Analysis of halogenated flame retardants in Canadian wastewater treatment plants using gas chromatography–tandem mass spectrometry (GC-MS/MS)

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ABSTRACT

An investigation of brominated flame retardants (BFRs), polybrominated diphenylethers (PBDEs), and chlorinated flame retardants was conducted in samples from Canadian wastewater treatment plants (WWTPs). The penta-BDE mixture and deca-BDE were most commonly detected. Median removal efficiencies of PBDEs by WWTPs were 71% to 99% and higher concentrations of PBDEs were found in influent samples in summer, compared to winter. Three novel brominated flame retardants (nBFRs) including 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTeBB or TBB), and bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP or TBPH) were detected in greater than 80% of influents and biosolids. Median removal efficiencies were 45% to 99% for BTBPE, 63% to 99% for TBB, and 88% to 99% for TBPH. Detection of total dechlorane plus ((DP) syn and anti) was greater than 90% in both wastewater and biosolids samples. However, median removal efficiencies were between 51% and 66% for total DP. Overall, PBDEs were effectively removed via different treatment processes, while BTBPE, TBB, and DP exhibited lower removal rates, which could be due to their physical chemical properties.

Key words | 1,2-bis(2,4,6-tribromophenoxy)ethane, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate, bis(2-ethyl-1-hexyl)tetrabromophthalate, dechlorane plus (DP), polybrominated diphenyl ethers, wastewater treatment plants

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INTRODUCTION

Halogenated flame retardants, including two main classes of commercial organobromine and organochlorine compounds, have been used in many industrial and domestic products for fire prevention (Alaee *et al.* 2003). However, concerns over the toxicity, persistence, and accumulation of some of the extensively used brominated flame retardants (BFRs), such as the polybrominated diphenyl ethers (PBDEs), have led to regulation and restriction of their production. Two of the three major PBDEs, penta-BDE and octa-BDE, have been banned under the Stockholm Convention on Persistent Organic Pollutants (POPs) in Europe and North America (Morf *et al.* 2005). Deca-BDE is no longer imported into Canada and is registered under the European Union's REACH program and has been designated as a persistent organic pollutant (POP) under the terms of the Stockholm Convention on POPs (http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx). As additive FRs, PBDEs are not covalently bound and can be released into the environment during

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production, application, and waste disposal processes. Due to restrictions in the utilization of PBDEs, the BFR industry has developed alternative and/or novel flame retardants (nFRs); replacements include bis(2-ethyl-1-hexyl)tetrabromophthalate (TBPH), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), dechlorane plus (DP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 1,2,3,4,5-pentabromobenzene (PBBZ), 2,3,5,6-tetrabromo-p-xylene (pTBX), and 3,4,5,6-tetrabromo-2-chlorotoluene (TBCT) (Papachlimitzou *et al.* 2012). Although hexabromocyclododecane was at one point the second-most heavily produced BFR globally and is included in monitoring programs for a wide range of environmental compartments, most laboratories globally have transitioned to methods based on liquid chromatography/mass spectrometry (LC/MS) that enables diastereomer-specific analysis (Marvin *et al.* 2011).

BTBPE, TBB, and TBPH are three novel BFRs used in commercial formulations (Covaci *et al.* 2011; Xiao *et al.* 2012; Houde *et al.* 2014). BTBPE is added in thermoplastics, thermoset resins, polycarbonate and coatings and has been used as a replacement for octa-BDE since 2005. Another commercial mixture contains the brominated components of TBB and TBPH and is used primarily in polyurethane foam, and found in furniture and baby products (Stapleton *et al.* 2008). All three nBFRs (BTBPE, TBB, and TBPH) have recently been identified in various biological and environmental matrices, including house dust, river sediment, sewage sludge, birds, mammals, and human serum (Covaci *et al.* 2011; Rocha-Gutierrez & Lee 2012; Lankova *et al.* 2013; Houde *et al.* 2014). Dechlorane plus (DP) is a chlorinated flame retardant introduced as a replacement for dechlorane (i.e., Mirex) (Sverko *et al.* 2008). In the DP technical mixture, two stereoisomers (syn and anti) are present at an approximate ratio of 1:2, respectively. DP is used mainly in cable coatings, plastic roofing materials, and hard connectors in computers and televisions (Qiu *et al.* 2007).

The growing human population and the expansion of industrial activities generate large volumes of wastewater which, in developed countries, is regularly treated by wastewater treatment plants (WWTPs) prior to discharge to the environment (Rocha-Gutierrez & Lee 2012, 2013). Although WWTPs are effective at removing many contaminants, such as nutrients and biodegradable organics, from residential, industrial, commercial, and institutional wastewater, WWTPs are not designed to remove POPs such as PBDEs (Kim *et al.* 2013a). Therefore, WWTP effluents and biosolids are considered to be pathways where organic pollutants, including PBDEs, are discharged to river ecosystems, to land and to lakes and oceans. Previous studies showed that lower concentrations of PBDEs were detected in treated effluent samples than in raw influents; this observation could be mainly due to the PBDEs' high partitioning affinity (octanol-water partition coefficient known as Log K_{ow}, $log\ K_{ow}$ *5–10*) to be adsorbed on suspended particles in wastewater (Song *et al.* 2006; Kim *et al.* 2013a). Despite the fact that PBDEs appear to be effectively removed in the liquid stream of WWTPs, the overall fate and occurrence of PBDEs during wastewater treatment requires further investigation. WWTP performance can be affected by environmental and operational parameters, including season, treatment time, and process complexity; however, only a handful of studies have investigated the relationship between the removal efficiency for PBDEs and varying environmental and/or operational conditions (Kim *et al.* 2013a, 2013b, 2014).

