



Halogenated organic contaminants of concern in urban-influenced waters of Lake Ontario, Canada: Passive sampling with targeted and non-targeted screening[☆]

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ARTICLE INFO

Article history:

Received 24 September 2019

Received in revised form

1 May 2020

Accepted 2 May 2020

Available online 5 May 2020

Keywords:

Flame retardants

Great Lakes

Polyethylene passive sampler

Methyl-triclosan

Halogenated anisoles

ABSTRACT

Passive samplers are useful tools for monitoring hydrophobic, persistent, and potentially bio-accumulative contaminants in the environment. In this study, low density polyethylene passive samplers were deployed in urban-influenced and background nearshore freshwaters of northwestern Lake Ontario and analyzed for a broad range of both legacy halogenated organic contaminants (HOCs) and halogenated flame retardants (HFRs). Non-targeted analysis was conducted for screening additional halogenated substances. For most compounds, concentrations were greatest in the industrialized Hamilton Harbour and more generally at sites that have stronger influences of wastewater effluent discharges and stormwater run-off through rivers and creeks. Polychlorinated biphenyls (PCBs) remain the dominant class of HOCs in water, with dissolved-phase concentrations ranging from 10 to 4100 pg/L (Σ PCBs), followed by polybrominated diphenylethers (Σ PBDEs; 14–960 pg/L) and the organochlorine pesticides (OCPs; 22–290 pg/L). Several non-PBDE brominated flame retardants (nBFRs) and chlorinated Decchlorane-related compounds were detected, with hexabromocyclododecanes (Σ HBCDD; sum of 3 diastereoisomers) the most abundant (1.0–21 pg/L). Non-targeted screening of samples by high resolution mass spectrometry using Kendrick mass defect plots for data analysis indicated that several other halogenated compounds were present in waters at relatively high abundances compared to the flame retardants, based on semi-quantitative estimates. These included methyl-triclosan, four halogenated anisoles (2,4,6-tribromoanisole, dimethyl-trichloroanisole, pentachloroanisole, and pentachloroanisole), and pentachloro-aniline. Dissolved-phase methyl-triclosan was estimated to contribute up to approximately 40% of the summed target HOC concentrations. Polyethylene passive samplers provided an excellent medium for both non-targeted screening of HOCs not currently included in monitoring programs and tracking brominated and chlorinated chemicals slated for reductions in uses and emissions through international (Stockholm Convention) and binational (Great Lakes) agreements.

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1. Introduction

Halogenated organic chemicals (HOCs) have been produced in

large quantities and used widely in industry, agriculture, commercial applications and consumer products since the first half of the 20th century. Many HOCs, such as dichloro-diphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCBs), are persistent when released to the environment with half-lives of many decades (Sun et al., 2018; Venier et al., 2016). Contamination from past uses was due in part to discharges and storage of waste

[☆] This paper has been recommended for acceptance by Charles Wong.

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from manufacturing processes, resulting in localized contaminated sites that remain subject to remedial activities. The widespread use of HOCs in infrastructure, such as PCBs in sealants (Robson et al., 2010) and transformers (Diamond et al., 2010) in the region, and flame retardants like hexabromocyclododecane (HBCDD) in foam insulation (Covaci et al., 2006) and polybrominated diphenylethers (PBDEs) in electronics, textiles, etc. (Alaee et al., 2003), has led to contamination associated with non-point sources across the built urban environment (Alaee et al., 2003; Harner et al., 2006; Melymuk et al., 2013). Due to the persistence, ability to bioaccumulate, potential for transport to remote regions, and known toxicity of many HOCs, the production and use of PCBs, PBDEs, organochlorine pesticides (OCPs), and several other HOCs are subject to use and emission reduction initiatives through the binational Great Lakes Water Quality Agreement (Barbiero et al., 2018) in the North American Great Lakes region, and internationally through the Stockholm Convention on Persistent Organic Pollutants (POPs) (United Nations Environmental Programme).

Extensive environmental monitoring of POPs and other HOCs has been conducted to understand their sources and environmental fate, and to evaluate the effectiveness of source control practices and remediation. In the North American Great Lakes, this has included binational efforts to monitor contaminant concentrations in sportfish and foodwebs, sediment, air, and water (Gewurtz et al., 2011; Hillery et al., 1998; Li et al., 2009). In recent years, passive samplers have been used as tools for monitoring of contaminants in air and water at the global scale (Pozo et al., 2006), as well as in the Great Lakes region (Gouin et al., 2005; Helm et al., 2012; Khairy et al., 2015). Polymer membrane passive samplers use, for example, polyethylene (PE) or polydimethylsiloxane as sampling media to measure the dissolved and bioavailable fractions of hydrophobic organic chemicals in water given the high partition coefficients of HOCs between water and the membranes. Deployed for weeks to months, passive samplers provide estimates of time-weighted average concentrations and a better representation of contamination conditions, particularly at sites subject to the influence of episodic events such as watershed inputs, discharges, and changes in currents. Passive samplers are considered cost-effective monitoring options, as they 1) provide lower detection limits by sampling greater volumes than typical grab and composite active samples; 2) are less susceptible to sample contamination due to reduced sample handling and processing; and 3) can provide greater spatial coverage and be archived for temporal and retrospective analyses (Lohmann et al., 2012; Petty et al., 2004).

The HOCs that are currently a priority for environmental monitoring, assessment, and regulation only represent a small fraction of the total number of organic chemicals produced and used daily in industry and everyday life (Hollender et al., 2017). Efforts to assess other chemicals in commerce that have persistent, bioaccumulative properties have noted that there are several hundred other compounds to consider, with a high percentage (98%) being halogenated (Howard and Muir, 2010; Scheringer et al., 2012). In addition to the chemicals currently subject to monitoring and assessment, there is a need to more broadly assess chemical contamination beyond the current known priority compounds (Howard and Muir, 2010). Recent developments in analytical mass spectrometry have made it possible to more efficiently conduct non-targeted screening for contaminants previously not known to be present in the environment (Hollender et al., 2017), including HOCs that may have characteristics similar to existing chemicals with known environmental hazards. Some of these advanced screening techniques have been applied to sediment (Pena-Abaurrea et al., 2014; Peng et al., 2015) and fish (Fernando et al., 2018; Jobst et al., 2013) in the Great Lakes region, and it has been recommended that non-targeted analysis techniques be

incorporated into monitoring strategies in the region (Crimmins et al., 2018). Since polymeric passive samplers accumulate bioavailable hydrophobic contaminants from water, they can serve as effective media for suspect and non-target screening (Allan et al., 2013; Rosenfelder et al., 2010), in addition to the advantages listed above.

In this study, polyethylene passive samplers were deployed in nearshore waters of northwestern Lake Ontario, Canada, part of the North American Great Lakes. The region is highly urbanized with commercial and industrial activities in adjacent watersheds containing a population of approximately 6 million people, and 4 of Canada's 10 largest cities. This nearshore area is influenced by urban runoff and receives municipal wastewater effluent of approximately half the population of the province of Ontario. Thus, it is an important region to assess the continued influence and inputs from land-based sources of legacy and current-use POPs (Melymuk et al., 2014). The objectives of this preliminary study were 1) to determine the bioavailable concentrations of HOCs in the urban-impacted nearshore waters of northwestern Lake Ontario, including legacy contaminants (PCBs, OCPs and PBDEs) and more recent HOC contaminants (e.g. non-PBDE brominated flame retardants (nBFRs), dechlorane compounds), and 2) to apply non-targeted screening using high resolution mass spectrometry (HRMS) to assess whether there are other HOCs of potential environmental concern.

2. Methods

2.1. Sampling and sample preparation

Passive samplers ($n = 3$) consisting of low-density polyethylene (PE) sheets ($5 \times 60 \text{ cm} \times 89 \mu\text{m}$ thickness; FilmGard, Tyco/Covallence Plastics; hereafter referred to as polyethylene devices or PEDs) were deployed at 10 sites in nearshore waters of northwest Lake Ontario (Fig. 1; site influences and details listed in Table S1 in Suppl. data) for one month from June to July 2010. Prior to deployment, PEDs were cleaned by soaking for 2–5 h in acetone, followed by two consecutive 24 h soaks in hexane, then short 1–2 h soaks in acetone and then methanol. The clean PEDs were infused with the performance reference compounds (PRCs; non-Aroclor PCBs not found in the environment; PCB-14, 30, 62, 104, 127, 166, 184, 197; UltraScientific, Inc.) following established protocols (Booij et al., 2002). Briefly, 11 PEDs were placed in each of four solvent-rinsed 1 L Erlenmeyer flasks containing 800 mL of 4:1 methanol:water and the PRC solution, and then equilibrated for 10 days by mixing on an oscillating table, covered, at ambient temperature. After equilibrating, PEDs were wiped with Kimwipes to remove residual solvent and water and placed into clean labeled glass jars and stored at -20°C until deployment. On station, the 3 PEDs were mounted within a perforated metal cage and secured beneath a buoy at about 4 m below the water's surface. PEDs from each batch were retained to determine initial PRC concentrations, while PED blanks were exposed to air at selected stations in the same manner as for deployed samplers.

Upon retrieval, PEDs were removed from their mounts, rolled, and placed into glass jars and stored frozen (-20°C) until analysis. Prior to extraction, PEDs were rinsed and wiped clean using a small amount of milli-Q water and Kimwipes, then placed into a clean 40 mL glass vial with Teflon-lined cap. Surrogate standards, 1,3,5-tribromobenzene (PCB/OCP; Muscalu et al., 2011) and mass-labeled halogenated flame retardants (listed in Megson et al. (2016); Tomy et al. (2005)), were spiked onto the surface of the PED, the standards allowed to sorb to the PED, then the vials were filled with 25 mL of hexane, shaken for 5 min to ensure solvent mixing across all surfaces and extracted via soaking overnight

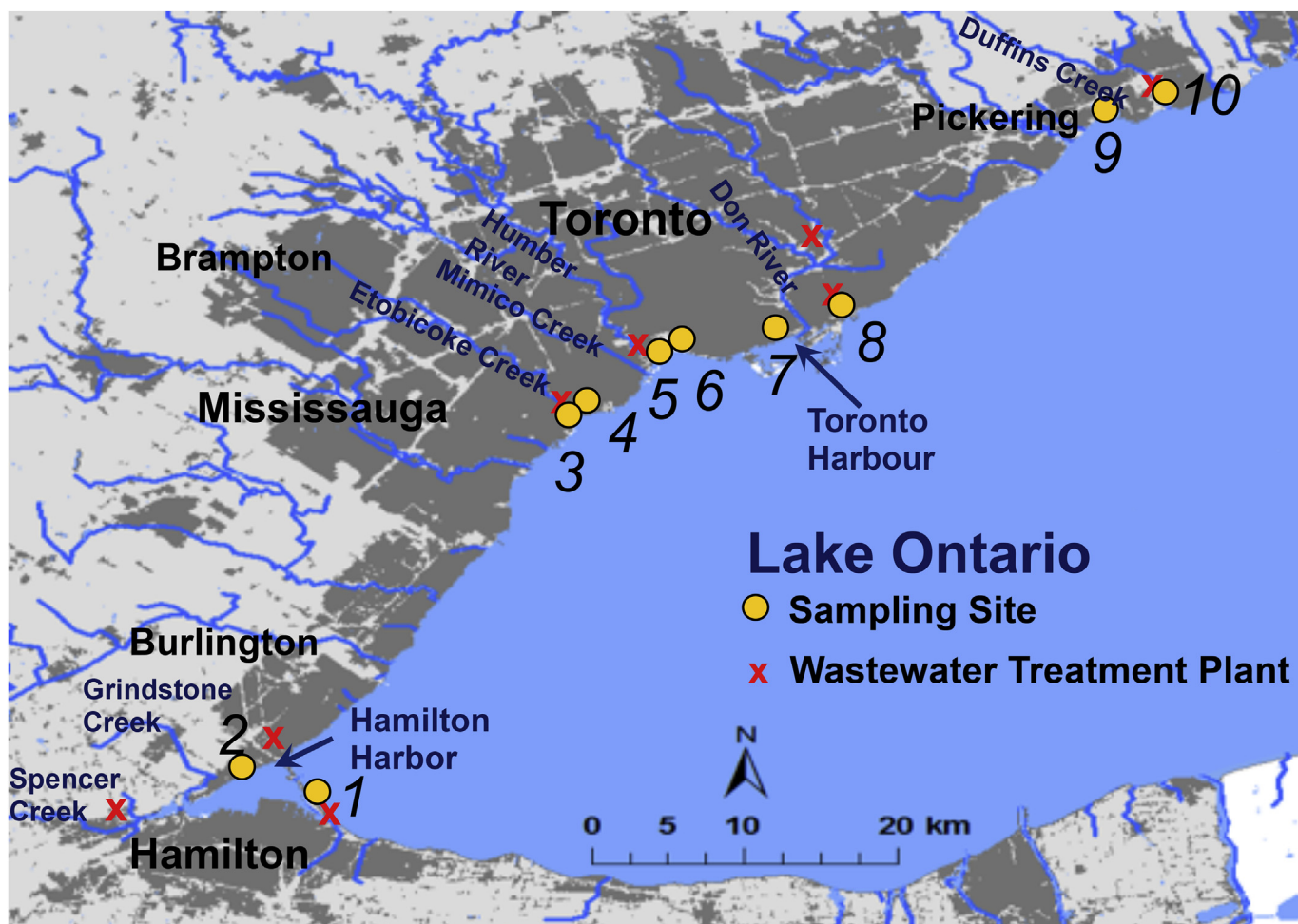


Fig. 1. Map indicating the ten nearshore Lake Ontario sites where polyethylene passive samplers were deployed, and nearby wastewater treatment plants.

