

## **(Yet more) challenges for water treatment plants: potential contribution of hypochlorite solutions to bromate, chlorate, chlorite and perchlorate in drinking water**

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### **ABSTRACT**

The aim of this study was to evaluate if chlorate, chlorite, perchlorate and bromate ions are found in treated water from 16 Canadian drinking water treatment plants (WTPs) that use hypochlorite as a disinfectant. The WTPs in this survey had unusually high concentrations of sodium, bromide and dissolved organic carbon in the source water and all used ammonium in the treatment train. Samples of hypochlorite solutions used in the disinfection process were collected in addition to source water and treated water. Chlorite was not detected in any of the samples (MDL 21 µg/L). Chlorate was found in 83% of source water samples (between 0.002 and 0.25 mg/L) and in treated water (between 0.002 and 0.96 mg/L), with the exception of one treated water sample (1.6 mg/L); 38% of them exceeded the US EPA health reference value of 0.210 mg/L. Perchlorate was detected in 47% of source water samples (between 0.06 and 0.2 µg/L) and in treated water (between 0.06 and 5.7 µg/L). Bromate was detected in only one source water sample and was found in treated water (between 0.5 and 11.2 µg/L). Only treated water samples from one WTP were above the US EPA maximum contaminant level of 10 µg/L.

**Key words** | drinking water, hypochlorite impurities, oxyhalides

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### **INTRODUCTION**

Drinking water disinfection represents one of the greatest achievements of public health protection. Chlorine can be used as a primary disinfectant to achieve microbial inactivation and/or as a secondary disinfectant to maintain chlorine residual in the distribution system to prevent bacterial regrowth. Chlorine is available in the gaseous form (as compressed elemental gas) or as hypochlorite salt solutions: sodium hypochlorite (NaOCl) and calcium hypochlorite (Ca(OCl)<sub>2</sub>). In drinking water treatment plants (WTPs) in the USA, sodium hypochlorite is predominantly used (Routt *et al.* 2008) since plants using gaseous

chlorine must develop a risk management plan due to safety and security concerns. In Canada, the vast majority of WTPs use some form of chlorine in the treatment process. Data obtained in 2005 from 3,590 drinking water facilities in Canada indicate that sodium hypochlorite was used in 78% of the WTPs, whereas 19% of the plants used chlorine gas, 1.4% used calcium hypochlorite and less than 0.5% applied alternative disinfectants (Health Canada 2009) such as chloramines and chlorine dioxide. Free chlorine concentrations in most Canadian drinking water distribution systems range from 0.04 to 2.0 mg/L (Health Canada 2009).

Hypochlorite solutions are known to contain impurities; thus, when hypochlorite is used in the water treatment process, these impurities may subsequently be found in drinking water. These contaminants are therefore additional challenges to be addressed by the drinking WTPs (Asami *et al.* 2009; Stanford *et al.* 2009). In Canada and the USA, most jurisdictions require that the hypochlorite solutions used in drinking water treatment be certified as compliant to NSF/ANSI Standard 60 – Drinking Water Treatment Chemicals – Health Effects (NSF/ANSI 2015). This standard establishes minimum health effects requirements, such as the Single Product Allowable Concentration (SPAC), for both the chemical and the chemical contaminants that are directly added to drinking water from drinking water treatment chemicals. SPACs for the various contaminants of hypochlorite have been established in NSF/ANSI 60, and hypochlorite additives must meet these health-based criteria in order to be certified as complying with NSF/ANSI 60. The SPAC for bromate is 0.0033 mg/L, which corresponds to 30% of the US EPA maximum contaminant level (MCL) of 0.010 mg/L at a 10 mg/L maximum use level (MUL); similarly, the SPAC for perchlorate is 0.005 mg/L, the SPAC for chlorite is 0.1 mg/L and the SPAC for chlorate is 0.3 mg/L (NSF/ANSI 2015). Additionally, the American Water Works Association (AWWA) developed a standard which sets out guidelines for the handling and storage of hypochlorite solutions (Stanford *et al.* 2011). In Canada, guidelines for drinking water quality have been established for bromate, chlorate and chlorite. For instance, the maximum acceptable concentration (MAC) for bromate in drinking water is 0.01 mg/L (10 µg/L) (Health Canada 2015). In the USA, the MCL is 10 µg/L (US EPA 2017), whereas the World Health Organization (WHO) has established a provisional guideline value of 10 µg/L (WHO 2005a).