Eight Canadian WWTPs, encompassing lagoon, primary, secondary, and advanced liquid treatment processes, were selected for the analysis of flame retardants in this study. An analytical method based on gas chromatography (GC) with tandem mass spectrometry (GC-MS/MS) was used for identification and quantification of 15 PBDEs and 16 alternative flame retardants in a total of 186 liquid and 58 solid samples, which were collected over a three-year period. In addition, the removal efficiencies of the various types of liquid treatment processes were investigated. This study also examined trends related to seasonal, annual, and input (industrial versus domestic) variations. To the best of our knowledge, this is the first study to report the concentration ranges of the alternative flame retardants TBB and TBPH in influent, effluent, and biosolids samples from WWTPs.

MATERIALS AND METHODS

Chemicals and reagents

Polybrominated diphenyl ether predominant congener mixture (PBDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). A custom mixture of brominated and chlorinated flame retardants, allyl 2,4,6-tribromophenyl ether (ATE), 2,3,5,6-tetrabromo-p-xylene (pTBX), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), 1,2,3,4,5-pentabromobenzene (PBBZ), 3,4,5,6-tetrabromo-2-chlorotoluene (TBCT), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBB), 2,2′,4,5,5′-pentabromobiphenyl (BB-101), pentabromobenzyl acrylate (PBBA), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethyl-1-hexyl)tetrabromophthalate (TBPH), anti-dechlorane plus (aDP), syn-dechlorane plus (sDP), and octabromotrimethylphenylindane (OBIND) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). The analytical grade organic solvents used in this study were purchased from Fisher Scientific (Fair Lawn, NJ, USA).

Sample information

All detailed WWTP characteristics and sampling procedures have been described in previous studies (Kim *et al.* 2013a, 2014). Briefly, wastewater samples were collected from eight WWTPs and biosolids samples were collected from five WWTPs in three different provinces in Canada (Table 1). Influent and effluent samples were collected at a rate of 200 mL per 15 mins over a 24-hr period using a refrigerated auto sampler (HACH Company, Loveland, CO, USA). Residential inputs comprised more than 50% of the total influent flow whereas the sum of the industrial, commercial, and institutional inputs comprised less than 50%. Average water flow ranged from 700 to over 400,000 m^3 day^{-1}. With respect to treatment processes, the eight WWTPs consisted of three secondary treatment (ST) plants, one chemically assisted primary treatment (PT) plant, two aerated lagoons (AL), one facultative lagoon (FL), and one advanced treatment (AT) biological nutrient removal (AT) plant. PT is usually the first stage of wastewater treatment, which is designed to remove suspended solids from raw influent, and removes approximately 40% to 50% of the suspended solids and 30% to 40% of the BOD (biochemical oxygen demand) in the wastewater. ST removes the dissolved organic matter via biological treatment processes followed by settling tanks to remove suspended solids, resulting in a BOD removal of at least 90%. Tertiary treatment includes removal of nutrient (nitrogen and phosphorus), and additional suspended solids. Disinfection with chlorine or by ultraviolet radiation can be the final step prior to discharge of the effluent. Lagoons are an efficient and cost-effective system for wastewater treatment extensively utilized in small communities with a population of <2,000 (Lishman *et al.* 2006; Holeton *et al.* 2011; Woudneh

Table 1 | Liquid and solid treatment processes for eight Canadian WWTPs (samples collected between 2013 and 2016)

WWTPs	Liquid treatment type	Solids treatment type	Percent industrial/ commercial/ institutional inputs
F	Secondary activated sludge	Alkaline	10
HG	Secondary activated sludge	Aerobic digestion	10
Q	Secondary activated sludge	Mesophilic anaerobic digestion	50
J	Facultative lagoon	None	0
E	Advanced biological nutrient removal with filtration	Dewatering	20
U	Primary with chemical addition	Dewatering	30
R	Aerated lagoon	None	10
TB	Aerated lagoon	None	2

et al. 2015). Treatment in lagoons is through a combination of physical, biological, and chemical processes. Although most of the treatment occurs naturally, some systems are equipped with aeration devices to increase the amount of oxygen in the wastewater. Sludge treatment types include digestion (aerobic/mesophilic anaerobic), dewatering, and alkaline stabilization; the treated biosolids from WWTPs are sent for land application to fertilize crops and can improve the quality of soil (Andrade *et al.* 2010). Sampling at all plants was conducted on three consecutive days once per year for the last three years to study annual variation, while two plants were selected to be sampled twice per year (again on three consecutive days) to investigate seasonal difference.

Sample pre-treatment, wastewater

Each wastewater sample (approximately 0.6 L and 1.6 L of sample for influent and effluent, respectively) was spiked with 100 ng of BDE-71 as a recovery standard or surrogate, and extracted sequentially with dichloromethane (DCM, 100 mL, 50 mL, and 50 mL) by liquid–liquid extraction. Following each extraction, the organic layers were dried over anhydrous Na_2SO_4 (granular certified ACS, fired in a 600 °C muffle furnace overnight) and combined. If emulsion was present, the emulsion layer was removed and centrifuged for 10 min at 2,500 rpm and 24 °C to isolate the organic layer, which was subsequently added to the existing extracts. The combined extract was solvent-exchanged to iso-octane and concentrated to approximately 1 mL using a rotary evaporator followed by evaporation with nitrogen. One laboratory blank (deionized water, no standards spiked) and spiked blank (target standards spiked in influent sample) was included for every six-sample batch. Individual samples, laboratory blanks and spiked blanks were spiked with BDE-71. Laboratory blanks reflected extraneous FRs present in the laboratory environment while spiked blanks accounted for matrix effects. It is acknowledged that labeled surrogate standards are now available for many of the analytes targeted in our schema, which is an approach we fully advocate; however, use of BDE-71 was standard practice during the period of time we began our method development.

