The presence of plasticizers, bisphenols, and flame retardants in potable water and their removal through conventional drinking water treatment

Leena Struzina

McGill University

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Abstract

Humans are regularly exposed to a wide array of chemicals everyday through consumer products. Many of these chemicals are at very low concentrations and do not present any significant health risk; however, some chemicals have the potential to cause serious adverse health effects even at low concentrations. Certain bisphenols, plasticizers, and flame retardants are receiving growing attention as they have recently been classified as proven or potential endocrine disrupting chemicals (EDCs), meaning they mimic hormones in the human body and can be associated with altered reproduction in males and females, abnormal growth patterns and neurodevelopmental delays in children. Governments around the world have implemented regulations regarding the production and importation of certain EDCs, such as bisphenol A (BPA), and this has led to the development of replacement chemicals. Unfortunately, these replacement chemicals are not always thoroughly tested for low-dose or long-term toxicity. Contaminated potable water, which can be caused by contaminated water sources, insufficient water treatment technologies, or contaminated piping and packaging, is one route of human exposure to flame retardants, bisphenols, and plasticizers.

The present Master's thesis quantified 39 contaminants including flame retardants, bisphenols, and plasticizers in potable water from Montreal and South Africa, and assessed the removal of these contaminants through a conventional drinking water treatment plant (DWTP). Human exposure to contaminants through potable water was assessed, which included five bottled water (BW) brands and three DWTPs in Montreal, and water from one urban DWTP located in Pretoria, and one rural DWTP located in Vhembe, along with water from the same DWTP which had been stored in small and large plastic containers in a rural area. A combination of legacy compounds, typically with proven toxic effects, and replacement compounds were investigated. Bisphenols, DEC-602, DEC-603, and s-DP were not detected in any water samples, and a-DP was only detected in one sample from Pretoria at a concentration of 1.09 ng/L. Lower brominated PBDEs were detected more frequently than higher brominated PBDEs, always at low concentrations < 2 ng/L, and total PBDE levels were statistically higher in South Africa than in Montreal. Replacement flame retardants, organophosphate esters (OPEs), were detected at statistically higher concentrations in Montreal's BW (68.6 ng/L), drinking water (DW) (421.5 ng/L) and in Vhembe (198.3 ng/L) than legacy PBDEs. Total OPE concentrations did not demonstrate any geographical trend; however levels were statistically higher in Montreal's DW than Montreal's BW. Plasticizers were frequently detected in all samples, with legacy compounds DEHP, DBP, and replacement DINCH being detected in 100% of samples with average concentrations ranging from 6.8 ng/L for DEHP in Pretoria to 175 ng/L for DINCH in Montreal's DW. Total plasticizer concentrations were higher in Montreal than in South Africa. The replacement plasticizers (DINCH, DINP, DIDA, and DEHA) were detected at similar frequencies and concentrations as legacy plasticizers (DEHP, DEP, DBP) and known toxic metabolite (MEHP).

The removal of these contaminants through conventional drinking water treatment was assessed in a DWTP in Montreal. The DWTP chosen utilized filtration, ultraviolet (UV) treatment, and chlorination, and 24h-composite daily sampling was performed between each treatment step over a three-day period. PBDEs, considered legacy flame retardants, were infrequently detected or at concentrations < 1 ng/L. Removal efficiencies for $\sum_7$ PBDEs was 48.5 and 94.1% on days 2 and 3, respectively, with BDE-183 and BDE-154 only detected in raw water. OPEs, considered replacement flame retardants, were frequently detected in all water samples. The total average concentration of $\sum_{15}$ OPEs was 500 ng/L in raw water and 159 ng/L in drinking water, with an average removal efficiency of 65.8%. The majority of OPE removal was attributed to filtration, which had significant removal of TCIPP (75.9%), TDCIPP (83.6%), and TPHP (94.5%). OPEs proved to be more persistent through drinking water treatment than legacy PBDEs as they were detected at higher frequencies and concentrations throughout the DWTP. Similar analysis for the removal of target plasticizers and bisphenols is on-going. While conventional drinking water treatment methods have demonstrated some removal of flame retardants, contributing to mitigating exposure to these contaminants, flame retardants are still present at concentrations in the ng/L range. Attention should be drawn to the potential health risks from the mixtures of flame retardants, plasticizers, and bisphenols found in potable water. The concentrations of target analytes found in potable water in this research should be combined with toxicological data for each component to accurately assess the health risk from the mixture of chemicals detected. Additionally, comprehensive toxicological investigations on the human health impact of replacement chemicals should be conducted considering that some of these compounds, such as OPEs, are consistently being detected in potable water throughout the world.

Résumé

Les humains sont régulièrement exposés à un large éventail de produits chimiques par l'entremise de produits de consommation. Bon nombre de ces produits chimiques sont présents à de très faibles concentrations et ne présentent pas de risque important pour la santé. Cependant, certains produits ont le potentiel de causer des effets néfastes sur la santé, même à de faibles concentrations. Certains bisphénols, plastifiants et retardateurs de flamme font l'objet d'une attention croissante car ils ont récemment été classés comme perturbateurs endocriniens (PE) avérés ou potentiels, ce qui signifie qu'ils imitent les hormones du corps humain et peuvent être associés à une altération de la reproduction chez les mâles et les femelles, à des schémas anormaux de croissance et des retards neurodéveloppementaux chez les enfants. Plusieurs gouvernements à travers le monde ont mis en place des réglementations concernant la production et l'importation de certains perturbateurs endocriniens, tels que le bisphénol A (BPA), ce qui a conduit au développement de produits chimiques alternatifs. Malheureusement, ces produits de remplacement ne sont pas toujours soigneusement testés avant leur mise en marché pour leur toxicité à faible dose ou à long terme. L'eau potable contaminée, qui peut être due à des sources d'eau contaminées, des technologies de traitement de l'eau insuffisantes ou des canalisations et des emballages contaminés, est une voie potentielle d'exposition humaine aux retardateurs de flamme, aux bisphénols et aux plastifiants.

Le présent mémoire de maîtrise présente la quantification de 39 contaminants, y compris des retardateurs de flamme, des bisphénols et des plastifiants dans l'eau potable de Montréal (Canada) et de Prétoria et Vhembe (Afrique du Sud), et l'élimination de ces contaminants lors d'un traitement d'eau potable (DWTP) conventionnel. La présence des contaminants dans l'eau potable a été quantifiées dans cinq marques d'eau embouteillée (BW) et trois stations d'épuration à Montréal, ainsi que dans l'eau d'une station de traitement urbaine située à Pretoria et d'une station de traitement rurale située à Vhembe. L'analyse inclut également l'eau de la même station de traitement de Vhembe qui avait été stockée dans des petits et grands conteneurs en plastique dans une zone rurale. Les composés cibles comportaient des composés utilisés depuis plusieurs années, ayant généralement des effets négatifs prouvés, et de composés de remplacement peu étudié jusqu'à maintenant.

Les bisphénols, DEC-602, DEC-603 et s-DP n'ont été détectés dans aucun échantillon d'eau, et l'a-DP n'a été détecté que dans un échantillon de Pretoria à une concentration de 1,09 ng/L. Les PBDE moins bromés ont été détectés plus fréquemment que les PBDE plus bromés, toujours à de faibles concentrations < 2 ng/L, et les niveaux de PBDE totaux étaient statistiquement plus élevés en Afrique du Sud qu'à Montréal. Les produits ignifuges de remplacement, les esters organophosphorés (OPE), ont été détectés à des concentrations statistiquement plus élevées dans le BW de Montréal (68,6 ng/L), l'eau potable (DW) (421,5 ng/L) et à Vhembe (198,3 ng/L) que les anciens PBDE. Les concentrations totales d'OPE n'ont démontré aucune tendance géographique; cependant, les niveaux étaient statistiquement plus élevés dans le DW de Montréal que dans le BW de Montréal. Des plastifiants ont été fréquemment détectés dans tous les échantillons, avec le DEHP, DBP et DINCH détectés dans 100 % des échantillons à des concentrations moyennes allant de 6,8 ng/L pour le DEHP à Pretoria à 175 ng/L pour le DINCH dans le DW de Montréal. Les concentrations totales de plastifiants étaient plus élevées à Montréal qu'en Afrique du Sud. Les plastifiants de remplacement (DINCH, DINP, DIDA et DEHA) ont été détectés à des fréquences et des concentrations similaires à celles des plastifiants traditionnels (DEHP, DEP, DBP et MEHP).

L'élimination de ces contaminants par le traitement conventionnel de l'eau potable a été évaluée dans une station d'épuration à Montréal. Le DWTP choisi utilisait une filtration, un traitement aux ultraviolets (UV) et une chloration, et un échantillonnage quotidien composite sur 24 heures a été effectué entre chaque étape de traitement sur une période de trois jours. Les PBDE, considérés comme des retardateurs de flamme traditionnels, ont été détectés peu fréquemment ou à des concentrations < 1 ng/L. L'efficacité d'élimination des $\sum_{7}$ PBDE était de 48,5 et 94,1 % aux jours 2 et 3, respectivement, le BDE-183 et le BDE-154 n'étant détectés que dans l'eau brute. Les OPE, considérés comme des retardateurs de flamme de remplacement, ont été fréquemment détectés dans tous les échantillons d'eau. La concentration moyenne totale des $\sum_{15}$ OPE était de 500 ng/L dans l'eau brute et de 159 ng/L dans l'eau potable, avec une efficacité d'élimination moyenne de 65,8 %. La majorité de l'élimination de l'OPE a été attribuée à la filtration, qui a entraîné une élimination significative du TCIPP (75,9 %), du TDCIPP (83,6 %) et du TPHP (94,5 %). Les OPE se sont avérés plus persistants dans le traitement de l'eau potable que les PBDE traditionnels, car ils ont été détectés à des fréquences et des concentrations plus élevées dans l'ensemble de la station de traitement. Une analyse similaire pour l'élimination des plastifiants et des bisphénols cibles est en cours. Bien que les méthodes conventionnelles de traitement de l'eau potable aient démontré une certaine élimination des retardateurs de flamme, contribuant à atténuer l'exposition à ces contaminants, les retardateurs de flamme sont toujours présents à des concentrations de l'ordre du ng/L. Il convient d'attirer l'attention sur les risques potentiels pour la santé des mélanges de retardateurs de flamme, de plastifiants et de bisphénols présents dans l'eau potable. Les concentrations d'analytes cibles trouvées dans l'eau potable dans cette recherche doivent être combinées avec des données toxicologiques pour chaque composant afin d'évaluer avec précision le risque pour la santé du mélange de produits chimiques détectés. De plus, des enquêtes toxicologiques approfondies sur l'impact sur la santé humaine des produits chimiques de remplacement devraient être menées étant donné que ces composés ont une fréquence élevée de détection dans l'eau potable à travers le monde.

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Abbreviations

Abbreviation	Definition
a-DP	Anti-dechlorane plus
BBOEP	Bis(2-butoxyethyl) phosphate
BCEP	Bis(2-chloroethyl) phosphate
BCPP	Bis(1-chloro-2-propyl) phosphate
BDCIPP	Bis(1,3-dichloro-2-propyl) phosphate
BEHP	Bis(2-ethylhexyl) phosphate
BPA	Bisphenol A
BPAF	Bisphenol AF
BPF	Bisphenol F
BPS	Bisphenol S
BW	Bottled water
DBP	Dibutyl phthalate
DC	Dechlorane
DCP	Di-cresyl phosphate
DEHA	Bis(2-ethylhexyl) adipate
DEHP	Bis(2-ethylhexyl) phthalate
DEC-602	Dechlorane 602
DEC-603	Dechlorane 603
DEP	Diethyl phthalate
DIDA	Diisodecyl adipate
DINCH	Bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate
DINP	Diisononyl phthalate
DMDCS	Dimethyldichlorosilane
DPHP	Diphenyl phosphate
DW	Drinking water
DWTP	Drinking water treatment plant
ECNI	Electron capture negative ionization
EDC	Endocrine disrupting chemical
GAC	Granulated activated carbon
GC	Gas chromotography
HCl	Hydrochloric acid
HRMS	High resolution mass spectrometry
IDL	Instrument detection limit
Ip-PPP	4-Isopropylphenyl phenyl phosphate
LOD	Limit of detection
LOQ	Limit of quantification
MDL	Method detection limit
MEHP	Mono(ethylhexyl) phthalate
MeOH	Methanol
MS	Mass spectrometry
MtBE	Methyl tert-butyl ether
ND	Non-detect
OPE	Organophosphate ester
PBDE	Polybrominated Diphenyl Ethers
s-DP	Syn-dechlorane plus
SIN	Single ion monitoring
TBOEP	Tris(2-butoxyethyl) phosphate
TCEP	Tris(2-chloroethyl) phosphate
TCIPP	Tris(1-chloro-2-propyl) phosphate
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate

TEHP	Tris(2-ethylhexyl) phosphate
TPHP	Triphenyl phosphate
UPLC	Ultra performance liquid chromatography
UV	Ultraviolet
WWTP	Wastewater treatment plant

Contribution of Authors

Manuscript 1 – Occurrence of flame retardants, bisphenols, and plasticizers in potable water in Montreal and South Africa

Submission to Science of the Total Environment in December 2021.

Author	Contribution
Leena Struzina	Primary author, performed sample preparation, data analysis and results interpretation, prepared the manuscript.
Viviane Yargeau	Contributed to the design of the study and interpretation of results, edited the manuscript.
Marco A. Pineda Castro	Developed methodology for sample extraction, performed analysis of plasticizers in water samples.
Cariton Kubwabo, Shabana Siddique, Gong Zhang	Developed method and performed analysis of PBDEs, OPEs, and dechloranes in water samples.
Mark Misunis	Developed method and performed analysis of PBDEs and dechloranes in Montreal's first campaign.
Lei Tian, Stephane Bayen	Developed method and performed analysis of bisphenols in water samples.
Natalie Aneck-Hahn, Riana Bornman, Jonathan Chevrier	Collected water samples in South Africa.

Manuscript 2 – Removal of flame retardants, bisphenols, and plasticizers through a conventional drinking water treatment plant

Will be submitted to the journal Science of the Total Environment when results for plasticizers and bisphenols will be finalized.

Author	Contribution
Leena Struzina	Primary author, design the study, performed sample collection and preparation, data analysis and results interpretation, prepared the manuscript.
Viviane Yargeau	Contributed to design of the study and the interpretation of results, edited the manuscript.

1 Introduction

1.1 Background

Humans are regularly exposed to a wide array of chemicals everyday through consumer products. Many of these chemicals are at very low concentrations and do not present any significant health risk; however, some chemicals have the potential to cause serious adverse health effects even at low concentrations. Endocrine disrupting chemicals (EDCs) disrupt the body's hormone systems and are associated with altered reproduction in males and females, abnormal growth patterns and neurodevelopmental delays in children, and changes in immune function. Certain bisphenols, plasticizers, and flame retardants are receiving growing attention as they have recently been classified as proven or potential EDCs and are used in a variety of consumer products. Governments around the world have implemented regulations regarding the production, importation and use of certain EDCs, such as bisphenol A (BPA), and this has led to the development of replacement chemicals. Unfortunately, these replacement chemicals are not always thoroughly tested for low-dose or long-term toxicity prior to use.

Contaminated potable water, which can be caused by contaminated water sources, insufficient water treatment technologies, or contaminated piping and packaging, is one route of human exposure to flame retardants, bisphenols, and plasticizers (WHO, 2017). Reporting levels of flame retardants, bisphenols, and plasticizers in potable water is important as this information is used in conjunction with toxicological data for risk assessments and the development of governmental policies such as drinking water quality guidelines. However, there are currently no limits on the concentrations of flame retardants, bisphenols, or plasticizers in Canada's Guidelines for Drinking water Quality (Health Canada, 2020). While some studies have reported EDCs in potable water from developed countries, there is a lack of information available for rural locations or developing countries, and few studies of replacement chemicals or metabolites. Even within a country there is potential for disparities in exposure to EDCs; for examples, some rural areas do not have easy access to potable water so it is collected and stored in plastic containers, which might result in higher risks of contamination.

Therefore, considering the widespread use and persistence of flame retardants, bisphenols, and plasticizers in the environment, it is necessary to quantify the exposure of humans

through drinking water in both urban and rural locations, and determine the efficiency of conventional drinking water treatment as a risk mitigation measure.

1.2 Literature Review

Thirty-nine (39) legacy and replacement EDCs were included in the present research, including proven and potential EDCs. Legacy flame retardants included eight polybrominated diphenyl ethers (PBDEs), while four dechloranes (DCs) and 15 organophosphate esters (OPEs), considered replacements, were also included. For OPEs, six parent compounds and 9 metabolites were studied. BPA was used as the legacy bisphenol, and BPAF, BPF, and BPS were considered replacement compounds. Finally, three phthalates were chosen as legacy plasticizers as well as one metabolite, and two adipates and two high molecular weight alternatives were chosen as replacements. These compounds were chosen in collaboration with the Healthy Environments and Consumer Safety Branch, and the Environmental Health Science & Research Bureau of Health Canada based on criteria detailed in the following sections. A summary of all compounds included in the research along with CAS numbers can be found in Table 1.

1.2.1 Use and health effects of flame retardants

Flame retardants are added to materials such as plastics, wood, paper, and textiles in consumer goods during the manufacturing process to prevent fire from igniting or spreading. An increase in the use of synthetic polymers in household and office products has driven the need for flame retardants, making exposure to these chemicals inevitable. PBDEs, OPEs, and DCs are considered additive flame retardants, meaning they are added into polymers via physical mixing instead of chemical bonding, and this makes them more likely to leach out into the environment (Barcelo and Kostianoy, 2011; Jianhua Li et al., 2019).

PBDEs consist of two phenol rings attached by an ether moiety. Any of the 10 hydrogen atoms on the phenol rings may be replaced by a bromine atom, resulting in 209 possible PBDE congeners. The bioaccumulation potential and level of toxicity is heavily dependent on the bromination level (Environmental Protection Agency, 2017), and studies on rats and mice showed that PBDEs can cause developmental neurotoxicity, endocrine disruption, and pancreas effects (Dorman et al., 2018; Linares et al., 2015). Eight common PBDEs were chosen for investigation in the current research and are listed in Table 1. BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 were chosen as they comprise the majority of the popular commercially available penta-BDE and octa-

BDE mixtures, while BDE-209 and BDE-28 were included to compare high and low bromination level PBDEs.

The environmental persistence, bioaccumulation potential, and toxicity of PBDEs led to a gradual discontinuation of their use in household items since 2004 (Dodson et al., 2012). In fact, the Great Lakes Chemical Corporation, which is the sole PBDE manufacturer in the U.S., discontinued the production of penta- and octa-BDE in 2005 (Great Lakes Chemical Corporation, 2005). These brominated flame retardants were replaced by alternative chemicals with similar properties, a popular commercial alternative being OPEs. Some OPEs are halogenated with chlorine atoms and combine flame retarding properties of both halogenated and phosphorus components (van der Veen and de Boer, 2012). Likewise, Dechlorane plus (DP) has been identified by the U.S. Environmental Protection Agency as a possible replacement for decaBDE (Environmental Protection Agency, 2014). DP and some of its analogs are persistent in some environmental media, however there is a considerable lack of monitoring and toxicity data available (Sverko et al., 2011). Health Canada published a screening assessment for DP in May 2019 and reported low concern for acute toxicity and no adverse health effects in repeated-dose toxicity-testing (Health canada and Environment and Climate Change Canada, 2019).

Various studies have confirmed the adverse health effects of some OPEs, however they do not investigate all 15 compounds of interest in the present research. The main areas of concern are neurotoxicity, endocrine disrupting effects and developmental and reproduction toxicity. Early developmental exposure to TPHP and TDCIPP in zebra fish was linked to behavioural impairment that lasted into adulthood (Yang et al., 2019). Studies comparing OPEs to several PBDEs have concluded that the new substances have similar adverse health effects to their legacy compounds (Behl et al., 2016; Dishaw et al., 2011; Schang et al., 2016). A weight-of-evidence assessment by the European Commission stated that an important effect of TCEP exposure is carcinogenicity, and reproductive toxicity has also been observed in several rat and mice studies (Government of Canada, 2009). Canada has since banned the production or importation of products made with polyurethane foam that contains TCEP and that are intended for children under the age of three (Government of Canada, 2010a).

1.2.2 Use and health effects of bisphenols

Bisphenol A (BPA) is widely used in industrial food applications, mainly as resin lining in food and beverage packaging, and in the manufacture of food additives. BPA is applied in food storage containers and as a lining in metal cans and has been shown to leach out of containers and into food and beverages, especially at high temperatures (Bae et al., 2002). There has been great controversy over low-dose toxicity of BPA and its continued use in the food packaging industry. While BPA has not shown high bioaccumulation potential (Corrales et al., 2015), it is considered an endocrine-disruptor and imitates estrogen in the body leading to adverse health effects, especially in pregnant women and children (T. Özdal and Yeşilcubuk, 2014). The toxicity of BPA has urged researchers to develop a range of new compounds similar to BPA in chemical structure and properties, but with reduced toxicity. Of the 16 bisphenol analogues, 4,4’-methylenediphenol (BPF), 4-hydroxyphenyl sulfone (BPS) and 4,4′-hexafluoroisopropylidene-diphenol (BPAF) are most commonly used in resin linings in place of BPA (Chen et al., 2016), and so were chosen as replacement compounds in the present research. Various studies have investigated the relative toxicity of BPAF, BPS and BPF to their legacy chemical BPA, and found that the substitutes are of similar toxicity, if not more toxic (Rochester and Bolden, 2015).

1.2.3 Use and health effects of plasticizers

Plasticizers are chemical additives that increase the plasticity and fluidity of a material. Plasticizers are frequently added to polymers with the most common application being polyvinyl chloride (PVC), however plasticizers are used in various other products including wires and cables, flooring, coatings, and personal care products (Cadogan, 1991). The Canadian Consumer Product Safety Act has restrictions on DEHP, DINP and DBP in the manufacturing of child care articles, and DEHP has been banned in cosmetics, medical devices and vinyl children’s toys (Minister of Justice, 2017). DEHP, DBP, and DEP were chosen as legacy plasticizers, as well as MEHP, which is a metabolite of DEHP and has demonstrated similar endocrine disrupting properties (Rowdhwal and Chen, 2018).

Plasticizers with higher molecular weights, such as di(isononyl)cyclohexane-1,2-dicarboxylate (DINCH) and DINP, have been introduced as replacements as they are less likely to migrate out of plastics, however recent studies find the toxicity similar to that of legacy compounds (Campioli et al., 2017; Nardelli, 2017). Adipates, classified as low temperature phthalates, have lower molecular weights than legacy phthalates making them ideal for low temperature storage. However, adipates have greater potential to leach relative to phthalates due to their lipophilic properties. Studies have shown that di(2-ethylhexyl) adipate (DEHA) and diisodecyl adipate (DIDA) have much lower toxicity and endocrine disrupting potential (Bui et al., 2016; Van Vliet et al., 2011). DEHA, DIDA, DINCH, and DINP were chosen as replacement plasticizers.

Table 1 – Target flame retardants, bisphenols, and plasticizers included in the present research.

Family	Analyte acronym	Target analyte	CAS number
Plasticizers	DEHP	Bis(2-ethylhexyl) phthalate	117-81-7
	DEP	Diethyl phthalate	84-66-2
	DBP	Dibutyl phthalate	84-74-2
	DEHA*	Bis(2-ethylhexyl) adipate	103-23-1
	DINCH*	Bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate	166412-78-8
	DIDA*	Diisodecyl adipate	27178-16-1
	DINP*	Diisononyl phthalate	68515-48-0
	MEHP†	Mono(ethylhexyl) phthalate	4376-20-9
Flame retardants – OPEs	TBOEP*	Tris(2-butoxyethyl) phosphate	78-51-3
	TCEP*	Tris(2-chloroethyl) phosphate	115-96-8
	TCIPP*	Tris(1-chloro-2-propyl) phosphate	13674-84-5
	TDCIPP*	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8
	TEHP*	Tris(2-ethylhexyl) phosphate	78-42-2
	TPHP*	Triphenyl phosphate	115-86-6
	DPHP†	Diphenyl phosphate	838-85-7
	Ip-PPP†	4-Isopropylphenyl phenyl phosphate	69415-02-7
	BCPP†	Bis(1-chloro-2-propyl) phosphate	789440-10-4
	BCEP†	Bis(2-chloroethyl) phosphate	3040-56-0
	BBOEP†	Bis(2-butoxyethyl) phosphate	14260-97-0
	BDCIPP†	Bis(1,3-dichloro-2-propyl) phosphate	72236-72-7
	BEHP†	Bis(2-ethylhexyl) phosphate	298-07-7
	BTBOEP†	Bis(2-butohexylethyl) 2-Hydroxyethyl Phosphate Triester	1477494-86-2
	DCP†	Di-cresyl phosphate	36400-46-1
Flame retardants – PBDEs	BDE 28	2,4,4'-Tribromodiphenyl ether	41318-75-6
	BDE 47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1
	BDE 99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9
	BDE 100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8
	BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2
	BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4
	BDE 183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5
	BDE 209	Decabromodiphenyl ether	1163-19-5
Flame retardants – Dechloranes	DEC-602*	Dechlorane 602	31107-44-5
	DEC-603*	Dechlorane 603	13560-92-4
	a-DP*	Anti-dechlorane plus	13560-89-9
	s-DP*	Syn-dechlorane plus	135821-03-3
Bisphenols	BPA	Bisphenol A	80-05-7
	BPAF*	Bisphenol AF	1478-61-1
	BPF*	Bisphenol F	620-92-8
	BPS*	Bisphenol S	80-09-1

* Denotes a compound considered a replacement, † Denotes metabolites.