The presence of bromate in drinking water is usually attributed to the disinfection processes (e.g. ozonation) of source waters containing bromide (Haag & Holgne 1983; Von Gunten & Hoigne 1994). The Canadian guideline also recognizes that bromate may be found in hypochlorite solutions and in drinking water treated with bromate-contaminated hypochlorite solutions. Hypochlorite is produced by electrolysis of sodium chloride solutions and high levels of bromide in the brine can lead to the formation

of bromate (Tynan *et al.* 1993; Weinberg *et al.* 2003; WHO 2005a). Bromate can also be formed in on-site generators of hypochlorite when high bromide salts are used (Health Canada 2015). The presence of bromate in treated water from treatment plants using hypochlorite solutions has been documented in the USA (Tynan *et al.* 1993), Canada (Health Canada 2015), Japan (Asami *et al.* 2009), Spain (Garcia-Villanova *et al.* 2010) and France (Bouland *et al.* 2005).

Chlorate and chlorite are disinfection by-products (DBPs) from the use of chlorine dioxide for the treatment of drinking water. Another source of chlorate and chlorite is the hypochlorite solution itself used in the treatment process, as it decomposes to chlorate, with chlorite ion as an intermediate (Gordon *et al.* 1995; Health Canada 2008). Hypochlorite transformation to chlorate is very fast (Bolyard & Snyder Fair 1992; Gordon *et al.* 1997), thus the chlorate concentration in the hypochlorite solutions increases during storage as a function of time, temperature and the presence of other impurities such as transition metals (Gordon *et al.* 1997). Chlorate was also found in treatment plants using on-site generated hypochlorite solutions in the USA (Stanford *et al.* 2012, 2013).

The MAC in Canada for chlorite and chlorate, based on a lifetime exposure from drinking water, is 1 mg/L for each ion (Health Canada 2008). WHO provisional guideline value for each ion is 0.7 mg/L (WHO 2005b). In the USA, the MCL for chlorite is 1 mg/L and currently there is no MCL for chlorate which was included in the EPA's fourth contaminant candidate list (CCL4) (Federal Register 2016). Alfredo *et al.* (2015) recently speculated that the MCL could potentially range from 210 µg/L (US EPA health reference level) to as high as 840 µg/L if a source contribution of 80% is adopted. They determined that if the US EPA chose to regulate chlorate in drinking water to the lower potential MCL, it would pose tremendous chlorate management challenges for WTPs. Chlorate has been found in finished water from treatment plants using hypochlorite solutions in Spain (Garcia-Villanova *et al.* 2010), India (Anupama *et al.* 2012) and the USA (Alfredo *et al.* 2014).

Perchlorate can be both a natural and anthropogenic contaminant and has been found to occur naturally in the USA and Chile. Perchlorate is also manufactured for use as an oxidizer in solid fuel propellants, munitions, fireworks and road

flares (Snyder *et al.* 2009). Perchlorate is formed in hypochlorite solutions as a direct result of the reaction between hypochlorite and chlorate ions. The rate of formation is a function of hypochlorite and chlorate concentration, as well as the ionic strength of the solution (Snyder *et al.* 2009). No drinking water guideline has been established for perchlorate in Canada. WHO established a guideline value of 0.07 mg/L (World Health Organization 2016).

The aim of this study was to evaluate if chlorate, chlorite, perchlorate and bromate are found in treated water from selected Canadian WTPs that use hypochlorite solutions as a disinfectant. It is important to note, however, that the WTPs included in this study were selected based on their unique water quality characteristics (Tugulea *et al.* 2016), which are not typical of Canadian WTPs. The plants in this study are representative of treatment plants using high levels of hypochlorite.

## SURVEY DESIGN

### Selection of WTPs

This study was part of a project which focused on WTPs with source waters containing high sodium concentrations. More details on the criteria for WTP selection, location and characteristics can be found elsewhere (Tugulea *et al.* 2016). Sixteen WTPs were selected, mainly based on source waters with high sodium concentration (ranging from 10 mg/L to 760 mg/L). All WTPs used ammonium in the treatment train and/or had naturally occurring ammonium and many had high dissolved organic carbon (DOC) in the source water. It should be noted that these WTPs do not represent the typical WTP in Canada but, rather, extreme cases.

