

**OCCURRENCE OF LEGACY AND REPLACEMENT PLASTICIZERS, BISPHENOLS,  
AND FLAME RETARDANTS IN POTABLE WATER IN MONTREAL AND SOUTH  
AFRICA**

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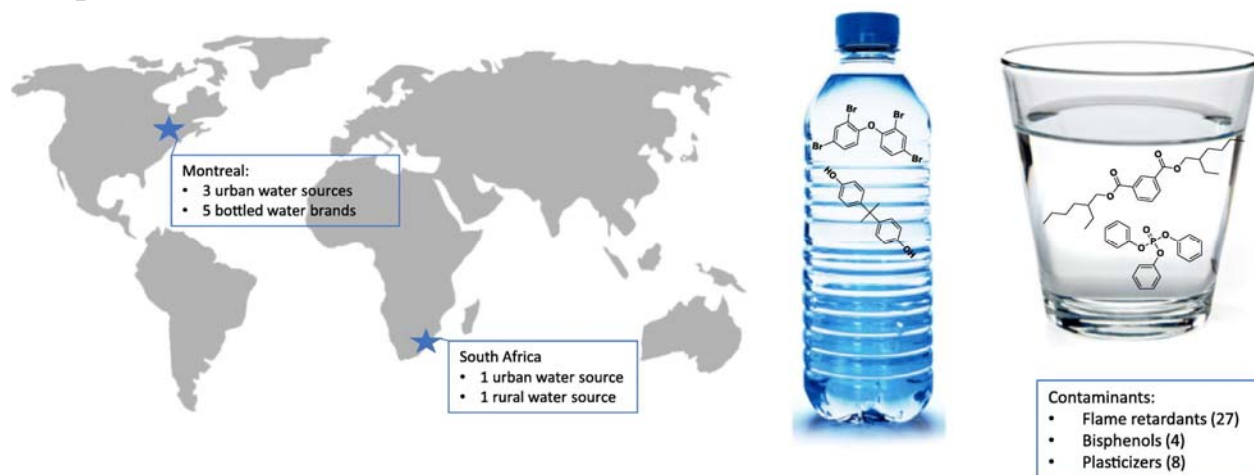
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## **Abstract**

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 (PBDE)s 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, MEHP). For the

compounds reported in earlier studies, the concentrations detected in the present study were similar to other locations. These compounds are not currently regulated in drinking water but their frequent detection, especially OPEs and plasticizers, and the presence of replacement compounds at similar or higher levels than their legacy compounds demonstrate the importance of further investigating the prevalence and the ecological or human health effects of these compounds.

## Graphical abstract



**Keywords:** Plasticizers, flame retardants, bisphenols, tap water, bottled water

## 1 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 synthetic 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; 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), 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 DINP 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 S4.

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, 2010) 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., 2019). Reports of bisphenols in potable water following the summary by Arnold et al. (2013) can be found in the Supplementary Information Table S5.

The objectives of the present research were: 1) To quantify the levels of 39 target flame retardants, plasticizers and bisphenols in potable water in Canada and South Africa; 2) To identify potential differences between locations – including rural and metropolitan areas, and between sources of water – tap and bottled water; 3) To 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.

## **2 Materials and Methods**

### **2.1 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.).

## **2.2 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°C until extraction. Water collected in South Africa was frozen and shipped



to Montreal on dry ice, and subsequently stored at -20°C until extraction. Samples were split into triplicates of 400 mL for each water source and extracted within 24 hours after thawing the sample.

### **2.3 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 °C 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, makes 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°C for 2 hours.

### **2.4 Sample preparation**

#### **2.4.1 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 (2M) 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 adjusted at pH 2.5 using 1N (2M) 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°C until completely evaporated. Samples were reconstituted using 200  $\mu$ L iso-octane and stored at -20°C until analysis.

#### **2.4.2 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  $\mu$ L of OPE (10 deuterated OPEs at 240  $\mu$ g/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°C until completely evaporated, reconstituted in 400  $\mu$ L of 5% MeOH solution in water, and stored at -20°C until analysis.