1.2.4 Presence of target analytes in potable water

Flame retardants, bisphenols, and plasticizers have frequently been detected in drinking water throughout the world. A detailed literature review on the presence of all target analytes in various types of potable water can be found in Manuscript 1: Occurrence of plasticizers, bisphenols, and flame retardants in potable water in Montreal and South Africa. A detailed review on the removal efficiencies of drinking water treatment techniques can be found in Manuscript 2: Removal of plasticizers, bisphenols, and flame retardants through a conventional drinking water treatment plant. A brief summary of the reviews follows.

For plasticizers and bisphenols – BPA has been detected in potable water from South Africa at levels ranging from 1.33 – 2.78 ng/L (Aneck-Hahn et al., 2018; Van Zijl et al., 2017), however was not detected above the limit of quantification in a recent study on Montreal's tap water (Goeury et al., 2019). Replacements bisphenols have only been reported in potable water from China and Hong Kong, at levels ranging from below the limit of detection (LOD) to 2.95 ng/L (Li et al., 2021; Wang et al., 2020; Zhang et al., 2019a). Plasticizers have been detected in South Africa's bottled and drinking water at concentrations ranging from <LOD to 3415 ng/L (Aneck-Hahn et al., 2018; Van Zijl et al., 2017), and in Egyptian bottled water from <LOD to 104 ng/L (Zaki and Shoeib, 2018). The only studies investigating potable water from Canada found the concentration in bottled water as high as 1720 ng/L for DBP (Cao, 2008), and concentrations as high as 188 ng/L for DEHP in drinking water (Chen et al., 2006).

For flame retardants – Legacy flame retardants PBDEs and replacement dechloranes have few reports on their presence in drinking water. Only four studies have ever quantified concentrations of PBDEs in drinking water, always at concentrations < 1 ng/L (Fontana et al., 2009; Khan et al., 2016a; L. Liu et al., 2019; Subedi et al., 2015). One study from Pakistan has assessed a-DP and s-DP in drinking water, finding very low concentrations <0.29 ng/L (Khan et al., 2016a), and there are currently no reports for DEC-602 or DEC-603. OPEs are more frequently detected in drinking water, however there are currently no studies from Africa or Canada. In the U.S.A., TCIPP has been detected as high as 220 ng/L in drinking water (Bacaloni et al., 2007), and TBOEP at 10 ng/L in tap water (Kim and Kannan, 2018).

1.2.5 Review of drinking water treatment technologies and their removal of target analytes from water

For bisphenols – BPA has demonstrated good removal through conventional drinking water treatment (72% in Taiwan (H W Chen et al., 2013) and 78.4% in South Korea (Nam et al., 2014)). Bisphenol analogs BPF and BPS has also demonstrated good removal in China, with an advanced drinking water treatment plant (DWTP) showing slightly higher removal efficiencies than a conventional DWTP (Zhang et al., 2013a). There are currently no reports on the removal efficiency of the bisphenol BPAF through drinking water treatment.

For plasticizers – Previously reported removal efficiencies for plasticizers through DWTPs have only included phthalates DEHP, DEP, and DBP, and were all located in Asia (Gou et al., 2016; Kong et al., 2017; Liu et al., 2013; Wang et al., 2015). Removal efficiencies varied between treatment technology and location, but primarily ranged from 35 – 68%.

For flame retardants – Removal efficiencies of OPEs through DWTPs have been reported in the U.S.A. (Padhye et al., 2013) and South Korea (Choo and Oh, 2020; Sim et al., 2021). Advanced treatment plants, including granulated activated carbon (GAC) adsorption have demonstrated removals from 38 – 70% for various OPEs. Few studies have investigated the removal from individual steps in a DWTP, and none have included OPE metabolites. Padhye et al. found that pre-ozonation/flocculation/sedimentation had the highest average removal efficiency (40.5%) for TCEP, followed by intermediate ozonation (38.9%) and filtration/chlorination (31.6%) (Padhye et al., 2013). There are currently no reports on the removal of PBDEs, dechloranes, or OPE metabolites through drinking water treatment.

Conventional drinking water treatment processes involve screening to remove large debris from the raw water, coagulation/flocculation, filtration, and chlorination. Using conventional methods, DWTPs can also apply advanced processes, such as ultraviolet (UV) treatment, ozonation, and GAC adsorption. This section provides a brief overview of the treatment steps.

Coagulation – flocculation is a pre-treatment step in drinking water purification to enhance the removal of suspended solids. The addition of a chemical (generally liquid aluminum polychloride or liquid aluminum chlorohydrate) to raw water helps destabilize the suspension and promote aggregation during flocculation. Gentle mixing helps accelerate the rate of flocculation, where unstable particles are further combined into larger precipitates (Yargeau, 2012). It is possible to apply an in-line coagulant before the filtration step if decanters will not be used in the water treatment process. In this case, decantation is performed directly on the filters.

Filtration removes particulate matter from the water, typically using a media such as sand or silica. Filtration can occur as slow filtration, where the water has a long contact time with the filtration media. Slow filtration is a biological removal process as a bacteria layer forms in the sand and degrades the contaminants, contributing to their removal. In rapid sand filtration, water is forced through the filters and contaminants are removed through the physical process.

Disinfection, which removes bacteria and viruses and leaves a residual disinfectant in the drinking water, is essential to provide safe drinking water and avoid contamination in the distribution system. Chlorination is the most used chemical process in disinfection because it deodorizes while disinfecting, is non-toxic to humans and animals, is commercially available, and is effective at ambient temperatures. Sodium hypochlorite is a common source of chlorine for disinfection as it is safer and less hazardous than chlorine gas and can be produced on-site or can be purchased commercially (Jeny and Naeem, 2008).

In addition to coagulation/flocculation, filtration, and chlorination, common advanced water treatment processes include GAC adsorption, ozonation and UV disinfection. GAC adsorption is the most widely used adsorption method because it is low cost and has a large surface available for adsorption of chemicals. Ozonation destroys bacteria by damaging bacteria cell walls or inhibiting enzyme activity, and leaves viruses inactive. UV disinfection is used to inactivate parasites, bacteria and viruses. The UV light acts directly on the DNA/RNA of cells which disrupts the cell function and reproduction rendering them harmless, and allows the removal of chlorine-resistant organisms.

2 Objectives

Considering the adverse health effects associated with proven and potential EDCs, and the lack of information regarding their presence in potable water or removal during drinking water treatment, there is a need to quantify EDCs in both urban and rural locations and assess their removal through conventional treatment processes. Therefore, the objectives of this research were to:

1. **Characterize potential exposure through bottled and drinking water to 39 targeted legacy and replacement flame retardants, bisphenols and plasticizers while taking into account geographical variations and potential differences between rural and urban areas.**
2. **Evaluate the efficiency of conventional water treatment methods to mitigate exposure to these targeted compounds and identify the most effective removal treatment steps.**

3 Manuscript 1: Occurrence of plasticizers, bisphenols, and flame retardants in potable water in Montreal and South Africa

3.1 Preface

This manuscript addresses the first objective of this Masters research – characterize potential exposure through bottled and drinking water to 39 targeted legacy and replacement flame retardants, bisphenols and plasticizers while taking into account geographical variations and potential differences between rural and urban areas. To address this objective, water samples from Montreal and South Africa were collected and multiple methods developed to analyze water samples for the target analytes.

To assess the difference in levels of contamination between geographical locations, potable water was collected from Montreal and South Africa. In Montreal, bottled water and water from three DWTPs was collected over 3 samples campaigns. In South Africa, water was collected from one urban DWTP (Pretoria), and one rural DWTP (Vhembe). In the rural location, water that was stored in small and large plastic containers was also collected as this is how drinking water is typically stored and consumed. Two sampling campaigns were performed in South Africa.

To detect the target analytes at such low concentrations, a method was required to concentrate the water samples. To achieve this, three solid-phase extraction (SPE) procedures were developed: plasticizers, OPEs, and BPs/PBDEs/dechloranes. Once concentrated, five methods were developed to analyse the concentrations of target analytes. The methods consisted of: gas chromatography coupled with mass spectrometry (GC-MS/MS) for PBDEs, GC-MS for DCs, ultra performance liquid chromatography (UPLC) coupled with mass spectrometry (MS) for OPEs, liquid chromatography coupled with MS for BPs, and liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS) for plasticizers.

The results showed some trends in concentrations of target analytes between locations as well as between replacement and legacy compounds. For flame retardants, replacement OPEs were detected at significantly higher concentrations than legacy PBDEs in Montreal's BW, DW, and South Africa's rural location. Dechloranes, which were also considered a replacement flame retardant, were only detected in one sample from South Africa. Plasticizers had similar concentrations of total legacy vs. replacement compounds in all four locations studied. While the total PBDE concentration was higher in Montreal's water than in South Africa, plasticizers were found at significantly higher concentrations in South Africa. No bisphenols were detected in any water samples.

3.2 Abstract

The occurrence of thirty-nine contaminants including plasticizers, bisphenols, and flame retardants in potable water from Montreal and South Africa was analyzed to determine their presence and concentrations in different water sources. In Montreal, five bottled water (BW) brands and three drinking water treatment plants (DWTP) were included. In South Africa, water was sampled from one urban DWTP located in Pretoria, Gauteng, and one rural DWTP located in Vhembe, along with water from the same rural DWTP which had been stored in small and large plastic containers. A combination of legacy compounds, typically with proven toxic effects, and replacement compounds was investigated. Bisphenols, Dechlorane-602, Dechlorane-603, and s-dechlorane plus (s-DP) were not detected in any water samples, and a-dechlorane plus (a-DP) was only detected in one sample from Pretoria at a concentration of 1.09 ng/L. Lower brominated polybrominated diphenyl ethers (PBDEs) were detected more frequently than higher brominated PBDEs, always at low concentrations of < 2 ng/L, and total PBDE levels were statistically higher in South Africa than in Montreal. Replacement flame retardants, organophosphate esters (OPEs), were detected at statistically higher concentrations in Montreal's BW (68.56 ng/L), drinking water (DW) (421.45 ng/L) and Vhembe (198.33 ng/L) than legacy PBDEs. Total OPE concentrations did not demonstrate any geographical trend; however, levels were statistically higher in Montreal's DW than Montreal's BW. Plasticizers were frequently detected in all samples, with legacy compounds DEHP, DBP, and replacement DINCH being detected in 100% of samples with average concentrations ranging from 6.89 ng/L for DEHP in Pretoria to 175.04 ng/L for DINCH in Montreal's DW. Total plasticizer concentrations were higher in Montreal than in South Africa. The replacement plasticizers (DINCH, DINP, DIDA, and DEHA) were detected at similar frequencies and concentrations as legacy plasticizers (DEHP, DEP, DBP) and known toxic metabolite (MEHP). The ubiquitous nature of many of these compounds in drinking water, especially OPEs and plasticizers, clearly indicate incomplete removal during drinking water treatment. Additionally, the presence of replacement compounds at similar or higher levels than their legacy compounds is of concern as there is generally less information available on the ecological or human health effects of these compounds.

3.3 Introduction

Endocrine disrupting chemicals (EDCs) are receiving growing attention because there is evidence that they have adverse effects on both human health and the ecosystem (Agas et al., 2013; Messerlian et al., 2016; Poston and Saha, 2019). Some proven and suspected EDCs are found in consumer products and packaging, including polybrominated diphenyl ethers (PBDEs) used as flame retardants in furniture and electronics, bisphenol A (BPA) used as a lining in food packaging and plastic water bottles, and phthalate esters used to alter the flexibility of synthetic materials. Amassed research on specific EDCs has led to government regulation or voluntary action by corporations; for example, the plasticizer bis(2-ethylhexyl) phthalate (DEHP) has been banned in cosmetics, medical devices and vinyl children's toys by the Canadian Consumer Product Safety Act (Minister of Justice, 2017). Replacement chemicals with similar structure and properties have been introduced as alternatives to the legacy EDCs, however there is usually little information available regarding their health and environmental effects. Organophosphate esters (OPEs) and dechloranes (DCs) were introduced as replacement flame retardants for legacy PBDEs (Brasseur et al., 2014; Lee et al., 2016), adipates have been introduced to replace phthalates as plastic additives (Bui et al., 2016), and various bisphenol analogues have replaced BPA (Chen et al., 2016).

Potable water is one source of human exposure to EDCs. Reporting levels of EDCs in potable water is essential for evaluating human exposure and environmental persistence. Some studies have been done in developed regions (Bach et al., 2020; Cao, 2008; Esteban et al., 2014) but there is little data available for EDC exposure from potable water in developing countries (Aneck-Hahn et al., 2018; Santhi et al., 2012; Van Zijl et al., 2017) and most replacement compounds have not been investigated. The World Health Organization (WHO) reports that only 5% of all investments in health research are spent in developing countries which experience over 90% of the global burden of disease (WHO, 2013). Even within a country there is potential for disparities in exposure between regions considering that in rural areas water is collected and stored in plastic containers as community taps can be unreliable, while tap water is the primary source of water for urban areas.

Flame retardants are added to materials such as plastics, wood, paper and textiles during the manufacturing process to prevent fire from igniting or spreading in consumer goods. An increase in the use of synthetics polymers in household and office products has driven the need for flame retardants, making exposure to these chemicals inevitable. Flame retardants such as PBDEs, OPEs, and DCs are added into polymers via physical mixing instead of chemical bonding making them more likely to leach into the environment (Barcelo and Kostianoy, 2011; Jianhua Li et al., 2019). Few studies have quantified levels of PBDEs in potable water. PBDEs were detected in Pakistan and New York, U.S.A., at concentrations below 1 ng/L (Khan et al., 2016b; Subedi et al., 2015), and two studies which tested for PBDEs in China and Argentina did not find any samples above the limit of detection (Fontana et al., 2009; L. Liu et al., 2019). There have been no studies which have tested dechloranes DEC-602 and DEC-603 in potable water, while a-DP and s-DP have only been studied and detected in Pakistan at levels below 1 ng/L (Khan et al., 2016b). Chlorinated OPEs, such as tris(1-chloro-2-propyl) phosphate (TCIPP), tris(2-chloroethyl) phosphate (TCEP), and tris(1,3-dichloro-2-propyl)phosphate (TDCIPP), and non-chlorinated OPEs such as tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), and tris(2-ethylhexyl) phosphate (TEHP) have frequently been detected in potable water (Kim and Kannan, 2018; Lee et al., 2016; Jiafu Li et al., 2019). TCIPP consistently had the highest detection frequency and concentration, with the highest concentration reaching 220 ng/L in the U.S.A. (Benotti et al., 2009). Most reporting of flame retardants in water occurs in North America, Europe, and Asia, and no data was found for Africa. Additionally, there was no data found in literature for OPE metabolites. A literature review of flame retardants in potable water can be found in the Supplementary Information Tables S1-S3.

Phthalate esters are common plastic additives which can be found in food wrappings, PVC interior surface coverings, and cosmetics. Di-2-ethylhexyl phthalate (DEHP), diethyl phthalate (DEP), and dibutyl phthalate (DBP) are commonly used phthalates for these applications. Mono(2-ethylhexyl)phthalate (MEHP) is a main metabolite of DEHP which has demonstrated similar endocrine toxicity (Rowdhwal and Chen, 2018). Higher molecular weight alternatives such as diisononyl phthalate (DINP) and bis(7-methyloctyl) cyclohexane-1,2-dicarboxylate (DINCH) were introduced as they are less likely to leach out of plastics, however the U.S. Consumer Product Safety Commission has banned children's toys and child care products with more than 0.1% DINP as it was determined to have harmful effects on male reproductive development (U.S. Consumer Product Safety Commission, 2017). Adipates, such as bis(2-ethylhexyl) adipate (DEHA) and diisodecyl adipate (DIDA), are phthalate alternatives with lower molecular weight and are typically used in low temperature applications (Bui et al., 2016). While DEHA has shown to leach from PVC into water, soapy water, and oil at a rate three times higher than DEHP, it has not demonstrated similar endocrine disrupting properties (Scientific Committee on Emerging and Newly-Identified Health Risks, 2016; Van Vliet et al., 2011). Legacy phthalates DEP, DBP, DEHP are frequently reported in potable water, but there is limited data for MEHP or replacements DINP and DEHA, and no data available for DIDA or DINCH. Europe and Asia provide the majority of data available for plasticizer concentrations in water, while there have been few reports for North America and Africa. A summary of plasticizer concentrations in potable water previously reported in the literature is presented in the Supplementary Information Table S6.

BPA is widely used in industrial food applications, mainly as resin lining in food and beverage packaging, and in the manufacture of food additives. Applied in food storage containers and as a lining in metal cans, BPA has been shown to leach out of containers and into food and beverages, especially at high temperatures (Bae et al., 2002). The regulation by many governments, including the Government of Canada, prohibiting the import and sale of baby bottles containing BPA (Government of Canada, 2010b) has led to the use of BPA analogues as replacements. Of the 16 bisphenol analogues, Bisphenol AF (BPAF), Bisphenol F (BPF), and Bisphenol S (BPS) are most commonly used in resin linings in place of BPA (Chen et al., 2016). Recently, studies have investigated the relative toxicity of BPAF, BPS and BPF to their legacy chemical BPA, and found that the substitutes are of similar toxicity, if not higher (Rochester and Bolden, 2015). There have been numerous reports on the concentration of BPA in potable water. A review paper published in 2013 found 30 studies quantifying the concentration of BPA in potable water, with 5% coming from North America, 52% from Europe and 59% from Asia (Arnold et al., 2013). Significantly less data is available for replacement compounds BPAF, BPF and BPS, with only three studies, two located in China and one from France (Colin et al., 2014; Wang et al., 2020; Zhang et al., 2019b). Reports of bisphenols in potable water following the summary by Arnold et al. (2013) can be found in the Supplementary Information Table S7.

The objectives of the present research were to quantify levels of 39 target flame retardants, plasticizers and bisphenols in potable water in Canada and South Africa, identify potential differences both between locations – including rural and metropolitan areas, and between sources of water – tap and bottled water, and compare the presence of replacement to legacy compounds.

To our knowledge, this is the first report of specific OPE metabolites, DCs, and replacement plasticizers in potable water, as well as the first report of many target analytes in African water. The data presented will aid in assessing human exposure to potential endocrine disruptors through various potable water sources.

3.4 Materials and Method

3.4.1 Chemicals and reagents

The list of analytical standards of all target analytes and their deuterated analogues, along with their acronym, CAS number and supplier, can be found in Supplementary Information Tables S6 and S7, respectively. LC-MS water, methanol (MeOH), acetone, hexanes, hydrochloric acid, formic acid, HPLC grade methyl tert-butyl ether (MtBE), pesticide grade isooctane, sulfuric acid, ammonium hydroxide, and hydrochloric acid were all purchased from Fisher Scientific (U.S.A.). Ultrapure water was prepared using a MilliQ water purification system purchased from Millipore Corporation (Billerica, MA, USA). Oasis HLB, Oasis WAX and glass Oasis HLB glass cartridges were all purchased from Waters (MA, U.S.A.).

3.4.2 Sampling

Three sampling campaigns took place in Montreal in April 2018, November 2018, and April 2019 and two sampling campaigns took place in South Africa in April 2018 and August 2019. In total, 32 potable water samples were collected, composed of 15 bottled water (BW) samples (five most common brands), 9 drinking water (DW) samples from three drinking water treatment plants (DWTP) located in Montreal, 2 drinking water samples from a DWTP located in an urban area in South Africa (Pretoria, Gauteng), and 6 drinking water samples from a rural area in South Africa (Vhembe), consisting of samples from a DWTP (n=2) and from water stored in small (n=2) and large (n=2) plastic containers. In this study, small containers were used to carry and store water from public taps inside the house and large containers or water tanks are used when people have access to a municipal water connection. According to the manufacturers, these tanks are made of polyethylene with pigment anti-oxidants and UV stabilizers to ensure and extend service life.

All five DWTPs included in this project used surface water as source water. The bottled water was purchased in 1L bottles from local grocery stores. Drinking water was collected as grab samples in 1L aluminum bottles from the outlet of the DWTPs or from the plastic containers.

Water collected in Montreal was put on ice and immediately transferred to a freezer where the water was stored at -20℃ until extraction. Water collected in South Africa was frozen and shipped to Montreal on dry ice, and subsequently stored at -20℃ until extraction. Samples were split into triplicates of 400 mL for each water source and extracted within 24 hours after thawing the sample.

3.4.3 Glassware cleaning and silanization

All glassware was cleaned thoroughly prior to contact with samples. Glassware was cleaned with hot water and soap, then rinsed with water and left to dry, and finally rinsed with pesticide grade acetone and hexane twice. Finally, glassware was baked at 500 ℃ for 4 hours and covered with aluminum foil until use. Silanized glassware was used when handling plasticizer samples to avoid adsorption of analytes to the glass surface. It is essential that glassware be free of any water particles before silanization, making degreasing the surface necessary. Glassware was soaked in 1:1 concentrated hydrochloric acid (HCl) to methanol (MeOH) for 30 minutes, rinsed with 18.2 Megaohm-cm dionized (MilliQ) water, soaked in concentrated sulfuric acid for 30 minutes, rinsed with MilliQ water, boiled in MilliQ water for 30 minutes, and left to dry overnight. Glassware was then silanized by soaking in dimethyldichlorosilane (DMDCS) solution (5% DMDCS in heptane) for 15 minutes, left to dry overnight, and baked at 70℃ for 2 hours.

3.4.4 Sample preparation

3.4.4.1 Sample preparation for PBDEs, DCs, and BPs

Water samples were prepared by SPE with Oasis HLB cartridges (5cc, 200 mg). Water samples (400 mL, unfiltered) were spiked with 100 μL of both PBDE and DC (eight deuterated PBDEs and three deuterated DCs at 240 ng/L), and BP (four deuterated BPs at 240 μg/L) internal standard mixture and brought to a pH of 2.5 using 1N sulfuric acid solution. Cartridges were conditioned by adding 6 mL of LC-MS grade methanol (MeOH), followed by 6 mL LC-MS grade acetone and finally 6 mL LC-MS grade water with pH 2.5 (1N sulfuric acid in water). Samples were loaded onto the cartridge ensuring a sample flow rate <5 mL/min and dried under vacuum for 10 minutes. Elution buffer (10% - 5% ammonium hydroxide in methanol, 45% - LC-MS grade hexane, 45% - pesticide residue grade dichloromethane) was added to the cartridge three times at a volume of 3 mL, allowing elution buffer to soak into cartridges for 5 minutes between additions. Samples were split into two equal parts for separate analysis (4.5 mL each) and dried under a gentle nitrogen stream at 50℃ until completely evaporated. Samples were reconstituted using 200 μL iso-octane and stored at -20℃ until analysis.

3.4.4.2 Sample preparation for OPEs

Water samples were prepared by SPE with Oasis WAX cartridges (6cc, 500 mg). Water samples (400 mL, unfiltered) were spiked with 100 μL of OPE (10 deuterated OPEs at 240 μg/L in MeOH) internal standard spiking mixture and brought to a pH of 1.5 using 95-98% sulfuric acid. Cartridges were conditioned by adding 3 mL LC-MS grade acetone, followed by 3 mL LC-MS grade MeOH, and finally 3 mL of LC-MS grade water with pH 1.5 (95-98% sulfuric acid in water). Samples were loaded onto the cartridge ensuring a sample flow rate <5 mL/min and dried under vacuum for 5 minutes. Elution buffer (2% ammonium hydroxide in LC-MS grade methanol) was added to the cartridges twice at a volume of 4 mL, allowing elution buffer to soak into cartridge for 10 minutes between additions. Samples were dried under a gentle nitrogen stream at 50℃ until completely evaporated, reconstituted in 400 μL of 5% MeOH solution in water, and stored at -20℃ until analysis.

3.4.4.3 Sample preparation for plasticizers

Water samples were prepared using SPE with Oasis HLB glass cartridges (5cc, 200 mg) based on a published method (Bissegger et al., 2018) which was modified to include DEHA, DINCH, DIDA, DINP, and MEHP. Water samples (400 mL, unfiltered) were spiked with 100 μL of plasticizer (five deuterated plasticizers at 240 μg/L in MeOH) internal standard spiking mixture and brought to a pH of 2.5 using 1N hydrochloric acid (HCl). Cartridges were conditioned by adding 5 mL of 5% LC-MS grade MeOH/95% LC-MS grade MtBE solution, followed by 3 mL LC-MS grade MeOH, and finally 3 mL LC-MS grade water with pH 2.5 (1N HCl). Samples were loaded onto the cartridges ensuring a sample flow rate <5 mL/min and dried under vacuum for 20 minutes. Elution buffer (10% LC-MS grade MeOH / 90% LC-MS grade MtBE) was added to the cartridges three times at a volume of 3 mL, allowing elution buffer to soak into cartridge for 10 minutes between additions. Samples were dried under a gentle nitrogen stream at 50℃ until completely evaporated, reconstituted in 400 μL of 40% LC-MS grade MeOH / 60% 2mmM ammonium formate in LC-MS grade water solution and stored at -20℃ until analysis.

3.4.5 Sample analysis

3.4.5.1 Analysis of PBDEs

Two different methods were used for the analysis of PBDEs. Method 1 was used for the samples collected during the first sampling campaign in Montreal and Method 2 for all the other campaigns.