Sample pre-treatment, biosolids

Approximately 1 g of biosolids sample was ground with 15 g of anhydrous Na_2SO_4 to a homogenous mixture. This solid mixture was transferred to a centrifuge tube, spiked with 100 ng of BDE-71 as a recovery standard, and then 25 mL of hexane:acetone (1:1) was added as the extraction solvent. The mixture was vortexed for 30 min at 2,500 rpm then centrifuged for 10 min at 2,000 rpm at 24 °C. The supernatant was collected and the remaining solid mixture was extracted twice more using the same vortex/centrifuge procedure. The combined extract was solvent-exchanged to iso-octane and reduced in volume to about 1 mL using a rotary evaporator followed by evaporation with nitrogen.

Column clean-up

Liquid and solid extracts were further pre-treated using an open column cleanup. A chromatography column was prepared containing 10 g of 5% deactivated silica gel (dried at 160 °C overnight prior to the deactivation), which was rinsed and saturated with hexane and topped with 2 g of anhydrous Na_2SO_4. The concentrated extract was loaded onto the column and eluted with an additional 45 mL of a 1:1 mixture of hexane:ethyl acetate. The extract was solvent exchanged into iso-octane and concentrated to 1 mL using a rotary evaporator followed by evaporation with nitrogen; the extracts were analyzed using GC with tandem mass spectrometry (MS/MS).

Instrumental parameters

All sample extracts were analyzed using an Agilent 7890A GC system equipped with an Agilent 7693 auto-sampler and interfaced with an Agilent 7000A Triple Quadrupole or tandem Mass Spectrometer (GC-EI-MS/MS, Agilent Technologies, Foster City, USA). Separation of flame retardants was achieved with a fused silica DB-5 HT capillary column (15 m, 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, CA, USA) with a constant flow rate of 1 mL/min. The injection was performed with 2 μL at pulsed splitless mode and the inlet temperature was set to 300 °C. The GC temperature program was as follows: hold at 80 °C for

1 min, then increase to 300 °C at 22 °C min^{-1} and hold for 7.5 min. Under multiple reaction monitoring scan type, primary and secondary ions (m/z) were used for quantification and confirmation of flame retardants in the samples, respectively. The MRM transitions and instrumental detection limits for the 31 flame retardants are shown in Table 2.

Quality assurance and quality control

Three main quality control criteria were used to confirm the correct identification of the target flame retardants: (i) the GC retention times of FRs must be matched within ±0.1 min of standards, (ii) the ratio between the quantifier (primary) and qualifier (secondary) ions must be

Table 2 | Instrumental detection limit and optimized GC-EI-MS-MS multiple reaction monitoring transitions for flame retardants and the average percent recovery ($n = 30$) of spike blanks containing flame retardant standards

Flame retardants	CAS number	Detection limit (ng/L)	% Recovery ±15	Precursor ion	Primary ion (Quantifier)	Secondary ion (Qualifier)
BDE17	147217-75-2	0.0058	110	406.0	248.0	246.0
BDE 28	41318-75-6	0.0031	110	406.0	248.0	246.0
BDE 33	NA	0.0031	110	406.0	248.0	246.0
BDE47	5436-43-1	0.0067	122	486.0	328.0	326.0
BDE66	189084-61-5	0.0041	114	486.0	328.0	326.0
BDE85	182346-21-0	0.0026	113	564.0	406.0	404.0
BDE99	60348-60-9	0.0049	101	564.0	406.0	404.0
BDE100	189084-64-8	0.0034	99	564.0	406.0	404.0
BB101	67888-96-4	0.0023	111	468.7	389.6	387.7
BDE138	182677-30-1	0.0036	110	484.0	377.0	324.0
BDE153	68631-49-2	0.0032	106	484.0	377.0	375.0
BDE154	207122-15-4	0.0033	112	484.0	377.0	375.0
BDE183	207122-16-5	0.0023	105	562.0	455.0	402.0
BDE190	189084-68-2	0.0019	111	562.0	455.0	453.0
BDE209	1163-19-5	0.0027	112	799.0	642.0	639.0
ATE	3278-89-5	0.0062	73	329.6	300.8	221.9
BATE	NA	0.0040	96	326.5	248.1	220.2
BTBPE	37853-59-1	0.0045	96	359.0	254.0	252.0
DPTE	35109-60-5	0.0058	99	327.8	220.9	219.9
HBB	87-82-1	0.0036	106	555.8	395.8	393.6
OBIND	155613-93-7	0.0074	118	772.1	453.7	451.9
PBBA	59447-55-1	0.0055	104	476.5	368.1	367.6
PBBE	608-90-2	0.0018	106	471.9	313.4	232.9
PBEB	85-22-3	0.0017	110	500.0	342.0	340.0
PBTO	87-83-2	0.0027	116	483.8	324.7	244.9
PTBX	23488-38-2	0.0053	83	419.8	341.0	259.8
TBPH	26040-51-7	0.0060	107	462.8	378.5	310.8
TBB	183658-27-7	0.0085	107	418.6	390.6	311.7
aDP	135821-74-8	0.0080	97	345.1	236.0	231.0
sDP	135821-74-8	0.0045	117	345.2	236.1	231.1
TBCT	39569-21-6	0.0019	100	445.9	204.5	203.0

within ±15% of the theoretical values, and (iii) the signal to noise ratio must be greater than 5 and the recovery of the surrogate (spiked in samples and blanks prior to extraction), BDE 71, must be greater than 75%. One spike blank (containing flame retardants standards) and one laboratory blank were included for every six samples. No target analytes were detected in the laboratory blanks and the recovery range of the spike blanks ($n = 30$) was between 73% and 117% (Table 2). The instrumental limits of detection (Table 2) and quantification were defined as the amount of analyte that resulted in signal to noise ratio of 3:1 and 10:1, respectively. Quantification was performed based on an external calibration method containing at least six standard levels, covering a dynamic range of five orders of magnitude with correlation coefficient greater than $R^2 > 0.991$.

Statistical analyses

Statistical analyses were carried out using SPSS 23.0 (IBM Corporation, USA) and Minitab 17 (Minitab Inc., PA, USA). The Shapiro–Wilk normality test showed that the data sets were not normally distributed and thus statistical data analysis was conducted using nonparametric methods such as the Mann–Whitney U test and the Kruskal–Wallis tests. Statistical significance was set as $p < 0.05$ unless otherwise specified.

