Total organic halogen (TOX) in treated wastewaters: an optimized method and comparison with target analysis

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Abstract

Wastewater effluents are complex mixtures that may potentially contain thousands of compounds that are not well removed from conventional wastewater treatment. There are more than 350,000 chemicals registered for production or use that can potentially end up in the environment. Quantification of emerging contaminants by target analysis has been extensively applied however, these methods are often limited by the availability of analytical standards and resources. The total organic halogen (TOX) method is a comprehensive evaluation of the total halogen content in water including emerging halogenated contaminants and disinfection by-products. In this study, an analytical method was developed to simultaneously quantify TOX as total organic fluorine (TOF), total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI). Halophenol recovery experiments were performed in secondary wastewater effluents for TOF, TOCl, TOBr, and TOI with recoveries between 61-105%. Also, nine halogenated contaminants were spiked into ultrapure water with recoveries between 19-107%. The TOX method was used to evaluate four secondary wastewater effluents prior to disinfection across 2 cities in Alberta, Canada. It was observed that TOF, TOCl, and TOBr ranged from 4.9 - 10.5 µg/L, 67.5 - 80.0 µg/L, and 5.0 – 9.0 µg/L, respectively whereas TOI was only detected in two samples at 1.8 and 6.1 µg/L. A sample was analyzed for 196 emerging contaminants (99 were halogenated) to characterize and identify TOX in wastewater for the first time. Target analysis with liquid chromatography tandem mass spectrometry only identified 1.5% of TOX which underlines the severe limitations of target analysis in wastewater samples. These results highlight the importance of the TOX method as an indicator of halogenated emerging contaminants in wastewater.

Keywords

Total organic halogen, wastewater, total organic iodine, total organic fluorine, micropollutants, halogenated contaminants

1. Introduction

Micropollutants (MPs) are priority anthropogenic contaminants found in the environment, which may include pharmaceuticals and personal care products (PPCPs), per- and polyfluoroalkyl substances (PFAS), pesticides, flame retardants, and industrial compounds.[1-5] There are over 350,000 registered chemicals for production or use that could potentially be released into the environment.[6] MPs are typically not well removed in wastewater facilities and can be discharged into surface water that may cause adverse environmental and human health effects.[5, 7] Another concern is that wastewater effluents are increasingly impacting surface waters used for drinking water and have been intentionally being reused for in water scarce areas. [8-11] These wastewater-impacted source waters contain high levels of MPs that could produce a different suite of disinfection by-products compared to pristine waters. One example is the antimicrobial agent triclosan, a component in daily personal care products such as toothpaste, soaps, and deodorants.[12, 13] Triclosan can react with free chlorine and chloramines to form chlorinated phenols 2,4-dichlorophenol and 2,4,6-trichlorophenol.[14] Iopamidol, another example of an emerging contaminant (EC), is an iodinated X-ray contrast media used in hospitals for organ imaging which is excreted and poorly removed during wastewater treatment. Iodinated X-ray contrast media has been found to react with chemical disinfectants to produce toxic iodinated DBPs (I-DBPs).[15-23]

Halogenated organic compounds are a group of MPs that contain a halogen in their molecule and have shown to be highly toxic, persistent in the environment, and potential to bioaccumulate in living organisms.[24] There are over 37,000 registered halogenated organic compounds that could contribute to the global pollution.[6] In a recent effort to prioritize the most concerning MPs based on their toxicity, occurrence frequency, and environmental concentrations reported in literature, 53 MPs were identified out of which 18 are halogenated.[5] However, MP quantification is limited to the availability of analytical standards.

Total organic halogen (TOX) is a comprehensive analytical method that can quantify all halogenated organic compounds and has been primarily used for drinking water analysis.[25] TOX includes *known* halogenated MPs that can be individually quantified, as well as *unknown* halogenated MPs that are still unidentified. This method is based on the adsorption of organic material onto activated carbon, combustion of activated carbon, and adsorption of produced gases into an aqueous solution. Halogen atoms attached to organic materials are released as acid halides (HF, HCl, HBr, HI), collected in an aqueous solution, and subsequently separated by ion chromatography. TOX can be quantified by halogen type as total organic fluorine (TOF), total organic chlorine (TOCl), total organic bromine (TOBr) and total organic iodine (TOI). The TOX measurement has the advantage that it can comprehensively quantify halogenated MPs in water, whereas target methods can only quantify a small subset of TOX. However, most of the existing TOX methods have been optimized for a subset of the TOX and do not analyze TOF, TOCl, TOBr, and TOI in one method.[25-37] The lowest detection limits that can simultaneously quantify TOCl, TOBr, and TOI in drinking water are 3, 2 and 1 µg/L as X^-, respectively.[28] Other methods have been optimized to either quantify TOF[26, 32, 34, 37] or TOI[30, 36] with detection limits as low as 0.3[26] and 0.95[36] µg/L as X^-, respectively. Additionally, the TOX method has also not been validated for wastewater secondary effluents.

The goals of this research was to optimize a method that can comprehensively capture halogenated contaminants by halogen type in treated wastewater effluents and identify the TOX fraction with target analysis. In this study, we tested the effect of absorption solution buffer composition, number of activated carbon columns, and sample volume. Percent recovery experiments of halogenated MPs spiked in ultrapure water or treated wastewater effluents were also performed. One treated wastewater sample was further analyzed for 196 targeted PCPPs, halogenated-flame retardants (HFRs), organophosphate flame retardants (OPFRs), and PFASs. This large-scale target analysis was completed to determine the TOX percentage of *known* and *unknown* halogenated MPs contained in wastewater, this is the first time to do this type of analysis to the best of our knowledge. This TOX method could be used to evaluate halogenated MPs found in treated wastewater effluents and recycled water.

2. Materials and Methods

2.1 Reagent and Solutions

Potassium iodide (99.0%), sodium chloride (99.0%), sodium bromide (99.0%), sodium fluoride (≥99%), hydrogen peroxide (30%), 2,4,6-trichlorophenol (≥98.3%), 2,4,6-tribromophenol (≥99%), 2,4,6-trifluorophenol (99%), 4-fluorophenol (99%), 4-iodophenol (≥99%), ofloxacin

(99%), BDE-99 (≥98%), BDE 209 (50 μg/mL), and iopamidol were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Nitric acid (Optima Grade), ammonium hydroxide (Optima Grade), ciprofloxacin (>98%), and triclosan (99%) were purchased from Fisher Scientific (Waltham, MA, USA). Whatman borosilicate 0.45 μm glass filters were purchased from VWR (Radnor, PA, USA).

Analytical standards for fluoride, chloride, bromide, and iodide were made by weighing halide salts on an analytical balance Mettler Toledo XS104 (Mississauga, ON, Canada). Each standard was weighed directly in a metal-free sterile 50 mL centrifuge tube (VWR, Radnor, PA, USA), filled with 20 μM ammonium hydroxide solution (absorbing solution), and weighed again to calculate the final concentration. The absorbing solution was prepared daily by adding 50 μL of trace-metal free hydrogen peroxide (30%) and 20 μL of ammonium hydroxide standard (0.5 M) and filled to the line with ultrapure water in a 500 mL volumetric flask. Analytical standards were covered in aluminum foil and stored in the dark at 4 °C. Analytical standards were found to be stable up to 4 months. A nitrate solution of concentration 5,000 mg/L as NO_3^- was used as washing solution to remove ions adsorbed to the AC. Ultrapure water (>18.1 MΩ•cm) was used to prepare all aqueous solutions in this study. Ultrapure water was obtained from DI water treated with a Barnstead B-Pure system followed by a Barnstead Micropure UV/UF System (Thermo Fisher Scientific, Waltham, MA, USA).

Halophenol standard stock solutions were prepared by weighing them in methanol (~4000 mg/L and stored in the freezer at -20 °C. Sub-stock solutions of 100 mg/L were made in methanol and prepared daily to be spiked directly into wastewater. Due to their different solubilities ciprofloxacin, ofloxacin, diclofenac, and iopamidol were dissolved in water; triclosan in acetone; BDE-99 and BDE-209 in methanol; and triiodomethane (TIM) in acetonitrile. Analyte stock solutions (~1000 mg/L) were stored at 4 °C in the dark. Working solutions were prepared daily by spiking the stock solutions into ultrapure water.

2.2 Wastewater Sample Collection

Halogenated phenol recovery, breakthrough, and volume optimization experiments were conducted using secondary wastewater effluent that was collected on January 9th, 2020. The secondary wastewater effluent was collected prior to disinfection as a 5-hour composite that flows into Advancing Canadian Wastewater Assets (ACWA), a full-scale research plant located in Calgary, Alberta, Canada. The wastewater was filtered with a 0.45 μm membrane filter. The developed method was used to analyze secondary wastewater effluents collected from two cities in Alberta, Canada. Both cities have conventional wastewater treatment process that includes screening and grit removal, primary clarifier, activated sludge reactor, secondary clarifier, and UV disinfection. Samples were collected prior to disinfection. City "A" wastewater was sampled on May 3rd, May 5th, and May 7th 2021 to evaluate TOX daily variations. A composite sample was obtained by collecting two bottles of 4 L of wastewater every hour for 5 hours and homogenized in two 20 L carboys. City "B" secondary wastewater effluent was collected on April 20th, 2021 in six 1 L HDPE bottles and homogenized in a 10 L carboy. The wastewater samples were stored in the dark at 4 °C until they were analyzed for TOX. City "A" and City "B" water were not filtered prior to analysis to minimize the removal of existing contaminants. Water quality parameters for collected samples are shown in Table 1.