Method 1 – Analysis was performed by gas chromatography coupled with high resolution mass spectrometry (GC-HRMS) using a Waters AutoSpec Ultima (Waters Milford, MA USA) mass spectrometer connected to a 6890 gas chromatograph with a Programmable temperature Vaporizing inlet (Agilent). The system was run in splitless injection mode with a constant pressure of 95 kPa, inlet temperature of 250℃, purge time of 1 minute, and purge flow of 50.0 mL/min. A 10 M x 0.18 mm x 0.18 μm Rxi-5ms column was used from Restek with a 1.0 M x 0.15 mm deactivated fused silica retention gap (Agilent) and a 1.0 M x 0.25 mm deactivated fused silica (Agilent) on the detector end to reduce cold spots in the transfer line. The oven temperature program used was as follows: from initial temperature 115℃ for 2 min to 250℃ at 25℃/min, to 320℃ at 8℃/min and hold for 2 minutes, to 350℃ at 10℃/min and hold for 2 minutes. Quantification by HRMS was run at 8000 resolution. Instrument detection limits (IDL) for PBDEs ranged from 0.12 – 9.61 ng/L and can be found in Supplementary Information Table S10 along with the retention times and mass-to-charge ratios.

Method 2 – Analysis was performed by gas chromatography coupled with mass spectrometry (GC-MS/MS) using a gas chromatograph (TSQ Quantum, Thermo Scientific, USA) coupled to a TSQ Quantum GC triple quadrupole mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA). The GC separation was carried out on a ZB-1HT Inferno column (15 m x 0.25 mm I.D., 0.1 µm film thickness) from Phenomenex (Torrance, CA, USA). GC oven temperature program used was as follows: from 120ºC to 230ºC at 15ºC /min, to 270ºC at 5ºC /min, to 320ºC at 10ºC/min and hold for 4 minutes. The source temperature was set at 180ºC and GC interface at 280ºC. The injection volume was 1 µL in splitless mode with surge, and the flow rate of the carrier gas (helium) was set at 1.0 mL/min. MS/MS was operated in positive EI mode at 70 eV. Censoring criteria for the positive identification of peaks were instrument signal-to-noise (s/n) ratio of at least 3 and ratio of the two monitored ions within the range of 70% to 130% from that of the standards, in addition to the match of retention times. Instrument detection limit (IDL) was determined by running 8 replicates of a standard solution at the lowest calibration level (0.025 ng/mL). Standard deviation

(SD) associated with the analysis multiplied by the Student's t value appropriate for a 99% confidence level was used to estimate the IDL, using the equation IDL = 2.998×SD. The calibration curves were linear over a concentration range from 0.025 ng/mL to 5.0 ng/mL with a coefficient of correlation (r^2) greater than 0.99 for most of the compounds. IDL values for PBDEs ranged from 0.01 – 0.02 ng/L and can be found in Supplementary Information Table S11 along with the transition ions monitored.

3.4.5.2 Analysis of DCs

Two different methods were used for the analysis of DCs. Method 3 was used for the samples collected during the first sampling campaign in Canada and Method 4 for all the other campaigns.

Method 3 – Analysis was performed using Method 1 (section 2.5.1). Limits of detection ranged from 0.19 – 0.44 ng/L and can be found with MS parameters in Supplementary Information Table S12.

Method 4 – Analysis was performed using an Agilent 6980 gas chromatographer (GC) coupled with a Waters Quattro micro triple quadrupole mass spectrometer (Waters Corp., Milford, MA, USA) operated in electron capture negative ionization (ECNI) mode. Methane was used as reagent gas. The ion source and GC interface temperatures were set at 180 °C and 280°C, respectively. The GC column was a Zebron ZB- 5HT (8 m × 0.25 mm i.d., 0.10 μm of film thickness) from Phenomenex (Torrance, CA, USA). The carrier gas was helium with a constant flow of 1 mL/min. The oven temperature was initially held at 80°C for 2 min, ramped to 200°C at 4°C/min, held at 200°C for 1 min, ramped to 300°C at 25 °C/min, held at 300°C for 2 min, ramped up to 330°C at 35°C/min, and finally held at 330°C for 10 min. The GC injector was equipped with a programmable-temperature vaporizer inlet (PTV) which was operated in solvent vent mode. The initial inlet temperature was held at 90°C for 0.04 min, ramped to 295°C at 700°C/min, and held at 295°C thereafter till the end of the GC/MS analysis. Vent pressure was set at 10 kPa with vent flow of 75 mL/min ending at 0.02 min. Purge flow was 50 mL/min after 1.25 min, and the injection volume was 2 μL. All target analytes were well separated and two ions were monitored for each analyte with MS operated in single ion monitoring (SIM) mode during analysis: one for quantitation (SIM-Q) and the other for confirmation (SIM-C). Analysis parameter and IDLs, which ranged from 0.9 – 2.4 ng/L, can be found in the Supplementary Information Table S13.

3.4.5.3 Analysis of OPEs

Analysis was carried out on an ultra performance liquid chromatography (UPLC) system from Waters (Milford, MA, USA) coupled to a Waters Xevo TQD MS/MS (Milford, MA, USA) operated in electrospray ionization (ESI) in positive or negative ion mode. Separation of metabolites was performed at 40°C using an Acquity UPLC BEH C18 column from Waters (1.7 µm, 2.1 mm x 50 mm) attached to a Waters Van Guard BEH C_{18} pre-column (1.7 µm, 2.1 x 5 mm). The mobile phase consisted of (A): 10 mM ammonium acetate in water and (B): methanol. The gradient programming was as follows: initial gradient 5% (B) hold for 1 minute, to 65% (B) in 1 minute, to 85% (B) in 6 minutes, to 100% (B) in 0.5 minute, hold at 100% (B) for 3.5 minutes, back to 5% B in 0.1 minute and hold for 2.4 minutes to re-equilibrate column. Flow rate was set at 0.22 mL/min. 1.5 µL of extracts were injected in full loop mode. Multiple reaction monitoring (MRM) transitions of the target analytes and internal standards used as well as associated collision energies are presented in Table S12. Source temperature, desolvation temperature, and desolvation gas flow were set at 150°C, 350°C and 650 L/hour, respectively.

The method detection limits (MDL) ranged from 0.03 – 0.70 ng/L in water samples and can be found with MS parameters in the Supplementary Information Table S14. MDL was determined by the standard deviation associated with eight replicate analyses of standard solution at 0.25 ng/mL per sample and multiplied by the Student's t value of 2.998. The relative percent recoveries were based on the recoveries of the labelled internal standards, which was greater than 70%. The calibration curves were linear over a concentration range from 0.5-500 ng/mL with correlation coefficient greater than 0.998 for all compounds of interest.

3.4.5.4 Analysis of BPs

Analysis of BPs was performed following a method previously outlined by Tian et al. (Tian et al., 2020). Briefly, samples were analyzed using an Agilent 1290 Infinity II LC system (Agilent Technologies, Santa Clara, CA) coupled to a 6545 quadrupole TOF-MS (Agilent Technologies, Santa Clara, CA) operating in negative (ESI-) electrospray ionization mode. The LC separation was conducted on a Poroshell 120 Phenyl Hexyl column (Agilent Technologies; 2.7 µm × 3.0 mm × 100 mm) fitted with a Poroshell 120 Phenyl Hexyl guard column (Agilent Technologies; 2.7 µm × 3.0 mm × 10 mm). The MDL was calculated as three times the standard deviation of procedural blanks divided by the slope of the matrix-matched calibration curve. Method detection limits ranged from 0.1 – 0.82 ng/L in water samples and can be found with MS parameters in the Supplementary Information Table S15.

3.4.5.5 Analysis of Plasticizers

The analysis of plasticizers in water samples was performed on a liquid chromatography – high resolution mass spectrometry (LC-HRMS). The chromatographic separation of target compounds followed the method described by Bissegger et al. (Bissegger et al., 2018). Briefly, chromatographic separation was performed on a Accela 600 LC system (Thermo Fischer, Waltham, MA, USA) with Zorbax HDHR Eclipse plus C18 column fitted with a C18 Eclipse plus (12.5 × 2.1 mm ID., 1.8 μm) guard column (Agilent Technologies, Santa Clara, CA, USA). Detection by MS was performed using a LTQ Orbitrap XL (Thermo Fisher Scientific, Waltham, MA, USA) with a heated electrospray ion source (HESI) operated in positive mode. Vaporization and capillary temperatures were set to 350℃ and 250℃, respectively, and helium was used as the collision gas. MS data was acquired in the 50-800 m/z range in high resolution (FTMS resolution @ 30,000). The ion of interest was extracted using a m/z range of $\pm$5ppm accuracy to quantify the target analyte and confirmed by MS/MS spectra. An eight-point calibration curve was constructed for each compound (1-150 ng/L) with a linear correlation coefficient of 0.990. Data analysis was performed by using Thermo Xcalibur software (Thermo Fisher, Waltham, MA, USA). Detection limits ranged from 1.29 – 1.93 ng/L in water samples and can be found with MS parameters in the Supplementary Information Table S16.

3.4.6 Quality control and assurance

For sample collection and preparation, care was taken to avoid sample contact with materials which are known to contain flame retardants, bisphenols, and plasticizers. All samples analyzed for plasticizers were handled under a biosafety cabinet to prevent contamination from dust particles. Additionally, all plasticizer samples were handled in silanized glassware only, and plastic tubing traditionally used to load samples to SPE was replaced by glass funnels. To prevent sample cross-contamination, all tubing was cleaned thoroughly by first passing milli-Q water for 2 minutes, followed by LC-MS grade MeOH for 2 minutes.

A procedure blank (LC-MS grade water spiked with internal standards) was included in every batch of extraction (1 blank for 9 water samples) to monitor contamination through SPE, as well as a positive control (LC-MS water spiked with native analytes and internal standards) to ensure adequate overall recoveries. Elution blanks (elution buffer only) and elution controls (elution buffer spiked with internal standards) were included with every SPE run to monitor for contamination during sample drying and analysis. Contamination through sample handling and extraction was only found in samples analysed for OPEs. To account for this, the concentration of contamination in the blank was subtracted from the concentration found in the sample for each extraction.

Samples were split for triplicate extraction and analysis to ensure reliable sample concentrations. The data presented in the manuscript is the average of triplicates. In the case that one or two replicates were below the limit of detection (LOD), the replicate was replaced with the value of the LOD divided by the square root of 2 (LOD/√2). Statistical analysis was performed to compare total concentrations of PBDEs, OPEs and plasticizers between location and water type. Specifically, comparisons were made between Montreal's BW and DW, between South Africa's urban and rural locations (Vhembe and Pretoria), and between Montreal's potable water (including BW and DW), and South Africa's potable water (including Vhembe and Pretoria). Each sampling campaign was considered an individual point in the analysis to account for variations between sampling campaigns. Statistical analyses were performed using the Wilcoxon rank sum test in JMP assuming unequal variances as this test relies on no distributional assumption and is preferred when handling small data sets. We considered two-sided p-values below 0.05 to be statistically significant.

3.5 Results and discussion

3.5.1 Overview of results

The measured average concentration and frequency of detection of each analyte are summarized in Table 2. Triplicates were not considered separately in the calculation of detection frequencies. If the concentration of a compound was determined to be above the limit of detection for any triplicate of a sample, the compound was considered detected in that sample. These data represent the average over the three campaigns for Montreal, and 2 campaigns for South Africa, and type of water – bottled water (BW) and drinking water (DW). BW is the average of five water brands, Montreal DW is the average of three DWTP finished water, Vhembe is the average of one DWTP finished water and water stored in small and large containers, and Pretoria is one DWTP finished water. BDE-183, BDE-209, DEC 602, DEC 603, s-DP BPA, BPAF, BPF, and BPS were not detected above the limit of detection in any potable water samples from any location. BDE-209 was only analysed in Montreal's first sampling campaign due to the change in method for PBDE analysis. The concentrations for the individual sampling campaigns are provided in Supplemental Information Tables S15-S17.

Due to the limit of single samples collected for each water source per campaign, along with the use of grab samples, the results are not intended to provide an insight into trends of analyte concentrations over time. The 2-year time period was intended to determine the presence and levels of contaminants in different types of water over an extended period of time. Comparisons of the present findings to previously reported concentrations from the literature will be made in the following sections, in addition to comparisons of total PBDE, OPE and plasticizer concentrations between location and water type, and comparisons between legacy compounds and their replacements.

Table 2 – Average concentration and detection frequency of each compound per location.

Family	Analyte	Montreal BW (n=15)		Montreal DW (n=9)		Pretoria (n=2)		Vhembe (n=6)	
		DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]
Flame retardants	BDE-28	33	<LOQ	44	0.03	100	<LOQ	33	0.05
	BDE-47	53	0.04	33	0.04	100	0.28	50	0.23
	BDE-99	13	0.02	0	ND	50	0.03	50	0.06
	BDE-100	7	0.01	11	0.01	50	0.08	67	0.07
	BDE-153	7	0.01	0	ND	0	ND	0	ND
	BDE-154	0	ND	11	0.03	0	ND	33	<LOQ
	BDE-183	0	ND	0	ND	0	ND	0	ND
	BDE-209	0	ND	0	ND	0	ND	0	ND
	DEC 602*	0	ND	0	ND	0	ND	0	ND
	DEC 603*	0	ND	0	ND	0	ND	0	ND
	a-DP*	0	ND	0	ND	50	1.09	0	ND
	s-DP*	0	ND	0	ND	0	ND	0	ND
	TBOEP*	73	4.58	100	15.30	50	4.76	50	0.94
	TCEP*	67	13.92	100	84.59	100	74.03	100	37.31
	TCIPP*	67	2.00	100	15.90	100	176.44	100	8.67
	TDCIPP*	80	5.25	100	46.58	100	66.93	83	46.45
	TEHP*	33	0.63	56	0.17	50	0.18	33	0.23
	TPHP*	100	1.30	100	11.11	100	4.41	100	3.15
	DPHP⁑	93	4.68	100	27.14	100	150.36	100	12.18
	Ip-PPP⁑	0	ND	22	0.27	100	0.33	17	<LOQ
	BCIPP⁑	33	0.22	100	163.38	100	114.74	100	66.33
	BCEP⁑	53	0.49	33	0.34	50	0.23	17	2.87
	BBOEP⁑	60	0.94	78	3.09	100	6.56	33	1.64
	BDCIPP⁑	47	0.85	56	2.88	0	ND	0	ND
	BEHP⁑	67	29.70	100	35.49	100	35.24	100	31.70
	BTBOEP⁑	93	0.88	100	7.54	100	13.27	50	0.49
	DCP⁑	73	0.41	67	0.48	50	0.35	83	0.30
Plasticizers	DEHP	100	153.25	100	133.44	100	6.89	100	8.14
	DEP	100	17.34	89	25.31	100	32.98	100	38.85
	DBP	100	56.22	100	66.93	100	16.37	100	27.26
	DEHA*	87	39.28	100	31.26	100	32.83	100	44.75
	DINCH*	100	156.59	100	175.04	50	36.61	100	21.68
	DIDA*	13	15.54	56	8.01	50	21.80	83	36.14
	DINP*	100	175.51	100	105.22	50	<LOQ	83	<LOQ
	MEHP⁑	33	4.96	33	6.35	100	5.97	83	5.78
Bisphenols	BPA	0	ND	0	ND	0	ND	0	ND
	BPAF*	0	ND	0	ND	0	ND	0	ND
	BPF*	0	ND	0	ND	0	ND	0	ND
	BPS*	0	ND	0	ND	0	ND	0	ND

ND: non-detect, <LOD: below limit of detection, <LOQ: below limit of quantification. * Denotes replacement compounds and ⁑ represents metabolites.

3.5.2 PBDEs in potable water

The concentrations of PBDEs in each water source, including bottled and drinking water in Montreal, and drinking water from South Africa are summarized in Figure 1(a). BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 were varyingly detected at concentrations ranging from 0.02 to 1.18 ng/L (Supplemental Information Table S17-S19). BDE-153 was only detected in one bottled water sample at a concentration of 0.02 ng/L (Supplemental Information Table S17), and BDE-154 was only detected above the limit of quantification in one Montreal DW sample at a concentration of 0.06 ng/L (Supplemental Information Table S18). BDE-183 was not detected in any samples. BDE-209, analyzed only using Method 1 for the sampling campaign in Montreal was also not detected. Typically, higher brominated PBDEs are less mobile in the environment as they are less water soluble and have a stronger adsorption to sediments (Watanabe and Sakai, 2003). This could explain the low detection frequencies observed for BDE-153, BDE-154, BDE-183 and BDE-209. These compounds are more likely to accumulate in the sediment while low brominated BDE-28, BDE-47, BDE-99, and BDE-100 are more likely to be present in water samples. All individual compounds, when detected, were present at concentrations below 1 ng/L except for one sample from Vhembe (BDE-47 found at 1.18 ng/L in water stored in small containers (Supplemental Information Table S19)). Lower bromination level PBDEs BDE-28 and BDE-47 had the highest overall detection frequencies (Table 2). BDE-47 had the highest concentration of all PBDEs for each location, with average concentrations over all campaigns of 0.28, 0.23, 0.04, and 0.04 ng/L for Pretoria, Vhembe, Montreal BW, and Montreal DW, respectively (Table 2 & Figure 1 (a)). The lower number of samples taken in South Africa may contribute to the overall higher detection frequencies than Montreal. Generally, total PBDE concentrations were similar in Pretoria and Vhembe, as seen in Figure 1(b). Likewise, Montreal saw similar total concentrations between bottled water and drinking water. Total PBDE concentrations in Vhembe, Pretoria, Montreal DW, and Montreal BW were 0.41, 0.39, 0.11, and 0.08 ng/L, respectively. There was no statistically significant difference between total PBDE concentrations of Montreal BW and DW, or between Vhembe and Pretoria, however, South Africa’s potable water had statistically higher PBDE concentrations than Montreal’s potable water ($p = 0.018$).

Previous reports from Argentina’s tap water (included BDE-47, BDE-99, BDE-100, and BDE-153) and China’s bottled water (included BDE-28, BDE-47, BDE-99, BDE-100, and BDE-154) did not find any PBDEs (Fontana et al., 2009; L. Liu et al., 2019). These findings agree with the present findings for BDE-153 and BDE-154 which were each only detected above the limit of quantification in one sample, however the present study found higher detection frequencies and concentrations for BDE-28, BDE-47, BDE-99, and BDE-100. Tap water from New York detected seven of the eight PBDEs included in the present study at concentrations ranging from 0.05 – 0.84 ng/L, and did not detect BDE-209 in any samples (Subedi et al., 2015). These concentrations are generally higher than what was found in the present study, except for BDE-47 which was detected above 1 ng/L in Vhembe. A detailed review of previously reported PBDE concentrations in potable water can be found in Supplemental Information Table S3.

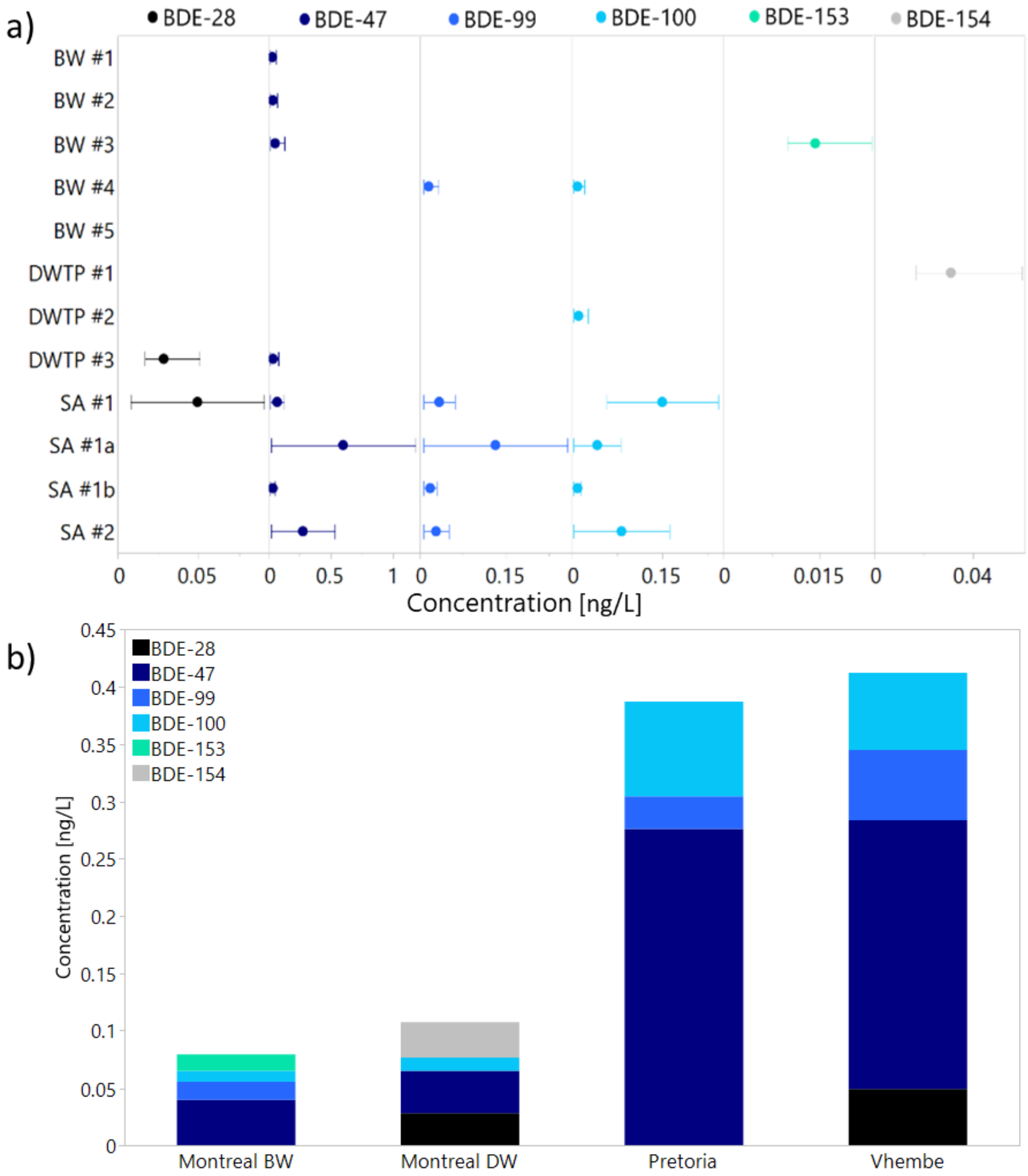

Figure 1 - Summary of PBDEs in potable water.

(a) Concentration per source. Marker represents average concentration and error bars represent range of concentrations detected over the campaigns. BW: bottled water, DW: Drinking water from Montreal, SA #1: Vhembe, SA #1a: Vhembe water stored in small containers, SA #1b: Vhembe water stored in large containers, SA #2: Pretoria (b)

Concentration averaged by location and water type. Montreal BW: average of 5 bottled water, Montreal DW: average of Montreal's 3 DWTPs, Vhembe: Average of Vhembe's three sources, Pretoria: single DWTP

3.5.3 Dechloranes in potable water

Of the four dechloranes, DEC-602, DEC-603, and s-DP were not detected in any water samples. a-DP was detected in one sample from Pretoria at a concentration of 1.09 ng/L. Only one previous study from Pakistan has quantified s-DP and a-DP in drinking water at maximum concentrations of 0.1 and 0.29 pg/L, respectively (Khan et al., 2016a), which are significantly lower than those found in the present study. No data is available for DEC-602 and DEC-603 in potable water and only a few studies are available on DP concentrations in surface water (Supplemental Information Table S4). The sum of a-DP and s-DP was reported in surface water from China at concentrations ranging from 1.4 – 3.5 ng/L and in Pakistan ranging from 0.01 – 4.58 ng/L (Chen et al., 2018; Mahmood et al., 2015). These reports of DP in surface water are in agreement with the level of a-DP detected in Pretoria in the present study. China has the highest portion of estimated production of DP related products at 31%, followed by North America, other Asia, and Western Europe at 27%, 16% and 14%, respectively (Hansen et al., 2020). Differences in environmental regulations between geographic regions could lead to the difference in detection levels in both surface water and potable water. It is expected that concentrations in potable water are reported at lower levels than in surface water as the water is treated prior to consumption.

3.5.4 OPEs in potable water

OPEs, which are employed as replacement flame retardants for legacy PBDEs, were more frequently detected at higher concentrations than PBDEs (TCEP ranging from 13.92 (Montreal BW) – 84.59 (Montreal DW) ng/L, TDCIPP ranging from 5.25 (Montreal BW) – 66.93 (Pretoria) ng/L, Table 2). The concentrations of OPEs for each source are summarized in Figure 2(a), where the metabolites are represented by the sum of the 9 target metabolites. Detection frequencies and concentrations per location for the individual metabolites are listed in Table 2. TCEP and TDCIPP were detected at the highest concentrations for both Montreal's BW (13.92 and 5.25 ng/L, respectively) and Montreal's DW (84.59 and 46.58 ng/L, respectively). In Vhembe and Pretoria, chlorinated OPEs TCEP, TCIPP, and TDCIPP were found at much higher concentrations than non-chlorinated OPEs (TBOEP, TEHP, and TPHP). TCIPP comprised more than half of the total parent OPE concentration for Pretoria at 176.44 ng/L. A study by Choo and Oh found that chlorinated OPEs are removed more effectively by granular activated carbon (GAC) filters than conventional drinking water treatment processes (Choo and Oh, 2020). GAC filters are not part of the water treatment process for any DWTPs included in the present study which could explain the high levels reported.