RESULTS

Overview of flame retardants analysis

In total, 31 flame retardants, including PBDEs and nFRs, were analyzed in 93 influent, 93 effluent, and 58 biosolids samples collected over three years (2013–2015) from eight WWTPs in Canada. Of all target flame retardants analyzed, PBDE congeners 47, 99, 100, 153, 154, and 209 and the nFRs, TBPH, BTBPE, TBB, and DP were detected frequently in the samples; their median, percentile, and maximum concentration values are shown in Table 3. In addition, the concentration ranges for all flame retardants from the eight WWTPs can be found in Tables 4 and 5. Moreover, removal

Table 3 | Statistical results of the most frequently detected PBDEs and nFRs in influent, effluent, and biosolids samples from eight WWTPs in Canada; units of median, maximum, 25th and 75th percentiles values for liquid and solid samples are in ng L^{-1} and ng g^{-1} dw (dry weight), respectively. The total number of samples analyzed is shown in parentheses

	BDE47	BDE99	BDE100	BDE153	BDE154	BDE209	BTBPE	TBB	TBPH	Total DP
Influent (93)										
Number of detects	93	93	93	79	93	93	93	93	76	93
25 percentile	25	22	9	2	2	20	2	67	40	39
Median	39	42	10	3	3	44	5	119	85	73
75 percentile	51	60	12	5	5	86	6	163	139	116
Maximum	79	126	38	14	18	443	25	477	326	247
Effluent (93)										
Number of detects	63	84	83	25	72	51	50	83	53	93
25 percentile	1	0.8	0.3	0.2	0.1	2	0.4	2	5	10
Median	2	3	0.8	0.2	0.4	4	0.7	5	10	27
75 percentile	7	7	1	0.4	0.7	9	1	12	19	42
Maximum	14	15	3	3	1	34	7	29	44	139
Biosolids (58)										
Number of detects	52	58	58	49	48	58	50	58	49	58
25 percentile	179	127	34	12	19	153	4	112	149	222
Median	276	319	56	29	28	395	7	181	279	340
75 percentile	365	458	73	43	41	641	14	402	710	443
Maximum	731	954	139	85	91	4,541	54	1,227	1,820	740

Table 4 | The detected concentration ranges for polybrominated diphenyl ethers (PBDEs) in influent (ng L^{-1}), effluent (ng L^{-1}), and biosolids (ng g^{-1}) samples from eight Canadian wastewater treatment plants, not detected (n.d) is below the instrumental detection limit (Table 2)

WWTPs	BDE17	BDE28 = 33	BDE47	BDE66	BDE85	BDE99	BDE100	BB101	BDE138	BDE153	BDE154	BDE183	BDE190	BDE209
Plant F														
Influent	n.d	n.d	38.6–55.3	n.d	1.85–3.9	50.0–100.0	8.4–18.4	n.d	n.d–0.6	3.0–6.5	3.6–10.5	n.d	n.d	11.0–327.1
Effluent	n.d	n.d	n.d–11.8	n.d	n.d–0.49	1.1–14.5	0.6–2.8	n.d	n.d–0.1	0.4–0.7	n.d–1.5	n.d	n.d	n.d–7.0
Biosolids	n.d	n.d	46.0–550.2	n.d	n.d	11.4–625.9	10.1–98.8	n.d	1.4–2.8	3.9–47.3	3.1–54.7	n.d	n.d–0.2	12.3–786.0
Plant HG														
Influent	n.d	n.d	13.5–78.7	n.d	0.7–5.9	17.9–126.0	3.2–33.1	n.d	n.d–3.2	1.3–14.0	0.7–18.0	n.d	n.d	7.1–124.6
Effluent	n.d	nd	n.d–0.9	n.d	n.d	n.d–0.89	n.d–1.0	n.d	n.d	n.d–0.7	n.d–0.66	n.d	n.d	n.d–2.0
Biosolids	n.d–28.0	n.d–11.5	88.7–730.5	n.d	n.d–16.2	75.1–954.1	18.3–139.0	n.d	3.2–8.4	5.5–34.4	6.4–91.2	n.d	n.d	25.3–4541.3
Plant Q														
Influent	n.d	n.d	9.3–43.6	n.d	n.d–2.7	0.4–59.4	2.9–11.5	n.d	n.d–0.6	0.8–4.3	0.8–4.3	n.d	n.d	9.6–123.8
Effluent	n.d	n.d	n.d–4.0	n.d	n.d–2.6	0.2–8.7	0.2–1.4	n.d	n.d	n.d–0.4	0.1–2.5	n.d	n.d	n.d–33.6
Biosolids	n.d–8.8	n.d–9.0	67.6–538.6	n.d	n.d–18.25	17.1–621.1	9.0–99.9	n.d	n.d–4.5	n.d–49.6	16.3–55.4	n.d	n.d	78.8–1404.0
Plant J														
Influent	n.d	n.d	19.5–56.5	n.d	0.6–2.8	0.9–70.9	3.9–13.1	n.d	n.d–0.5	2.0–7.9	0.8–7.9	n.d	n.d	22.6–139.6
Effluent	n.d	n.d	n.d–1.9	n.d	n.d	n.d–0.4	n.d–1.2	n.d	n.d	n.d–0.7	n.d–0.7	n.d	n.d	n.d–2.2
Plant E														
Influent	n.d	n.d	20.8–70.8	n.d	2.5–8.3	n.d–83.9	1.3–17.1	n.d	n.d	0.4–4.4	0.9–7.1	n.d	n.d	21.1–307.7
Effluent	n.d	n.d	n.d–1.3	n.d	n.d–0.2	n.d–1.5	n.d–0.8	n.d	n.d	n.d–0.3	n.d–0.3	n.d	n.d	n.d–1.4
Biosolids	n.d	n.d	158.7–533.9	n.d	n.d–16.1	212.3–629.1	41.1–95.9	n.d	n.d–4.0	21.8– 41.4	14.5–50.4	n.d	n.d	386.5–2620.3
Plant U														
Influent	n.d	n.d	12.8–39.2	n.d	0.4–16.2	0.6–42.4	2.6–9.8	n.d	n.d	0.8–3.6	1.1–3.8	n.d	n.d	5.9–129.7
Effluent	n.d	n.d	2.4–12.2	n.d	n.d–11.8	0.6–14.8	0.7–3.4	n.d	n.d	0.4–1.1	0.3–1.4	n.d	n.d	n.d–11.2
Biosolids	n.d	n.d	n.d–166.0	n.d	n.d	8.7–187.3	2.7–34.5	n.d	n.d–1.3	1.2–13.5	3.4–18.5	n.d	n.d	8.3–544.6
Plant R														
Influent	n.d	n.d	20.6–70.6	n.d	0.3–6.0	1.3–93.7	4.8–38.1	n.d	n.d	0.3–7.4	2.1–11.8	n.d	n.d	7.7–197.0
Effluent	n.d	n.d	n.d–2.0	n.d	n.d	n.d–2.0	0.2–1.1	n.d	n.d	n.d–0.2	n.d–0.1	n.d	n.d	n.d–1.9
Plant TB														
Influent	n.d	n.d	23.4–224.9	n.d	0.9–2.6	0.9–94.5	6.3–24.7	n.d	n.d–0.5	0.23–7.2	0.6–5.4	n.d	n.d	27.1–443.7
Effluent	n.d	n.d	n.d–9.2	n.d	n.d–0.5	3.2–14.7	0.9–2.6	n.d	n.d–0.1	n.d –.4	n.d–1.5	n.d	n.d	n.d–32.3