2.3 Analytical Methods and Instrumentation

The TOX method was followed as outlined in Kimura et al[27] with modifications using a Mitsubishi TOX system (Chigasaki, Japan) and a decoupled Dionex Integrion Ion Chromatograph (IC) (Thermo Fisher Scientific, Waltham, MA). Samples were passed through activated carbon

(AC) columns (Mitsubishi TXAPPC4, 40 mg) (Chigasaki Japan) using an adsorption unit (Mitsubishi TXA-04) (Chigasaki, Japan) without pH adjustment to minimize the oxidation of I^- to I_2 under acidic conditions.[38] A 15 mL washing solution of 5000 mg/L as NO_3^- was used to wash inorganic anions from the ACs. The ACs were then transferred to ceramic boats where a solid autosampler (ASC-240S) that introduced the ACs into the automatic quick furnace (AQF-2100H). The following program was used to combust the ACs: 500 s at the end position (1000 °C), 200 s at the cooling position (900 °C), and 200 s at the home position (room temperature) at an argon and oxygen flow rate of 200 and 400 mL/min. Combustion off-gases were collected using an AU-250 absorption carousel that held a centrifuge tube with a buffer solution.

The efficiency to absorb all halides by the absorption solution was assessed by testing two different buffers (ammonium hydroxide and potassium phosphate). A 5 µL standard mix of 50 mg/L as X^- that contained sodium fluoride, sodium chloride, potassium bromide, and potassium iodide was directly injected into a ceramic boat that contained quartz wool. The ceramic boat was placed into the instrument autosampler. Two buffer concentrations were also evaluated: 10 µM and 20 µM. The absorption solution containing the pyrolysis off-gases was then analyzed by IC for fluoride, chloride, bromide, and iodide. All experiments were done in triplicate.

Two sample volumes were tested for breakthrough analysis: 50 and 80 mL. The goal was to recover TOCl, TOBr and TOI within two ACs. Two ACs were used because the ceramic boats used for the pyrolysis unit ASC-240S can only fit two ACs per run. To do this, secondary wastewater effluents samples were passed through three ACs in series. Each AC was pyrolyzed individually with the quick furnace and the produced gases from each AC were collected separately into individual containers (C#1, C#2, C#3). The breakthrough percentage was calculated by dividing the TOX amount in the third AC by total TOX from all three ACs. Due to the low concentration of TOF in wastewater samples, the TOF breakthrough experiments were performed by spiking 2,4,6-trifluorophenol (246TFP) (30 µg/L as F^-) to 50 mL of sample. All samples were tested in triplicate.

Two separate ion chromatography methods were utilized to optimize separation and quantification of halide ions (Figure S1 and S2 in Support Information). The first method analyzed chloride, bromide, and iodide using a Dionex IonPac AS20 microbore analytical column (2 x 250 mm), AG20 guard column, and a sample loop size of 250 µL. The mobile phase was potassium hydroxide introduced at a flow rate of 0.250 mL/min. The separation gradient program started at 5 mM KOH for 10 minutes, increased to 35 mM KOH for 8 minutes, and a final 5 mM KOH for 12 minutes. The column and detector temperatures were set to 35 °C and 30 °C, respectively. The second method analyzed fluoride using a Dionex IonPac AS15 microbore analytical column (2 x 250 mm), AG15 guard column, and a sample loop size of 250 µL. The mobile phase was KOH and introduced at a flow rate of 0.300 mL/min. The separation gradient program was programmed to start at 5 mM KOH for 12 minutes, followed by 25 mM for 15 minutes, 50 mM for 12 minutes, and reduced to a final 5 mM KOH for 7 minutes. The column and detector temperatures were set to 30 °C. Seven calibration standards were used within the range of 5-500 µg/L with a coefficient of determination (R^2) > 0.99 for both methods.

Detection limits (DLs) for the IC were calculated by the standard deviation of n=7 replicates multiplied by the 99% confidence interval of a one-sided Student's t-test as explained elsewhere[39]. Briefly, DLs were calculated using the equation below, where *C* is the concentration of all replicates in µg/L, *F* is the concentration factor during extraction, $t_{N—1,1—\alpha=0.99}$ is the 99% confidence level of N-1 Student's t-value, $SD_{PeakArea}$ is the standard deviation of the peak areas, and $AV_{PeakArea}$ is the average peak area. Method detection limits (MDLs) were estimated from IC detection limits. MDL for TOF is estimated to be 1 μg/L based on the lowest calibration point and concentration factor.

$$DL = t_{N-1,1-\alpha=0.99}(C)\frac{SD_{PeakArea}}{AV_{PeakArea}(F)}$$

The TOX method was tested to determine the recovery of 4 halophenols spiked into secondary wastewater effluents. Levels of 30 μg/L of 2,4,6-trifluorophenol (246TFP) as F^-, 30 μg/L of 4-fluorophenol (4FP) as F^-, 200 μg/L of 2,4,6-trichlorphenol (246TCP) as Cl^-, 50 μg/L of 2,4,6-tribromophenol (246-TBP) as Br^-, and 30 μg/L of 4-iodophenol (4IP) as I^- were spiked directly into wastewater effluents. 4FP and 246TFP were spiked and recoveries were evaluated separately. A wastewater control without spiked analytes was evaluated.

Dissolved organic carbon was measured using a Shimadzu TOC-V (Kyoto, Japan) according to Standard Method 5310 B[40]. Turbidity, SUVA 254, and pH were determined with a Hach 2100AN Turbidimeter (Loveland, CO, USA), Shimadzu UV-2700 (Columbia, MD, USA), and Mettler Toledo Seven Compact pH meter (Mississauga, ON, Canada), respectively.

2.5 Micropollutant quantification

Targeted analysis for 196 different PCPPS, HFRs, OPFRS, PFAS were performed by SGS AXYS Analytical Services Ltd (Sidney, BC, Canada) with four analytical methods. These compounds were chosen because the 4 selected methods contained the largest number of halogenated analytes of interest. PCPPs analysis was performed by electrospray ionization liquid chromatography with triple-quadrupole mass spectrometry (LC-ESI-MS/MS) according to SGS AXYS method MLA-075 REV 09 VER 01. OPFRs analysis was performed by LC-MS/MS according to SGS AXYS method MLA-098 REV.01 VER.03. PFAS analysis was performed by LC-MS/MS according to SGS AXYS method MLA-110 REV.02 VER.11. HFRs analysis was performed by gas chromatography electron capture negative ion mass spectrometry (GC-(ECNI)-

MS) according to SGS AXYS method MLA-096 REV. 01 VER. 07. PFAS and PCPPs were preconcentrated with solid phase extraction and OPFRs and HFRs analysis were extracted with liquid-liquid extraction. Detailed information on these methods including procedure, target analytes, and detection limits can be found in Supporting Information.

3. Results and Discussion

3.1 Absorption Solution Composition

The combustion of activated carbon in the quick furnace produces an off-gas that contain hydrogen halides (i.e., HF, HCl, HBr, HI). The off-gas is collected by bubbling it into an absorption solution that contains a buffer and hydrogen peroxide. The composition of the absorption solution is important because the solution needs to efficiently capture the products from the off-gas and should not affect the subsequent ion chromatography analysis[27]. Two different buffers (ammonium hydroxide and phosphate) were tested for fluoride, chloride, bromide and iodide. Fluoride, chloride, and bromide concentrations did not differ significantly between buffer composition or concentration (data not shown). Fluoride recovery ranged between 107-109%, chloride recovery ranged between 104-108%, and bromide recovery ranged between 101-108% over all trials. However, there was significant difference with the iodide recovery as shown in Figure 1. The average iodide recoveries were 30 ± 8% for phosphate buffer and 75 ± 6% for ammonium hydroxide buffer. Ammonium hydroxide was shown to perform better than phosphate buffer with a recovery improvement of 45% and excellent precision between the replicates. The effect of ammonium hydroxide concentration was also analyzed at two concentrations: 10 and 20 µM. When the concentration of ammonium hydroxide doubled, the iodide recovery increased from 75 ± 6 to 86 ± 2%. Furthermore, the IC system uses potassium hydroxide as the eluent which contributes to the background noise. However, it was observed that ammonium hydroxide had lower background noise compared to the phosphate buffer solution. For these reasons, ammonium hydroxide (20 µM) was chosen for this study.

3.2 Breakthrough tests

The TOX method relies on organic matter being retained in the AC columns. When the AC fail to retain the organic matter, it can pass through the cartridge or breakthrough. Results for the two sample volumes tested (50 and 80 mL) are shown in Figure 2. The results show the chloride, bromide, and iodide concentrations measured from the absorption solution that represents the recovered total organic halide from each activated carbon. For 50 mL, the recovery in the first two AC columns were 92%, 90%, and 80% for chloride, bromide and iodide, respectively (Figure 2). The TOI breakthrough was higher than TOCl and TOBr because the TOI concentration is significantly lower than the other two measurements with a signal to noise ratio of 2. The iodide background concentration for each AC from the blank was 2.24 µg/L ± 0.4. A signal to noise ratio of 2 made it difficult to differentiate between the signal and the noise. However, a previous study that analyzed TOX in urine with a sample volume of 50 mL, a complex mixture, showed that TOI was primarily captured in the first AC.[27] For the 80 mL sample volume, the recovery in the first two AC columns were 88, 86, and 80% for TOCl, TOBr, and TOI, respectively as shown in Figure 2. Due to the lower recovery (higher breakthrough) in 80 mL sample volume, 50 mL was chosen as the sample volume.