A comparison of OPE concentrations between locations is depicted in Figure 2(b). The average total OPE concentration in Montreal BW, Montreal DW, Pretoria, and Vhembe were 68.56, 421.45, 647.81, and 198.33 ng/L, respectively. There was no statistically significant difference in total OPE concentrations between Vhembe and Pretoria, or between Montreal's potable water and South Africa's potable water, however Montreal's DW was statistically higher than Montreal's BW ($p = 0.0021$). Metabolites DCPs and ip-PPP were detected at low concentrations <1 ng/L. TMPP, the parent compound of DCPs, were not detected in previous studies from Italy (Rodil et al., 2012), China (Kim and Kannan, 2018), or South Korea (Park et al., 2018). There are no reports of IPPP (parent of ip-PPP) in drinking water. In Montreal BW and DW, and Vhembe, non-chlorinated metabolite BEHP was detected at statistically higher concentrations than its parent compound TEHP (BW: $p = 0.006$, DW: $p = 0.0003$, Vhembe: $p = 0.004$), while chlorinated metabolites DCEP (BW: $p = 0.0006$, DW: $p = 0.0003$, Vhembe: $p = 0.004$) (parent TCEP) and BDCIPP (BW: $p = 0.017$, DW: $p = 0.0005$, Vhembe: $p = 0.0028$) (parent TDCIPP) were detected at lower concentrations than parent compounds. A graphical comparison between parent OPEs and their metabolites can be found in Supplemental Information Figure S1.

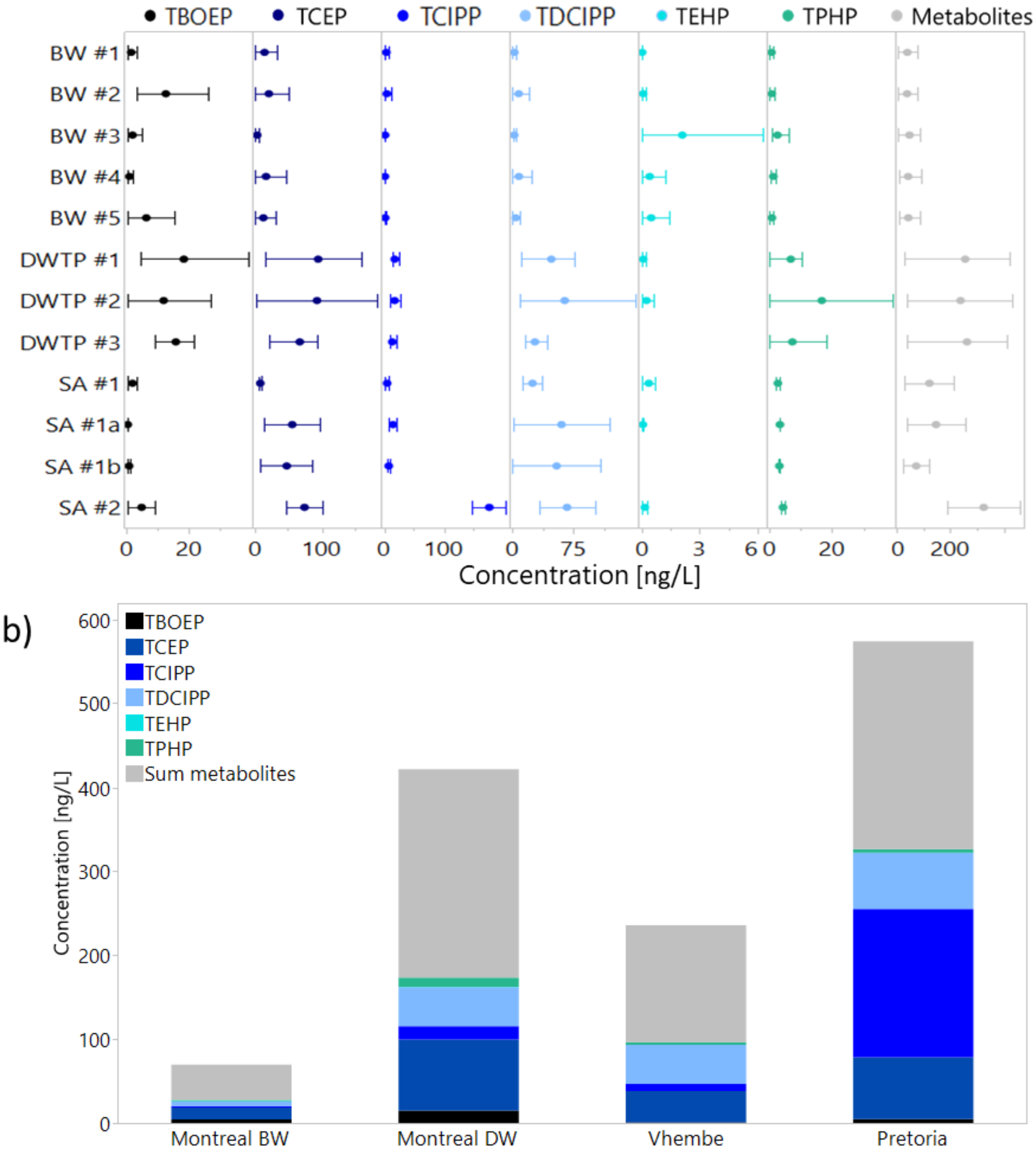

Figure 2 - Summary of OPEs in potable water.

(a) Concentration per source. Marker represents average concentration and error bars represent range of concentrations detected. BW: Bottled water, DW: Drinking water from Montreal, SA #1: Vhembe, SA #1a: Vhembe water stored in small containers, SA #1b: Vhembe water stored in large containers, SA #2: Pretoria. (b) Concentration averaged by location and water type. BW: average of 5 bottled water, DW: average of Montreal's 3 DWTPs, Vhembe: Average of Vhembe's 3 sources, Pretoria: Pretoria DWTP.

Numerous studies have quantified OPE concentrations in potable water (Supplemental Information Table S5), although none included water from Africa. In North America, New York tap water had similar levels of TBOEP, TCIPP, TDCIPP, TEHP, and TPHP as Montreal's bottled and drinking water (0.12 ng/L for TEHP to 11.6 ng/L for TCIPP) but lower concentrations of TCEP (0.45 ng/L) (Kim and Kannan, 2018). OPE concentrations in bottled water is less frequently reported, with one study from China detecting TBOEP, TCEP, TCIPP, and TPHP at concentration ranges of 19.5-81.7, ND-48.8, 1.33-16.2, and 2.57-14.8 ng/L, respectively, while TDCIPP and TEHP were not detected in any samples (Li et al., 2014). These findings generally agree with the concentrations found in Montreal BW, except for TDCIPP which was detected in 80% of Montreal's BW samples at an average concentration of 5.3 ng/L. OPE metabolites are often overlooked when reporting concentrations in potable water. Only one study of Spanish tap water included TPHP and metabolite DPHP, however neither compounds were found above the limit of detection (Rodil et al., 2012). Pretoria had high TCIPP and TDCIPP concentrations of 176 and 66.9 ng/L, respectively. These were higher than concentrations found in tap water from China (TCIPP: 2.39 – 101 ng/L, TDCIPP: <LOD – 22.3 ng/L) (Jiafu Li et al., 2019), South Korea (TCIPP : 49.5 ng/L, TDCIPP : 2 ng/L) (Park et al., 2018), or potable water from Pakistan (TCIPP : <LOD – 86 ng/L, TDCIPP : <LOD – 21.4 ng/L) (Khan et al., 2016b).

3.5.5 Bisphenols in potable water

No bisphenols were detected in any of the water samples, despite limits of detection below 1 ng/L. This agrees with a recent study by Goeury et al., where BPA was not detected in tap water from Quebec, and detected below the limit of detection (1.5 ng/L) in 50% of tap water samples from Ontario (Goeury et al., 2019). However, BPA has been frequently detected in potable water from around the world (Radwan et al., 2019; Santhi et al., 2012; Zhang et al., 2019b), notably in South Africa's bottled water at a concentration of 2.78 ng/L (Aneck-Hahn et al., 2018) and drinking water at concentrations of 1.45 and 1.33 ng/L from Cape Town and Pretoria, respectively (Van Zijl et al., 2017). Bisphenol analogues have recently been reported in Chinese drinking water at low concentrations of 0.4, 0.04, and 0.1 ng/L for BPAF, BPF, and BPS, respectively (Zhang et al., 2019b), and bottled water ranging from ND-4.9 ng/L for BPAF, ND-10.6 ng/L for BPS, while BPAF was not detected (Wang et al., 2020).

3.5.6 Plasticizers in potable water

Plasticizers were frequently detected in water samples from Montreal and South Africa (13-100%). Concentrations of the eight target plasticizers in each water source are summarized in Figure 3(a). Legacy compounds DEHP and DBP, and replacement compound DINCH were detected in 100% of samples. In Montreal's BW, DINP, DINCH and DEHP had the highest concentrations of total plasticizers up to 175.51 ng/L, 156.59 ng/L, and 153.25 ng/L, respectively. Similarly, in Montreal's DW, DINCH, DEHP, and DINP were at the highest concentrations of total plasticizers at 175.04 ng/L, 133.44 ng/L, and 105.22 ng/L, respectively. Pretoria and Vhembe had a very different composition of plasticizers, and statistically lower concentrations of total plasticizers than Montreal ($p = 0.0001$). The most prevalent compounds were DEHA (44.75 ng/L), DEP (38.85 ng/L) and DIDA (36.14 ng/L) for Vhembe, and DINCH (36.61 ng/L), DEHA (32.83 ng/L) and DEP (32.98 ng/L) in Pretoria. DINP was not detected above the limit of quantification for any South Africa samples. There was no statistical difference between Montreal BW and DW, or between Vhembe and Pretoria. Total concentrations of replacement plasticizers (DEHA, DINCH, DINP, and DIDA) were statistically higher than legacy plasticizers in Montreal's BW ($p = 0.0048$), as seen in Figure 3(b).

Previous reports of DEHP, DEP, and DBP in Canadian water align with concentrations found in the present study (Supplemental Information Table S6). DEHP and DBP were previously detected between 103-188 ng/L and 46-50 ng/L, respectively, in drinking water outlets from Canada (Chen et al., 2006), and DEHP, DBP, and DEP were detected at levels of 118, 138, and 80 ng/L in Canadian bottled water (Cao, 2008). However, no DIDA was detected in Canadian bottled water, while DIDA was detected in 13% of bottled water samples in the present study at an average concentration of 16 ng/L. In South Africa, a previous study did not detect DEHP, DBP or DEHA in any bottled water samples (Aneck-Hahn et al., 2018), and concentrations of DEHP, DBP, DEHA and DINP in drinking water ranged from 60-3415, 176-629, 1.97-4.07, and 8.34-350 ng/L, respectively (Van Zijl et al., 2017). The previously reported South African drinking water concentrations are higher than those found in this study, both in Pretoria and Vhembe, with the exception of DEHA which was consistently detected at higher levels in the present study. Studies of bottled water from Egypt detected DEHP at 104 ng/L and DBP at 82 ng/L, however did not detect DEP, which was detected in all samples from South Africa in the present study (Zaki and

Shoeib, 2018). MEHP is not often reported in literature, but was included in a study of Chinese drinking water which found an average concentration of 9.86 ng/L (Ding et al., 2019a), similar to levels reported in Montreal's BW (4.96 ng/L), Montreal's DW (6.35 ng/L), Vhembe (5.78 ng/L), and Pretoria (5.97 ng/L).

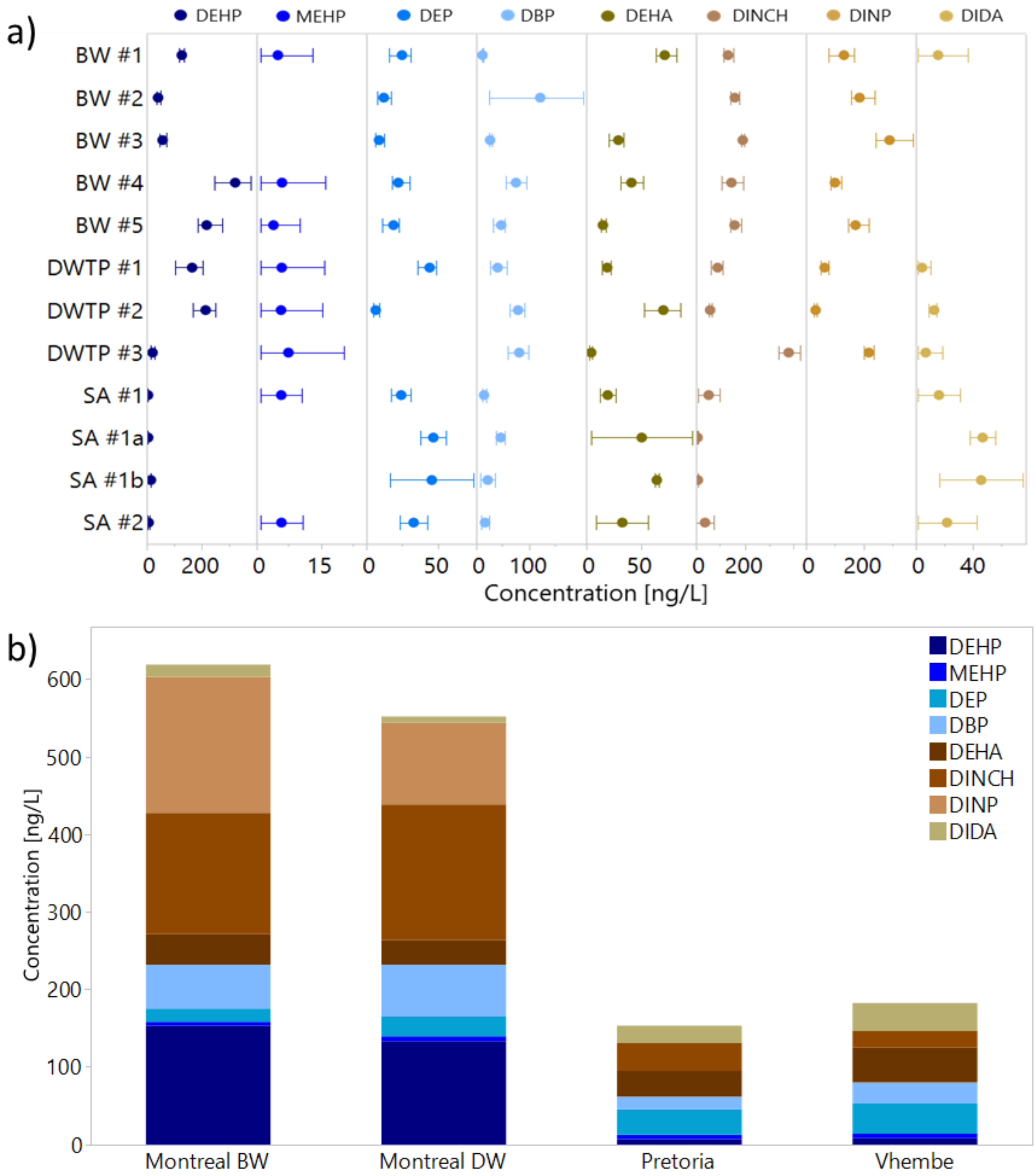

Figure 3 - Summary of plasticizers in potable water.

Blue tones are legacy compounds and brown tones are replacement compounds (a) Concentration per source. Marker represents average concentration and error bars represent range of concentrations detected. BW: Bottled water, DW: Drinking water from Montreal, SA #1: Vhembe, SA #1a: Vhembe water stored in small containers, SA #1b: Vhembe water stored in large containers, SA #2: Pretoria. (b) Concentration averaged by location and water type. Montreal BW: average of 5 bottled water, Montreal DW: average of Montreal's 3 DWTPs, Vhembe: Average of Vhembe's 3 sources, Pretoria: Pretoria DWTP.

3.5.7 Comparison of legacy compounds and replacement compounds

While legacy plasticizers DEHP, DBP, and DEP had the highest overall detection frequencies in potable water samples (100%, 100%, and 97%, respectively), replacement plasticizers DINCH, DINP, DEHA, and DIDA were still frequently detected (97%, 94%, 94%, and 41%, respectively). DINCH and DINP were detected in all of Montreal's BW and DW samples. The total concentration of replacement compounds was statistically higher in Montreal's BW ($p = 0.0048$). It is crucial to thoroughly characterize the toxicity of replacement plasticizers as they are frequently present at similar concentrations to their legacy compounds throughout potable water samples.

Legacy flame retardants, PBDEs, were infrequently detected in potable water samples or at concentrations typically below 1 ng/L. Dechloranes, which are considered replacement flame retardants, were less present than PBDEs in potable water. a-DP was only detected in one sample from Pretoria at a concentration of 1.09 ng/L (Supplemental Information Table S19), and DEC 602, DEC-603, and s-DP were not detected in any water samples. On the contrary, OPEs, which were also considered as replacement flame retardants, were frequently detected throughout all locations. A statistical analysis was performed to compare total concentrations of parent OPEs (6 compounds) to PBDEs (8 compounds) and determined that OPEs were statistically higher than PBDEs in Montreal BW ($p = 0.001$), DW ($p = 0.0003$), and Vhembe ($p = 0.005$). It should be noted that no statistical analysis performed on Pretoria resulted in a significant finding, which could be due to the low number of samples ($n=2$). While replacement compounds are intended to offer a safer alternative to chemicals which have been shown to have negative impacts on the environment and/or human health, incomplete evaluations of the persistence and toxicity of the replacements is a problem. OPEs were originally introduced as safer alternatives to PBDEs, but have since been proven to demonstrate developmental toxicity, neurotoxicity, and endocrine disrupting effects (Yang et al., 2019). Additionally, OPEs have higher mobility once in water than PBDEs, as PBDEs are not very water soluble and tend to accumulate in the soil (Rodgers et al., 2018). The combination of persistence in the aquatic environment, initial toxicity reports for OPEs, and significantly higher levels detected in Montreal's potable water and Vhembe indicates that OPEs should not be considered as a safe alternative to PBDEs.

3.6 Conclusion

The results of the present study demonstrate concentrations of OPE metabolites and plasticizers DINCH and DIDA in potable water for the first time. DINCH was detected in 100% of the samples from Montreal BW (156.59 ng/L), Montreal DW (175.04 ng/L), and Vhembe (21.68 ng/L), and in 50% of samples from Pretoria (36.61 ng/L). Total OPE metabolites were found in similar concentrations to the total of the parent compounds, although there was variability in concentrations between individual compounds and their metabolites. The data shows that replacement flame retardant/plasticizer OPEs are being detected at higher concentrations than legacy PBDEs in Montreal's BW, DW and Pretoria. Replacement plasticizers were found at similar total concentrations and detection frequencies as legacy compounds and were significantly higher only in Montreal's BW. Bisphenols and dechloranes were not detected in any samples, with the exception of a-DP in one South African sample at a concentration of 1.09 ng/L.

When considering Montreal's bottled and drinking water, there was no significant difference in the concentration of total plasticizers or PBDEs, however OPEs were found at statistically higher concentrations in drinking water. There was no significant difference in total plasticizer, PBDE, or OPE concentrations when comparing Vhembe and Pretoria. Montreal potable water had statistically higher concentrations of total plasticizers and PBDEs than South Africa's potable water. The ubiquitous nature of many of these compounds in potable water, especially OPEs and plasticizers, indicates inadequate removal during drinking water treatment. Further laboratory research and field studies should be implemented to investigate the efficiency of different treatment processes on such contaminants of emerging concern.

Attention should be drawn to the potential health risks from the mixtures of flame retardants, plasticizers, and bisphenols found in drinking water. The cumulative effect of mixtures of chemicals is more complex than a simple dose or effect addition (Sarigiannis and Hansen, 2012). The concentrations of target analytes found in potable water in the present study should be combined with toxicological data for each component to accurately assess the health risk from the mixture of chemicals detected. Additionally, comprehensive toxicological investigations on the human health impact of replacement chemicals should be conducted considering that these compounds are consistently being detected in potable water throughout the world.

3.7 Acknowledgements

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3.8 Supplemental Information

Table S3 – Concentrations of PBDEs in drinking water published prior to October 2021.

Location (year published)	Water Type	Total # of samples	BDE-28		BDE-47		BDE-99		BDE-100		BDE-153		BDE-154		BDE-183		BDE-209	
			DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]
Argentina(Fontana et al., 2009) (2009)	TW	1	-	-	0	<LOD (1.2)	0	<LOD (1.5)	0	<LOD (1.0)	0	<LOD (2.0)	-	-	-	-	-	-
U.S.A(Subedi et al., 2015) (2015)	TW	27	33	0.5	81	0.84	81	0.81	81	0.33	33	0.05	52	0.11	15	0.36	0	<LOD (1.0)
Pakistan(Khan et al., 2016b) (2016)	PW	39	41	<LOD (0.00003) – 0.00028	64	<LOD (0.00002) – 0.00059	56	<LOD (0.000017) – 0.0006	31	<LOD (0.00003) – 0.000082	44	<LOD (0.00003) – 0.00025	26	<LOD (0.00003) – 0.00058	51	<LOD (0.00003) – 0.0007	51	<LOD (0.000024) – 0.0007
China(L. Liu et al., 2019) (2019)	BW	NS	0	<LOD (0.0075)	0	<LOD (0.0058)	0	<LOD (0.0063)	0	<LOD (0.0099)	-	-	0	<LOD (0.0022)	-	-	-	-

TW: Tap water, BW: Bottled water, DF: Detection frequency, NS: Not specified, <LOD(): Limit of detection, “-“ compound not included in study.

Table S4 – Concentrations of Dechloranes in drinking water prior to October 2021.

Location (year published)	Water Type	Total # of samples	a-DP		s-DP	
			DF [%]	Conc. [pg/L]	DF [%]	Conc. [pg/L]
Pakistan(Khan et al., 2016b) (2016)	PW	41	36	<LOD (0.031) – 0.29	31	<LOD (0.03) – 0.1

TW: Tap water, DF: Detection frequency, <LOD(): Limit of detection.

Table S5 – Concentrations of OPEs in drinking water prior to October 2021.

Location (year published)	Water Type	Total # of samples	TBOEP		TCEP		TCIPP		TDCIPP		TEHP		TPHP		DPHP	
			DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]
U.S. A(Stackelberg et al., 2004) (2004)	DW	12	83	350	100	99	-	-	100	250	-	-	0	<LOD (500)	-	-
Germany(Andresen and Bester, 2006) (2006)	DW	5	0	<LOD (3)	100	99	-	-	100	2	-	-	-	-	-	-
Italy(Bacaloni et al., 2007) (2007)	TW	6	NS		0	<LOD (1.5)	0	<LOD (1)	0	<LOD (0.7)	-	-	-	-	-	-
U.S. A(Benotti et al., 2009)	DW	15	-	-	40	150	40	220	-	-	-	-	-	-	-	-

(2009)															
Spain(Rodil et al., 2012) (2012)	TW	28	-	-	71	7	92	50	0	<LOD (NS)	-	-	0	<LOD (NS)	0	<LOD (NS)
China(Li et al., 2014) (2014)	TW	39	NS	70.1	NS	12.5	NS	33.4	0	<LOD (1)	0	<LOD (0.5)	NS	40	-	-
	BW	8	100	19.5 – 81.7	25	<LOD (1) – 48.8	100	1.33– 16.2	0	<LOD (1)	0	<LOD (0.5)	100	2.57 – 14.8	-	-
Spain(Esteban et al., 2014) (2014)	TW	6	50	<LOD (0.002) – 33.5	67	<LOD (0.034 – 165.4	50	<LOD (0.002) – 37.1	-	-	-	-	-	-	-	-
China(Ding et al., 2015) (2015)	BW	23	91	0.3	100	0.5	96	0.6	87	0.6	-	-	100	0.8	-	-
	TW	21	100	3.7	100	48.5	100	43	100	5.8	-	-	100	1.4	-	-
South Korea(Lee et al., 2016) (2016)	Various	127	59	26.1	75	38.8	82	67	9	4.46	2	0.94	26	2.12	-	-
Pakistan(Khan et al., 2016b) (2016)	PW	39	-	-	69	<LOD (0.03) – 29.7	74	<LOD (0.03) – 86	64	<LOD (0.03) – 21.4	44	<LOD (0.03) – 8.14	34	<LOD (0.03) – 7.86	-	-
U.S.A.(Kim and Kannan, 2018) (2018)	TW	58	90	10	9	0.45	91	11.6	38	4.75	21	0.12	53	3.72	-	-
South Korea(Park et al., 2018) (2018)	TW	44	100	43.9	100	39.5	100	49.5	18	2	0	<LOD (0.31)	98	23	-	-
China(X. Liu et al., 2019) (2019)	TW	18	-	-	100	15.1 – 160	100	7.4 – 132	11	<LOD (6.2) – 16	11	<LOD (1.4) – 17.9	17	<LOD (7.8) – 45.6	-	-

China(Jiafu Li et al., 2019) (2019)	TW	79	36	<LOD (0.42) – 20.6	100	0.78 – 89	100	2.39 – 101	85	<LOD (1.4) – 22.3	71	<LOD (1.32) – 59	70	<LOD (1.28) – 37.6	-	-
South Korea(Choo and Oh, 2020) (2020)	DW	6	NS	5.66 – 13.0	NS	13.5 – 21.8	NS	15.0 – 35.9	NS	2.17 – 3.23	NS	3.05 – 3.07	NS	305 – 7.47	-	-
South Korea(Sim et al., 2021) (2021)	DW	36	100	8.32	100	17.3	100	17.9	11	0.15	53	0.27	67	1.73	-	-
China(Zhang et al., 2021) (2021)	TW	1	-	-	100	0.31	100	8.99	-	-	-	-	100	7.47	-	-

Table S6 – Concentrations of plasticizers in drinking water prior to October 2021.