#### **2.4.3 Sample preparation for plasticizers**

Water samples were prepared using SPE with Oasis HLB glass cartridges (5cc, 200 mg) based on a published method (Bisseger et al., 2018) which was modified to include DEHA, DINCH, DIDA, DINP, and MEHP. Water samples (400 mL, unfiltered) were spiked with 100  $\mu$ L of

plasticizer (five deuterated plasticizers at 240  $\mu\text{g/L}$  in MeOH) internal standard spiking mixture and brought to a pH of 2.5 using 1N (1M) 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 at pH 2.5 adjusted using 1N (1M) 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°C until completely evaporated, reconstituted in 400  $\mu\text{L}$  of 40% LC-MS grade MeOH / 60% 2mM ammonium formate in LC-MS grade water solution and stored at -20°C until analysis.

## **2.5 Sample analysis**

### **2.5.1 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 injection mode was splitless with a constant pressure of 95 kPa, inlet temperature of 250°C, purge time of 1 minute, and purge flow of 50.0 mL/min. A 10 M x 0.18 mm x 0.18  $\mu\text{m}$  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°C for 2 min to 250°C at 25°C/min, to 320°C at 8°C/min and hold for 2 minutes, to 300°C at 8°C/min and hold for the remainder of the run. 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 S8 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 120°C to 230°C at 15°C /min, to 270°C at 5°C /min, to 320°C at 10°C/min and hold for 4 minutes. The source temperature was set at 180°C and GC interface at 280°C. 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  $IDL = 2.998 \times SD$ . 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 S9 along with the transition ions monitored.

### **2.5.2 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 S10.

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 S11.

### 2.5.3 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<sub>18</sub> 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 S12. 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.

#### **2.5.4 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  $\mu\text{m}$   $\times$  3.0 mm  $\times$  100 mm) fitted with a Poroshell 120 Phenyl Hexyl guard column (Agilent Technologies; 2.7  $\mu\text{m}$   $\times$  3.0 mm  $\times$  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 S13.

#### **2.5.5 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  $\times$  2.1 mm ID., 1.8  $\mu\text{m}$ ) 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°C and 250°C, 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  $\pm 5$  ppm 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 S14.

## **2.6 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 ( $LOD/\sqrt{2}$ ). 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 Results and Discussion**

#### **3.1 Overview of the results**

The measured average concentration and frequency of detection of each analyte are summarized in Table 1. 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 1** – 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
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
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

DF: Detection frequency, ND: non-detect, <LOD: below limit of detection, <LOQ: below limit of quantification. \* Denotes replacement compounds and ‡ represents metabolites.