Recovery of TOF was also difficult to assess because each AC was very close to the background concentration. Therefore, wastewater was spiked with 246TFP (30 µg/L as F^-) and recoveries are shown in Figure 3. Results suggest that the organic fluorine was primarily adsorbed within the first AC. A high recovery of 96% was observed in the first two columns.

3.3 Recovery of Standards

Recovery of analytical standards were completed using the improved method. The improved method included 50 mL sample volume, 2 AC columns in series, and 20 µM ammonium hydroxide buffered absorption solution. MDLs for TOCl, TOBr, TOI, and TOF were 0.5, 0.2, 0.2 and 1 µg/L, respectively.

The recovery of halogenated phenols spiked in secondary wastewater effluent ranged from 61 to 105% as shown in Figure 4. TOF had a recovery of 78 ± 10% for 4-fluorophenol (4FP) and 89 ± 2% for 2,4,6-trifluorophenol (246TFP), TOCl had a recovery of 98 ± 1% for 246TCP, TOBr had a recovery of 105 ± 1% for 246TBP, and TOI had a recovery of 61 ± 8% for 4IP. A lower TOI recovery compared to TOCl and TOBr has been previously reported in complex mixtures such as urine[27] and groundwater[28], which agrees with the results found in our study. Kristiana et al tested the effect of inorganic ions on halophenol recovery however, they did not observe any significant effects and needs to be further investigated.[28]

Additionally, the improved method was used to determine the recovery of 9 emerging contaminants spiked into ultrapure water (Figure S3 in Supporting Information). Two emerging contaminants were selected for each halogen type that are commonly present in wastewaters effluents (except TIM) due to their poor removal from wastewater treatment. The analytes were individually spiked into ultrapure water at a concentration of 50 µg/L. The recoveries of these compounds are shown in Figure 5.

Fluorinated compounds had a recovery of 85-88%. A previous study by Willach *et al.* reported that ciprofloxacin recovery in ultrapure water of 90-100% could be achieved, while a similar recovery of 85% was observed in this study.[41] The chlorinated compounds, which include diclofenac, and triclosan, had high percent recoveries of 91-107%. The brominated compounds, which include two flame retardants, BDE-99 and BDE-209, had low percent recoveries of 23-53%. A possibly explanation is that BDE-209 has five more bromine atoms than BDE-99, making BDE-209 a more polar molecule that results in its low adsorption to the AC. Oleksy-Frenzel *et al.* found that highly polar, linear compounds had limited adsorption to AC[42]. The iodinated compounds (iopamidol and TIM) had percent recoveries of 19-26%, which are the lowest of the halogenated groups. Previous studies have reported recoveries of 100%[28] and 92%[43] for TIM. Further, iopamidol was reported to have a recovery of 99%[28], which is significantly higher compared to results found in this study. There are a few possible reasons for this discrepancy. Kristiana *et al.* adjusted the sample pH to 2 prior to extraction, used a different brand of activated carbon, and their spike concentration was not reported.[28] Kinani *et al.* also adjusted the sample pH to 2, used a higher spiked concentration (50 µg/L as Cl^- compared to 50 µg/L of analyte), and did not report what type of AC was used.[43] Low pH favors the protonation of HX that leads to a better adsorption which result in higher recoveries. Furthermore, the type of AC has a significant influence on the recovery of analytes.[26] The AC used in this study was provided by the vendor which is readily accessible to any user that wants to use this technique.

3.4 Quantification of TOF, TOCl, TOBr, and TOI in secondary wastewater effluents

Secondary wastewater effluents from two cities in Alberta, Canada were processed individually in triplicate to determine TOF, TOCl, TOBr, and TOI. Results are shown in Figure 6. TOF concentrations of the four water samples were 7.3 ± 2.8, 4.9 ± 0.8, and 5.0 ± 1.9 µg/L as F^- for City "A" and 10.5 ± 2.3 µg/L as F^- for City "B", which is a similar concentration range reported in previous studies[37, 41]. A study by Willach *et al.* in Germany reported that a municipal wastewater treatment effluent had a TOF value of 1.98 µg/L[41]. Another study in Germany by von Abercron *et* *al.* reported that 85% (n=117) municipal wastewater treatment plants detected concentrations between 2.0 and 8.5 µg/L[37].

Similarily, TOCl, TOBr, and TOI values found in this study are similar to values reported previously by our research group[44]. TOCl and TOBr concentrations of the four water samples were between 62.8-80.0 µg/L as Cl^- and 5.0-8.9 µg/L as Br^-, respectively. Ortega-Hernandez *et al.* reported a TOCl and TOBr concentration of 102.4 ± 2.0 µg/L as Cl^- and 7.1 ± 0.1 µg/L as Br^- in a Canadian secondary wastewater effluent,[44] respectively which are within range. However, TOI was detected in two of the four samples with concentration of 6.1 ± 1.8 µg/L as I^- for City "A" and 1.8 ± 0.5 µg/L as I^- for City "B". Ortega-Hernandez *et al.* reported a TOI concentration of 5.6 ± 2.9 µg/L as I^- , similar values compared to what was found in this study[44]. Water quality parameters in Table 1 indicate that City "B" (10 mg/L) had higher TOC values than City "A" (5.6-5.9 mg/L) samples by almost 40%. However, the elevated TOC did not correlate to a higher percentage of TOX in the sample.

3.5 Known and unknown composition of TOX

Wastewater is a complex matrix that contains many natural and anthropogenic contaminants. However, there is limited information about the total composition of these waters. For the first time, our study has attempted to characterize emerging contaminants that are included in TOX. One wastewater sample (City A – May 7/21) was analyzed for 196 emerging contaminants which included 25 HFRs, 13 OPFRs, 40 PFAS, and 118 PCPPs. The full list of compounds and their reporting concentration limits are listed in Tables S1-S4 in Supporting Information. However, of the 196 compounds (99 analytes contain at least one halogen) that were analyzed, 87 were detected as shown in Table 2 (35 halogenated, 52 non-halogenated).

Targeted fluorinated compounds only contributed 1.1% of the TOF (4.9 μg/L as F^-) quantified in City "A" May 5th sample (Figure 7a, Table 2). Within the known fraction, PFAS and PCPPs contributed 57.0% and 43.0%, respectively. Perfluoropentanoate (PFPeA) and perfluorohexanoate (PFHxA) had the highest PFAS concentrations at 17.2 ng/L and 13.1 ng/L, respectively. A study in China reported that PFPeA was the predominant PFAS in influent and effluent wastewaters at concentrations of 754 and 68.7 ng/L, respectively[45]. A recent study by Han *et al.* reported that targeted PFAS analysis contributed between 0.4-29% of TOF across different environmental water samples, including drinking water, tap water, ground water, and storm water[46]. In the targeted analysis performed in our study, the 12 PFAS detected contributed to 0.65% of TOF, which falls within the reported range. Additionally, out of the 14 fluorinated target PCPPs only half were detected. Ciprofloxacin (antibiotic) and fluoxetine (antidepressant known as Prozac) were the highest detected fluorinated PCPPs at concentrations of 192 ng/L and 46.8 ng/L. Ciprofloxacin has previously been reported in wastewater effluent at concentrations up to 160 ng/L[47]. Ciprofloxacin is excreted in large quantities unmetabolized, which makes it commonly found in domestic wastewater at significant quantities[48]. Fluoxetine has been reported in secondary wastewater effluent at concentrations ranging from 0.6 – 8.4 ng/L[49, 50]. Fluoxetine has been commonly quantified in wastewater in Europe and North America[51-53].

Targeted chlorinated compounds contributed 1.1% of TOCl (67.5 μg/L as Cl^-) quantified in this study (Figure 7b, Table 2) composed of chlorinated flame retardants (78.6%) and PCPPs (21.4%). Chlorinated flame retardants (FRs) analysis was broken into two types: organophosphates (OPFRs) and halogenated flame retardants (HFRs). OPFRs made up 99.99% of the total FRs detected, with HFRs contributing a negligible amount. Tris-chloroisopropyl phosphate (TCPP) and tris(1,3-dichloro-2-propyl)phosphate (TDCPP), two flame retardants found in consumer products and electronics that are ubiquitous in nature[54, 55], had the highest concentrations. TCPP and TDCPP were detected at concentrations of 1210 ng/L and 290 ng/L, respectively. In a study by Bester *et al.*, TCPP was monitored in the wastewater effluent in Germany over five days and reported a concentration range of 230-610 ng/L[56], at least two times lower compared to what was quantified in our study. In a study by Hao *et al.*, TDCPP was detected in wastewater effluent in Ontario, Canada with a reported concentration range of 210-400 ng/L[57].TDCPP has also been reported in the United States at concentrations as high as 65,600 ng/Lin laundry wastewater.[58] Furthermore, out of 14 chlorinated PCPPs, 10 were detected. Hydrochlorothiazide, a diuretic medication used to treat high blood pressure, was detected with the highest concentration of 995 ng/L. In a nationwide study across 50 wastewater treatment plants in the United States, hydrochlorothiazide was detected in all 50 effluents with a mean concentration of 1100 ng/L[59]. A full list of all the compounds detected in the analysis and their concentrations can be found in Table 2.