(minimum 16 h). The solvent was transferred to a clean 60 mL vial, and then PEDs were re-extracted with another 25 mL of hexane overnight. The combined extracts were then reduced in volume to approximately 2 mL using a Rapidvap Vortex Evaporator (Labconco, Kansas City, MO, USA), passed through a 1 g Na_2SO_4 solid phase extraction cartridge (SPE, Bond Elute, Agilent, USA), further reduced in volume to 1 mL or 200 μL , and transferred to GC vial and spiked with injection standards. Extraction test results are provided in [Tables S2 and S3](#) of Supplementary Materials. All solvents used for PED preparation and extraction were Distilled in Glass or HPLC grade (Fisher Scientific, Ottawa, ON, Canada). Two replicate PEDs from each site were subjected to PCB and OCP analysis, including PRC determination, while the remaining PED from each site was analyzed for flame retardants and subjected to non-target analysis.

2.2. Targeted HOC analysis

The analytes for targeted HOC analysis included legacy PCBs and OC pesticides, brominated and chlorinated flame retardants including PBDEs, HBCDD, dechlorane compounds, and other non-BDE flame retardants (nBFRs). PCBs and OC pesticides were analyzed via comprehensive two-dimensional gas chromatography (GCxGC) coupled with micro-electron capture detector (μECD) (LECO Corporation, Benton Harbour, MI, USA). The stationary phases, instrument conditions, and quantitation details are given in ([Muscalu et al., 2011](#)). The method detection limits of 0.1–1 ng/g of

matrix analyzed were determined by statistical analysis repeated replicates spikes of the lowest calibration standard, and a method quantitation limit of 1 ng/sample per PCB congener and OCP compound was set based on the lowest quantitation standard since quadratic fits were applied to quantitation ([Muscalu et al., 2011](#)) ([Table S4 in Supplementary data](#)).

PBDEs, nBFRs and Dechloranes analyses were carried out using a Waters AutoSpec (Milford, MA, USA) HRMS equipped with an Agilent (Wilmington, DE, USA) 6890 gas chromatograph (GC). Chromatographic separation was carried out using a 15 m DB-5HT column (0.25 mm i.d., 0.10 μm film thickness, J&W Scientific). The HRMS system was operated in electron ionisation mode at a resolving power of >10,000 (10% valley), and additional details have been published previously ([Megson et al., 2016](#); [Shen et al., 2011](#)). HBCDD analyses were conducted using a Sciex 4000 QTrap mass spectrometer (AB Sciex LP, Concord, ON, Canada) coupled to an Agilent 1200 LC system in tandem MS/MS mode as per [Tomy et al. \(2005\)](#). Quantitation of flame retardants was via isotope dilution using mass-labeled surrogate and injection standards ([Megson et al., 2016](#); [Shen et al., 2011](#); [Tomy et al., 2005](#)). Instrument detection limits for PBDEs and nBFRs, determined based on serial dilutions of standards and a signal to noise ratio of 10, ranged from 2.2 (BDE15) to 2100 (BDE209) pg/sampler for PBDEs, and 10 pg/sampler for TBP-DBPE to 8000 pg/sampler for DBDPE ([Megson et al., 2016](#)). Instrument detection limits for Dechlorane-related compounds were 10 pg/sampler based on a 5:1 signal to noise

ratio (Shen et al., 2011), and 16–18 pg/sampler for syn/anti-Dechlorane Plus based on a 10:1 signal to noise ratio (Megson et al., 2016). Instrument limits for HBCDD isomers were based on a 3:1 signal:noise ratio, based on the lowest quantitation standard, ranging 3.8 pg/sampler for α -HBCDD to 4.3 pg/sampler for γ -HBCDD. Table S5 lists the detection limits and estimated method detection limits on a water concentration basis.

2.3. Non-targeted PED screening

Non-targeted screening was carried out using a GCxGC system comprised of an Agilent 6890 gas chromatograph coupled with a Waters GCT Premier time-of-flight mass spectrometer (ToFMS). The GCxGC system consisted of a single jet loop modulator (Zoex Corporation, Houston, USA), an Rtx-5MS first dimension column (30 m \times 0.25 mm ID \times 0.25 μ m) and an Rtx-50 second dimension column (2.3 m \times 0.18 mm ID \times 0.2 μ m; Restek Corporation, Bellefonte, USA) operating with a 4s modulation time. All samples were analyzed in full scan mode (150–800 m/z) using electron impact (EI) ionisation at an approximate mass resolution of 7000 at full width at half maximum. The mass spectral data were filtered and interpreted using the Kendrick mass defect plot, which was pioneered by Kendrick (1963) and later modified by using + Cl(Br)/-H for screening halogenated organic compounds (Jobst et al., 2013; Taguchi et al., 2010). Kendrick mass defect plots isolate halogenated compounds within a given region on the mass defect plot. The number of Br and Cl atoms in a molecule were determined by isotope distributions, and elemental compositions of peak clusters were assigned using the software Elemental Composition Calculator (Varian Inc. version 2.1) and confirmed with theoretical isotope distributions. Specific compounds associated with the elemental compositions were proposed for peaks that were detected (not present in the two blanks) in a majority of sample extracts (>50%). The tentative assignments for the six most abundant peaks, determined by manual inspection, are reported here, with 5 compounds verified by comparing their retention times and MS characteristics with analytical standards. Semi-quantitative concentrations of these compounds were derived based on the response factors of the confirmed chemicals in solution relative to that of PCB28, which elutes centrally among the identified compounds, and adjusted using the ^{13}C -BDE28 surrogate within the extracts.

2.4. QA/QC

For PCBs and OCPs, peaks were integrated after adjusting for markers using retention time references (Muscalu et al., 2011), and amounts reported that exceeded the 1 ng/sample method quantitation limit (MQL). Field blanks ($n = 4$) and preparation/PRC reference blanks ($n = 7$) did not contain PCBs or OCPs present at levels above the MQL, so no subtraction was undertaken. For PBDEs, Dechloranes, and nBFRs, chromatographic peaks in samples were accepted when the signal-to-noise ratios were greater than 3:1, the peak retention time was within 0.1 min of the appropriate standards, and ion ratios were within 15% of the theoretical value for the target analytes. Measured amounts in samples were reported if they exceeded the reported instrument detection limits (IDLs; based on 5:1–10:1 signal to noise ratios) for PBDEs, Dechloranes and nBFRs. One field blank and one lab preparation blank were included in the analyses but did not have PBDEs, Dechloranes, or nBFRs present above IDLs. HBCDD isomers were present in blanks above IDL values at 21–34 pg/sample maximum, and amounts present above IDLs (3:1 signal to noise) were blank subtracted using the maximum value prior to concentration calculations. Method quantitation limits, instrument detection limits, water

concentration-based method detection limits, and blank values are listed in Tables S4 and S5 in the Suppl. data.

Extraction efficiency was evaluated at the beginning of the project by infusing native target analytes (PCBs and PBDEs) into PEDs in the same manner as for PRCs. After storing frozen, spiked PEDs were extracted using the protocol described above, followed by a subsequent overnight soak in dichloromethane (DCM) to demonstrate exhaustive extraction. More than 95% of PCBs and 99% of PBDEs were extracted in two hexane soaks demonstrating high extraction efficiencies, and this was confirmed in a re-extraction of selected field samples with no target analytes detectable in re-extracted PEDs. PCB congeners and OCP compounds were not recovery-corrected, but were only reported if surrogate recoveries (of 1,3,5-tribromobenzene) were within the method acceptance criteria of $\pm 50\%$ target value (Muscalu et al., 2011). PBDEs, Dechloranes, HBCDD, and nBFRs were corrected for recoveries and responses using the mass-labeled surrogates when reporting amounts (Megson et al., 2016; Tomy et al., 2005).

Replicate analyses were conducted on samplers via PCB/OCP analysis to assess variability and consistency within the deployment cages, particularly for the PCB PRCs for calculating site-specific sampling rates. Analysis of replicate pre-deployment PEDs for time = 0 PRC values demonstrated a high degree of consistency among preparation batches with relative standard deviations ranging from 2.8% to 7.3% for PCBs-14, 30, 62, 127, 166, 184, and 197, but an RSD of 13.2% was observed for PCB-104. These RSDs were within the range of within-run and between-run RSDs for the analytical method for both standard injections and spike matrix recoveries. The PRCs in field blanks were not different from pre-deployment PRCs, and the RSDs were in the same range. Replicate PRC determinations also agreed very well among PEDs within a site. Median percent differences ranged from 0.6% to 7.1% for 7 PRCs across 9 of the 10 sites. One site had a higher median of 11.2% difference. PCB-14 could not be included as a PRC due to interferences in the environment-exposed samplers. The median percent differences between replicates for detected analytes within a site ranged from 4.8% to 15.4% for PCB congeners and 1.4%–11.9% OCP compounds, demonstrating very good agreement among the PEDs within a deployment cage.

2.5. Determination of sampling rates and aqueous concentrations

Freely dissolved concentrations of the target analytes were calculated using the retained fraction (f) from the dissolution of the PRCs (PCB #30, 62, 104, 127, 166, 184 and 197) from deployed PEDs. Nonlinear least squares (NLS) estimation was used to solve for the site specific sampling rate, R_S , and site specific coefficient, β_{MW} , based on the approach of, and using spreadsheet calculations provided by, Booij and Smedes (2010) (Excel Solver add-in) with equations (1) and (2) below.

$$f = \exp[-(R_S \cdot t)/(K_{PEW} \cdot m_{PE})] \quad (1)$$

$$R_S = \beta_{MW} \cdot MW^{-0.35} \quad (2)$$

The time PEDs were deployed is t (days), R_S is in L/day, K_{PEW} (L/kg) is the sampler-water partition coefficient, m_{PE} (kg) is the mass of a PED, and MW is the molecular weight of the particular compound. K_{PEW} values were derived from Eq. (3) that was determined from values listed in Lohmann (2012) for PCBs, PBDEs, and PAHs (non-polar compounds with no functional groups):

$$\log K_{PEW} = 1.041 \cdot \log K_{OW} - 0.392 \quad (3)$$

where K_{OW} is the octanol-water equilibrium partition coefficient of

a chemical (listed in Tables S6–S9). After determining the site parameter β_{MW} using the PRC compounds, the sampling rates for individual compounds were adjusted using equation (2), and then the dissolved water concentration, C_W , was calculated for each compound based on the amount (N) of an analyte accumulated in the PED (Booij & Smedes, 2010) using equation (4):

$$C_W = N / K_{PEW} \cdot m_{PE} \left[1 - \exp \left[(-\beta_{MW} \cdot t) / (K_{PEW} \cdot MW^{0.35} \cdot m_{PE}) \right] \right] \quad (4)$$

The average fraction of PRCs retained in deployed PEDs varied from 0.23 to 0.47 for PCB-30, 0.50–0.98 for PCB-104, and 0.85–1.28 for PCB-184 as examples. The average estimated percent equilibrium obtained by compound are listed in Tables S4–5. Given the 1-month deployment duration, most compounds were in the kinetic uptake phase. The site specific β_{MW} values calculated from the PRCs via NLS ranged from 70.6 to 170 (Table S6), with relative standard error of β_{MW} calculated as per Booij & Smedes (2010), ranging 5–48%. The sites with the greatest variability were those most influenced by wastewater and runoff (sites 1, 7, and 8), likely due to interferences impacted PRCs. Calculated sampling rates varied by chemical across the ten sites ranged from 5.5 L/d for BDE-209 to 25.6 L/d for PCBs 4, 6, and 8 (Tables S6–S9; Suppl. data). For nontarget screening results, the semi-quantitatively estimated amounts of chemical per sample were converted to water concentrations using the site-specific β_{MW} using log K_{PEW} values estimated according to Eq. (3) from log K_{OW} values listed in Table 1.