Location (year published)	Water Type	Total # of samples	DBP		DEHP		DEP		DEHA		DINP		MEHP	
			DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]
Germany(Luks-Betlej et al., 2001) (2001)	TW	1	100	380	100	50	100	200	-	-	-	-	-	-
Poland(Luks-Betlej et al., 2001) (2001)	TW	1	100	640	100	60	100	160	-	-	-	-	-	-
Portugal(Serôdio and Nogueira, 2006) (2006)	TW	NS	NS	520	NS	60	NS	190	NS	90	-	-	-	-
	BW	NS	NS	350	NS	170	NS	40	NS	150	-	-	-	-
Canada(Chen et al., 2006) (2006)	DW	NS	NS	50	NS	188	-	-	-	-	-	-	-	-
	DW	NS	NS	46	NS	103	-	-	-	-	-	-	-	-
Canada(Cao, 2008) (2008)	BW	1	100	1720	100	223	100	67	0	<LOD (17)	-	-	-	-

	BW	6	100	138	100	118	100	80	0	<LOD (17)	-	-	-	-
Italy(Montuori et al., 2008) (2008)	BW	142	NS	210	NS	20	NS	170	-	-	-	-	-	-
Greece(Amiridou and Voutsa, 2011) (2011)	BW	6	NS	44	NS	350	NS	33	-	-	-	-	-	-
Portugal(Santana et al., 2013) (2013)	TW	4	0	<LOD (10)	50	<LOD (10) – 130	-	-	-	-	-	-	-	-
	BW	1	100	1890	100	20	-	-	-	-	-	-	-	-
	BW	5	100	100-1420	100	80-180	-	-	-	-	-	-	-	-
Hungary(Keresztes et al., 2013) (2013)	BW	3	NS	<LOQ (6.6) – 800	NS	<LOQ (16) – 1700	NS	<LOQ (22.2)	-	-	-	-	-	-
France(Dévier et al., 2013) (2013)	BW	2	0	<LOQ (20)	0	<LOQ (10)	0	<LOQ (30)	-	-	-	-	-	-
China(Hu et al., 2013) (2013)	DW	8	100	68 – 200	100	10 – 61	100	5.6 – 54	-	-	-	-	-	-
Spain(Guart et al., 2014a) (2014)	BW	362	0	736	8	985 – 5510	4	920 – 9340	3	182 – 2040	-	-	-	-
International(Guart et al., 2014b) (2014)	BW	77	5	100	0	<LOD (66)	-	-	-	-	91	<LOD (1) – 447	-	-
Taiwan(Yang et al., 2014) (2014)	TW	23	92	<LOD (1) – 103	100	131 – 239	54	<LOD (1) – 7	-	-	85	<LOD (1) – 316	-	-
	DWF	20	100	12 – 47	100	34 – 283	45	<LOD (1) – 3	-	-	-	-	-	-
Spain(Domínguez-Morueco et al., 2014) (2014)	TW	7	100	633	0	<LOD (460)	14	<LOD (330) – 381	-	-	-	-	-	-
China(Liu et al., 2015) (2015)	DW	225	100	350	94	770	88	35	-	-	-	-	-	-
Iran(Jeddi et al., 2015) (2015)	BW	12	NS	135	NS	217	-	-	-	-	NS	<LOD (420)	-	-

Taiwan(Gou et al., 2016) (2016)	DW	109	NS	<LOQ (610 –840	NS	<LOQ (930) – 2880	-	-	-	-	NS	<LOD (NS)	-	-
China(Kong et al., 2017) (2017)	DW	NS	NS	17	NS	150	NS	<LOQ (NS)	-	-	-	-	-	-
South Africa(Van Zijl et al., 2017) (2017)	DW	20	100	176 – 629	100	60 – 3415	-	-	100	1.97 – 4.07	100	8.34-350	-	-
South Africa(Aneck-Hahn et al., 2018) (2018)	BW	10	0	<LOD (5.7)	0	<LOD (4.4)	-	-	0	<LOD (8.7)	-	-	-	-
Iran(Gheisari et al., 2018) (2018)	TW	66	21	<LOD (0.01) – 67	67	<LOD (0.06) – 606	29	<LOD (0.14) – 113	-	-	-	-	-	-
Egypt(Zaki and Shoeib, 2018) (2018)	BW	12	58	82	50	104	0	<LOD (12)	-	-	-	-	-	-
Iran(Abtahi et al., 2019) (2019)	DW	40	NS	90	NS	150	NS	50	-	-	-	-	-	-
	BW	10	NS	70	NS	100	NS	180	-	-	-	-	-	-
China(Ding et al., 2019a) (2019)	DW	146	86	596	77	178	65	5.9	-	-	-	-	37	9.86
China(Hui Li et al., 2019) (2019)	BW	60	NS	200	NS	18	NS	23	-	-	NS	20	-	-
France(Bach et al., 2020) (2020)	DW	89	100	951	0	<LOD (500)	100	255	0	<LOD (500)	-	-	-	-
China(Xue et al., 2021) (2021)	DW	NS	NS	153	NS	645	NS	8.69	-	-	-	-	-	-
China(Wang et al., 2021) (2021)	TW	6	100	340 – 670	100	1097 – 1505	0	<LOD (21)	-	-	-	-	-	-
China(Wang et al., 2021) (2021)	BW	6	100	465 - 517	100	880 – 1257	0	<LOD(21)	-	-	-	-	-	-
Hong Kong(Li et al., 2021)	TW	12	83	346	25	85.3	100	102	-	-	-	-	-	-

(2021)														
Hong Kong(Li et al., 2021) (2021)	BW	3	100	95	0	<LOD(0.8)	100	38.7		-	-	-	-	-

TW: Tap water, BW: Bottled water, DW: Drinking water, DWF: drinking water fountain DF: Detection frequency, <LOD(): Limit of detection, <LOQ(): Limit of quantification, “**-**“ compound not included in study.

Table S7 – Concentrations of Bisphenols in drinking water between 2012 – October 2021.

Location (year published)	Water Type	Total # of samples	BPA		BPAF		BPF		BPS	
			DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]	DF [%]	Conc. [ng/L]
Italy(Maggioni et al., 2012) (2012)	DW	35	29	<LOD(0.73) – 102	-	-	-	-	-	-
	BW	5	40	<LOD(0.73) – 1.13	-	-	-	-	-	-
Malaysia(Santhi et al., 2012) (2012)	TW	30	100	14.1	-	-	-	-	-	-
Taiwan(H W Chen et al., 2013) (2013)	DW	NS	NS	<LOQ (4.3) - 38	-	-	-	-	-	-
France(Colin et al., 2014) (2014)	TW	291	4	<LOD(25) – 1430	-	-	0	<LOD(25)	-	-
Spain(Guart et al., 2014a) (2014)	BW	362	10	<LOD(NS) – 24200	-	-	-	-	-	-
Lebanon(Dhaini and Nassif, 2014) (2014)	BW	22	59	169	-	-	-	-	-	-
Korea(Nam et al., 2014) (2014)	DW	25	40	<LOD (1.99) - 324	-	-	-	-	-	-
India(Saini et al., 2015) (2015)	TW	1	100	11.83	-	-	-	-	-	-
Cape Town(Van Zijl et al., 2017) (2017)	DW	40	93	1.45	-	-	-	-	-	-
Pretoria(Van Zijl et al., 2017) (2017)	DW	40	90	1.33	-	-	-	-	-	-
South Africa(Aneck-Hahn et al., 2018) (2018)	BW	10	90	2.78	-	-	-	-	-	-
China(Xu et al., 2018) (2018)	DW	2	0	<LOD (0.3)	-	-	-	-	-	-
Egypt(Radwan et al., 2019) (2019)	DW	446	15	36.1	-	-	-	-	-	-
Canada(Goeury et al., 2019) (2019)	TW	11	0	<LOQ(1.5)	-	-	-	-	-	-
China(Zhang et al., 2019a) (2019)	DW	20	40	1.6	30	0.4	5	0.04	25	0.1
China(Wang et al., 2020) (2020)	BW	21	100	675	33	<LOD(1.56) – 4.9	0	<LOD(0.91)	10	<LOD(2.3) – 10.6

China(Hao, 2020) (2020)	DW	52	67	<LOD (7) – 898.7	-	-	-	-	-	-
Italy(Valbonesi et al., 2021) (2021)	DW	12	100	<LOQ (0.99) – 6.27	-	-	-	-	-	-
Hong Kong(Li et al., 2021) (2021)	TW	12	-	-	83.7	0.96	83	1.51	33	2.95
Hong Kong(Li et al., 2021) (2021)	BW	3	-	-	100	0.96	67	1.52	0	<LOD(0.5)

TW: Tap water, DW: Drinking water, BW: Bottled water, DF: Detection frequency, <LOD(): Limit of detection, <LOQ(): Limit of quantification, “-“ compound not included in study

Table S8 – List of target analytes with CAS number and supplier of native standards

Family	**Analyte acronym**	**Target analyte**	**CAS number**	**Supplier**
Plasticizer	DEHP	Bis(2-ethylhexyl) phthalate	117-81-7	Sigma Aldrich
Plasticizer	DEP	Diethyl phthalate	84-66-2	Sigma Aldrich
Plasticizer	DBP	Dibutyl phthalate	84-74-2	Sigma Aldrich
Plasticizer	DEHA	Bis(2-ethylhexyl) adipate	103-23-1	Toronto Research Chemicals
Plasticizer	DINCH	Bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate	166412-78-8	Toronto Research Chemicals
Plasticizer	DIDA	Diisodecyl adipate	27178-16-1	Sigma Aldrich
Plasticizer	DINP	Diisononyl phthalate	68515-48-0	Sigma Aldrich
Plasticizer	MEHP	Mono(ethylhexyl) phthalate	4376-20-9	Toronto Research Chemicals
OPEs	TBOEP	Tris(2-butoxyethyl) phosphate	78-51-3	Sigma Aldrich
OPEs	TCEP	Tris(2-chloroethyl) phosphate	115-96-8	Sigma Aldrich
OPEs	TCIPP	Tris(1-chloro-2-propyl) phosphate	13674-84-5	Cambridge Isotope Lab. Inc
OPEs	TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	Toronto Research Chemicals Inc.
OPEs	TEHP	Tris(2-ethylhexyl) phosphate	78-42-2	Wellington Laboratories
OPEs	TPHP	Triphenyl phosphate	115-86-6	Supelco Analytical
OPEs – metabolite	DPHP	Diphenyl phosphate	838-85-7	Sigma Aldrich
OPEs – metabolite	Ip-PPP	4-Isopropylphenyl phenyl phosphate	69415-02-7	Toronto Research Chemicals
OPEs – metabolite	BCPP	Bis(1-chloro-2-propyl) phosphate	789440-10-4	Toronto Research Chemicals
OPEs – metabolite	BCEP	Bis(2-chloroethyl) phosphate	3040-56-0	Toronto Research Chemicals
OPEs – metabolite	BBOEP	Bis(2-butoxyethyl) phosphate	14260-97-0	Toronto Research Chemicals
OPEs – metabolite	BDCIPP	Bis(1,3-dichloro-2-propyl) phosphate	72236-72-7	Wellington Laboratories
OPEs – metabolite	BEHP	Bis(2-ethylhexyl) phosphate	298-07-7	Toronto Research Chemicals
OPEs – metabolite	BTBOEP	Bis(2-butohexylethyl) 2-Hydroxyethyl Phosphate Triester	1477494-86-2	Toronto Research Chemicals
OPEs – metabolite	DCP	Di-cresyl phosphate	36400-46-1	Toronto Research Chemicals
PBDE	BDE 28	2,4,4'-Tribromodiphenyl ether	41318-75-6	Wellington Laboratory
PBDE	BDE 47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1	Wellington Laboratory
PBDE	BDE 99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9	Wellington Laboratory
PBDE	BDE 100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8	Wellington Laboratory
PBDE	BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2	Wellington Laboratory
PBDE	BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4	Wellington Laboratory
PBDE	BDE 183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5	Wellington Laboratory
PBDE	BDE 209	Decabromodiphenyl ether	1163-19-5	Wellington Laboratory
Dechlorane	DEC-602	Dechlorane 602	31107-44-5	Toronto Research Chemicals
Dechlorane	DEC-603	Dechlorane 603	13560-92-4	Toronto Research Chemicals
Dechlorane	a-DP	Anti-dechlorane plus	13560-89-9	Toronto Research Chemicals
Dechlorane	s-DP	Syn-dechlorane plus	135821-03-3	Cambridge Isotope Lab. Inc.
Bisphenol	BPA	Bisphenol A	80-05-7	Toronto Research Chemicals
Bisphenol	BPAF	Bisphenol AF	1478-61-1	Sigma Aldrich
Bisphenol	BPF	Bisphenol F	620-92-8	Toronto Research Chemicals
Bisphenol	BPS	Bisphenol S	80-09-1	Sigma Aldrich

Table S9 – Labelled surrogates used for recovery and matrix effect in each sample with CAS numbers and suppliers

Family	**Analyte acronym**	**Target analyte**	**CAS number**	**Supplier**
Plasticizer	DEHP-d4	Bis(2-ethylhexyl) phthalate-d4	117-81-7	Toronto Research Chemicals
Plasticizer	DEP-d4	Diethyl phthalate-d4	84-66-2	Toronto Research Chemicals
Plasticizer	DBP-d4	Dibutyl phthalate-d4	84-74-2	Toronto Research Chemicals
Plasticizer	DEHA-d4	Bis(2-ethylhexyl) adipate-d4	103-23-1	Toronto Research Chemicals
Plasticizer	DINP-d4	Diisononyl phthalate-d4	68515-48-0	Toronto Research Chemicals
Plasticizer	DINCH-13C4	Bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate-13C4	166412-78-8	Toronto Research Chemicals
Plasticizer	MEHP-d4	Mono(ethylhexyl) phthalate-d4	4376-20-9	Toronto Research Chemicals
OPEs	TEHP-d51	Tris(2-ethylhexyl) phosphate-d51	1259188-37-8	Toronto Research Chemicals
OPEs	TCEP-d12	Tris(2-chloroethyl) phosphate-d12	115-96-8	Wellington Laboratories
OPEs	TDCIPP-d15	Tris(1,3-dichloro-2-propyl) phosphate-d15	1447569-77-8	Wellington Laboratories
OPEs	TPHP-d15	Triphenyl phosphate	1173020-30-8	Wellington Laboratories
OPEs – metabolite	DPHP-d10	Diphenyl phosphate-d10	1477494-97-5	Toronto Research Chemicals Inc.
OPEs – metabolite	Ip-PPP-d7	4-Isopropylphenyl phenyl phosphate-d7	69415-02-7	Toronto Research Chemicals Inc.
OPEs – metabolite	BCPP-d12	Bis(1-chloro-2-propyl) phosphate-d12	789440-10-4	Toronto Research Chemicals Inc.
OPEs – metabolite	BBOEP-d8	Bis(2-butoxyethyl) phosphate-d8	14260-97-0	Toronto Research Chemicals Inc.
OPEs – metabolite	BEHP-d34	Bis(2-ethylhexyl) phosphate-d34	1773493-20-1	Toronto Research Chemicals Inc.
OPEs – metabolite	DCP—d14	Di-cresyl phosphate-d14	36400-46-1	Toronto Research Chemicals Inc.
PBDE	BDE 28-13C12	2,4,4'-Tribromodiphenyl ether-13C12	41318-75-6	Wellington Laboratory
PBDE	BDE 47-13C12	2,2',4,4'-Tetrabromodiphenyl ether-C13C12	5436-43-1	Wellington Laboratory
PBDE	BDE 99-13C12	2,2',4,4',5-Pentabromodiphenyl ether-13C12	60348-60-9	Wellington Laboratory
PBDE	BDE 100-13C12	2,2',4,4',6-Pentabromodiphenyl ether-13C12	189084-64-8	Wellington Laboratory
PBDE	BDE 153-13C12	2,2',4,4',5,5'-Hexabromodiphenyl ether-13C12	68631-49-2	Wellington Laboratory
PBDE	BDE 154-13C12	2,2',4,4',5,6'-Hexabromodiphenyl ether-13C12	207122-15-4	Wellington Laboratory
PBDE	BDE 183-13C12	2,2',3,4,4',5',6-Heptabromodiphenyl ether-13C12	207122-16-5	Wellington Laboratory
PBDE	BDE 209-13C12	Decabromodiphenyl ether-13C12	1163-19-5	Wellington Laboratory
Dechlorane	DEC-602-13C10	Dechlorane 602-13C10	31107-44-5	Cambridge Isotope Lab. Inc.
Dechlorane	a-DP-13C10	Anti-dechlorane plus-13C10	135821-74-8	Cambridge Isotope Lab. Inc.
Dechlorane	s-DP-13C10	Syn-dechlorane plus-13C10	135821-03-3	Cambridge Isotope Lab. Inc.
Bisphenol	BPA-C13	Bisphenol A-C13	80-09-1	Toronto Research Chemicals Inc.
Bisphenol	BPAF-d4	Bisphenol AF-d4	263261-65-0	Toronto Research Chemicals Inc.
Bisphenol	BPF-C13	Bisphenol F-C13	1410794-06-7	Toronto Research Chemicals Inc.
Bisphenol	BPS-C13	Bisphenol S-C13	80-09-1	Toronto Research Chemicals Inc.

Table S10 – Analysis parameters and instrument detection limits for PBDEs used in Montreal campaign 1

Compound	**Analyte**		**Internal standard**		**IDL [ng/L]**	**Recovery [%]**	**Retention time [min]**
	SIM-Q (m/z)	**SIM-C (m/z)**	**SIM-Q (m/z)**	**SIM-C (m/z)**			
BDE-28	405.8	407.8	417.8	419.8	0.12	77.9	6.42
BDE-47	483.7	485.7	497.8	499.7	0.52	75.3	7.27
BDE-99	563.6	565.6	575.6	577.7	0.41	75.0	8.16
BDE-100	641.5	643.5	653.6	655.6	0.28	72.9	7.94
BDE-153	721.4	723.4	733.5	735.5	1.09	64.8	9.27
BDE-154	799.4	801.3	811.4	813.4	0.80	66.5	8.87
BDE-183	879.3	881.3	891.3	893.3	0.58	70.1	10.61
BDE-209	957.2	959.2	971.2	973.2	9.61	100.1	16.93

Table S11 – SRM transition and instrument detection limits for PBDEs used in all campaigns except Montreal campaign 1 (Montreal campaigns 2-3 and South Africa campaigns 1-2)

Compound	**Transition ions monitored**		**IDL [ng/L]**
	Congener	**Internal standard**	
BDE-28	407.8 → 247.9	419.8 → 260.0	0.02
BDE-47	485.7 → 325.9	497.8 → 337.8	0.02
BDE-99	403.8 → 137.0	415.8 → 148.0	0.01
BDE-100	403.8 → 137.0	415.8 → 148.0	0.01
BDE-153	643.5 → 483.7	655.6 → 495.7	0.01
BDE-154	643.5 → 483.7	655.6 → 495.7	0.04
BDE-183	723.4 → 563.6	733.5 → 573.6	0.01

Table S12 – Analysis parameters and instrument detection limits for dechloranes in Montreal campaign 1

Compound	**Analyte**		**Internal standard**		**Recovery [%]**	**IDL [ng/L]**	**Retention time [min]**
	SIM-Q (m/z)	**SIM-C (m/z)**	**SIM-Q (m/z)**	**SIM-C (m/z)**			
DEC 602	271.8	273.8	276.9	278.8	36.9	0.10	8.13
DEC 603	260.8	262.8	-	-	35.9	0.27	10.18
a-DP	271.8	273.8	276.9	278.8	158.3	0.16	12.45
s-DP	271.8	273.8	-	-	46.7	0.04	11.94

Table S13 – Analysis parameters and instrument detection limits for all campaigns except Montreal campaign 1 (Montreal campaigns 2-3 and South Africa campaigns 1-2).

Compound	**Retention time [min]**	**SIM-Q (m/z)**	**SIM-C (m/z)**	**Internal standard (m/z)**	**IDL [ng/L]**
Dechlorane 602	29.69	614	612	624	1.0
Dechlorane 603	34.89	638	636	624	2.4
s-DP	35.99	654	652	664	1.7
a-DP	36.19	654	652	664	0.9

SIM-Q is quantification and SIM-C is confirmation.

Table S14 – Analysis parameters and instrument detection limits for OPEs

	Analyte		**Internal standard**				
Compound	MRM transition [Collision energy, eV]	Cone Voltage (V)	MRM transition [Collision energy, eV]	Cone Voltage (V)	**Ionisation mode**	**Recovery [%]**	**IDL [ng/L]**
TBOEP	399.37 → 45.04 [22]	38	426.42 → 208.09 [16]	36	ESI+	60.7	0.34
TCEP	287.10 → 99.01 [24]	36	299.17 → 67.10 [26]	40	ESI+	78.1	0.48
TCIPP	329.18 → 99.01 [20]	32	342.19 → 81.82 [40]	64	ESI+	83.1	0.70
TDCIPP	431.04 → 99.01 [22]	36	446.14 → 102.00 [26]	40	ESI+	112.1	0.18
TEHP	435.53 → 99.00 [16]	18	486.85 → 102.19 [22]	28	ESI+	419.4	0.03
TPHP	327.18 → 77.13 [38]	56	342.19 → 81.82 [40]	64	ESI+	118.7	0.11
BDCIPP	318.64 → 34.42 [8]	18	328.71 → 34.74 [8]	8	ESI-	159.9	0.55
DPHP	249.03 → 93.03 [24]	56	259.15 → 98.04 [26]	54	ESI-	115.3	0.24
BCPP	253.00 → 98.81 [20]	25	264.98 → 100.88 [14]	26	ESI+	140.0	0.17
BCEP	222.93 → 98.86 [18]	32	230.9 → 100.9 [18]	36	ESI+	84.3	0.23
DCPs	279.21 → 91.13 [30]	46	293.30 → 97.25 [30]	56	ESI+	85.6	0.24
ip-PPPs	293.24 → 77.08 [36]	46	293.30 → 97.25 [30]	56	ESI+	81.8	0.21
BTBOEP	343.15 → 44.88 [18]	22	347.14 → 44.95 [18]	32	ESI+	75.8	0.28
BBOEP	299.28 → 45.04 [18]	34	307.33 → 49.01 [18]	32	ESI+	99.7	0.26
BEHP	321.01 → 78.88 [32]	58	355.41 → 227.26 [24]	60	ESI-	187.4	0.25

Table S15 – Analysis parameters and instrument detection limits for bisphenols

Compound	Analyte Retention time [min]	m/z	Internal standard Retention time [min]	m/z	Linearity	Recovery [%]	IDL [ng/L]
BPA	14.9	227.10	14.9	239.15	0.99	140	0.32
BPAF	15.5	335.05	15.5	339.08	0.99	108	0.1
BPF	13.9	199.08	13.9	211.12	0.99	126	0.71
BPS	12.2	249.02	12.2	261.06	0.98	57.0	0.82

Table S16 – Analysis parameters and method detection limits for plasticizers.

Compound	Retention time [min]	SIM-Q m/z	SIM-C m/z	Linearity	Recovery [%]	IDL [ng/L]
DEHP	8.54	391.28	278.9	0.99	82.8	1.35
MEHP	6.95	279.16	167.0	0.99	77.5	1.32
DEP	6.60	223.10	163.0	0.99	83.4	1.29
DBP	6.80	279.16	205.1	0.99	77.7	1.70
DEHA	8.60	371.32	129.0	0.99	85.7	1.54
DINCH	9.80	425.36	155.9	0.99	76.0	1.93
DINP	9.20	419.32	129.2	0.99	87.9	1.68
DIDA	9.50	427.38	269.1	0.99	82.4	1.68

SIM-Q is used for quantification and SIM-C is used for confirmation. MS2 was used for confirmation with the exception of MEHP which used MS3.

Table S17 – Concentration of target analytes in Montreal bottled water.