Out of the 19 targeted brominated-compounds, only 3 brominated FRs were detected with a maximum concentration of 0.145 ng/L. All three compounds detected were brominated FRs: hexabromobenzene (0.12 ng/L), pentabromotoluene (0.145 ng/L), and pentabromoethylbenzene (0.045 ng/L). The targeted brominated compounds only contributed 0.005% of TOBr (5.0 µg/L as Br^-). Unfortunately, the polybrominated diphenyl ether flame retardants were not analyzed in this study.

The halogenated target analytes were converted to equivalents of Cl^- and TOX was evaluated as a sum of TOF, TOCl, and TOBr as Cl^-. Overall, the targeted methods only accounted 1.5% of TOX, with 98.5% still unknown (Figure 7c). Wastewater is a complex mixture that may contain many PCPPs, FRs, natural organic matter, among other anthropogenic and natural compounds. According to Wang et al, there are over 350,000 chemicals that have been registered in 19 countries that could enter the environment and contribute to the chemical pollution[6]. This targeted analysis only targeted 196 emerging contaminants, which represents only a fraction of chemicals that could be contained in wastewater and therefore only constitutes 1.5% of TOX. Additional analysis that includes a wider range of other emerging contaminants would need to be performed including herbicides, pesticides, flame retardants, fungicides, microplastics (specifically polyvinyl chloride), and DBPs. However, target methods for emerging contaminants are expensive, resource intensive, and advanced analytical instrumentation that make them difficult to study. Therefore, the advantage of the TOX method reported by halogen type developed in this study can provide an alternative parameter that quantifies the total amount of halogenated organic compounds found in wastewater.

A major limitation of the TOX method is that it cannot quantify non-halogenated compounds of concern. Target analysis quantified 35 halogenated and 52 non-halogenated compounds that make up 28% and 72% of the total molar micropollutant concentration, respectively. However, the halogenated versus non-halogenated percentages will depend on the initial target analyte list and water samples. Of the non-halogenated compounds detected in our analysis metformin, azithromycin, carbamazepine, clarithromycin, and trimethoprim were the top five compounds with the highest concentrations. Metformin, a medication used to treat type 2 diabetes, was detected at concentration of 1160 ng/L. Carbamazepine, an anticonvulsant used to treat epilepsy and schizophrenia, was detected at a concentration of 398 ng/L. Three antibiotics were detected including azithromycin (879 ng/L), clarithromycin (334 ng/L), and trimethoprim (276 ng/L).

4. Conclusions

An optimized method that simultaneously quantifies total organic fluorine, chlorine, bromine, and iodine in treated wastewater effluent has been developed. The TOX method include the following: 50 mL of sample, 2 activated carbons, 15 mL of nitrate wash, and 20 μM ammonium hydroxide buffer solution. MDLs for TOCl, TOBr, and TOI were 0.5, 0.2, and 0.2 μg/L, respectively. MDL for TOF was estimated to be 1 μg/L. The TOX method was tested on four secondary wastewater effluents from two cities in Alberta, Canada. Further, a target analysis was performed on one of the wastewater samples that included 99 halogenated compounds including PFAS, PCPPs, FRs, and OPFRs. The results showed that only 1.5% of TOX (~1.1% of TOF and TOCl) was identified with target analysis and 98.5% of TOX remained unknown. The halogenated compounds that were detected with the highest concentrations were: perfluoropentanoate, perfluorohexanoate, ciprofloxacin, fluoxetine, tris-chloroisopropyl phosphate, tris(1,3-dichloro-2-propyl)phosphate, and hydrochlorothiazide.

Conflicts of interest

The authors of this manuscript have no competing financial interests or personal relationships that could have influenced the outcomes of this study.

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References

1. S. D. Richardson and T. A. Ternes, Water Analysis: Emerging Contaminants and Current Issues, *Anal. Chem.*, 2022, **94**, 382-416.
2. S. D. Richardson and S. Y. Kimura, Water Analysis: Emerging Contaminants and Current Issues, *Anal. Chem.*, 2020, **92**, 473-505.
3. S. D. Richardson and T. A. Ternes, Water Analysis: Emerging Contaminants and Current Issues, *Anal. Chem.*, 2018, **90**, 398-428.
4. S. D. Richardson and S. Y. Kimura, Water Analysis: Emerging Contaminants and Current Issues, *Anal. Chem.*, 2016, **88**, 546-582.
5. Y. Yang, X. Zhang, J. Jiang, J. Han, W. Li, X. Li, K. M. Yee Leung, S. A. Snyder and P. J. J. Alvarez, Which Micropollutants in Water Environments Deserve More Attention Globally?, *Environ. Sci. Technol.*, 2022, **56**, 13-29.
6. Z. Wang, G. W. Walker, D. C. G. Muir and K. Nagatani-Yoshida, Toward a Global Understanding of Chemical Pollution: A First Comprehensive Analysis of National and Regional Chemical Inventories, *Environ. Sci. Technol.*, 2020, **54**, 2575-2584.
7. Y. Luo, W. Guo, H. H. Ngo, L. D. Nghiem, F. I. Hai, J. Zhang, S. Liang and X. C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Sci. Total Environ.*, 2014, **473-474**, 619-641.

8. A. Ortega-Hernandez, R. Acayaba, C. Verwold, C. C. Montagner and S. Y. Kimura, Emerging investigator series: emerging disinfection by-product quantification method for wastewater reuse: trace level assessment using tandem mass spectrometry, *Environ. Sci.-Wat. Res.*, 2021, DOI: 10.1039/D0EW00947D, 285-297.

9. R. J. Weisman, L. B. Barber, J. L. Rapp and C. M. Ferreira, De facto reuse and disinfection by-products in drinking water systems in the Shenandoah River watershed, *Environ. Sci.-Wat. Res.*, 2019, **5**, 1699-1708.

10. K. Doederer, W. Gernjak, H. S. Weinberg and M. J. Farre, Factors affecting the formation of disinfection by-products during chlorination and chloramination of secondary effluent for the production of high quality recycled water, *Water Res.*, 2014, **48**, 218-228.

11. J. Rice, A. Wutich and P. Westerhoff, Assessment of De Facto Wastewater Reuse across the U.S.: Trends between 1980 and 2008, *Environ. Sci. Technol.*, 2013, **47**, 11099-11105.

12. M.-F. Yueh and R. H. Tukey, Triclosan: A Widespread Environmental Toxicant with Many Biological Effects, *Annual Review of Pharmacology and Toxicology*, 2016, **56**, 251-272.

13. A. M. Calafat, X. Ye, L.-Y. Wong, J. A. Reidy and L. L. Needham, Urinary Concentrations of Triclosan in the U.S. Population: 2003–2004, *Environmental Health Perspectives*, 2008, **116**, 303-307.

14. P. Canosa, S. Morales, I. Rodríguez, E. Rubí, R. Cela and M. Gómez, Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine, *Anal. Bioanal. Chem.*, 2005, **383**, 1119-1126.

15. S. E. Duirk, C. Lindell, C. C. Cornelison, J. Kormos, T. A. Ternes, M. Attene-Ramos, J. Osiol, E. D. Wagner, M. J. Plewa and S. D. Richardson, Formation of Toxic Iodinated Disinfection By-Products from Compounds Used in Medical Imaging, *Environmental Science & Technology*, 2011, **45**, 6845-6854.

16. X. J. Kong, J. Jiang, J. Ma, Y. Yang and S. Y. Pang, Comparative investigation of X-ray contrast medium degradation by UV/chlorine and UV/H2O2, *Chemosphere*, 2018, **193**, 655-663.

17. C. Postigo, D. M. DeMarini, M. D. Armstrong, H. K. Liberatore, K. Lamann, S. Y. Kimura, A. A. Cuthbertson, S. H. Warren, S. D. Richardson, T. McDonald, Y. M. Sey, N. O. B. Ackerson, S. E. Duirk and J. E. Simmons, Chlorination of Source Water Containing Iodinated X-ray Contrast Media: Mutagenicity and Identification of New Iodinated Disinfection Byproducts, *Environ. Sci. Technol.*, 2018, **52**, 13047-13056.

18. I. Pantelaki and D. Voutsa, Formation of iodinated THMs during chlorination of water and wastewater in the presence of different iodine sources, *Sci. Total Environ.*, 2018, **613-614**, 389-397.

19. C. H. Jeong, E. J. Machek, M. Shakeri, S. E. Duirk, T. A. Ternes, S. D. Richardson, E. D. Wagner and M. J. Plewa, The impact of iodinated X-ray contrast agents on formation and toxicity of disinfection by-products in drinking water, *J. Environ. Sci.*, 2017, **58**, 173-182.

20. F. X. Tian, B. Xu, Y. L. Lin, C. Y. Hu, T. Y. Zhang, S. J. Xia, W. H. Chu and N. Y. Gao, Chlor(am)ination of iopamidol: Kinetics, pathways and disinfection by-products formation, *Chemosphere*, 2017, **184**, 489-497.