There are uncertainties to consider in using passive samplers for concentration estimates, including variability in chemical analyses and in sampling rate determination, the latter due to the choice of model used to estimate R_S and the chosen values of K_{PEW} (Booij et al., 2016). Although the use of log K_{OW} –log K_{PEW} relationships are well established (e.g. (Booij et al., 2014)), there is likely to be more uncertainty in the K_{PEW} for the nBFRs and OCPs that have additional functional groups with some polarity (Lohmann, 2012). As well, the K_{OW} for highly hydrophobic compounds (e.g. Dechloranes, BDE-209, DBDPE) are greater than the validated range in log K_{OW} –log K_{PEW} relationships, resulting in extrapolation. However, error in the K_{PEW} is more impactful for PRCs in calculating R_S than for individual target compounds (Booij and Smedes, 2010). It should be noted that differences in sources of log K_{OW} can create significant uncertainty. For example, log K_{OW} for α -, β -, and γ -

HBCDD used in calculations (5.07, 5.12 and 5.47, respectively) (Hayward et al., 2006) are more than two orders of magnitude lower than those calculated and listed in Bergman et al. (2012) (7.92 for each compound). Concentration estimates of approximately a factor two lower result when the latter value is used.

3. Results and discussion

3.1. General trends and legacy POPs

The PED-derived, freely dissolved concentrations of the HOCs in water are summarized in Fig. 2 and listed in Tables S10–13 in Supplement data. Total concentrations of HOCs (Σ HOCs) ranged from 43 pg/L at site 9 to 5400 pg/L at site 1. After site 1, the next highest Σ HOC concentrations were at site 2 (850 pg/L), site 7 (590 pg/L), site 5 (270 pg/L), and site 10 (130 pg/L). Site 1 in Hamilton Harbour, at the west end of Lake Ontario, was directly influenced by wastewater effluent and urban run-off through Red Hill Creek, and industrial activities adjacent to the deployment location. Site 2 is in the center of Hamilton Harbour further removed from direct influences. Similarly, sites 5, 7, and 10 are in closer proximity to wastewater effluent discharges and run-off from urbanized watersheds. The Σ PCBs (10–4100 pg/L), Σ OCPs (22–290), and Σ PBDEs (14–960 pg/L) were the three most abundant HOC classes (Fig. 2a), and all the classes of compounds were the highest in concentrations at site 1, except for the Dechloranes (the highest concentrations at site 7) (Fig. 2b).

Some variation in distributions across the sampling sites was apparent among the compound classes. The Σ PCB and Σ PBDE concentrations had coefficients of variance (CV) of 2.4 and 2.3, respectively, across the 10 sites, while the CVs for Σ nBFRs (1.3), Σ DECs (1.2) and Σ OCPs (1.1) were lower by a factor of 2. Statistically significant correlations were observed between Σ PCBs and Σ OCPs, Σ PBDEs and Σ nBFRs, as well as Σ PBDEs and Σ nBFRs (Spearman correlation coefficient >0.75) (Fig. 3). Σ OCPs were moderately but significantly correlated with the other compound classes (Spearman >0.5 but <0.75), including the Σ DECs, which were not correlated with the PCBs or other flame retardants. Correlations among the compound classes are driven by the ranking of concentrations at sites 1, 2, 5, 7, and 10, illustrating the ongoing contributions of wastewater effluent and urban runoff for both legacy contaminants (OCPs and PCBs) and the more recently regulated

Table 1
Halogenated organic compounds identified in polyethylene passive samplers by non-targeted screening with high-resolution mass spectrometry.

Mass Detected (Da)	Elemental Composition	log K_{OW} ^a	log K_{PEW} ^b	Theoretical Mass (Da)	Mass Error (Da)	Relative Retention Time ^c		Compound	Semi-quantitative Concentrations at Sampling Sites (pg/L) ^e									
						Sample	Standard		1	2	3	4	5	6	7	8	9	10
279.861	C7H3OCI5	5.3	5.1	279.859	0.002	0.87	0.86	Pentachloroanisole	421	57	8.0	2.6	18	2.7	22	0.6	1.2	13
295.841	C7H3SCI5	5.9	5.8	295.837	0.004	1.07	1.06	Pentachlorothioanisole	230	34	7.4	3.2	18	2.7	17	0.2	0.4	4.5
301.968	C13H9O2Cl3	5.2	5.0	301.967	0.001	1.22	1.23	Methyl-triclosan	2166	122	28	17	32	3.1	61	1.4	2.4	38
343.783	C7H5OBr3	4.5	4.3	343.787	-0.004	0.78	0.77	2,4,6-tribromoanisole	1004	156	3.0	0.4	36	1.2	27	0.3	0.6	15
264.864	C6H2NCI5	4.8	4.6	264.86	0.004	0.98	0.98	Pentachloroaniline	188	34	2.4	1.5	15	1.3	3.1	0.02	0.5	2.4
237.974	C9H9OCI3	5.1	4.9	237.972	0.002	0.76	na	Dimethyl-trichloroanisole ^d	949	56	8.0	0.4	12	0.4	24	0.4	0.5	22

a. EPISuite KOWWin1.68

b. Based on Equation 3

c. Retention time relative to 2,4,4'-trichlorobiphenyl (PCB-28)

d. Inferred from elemental composition without confirmation by comparing with standards

e. Concentrations determined using the semi-quantitative approach described in the method section. The red-yellow-blue color scale represents concentrations ranging from <=1 to 10 to >=1000 pg/L

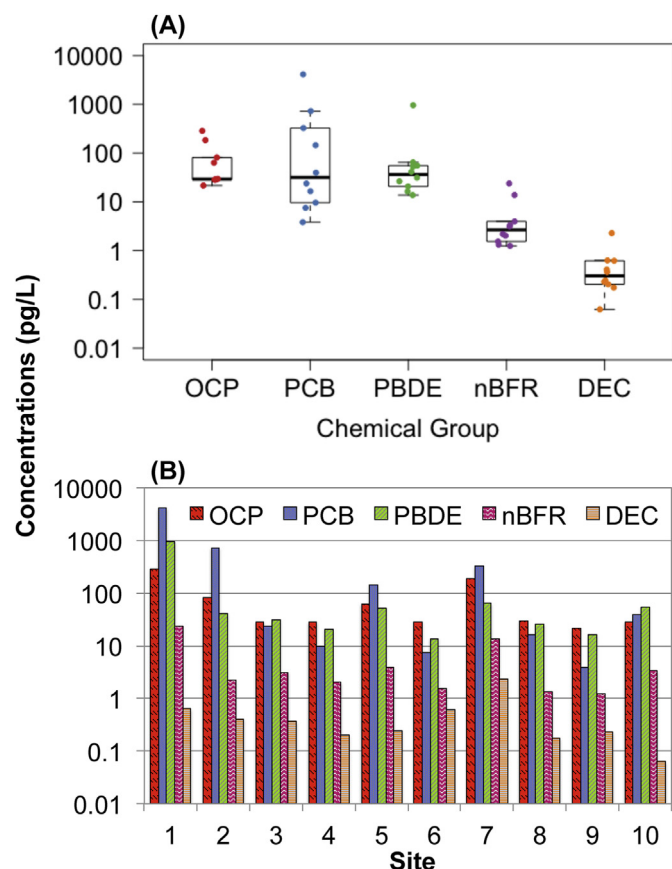


Fig. 2. Summed concentrations of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCP), polybrominated diphenyl ethers (PBDE), non-BDE brominated flame retardants (nBFR) and Dechlorane compounds (DEC) A) summarized across all sites, and B) at the ten sampling sites.

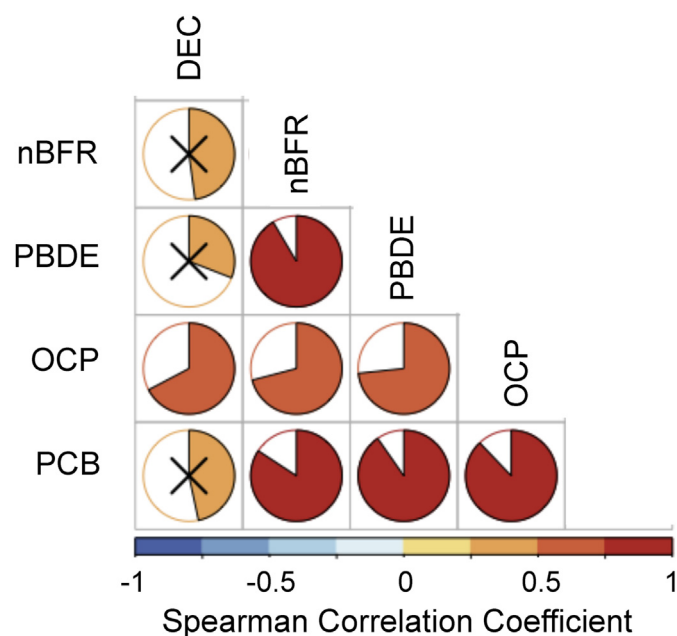


Fig. 3. Correlations between summed concentrations of organochlorine pesticides (OCP), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE), non-BDE brominated flame retardants (nBFR), and dechloranes (DEC). Symbol "X" indicates the correlation is not significant at 95% confidence interval.

(PBDEs and HBCDD). This is consistent with reports of urban loadings of POPs to nearshore waters in the region (Melymuk et al., 2014) and greater POPs concentrations near other urban centers in the Great Lakes region (Liu et al., 2016; McDonough et al., 2016; Melymuk et al., 2014).

PCBs and OCPs represent legacy contamination in the region, with PCBs remaining an important contaminant class in Lake Ontario as the primary drivers of sportfish consumption advisories (Bhavsar et al., 2007). A steep gradient was found for Σ PCBs between sites 1 and 2 (4100 and 730 pg/L, respectively) with strong industrial, wastewater, and runoff influences, across the more moderately-impacted sites 3, 5, 7, 8 and 10 (17–330 pg/L) influenced by riverine and wastewater, to the remaining sites (4, 6, 9) more reflective of lake background (4–10 pg/L). The concentrations at background sites and other locations outside Hamilton Harbour were comparable to the 6–105 pg/L found using PEDs at central Lake Ontario and shore-based locations on the US side of the lake (Liu et al., 2016). The OCP compounds Dieldrin (14–45 pg/L), p,p'-DDE (3–70 pg/L) and Heptachlor epoxide (4–38 pg/L) were detected at all sites, while p,p'-DDD (<DL-25 pg/L), p,p'-DDT (<DL-13 pg/L), α -Chlordane (<DL-20 pg/L) and γ -Chlordane (<DL-31 pg/L) were detected at 5 or more sites. Concentrations were generally greatest at site 1 followed closely by site 7, but gradients weren't as steep. Similar OCP concentrations were observed using PEDs in waters along the south side of Lake Ontario for the more frequently detected Dieldrin, p,p'-DDE, and Heptachlor epoxide, ranging up to 53, 22, and 2 pg/L, respectively (Khairy et al., 2015). The distribution across the stations reflect historic inputs to the lake. Hexachlorocyclohexane (HCH) isomers, usually among the abundant OCPs in Great Lakes waters (Venier et al., 2014), do not partition as strongly to polyethylene ($\log K_{OW} < 4$; Table S6) and were not detected in this study, nor by Khairy et al. (2015).

The PEDs captured spatial trends and current status of PCB and OCP source inputs. The greater variation for Σ PCBs was driven in part by a high value (site 1) resulting from stormwater and wastewater impacted by known legacy contamination in the Hamilton area. Greater contributions of lower molecular weight (MW) PCBs (diCBs to tetraCBs) compared to higher MW PCBs (Table S10) is indicative of fresh inputs to water from PCB mixtures, relative to the profile accumulated from historical sediment contamination or soils in runoff at site 7 (Fig. S2 in Suppl. data) (Dang et al., 2013). The physical limnology of the area also contributes to the rapid decline to background levels from source areas, as upwelling of colder, cleaner deep waters outside of the harbours is common (Howell et al., 2012) (Fig. S1 in Suppl. data). Longer deployments or PCB analysis with lower detection limits are necessary for more detailed congener-based source apportionment. Sampling within watersheds can better isolate contaminated sites (Benoit et al., 2016) or specific land-uses contributions as was done for air in the region (Melymuk et al., 2013). In contrast, the smaller gradient for Σ OCPs ($CV = 1.1$) across sites compared to Σ PCBs ($CV = 2.4$) suggests a diminished role for riverine runoff and wastewater inputs relative to historical contamination and atmospheric transport/deposition (Hillery et al., 1998). Dieldrin has the lowest CV (0.5) with relatively consistent concentrations across background and impacted sites, as was found in open Lake Ontario and the other Great Lakes (Venier et al., 2014), reflecting former widespread use of Aldrin and Dieldrin in agriculture. However, the other frequently detected pesticides (e.g. p,p'-DDE, p,p'-DDD, Heptachlor epoxide, and Chlordane) had concentrations 3–10 times higher at sites 1 and 7 compared to other sites (Table S10), indicating some runoff and wastewater influences. Chlordane and related compounds were used as termiticides and DDT for mosquito control in urban areas decades ago, contributing to the urban signature, in addition to agricultural uses. The prevalence of p,p'-

DDD and p,p'-DDE over p,p'-DDT indicate an aged, degraded residues. Passive sampling near or in sediment beds, coupled with water and air measurements, e.g. Khairy et al. (2015); Liu et al. (2016) would provide a more detailed understanding of the relative contributions of past and ongoing inputs.