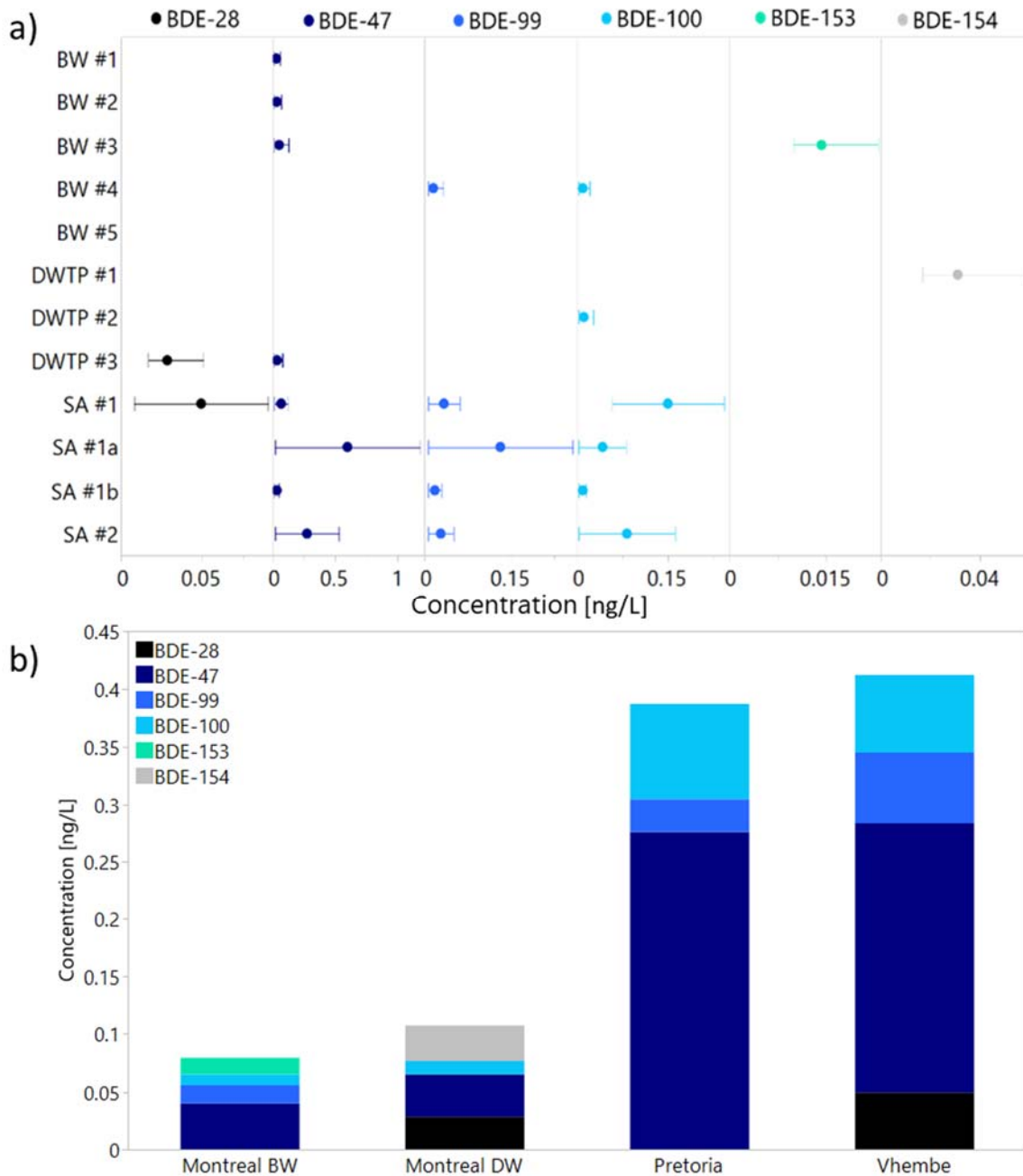
### 3.2 PBDEs in potable water

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 S15-S17). BDE-153 was only detected in one bottled water sample at a concentration of 0.02 ng/L (Supplemental Information Table S15), 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 S16). 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 S17)). Lower bromination level PBDEs BDE-28 and BDE-47 had the highest overall detection frequencies (Table 1). 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 1 & 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; 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 S1.



**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

### **3.3 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 S2). 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.

