) were calculated for Hamilton Harbour samples (site W13). To evaluate these empirical K_{oc} values, they were compared to those estimated from the octanol–water partition coefficient (K_{ow}) by the simple relationship (46): $K_{oc} = 0.41 \times K_{ow}$.

K_{ow} values of OH-PBDEs were estimated according to the fragment constant method (47), using K_{ow} values of PBDEs with the same number of bromines (5), because to our knowledge there are no directly measured values. The observed and predicted K_{oc} values agreed within a factor of 0.8 log units for tetra- and penta-brominated congeners, and were generally lower than predicted values (Figure 4: individual data is available in SI Table S12). It has been reported that environmental K_{oc} values of organic pollutants are lower than estimated values, and this discrepancy may be due to partitioning to a colloidal third phase, as observed in studies of PCBs and PBDEs in Lake Michigan (14, 48). In addition, the pK_a of OH-PBDEs can be an important factor by influencing the partitioning behavior. It was suggested that OH-PCB congeners with pK_a values around 7 could be 50% in the anionic form at the pH of Lake Ontario and Hamilton Harbour water (pH 7.4–8.2), which could result in a lower observed K_{oc} for those congeners, assuming the anionic form did not bind to POC (33). With pK_a values for tetrabromo OH-PBDEs ranging from 6.8 to 8.1 and 7.8 (37), some OH-PBDEs (e.g., a major congener such as 3-OH-BDE47; $pK_a = 6.8$) may be more than 50% in the anionic form at the pH of Lake Ontario and Hamilton Harbour water.

In summary, this study detected OH-PBDEs in rain, snow, and water, and the results suggest OH-PBDEs are ubiquitous contaminants in the abiotic environment. Given their relatively hydrophobic characteristics, bioaccumulation from water and food could be another exposure route for aquatic organisms, in addition to metabolism of precursor PBDEs. Further research is required to determine the sources, fate and bioavailability of these compounds.

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Supporting Information Available

Full method (text); sampling map, geographical distribution of PBDEs fluxes/concentrations (figures); fluxes/concentrations and RRT of individual congeners, calculated Koc (Tables). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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