21. S. Allard, J. Criquet, A. Prunier, C. Falantin, A. Le Person, J. Y. M. Tang and J. P. Croue, Photodecomposition of iodinated contrast media and subsequent formation of toxic

iodinated moieties during final disinfection with chlorinated oxidants, *Water Res.*, 2016, **103**, 453-461.

22. F. M. Wendel, T. A. Ternes, S. D. Richardson, S. E. Duirk, J. A. Pals, E. D. Wagner and M. J. Plewa, Comparative Toxicity of High-Molecular Weight Iopamidol Disinfection Byproducts, *Environ. Sci. Technol. Lett.*, 2016, **3**, 81-84.
23. F. M. Wendel, C. Lütke Eversloh, E. J. Machek, S. E. Duirk, M. J. Plewa, S. D. Richardson and T. A. Ternes, Transformation of Iopamidol during Chlorination, *Environ. Sci. Technol.*, 2014, **48**, 12689-12697.
24. A. E. Artabe, H. Cunha-Silva and A. Barranco, Enzymatic assays for the assessment of toxic effects of halogenated organic contaminants in water and food. A review, *Food and Chemical Toxicology*, 2020, **145**, 111677.
25. I. Kristiana, S. McDonald and C. A. Joll, The forest or the trees: a critical review on the analysis of total organic halogen (TOX) in drinking waters and its utility as a water quality parameter, *Environ. Sci.-Wat. Res.*, 2020, **6**, 2313-2330.
26. Y. Han, V. F. Pulikkal and M. Sun, Comprehensive Validation of the Adsorbable Organic Fluorine Analysis and Performance Comparison of Current Methods for Total Per- and Polyfluoroalkyl Substances in Water Samples, *ACS ES&T Water*, 2021, **1**, 1474-1482.
27. S. Y. Kimura, W. Zheng, T. N. Hipp, J. M. Allen and S. D. Richardson, Total organic halogen (TOX) in human urine: A halogen-specific method for human exposure studies, *J. Environ. Sci.*, 2017, **58**, 285-295.
28. I. Kristiana, S. McDonald, J. Tan, C. Joll and A. Heitz, Analysis of halogen-specific TOX revisited: Method improvement and application, *Talanta*, 2015, **139**, 104-110.

29. Y. Yang, Y. Komaki, S. Y. Kimura, H.-Y. Hu, E. D. Wagner, B. J. Mariñas and M. J. Plewa, Toxic Impact of Bromide and Iodide on Drinking Water Disinfected with Chlorine or Chloramines, *Environ. Sci. Technol.*, 2014, **48**, 12362-12369.

30. Y. Pan and X. Zhang, Total organic iodine measurement: A new approach with UPLC/ESI-MS for off-line iodide separation/detection, *Water Res.*, 2013, **47**, 163-172.

31. T. Gong and X. Zhang, Determination of iodide, iodate and organo-iodine in waters with a new total organic iodine measurement approach, *Water Res.*, 2013, **47**, 6660-6669.

32. A. Wagner, B. Raue, H.-J. Brauch, E. Worch and F. T. Lange, Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography, *J. Chromatogr. A*, 2013, **1295**, 82-89.

33. E. M. Smith, M. J. Plewa, C. L. Lindell, S. D. Richardson and W. A. Mitch, Comparison of byproduct formation in waters treated with chlorine and iodine: relevance to point-of-use treatment, *Environ. Sci. Technol.*, 2010, **44**, 8446-8452.

34. Y. Miyake, N. Yamashita, P. Rostkowski, M. K. So, S. Taniyasu, P. K. S. Lam and K. Kannan, Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water, *J. Chromatogr. A*, 2007, **1143**, 98-104.

35. G. H. Hua and D. A. Reckhow, Determination of TOCl, TOBr and TOI in drinking water by pyrolysis and off-line ion chromatography, *Anal. Bioanal. Chem.*, 2006, **384**, 495-504.

36. R. Sayess and D. A. Reckhow, An improved method for total organic iodine in drinking water, *Water Res.*, 2017, **108**, 250-259.

37. E. von Abercron, S. Falk, T. Stahl, S. Georgii, G. Hamscher, H. Brunn and F. Schmitz, Determination of adsorbable organically bound fluorine (AOF) and adsorbable organically bound halogens as sum parameters in aqueous environmental samples using combustion ion chromatography (CIC), *Sci. Total Environ.*, 2019, **673**, 384-391.

38. A. B. Couto, D. C. de Souza, E. R. Sartori, P. Jacob, D. Klockow and E. A. Neves, The Catalytic Cycle of Oxidation of Iodide Ion in the Oxygen/Nitrous Acid/Nitric Oxide System and Its Potential for Analytical Applications, *Analytical Letters*, 2006, **39**, 2763-2774.

39. S. Y. Kimura, A. A. Cuthbertson, J. D. Byer and S. D. Richardson, The DBP exposome: Development of a new method to simultaneously quantify priority disinfection by-products and comprehensively identify unknowns, *Water Research*, 2019, **148**, 324-333.

40. R. Baird, L. Bridgewater, A. American Public Health, A. American Water Works and F. Water Environment, *Standard methods for the examination of water and wastewater*, Washington, D.C. : American Public Health Association, 23rd edn., 2017.

41. S. Willach, H.-J. Brauch and F. T. Lange, Contribution of selected perfluoroalkyl and polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and in a highly contaminated groundwater, *Chemosphere*, 2016, **145**, 342-350.

42. J. Oleksy-Frenzel, S. Wischnack and M. Jekel, Application of ion-chromatography for the determination of the organic-group parameters AOCl, AOBr and AOI in water, *Fresenius' Journal of Analytical Chemistry*, 2000, **366**, 89-94.

43. A. Kinani, H. SaLhi, S. Bouchonnet and S. Kinani, Determination of adsorbable organic halogens in surface water samples by combustion–microcoulometry versus combustion–ion chromatography titration, *Journal of Chromatography A*, 2018, **1539**, 41-52.

44. A. Ortega-Hernandez, R. Acayaba, C. Verwold, C. C. Montagner and S. Y. Kimura, Emerging investigator series: emerging disinfection by-product quantification method for wastewater reuse: trace level assessment using tandem mass spectrometry, *Environmental Science: Water Research & Technology*, 2021, **7**, 285-297.

45. C. Zhang, H. Yan, F. Li and Q. Zhou, Occurrence and fate of perfluorinated acids in two wastewater treatment plants in Shanghai, China, *Environmental Science and Pollution Research*, 2015, **22**, 1804-1811.

46. Y. Han, V. F. Pulikkal and M. Sun, Comprehensive Validation of the Adsorbable Organic Fluorine Analysis and Performance Comparison of Current Methods for Total Per- and Polyfluoroalkyl Substances in Water Samples, *ACS ES&T Water*, 2021, DOI: 10.1021/acsestwater.1c00047.

47. L. Mijangos, H. Ziarrusta, O. Ros, L. Kortazar, L. A. Fernández, M. Olivares, O. Zuloaga, A. Prieto and N. Etxebarria, Occurrence of emerging pollutants in estuaries of the Basque Country: Analysis of sources and distribution, and assessment of the environmental risk, *Water Research*, 2018, **147**, 152-163.

48. L. J. M. Githinji, M. K. Musey and R. O. Ankumah, Evaluation of the Fate of Ciprofloxacin and Amoxicillin in Domestic Wastewater, *Water, Air, & Soil Pollution*, 2011, **219**, 191-201.

49. R. A. Trenholm, B. J. Vanderford, J. C. Holady, D. J. Rexing and S. A. Snyder, Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry, *Chemosphere*, 2006, **65**, 1990-1998.

50. T. Vasskog, T. Anderssen, S. Pedersen-Bjergaard, R. Kallenborn and E. Jensen, Occurrence of selective serotonin reuptake inhibitors in sewage and receiving waters at Spitsbergen and in Norway, *Journal of Chromatography A*, 2008, **1185**, 194-205.

51. A. L. N. van Nuijs, I. Tarcomnicu, W. Simons, L. Bervoets, R. Blust, P. G. Jorens, H. Neels and A. Covaci, Optimization and validation of a hydrophilic interaction liquid chromatography–tandem mass spectrometry method for the determination of 13 top-prescribed pharmaceuticals in influent wastewater, *Anal. Bioanal. Chem.*, 2010, **398**, 2211-2222.

52. S. L. MacLeod, P. Sudhir and C. S. Wong, Stereoisomer analysis of wastewater-derived β-blockers, selective serotonin re-uptake inhibitors, and salbutamol by high-performance liquid chromatography–tandem mass spectrometry, *Journal of Chromatography A*, 2007, **1170**, 23-33.

53. A. Lajeunesse, C. Gagnon and S. Sauvé, Determination of Basic Antidepressants and Their N-Desmethyl Metabolites in Raw Sewage and Wastewater Using Solid-Phase Extraction and Liquid Chromatography−Tandem Mass Spectrometry, *Analytical Chemistry*, 2008, **80**, 5325-5333.

54. C. Wang, H. Chen, H. Li, J. Yu, X. Wang and Y. Liu, Review of emerging contaminant tris(1,3-dichloro-2-propyl)phosphate: Environmental occurrence, exposure, and risks to organisms and human health, *Environment International*, 2020, **143**, 105946.