Compound	BW #1			BW #2			BW #3			BW #4			BW #5		
	Camp. 1	Camp. 2	Camp. 3	Camp. 1	Camp. 2	Camp. 3	Camp. 1	Camp. 2	Camp. 3	Camp. 1	Camp. 2	Camp. 3	Camp. 1	Camp. 2	Camp. 3
Flame retardants															
BDE-28	ND	<LOQ	ND	<LOQ	ND	<LOQ	<LOQ	ND	ND	ND	<LOQ	ND	ND	ND	ND
BDE-47	ND	<LOQ	0.06	ND	<LOQ	0.07	ND	ND	0.13	ND	ND	<LOQ	ND	<LOQ	<LOQ
BDE-99	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	0.03	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND	ND	ND	ND
TBOEP	0.57	3.40	ND	8.11	26.33	3.14	5.00	ND	ND	2.11	ND	ND	15.40	ND	3.13
TCEP	ND	33.54	10.41	ND	51.45	11.53	ND	4.71	6.47	ND	46.31	4.23	ND	32.09	6.44
TCIPP	ND	8.24	0.52	ND	11.17	0.37	ND	1.02	1.61	ND	0.69	0.95	ND	2.45	0.56
TDCIPP	5.12	2.08	0.97	ND	21.24	2.92	4.81	1.16	1.54	ND	24.59	0.23	ND	9.89	3.86
TEHP	ND	ND	0.06	ND	ND	0.21	ND	ND	6.28	ND	ND	1.22	ND	ND	2.01
TPHP	1.01	1.19	0.62	0.46	1.92	0.80	0.87	0.79	0.85	0.61	2.20	1.09	0.22	0.99	0.67
BDCIPP	0.66	3.72	ND	0.39	8.32	ND	0.51	ND	ND	ND	ND	ND	0.73	7.14	ND
DPHP	2.68	5.11	3.05	ND	5.11	2.29	0.16	16.91	5.77	6.54	4.23	3.30	7.30	6.77	0.72
BCIPP	ND	ND	<LOQ	ND	ND	0.43	ND	ND	0.44	ND	ND	0.53	ND	ND	0.27
BCEP	1.37	ND	0.26	1.58	ND	0.68	1.12	ND	ND	0.37	ND	0.68	1.17	ND	ND
DCPs	0.86	<LOQ	0.31	ND	<LOQ	<LOQ	ND	0.68	<LOQ	ND	<LOQ	<LOQ	ND	<LOQ	<LOQ
BTBOEP	0.55	1.15	0.13	1.17	3.72	0.23	0.76	0.74	0.83	0.39	2.45	ND	0.45	0.38	0.53
BBOEP	0.27	0.92	ND	0.86	4.08	0.51	0.94	0.17	1.10	ND	1.81	ND	ND	ND	ND
BEHP	ND	66.78	27.87	ND	53.54	30.33	ND	66.73	42.98	ND	81.45	28.92	ND	70.71	25.80
Plasticizers															
DEHP	128.73	137.38	116.50	39.32	34.09	59.97	45.78	55.21	71..89	247.12	339.86	378.83	247.12	340.86	274.43
MEHP	ND	ND	13.08	ND	ND	<LOQ	ND	ND	<LOQ	ND	ND	15.98	ND	ND	10.02
DEP	30.94	15.50	27.98	10.98	7.82	17.50	8.10	12.05	6.08	18.26	18.24	30.11	11.25	22.73	22.61
DBP	10.17	13.74	10.41	137.69	23.93	202.94	24.36	24.15	29.07	73.05	56.39	96.11	54.32	54.60	32.40
DEHA	67.95	63.92	82.49	ND	ND	<LOQ	33.94	33.65	20.26	40.53	51.53	31.41	13.16	14.53	17.95
DINCH	112.63	125.22	154.53	175.35	158.54	142.40	195.89	193.96	183.35	136.96	104.92	192.43	147.16	140.06	185.42
DINP	168.03	146.43	79.64	162.19	156.59	237.11	257.79	241.16	368.64	84.77	94.79	121.22	146.87	151.31	216.05
DIDA	36.34	9.09	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND represents samples which had non-detect, <LOQ represents samples which were detected but below the limit of quantification. Compounds not detected in any samples: BDE-154, BDE-183, BDE-209, DEC 602, DEC 603, a-DP, s-DP, and ip-PPP, BPA, BPAF, BPF, BPS

Table S18 – Concentration of target analytes in Montreal drinking water.

Compound	**DWTP #1**			**DWTP #2**			**DWTP #3**		
	Camp. 1	**Camp. 2**	**Camp. 3**	**Camp. 1**	**Camp. 2**	**Camp. 3**	**Camp. 1**	**Camp. 2**	**Camp. 3**
Flame retardants									
BDE-28	ND	<LOQ	ND	ND	ND	<LOQ	ND	0.05	ND
BDE-47	ND	ND	ND	ND	<LOQ	ND	ND	0.08	ND
BDE-100	ND	ND	ND	ND	ND	0.03	ND	ND	ND
BDE-154	ND	0.06	ND	ND	ND	ND	ND	ND	ND
TBOEP	11.14	39.13	4.64	26.82	8.16	0.47	21.76	16.41	9.02
TCEP	107.87	159.05	15.92	182.78	91.90	2.94	86.96	92.57	21.35
TCIPP	13.56	24.11	14.39	26.36	16.14	8.73	19.88	10.82	9.08
TDCIPP	55.79	76.34	11.34	149.76	32.24	10.33	16.38	42.97	24.09
TEHP	0.23	ND	0.06	0.62	ND	0.23	ND	ND	9.50
TPHP	10.17	10.39	3.25	39.18	10.92	1.75	3.86	18.30	2.13
BDCIPP	3.70	3.49	ND	11.13	4.51	ND	8.25	ND	ND
DPHP	36.49	49.80	2.65	50.69	19.59	1.04	31.64	50.94	1.42
BCIPP	204.90	287.46	1.47	303.34	154.15	1.53	223.04	293.47	1.10
BCEP	ND	ND	0.53	ND	ND	0.84	ND	ND	0.69
DCPs	ND	1.11	<LOQ	ND	<LOQ	<LOQ	<LOQ	<LOQ	ND
BTBOEP	6.81	15.38	1.27	12.91	3.63	0.58	12.76	10.69	3.83
BBOEP	2.50	9.08	ND	6.95	0.35	ND	3.56	3.19	1.76
BEHP	59.94	49.21	26.32	40.85	58.69	22.73	50.96	49.61	30.15
Ip-PPP	0.60	ND	ND	ND	ND	ND	ND	0.41	ND
Plasticizers									
DEHP	204.28	185.17	105.37	225.39	168.30	249.01	13.47	22.26	27.71
MEHP	ND	ND	15.75	ND	ND	15.34	ND	ND	20.47
DEP	35.83	48.83	47.84	5.6	4.83	8.94	<LOQ	ND	<LOQ
DBP	26.49	57.50	36.68	84.10	62.60	90.83	98.96	86.03	59.19
DEHA	20.69	14.39	22.11	85.63	71.96	52.98	5.08	<LOQ	5.83
DINCH	96.70	108.37	60.07	65.34	55.20	51.53	426.09	339.31	372.74
DINP	64.72	49.62	79.89	36.30	37.38	26.73	199.48	218.41	234.47
DIDA	ND	ND	10.59	9.26	14.57	14.46	ND	ND	18.43

ND represents samples which had non-detect, <LOQ represents samples which were detected but below the limit of quantification. Compounds not detected in any samples: BDE-153, BDE-183, BDE-209, DEC 602, DEC 603, a-DP, s-DP, BPA, BPAF, BPF, BPS

Table S19 – Concentration of target analytes in South Africa water.

Compound	**Vhembe**		**Vhembe – small containers**		**Vhembe – large containers**		**Pretoria**	
	Camp. 1	**Camp. 2**	**Camp. 1**	**Camp. 2**	**Camp. 1**	**Camp. 2**	**Camp. 1**	**Camp. 2**
Flame retardants								
BDE-28	0.09	ND	<LOQ	ND	ND	ND	<LOQ	<LOQ
BDE-47	0.12	ND	1.18	ND	0.05	ND	0.53	<LOQ
BDE-99	0.06	ND	0.26	ND	0.03	ND	0.05	ND
BDE-100	0.06	0.24	0.08	ND	0.02	ND	0.16	ND
BDE-154	<LOQ	ND	<LOQ	ND	ND	ND	ND	ND
a-DP	ND	ND	ND	ND	ND	ND	ND	1.09
TBOEP	ND	3.37	ND	0.37	ND	1.17	ND	9.28
TCEP	9.97	6.94	97.55	14.06	86.0	9.03	100.37	47.69
TCIPP	1.40	7.55	21.58	7.16	9.70	4.61	204.49	148.39
TDCIPP	36.86	12.93	119.19	1.21	108.40	ND	100.77	33.09
TEHP	ND	0.74	ND	0.13	ND	ND	ND	0.33
TPHP	2.03	3.51	3.49	3.37	3.39	3.11	3.93	4.90
DPHP	29.52	0.77	28.81	0.36	12.82	0.82	172.58	128.13
BCIPP	138.63	0.83	184.31	0.34	73.81	0.08	215.35	14.13
BCEP	ND	ND	5.58	ND	ND	ND	ND	0.29
DCPs	0.42	<LOQ	<LOQ	<LOQ	ND	<LOQ	0.53	ND
BTBOEP	ND	0.77	ND	0.65	ND	0.94	11.98	14.55
BBOEP	ND	ND	ND	ND	2.85	0.44	11.14	1.97
BEHP	42.98	26.87	34.96	34.35	29.85	21.22	44.17	26.32
Ip-PPP	ND	ND	ND	<LOQ	ND	ND	0.512	<LOQ
Plasticizers								
DEHP	4.79	4.27	4.99	5.04	15.71	14.03	9.71	4.07
MEHP	10.56	<LOQ	ND	<LOQ	<LOQ	<LOQ	10.73	<LOQ
DEP	17.44	31.05	37.55	55.83	16.76	74.48	23.55	42.42
DBP	10.22	18.36	54.51	37.82	7.99	34.67	8.72	24.02
DEHA	12.35	26.70	4.32	96.66	66.16	62.32	8.98	56.68
DINCH	94.78	8.35	2.42	9.95	6.70	7.89	71.85	ND
DINP	<LOQ	ND	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
DIDA	ND	31.05	37.55	55.83	16.76	74.48	ND	42.42

ND represents samples which had non-detect, <LOQ represents samples which were detected but below the limit of quantification. Compounds not detected in any samples: BDE-153, BDE-183, DEC 602, DEC 603, a-DP, BDCIPP, BPA, BPAF, BPF, BPS

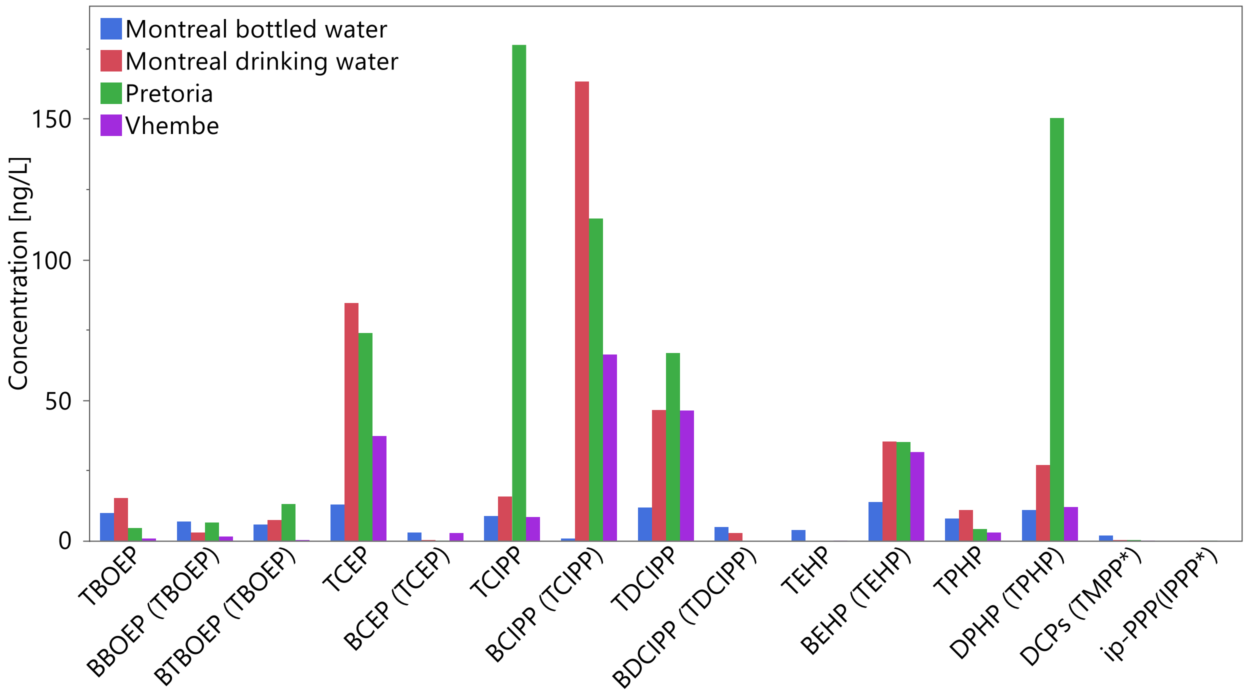

Figure S4 – Comparison of concentrations of OPE parent compounds and their metabolites.

For the metabolites, their parent compound is specified in brackets. *Denotes parent compounds which were not included in the present study.

4 Manuscript 2: Removal of plasticizers, bisphenols, and flame retardants through a conventional drinking water treatment plant

4.1 Preface

In the previous manuscript, the levels of flame retardants, bisphenols, and plasticizers were measured in potable water from Montreal and South Africa. The results were essential for determining the presence and concentrations of target analytes in potable water from different geographic locations, as well as for comparing legacy and replacement compounds. The present manuscript addresses the second objective of this master's research - evaluate the efficiency of conventional water treatment methods to mitigate exposure to these targeted compounds and identify the most effective removal treatment steps.

Sampling was performed in a DWTP located in Montreal to determine the removal of target analytes through filtration, UV disinfection, and chlorination, the most common conventional treatment steps. Twenty-four-hour composite daily sampling was performed over a 3-day period, accounting for the residence time of each unit. Samples were concentrated using the SPE methods developed and reported in manuscript 1. Analysis of OPEs, DCs, and PBDEs were performed following the methods developed and reported in manuscript 1. Methods for the analysis of plasticizers and BPs are being developed on a new instrument, a Vanquish UHPLC-RTC system (Thermo Scientific, Germany) coupled with an Exploris 120 HRMS (Thermo Scientific, Germany). The results for plasticizers and bisphenols were not yet available to include in this thesis but will be added to manuscript 2 before publication.

BDE-209, which was only included in the first sampling campaign in manuscript 1, was not included in the second manuscript as it could not be analyzed at Health Canada's laboratory. Concentrations of target analytes were analysed using statistical methods to determine significant removal efficiencies for each treatment step. With only three replicates (3 days of sampling), a different statistical analysis was used in this manuscript than what was used in Manuscript 1. The Wilcoxon rank-sum test could be used in Manuscript 1 as it assumes unequal variances and does not rely on distributional assumptions but requires a higher number of replicates to find significance, which were not available in Manuscript 2. Thus, a paired t-test was used in

Manuscript 2, where the data was first tested for normal distribution using the Shapiro-Wilk test, which is more suitable for small data sets.

Removal efficiencies for PBDEs could not be calculated as they had very low detection frequencies. Concentrations of PBDEs were similar to concentrations found in Montreal's DW in our previous sampling campaigns (manuscript 1). No dechloranes were detected in any water samples. OPEs were frequently detected, and significant overall removal efficiencies ranged from 35.0% for BEHP to 90.7% for TPHP. The overall removal of total OPEs was 65.8%, with filtration accounting for 66.6% of that removal. Due to delays caused by the pandemic and the necessity to use a new analytical system replacing the old system that stopped working, results were unavailable for plasticizers and bisphenols at the time of thesis submission but will be included in the manuscript prior to submission for publication.

4.2 Abstract

The occurrence of thirty-eight contaminants, including flame retardants, bisphenols, and plasticizers throughout treatment steps in a conventional drinking water treatment plant (DWTP) was analyzed to assess removal efficiencies of filtration, ultraviolet (UV) treatment, and chlorination. Both legacy compounds and popular replacements were included to compare their presence in drinking water and persistence through water treatment. Twenty-four-hour composite daily sampling was performed at a DWTP in Montreal, Canada over a three-day period. Polybrominated diphenyl ethers (PBDEs), considered legacy flame retardants, were infrequently detected or at concentrations < 1 ng/L. When overall removal efficiencies could be calculated, the removal of $\sum_7$ PBDEs was 48.5 and 94.1%. No removal could be calculated on day 1 as PBDEs were only detected in finished drinking water. Higher brominated PBDEs BDE-183 and BDE-154 were only detected in raw water. Organophosphate esters (OPEs), considered replacement flame retardants, were frequently detected in all water samples. The total average concentration of $\sum_{15}$ OPEs was 501 ng/L in raw water and 162 ng/L in drinking water, with an average removal efficiency of 66.6%. OPEs were mainly removed during filtration, with TCIPP, TDCIPP, and TPHP showing statistically significant removal of 75.9, 83.6, and 94.5%, respectively. Conventional drinking water treatment decreases the concentration of these contaminants in drinking water but was less effective in removing flame retardants than bisphenols and plasticizers,

as indicated by their higher number of PBDEs detected and higher concentrations of OPEs measured.

4.3 Introduction

Endocrine disrupting chemicals (EDCs) interfere with the function of natural hormones in the human body causing health risks and, even low doses have shown potent effects on the endocrine system, prompting concern about the risks of life-long exposure to these chemicals (Yilmaz et al., 2020). Among the list of proven endocrine disruptors are certain plasticizers, bisphenols, and flame retardants which are used in a range of applications from flexible vinyl to food packaging. Amassed research on certain chemicals can lead to regulations on their importation and use in the manufacturing of consumer products to limit human exposure. The FDA has banned the use of bisphenol-A (BPA) in polycarbonate resins in baby bottles and sippy cups, while bis(2-ethylhexyl) phthalate (DEHP) has been banned in cosmetics, medical devices and vinyl children's toys by the Canadian Consumer Product Safety Act (Minister of Justice, 2017). Restricted chemicals are replaced with chemicals that have similar structure and properties, which could cause similar adverse health effects. A list of 38 plasticizers, bisphenols, and flame retardants including proven endocrine disruptors and emerging replacements are included in the present study chosen in collaboration with the Healthy Environments and Consumer Safety Branch, and the Environmental Health Science & Research Bureau of Health Canada.

EDCs have become ubiquitous contaminants in the environment due to their use in a wide range of consumer products. Ingestion of contaminated food and beverages is a common form of human exposure to these chemicals (Diamanti-Kandarakis et al., 2009). This includes contaminated drinking water, which can occur when insufficient water treatment technologies are used. Popular plasticizers diethyl phthalate (DEP), DEHP, and dibutyl phthalate (DBP) have been frequently detected in drinking water at the mid ng/L level (Chen et al., 2006; Ding et al., 2019; Hu et al., 2013; Yang et al., 2014). Replacement flame retardants diisodecyl adipate (DIDA), bis(2-ethylhexyl) adipate (DEHA), diisononyl phthalate (DINP) and bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate (DINCH) have recently been detected in Montreal's drinking water at concentrations of 8, 31, 105, and 175 ng/L, respectively (Manuscript 1). Legacy flame retardants, polybrominated diphenyl ethers (PBDEs), are not frequently detected in drinking water (Khan et al., 2016b; L. Liu et al., 2019; Subedi et al., 2015). The absence of PBDEs in drinking water could be due to their hydrophobicity, leading to their presence in other environmental media such as wastewater sludge or sediments (Rodgers et al., 2018). However, PBDEs were recently detected in Montreal's drinking water and bottled water at low concentrations of 0.11 and 0.08 ng/L, respectively (Manuscript 1). Replacement flame retardants, organophosphate esters (OPEs), have been detected in tap water from Spain (Esteban et al., 2014), U.S.A. (Kim and Kannan, 2018), South Korea (Park et al., 2018), and China (X. Liu et al., 2019). The total of six parent compounds and 9 metabolites were recently detected in Montreal's drinking and bottled water at concentrations of 69 and 421 ng/L, respectively (Manuscript 1). BPA has been detected in tap water from Malaysia (Santhi et al., 2012), France (Colin et al., 2014), and South Africa (Van Zijl et al., 2017), however was not detected in Montreal's tap (Goeury et al., 2019), drinking, or bottled water (Manuscript 1). Replacement's bisphenol-AF (BPAF), bisphenol-F (BPF), and bisphenol-S (BPS) are not typically monitored in drinking water, but have recently been detected at low concentrations in Chinese bottled and drinking water (Wang et al., 2020; Zhang et al., 2019a).

There is limited information available on the removal efficiencies of plasticizers, bisphenols and flame retardants through conventional drinking water treatment technologies. A summary of previous reported data is presented in Table 20. Plasticizers have proven to have low removal efficiencies, ranging from 35% for DEP to 68% for DEHP, when conventional water treatment technologies such as coagulation/sedimentation and filtration are applied. This results in residual plasticizer contamination in finished drinking water with concentrations as high as 7800 ng/L for DEHP (Liu et al., 2013). Similarly, Gou et al. performed a study on 10 drinking water treatment plants (DWTPs) from Taiwan and found significant concentrations of plasticizers in finished water (maximum of 2880 ng/L of DEHP and 840 ng/L of DBP), with removal efficiencies ranging from -93% to 100% (Gou et al., 2016).

Table 20 – Previously reported removal efficiencies of plasticizers, flame retardants and bisphenols through drinking water treatment.

Family	Location	Sampling method (# of samples)	Treatment steps	Compound	Inlet Conc. [ng/L]	Outlet Conc. [ng/L]	Removal efficiency [%]	Reference
Plasticizers	China - Mopanshan	NS (3)	Coag./sed., filt.	DEHP	11000	7480	68	(Liu et al., 2013)
				DEP	100	55	55	
				DBP	1200	780	65	

	China – Songhua River	NS (3)	Coag./sed., filt.	DEHP	12000	7800	65	
				DEP	150	52.5	35	
				DBP	850	442	52	
	China	Grab (12)	Coag./sed., filt.	DEHP	256	150	59	(Kong et al., 2017)
				DBP	27	17.2	65	
	China	Grab (1)	Coag./sed., filt.	DEHP	0.33	0.35	-6	(Wang et al., 2015)
				DBP	0.14	0.14	0	
				DEP	<LOD	<LOD	NA	
	Taiwan	Grab (28)	NS	DEHP	<LOD-2500	<LOD-2880	-93 – 46[a]	(Gou et al., 2016)
				DBP	<LOD-760	<LOD-840	0 – 100[a]	
OPEs	U.S.A.	24-hr composite (8)	Pre-oz./flocc./sed.	TCEP	2.6 – 43.6	0.4 – 37.8	40.5[b]	(Padhye et al., 2013)
			Inter.-oz		0.4 – 37.8	0.9 – 9.9	38.9[b]	
			Filt./chlor.		0.9 – 9.9	0.2 – 20.4	31.6[b]	
	South Korea	Grab (4)	Pre-chlor., pre-oz., sed., filt., post-oz., GAC	TCIPP	29.6[b]	15.0	48	(Choo and Oh, 2020)
				TCEP	27.8	15.7	38	
				TDCIPP	3.76	2.17	NA	
				TBOEP	18.1	5.66	70	
				TEHP	3.05	3.05	NA	
				TPHP	5.69	2.79	53	
	South Korea	Grab (36)	Coag./sed., filt., oz., GAC., chlor.	TCIPP	45.5	24.0	NS	(Sim et al., 2021)
				TCEP	32.5	18.4	NS	
				TDCIPP	3.83	3.03	NS	
				TBOEP	22.8	9.61	NS	
				TEHP	3.07	3.06	NS	
				TPHP	9.33	4.28	NS	
BPs	France	Composite (8)	NS	BPA	6.7 - 29.7	2.0 – 16.9	37 - 79	(Dupuis et al., 2012)
	China	Grab (2)	Coag./flocc., clarif., filt., chlor.	BPA	7.44	1.12	85[a]	(Zhang et al., 2013b)
				BPF	19.49	0.32	98[a]	
				BPS	1.36	<LOD	100[a]	
		Grab (2)	Pre-oz., tube settling, filt., post-oz., GAC, UV	BPA	8.26	0.56	93[a]	
				BPF	20.94	<LOD	100[a]	
				BPS	0.98	<LOD	100[a]	
	U.S.A.	24-hr composite (8)	Pre-oz./flocc./sed.	BPA	<LOD – 70.4	<LOD – 25.5	28[b]	(Padhye et al., 2013)
			Inter.-oz		<LOD – 25.5	<LOD – 58.1	44[b]	
			Filt./chlor.		<LOD – 58.1	<LOD – 44.3	31[b]	
	Taiwan	Grab (206)	Sed., filt., chlor.	BPA	29	8	72	(H. W. Chen et al., 2013)
	Korea	NS (25)	Coag./floc., sed., filt., chlor.	BPA	88	19	78.4	(Nam et al., 2014)

NS: Not specified
<LOD: Below limit of detection
Coag.: coagulation, sed.: sedimentation, filt.: filtration, Pre-oz: pre-ozonation, flocc.: flocculation, inter-oz.: intermediate ozonation, chlor.: chlorination, pre-chlor.: pre-chlorination, post-oz. post ozonation, GAC: granulated activated carbon adsorption, clarif.: Clarification,
a: removal efficiencies calculated based of concentrations,
b: mean removal efficiencies provided

When analysing tris(2-chloroethyl) phosphate (TCEP) removal between individual steps in a conventional drinking water treatment process, Padhye et al. found that pre-ozonation/flocculation/sedimentation had the highest average removal efficiency (40.5%), followed by intermediate ozonation (38.9%) and filtration/chlorination (31.6%) (Padhye et al., 2013). These removal efficiencies are similar to those found in five advanced DWTPs from South Korea, which had overall removals ranging from 13.7 – 82%. However, Choo and Oh found negative removal efficiencies for both chlorinated OPEs TCEP (-139 to -75.9%) and tris(1-chloro-2-propyl) phosphate (TCIPP) (-70 to -13.5%) in conventional DWTPs, indicating that advanced treatment options such as granular activated carbon (GAC) adsorption and ozonation might be necessary for the removal of chlorinated OPEs (Choo and Oh, 2020). Generally, BPA has demonstrated good removal during conventional drinking water treatment (H W Chen et al., 2013; Nam et al., 2014). Both conventional and advanced DWTPs in China showed high removal efficiencies of BPA, BPF, and BPS, ranging from 85% for BPA through conventional DWTP to 100% for BPF in both conventional and advanced DWTPs (Zhang et al., 2013b).

A proper sampling strategy is crucial when assessing removal efficiencies through water treatment technologies, whether it be wastewater treatment plants (WWTPs) or DWTPs. Ort et al. reviewed 87 papers monitoring pharmaceutical and personal care products (PPCPs) in wastewater systems and found that only 11% addressed sampling strategy explicitly (Ort et al., 2010b). Without a proper sampling strategy, findings can have significant uncertainty, especially when studying compounds which might have temporal fluctuations. Notably, negative removal efficiencies can be found when not accounting for the hydraulic retention time of the water treatment plant (Rodayan et al., 2014a). Grab samples can play a large role in negative removal efficiencies as they only capture a snapshot of the concentration in time, and do not necessarily sample the same water pocket as it passes through the DWTP. Thus, sampling is of utmost importance when considering compounds which have been reported in drinking water at varying detection frequencies and concentrations, as is the case of plasticizers, bisphenols, and flame retardants.