3.2. Distributions and composition of halogenated flame retardants

Concentrations of the halogenated flame retardants, including the PBDEs, non-BDE brominated flame retardants (nBFRs), and dechlorane-related compounds (DECs), are summarized in Fig. 2 as classes, Fig. 4 for individual PBDE congeners and HBCDD isomers, and in Tables S12–13. The Σ PBDEs were the most abundant halogenated flame retardants, ranging from 14 to 960 pg/L, followed by the Σ nBFRs (1–24 pg/L) and then the Σ DECs (0.1–2.3 pg/L) at very low concentrations. Site 1 in Hamilton Harbour (Windemere) had the highest concentrations of PBDEs and nBFRs, followed by Toronto Harbour (site 7) and sites 3, 5, 10 which were influenced by wastewater. Σ DECs were most abundant in Toronto Harbour.

The Σ PBDE concentrations observed at sites outside of Hamilton Harbour ranged 14–65 pg/L (Table S11) and were slightly greater than the 1.1–18 pg/L previously reported for PEDs in nearshore and offshore Lake Ontario (McDonough et al., 2016). The difference may be attributed to the closer proximity of sites to wastewater discharges in our study. Concentrations in active samples from Lake Ontario in 2012 averaged 227 ± 150 pg/L ($n = 4$) (Venier et al., 2014). PEDs from all sites contained congeners BDE-15, -28, -47, -99, -100, -119, -153, and -154, accounting for 62–100% of Σ PBDEs. BDE-47 and -99 were the two most abundant congeners (4.7–530 and 2.7–240 pg/L, respectively), accounting for 29–55% and 16–28% of Σ PBDEs. This congener profile pattern was consistent with those observed for PEDs in water across Lake Ontario and Lake Erie (McDonough et al., 2016), but varied from that measured by Venier et al. (2014) in active samples, with the latter having greater BDE-99 contributions than BDE-47. BDE-209 was not detected in the PEDs, but was detected in active samples (average 16.8 pg/L) (Venier et al. (2014) in Lake Ontario.

Of the nBFRs included in the analyses, only the α -, β -, and γ -HBCDD diastereoisomers and 2,4,6-tribromophenyl allyl ether (TBP-AE) were frequently detected (Table S12). Σ HBCDD concentrations were 21 and 13 pg/L at sites 1 and 7, respectively, and ranged 1–4 pg/L across the other sites. TBP-AE, detected at 9 of 10 sites, ranged from <DL to 0.7 pg/L in Toronto Harbour. In comparison, total HBCDD concentrations averaged 4.2 pg/L in 2 active samples of Lake Ontario waters (Venier et al. (2014). The α -HBCDD diastereoisomer was dominant in Lake Ontario nearshore PEDs,

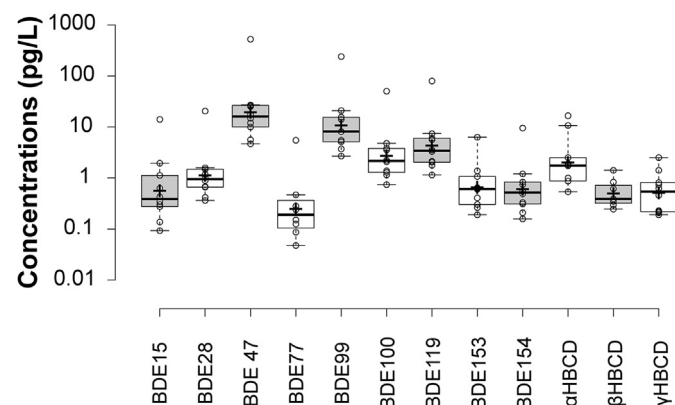


Fig. 4. Concentration ranges and distributions of the major individual PBDE and HBCDD congeners measured in nearshore waters of northwest Lake Ontario.

accounting for 53–90% of Σ HBCDD. Although γ -HBCDD is prevalent in technical mixtures (Marvin et al., 2011), thermal isomerization (Köppen et al., 2008), photo-reaction in the environment (Harrad et al., 2009), and physico-chemical property differences (e.g. log K_{OW}) can all contribute to the prevalence of α -HBCDD. Several nBFRs were detected only at site 1 and one or two other sites (Table S12). BTBPE (1,2-bis(2,4,6-tribromo-phenoxy)ethane) was present at 1.1 pg/L (site 1 only), and TBP-DBPE (2,4,6-tribromophenyl-2,3-dibromopropyl ether) was detected at three sites, at a maximum of 0.33 pg/L at site 1. BTBPE has been detected in Great Lakes waters (averaging 0.30–0.72 pg/L), but it was not detected in Lake Ontario (Venier et al., 2014), nor was it detected in PEDs from across Lake Ontario (McDonough et al., 2016). Concentrations of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), the dominant component of Firemaster 550 and BZ-54 mixtures (Bearr et al., 2010; Ma et al., 2011), ranged from 0.10 to 0.70 at three wastewater-influenced sites (1, 5, and 10). The other main mixture component was not detected (BEH-TEBP; bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate). Venier et al. (2014) similarly found EH-TBB (TBB) in Toronto and Hamilton harbours (0.7–1.6 pg/L), but BEH-TEBP (TBP) was not detected. The legacy brominated flame retardants pentabromoethylbenzene (PBB), hexabromobenzene (HBB), and 2,2',4,4',5,5'-hexabromobiphenyl (PBB153; FireMaster FF1) were only detected in the Hamilton area, and at concentrations <0.25 pg/L. McDonough et al. (2016) detected PBB at similar levels in PEDs from Lake Ontario. Decabromodiphenylethane (DBDPE), 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (DBE-DBCH; or TBECH), or 1,2,5,6-tetrabromocyclooctane (TBCO) were not detected at any sites.

PBDE congener and HBCDD compound profile differences among sites were examined via cluster analysis, with grouping observed based in part on source origins and degree of bromination (Fig. 5). For example, tetraBDEs (47, 77), pentaBDEs (99, 100, 119) and hexaBDEs (153, 154) each grouped together, and α - and γ -HBCDD grouped with the hexaBDEs. The di- and triBDE congeners

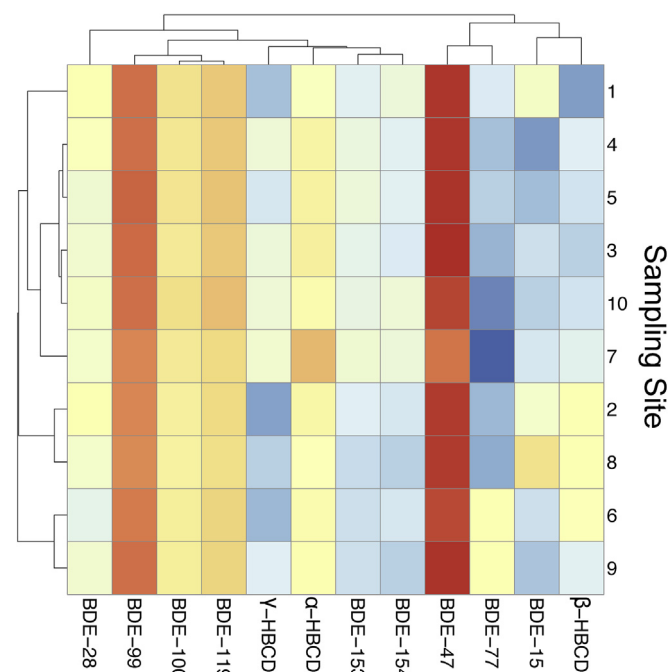


Fig. 5. Hierarchical cluster analysis of composition profiles of polybrominated diphenyl ethers (PBDEs) and hexabromododecanes (HBCDDs). Concentrations were centered with unit variance scaling for each sample before analysis. Both rows and columns are clustered using correlation distance and average linkage.

and β -HBCDD did not specifically group with the other compounds. The sites clustered mostly by apparent influence of wastewater (eg. 3,4,5,10). Site 1 and site 7 clustered separately from other sites given their unique source attributions, likely due to their more immediate proximity to run-off and wastewater influences, compared to the other sites. Sites 6 and 9 were grouped and are both more representative of local background nearshore conditions. Sites 2, 8, and 1 also had varying patterns BDE-15 and β -HBCDD contributing to their separate groupings. Perhaps processes such as debromination contribute to varying degrees (e.g. BDE-15 is a debromination product of BDE-28) (Zhao et al., 2014).

The frequently detected compounds (7–10 sites) comprising Σ DEC (Fig. 2) were mirex, photomirex, and syn- and anti-Dechlorane Plus (DP), but concentrations were very low, generally 0.2 pg/L or less (Table S12). Syn- and anti-DP were generally the more abundant compounds, with concentrations ranging <DL-0.44 and <DL-1.7 pg/L, respectively, with the highest concentrations found in Toronto Harbour. Given their use in building materials (wire, roofing; (Sverko et al., 2007)), greater contamination of Toronto Harbour through combined sewer (stormwater) discharges and runoff via the highly urbanized Don River is plausible. DP was not detected in previously reported PED measurements for Lake Ontario (McDonough et al., 2016), while active sampling found a mean concentration of 13.9 pg/L (Venier et al., 2014). The syn-/anti-DP ratios in PEDs ranged 0.3–1.3, higher than the 1/3 ratio in the technical mixture, consistent with the more rapid loss of anti-DP than syn-DP via photolysis (Sverko et al., 2007). Dechlorane 602 (Dec602) was detected only at the two Hamilton Harbour sites, while Dechlorane 603 and 604 were not detected in the PEDs. Mirex (also called Dechlorane) and its photodegradation product, photomirex, had concentrations ranging <DL-0.19 and <DL-0.20 pg/L, respectively. Their presence in PEDs is likely due to widespread contamination of Lake Ontario from manufacturing upstream in the Niagara region, as with other Dechlorane compounds (Shen et al., 2011).

The relative abundances of various halogenated flame retardants (HFRs) measured in the PEDs reflect their bioavailability for exposure and accumulation in organisms, and demonstrates the influence of wastewater and stormwater runoff pathways for delivering HFRs to the lakes. Compound accumulation profiles were generally consistent with observations in Great Lakes fish. For example, the PBDE profile of PED-based water concentrations were similar to those in Great Lakes fish (Gandhi et al., 2017; Guo et al., 2017). However, BDE-119 was more prevalent in PEDs than in fish, and BDE-209 was not detected in PEDs but was found as a significant contributor to Σ PBDEs in some species (Gandhi et al., 2017). As in the PEDs, Σ HBCDD is the most abundant HFR present in Lake Ontario lake trout after Σ PBDEs (Guo et al., 2017; Ismail et al., 2009; Su et al., 2017). Also similar to the PEDs, other nBFRs were detected at very low concentrations (generally <1 ng/g lipid weight [lw]) in Lake Ontario fish in several studies (Guo et al., 2017; Su et al., 2017; Wu et al., 2019). However, Kurt-Karakus et al. (2019) found TBP-DBPE to be the most abundant nBFR of those analyzed in Lake Ontario lake trout (0.11–8.4 ng/g lw), and that this compound also had a prey-adjusted biomagnification factor similar to those of the PBDEs. In contrast, this compound was only detected in PEDs at site 1. Of the Dechlorane-related compounds, mirex, photomirex, Dec602, and syn- and anti-DP were detected by PEDs, and are also the compounds detected at higher concentration in fish. In lake trout from Lake Ontario, mirex and photomirex were more abundant, followed by Dec602, and then syn-/anti-DP which had concentrations that were two orders of magnitude lower than Dec602 (Shen et al., 2011). Dec603 and Dec604 were very low, if detected (Shen et al., 2011). While the predicted dissolved-phase concentrations of the Dechlorane-related compounds are similar in

magnitude, the amount profiles of each accumulated within the strips on a mass basis are consistent with lipid-weight adjusted concentration profiles in fish.

PBDEs remain the most abundant flame retardants present and bioavailable in the water column at the highest concentrations. As formerly high production volume chemicals, and classified as persistent, bioaccumulative and toxic compounds, PBDEs and HBCDD are now regulated under national and international programs, and both are Chemicals of Mutual Concern subject to risk management measures under the Canadian and U.S. binational Great Lakes Water Quality Agreement. The PEDs will be effective tools for assessing the effectiveness of bans and subsequent reductions. For example, with HBCDD now excluded from polystyrene insulation boards (Government of Canada), reductions in future sampling may be observed. PEDs also provided for low but detectable concentrations at some sites for several compounds, including EH-TBB, BEH-TEBP, and BTBPE, which are suggested to be metabolized by trout (Guo et al., 2017) and diluted through the food web likely due to metabolism (Kurt-Karakus et al., 2019), thus PEDs may provide better measures of exposure for such compounds. This preliminary study demonstrates that alternative (non-PBDE) flame retardants are present but at much lower abundances, reflecting more limited use and less environmental availability through the water column. Future monitoring with passive sampling for these compounds will require longer deployment periods to enhance detection, or more focus on source pathways (wastewater, rivers) in addition to Great Lakes receiving waters.