55. T. Xu, P. Li, S. Wu, L. Lei and D. He, Tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloropropyl) phosphate (TCPP) induce locomotor deficits and dopaminergic degeneration in Caenorhabditis elegans, *Toxicol Res (Camb)*, 2016, **6**, 63-72.

56. K. Bester, Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant—comparison of sewage sludge from 20 plants, *Journal of Environmental Monitoring*, 2005, **7**, 509-513.

57. C. Hao, P. A. Helm, D. Morse and E. J. Reiner, Liquid chromatography-tandem mass spectrometry direct injection analysis of organophosphorus flame retardants in Ontario surface water and wastewater effluent, *Chemosphere*, 2018, **191**, 288-295.

58. E. D. Schreder and M. J. La Guardia, Flame Retardant Transfers from U.S. Households (Dust and Laundry Wastewater) to the Aquatic Environment, *Environmental Science & Technology*, 2014, **48**, 11575-11583.

59. M. S. Kostich, A. L. Batt and J. M. Lazorchak, Concentrations of prioritized pharmaceuticals in effluents from 50 large wastewater treatment plants in the US and implications for risk estimation, *Environmental Pollution*, 2014, **184**, 354-359.

Tables and Figures

Table 1: Secondary wastewater effluent water quality parameters.

	City "A" #1	City "A" #2	City "A" #3	City "B"	ACWA Sample*
Date	May 5, 2021	May 7, 2021	May 9, 2021	April 20, 2021	January 9, 2020
pH	8.37	8.38	8.62	7.96	7.51
Turbidity (NTU)	36.3	57.0	25.9	47.9	0.695
DOC (mg/L)	5.8 ± 0.2	6.0 ± 0.1	5.8 ± 0.2	10 ± 0.1	7.6
SUVA 254 (L/mg-m)	3.0	2.7	2.7	2.2	0.454
Fluoride (µg/L)	244	283	728	487	N/A
Chloride (mg/L)	144	147	147	141	151
Bromide (µg/L)	72.9	80.4	76.6	90.5	75.3

* Filtered with 0.45 µm membrane filter
Iodide was not detected in samples

Table 2: Target analytes quantified in secondary wastewater effluents.

Name	Halogen (#)	Conc. (ng/L)
HFRs		
HBB	Br (6)	0.12
PBT	Br (5)	0.145
PBEB	Br (5)	0.045
Dechlorane	Cl (12)	0.097
PFASs		
PFBA	F (7)	3.57
PFPeA	F (9)	13.1
PFHxA	F (11)	17.2
PFHpA	F (13)	1.2
PFOA	F (15)	5.53
PFNA	F (17)	0.503
PFDA	F (23)	0.848
PFBS	F (9)	1.43
PFPeS	F (11)	2.17
PFHxS	F (13)	0.917
PFOS	F (17)	0.93
PFOSA	F (17)	0.737
OPFRs		
TEP	N/A	506
TCEP	Cl (3)	116
TCPP	Cl (3)	1210
V6	Cl (6)	13.3
TDCPP	Cl (6)	290
TBP	N/A	126
TBEP	N/A	57.3
TEHP	N/A	13.7
TPP	N/A	18.5
PCPPs		
Furosemide	Cl (1)	94.6
Gemfibrozil	N/A	3.18
Hydrochlorothiazide	Cl (1)	995
2-Hydroxy-ibuprofen	N/A	106
Ibuprofen	N/A	3.97
Naproxen	N/A	39.9
Triclosan	Cl (3)	12.5
Warfarin	N/A	1.65
Azithromycin	N/A	879
Caffeine	N/A	21.9
Carbamazepine	N/A	398
Erthromycin-H_2O	N/A	46.7
Fluoxetine	F (3)	46.8
Miconazole	Cl (4)	1.85
Ofloxacin	F (1)	52.2
1,7-Dimethylxanthine	N/A	128
Sulfadimethoxine	N/A	1.15
Sulfamethoxazole	N/A	260
Sulfanilamide	N/A	20.5
Thiabendazole	N/A	36.9
Trimethoprim	N/A	276
Alprazolam	Cl (1)	0.424
Amitriptyline	N/A	58.1
Amlodipine	Cl (1)	18.6
Benzoylecgonine	N/A	21.3
Betamethason	F (1)	2.28
Cocaine	N/A	1.92
DEET	N/A	103
Desmethyldiltiazem	N/A	62.4
Diazepam	Cl (1)	0.573
10-hydroxy-amitriptyline	N/A	16.5
Metoproplol	N/A	242
Norfluoxetine	F (3)	2.83
Norverapamil	N/A	3.8
Paroxetine	F (1)	4
Propanolol	N/A	52.9
Sertraline	Cl (2)	78.1
Theophylline	N/A	87.5
Triamterene	N/A	17.2
Valsartan	N/A	75.8
Verapamil	N/A	23.7
Doxycycline	N/A	65.6
4-Epitetracycline	N/A	8.8
Tetracycline	N/A	13.9
Albuterol	N/A	7.32
Amphetamine	N/A	0.593
Atenolol	N/A	261
Atrovastatin	F (1)	19.1
Cimetidine	N/A	34.6
Clonidine	Cl (2)	1.65
Codeine	N/A	124

Ciprofloxacin	F (1)	192	Cotinine	N/A	26.5
Clarithromycin	N/A	334	Hydrocodone	N/A	7.2
Cloxacillin	Cl (1)	30.3	Metformin	N/A	1160
Dehydronifedipine	N/A	19.1	Oxycodone	N/A	46.3
Diphenhydramine	N/A	255	Ranitidine	N/A	70.7
Diltiazem	N/A	131			

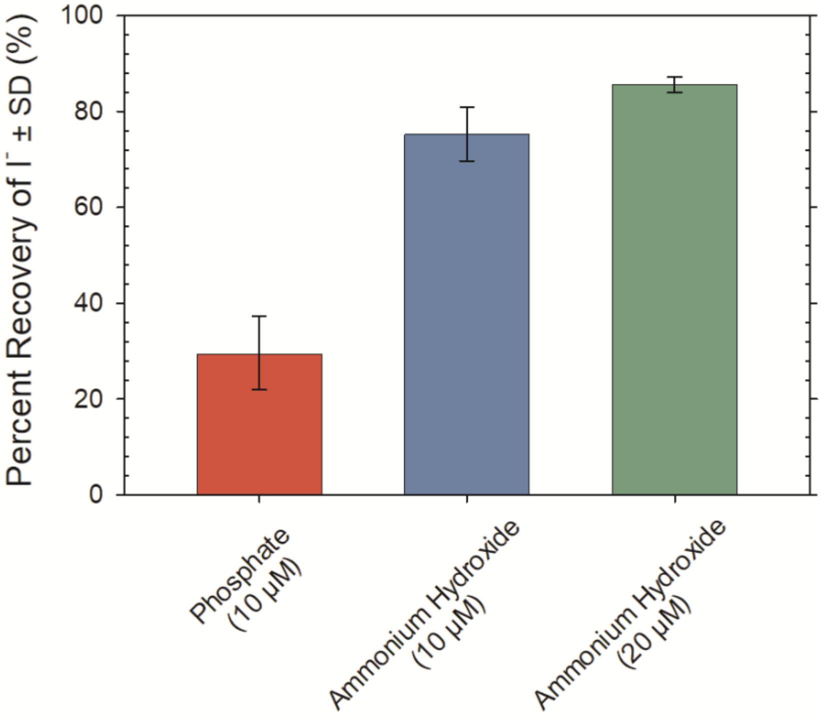

Figure 1: Percent recovery of iodide for comparison of buffer composition and concentration. Analysis was performed in triplicate and results are shown as the mean and standard deviation

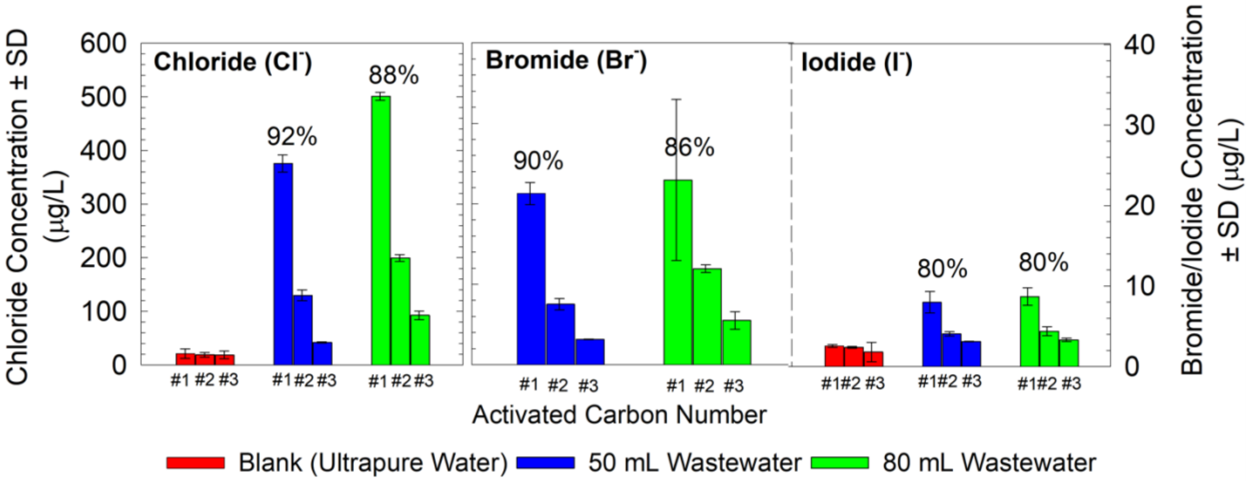

Figure 2: Breakthrough analysis for total organic chlorine, total organic bromine, and total organic iodine on three activated carbon columns in series for 50 mL (left) and 80 mL (right) of wastewater sample volume. Shown results are chloride, bromide and iodide concentrations measured from the absorption solution that represents the recovered organic chlorine, organic bromine, and organic iodine as the result from the pyrolysis of each individual activated carbon. Percent recoveries are shown at top of each column. Organic bromine in blank was below detection limits. All measurements were performed in triplicate and are shown as the mean and standard deviation.