Table 5 | The detected concentration ranges for novel brominated and chlorinated flame retardants in influent (ng L^{-1}), effluent (ng L^{-1}), and biosolids (ng g^{-1}) samples from eight Canadian wastewater treatment plants, not detected (n.d) is below the instrumental detection limit (Table 2)

WWTPs	ATE	BATE	BTBPE	DPTE	HBB	OBIND	PBBA	PBBE	PBEB	PBTO	PTBX	TBB	TBPH	Total DP	TBCT
Plant F															
Influent	n.d	n.d	2.3–6.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	155.4–289.7	77.0–174.0	29.0–173.5	n.d
Effluent	n.d	n.d	n.d–1.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	5.4–29.2	6.8–54.0	6.8–54.0	n.d
Biosolids	n.d	n.d	n.d–11.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	72.3–1,226.8	n.d–384.8	163.9–384.8	n.d
Plant HG															
Influent	n.d	n.d	1.2–13.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	44.2–172.6	37.6–180.0	18.4–146.6	n.d
Effluent	n.d	n.d	n.d–0.9	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d–1.5	n.d–8.0	2.0–49.5	n.d
Biosolids	n.d	n.d	n.d–23.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	5.4–540.1	n.d–1,820.3	219.0–739.6	n.d
Plant Q															
Influent	n.d	n.d	0.6–8.5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	14.8–141.6	0.4–180.1	29.3–212.7	n.d
Effluent	n.d	n.d	n.d–1.8	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.0–11.3	n.d–19.3	10.4–95.6	n.d
Biosolids	n.d	n.d	n.d–54.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	92.3–910.2	n.d–1,315.9	171.4–623.4	n.d
Plant J															
Influent	n.d	n.d	0.5–4.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	51.9–476.8	1.8–272.9	55.9–99.7	n.d
Effluent	n.d	n.d	n.d–0.5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d–3.0	n.d	22.2–33.2	n.d
Plant E															
Influent	n.d	n.d	2.8–3.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	113.2–222.2	2.3–325.9	35.9–78.4	n.d
Effluent	n.d	n.d	n.d–0.6	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d–4.7	n.d–8.8	7.8–49.9	n.d
Biosolids	n.d	n.d	n.d–24.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	123.2–1,019.8	n.d–993.6	153.5–515.6	n.d
Plant U															
Influent	n.d	n.d	0.6–9.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	11.2–87.6	10.2–172.9	17.2–177.9	n.d
Effluent	n.d	n.d	n.d–6.9	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	4.6–23.9	n.d–21.5	8.4–103.8	n.d
Biosolids	n.d	n.d	n.d–8.9	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	23.3–333.0	n.d–254.2	96.4–458.2	n.d
Plant R															
Influent	n.d	n.d	5.3–20.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	81.7–351.4	35.9–231.7	25.2–201.7	n.d
Effluent	n.d	n.d	n.d–1.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.5–5.5	n.d–16.1	3.9–31.4	n.d
Plant TB															
Influent	n.d	n.d	1.3–12.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	13.2–163.4	7.7–166.0	26.8–246.6	n.d
Effluent	n.d	n.d	n.d–3.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.2–21.0	n.d–44.3	4.3–138.6	n.d

efficiency of total PBDEs and nFRs in wastewater samples from different types of liquid treatment processes was investigated (Figure 1) and correlations between seasonal, annual, and input variations were also examined.