3.3. Nontargeted screening for HOCs

Mass spectral data of samples acquired using the HRTof mass spectrometer were compiled and organized using the +Cl/-H Kendrick mass defect (KMD) plot (Jobst et al., 2013; Taguchi et al., 2010). Fig. 6a depicts the KMD plot for the PED extract for site 1. HOCs primarily distribute in the region with KMD between 0.1 and 0.35 which are distinguished from other groups such as silicone-containing compounds and hydrocarbons from GC column bleed and sample matrix, and fluorine-containing compounds used for the lock mass. On the +Cl/-H KMD plot, the homologous series of chemicals such as PCBs and PBDEs distribute as horizontal clusters.

Along with the legacy halogenated compounds included for targeted analyses, other individual and homologous series of HOCs with relatively higher intensities were found which have elemental compositions of $C_7H_{8-n}OCl_n$, $C_7H_{8-n}SCl_n$, $C_{13}H_{12-n}O_2Cl_n$ ($n = 3-5$), $C_7H_3OBr_5$, $C_6H_2NCl_5$. We infer that these compounds are chlorinated anisoles and thioanisoles, methyl triclosan, brominated anisoles and chlorinated aniline, based on the likely structures from the elemental of the postulated identities (mass errors <0.005 Da; Table 1). The identities of pentachloroanisole, pentachlorothioanisole, 2,4,6-tribromoanisole, pentachloroaniline and methyl-triclosan were subsequently confirmed by analyzing solutions made from neat standards and comparing the mass spectral characteristics and chromatographic retention times of the suspect peak(s) with those of the neat compounds.

Dissolved-phase water concentrations were estimated for the six identified HOCs based on semi-quantitated amounts in the extracts, estimated log K_{OW} (EPIsuite KOWWin1.68, US Environmental Protection Agency, 2017), and using equations (3) and (4) with the site specific β_{MW} values (Table 1). Methyl-triclosan exhibited the highest estimated concentrations (1.4–2170 pg/L), followed by 2,4,6-tribromoanisole (<1–1000 pg/L) and dimethyl-trichloroanisole (<1–950 pg/L). As was the case for legacy compounds and several of the flame retardants, sites 1 and 2 tended to have higher concentrations, followed by sites influenced by wastewater and stormwater discharges (3, 5, 7, 10) and then

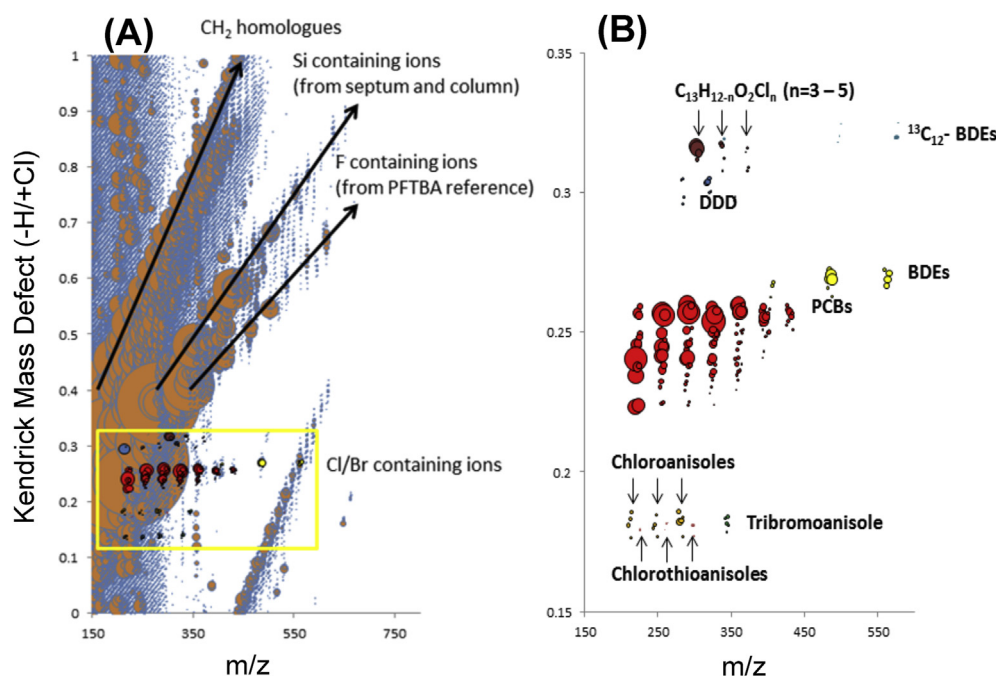


Fig. 6. Kendrick mass defect (+Cl/-H) plot showing peaks from mass spectra acquired from the high-resolution time of flight mass spectrometer. Halogenated compounds primarily distribute in the region with Kendrick mass defect (+Cl/-H) between 0.1 and 0.35 (yellow square in panel a and in panel b). The sizes of dots on the plot represent their relative intensities. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

background sites. This suggests that wastewater and/or urban stormwater are important pathways to the lake for the 6 identified compounds as well. The identified compounds were statistically correlated with Σ PCBs, Σ PBDEs and Σ nBFRs (Spearman coefficient >0.75 ; $p < 0.5$) and moderately correlated with Σ OCPs, but not Σ DECs (Table S14). A concentration of 100 pg/L for methyl-triclosan has been measured in Lake Ontario (Andresen et al., 2007), consistent with estimated PED estimates. The observed spatial patterns are also consistent with the knowledge that methyl-triclosan can be formed from triclosan during wastewater treatment (Lozano et al., 2013). We are not aware of recent measurements of the remaining 5 compounds in the Great Lakes region. Pentachloroanisole, a metabolite of pentachlorophenol, was measured in Great Lakes fish in the 1980s, with a median of 29 ng/g lw concentration at sites around Lake Ontario (Jaffe and Hites, 1986), and low (3–9 ng/g lw) concentrations in Siskiwit Lake fish (Isle Royale, Lake Superior) (Swackhamer and Hites, 1988). Fish collected from Lake Ontario did not contain 2,4,6-tribromoanisole, except for common carp from one tributary which had mean concentrations of 600 ng/g lipid weight (Jaffe and Hites, 1986).

Our results support the use of polymer membrane passive samplers for screening and prioritization exercises as part of monitoring programs. Our initial results for HOCs indicate that there are additional individual compounds present at estimated concentrations that are on the order of Σ PCBs and Σ PBDEs, and greater than other nBFRs. This suggests there is merit in having a better understanding of their environmental occurrence, and whether their presence is a legacy issue or the result of ongoing use and emissions. Methyl-triclosan concentrations were relatively higher near WWTP discharges, and are estimated in this study to comprise up to approximately 40% of the summed targeted HOC concentrations. Given their widespread use in consumer products, it may serve as a tracer for wastewater inputs. However, while methyl-triclosan is present in WWTP effluents, concentrations are generally low (Lindström et al., 2002; McAvoy et al., 2002). Methyl-

triclosan can also be formed water and sediment (Huang et al., 2014), and is now subject to regulation (Halden et al., 2017; Hogue, 2018), which would impact its use as a tracer. Methyl triclosan is also much less susceptible to environmental degradation than triclosan (Lindström et al., 2002) and is present in fish at concentrations up to about 90 times greater than triclosan (Boehmer et al., 2004). Pentachloroanisole, along with its parent pentachlorophenol, is listed as a POP under the Stockholm Convention on POPs (Pentachlorophenol and its salts and esters) (United Nations Environmental Programme), and is considered a legacy contaminant from wide use as a wood preservative. Pentachlorothioanisole and pentachloroaniline are known degradation products of the fungicide pentachloronitrobenzene (Montgomery and Crompton, 2017), which was restricted to specific uses in 2009 in Canada, and as of 2015 is no longer registered for use as a pesticide (Pest Management Regulatory Agency, 2014). The compound 2,4,6-tribromoanisole is a metabolite of 2,4,6-tribromophenol, which is a flame retardant and an intermediate in flame retardant production, as well as a degradation product of several other current-use flame retardants (Howard and Muir, 2010). 2,4,6-tribromoanisole is also a natural compound in the marine environment (Bidleman et al., 2014). A similar compound, 1,3,5-tribromo-2-methoxy-4-methylbenzene (also an anisole) was detected and relatively abundant in Lake Ontario lake trout compared to other nBFRs (Kurt-Karakus et al., 2019). Several halogenated methoxyphenols were detected in nontargeted screening of Great Lakes lake trout, with some having considerable abundance compared to PCBs (Fernando et al., 2018). The frequent detection of halogenated anisoles and their abundance in PEDs, the accumulation of similar compounds in fish, and their apparent source pathways through wastewater and stormwater, suggest that further assessment of sources is merited. The PEDs will be useful tools to assess inputs, and to monitor for changes with regulation of triclosan (Halden et al., 2017; Hogue, 2018) and those under the Stockholm Convention (Lohmann et al., 2017).

4. Conclusions

Passive samplers such as polyethylene devices (PEDs) provide a medium for tracking POPs in water. In this study, we have demonstrated their utility for screening activities using non-targeted analysis for compounds that may be present in significant amounts but are not included in monitoring programs. The nearshore waters of northwestern Lake Ontario, which are impacted by stormwater through urban creeks and rivers and wastewater treatment plant effluents from half the population of Ontario, had widespread occurrence of several classes of halogenated organic compounds, including PCBs, PBDEs, OCPs, and several non-PBDE flame retardants. The PEDs accumulated Great Lakes chemicals of concern and POPs listed in the Stockholm Convention, including PBDEs, HBCDD, and PCBs, allowing the tracking of sources and effectiveness of use/emission reduction efforts to the aquatic environment. Correlations were observed among PCBs, PBDEs, and nBFRs, supporting the notion that wastewater and stormwater remain important pathways to the lake for many HOCs. Non-targeted screening of PEDs using high resolution mass spectrometry identified several additional HOCs including methyl-triclosan, 2,4,6-tribromoanisole, trichlorothionanisole, pentachloroanisole, pentachloroaniline, and dimethyl-trichloroanisole. These HOC were estimated to be relatively abundant compared to the target analytes. The non-targeted screening can help prioritize additional analytes for monitoring and risk assessment, and can facilitate assessment of sources and fate of past and in-use chemicals.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Xianming Zhang: Data curation, Validation, Formal analysis, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Matthew Robson:** Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Karl Jobst:** Methodology, Validation, Formal analysis, Investigation. **Miren Pena-Abaurrea:** Methodology, Investigation. **Alina Muscalu:** Methodology, Investigation. **Sri Chaudhuri:** Methodology, Investigation. **Chris Marvin:** Investigation, Resources. **Ian D. Brindle:** Funding acquisition, Investigation. **Eric J. Reiner:** Investigation, Resources. **Paul Helm:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Project administration.

Acknowledgements

We are grateful for the comments from three anonymous reviewers who helped improve the manuscript. We thank Great Lakes Unit field staff aboard the Ministry of the Environment, Conservation and Parks' Great Lakes Guardian for sampler deployment. This research was supported in part by the Province of Ontario with funding to I.D. Brindle under the Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114733>.

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Supplementary Material

Halogenated Organic Contaminants of Concern in Urban-influenced Waters of Lake Ontario, Canada: Passive Sampling with Targeted and Non-targeted Screening

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Table S1: Deployment location and temperature information.