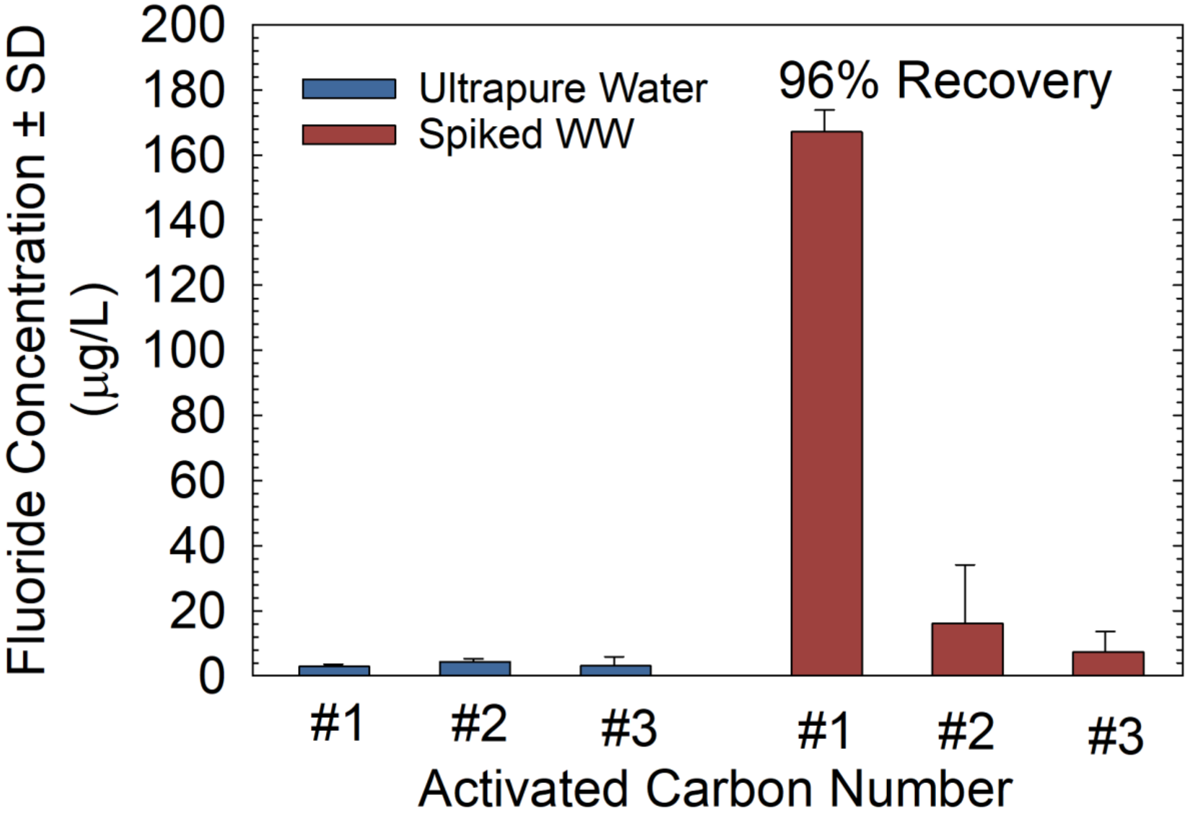

Figure 3: Breakthrough analysis for total organic fluorine on three activated carbon columns in series for an ultrapure water control and wastewater spiked with 246TFP (30 µg/L as F^-). Shown results are fluoride concentrations measured from the absorption solution that represents the recovered organic fluoride as the result from the pyrolysis of each individual activated carbon. The spike wastewater was sampled January 9th, 2020 from ACWA. The analysis was performed in triplicate using 50 mL of sample and the results are shown as the mean and standard deviation.

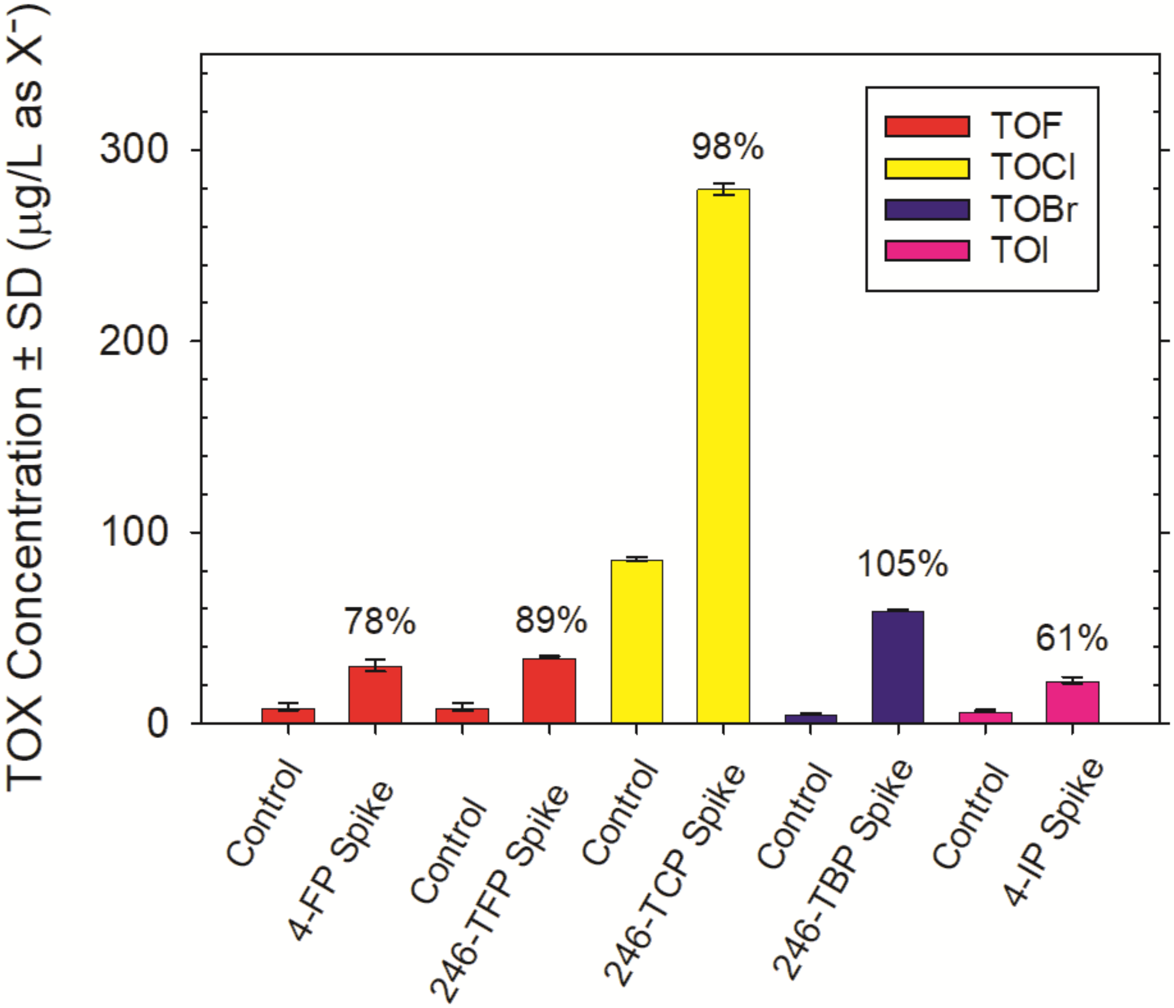

Figure 4. Total organic chlorine, bromine, iodine, and fluorine halophenol recoveries spiked into secondary wastewater effluent samples from ACWA on January 9th, 2020. TOF was spiked with 30 µg/L 246TFP as F^- and 30 µg/L 4-FP as F^- in separate recovery experiments, TOCl was spiked with 200 µg/L 246TCP as Cl^-, TOBr was spiked with 50 µg/L 246TBP as Br^-, and TOI was spiked with 30 µg/L 4-IP as I^-. All experiments were performed in triplicate and results are shown as the mean and standard deviation.