As a consequence, the goals of this study were to determine the levels of 38 plasticizers, flame retardants, and bisphenols in the influent and effluent as well as between each step in a conventional drinking water treatment plant located in Southeastern Canada, using a proper sampling strategy. To our knowledge, it is the first report on removal efficiencies through a conventional DWTP for PBDEs, plasticizer replacements (DEHA, DIDA, DINCH, DINP), and OPE metabolites.

4.4 Methods

4.4.1 Chemicals and reagents

Analytical standards and deuterated analogs of all target analytes are provided with supplier information in the Supplemental Information Table SI24 and SI25, respectively. Limit of detection and recoveries for each compound can be found in Supplemental Information Table SI26. High performance liquid chromatography (HPLC) grade methyl tert-butyl ether (MtBE), optima grade liquid chromatography-mass spectrometry (LC-MS) grade water, methanol (MeOH), acetone, hexanes, hydrochloric acid, and formic acid, and pesticide grade isooctane, sulfuric acid, ammonium hydroxide, and hydrochloric acid were all purchased from Fisher Scientific (Ottawa, ON, Canada). Ultrapure water was produced on a MilliQ water purification system purchased from Millipore Corporation (Billerica, MA, USA) and Oasis HLB, Oasis WAX, and glass Oasis HLB cartridges were purchased from Waters.

4.4.2 Sampling and DWTP characteristics

All samples were obtained from a DWTP in Montreal, QC, Canada, that uses source water from the Saint-Lawrence River. The DWTP employs in-line coagulant, sand filtration, ozonation, UV-disinfection, and chlorination. The ozonation system was not functioning at the time of sampling and was therefore not included in the study. Sand filtration at the DWTP had 93 available filters all of which have a filter area of 110m^2 and depth of 0.75m. The sand is made of silica with a diameter of 0.6mm and was originally colonized with zooglea bacteria to improve the removal of organic matter. Particulates remain trapped in the sand bed as water passes through at a nominal rate of 5 $m^3/m^2/h$. For UV treatment, the DWTP contains fourteen Sentinel UV reactors (CalgonCarbon) which are 1.2 m in diameter and contain 6 UV lamps. Sampling occurred at the exit of screening (RW), at the exit of the filtration tank (FW), at the exit of the UV system (UW), and from the holding tank of finished drinking water (DW), as denoted in Figure 5.

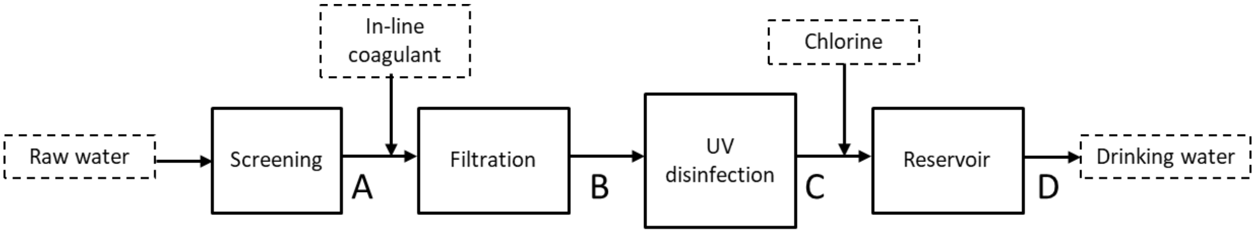

Figure 5 – Schematic of the DWTP train with sampling locations: A – Raw water (RW), B – Filtered water (FW), C – UV disinfected water (UW), D – finished drinking water (DW)

Sampling took place on August 3rd – August 5th, 2020, during which the average flow was estimated as 253,267 m^3/day. The inlet water had an average temperature of 25.7±0.5℃, pH of 7.9±0.09, and turbidity of 1.2±0.14 NTU. Complete raw water characteristics are provided in

Table 21. Filtration reduced the turbidity of water to 0.15 NTU, and finished drinking water had a turbidity of 0.10 NTU, pH of 7.7, and chlorination of 1.02 ppm. UV treatment applied a dosage 4.2 mJ/cm^2. The outlet flow over the three-day sampling period was relatively constant with an average of 250,560±69,000 m^3/day.

Table 21 – Water characteristics in DWTP during sampling period.

Characteristic	**Raw water**
Temperature [℃]	25.7
pH	7.9
Turbidity [NTU]	1.2
Conductivity [μS/cm]	407
UV absorbance [cm^{-1}]	5.6
Hydrocarbons [ppb]	7.4

4.4.2.1 Sampling strategy

Grab samples were not considered for the present study as they are more likely to produce negative removal efficiencies and are recommended for providing “instantaneous concentrations of pollutants at a specific time” (United States Environmental Protection Agency, 2010). The relatively constant flow rate of inlet water at the DWTP favours time-proportional over flow-proportional composite sampling, and is reliable when a high sampling frequency (<15 minutes) is used (Ort et al., 2010a). Therefore, the present study applied 24-hour time-proportional composite daily sampling over a three-day period coupled with a high sampling frequency (15 minutes). Additionally, residence times for each treatment unit were provided and used to offset the start of the composite sampling to further optimize the sampling strategy, as recommended in our earlier work (Rodayan et al., 2014b) . The filtration unit had a residence time between 26 – 53 minutes, followed by UV disinfection at 0.03 – 0.04 minutes, and chlorination at 18 – 69 minutes. Samples were collected using Teledyne ISCO 6712 Portable Samplers (Lincoln, NE, USA) equipped with a 10L silanized glass collection bottle. The start of sampling was delayed to account for residence times as follows: filtered water was collected 25 minutes after raw water, UV treated water was collected 5 minutes after filtered water, and chlorinated water was collected 15 minutes after UV treated water. Samplers were programmed to retrieve 90 mL of water every 15 minutes, for a final volume of roughly 8L after the 24-hour collection period. The water was then transferred to 1L aluminum bottles, placed on ice for transportation and stored at -20℃ until extraction.

4.4.3 Sample preparation

Samples of raw water, filtered water, and UV disinfected water were vacuum filtered using 1.5μm glass fiber filters to remove suspended particles. Water samples were concentrated using solid phase extraction following the method previously described in (Manuscript 1). Briefly, PBDEs, dechloranes, and BPs were concentrated on OASIS HLB cartridges (5cc, 200 mg), plasticizers on Oasis HLB glass cartridges (5cc, 200 mg), and OPEs on OASIS WAX cartridges (6cc, 500 mg). An initial sample volume of 400 mL was used, spiked with 100 uL of labelled surrogates at a concentration of 240 ug/L (Supplemental Information Table SI25). The final elution volume was 9 mL. After elution, PBDEs, dechloranes, and BPs were split into two equal volumes to be analysed separately. All samples were dried under a gentle nitrogen stream at 50℃ until completely evaporated, reconstituted in 400 μL of buffer and stored at -20℃ until analysis.

4.4.4 Sample analysis

4.4.4.1 Analysis of PBDEs

Analysis of PBDEs used gas chromatography mass spectrometry (GC-MS/MS) and followed the method previously described in Manuscript 1. Briefly, analysis was carried out by gas chromatography (GC) (TSQ Quantum, Thermo Scientific, USA) on a ZB-1HT Inferno column (15 m x 0.25 mm I.D., 0.1 µm film thickness) from Phenomenex (Torrance, CA, USA), and coupled with a TSQ Quantum GC triple quadrupole mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA). MS/MS was operated at 70 eV in positive EI mode. IDL values for PBDEs ranged from 0.01 – 0.02 ng/L and can be found in Supplementary Information Table SI26, along with recoveries and LOQ values.

4.4.4.2 Analysis of Dechloranes

Analysis of dechloranes used GC-MS on an Agilent 6980 gas chromatographer on a Zebron ZB-5HT column (8 m × 0.25 mm i.d., 0.10 µm of film thickness) from Phenomenex (Torrance, CA, USA) coupled with a Waters Quattro micro triple quadrupole mass spectrometer (Waters Corp., Milford, MA, USA), as previously described Manuscript 1. The MS was operated in single ion monitoring (SIM) mode during analysis and monitored two ions for each compound, one for quantification (SIM-Q) and one for confirmation (SIM-C). IDL values for dechloranes ranged from 0.08 – 0.20 ng/L and can be found in Supplementary Information Table SI26, along with recoveries and LOQ values.

4.4.4.3 Analysis of OPEs

Analysis of OPEs followed the method previously described in Manuscript 1. Briefly, analysis was performed on an ultra-performance liquid chromatography (UPLC) system from Waters (Milford, MA, USA) with an Acquity UPLC BEH C18 column from Waters (1.7 µm, 2.1 mm x 50 mm) attached to a Waters Van Guard BEH C_{18} pre-column (1.7 µm, 2.1 x 5 mm). MS was carried out on a Waters Xevo TQD MS/MS (Milford, MA, USA) operated in electrospray ionization (ESI) in positive or negative ion mode. IDL values for PBDEs ranged from 0.03 – 0.70 ng/L and can be found in Supplementary Information Table SI26, along with recoveries and LOQ values.

4.4.5 Quality control and assurance

Special care was taken to reduce the risk of contamination of samples by materials which are known to contain plasticizers, flame retardants or bisphenols. Plasticizers can adsorb onto glass materials and leach out of plastic tubing. Thus, all glassware used for handling samples for plasticizers analysis was silanized using dimethyldichlorosilane (DMDCS) solution (5% DMDCS in heptanes) following the method previously developed by Struzina et al. (Manuscript 1). In addition, SPEs of samples for plasticizers analysis were performed using glass funnels to avoid the use of plastic tubing. Possible contamination due to the sampler pumping system was taken into consideration through controls, which involved running the sampler in the laboratory using LC-MS grade water. Additionally, all plasticizer and OPE samples were handled in a biosafety cabinet to prevent contamination from the lab environment.

For SPEs performed for the other classes of contaminants, for which plastic tubing was used, the tubing was thoroughly cleaned between each sample using MilliQ water pumped through the tubing for 2 minutes followed by MeOH for 2 minutes. Glassware was cleaned with hot water and soap, then rinsed with water and left to dry, then rinsed with pesticide grade acetone followed by hexane, twice. Glassware was then baked at 500 ℃ for 4 hours and covered with aluminum foil until use.

Field blanks (n=3) were prepared using LC-MS grade water in aluminum bottles. On the first day of sample collection, the aluminum bottles containing field blanks were opened to expose the water to the sampling environment for the duration of sample transfer between the 10L collection bottle and aluminum bottles. One field blank was deployed for both filtered water and UV treated water as the sampling points were in the same room, roughly 15m apart. The field blanks were then sealed and extracted following the same method as water samples. Each SPE batch included a lab blank (LC-MS water spiked with internal standards) to monitor contamination through sample preparation as well as a positive control (LC-MS water spiked with native and internal standard) to regularly checked that the methods were efficient. Elution controls (elution buffer spiked with internal standard) and elution blanks (elution buffer only) were prepared for each SPE to account for contamination through sample drying and analysis.

Samples were extracted in triplicates. The average of the triplicates was taken as one value for each sample. If one of the replicates was above the limit of detection, the sample was considered a detect for calculation of detection frequency. When one or two of the replicates were below the LOD, these replicates were assigned a value of the LOD divided by the square root of two (LOD/√2), as recommended by Hornung and Reed (Hornung and Reed, 1990). However, if a replicate was between the LOD and LOQ, while one or more replicated were at quantifiable concentrations, the value measured was used for calculating the average as this is considered the best estimate of the concentration of that replicate. Statistical analyses were performed to determine significant removal efficiencies. A paired t-test was chosen as the inlet and outlet concentrations of a given compound are considered dependent. A one-tailed paired t-test was executed in JMP assuming a p-value of 0.05. As the paired t-test assumes the data is normally distributed, the Shapiro-Wilk test for normal distribution was run on all data sets prior to performing the t-tests.

4.5 Results and Discussion

4.5.1 Overview of the results

The measured average concentration of each analyte per location in the drinking water treatment plant is summarized in Table 22. When calculating the average over 3 days of sampling, non-detects were assigned a value of LOD/√2 if at least one of the daily concentrations is above the limit of detection. The individual analyte concentrations for each day can be found in Supplemental Information Table SI27, along with the concentrations found in field blanks. Dechloranes DEC-602, DEC-603, a-DP, and s-DP were not detected above the limit of detection in any samples throughout the DWTP.

The average removal efficiencies of each step for each analyte are presented in Table 23. If one or more daily concentrations were below the limit of quantification, the removal efficiency for that treatment unit was not calculated and reported as not available (NA). This was done to reduce the risk of false reporting of removal efficiencies when limited data is available. Comparisons of removal efficiencies to previously reported data, along with comparisons of the persistence between legacy compounds and their replacements will be discussed in the following sections.

Table 22 – Average concentration of each compound per treatment step.

Compound	Raw water			Filtered water			UV water			Drinking water		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
BDE-28	ND	ND	ND	ND	<LOQ	<LOQ	ND	ND	ND	<LOD	0.06	0.03
BDE-47	ND	0.11	0.05	ND	0.04	0.03	ND	ND	ND	ND	0.02	0.02
BDE-99	ND	0.46	0.16	ND	0.04	0.02	ND	0.02	0.01	ND	0.01	0.01
BDE-100	ND	ND	ND	ND	0.04	0.03	ND	0.02	0.01	ND	0.01	ND
BDE-153	ND	0.03	0.01	ND	0.03	0.01	ND	ND	ND	ND	0.08	0.03
BDE-154	ND	0.02	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-183	ND	0.04	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
DEC 602*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DEC 603*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
a-DP*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
s-DP*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TBOEP*	24.57	41.36	31.31	16.28	23.21	19.47	12.78	36.50	24.28	8.40	23.16	16.43
TCEP*	83.73	303.31	171.45	7.21	13.04	10.28	7.23	8.37	7.67	5.28	9.39	7.57
TCIPP*	42.07	77.41	56.03	12.50	12.79	12.63	17.25	20.68	18.61	20.30	24.50	22.46
TDCIPP*	65.49	97.45	86.47	13.40	14.28	13.76	11.76	33.26	20.19	7.49	14.28	10.85
TEHP*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.61	0.21
TPHP*	19.82	24.11	21.39	0.85	1.49	1.20	2.72	2.90	2.83	1.66	2.23	1.98
DPHP⁑	12.66	36.46	24.79	5.17	5.67	5.39	26.06	36.31	32.48	10.83	38.46	23.93
Ip-PPP⁑	0.10	0.30	0.19	0.09	0.21	0.16	0.08	0.19	0.13	0.11	0.20	0.14
BCPP⁑	1.76	2.31	1.36	0.07	1.59	0.81	0.73	2.27	1.32	0.18	1.53	0.94
BCEP⁑	ND	0.67	0.29	ND	0.63	0.36	<LOD	1.46	0.79	<LOD	0.69	0.41
BBOEP⁑	11.22	19.23	16.39	10.92	13.01	11.66	5.50	13.12	8.80	6.26	10.03	7.57
BDCIPP⁑	2.63	2.63	0.98	2.17	2.17	0.82	1.44	10.40	6.58	2.81	19.97	7.64
BEHP⁑	78.82	94.36	86.06	76.95	80.61	78.58	59.79	73.31	68.39	52.13	59.71	55.54
BTBOEP⁑	2.92	3.52	3.23	2.52	4.15	3.15	2.17	3.46	2.64	1.59	3.33	2.57
DCP⁑	0.07	0.39	0.21	0.01	0.13	0.06	0.02	0.22	0.14	0.05	0.57	0.21

ND: non-detect, <LOD: below limit of detection, <LOQ: below limit of quantification. * Denotes replacement compounds and ⁑ represents metabolites.

Table 23 – Removal efficiencies of OPEs through filtration, UV treatment, chlorination, and overall treatment.

Analyte	**Average filtration removal efficiency [%]**	**Average UV removal efficiency [%]**	**Average chlorination removal efficiency [%]**	**Average total removal efficiency [%]**
TBOEP	33.6	-20.1	20.7	46.7
TCEP	92.9	19.6	2.1	94.0
TCIPP	75.9*	-47.3*	-22.0	56.5
TDCIPP	83.6*	-48.3	39.1	86.5*
TEHP	NA	NA	NA	NA
TPHP	94.5*	-151*	19.5*	90.7*
DPHP	73.9	-503*	19.5	-36.1
Ip-PPP	-6.6	13.8	-11.3	7.0
BCPP	89.6†	-370	30.0	78.2†
BCEP	NA	NA	NA	NA
BBOEP	25.3	26.0	-10.2	44.3
BDCIPP	NA	NA	NA	NA
BEHP	8.1	13.0	18.4*	35.0*
BTBOEP	3.0	15.8*	-1.1	21.0
DCPs	62.1	-538	NA	NA
Total OPEs	66.6*	-23.3	16.8	65.8*

NA: Not available (one or more days had concentrations <LOD). *Statistically significant removal. † Removal calculated off 2 days of data only.

4.5.2 Presence and removal of PBDEs through drinking water treatment

Average concentrations over the three days of sampling for individual compounds ranged from below the limit of detection to 0.46 ng/L (BDE-99 in raw water). The average sum of the seven target PBDEs in raw water, filtered water, UV treated water, and drinking water were 0.23, 0.07, 0.02, and 0.06 ng/L, respectively. PBDEs were infrequently detected across all water samples, with the highest detection rates for BDE-47, BDE-99, and BDE-100 being 42%. Due to low detection frequencies, removal efficiencies could not be calculated for PBDEs, however the total PBDE removal for days 2 and 3 were 48.5% and 94.1%, respectively. On day 1, no PBDEs were detected in raw water, filtered water, or UV treated water, while BDE-28, BDE-47, and BDE-153 were detected in drinking water at <LOQ, 0.02ng/L, and 0.08 ng/L, respectively. Figure 6 depicts the average concentrations of PBDEs throughout the DWTP. BDE-28 was detected in 66% of drinking water samples, although only detected above the limit of quantification on day 2 at 0.06 ng/L. Interestingly, BDE-28 was not detected above the limit of quantification in any raw, filtered, or UV treated water samples. BDE-99 was the only compound detected in all water types, with the highest concentration detected in raw water at 0.46 ng/L (Supplemental Information Table SI27). The average concentration of BDE-99 in filtered, UV treated, and drinking water was 0.02, 0.01, and 0.01 ng/L, respectively, which is considerably lower than the concentration found in raw water. Similarly, BDE-154 and BDE-183 were detected in raw water at average concentrations of 0.2 ng/L, however were not detected in any other water samples. UV treated water had the lowest total PBDE concentration as well as the fewest number of PBDEs detected. In UV treated water, BDE-99 and BDE-100 were both found at average concentrations of 0.01 ng/L.

There are no prior studies on the removal of PBDEs from drinking water treatment. However, Subedi et al. reported all seven of the PBDEs included in the present study in New York tap water at concentrations ranging from 0.05 ng/L for BDE-153 to 0.84 ng/L for BDE-47 (Subedi et al., 2015). These values are higher than the average PBDE concentrations found in drinking water in the present study. The sum of the seven target PBDEs have previously been detected in Montreal's bottled water (0.08 ng/L) and drinking water (0.11 ng/L) at concentrations slightly higher than found in drinking water in the present study (0.06 ng/L) (Manuscript 1). Samples from Argentina did not show any BDE-47, BDE-99, BDE-100, or BDE-153 in tap water however this could be attributed to their relatively high limit of detection of 1 – 2 ng/L (Fontana et al., 2009). Similarly, a study of bottled water from China did not detect any BDE-28, BDE-47, BDE-99, BDE-100, or BDE-154 (L. Liu et al., 2019).

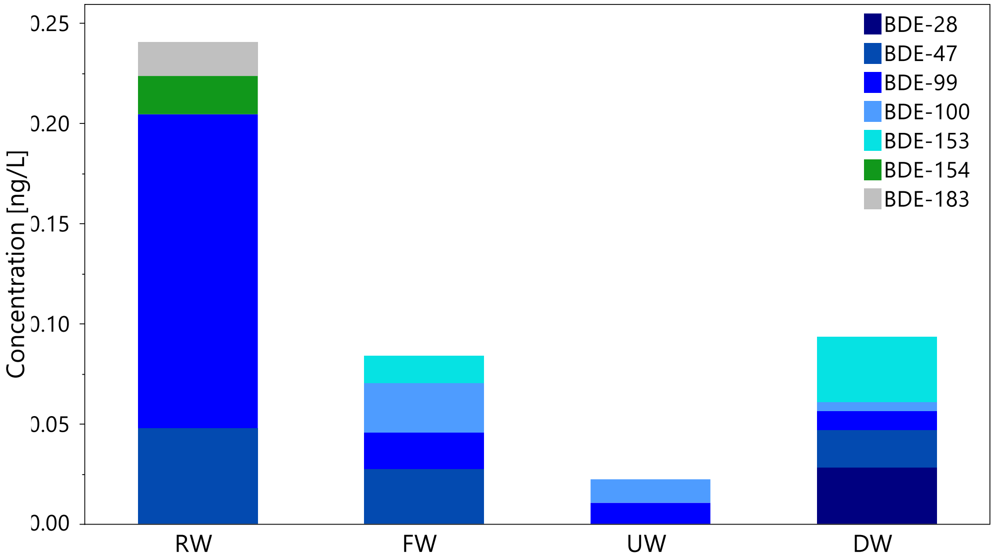

Figure 6 – PBDE concentrations throughout DWTP.

4.5.3 Presence and removal of OPEs through drinking water treatment

Total OPE concentrations are presented in Figure 7, and removal efficiencies are provided in Table 23. Average total OPE concentrations (6 parent compounds and 9 metabolites) in raw, filtered, UV treated, and drinking water were 501, 158, 194, and 162 ng/L, respectively. Most of the OPEs had high detection frequencies across all water samples (>90%), except parent compound TEHP (8%), and metabolites BCEP (58%) and BDCIPP (58%). This supports previous reports of OPEs in drinking water from Canada (Manuscript 1), which included the same 15 target OPEs, and South Korea (Choo and Oh, 2020) and the U.S.A. (Kim and Kannan, 2018), which only included the six target parent OPEs. OPEs were consistently detected in field blanks for all three sampling locations, typically at lower concentrations than in water samples. Only DCPs and BCPP, both OPE metabolites, were detected at higher concentrations in field blanks for more than 50% of water samples. Detailed field blank concentrations can be found in Supplemental Information Table SI28, and the average sum of field blanks is shown in Figure 7.

Chlorinated OPEs TCEP, TCIPP and TDCIPP were the dominant contributors to total OPE in raw water with average concentrations of 171, 56, and 86 ng/L, respectively. In drinking water, non-chlorinated metabolites BEHP and DPHP had the highest average concentrations at 55 ng/L and 23 ng/L, respectively. In filtered and UV treated water, the total concentration of metabolites is statistically higher than the total concentration of parent compounds. The concentration of total OPEs in the present study is lower than previously reported in Montreal's drinking water (423 ng/L), while the dominance of chlorinated OPEs in total OPE concentration was similar (Manuscript 1). Analyses of New York tap water (TCEP 0.45 ng/L, TCIPP 11.6 ng/L, and TDCIPP 4.75 ng/L) indicated slightly lower concentrations of chlorinated OPEs than in the present study, and similar concentration of alkyl- and aryl-OPEs (TBOEP 10.2 ng/L, TEHP 0.12 ng/L, and TPHP 3.72 ng/L) (Kim and Kannan, 2018).

The average removal efficiency per treatment step is reported in Table 23, and specific daily removals can be found in Supplemental Information Table SI29. The average removal efficiency of total OPEs was 65.8%, where filtration, UV treatment, and chlorination accounted for 66.8, -23.1, and 16.8% of the total removal, respectively. However, only the removal from filtration and overall removal was statistically significant. Average overall removal per compound ranged from -36.1% for DPHP to 94.0% for TCEP. Most statistically significant positive removal efficiencies were found for filtration, with 94.5, 83.6, and 75.9% removal of TPHP, TDCIPP, and TCIPP, respectively. UV treatment had a significant positive removal of 15.8% for BTBOEP, while chlorination had significantly positive removals of 19.5 and 18.4% for TPHP and BEHP, respectively.

TPHP had the highest overall removal at 90.7%, while TPHPs metabolite DPHP was the only OPE to demonstrate an overall negative removal efficiency. The negative overall average removal stems from a high concentration of DPHP in drinking water on day 3 (38.5 ng/L), and relatively low concentrations in the raw water on the same day (12.7 ng/L). The removal efficiencies of DPHP on day 1 (38.3%) and day 2 (57.1%) were much more agreeable. However, concentrations of the metabolite DPHP were higher than parent TPHP across all water samples, except drinking water on day 3, which could be caused by the transformation of TPHP. While there is little knowledge of the major pathways and mechanisms of biodegradation processes of TPHP under aerobic conditions, DPHP was proven to be an important transformation product which accounted for 47.8 – 56.4% of TPHP removal from wastewater treatment plant (WWTP) sludge (Hou et al., 2021). This suggests that DPHP may also be formed and released from the biological layer of the filtration unit in the studied DWTP. BEHP was the only other OPE metabolite to be detected at higher concentrations than parent compound TEHP across all water samples.