### **3.4 OPEs in potable water**

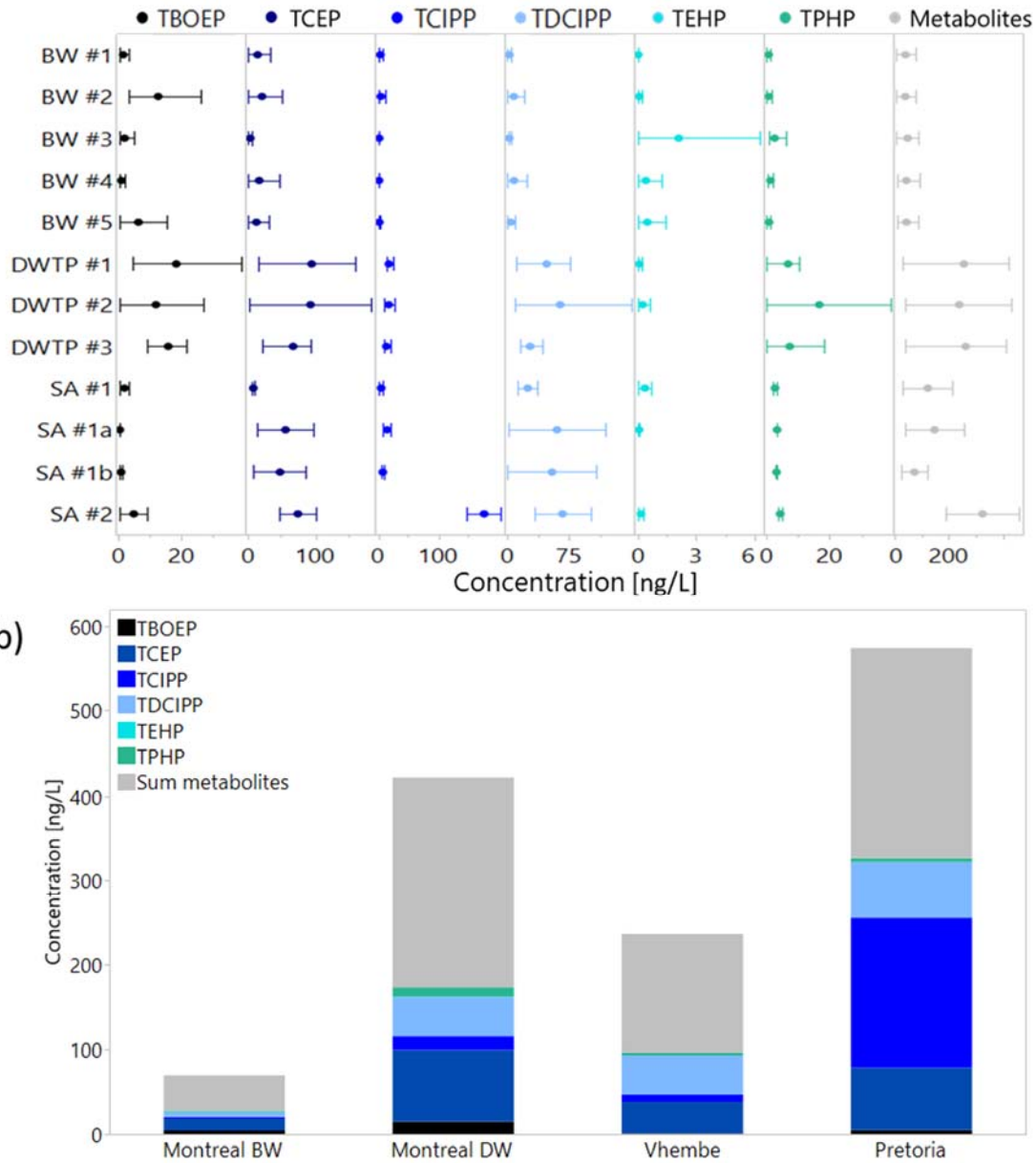
OPEs, which are employed as replacement flame retardants for legacy PBDEs, were more frequently detected at higher concentrations than PBDEs (TCEP ranging from 13.92 (Montreal BW) – 84.59 (Montreal DW) ng/L, TDCIPP ranging from 5.25 (Montreal BW) – 66.93 (Pretoria) ng/L, Table 1). The concentrations of OPEs for each source are summarized in Figure 2(a), where the metabolites are represented by the sum of the 9 target metabolites. A detailed list of OPEs and

their respective metabolites can be found in Supplementary Information Table S6.1. Detection frequencies and concentrations per location for the individual metabolites are listed in Table 1. 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 South 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 BCEP (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 S3), 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).