Site	Description	Location Coordinates ^a		Dates		Duration (days, d)	Temperature (°C)	
		Latitude (N)	Longitude (W)	Deploy	Retrieve		Mean	StDev ^b
1	Hamilton Harbour, Windemere Arm (creek, storm and WWTP influence)	43° 16' 06.9"	79° 46' 53.4"	15-Jun	14-Jul	29	22.1	1.5
2	Hamilton Harbour Index (central harbour area reference)	43° 17' 26.2"	79° 50' 10.9"	15-Jun	14-Jul	29	21.2	0.9
3	Lakeview (some WWTP, river influence)	43° 34' 45.7"	79° 31' 17.3"	15-Jun	13-Jul	28	13.2	3.6
4	Etobicoke Creek Index (area reference, possible WWTP, river influence)	43° 34' 28.5"	79° 30' 59.9"	15-Jun	13-Jul	28	13.6	3.6
5	Humber Bay (WWTP, river influence)	43° 37' 40.1"	79° 27' 51.2"	14-Jun	13-Jul	29	12.3	3.6
6	Humber Bay Index (area reference)	43° 37' 20.1"	79° 26' 42.5"	14-Jun	13-Jul	29	11.3	4.3
7	Toronto Harbour Index (stormwater, river, upstream WWTP influence)	43° 37' 55.1"	79° 22' 04.4"	14-Jun	13-Jul	29	15.8	2.1
8	Ashbridges Bay (WWTP influence)	43° 38' 59.7"	79° 18' 29.7"	14-Jun	12-Jul	28	12.8	3.8
9	Pickering Index (area reference)	43° 47' 33.3"	79° 04' 57.0"	14-Jun	12-Jul	28	13.8	3.4
10	Duffins Creek (WWTP, creek influence)	43° 48' 25.3"	79° 02' 20.3"	14-Jun	12-Jul	28	12.9	3.3

a – coordinates in degrees, minutes, seconds (dd mm ss.s); b – standard deviation

Extraction Efficiencies

Extraction efficiencies of non-polar HOCs were verified for this study using multiple extractions. Diffusion-spiked PEDs were prepared as per PRCs loading protocols (Booij et al., 2002) by adding a solution of individual PCB congeners (Table S1) or a solution PBDE congeners (Table S2; RoHS Solution, Cambridge Isotope Laboratories, USA) into 1 L of 80:20 methanol:water. PEDs were mixed with the solutions for approximately 2 weeks, then removed, wiped dry, and subjected to extraction tests using hexane. Extraction 1 was performed as per sample extractions described in the methods section of the manuscript. Extraction 2 consisted of an additional overnight extraction in hexane. Results were expressed as percent of amount remaining in the 2nd extraction relative to the amount obtained in extraction 1.

Table S2. Extraction efficiency test results for PCBs from PEDs using hexane.

PCB Congener	Amounts (ng / PED)						% in 2nd extraction		
	PCB-A	PCB-B	PCB-C	PCB-A2	PCB-B2	PCB-C2	A	B	C
PCB8	13.8	14.5	12.8	<DL	0.93	0.98	<DL	6.4	7.6
PCB15	23.5	26.9	24.3	<DL	1.34	2.16	<DL	5.0	8.9
PCB28	7.18	8.18	7.44	<DL	<DL	<DL	<DL	<DL	<DL
PCB44	4.04	4.28	3.81	<DL	<DL	<DL	<DL	<DL	<DL
PCB52	5.79	6.68	6.07	<DL	<DL	<DL	<DL	<DL	<DL
PCB70	6.55	7.38	6.4	<DL	<DL	<DL	<DL	<DL	<DL
PCB95	3.53	3.88	4.04	<DL	<DL	<DL	<DL	<DL	<DL
PCB104	4.39	5.03	4.34	<DL	<DL	<DL	<DL	<DL	<DL
PCB105	5.67	6.53	6.02	<DL	<DL	<DL	<DL	<DL	<DL
PCB110	2.57	3.24	2.74	<DL	<DL	<DL	<DL	<DL	<DL
PCB138	6.25	7.26	6.35	<DL	<DL	<DL	<DL	<DL	<DL
PCB149	5.66	6.46	5.66	1.04	<DL	<DL	18.4	<DL	<DL
PCB153	25.9	32.4	26.5	<DL	2.18	2.18	<DL	6.7	8.2
PCB174	6.23	7.71	6.6	<DL	<DL	<DL	<DL	<DL	<DL
PCB180	10.9	13.1	11.7	<DL	<DL	1.02	<DL	<DL	8.7
PCB200	9.39	10.2	10.0	<DL	<DL	<DL	<DL	<DL	<DL
PCB203	13.12	14.6	12.8	<DL	1.24	1.24	<DL	8.5	9.7
PCB206	16.13	17.7	15.6	<DL	1.63	1.55	<DL	9.2	10.0
PCB209	20.95	23.3	21.3	<DL	2.33	2.11	<DL	10.0	9.9

Table S3. Extraction efficiency test results for PBDEs from PEDs using hexane.

PBDE Congener	Amounts (ng / PED)				% in 2nd extraction	
	BDE-A	BDE-B	BDE-A2	BDE-B2	A	B
BDE 28	2.69	2.87	0.007	0.006	0.25	0.22
BDE 47	4.11	4.31	0.021	0.032	0.52	0.74
BDE 99	7.33	7.43	0.023	0.055	0.32	0.73
BDE 154	10.4	11.1	0.029	0.032	0.28	0.29
BDE 153	10.7	9.19	0.030	0.026	0.28	0.29
BDE 183	12.5	13.6	0.039	0.047	0.31	0.35
BDE 197	22.1	26.8	0.078	0.084	0.36	0.31
BDE 208	61.2	74.3	0.245	0.282	0.40	0.38
BDE 207	66.9	80.4	0.330	0.313	0.49	0.39
BDE 206	103	127	0.516	0.495	0.50	0.39
BDE 209	412	415	1.821	1.784	0.44	0.43

Table S4: Method quantitation limits (MQL) and blank values for polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs)

PCB ^a	MQL ^b	MQL ^c	Max Blank (n=4)	Average %	Organochlorine Pesticide	MQL ^b	MQL ^c	Max Blank (n=4)	Average %
Congener	pg/sample	pg/L	pg/sample	Equilibrium	Compound	pg/sample	pg/L	pg/sample	Equilibrium
8	1000	6.50	<DL	89.2 ±5.9	o,p-DDT	1000	2.95	<DL	4.23 ±1.28
18	1000	5.03	<DL	76.4 ±8.9	p,p'-DDD	1000	2.98	<DL	12.6 ±3.58
28	1000	3.35	<DL	41.3 ±9.0	p,p'-DDE	1000	2.81	<DL	2.27 ±0.70
31	1000	3.35	<DL	41.3 ±9.0	p,p'-DDT	1000	3.05	<DL	10.6 ±3.07
44	1000	3.32	<DL	34.5 ±8.1	Aldrin	1000	3.01	<DL	6.37 ±1.90
52	1000	3.19	<DL	77.3 ±8.7	Dieldrin	1000	4.50	<DL	58.4 ±10.1
70	1000	2.90	<DL	13.6 ±3.8	Endosulfan 1	1000	13.2	<DL	97.8 ±2.03
95	1000	3.04	<DL	15.2 ±4.3	Endosulfan 2	1000	12.1	<DL	96.9 ±2.57
99	1000	2.93	<DL	8.51 ±2.50	Endos. Sulfate	1000	7.39	<DL	86.1 ±6.90
118	1000	2.86	<DL	3.78 ±1.15	Endrin	1000	5.63	<DL	75.1 ±9.07
138	1000	2.95	<DL	2.96 ±0.90	Heptachlor	1000	3.20	<DL	15.6 ±4.34
149	1000	2.97	<DL	4.30 ±1.30	α-HCH	1000	121	<DL	100 ±0
153	1000	2.94	<DL	2.39 ±0.73	β-HCH	1000	113	<DL	100 ±0
156	1000	2.92	<DL	1.29 ±0.40	γ-HCH	1000	158	<DL	100 ±0
168	1000	2.93	<DL	1.52 ±0.47	Oxychlordane	1000	3.12	<DL	3.15 ±0.96
180	1000	3.01	<DL	0.81 ±0.25	α-Chlordane	1000	3.29	<DL	15.1 ±4.23
193	1000	3.01	<DL	0.55 ±0.17	γ-Chlordane	1000	3.22	<DL	11.4 ±3.26
199	1000	3.09	<DL	0.42 ±0.13	cis-Nonachlor	1000	3.15	<DL	2.03 ±0.62
203	1000	3.09	<DL	0.39 ±0.12	trans-Nonachlor	1000	3.15	<DL	1.76 ±0.54
209	1000	3.25	<DL	0.11 ±0.03	H-Epoxyde	1000	4.52	<DL	58.1 ±10.1

a - selected PCB congeners shown

b - Set quantitation limits based on lowest quantitation level for PCBs and OC pesticides by GCxGC-μECD (Muscalu et al., 2011)

c - Calculated based on median β_{MV} = 96.6 for the 10 sites

Table S5: Instrument quantitation limits (IDL), method detection limits (MDLs) and blank values for polybrominated diphenylethers (PBDEs) and non-PBDE flame retardants (nBFRs).

PBDE Congener	IDL ^a pg/sample	MDL ^b pg/L	Max Blank (n=2) pg/sample	Average % Equilibrium	Compound	IDL ^a pg/sample	MDL ^b pg/L	Max Blank (n=2) pg/sample	Average % Equilibrium
BDE 3	63	2.29	<DL	100 ±0	αHBCD	4	0.03	31 (0.23) ^c	79.2 ±8.4
BDE 15	2.2	0.02	<DL	96.2 ±3.0	βHBCD	3	0.02	21 (0.14) ^c	75.4 ±9.0
BDE 28	5.7	0.02	<DL	20.5 ±5.5	γHBCD	4	0.02	34 (0.16) ^c	46.4 ±9.5
BDE 47	14	0.04	<DL	3.15 ±1.0	TBP-AE	22	0.16	<DL	86.6 ±6.7
BDE 77	7.7	0.03	<DL	24.9 ±6.4	TBP-DBPE	10	0.04	<DL	25.3 ±6.5
BDE 99	10	0.03	<DL	0.89 ±0.28	TBCO	70	0.36	<DL	67.1 ±9.8
BDE 100	16	0.05	<DL	0.53 ±0.16	HBB	20	0.07	<DL	13.5 ±3.8
BDE 119	13	0.04	<DL	1.50 ±0.46	PBEB	32	0.11	<DL	3.11 ±0.95
BDE 126	19	0.07	<DL	3.44 ±1.05	EH-TBB	48	0.16	<DL	0.30 ±0.09
BDE 138	49	0.18	<DL	0.40 ±0.12	BEH-TEBP	58	0.21	<DL	0.01 ±0.00
BDE 153	21	0.08	<DL	0.41 ±0.13	BTBPE	112	0.41	<DL	0.07 ±0.02
BDE 154	21	0.07	<DL	0.19 ±0.06	DBDPE	8000	32.8	<DL	0.00 ±0.00
BDE 169	86	0.31	<DL	1.44 ±0.44	PBB153	13	0.05	<DL	0.05 ±0.01
BDE180	125	0.46	<DL	0.10 ±0.03	DBE-DBCH	62	0.69	<DL	95.7 ±3.3
BDE 183	64	0.24	<DL	0.06 ±0.02	PhotoMirex	10 ^d	0.03	<DL	0.02 ±0.00
BDE 197	114	0.44	<DL	0.04 ±0.01	Mirex	10 ^d	0.03	<DL	1.32 ±0.41
BDE 205	194	0.75	<DL	0.05 ±0.02	Dec602	10 ^d	0.03	<DL	0.07 ±0.02
BDE 207	230	0.91	<DL	0.01 ±0.00	Dec603	10 ^d	0.04	<DL	0.01 ±0.00
BDE 209	2105	8.61	<DL	0.01 ±0.00	Dec604	10 ^d	0.07	<DL	0.00 ±0.00
					Syn-DP	18	0.06	<DL	0.00 ±0.00
					Anti-DP	16	0.06	<DL	0.00 ±0.00

a - Instrument detection limit based on 10:1 signal to noise ratio (Megson et al., 2016)

b – Calculated based on median β_{MV} = 96.6 for the 10 sites; c - blank concentration in pg/L based on median β_{MV} in parentheses

d - Instrument detection limits reported previously (Shen et al., 2011)

Table S6: Compound properties and site/compound-specific sampling rates (R_s) of the polychlorinated biphenyls (PCBs).

PCB Congener	MW ^a	log K_{OW} ^b	log K_{PEW} ^c	Site β_{MW} ^d	Sampling Rates (L/d)									
					1 99.0	2 101.9	3 94.1	4 110.5	5 70.6	6 89.1	7 61.2	8 169.9	9 99.8	10 72.5
4	223.1	4.65	4.45		14.9	15.3	14.2	16.6	10.6	13.4	9.2	25.6	15.0	10.9
6	223.1	5.06	4.88		14.9	15.3	14.2	16.6	10.6	13.4	9.2	25.6	15.0	10.9
8	223.1	5.07	4.89		14.9	15.3	14.2	16.6	10.6	13.4	9.2	25.6	15.0	10.9
15	223.1	5.3	5.13		14.9	15.3	14.2	16.6	10.6	13.4	9.2	25.6	15.0	10.9
16	257.5	5.16	4.98		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
18	257.5	5.24	5.06		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
19	257.5	5.02	4.83		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
22	257.5	5.58	5.42		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
28	257.5	5.67	5.51		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
31	257.5	5.67	5.51		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
33	257.5	5.6	5.44		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
37	257.5	5.83	5.68		14.2	14.6	13.5	15.8	10.1	12.8	8.8	24.3	14.3	10.4
40	292	5.66	5.50		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
41	292	5.69	5.53		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
44	292	5.75	5.59		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
49	292	5.85	5.70		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
52	292	5.84	5.69		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
54	292	5.21	5.03		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
66	292	6.2	6.06		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
70	292	6.2	6.06		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
77	292	6.36	6.23		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
81	292	6.36	6.23		13.6	14.0	12.9	15.1	9.7	12.2	8.4	23.3	13.7	9.9
84	326.4	6.04	5.90		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
85	326.4	6.3	6.17		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
87	326.4	6.29	6.16		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
90	326.4	6.36	6.23		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
95	326.4	6.13	5.99		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6

Table S6 (Cont'd): Compound properties and site/compound-specific sampling rates (R_s) of the polychlorinated biphenyls (PCBs).