PBDEs

Although octa-BDE and penta-BDE have been banned in use of all applications since 2004, PBDEs have not been fully removed from the environment due to continual release from in-use products. Herein, the percent detection of frequently found PBDE congeners, the penta-BDE mixture (47, 99, 100, 153, and 154) and the major deca-BDE (209), in the influent wastewater samples was 100%, 100%, 100%, 85%, 100%, and 100%, respectively. The total concentration of ΣPBDE (BDE 47, 99, 100, 153, and 154) ranged from 39 to 262 ng L^{-1} in influent and from not detected (nd) to 33 ng L^{-1} in effluent, while the concentrations of BDE 209 ranged from 6 to 443 ng L^{-1} in influent and from not detected to 34 ng L^{-1} in effluent

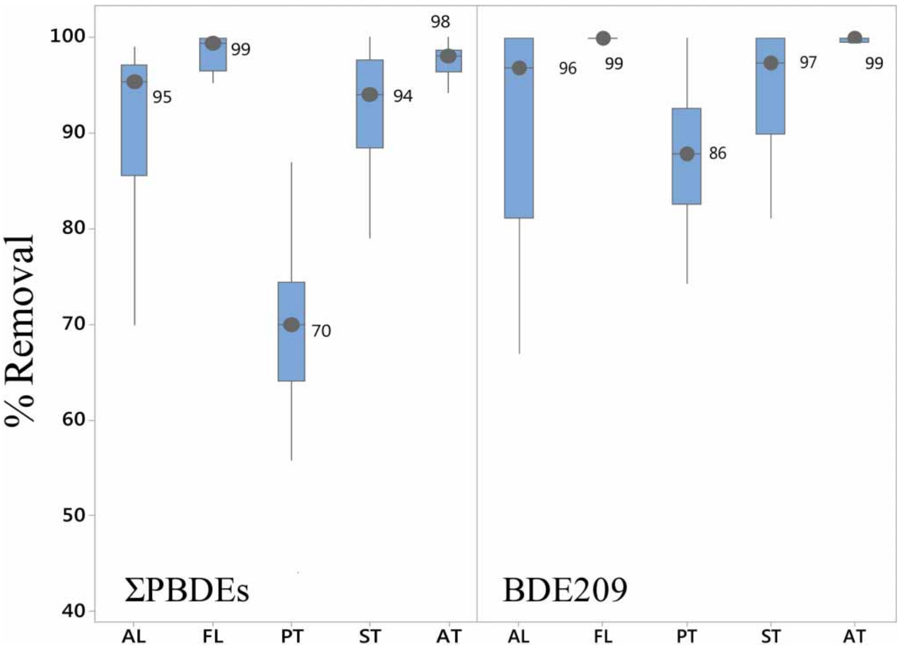

Figure 1 | Boxplots of removal efficiencies for ΣPBDEs (BDE 47, 99, 100, 153, and 154) and BDE209 via different types of liquid treatments, aerated lagoons (AL), facultative lagoons (FL), primary treatment (PT), secondary treatment (ST), and advanced treatment (AT). Percentiles are shown: minimum, 25th, 75th, and maximum. The horizontal line, dot, and numbers shown next to boxplots are median values.

samples. The total concentration of ΣPBDE from this study is comparable with a previous study (Kim *et al.* 2013a) in which ΣPBDE (BDE 47, 99, 100, 153, 154, and 209) in influent and effluent collected from 20 Canadian WWTPs ranged from 21 to 1,000 ng L^{-1} and from 3 to 270 ng L^{-1}, respectively.

Removal efficiencies of total PBDEs and BDE 209 in wastewater by various treatment types, including AL, FL, PT, ST, and AT are presented in Figure 1. Greater than 94% median removal efficiencies of PBDEs were observed in AL, FL, ST, and AT, while the PT rendered a median of 70% removal. Similarly, greater than 96% median removal efficiencies of BDE 209 were observed in AL, FL, ST, and AT, while there was removal of a median of 86% in the PT. However, PBDE removal rates can be strongly influenced by environmental and operational factors, such as season (summer vs. winter water temperatures), treatment type (biological vs. physical/chemical), size (urban with residential and industrial contributions vs. semi-rural with only residential contributions), and configurations and process complexity (aerobic treatment only vs. aerobic/anoxic/anaerobic treatment); a recent study investigated the influence of these factors on PBDE removal (Kim *et al.* 2013a). In this study, a higher concentration of ΣPBDE was observed in the influent collected in summer than in winter, while no statistically significant annual variations or domestic vs. industrial input variations were observed over three years (2013–2015, $p < 0.05$, data not shown).

PBDEs are adsorbed onto suspended solids in wastewater due to their physico-chemical properties such as a high octanol-water partition coefficient (K_{ow}) and a high organic carbon-water partition coefficient (K_{oc}). In this study, 58 treated biosolids samples were collected over a three-year period (2013–2015) from five WWTPs. The percent detection of frequently found PBDE congeners, BDE – 47, 99, 100, 153, 154, and 209, in the biosolids were 90%, 100%, 100%, 84%, 83%, and 100%, respectively as shown in Table 3. The total concentrations of major PBDE congeners in biosolids samples were in the range of 70 to 6,390 ng g^{-1} dry weight (dw), falling in the range previously reported for North America as shown in Table 6 (Hale *et al.* 2001; North 2004; Rayne & Ikonomou 2005; Song *et al.* 2006). In addition, deca-BDE (BDE 209) was the predominant congener found in the wastewater and biosolids samples as shown in Table 6.

Table 6 | Comparison of range PBDE concentrations (ng g^{-1}, dry weight) in biosolids from this study (Canadian WWTPs) with those reported in other regions in Canada and United States

Locations	**BDE47**	**BDE99**	**BDE100**	**BDE153**	**BDE154**	**BDE209**	**ΣPBDE**
Present study (8 WWTPs), Canada	92–731	100–954	16–139	7.0–85	7.0–91	140–4,541	362–6,541
Windsor STP ON, Canada	407–971	540–1,267	89–211	69–145	36–145	n.d	1,141–2,739[a]
Kelowna STP BC, Canada	518	675	103	101	57	n.d	1,455[b]
Palo Alto STP CA, USA	722–778	894–973	158–172	83–91	61–72	1,010–1,440	2,928–3,535[c]
Samples from Virginia, Mayland, New York and California (11 samples)	359–754	931–1,157	89–255	56–199	58–173	85–4,890	1,578–7,428[d]

[a] Song *et al.* (2006).
[b] Andrade *et al.* (2010).
[c] North (2004).
[d] Hale *et al.* (2001).