A study by Sim et al., studying 18 advanced DWTPs in South Korea, generally found removal efficiencies from 0 – 80% for TCIPP, TCEP, and TBOEP, however some negative removals were reported (Sim et al., 2021). This agrees with removal efficiencies of TCIPP and TBOEP found in the present study, which ranged from 46 – 74% and 17 – 66%, respectively, however the overall removal of TCEP in the present study was higher, ranging from 89 – 97%. Conventional DWTPs have previously demonstrated poor removal of chlorinated OPEs (Choo and Oh, 2020; Padhye et al., 2013). Choo et al. reported overall TCIPP removal of -70.0 to -13.5% and TCEP removal of -135 to -75.9% through conventional treatment (chlorination, coagulation, sedimentation, and filtration). Filtration, considered a conventional treatment method, demonstrated the highest removal rates for chlorinated OPEs in the present study.

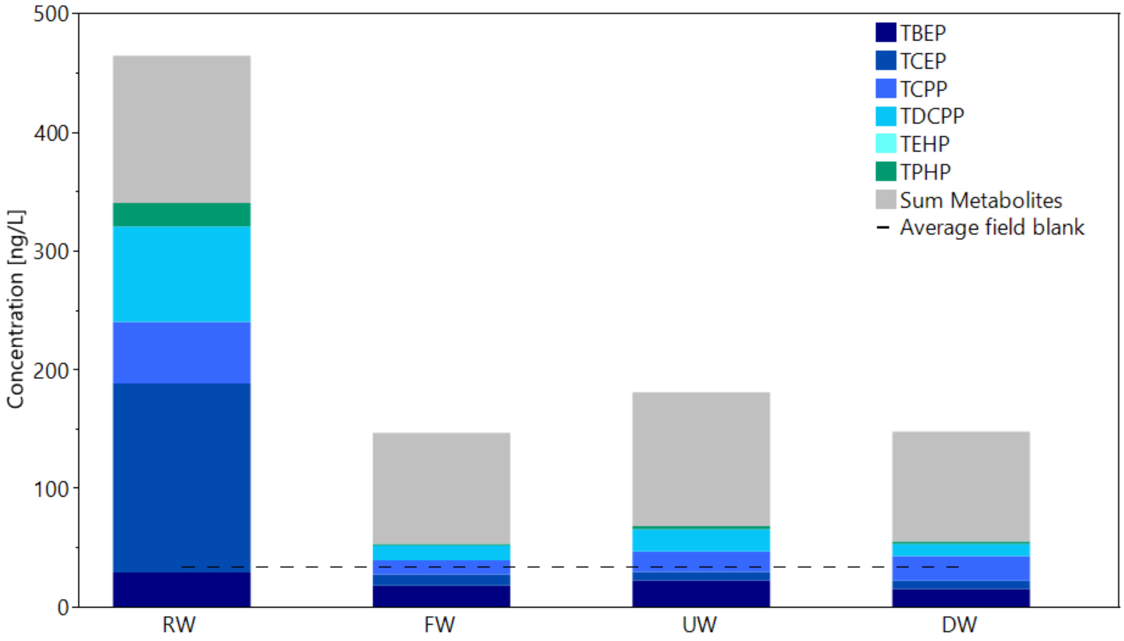

Figure 7 – OPE concentrations throughout DWTP

4.6 Conclusion

Little information is available on flame retardant, bisphenol, and plasticizer removal efficiencies through drinking water treatment. The results of the present study demonstrate the removal of PBDEs and OPE metabolites through a conventional DWTP for the first time. PBDEs were present at all sampling locations throughout the DWTP, albeit at low detection frequencies and concentrations. Lower brominated PBDEs were detected more frequently in all water samples, with BDE-183 and BDE-154 only detected in raw water. Total PBDE removal was found as 48.5% and 94.1% for days 2 and 3, respectively. It was not possible to calculate removal of individual PBDEs through each treatment step due to the low detection frequencies of individual compounds. OPEs were frequently detected in all water types. Conventional drinking water treatment technologies show good removal of total OPE concentrations (65.8%), however the removal varied per compound. Statistically significant overall removals were only found for TDCIPP (86.5%), TPHP (90.7%), and BEHP (35.0%), and some compounds showed very low or negative overall removal efficiencies (DPHP: -36.1%, ip-PPP: 7.0%, BTBOEP: 21.1%) Filtration proved to be the most effective treatment step for OPEs, although considerable concentrations were still present in finished drinking water. Conventional drinking water treatment technologies have proven to reduce the total concentration of both legacy ($\sum_{7}$ PBDEs) and replacement ($\sum_{15} O$PEs) flame retardants in finished drinking water, contributing to mitigating exposure to these contaminants. However, removal efficiencies varied between compounds and treatment type, with some compounds detected at higher concentrations in drinking water than raw water. Further laboratory and field studies should be performed to investigate the removal efficiencies from different treatment processes and their effects on flame retardant concentrations in drinking water.

4.7 Supplemental Information

Table SI24 – List of target analytes with CAS number and supplier information

Family	**Analyte acronym**	**Target analyte**	**CAS number**	**Supplier**
Plasticizer	DEHP	Bis(2-ethylhexyl) phthalate	117-81-7	Sigma Aldrich
Plasticizer	DEP	Diethyl phthalate	84-66-2	Sigma Aldrich
Plasticizer	DBP	Dibutyl phthalate	84-74-2	Sigma Aldrich
Plasticizer	DEHA	Bis(2-ethylhexyl) adipate	103-23-1	Toronto Research Chemicals
Plasticizer	DINCH	Bis(7-methyloctyl) Cyclohexane-1,2-dicarboxylate	166412-78-8	Toronto Research Chemicals
Plasticizer	DIDA	Diisodecyl adipate	27178-16-1	Sigma Aldrich
Plasticizer	DINP	Diisononyl phthalate	68515-48-0	Sigma Aldrich
Plasticizer	MEHP	Mono(ethylhexyl) phthalate	4376-20-9	Toronto Research Chemicals
OPEs	TBOEP	Tris(2-butoxyethyl) phosphate	78-51-3	Sigma Aldrich
OPEs	TCEP	Tris(2-chloroethyl) phosphate	115-96-8	Sigma Aldrich
OPEs	TCIPP	Tris(1-chloro-2-propyl) phosphate	13674-84-5	Cambridge Isotope Lab. Inc
OPEs	TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	Toronto Research Chemicals Inc.
OPEs	TEHP	Tris(2-ethylhexyl) phosphate	78-42-2	Wellington Laboratories
OPEs	TPHP	Triphenyl phosphate	115-86-6	Supelco Analytical
OPEs – metabolite	DPHP	Diphenyl phosphate	838-85-7	Sigma Aldrich
OPEs – metabolite	Ip-PPP	4-Isopropylphenyl phenyl phosphate	69415-02-7	Toronto Research Chemicals
OPEs – metabolite	BCPP	Bis(1-chloro-2-propyl) phosphate	789440-10-4	Toronto Research Chemicals
OPEs – metabolite	BCEP	Bis(2-chloroethyl) phosphate	3040-56-0	Toronto Research Chemicals
OPEs – metabolite	BBOEP	Bis(2-butoxyethyl) phosphate	14260-97-0	Toronto Research Chemicals
OPEs – metabolite	BDCIPP	Bis(1,3-dichloro-2-propyl) phosphate	72236-72-7	Wellington Laboratories
OPEs – metabolite	BEHP	Bis(2-ethylhexyl) phosphate	298-07-7	Toronto Research Chemicals
OPEs – metabolite	BTBOEP	Bis(2-butohexylethyl) 2-Hydroxyethyl Phosphate Triester	1477494-86-2	Toronto Research Chemicals
OPEs – metabolite	DCP	Di-cresyl phosphate	36400-46-1	Toronto Research Chemicals
PBDE	BDE 28	2,4,4'-Tribromodiphenyl ether	41318-75-6	Wellington Laboratory
PBDE	BDE 47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1	Wellington Laboratory

PBDE	BDE 99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9	Wellington Laboratory
PBDE	BDE 100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8	Wellington Laboratory
PBDE	BDE 153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2	Wellington Laboratory
PBDE	BDE 154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4	Wellington Laboratory
PBDE	BDE 183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5	Wellington Laboratory
Dechlorane	DEC-602	Dechlorane 602	31107-44-5	Toronto Research Chemicals
Dechlorane	DEC-603	Dechlorane 603	13560-92-4	Toronto Research Chemicals
Dechlorane	a-DP	Anti-dechlorane plus	13560-89-9	Toronto Research Chemicals
Dechlorane	s-DP	Syn-dechlorane plus	135821-03-3	Cambridge Isotope Lab. Inc.
Bisphenol	BPA	Bisphenol A	80-05-7	Toronto Research Chemicals
Bisphenol	BPAF	Bisphenol AF	1478-61-1	Sigma Aldrich
Bisphenol	BPF	Bisphenol F	620-92-8	Toronto Research Chemicals
Bisphenol	BPS	Bisphenol S	80-09-1	Sigma Aldrich

Table SI25 – Labelled surrogates used for each compound to account for recovery during extraction and matrix effects with CAS number and supplier information

Family	**Analyte acronym**	**Target analyte**	**CAS number**	**Supplier**
Plasticizer	DEHP-d4	Bis(2-ethylhexyl) phthalate-d4	117-81-7	Toronto Research Chemicals
Plasticizer	DEP-d4	Diethyl phthalate-d4	84-66-2	Toronto Research Chemicals
Plasticizer	DBP-d4	Dibutyl phthalate-d4	84-74-2	Toronto Research Chemicals
Plasticizer	DEHA-d4	Bis(2-ethylhexyl) adipate-d4	103-23-1	Toronto Research Chemicals
Plasticizer	DINP-d4	Diisononyl phthalate-d4	68515-48-0	Toronto Research Chemicals
OPEs	TEHP-d51	Tris(2-ethylhexyl) phosphate-d51	1259188-37-8	Toronto Research Chemicals
OPEs	TCEP-d12	Tris(2-chloroethyl) phosphate-d12	115-96-8	Wellington Laboratories
OPEs	TDCIPP-d15	Tris(1,3-dichloro-2-propyl) phosphate-d15	1447569-77-8	Wellington Laboratories
OPEs	TPHP-d15	Triphenyl phosphate	1173020-30-8	Wellington Laboratories
OPEs – metabolite	DPHP-d10	Diphenyl phosphate-d10	1477494-97-5	Toronto Research Chemicals
OPEs – metabolite	Ip-PPP-d7	4-Isopropylphenyl phenyl phosphate-d7	69415-02-7	Toronto Research Chemicals
OPEs – metabolite	BCPP-d12	Bis(1-chloro-2-propyl) phosphate-d12	789440-10-4	Toronto Research Chemicals
OPEs – metabolite	BBOEP-d8	Bis(2-butoxyethyl) phosphate-d8	14260-97-0	Toronto Research Chemicals
OPEs – metabolite	BEHP-d34	Bis(2-ethylhexyl) phosphate-d34	1773493-20-1	Toronto Research Chemicals
OPEs – metabolite	DCP—d14	Di-cresyl phosphate-d14	36400-46-1	Toronto Research Chemicals
PBDE	BDE 28-13C12	2,4,4'-Tribromodiphenyl ether-13C12	41318-75-6	Wellington Laboratory

PBDE	BDE 47-13C12	2,2',4,4'-Tetrabromodiphenyl ether-C13C12	5436-43-1	Wellington Laboratory
PBDE	BDE 99-13C12	2,2',4,4',5-Pentabromodiphenyl ether-13C12	60348-60-9	Wellington Laboratory
PBDE	BDE 100-13C12	2,2',4,4',6-Pentabromodiphenyl ether-13C12	189084-64-8	Wellington Laboratory
PBDE	BDE 153-13C12	2,2',4,4',5,5'-Hexabromodiphenyl ether-13C12	68631-49-2	Wellington Laboratory
PBDE	BDE 154-13C12	2,2',4,4',5,6'-Hexabromodiphenyl ether-13C12	207122-15-4	Wellington Laboratory
PBDE	BDE 183-13C12	2,2',3,4,4',5',6-Heptabromodiphenyl ether-13C12	207122-16-5	Wellington Laboratory
Dechlorane	DEC-602-13C10	Dechlorane 602-13C10	31107-44-5	Cambridge Isotope Lab. Inc.
Dechlorane	a-DP-13C10	Anti-dechlorane plus-13C10	135821-74-8	Cambridge Isotope Lab. Inc.
Dechlorane	s-DP-13C10	Syn-dechlorane plus-13C10	135821-03-3	Cambridge Isotope Lab. Inc.
Bisphenol	BPA-C13	Bisphenol A-C13	80-09-1	Toronto Research Chemicals
Bisphenol	BPAF-d4	Bisphenol AF-d4	263261-65-0	Toronto Research Chemicals
Bisphenol	BPF-C13	Bisphenol F-C13	1410794-06-7	Toronto Research Chemicals
Bisphenol	BPS-C13	Bisphenol S-C13	80-09-1	Toronto Research Chemicals

Table SI26 – Limits of detection and quantification for target analytes

Analyte acronym	**Recovery [%]**	**Limit of detection [ng/L]**	**Limit of quantification [ng/L]**
TBOEP	38.9	0.34	1.13
TCEP	65.3	0.48	1.60
TCIPP	80.6	0.70	2.33
TDCIPP	65.9	0.18	0.60
TEHP	419.4	0.03	0.10
TPHP	99.9	0.11	0.37
BDCIPP	192.4	0.55	1.83
DPHP	53.0	0.24	0.80
BCPP	128.5	0.17	0.57
BCEP	85.4	0.23	0.77
DCPs	86.1	0.24	0.80
Ip-PPPS	87.9	0.21	0.70
BTBOEP	99.0	0.28	0.93
BBOEP	122.2	0.26	0.87
BEHP	21.1	0.25	0.83
BDE 28	77.9	0.02	0.07
BDE 47	75.3	0.02	0.07
BDE 99	75.0	0.01	0.03
BDE 100	72.9	0.01	0.03
BDE 153	64.8	0.01	0.03
BDE 154	66.5	0.02	0.07
BDE 183	70.1	0.01	0.03
DEC-602	36.9	0.08	0.26
DEC-603	35.9	0.20	0.67
a-DP	158.3	0.13	0.43
s-DP	46.7	0.14	0.47

Table SI27 – Daily concentrations of target analytes in raw, filtered, UV treated, and drinking water.

Compound	Raw water			Filtered water			UV treated water			Drinking water		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
BDE-28	ND	ND	ND	ND	ND	<LOQ	ND	ND	ND	<LOQ	0.06	<LOD
BDE-47	ND	0.02	0.11	ND	0.04	0.03	ND	ND	ND	0.02	ND	ND
BDE-99	ND	ND	0.46	ND	0.04	0.01	ND	0.02	ND	ND	ND	0.01
BDE-100	ND	ND	ND	ND	0.04	0.03	ND	0.02	0.01	ND	ND	0.01
BDE-153	ND	0.03	ND	ND	ND	0.03	ND	ND	ND	0.08	ND	ND
BDE-154	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-183	ND	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DEC 602	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DEC 603	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
a-DP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
s-DP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TBOEP	24.58	27.99	41.36	18.92	23.21	16.28	23.54	36.50	12.78	8.40	23.21	17.74
TCEP	303.31	83.73	127.30	13.04	7.21	10.59	7.39	8.37	7.23	8.03	9.39	5.28
TCIPP	77.41	42.07	48.60	12.79	12.50	12.60	20.68	17.25	17.91	20.30	22.60	24.50
TDCIPP	97.45	65.49	96.46	14.28	13.40	13.62	11.76	33.26	15.54	10.76	14.29	7.49
TEHP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.61	ND
TPHP	24.11	19.82	20.23	1.49	0.85	1.25	2.89	2.90	2.72	2.23	2.04	1.66
DPHP	36.46	25.24	12.66	5.67	5.17	5.33	35.06	36.31	26.06	22.50	10.83	38.46
Ip-PPP	0.17	0.10	0.30	0.21	0.17	0.09	0.18	0.13	0.08	0.20	0.13	0.11
BCPP	4.61	1.76	ND	0.78	0.07	1.59	2.26	0.73	0.95	1.53	0.18	1.12
BCEP	ND	ND	0.66	ND	0.63	0.35	0.81	<LOD	1.46	0.69	0.43	<LOD
BBOEP	19.23	11.22	18.73	13.01	10.92	11.04	13.12	7.78	5.50	6.26	10.03	8.45
BDCIPP	5.11	ND	ND	2.17	ND	ND	10.40	1.44	7.89	2.81	ND	29.97
BEHP	85.01	94.36	78.82	78.18	76.95	80.61	59.79	73.31	72.07	52.13	54.78	59.71
BTBOEP	2.82	3.52	3.24	2.78	4.15	2.52	1.23	3.46	2.17	1.59	2.80	3.33
DCPs	0.01	0.13	0.07	0.22	0.18	0.06	ND	0.18	0.02	0.04	0.05	0.57

Concentrations reported in [ng/L]. ND: Not detected, <LOD: Below limit of detection, <LOQ: Below limit of quantification.

Table SI28 – Concentration of target analytes in field blank.

Compound	Raw water	Filtered/UV treated water	Chlorinated water
BDE-28	ND	ND	ND
BDE-47	ND	ND	ND
BDE-99	ND	ND	ND
BDE-100	ND	ND	0.03
BDE-153	ND	0.04	ND
BDE-154	ND	ND	ND
BDE-183	ND	ND	ND
DEC 602	ND	ND	ND
DEC 603	ND	ND	ND
a-DP	ND	ND	ND
s-DP	ND	ND	ND
TBOEP	7.68	8.59	12.33
TCEP	6.68	3.48	6.35
TCIPP	5.02	3.59	1.99
TDCIPP	5.96	0.28	9.27
TEHP	ND	ND	ND
TPHP	<LOD	0.08	0.42
DPHP	2.48	1.47	ND
Ip-PPP	0.31	0.07	0.05
BCPP	1.91	1.25	0.49
BCEP	0.95	5.06	ND
BBOEP	3.42	1.56	0.10
BDCIPP	ND	ND	ND
BEHP	3.56	ND	5.05
BTBOEP	0.38	0.32	0.69
DCPs	0.50	0.32	0.14

One field blank was collected at each location on day 1 of sampling. Concentrations reported in ng/L. ND: Not detected, <LOD: Below limit of detection.

Table SI29 – Daily removal efficiencies [%] of OPEs by treatment step.

Compound	Filtering			UV treatment			Chlorination			Overall		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
TBOEP	23.0	17.1	60.6	-24.4	-57.3	21.5	64.3	36.6	-38.8	65.8	17.3	57.1
TCEP	95.7	91.4	91.7	43.3	-16.2	31.8	-8.6	-12.1	26.9	97.4	88.8	95.9
TCIPP	83.5	70.3	74.1	-61.7	-38.0	-42.1	1.8	-31.1	-36.8	73.8	46.3	49.6
TDCIPP	85.3	79.5	85.9	17.8	-148	85.9	8.5	57.0	51.8	89.0	78.2	92.2
TEHP	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
TPHP	93.8	95.7	93.8	-94.0	-241	-118	22.6	29.4	39.0	90.7	89.7	91.8
DPHP	84.5	79.5	57.9	-519	-602	-389	35.8	70.2	-47.6	38.3	57.1	-204
Ip-PPP	-23.2	67.0	70.3	10.2	21.3	9.9	-7.9	5.1	-31.2	-19.3	-24.7	64.8
BCPP	83.1	96.1	NA	-190.8	-959	40.4	32.6	74.9	-17.5	66.9	89.6	NA
BCEP	NA	NA	47.7	NA	NA	-322	14.9	NA	NA	NA	NA	NA
BBOEP	32.3	2.6	41.0	-0.80	28.8	50.2	52.3	-29.0	-53.8	67.5	10.6	54.9
BDCIPP	57.6	NA	NA	-380	NA	NA	73.0	NA	-153.1	45.0	NA	NA
BEHP	8.0	18.4	-2.3	23.5	4.7	10.6	12.8	25.3	17.2	38.7	41.9	24.2
BTBOEP	4.7	-17.9	22.3	17.3	16.6	13.6	30.8	19.2	-53.3	45.5	20.5	-2.9
DCPs	92.9	68.3	25.0	NA	-46.6	71.1	NA	71.4	-3449	NA	86.7	-668
Total OPE	76.0	58.7	65.2	-16.6	-42.7	-10.6	27.8	31.7	-9.3	79.8	59.7	58.0

NA: Removal not available due to data below limit of detection or quantification.

5 Conclusion

This research focused on the quantification of thirty-nine legacy and replacement contaminants, including flame retardants, bisphenols, and plasticizers in potable water from Montreal and South Africa, and determined the removal efficiency of a conventional DWTP. Legacy flame retardant PBDEs were infrequently detected in all potable water samples, with lower brominated PBDEs typically detected at higher frequencies. Replacement flame retardant OPEs were detected frequently in water from Montreal and South Africa at total average concentrations ranging from 68.4 ng/L (Montreal BW) to 647.4 ng/L (Pretoria). There were significantly higher concentrations of total OPEs in Montreal's DW than Montreal's BW. Total OPE concentrations were significantly higher than PBDEs in Montreal's potable water and Vhembe, indicating replacement chemicals are more present in potable water than legacy PBDEs. OPEs should be reconsidered as safe alternatives to PBDEs based on initial toxicity data and their presence at higher concentrations than PBDEs. The other class of replacement flame retardants, dechloranes, might be less of a concern considering that they were not detected in any water samples from Montreal (including manuscript 1 and 2), while a-DP was detected in one South African sample at a concentration of 1.09 ng/L. Bisphenols were also not detected in any water samples from Montreal or South Africa. Plasticizers were frequently detected in potable water samples from all locations. The total of the eight target plasticizers ranged from 152 ng/L in Pretoria to 606 ng/L in Montreal's bottled water. Notably, legacy phthalates DEHP and DBP were detected in 100% of potable water samples, while replacements DINCH, DINP, DEHA were detected at similar detection frequencies of 97%, 94%, and 94%, respectively. Moving forward, it is crucial to thoroughly characterize the toxicity of replacement plasticizers as they were frequently found at similar concentrations to their legacy compounds throughout potable water samples.

The low detection frequency of PBDEs throughout the drinking water treatment train did not allow for the determination of accurate removal efficiencies of individual compounds during drinking water treatment. Total PBDE removal was calculated as 48.5 and 94.1% for days 2 and 3, respectively, while no removal could be calculated for day 1 as PBDEs were only detected in finished drinking water. While higher brominated PBDE's BDE-183 and BDE-154 were only detected in raw water, lower brominated PBDEs BDE-28, BDE-47 and BDE-99 were detected in finished drinking water. The total of 15 target OPEs were significantly removed through the conventional DWTP (65.8%), with filtration being the most effective treatment method, accounting for 66.6% of the removal of the total OPEs. Some negative removal efficiencies were found, even though an optimized sampling strategy was implemented. Overall removal of individual OPEs ranged from -36.1% (DPHP) to 94.0% (TCEP). Although significant removal was measured for many individual OPEs, significant concentrations were still present in finished drinking water (55 ng/L for BEHP, 23.9 ng/L for DPHP, and 22.5 ng/L TCIPP). Analysis methods for the detection of plasticizers and bisphenols is being developed to determine removal efficiencies through the DWTP. While conventional drinking water treatment methods have demonstrated some removal of flame retardants, contributing to mitigating exposure to these contaminants, flame retardants are still present at concentrations in the ng/L range. Considering flame retardants were detected in potable water at concentrations ranging from ND to 59.7 ng/L, it is essential to assess the potential toxicity of individual compounds as well as mixtures of compounds at these concentrations. Further laboratory and field studies should be conducted on different water treatment technologies to optimize the removal of these contaminants and ultimately eliminate human exposure through drinking water.

6 Limitations and recommendations

The sampling strategy, although optimized for part of the work, had limitations in some sampling campaigns. Only one sample was collected from Pretoria in each sampling campaign, resulting in a total of two samples for the location. All comparisons between Pretoria and other geographical locations resulted in insignificant conclusions, likely due to the low number of samples at Pretoria. Sampling from multiple DWTPs in Pretoria would have increased the sample size and resulted in more statistically significant results. Another sampling limitation was the difficulty in procuring samples from the rural area of Vhembe in South Africa. The water must be frozen immediately after sampling and remain frozen until extraction, which was difficult given the lack of reliable power and freezers in Vhembe. While three sampling campaigns were initially planned for South Africa, only two were accomplished because the extraction could not be done on site as initial planned, which resulted in very high costs of shipping frozen water from South Africa to Canada. Capacity building for extraction and/or analysis with a collaborator in South Africa would eliminate such obstacles.

Limitations in the sampling method of manuscript two resulted in some negative removals reported for both PBDEs and OPEs. Although time-shifted composite sampling accounted for the residence times of each treatment unit, a continuous sampling method over an extended period of time might be best to investigate these compounds present at trace levels. Implementing passive samplers, such a polar organic chemical integrative sampler (POCIS), would however require significant method development as the only commercially available sorbent's target pharmaceuticals or pesticides. Additionally, some of the target analytes in this thesis are non-polar and would not be compatible with any POCIS system.

The time constraint in terms of sample preparation and analysis was another considerable limitation of the thesis. Due to the low concentrations of target analytes in drinking water, a large volume of water (400 mL) was required to pass through SPE. Additionally, three separate extractions were necessary for each water sample to account for the difference in chemical properties of the wide range of target analytes. Contamination was also found in the procedure blanks of OPEs, which was possibly due to SPE, even though care was taken to handle OPEs under a laminar flow hood. Future work should consider using a mass-spectrometer with on-line SPE to streamline the process and reduce the risks of contamination during sample preparation.

The implementation of a new mass spectrometer for the analysis of plasticizers and bisphenols due to the breakdown of the old instrument delayed the availability of these results for inclusion in the thesis. However, these results will be added to the manuscript prior to submission to a journal of consideration for publication.

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