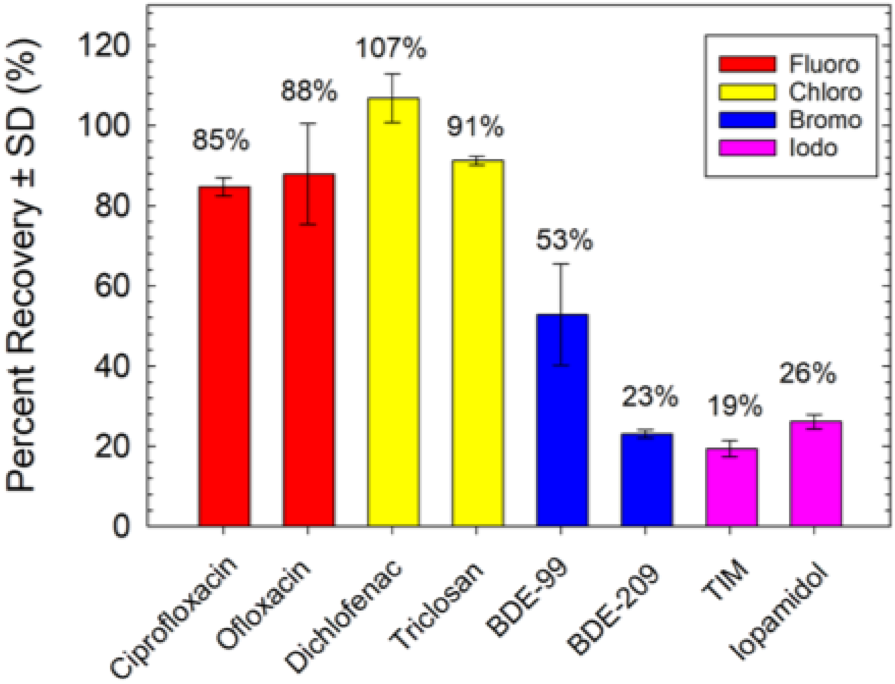

Figure 5. Halogenated emerging contaminants recovery in ultrapure water performed in triplicate. The results are shown as the mean and standard deviation.

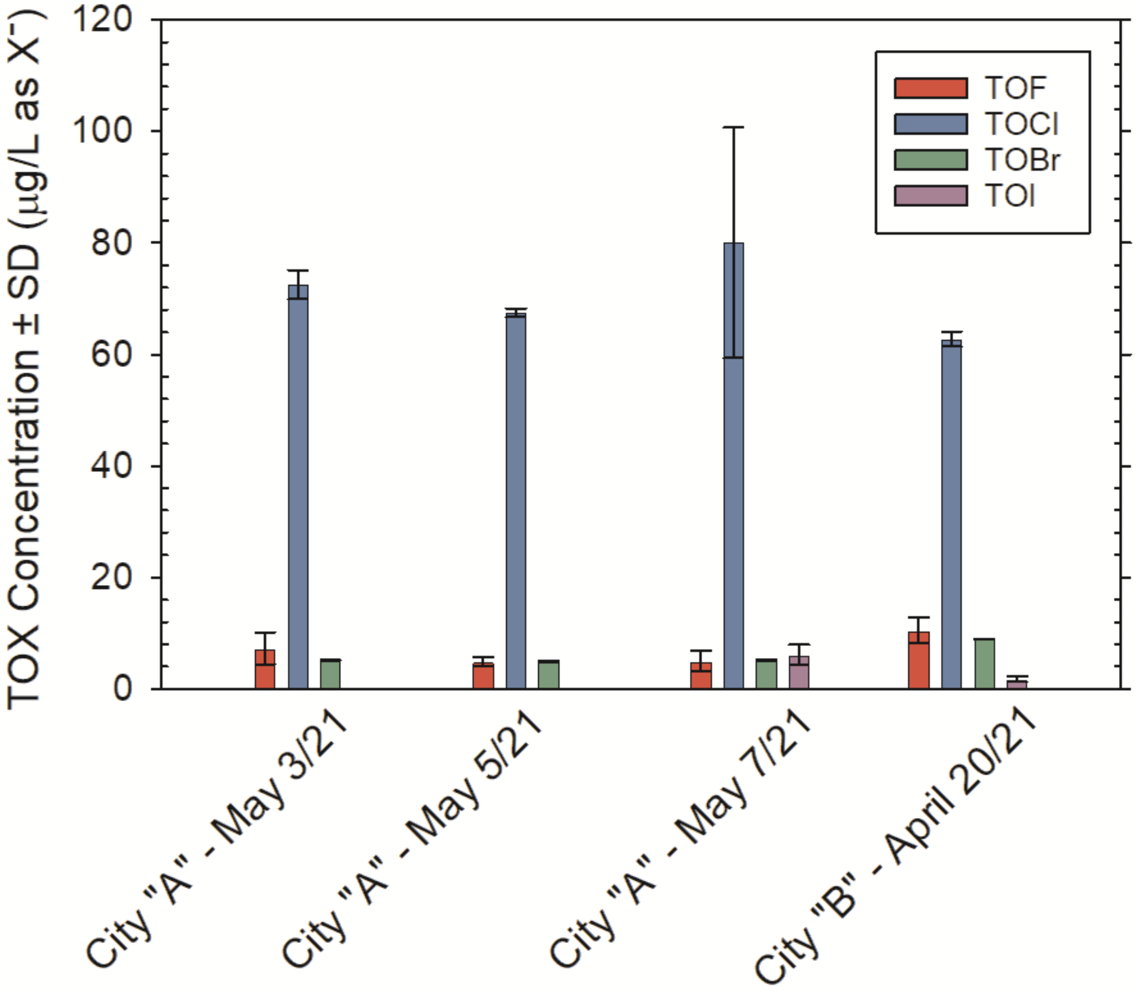

Figure 6. TOX for each 4 sampling events across two cities in Alberta, Canada. The analysis were performed in triplicate and results are shown as the mean and standard deviation.

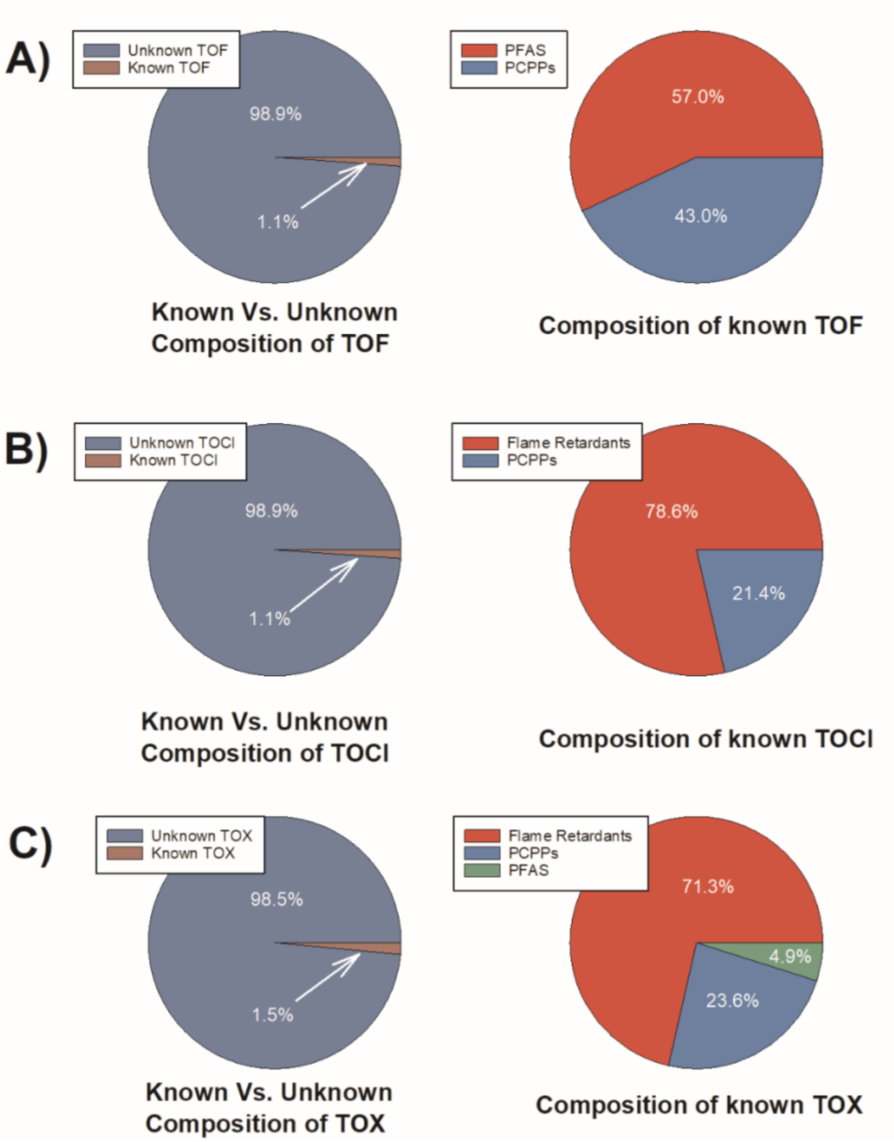

Figure 7. Comparison of known vs. unknown portion of a) TOF b) TOCl, and c) TOX represented as Cl^- (left). Right-side figures show the composition of the known portion of TOF, TOCl, and TOX that was quantified using targeted methods. The calculated known portion of TOBr was found to be negligible. Only 3 brominated-FRs were detected out the brominated-compounds targeted. TOI was not detected in the wastewater used in this analysis. Further, no iodinated compounds were included in the targeted method.