PCB Congener	MW ^a	log K_{OW} ^b	log K_{PEW} ^c	Site β_{MW} ^d	Sampling Rates (L/d)									
					1 99.0	2 101.9	3 94.1	4 110.5	5 70.6	6 89.1	7 61.2	8 169.9	9 99.8	10 72.5
97	326.4	6.29	6.16		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
99	326.4	6.39	6.26		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
105	326.4	6.65	6.53		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
110	326.4	6.48	6.35		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
118	326.4	6.74	6.62		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
119	326.4	6.58	6.46		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
123	326.4	6.74	6.62		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
126	326.4	6.89	6.78		13.1	13.4	12.4	14.6	9.3	11.7	8.1	22.4	13.2	9.6
128	360.9	6.74	6.62		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
129	360.9	6.73	6.61		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
135	360.9	6.64	6.52		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
137	360.9	6.83	6.72		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
138	360.9	6.83	6.72		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
141	360.9	6.82	6.71		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
149	360.9	6.67	6.55		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
151	360.9	6.64	6.52		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
153	360.9	6.92	6.81		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
155	360.9	6.41	6.28		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
156	360.9	7.18	7.08		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
157	360.9	7.18	7.08		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
158	360.9	7.02	6.92		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
167	360.9	7.27	7.18		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
168	360.9	7.11	7.01		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
169	360.9	7.42	7.33		12.6	13.0	12.0	14.1	9.0	11.3	7.8	21.6	12.7	9.2
170	395.3	7.27	7.18		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
174	395.3	7.11	7.01		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9

Table S6 (Cont'd): Compound properties and site/compound-specific sampling rates (R_s) of the polychlorinated biphenyls (PCBs).

PCB Congener	MW ^a	$\log K_{OW}$ ^b	$\log K_{PEW}$ ^c	Site β_{MW} ^d	Sampling Rates (L/d)									
					1 99.0	2 101.9	3 94.1	4 110.5	5 70.6	6 89.1	7 61.2	8 169.9	9 99.8	10 72.5
177	395.3	7.08	6.98		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
178	395.3	7.14	7.04		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
180	395.3	7.36	7.27		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
183	395.3	7.2	7.10		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
187	395.3	7.17	7.07		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
188	395.3	6.82	6.71		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
189	395.3	7.71	7.63		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
191	395.3	7.55	7.47		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
193	395.3	7.52	7.44		12.2	12.6	11.6	13.6	8.7	11.0	7.5	21.0	12.3	8.9
194	429.8	7.8	7.73		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
199	429.8	7.62	7.54		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
200	429.8	7.2	7.10		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
201	429.8	7.27	7.18		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
202	429.8	7.24	7.14		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
203	429.8	7.65	7.57		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
205	429.8	8	7.94		11.9	12.2	11.3	13.2	8.5	10.7	7.3	20.3	12.0	8.7
206	464.2	8.09	8.03		11.5	11.9	11.0	12.9	8.2	10.4	7.1	19.8	11.6	8.4
207	464.2	7.74	7.67		11.5	11.9	11.0	12.9	8.2	10.4	7.1	19.8	11.6	8.4
208	464.2	7.71	7.63		11.5	11.9	11.0	12.9	8.2	10.4	7.1	19.8	11.6	8.4
209	498.7	8.18	8.12		11.3	11.6	10.7	12.6	8.0	10.1	7.0	19.3	11.3	8.2

a – MW – molecular weight; b – \log octanol-water partition coefficient (Hawker & Connell, 1988);c – Calculated using $\log K_{PEW} = 1.041 \log K_{OW} - 0.392$ from properties for PCBs, PBDEs, and PAHs listed in Lohmann et al. (2012)d – β_{MW} – site-specific proportionality constant determined from performance reference compound (PRC) data (Booij and Smedes, 2010)

Table S7: Compound properties and site/compound-specific sampling rates (R_s) of the organochlorine pesticides.

Organochlorine Pesticide Compound		MW ^a	log K_{OW} ^b	log K_{PEW} ^c	Site β_{MW} ^d	Sampling Rates (L/d)									
						1	2	3	4	5	6	7	8	9	10
						99.0	101.9	94.1	110.5	70.6	89.1	61.2	169.9	99.8	72.5
o,p-DDT		354.5	6.68	6.56		12.7	13.1	12.1	14.2	9.0	11.4	7.8	21.8	12.8	9.3
p,p'-DDD		321	6.22	6.08		13.1	13.5	12.5	14.7	9.4	11.8	8.1	22.5	13.2	9.6
p,p'-DDE		319	6.96	6.85		13.2	13.5	12.5	14.7	9.4	11.8	8.1	22.6	13.3	9.6
p,p'-DDT		354.5	6.28	6.15		12.7	13.1	12.1	14.2	9.0	11.4	7.8	21.8	12.8	9.3
Aldrin		364.9	6.50	6.37		12.6	12.9	11.9	14.0	9.0	11.3	7.8	21.5	12.7	9.2
Dieldrin		380.9	5.40	5.23		12.4	12.7	11.8	13.8	8.8	11.1	7.6	21.2	12.5	9.1
Endosulfan 1		406.9	4.74	4.54		12.1	12.4	11.5	13.5	8.6	10.9	7.5	20.7	12.2	8.8
Endosulfan 2		406.9	4.78	4.58		12.1	12.4	11.5	13.5	8.6	10.9	7.5	20.7	12.2	8.8
Endos. Sulfate		422.9	5.03	4.84		11.9	12.3	11.3	13.3	8.5	10.7	7.4	20.5	12.0	8.7
Endrin		380.9	5.20	5.02		12.4	12.7	11.8	13.8	8.8	11.1	7.6	21.2	12.5	9.1
Heptachlor		373.4	6.10	5.96		12.5	12.8	11.8	13.9	8.9	11.2	7.7	21.4	12.6	9.1
α -HCH		290.9	3.81	3.57		13.6	14.0	12.9	15.2	9.7	12.2	8.4	23.3	13.7	10.0
β -HCH		290.9	3.84	3.61		13.6	14.0	12.9	15.2	9.7	12.2	8.4	23.3	13.7	10.0
γ -HCH		290.9	3.70	3.46		13.6	14.0	12.9	15.2	9.7	12.2	8.4	23.3	13.7	10.0
Oxychlordane		423.8	6.78	6.67		11.9	12.3	11.3	13.3	8.5	10.7	7.4	20.4	12.0	8.7
α -Chlordane		409.8	6.10	5.96		12.1	12.4	11.5	13.5	8.6	10.8	7.4	20.7	12.2	8.8
γ -Chlordane		409.8	6.23	6.09		12.1	12.4	11.5	13.5	8.6	10.8	7.4	20.7	12.2	8.8
cis-Nonachlor		442.2	6.96	6.85		11.7	12.1	11.2	13.1	8.4	10.6	7.3	20.1	11.8	8.6
trans-Nonachlor		442.2	7.02	6.92		11.7	12.1	11.2	13.1	8.4	10.6	7.3	20.1	11.8	8.6
H. Epoxide		389.2	5.40	5.23		12.3	12.6	11.7	13.7	8.8	11.0	7.6	21.1	12.4	9.0

a – MW – molecular weight; b – log octanol-water partition coefficient (calculated from SPARC)

c – Calculated using $\log K_{PEW} = 1.041 \log K_{OW} - 0.392$ from properties for PCBs, PBDEs, and PAHs listed in Lohmann et al. (2012)d – β_{MW} – site-specific proportionality constant determined from performance reference compound (PRC) data (Booij and Smedes, 2010)

Table S8: Compound properties and site/compound-specific sampling rates (R_s) of the polybrominated diphenylethers (PBDEs).

PBDE Congener	MW ^a	log K_{OW} ^b	log K_{PEW} ^c	Site β_{MW} ^d	Sampling Rates (L/d)									
					1 99.0	2 101.9	3 94.1	4 110.5	5 70.6	6 89.1	7 61.2	8 169.9	9 99.8	10 72.5
BDE 3	249	4.31	4.09		14.4	14.8	13.6	16.0	10.2	12.9	8.9	24.6	14.5	10.5
BDE 15	328	4.84	4.65		13.0	13.4	12.4	14.5	9.3	11.7	8.1	22.4	13.1	9.5
BDE 28	406.9	5.96	5.81		12.1	12.4	11.5	13.5	8.6	10.9	7.5	20.7	12.2	8.8
BDE 47	485.8	6.76	6.65		11.4	11.7	10.8	12.7	8.1	10.2	7.0	19.5	11.5	8.3
BDE77	485.8	5.84	5.69		11.4	11.7	10.8	12.7	8.1	10.2	7.0	19.5	11.5	8.3
BDE 99	564.7	7.27	7.18		10.8	11.1	10.2	12.0	7.7	9.7	6.7	18.5	10.9	7.9
BDE 100	564.7	7.49	7.41		10.8	11.1	10.2	12.0	7.7	9.7	6.7	18.5	10.9	7.9
BDE 119	564.7	7.05	6.95		10.8	11.1	10.2	12.0	7.7	9.7	6.7	18.5	10.9	7.9
BDE 126	564.7	6.7	6.58		10.8	11.1	10.2	12.0	7.7	9.7	6.7	18.5	10.9	7.9
BDE 138	643.6	7.59	7.51		10.3	10.6	9.8	11.5	7.3	9.3	6.4	17.7	10.4	7.5
BDE 153	643.6	7.58	7.50		10.3	10.6	9.8	11.5	7.3	9.3	6.4	17.7	10.4	7.5
BDE 154	643.6	7.89	7.82		10.3	10.6	9.8	11.5	7.3	9.3	6.4	17.7	10.4	7.5
BDE 169	643.6	7.05	6.95		10.3	10.6	9.8	11.5	7.3	9.3	6.4	17.7	10.4	7.5
BDE 180	722.5	8.15	8.09		9.9	10.2	9.4	11.0	7.1	8.9	6.1	17.0	10.0	7.2
BDE 183	722.5	8.35	8.30		9.9	10.2	9.4	11.0	7.1	8.9	6.1	17.0	10.0	7.2
BDE 197	801.4	8.53	8.49		9.5	9.8	9.1	10.6	6.8	8.6	5.9	16.4	9.6	7.0
BDE 205	801.4	8.43	8.38		9.5	9.8	9.1	10.6	6.8	8.6	5.9	16.4	9.6	7.0
BDE 207	880.3	9.03	9.01		9.2	9.5	8.8	10.3	6.6	8.3	5.7	15.8	9.3	6.8
BDE 209	959.2	9.31	9.30		9.0	9.2	8.5	10.0	6.4	8.1	5.5	15.4	9.0	6.6

a – MW – molecular weight; b – log octanol-water partition coefficient (Yue and Li, 2013);

c – Calculated using $\log K_{PEW} = 1.041 \log K_{OW} - 0.392$ from properties for PCBs, PBDEs, and PAHs listed in Lohmann et al. (2012)d – β_{MW} – site-specific proportionality constant determined from performance reference compound (PRC) data (Booij and Smedes, 2010)

Table S9: Compound properties and site/compound-specific sampling rates (R_S) of the non-PBDE flame retardants (nBFRs) and Dechlorane-related compounds.