2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethyl-1 hexyl)tetrabromophthalate (TBPH)

TBB and TBPH are two major components in a commercial mixture which is a replacement for penta-BDE in polyurethane foam applications (Houde *et al.* 2014). Both of these chemicals have been previously detected in house dust, air, and biosolids or sludge samples at concentrations approaching the concentration of PBDEs (Table 7) (Klosterhaus *et al.* 2008; Stapleton *et al.* 2008; Covaci *et al.* 2011; Davis *et al.* 2012; Lankova *et al.* 2013; Houde *et al.* 2014). To the best of our knowledge, this study is the first to report concentrations of TBB and TBPH in influent, effluent, and biosolids samples, as well as their removal efficiency via various types of treatments in Canadian WWTPs. The concentrations of TBB ranged from 11 to 477 ng L^{-1}, nd to 29 ng L^{-1}, and 5 to 1,227 ng g^{-1} dw, while the concentrations of TBPH ranged from 0.4 to 326 ng L^{-1}, nd to 44 ng L^{-1}, and 56 to 1,820 ng g^{-1} dw in influent, effluent, and biosolids samples, respectively, as shown in Table 7. The concentrations of TBB and TBPH measured in influent, effluent, and biosolids in this study are comparable to the ranges reported in a previous study from North America, as shown in Table 7 (Schreder & La Guardia 2014).

The mass ratio of TBB/TBPH in a commercial mixture is approximately 4:1; however, among the biosolids samples analyzed the ratio was 1:7. The lower ratio of TBB/TBPH in the biosolids samples suggests contributions from sources other than the commercial mixture. For instance, TBPH is the sole component of a liquid flame retarded plasticizer (Xiao *et al.* 2012); the use of TBPH in other unknown commercial products could have contributed to the TBPH levels in the biosolids. In addition, the discrepancy ratio of TBB/TBPH in biosolids from this study may suggest different migration or degradation behaviors of TBB relative to TBPH, both in consumer products and during the wastewater treatment process.

Greater than 96% median removal efficiency of TBB was observed for AL, FL, ST, and AT, while the PT rendered a median of 63% removal, presented in Figure 2. In contrast, a median of over 88% removal efficiency of TBPH was

Table 7 | Comparison of concentration ranges of novel brominated flame retardants (BTPBPE, TBB, and TBPH) in wastewater (ng L^{-1}) and biosolids (ng/g, dry weight) samples from Canadian WWTPs in this study with those reported in other regions in Canada, United States and China (house dust, ng g^{-1} or μg kg^{-1}, dw)

Locations	**BTBPE**	**TBB**	**TBPH**
Present study (8 WWTPs): Influent	0.6–25	11–477	0.4–326
Effluent	n.d–7	n.d–29	n.d–44
Biosolid	2.0–54	5.0–1,227	56–1,820
USA (sewage sludge)	no data	120–3,749	206–1,631[a]
Lake Ontario surface sediment	2.7–3.8	no data	no data[b]
China (sewage sludge samples from 21 provinces)	0.1–2.26	no data	no data[c]
USA (house dust)	1.6–789	6.6–15,030	1.5–10,630[d]
Canada (house dust)	no data	no data	15–22,251[e]

[a] Davis *et al.* (2012).
[b] Zeng *et al.* (2014).
[c] Davis *et al.* (2015).
[d] Stapleton *et al.* (2008).
[e] Yang *et al.* (2012).

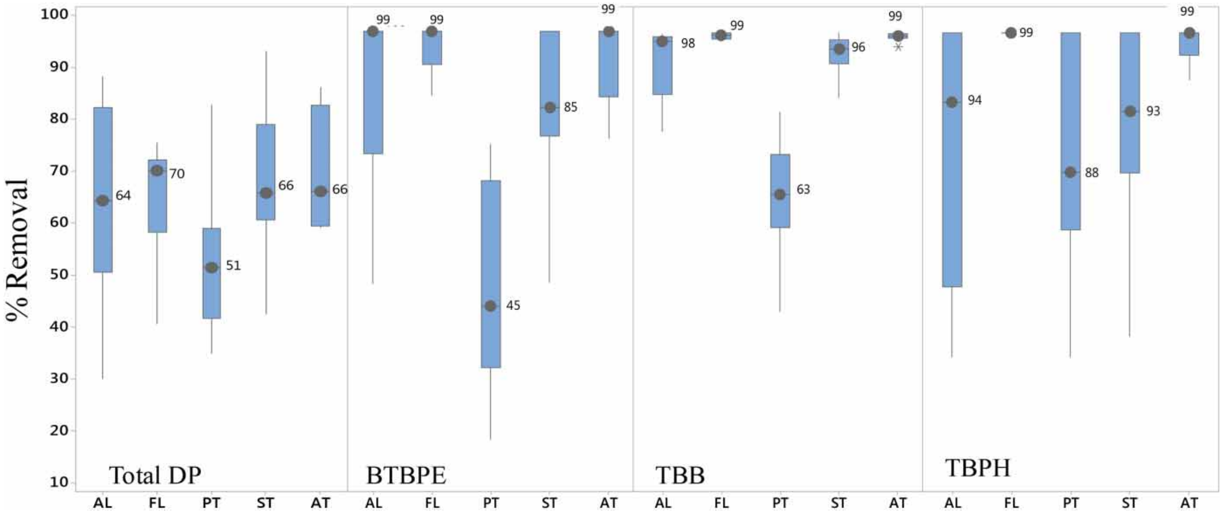

Figure 2 | Boxplots of removal efficiencies for novel brominated flame retardants (BTBPE, TBB, and TBPH) and chlorinated flame retardant, dechlorane plus (syn- and anti-DP), via different types of liquid treatment processes, aerated lagoons (AL, $n = 26$), facultative lagoons (FL, $n = 8$), primary treatment (PT, $n = 11$), secondary treatment (ST, $n = 39$), and advanced treatment (AT, $n = 9$). Percentiles are shown: minimum, 25th, 75th, and maximum. The horizontal line, dot, and numbers shown next to boxplots are median values and asterisks inside the box represent outliers.

observed for PT, AL, FL, ST, and AT. The lower removal efficiency of TBB relative to TBPH in PT may be governed by differences in their physico-chemical properties, including water solubility constant (Log S), octanol-water partition coefficient (Log K_{ow}) and soil organic carbon-normalized adsorption constant (Log K_{OC}). TBB has a higher water solubility constant (Log S: 8.21) but lower octanol-water partition and organic carbon adsorption constants (Log K_{ow}: 8.8 and Log K_{OC}: 5.7) than does TBPH (Log S: 11.6, Log K_{ow}: 12, and Log K_{OC}: 7.4) (Davis *et al.* 2012, 2015).