### 1 **3.5 Bisphenols in potable water**

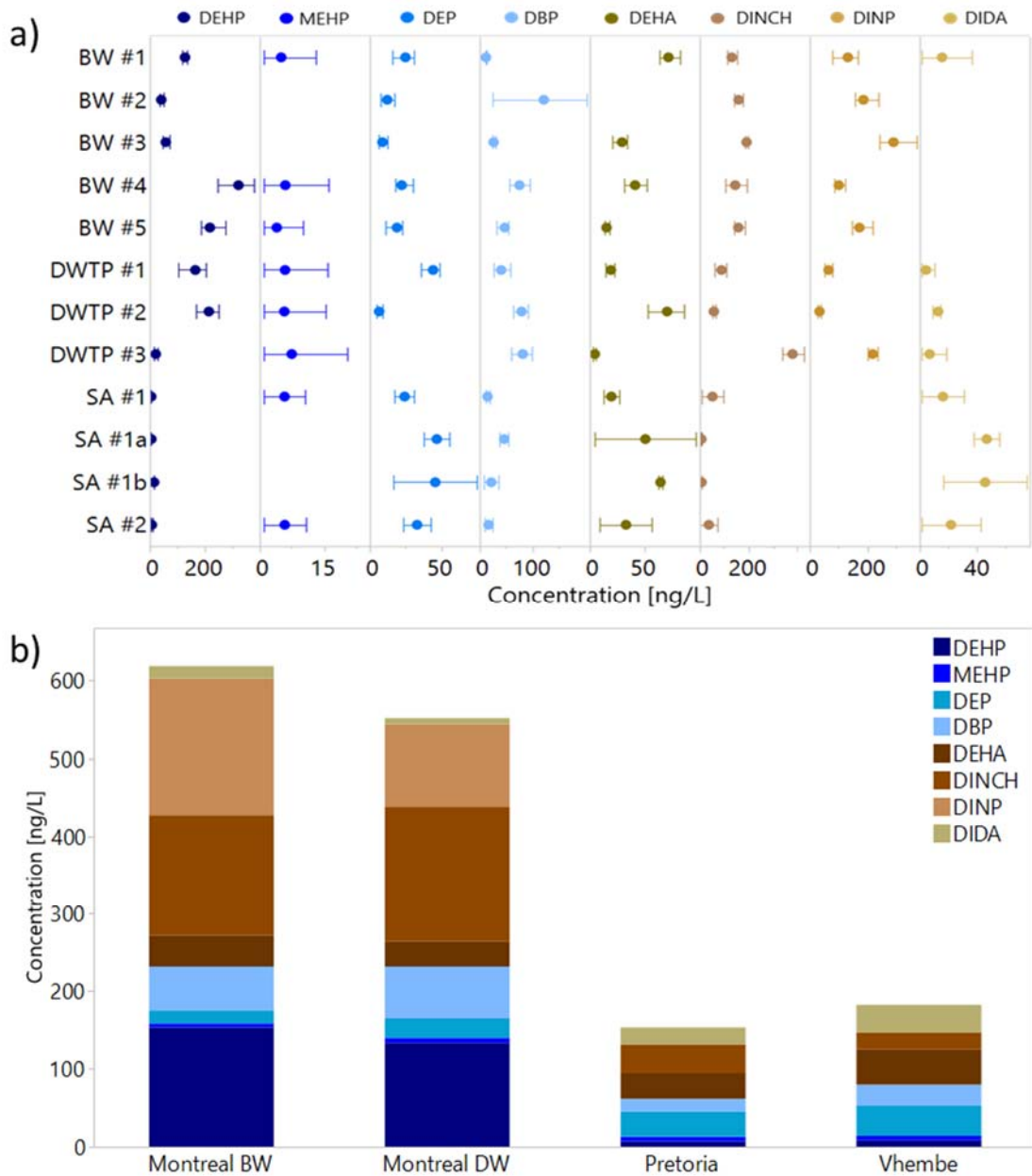
No bisphenols were detected in any of the water samples, despite limits of detection below 1 ng/L. This agrees with a recent study by Goeury et al., where BPA was not detected in tap water from Quebec, and detected below the limit of detection (1.5 ng/L) in 50% of tap water samples from Ontario (Goeury 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., 2019), 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., 2019), 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).

### 3.6 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 S4). 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., 2019), 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.

### **3.7 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 S17), 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 (8 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 mobilities 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.

#### **4 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. For a subset of compounds included in the study, it was possible to compare the concentrations measured to the ones reported for other locations and the range of concentrations were similar. There is however limited information in literature for several compounds considering that these are not regulated. Some preliminary work (data not shown) indicated that these compounds can be removed by the treatment process used in drinking water treatment but further laboratory research and field studies should be implemented to investigate their respective efficiency of removal of these contaminants.

Attention should be drawn to the potential health risks from the mixtures of flame retardants, plasticizers, and bisphenols found in drinking water, as 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, reduction at the source strategies and 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.

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