nBFR					Sampling Rates (L/d)									
Compound	MW ^a	log <i>K</i> _{OW} ^b	log <i>K</i> _{PEW} ^c	Site β _{MW} ^d	1 99.0	2 101.9	3 94.1	4 110.5	5 70.6	6 89.1	7 61.2	8 169.9	9 99.8	10 72.5
<i>nBFRs</i>														
αHBCD	641.7	5.07 ^e	4.89		10.3	10.6	9.8	11.5	7.4	9.3	6.4	17.7	10.4	7.5
βHBCD	641.7	5.12 ^e	4.94		10.3	10.6	9.8	11.5	7.4	9.3	6.4	17.7	10.4	7.5
γHBCD	641.7	5.47 ^e	5.30		10.3	10.6	9.8	11.5	7.4	9.3	6.4	17.7	10.4	7.5
TBP-AE	370.8	5.04	4.85		12.5	12.8	11.9	13.9	8.9	11.2	7.7	21.4	12.6	9.1
TBP-DBPE	530.7	5.82	5.67		11.0	11.3	10.5	12.3	7.9	9.9	6.8	18.9	11.1	8.1
TBCO	427.8	5.28	5.10		11.9	12.2	11.3	13.3	8.5	10.7	7.3	20.4	12.0	8.7
HBB	551.5	6.11	5.97		10.9	11.2	10.3	12.1	7.8	9.8	6.7	18.6	11.0	8.0
PBEB	500.7	6.76	6.65		11.2	11.6	10.7	12.5	8.0	10.1	6.9	19.3	11.3	8.2
EH-TBB	549.9	7.73	7.65		10.9	11.2	10.3	12.1	7.8	9.8	6.7	18.7	11.0	8.0
BEH-TEBP	706.1	9.34	9.33		10.0	10.3	9.5	11.1	7.1	9.0	6.2	17.1	10.0	7.3
BTBPE	687.6	8.31	8.26		10.1	10.3	9.6	11.2	7.2	9.0	6.2	17.3	10.1	7.4
DBDPE	971.2	11.1	11.16		8.9	9.2	8.5	9.9	6.4	8.0	5.5	15.3	9.0	6.5
PBB153	627.6	8.50	8.46		10.4	10.7	9.9	11.6	7.4	9.3	6.4	17.8	10.5	7.6
DBE-DBCH	427.8	4.82	4.63		11.9	12.2	11.3	13.3	8.5	10.7	7.3	20.4	12.0	8.7
<i>Dechloranes</i>														
PhotoMirex	511.1	8.99	8.97		11.2	11.5	10.6	12.5	8.0	10.0	6.9	19.1	11.2	8.2
Mirex	545.5	9.69	7.01		10.9	11.2	10.4	12.2	7.8	9.8	6.7	18.7	11.0	8.0
Dec602	613.6	8.30	8.25		10.5	10.8	9.9	11.7	7.5	9.4	6.5	18.0	10.6	7.7
Dec603	673.7	9.14	9.12		10.1	10.4	9.6	11.3	7.2	9.1	6.3	17.4	10.2	7.4
Dec604	692.5	10.24	10.27		10.0	10.3	9.5	11.2	7.2	9.0	6.2	17.2	10.1	7.3
Syn-DP	653.7	10.12	10.14		10.2	10.5	9.7	11.4	7.3	9.2	6.3	17.6	10.3	7.5
Anti-DP	653.7	10.12	10.14		10.2	10.5	9.7	11.4	7.3	9.2	6.3	17.6	10.3	7.5

a – MW – molecular weight; b – \log octanol-water partition coefficient (calculated, listed in Bergman et al., 2012);

c – Calculated using $\log K_{PEW} = 1.041 \log K_{OW} - 0.392$ from properties for PCBs, PBDEs, and PAHs listed in Lohmann et al. (2012)

d – β_{MW} – site-specific proportionality constant determined from performance reference compound (PRC) data (Booij and Smedes, 2010)

e – $\log K_{OW}$ values for HBCDD isomers from Hayward et al. (2006)

Table S10: Dissolved phase water concentrations (pg/L) of polychlorinated biphenyls (PCBs) determined from polyethylene passive samplers.

Congener	Sampling Rates (L/d)									
	1	2	3	4	5	6	7	8	9	10
4	144	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
6	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
8	99.3	10.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
15	87.8	17.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
16	297	39.0	<DL	<DL	<DL	<DL	11.5	<DL	<DL	<DL
18	320	50.7	<DL	<DL	6.06	<DL	14.8	4.33	<DL	<DL
19	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
22	30.4	3.92	<DL	<DL	<DL	<DL	6.36	<DL	<DL	<DL
28	301	36.7	4.15	<DL	9.00	<DL	14.6	<DL	<DL	4.69
31	268	28.2	3.60	<DL	8.25	<DL	13.0	<DL	<DL	4.23
33	142	13.3	<DL	<DL	4.56	<DL	7.29	<DL	<DL	5.66
37	65.0	7.40	<DL	<DL	<DL	<DL	6.17	<DL	<DL	<DL
40	28.9	4.63	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
41	12.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
44	128	29.0	4.22	<DL	10.1	<DL	20.2	<DL	<DL	<DL
49	126	19.9	<DL	<DL	5.20	<DL	7.85	<DL	<DL	<DL
52	190	39.2	4.81	3.58	13.4	3.43	18.8	2.87	<DL	<DL
54	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
66	114	19.9	<DL	<DL	7.43	<DL	13.2	<DL	<DL	<DL
70	137	23.4	<DL	<DL	6.71	<DL	13.2	<DL	<DL	<DL
77	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
81	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
84	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
85	17.8	3.52	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
87	62.1	13.3	<DL	<DL	5.99	<DL	8.72	1.78	<DL	<DL
90	134	32.4	<DL	<DL	8.12	<DL	17.6	<DL	<DL	<DL
95	192	61.2	<DL	3.14	13.6	4.08	26.1	<DL	<DL	<DL
97	37.8	7.38	<DL	<DL	<DL	<DL	6.01	<DL	<DL	<DL
99	55.5	11.2	<DL	<DL	4.83	<DL	6.24	<DL	<DL	<DL
105	37.2	6.84	<DL	<DL	4.04	<DL	6.20	<DL	<DL	<DL
110	109	23.6	3.23	<DL	11.3	<DL	24.8	2.02	<DL	<DL
118	70.4	14.9	<DL	<DL	5.37	<DL	8.31	<DL	<DL	<DL
119	7.01	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
123	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
126	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
128	20.0	3.55	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
129	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
135	45.4	6.59	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
137	12.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	6.89
138	106	29.8	<DL	<DL	7.31	<DL	13.4	<DL	<DL	<DL

[illegible]

Table S11: Dissolved phase water concentrations (pg/L) of organochlorine pesticides determined from polyethylene passive samplers.

Compound	Concentrations (pg/L)									
	1	2	3	4	5	6	7	8	9	10
o,p-DDT	<DL	3.12	<DL	<DL	<DL	<DL	7.18	2.04	<DL	<DL
p,p'-DDD	15.4	7.46	<DL	2.68	5.70	<DL	24.5	<DL	<DL	<DL
p,p'-DDE	70.5	17.4	3.85	3.23	7.42	3.44	21.1	2.28	3.01	4.49
p,p'-DDT	12.5	4.24	<DL	<DL	5.53	<DL	13.4	1.85	<DL	<DL
Aldrin	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Dieldrin	44.7	18.1	15.4	14.5	21.6	15.9	38.7	13.6	13.5	17.9
Endosulfan 1	23.1	<DL	<DL	<DL	<DL	<DL	17.6	<DL	<DL	<DL
Endosulfan 2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Endos. sulfate	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Endrin	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Heptachlor	3.75	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
α -HCH	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
β -HCH	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
γ -HCH	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Oxychlordane	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
α -Chlordane	20.1	5.98	<DL	<DL	5.18	<DL	17.2	3.19	<DL	<DL
γ -Chlordane	31.4	7.16	3.72	3.11	6.53	3.76	17.8	2.65	<DL	<DL
cis-Nonachlor	10.5	3.84	<DL	<DL	<DL	<DL	6.94	<DL	<DL	<DL
trans-Nonachlor	15.5	4.16	<DL	<DL	4.68	<DL	10.4	<DL	<DL	<DL
H-Epoxyde	38.0	9.85	5.90	4.92	6.70	5.64	9.51	4.00	5.14	6.23

[illegible]

Table S13: Dissolved phase water concentrations (pg/L) of non-PBDE flame retardants (nBFRs) and Dechlorane-related compounds determined from polyethylene passive samplers.

Congener	Concentrations (pg/L)									
	1	2	3	4	5	6	7	8	9	10
<i>nBFRs</i>										
α HBCD	16.5	1.89	1.78	1.01	2.49	0.87	10.7	0.86	0.54	1.75
β HBCD	1.41	<blk	0.35	0.29	0.62	<blk	0.83	<blk	0.25	0.39
γ HBCD	2.53	0.22	0.74	0.46	0.64	0.19	1.43	0.21	0.23	0.80
TBP-AE	0.60	<DL	0.26	0.27	0.22	0.33	0.74	0.25	0.23	0.27
TBP-DBPE	0.33	<DL	<DL	<DL	<DL	0.05	0.12	<DL	<DL	<DL
TBCO	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
HBB	0.20	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
PBEB	0.19	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
EH-TBB	0.70	<DL	<DL	<DL	0.10	<DL	<DL	<DL	<DL	0.11
BEH-TEBP	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BTBPE	1.10	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
DBDPE	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
PBB153	0.24	0.08	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
DBE-DBCH	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<i>Dechloranes</i>										
PhotoMirex	0.20	0.06	0.05	0.03	0.06	0.07	<DL	0.03	<DL	<DL
Mirex	0.13	0.09	0.06	0.06	0.09	0.10	0.19	0.03	0.05	0.06
Dec602	0.06	0.04	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Dec603	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Dec604	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Syn-DP	0.09	0.10	0.13	<DL	<DL	0.26	0.44	0.04	0.09	<DL
Anti-DP	0.15	0.12	0.13	0.11	0.10	0.20	1.65	0.07	0.09	<DL

Figure S2: PCB congener concentration (pg/L) profiles at Site 1 and Site 7.

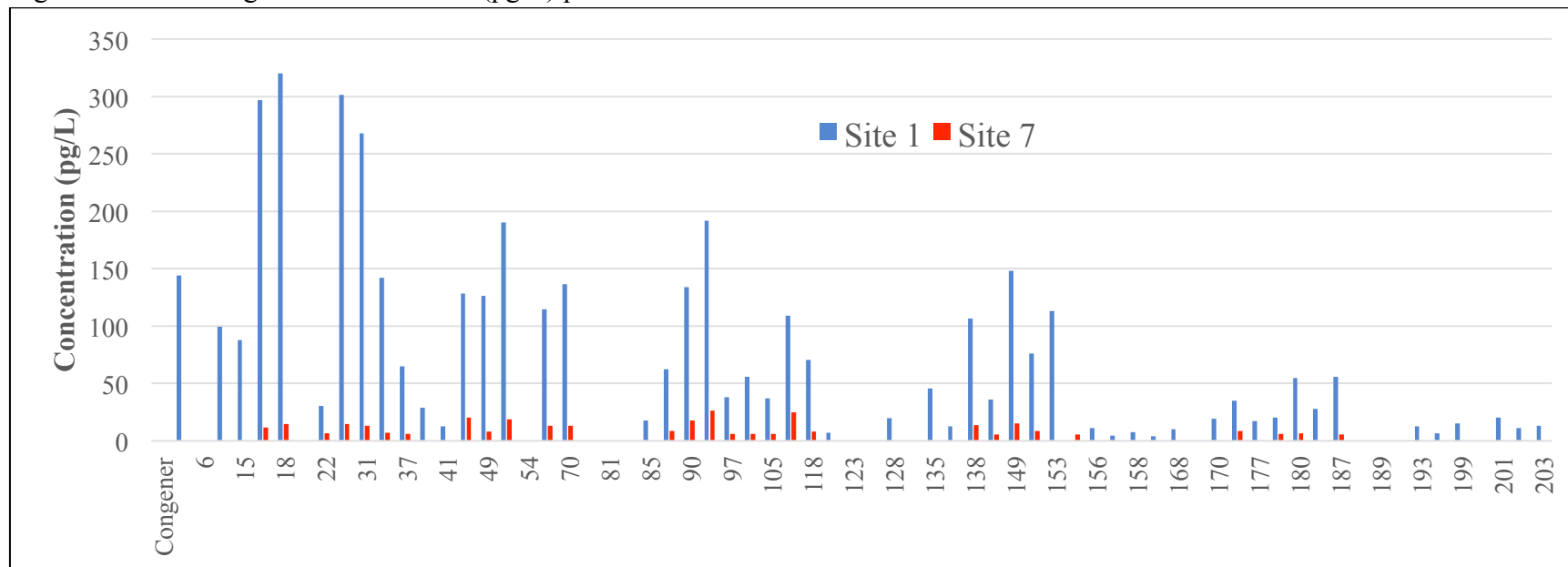


Table S14. Spearman correlation coefficients and p values between the chemicals detected via nontargetd screening and the target compound groups

Compound	Spearman Correlation Coefficient				
	PCB	PBDE	OCP	nBFR	DEC
Pentachloroanisole	0.92	0.81	0.77	0.85	0.64
Pentachlorothioanisole	0.90	0.77	0.75	0.84	0.58
Methyl trichlosan	0.92	0.84	0.70	0.85	0.53
2,4,6-tribromoanisole	0.88	0.77	0.73	0.81	0.59
Penachloraniline	0.92	0.81	0.72	0.85	0.52
Dimethyl-trichloroanisole	0.90	0.88	0.67	0.78	0.42

	p-value				
	PCB	PBDE	OCP	nBFR	DEC
Pentachloroanisole	0.0005	0.008	0.014	0.004	0.054
Pentachlorothioanisole	0.0009	0.014	0.018	0.004	0.088
Methyl trichlosan	0.0005	0.004	0.031	0.004	0.123
2,4,6-tribromoanisole	0.0020	0.014	0.021	0.008	0.080
Penachloraniline	0.0005	0.008	0.024	0.004	0.133
Dimethyl-trichloroanisole	0.0009	0.002	0.039	0.012	0.232

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