1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)

BTBPE (log $K_{ow} \sim 7.88 \pm 0.86$) is an additive FR used as a replacement for octa-BDE since 2005 (Covaci *et al.* 2011). The major applications of BTBPE as an additive are in high impact polystyrene (HIPS), thermoplastics, textiles, acrylonitrile butadiene styrene (ABS), polypropylene, and polycarbonate; estimated worldwide production and usage of BTBPE was approximately 16,710 tons in 2001 (Xiao *et al.* 2012; Zeng *et al.* 2014). It was previously reported that BTPBE was frequently detected in the environment, for example, in indoor dust, sludge, sediment, and biota; high concentrations of BTPBE were detected in indoor dust samples in Europe, the United States, and China (octanol-air partition constant, $K_{OA} \sim 15$) (Stapleton *et al.* 2008; Xiao *et al.* 2012; Yang *et al.* 2012; Zeng *et al.* 2014 ; Peng *et al.* 2015). In this study, the concentrations of BTBPE ranged from 0.6 to 25 ng L^{-1}, nd to 7 ng L^{-1}, and 2–54 ng g^{-1} dw in influent, effluent, and biosolids samples, respectively (Table 7). It was recently reported that the concentrations of BTBPE found in biosolids samples from 20 different Canadian WWTPs ranged from 0.005 to 140 ng g^{-1}, which was approximately three times higher than the concentrations found in this study. In contrast, the concentrations of BTBPE found in surface sediment from Lake Ontario (2.7 to 3.8 ng g^{-1}) were about an order of magnitude lower than BTBPE concentrations found in biosolids from this study. Furthermore, it was reported that median removal efficiencies of BTBPE across 20 Canadian WWTPs ranged from 61% to 97%, whereas in this study a greater than 85% median removal efficiency of BTPBE was observed in AL, FL, ST, and AT, but the PT removed a median of only 45% of BTPBE as shown in Figure 2.

Dechlorane plus (DP)

Two stereoisomers, syn and anti, are present at an approximate ratio of 1:2, respectively, in the dechlorane plus (DP) technical mixture (De la Torre *et al.* 2011). It was previously shown that the total DP concentration in suspended sediment samples collected from the Niagara River had been declining, from 89 ng g^{-1} to 7.0 ng g^{-1}, for over two decades (1980 to 2002) (Qiu *et al.* 2007; Sverko *et al.* 2008; De la Torre *et al.* 2011). However, a recent study reported the presence of DP in the eggs of peregrine falcons nesting in the Canadian Great Lakes and the Maritimes; DP was detected in all eggs with concentration ranging from 6.3 to 209 ng/g lw (lipid weight) (Guerra *et al.* 2011). The present study investigated the presence of syn- and anti-DP in wastewater and biosolids samples collected over a three-year period. The pre-treated (extraction/column clean up) wastewater and biosolids samples were stored in iso-octane at −20 °C. The percent detection of total DP was greater than 90% in both wastewater and biosolids samples, ranged from 17 to 247 ng L^{-1}, 2 to 139 ng L^{-1}, and 96 to 740 ng g^{-1} dw in influent, effluent, and biosolids, respectively. Similar to PBDEs, DP also has a relatively high affinity for lipids and solid particles due to its high molecular weight and high log Kow (9.3). Unlike the PBDEs, DP median removal efficiencies were lower and ranged from 51% to 70% for AL, FL, ST, PT, and AT treatment processes as shown in Figure 2. In addition, higher concentrations of total DP were found in influent samples collected in winter relative to summer, whereas no statistically significant correlations were found between total DP concentrations and annual or input variations ($p < 0.05$, data not shown). Syn-DP not being detected in any of the wastewater or biosolids samples could be due to conversion of syn-DP to anti-DP under extended storage conditions. This hypothesis was tested by analyzing pre-treated influent samples that were only stored for a few days at −20 °C, and syn-DP was detected in those samples. However, the conversion of syn-DP to anti-DP under extended storage conditions and low removal efficiency of DP within different liquid treatment processes in WWTPs will be investigated further.

CONCLUSIONS

This study evaluated the concentrations of PBDEs and novel halogenated flame retardants in wastewater and biosolids samples collected over a three-year period from eight Canadian WWTPs, representing a diverse range of treatment processes including two AL, one facultative lagoon, one PT plant, three ST plants, and one AT plant. Among the 15 PBDEs analyzed, the highest concentrations detected were deca-BDE (BDE-209) in influent and biosolids samples. Furthermore, three novel BFRs, TBPH, BTBPE, and TBB, were frequently detected in influent and biosolids samples, although at lower concentrations than BDE-209. All WWTPs reduced levels of TBB and BTBPE in wastewater; however, the PT process had relatively low removal efficiency for these compounds. In addition, WWTPs did not effectively remove high levels of the DP found in influent and biosolids samples; only 66% median removal of DP was observed in AT. Despite the effective removal of PBDEs in WWTPs, some nFRs, including BTBPE, TBB, and DP, have lower removal rate in WWTPs, which could be due to their physical/chemical properties. Further study is required to investigate conditions that would improve the removal efficiency of these nFRs both in biosolids and in effluent samples prior to discharge to the environment.

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