### Target analytes

In addition to chlorite, chlorate, bromate, and perchlorate, the following DBPs were also analysed: trihalomethanes (THM), haloacetaldehydes, haloacetonitriles, haloketones, 7 nitrosamines, chloropicrin and some DBP precursors (bromide) and auxiliary parameters (specific UV absorbance (SUVA), DOC, total organic carbon (TOC), ammonium).

Free chlorine, total chlorine, water temperature, turbidity and water pH were determined on site.

### Sampling schedule

Water samples were collected in 2012/2013 at the drinking water treatment facilities, in duplicate, before treatment (raw, R), after treatment but before distribution (treated, T), and at the mid-point of the distribution system (distributed, D). In order to capture the seasonal variation of analyte concentrations in drinking water during the year, samples were collected during winter and summer (twice in the same year). The characteristics of the water treatment process at the time of sampling, including disinfection procedures and handling of hypochlorite solutions were recorded using a questionnaire but the hypochlorite concentration or its age were not determined or available at the time of the survey.

## MATERIALS AND METHODS

### Chemicals

Certified reference solutions of perchlorate, chlorate, chlorite and bromate ions were obtained from SPEX CertiPrep (Fisher Scientific, Ottawa, ON) and were used to construct the calibration curves. Certified reference solutions of bromate, chlorate, and chlorite obtained from Ultra Scientific (North Kingstown, RI) and perchlorate from Sigma-Aldrich (St. Louis, MO) were used as a secondary source of standards. The stable isotope labeled internal standard for perchlorate ( $\text{Cl}^{18}\text{O}_4^-$ ) was purchased from Thermo Scientific (Bannockburn, IL) and bromate ( $\text{Br}^{18}\text{O}_3^-$ ) from Icon Isotopes (Summit, NJ). No isotope labeled chlorate and chlorite ions were available, so they were quantified using the isotope labeled perchlorate as an internal standard. Malonic acid and nitric acid (10% *v/v*) were obtained from Fisher Scientific (Ottawa, Canada). Deionized water was generated in house using a Milli-Q system (Millipore, Billerica, MA).

### Sample collection

Samples were collected in 60 mL high-density polyethylene (HDPE) pre-washed bottles, spiked with 13  $\mu\text{L}$  0.5 M malonic

acid as a quenching agent (Pisarenko *et al.* 2010). Hypochlorite solution used in the disinfection process was collected in 30 mL HDPE bottles with no quenching solution. Samples were placed in coolers containing ice packs and sent to the laboratory by overnight courier. During shipment, water samples were kept at less than 10 °C.

### Sample preparation

Five mL of each hypochlorite solution was transferred to a 40 mL glass vial and quenched with 0.74 g malonic acid. The resulting solutions were then diluted 5,000 times with deionized water.

All water samples (R, T and D) were passed through OnGuard Ba/Ag/H cartridges from Thermo Fisher Scientific (Mississauga, ON) to remove interfering ions (Snyder *et al.* 2005). Water samples and diluted hypochlorite solutions were then spiked with the internal standards before injection into the analytical system.

### Oxyhalide analysis

The analysis of oxyhalides was carried out using the method described by Pisarenko *et al.* (2010). A 20 µL sample was loaded onto a 75 mm × 4.6 mm Synergi MAX-RP C12 column with 4 µm particle size (Phenomenex, Torrance, CA). The mobile phase consisted of 0.1% formic acid in water (A) and 100% methanol (B) at a flow rate of 700 µL/min. The gradient program started with 98%A which was held for 1 min, changed to 85%A in 1 min, then to 5%A in 3 min, held for 1 min, changed to 98%A again in 0.5 min and allowed to equilibrate for 5 min. The diverting valve was set to 'detector' from 0 to 5 min. The selected reaction monitoring (SRM) mode of each ion was detected using TSQ Quantum Ultra triple quadrupole mass spectrometer (Thermo Scientific, Bannockburn, IL), operated in negative mode. The following precursor/product ion transitions were monitored for quantitation purposes: perchlorate  $m/z$  99 → 83 ( $^{35}\text{ClO}_4^-$  to  $^{35}\text{ClO}_3^-$ ), chlorate  $m/z$  83 → 67 ( $^{35}\text{ClO}_3^-$  to  $^{35}\text{ClO}_2^-$ ), chlorite  $m/z$  67 → 51 ( $^{35}\text{ClO}_2^-$  to  $^{35}\text{ClO}^-$ ) and bromate  $m/z$  127 → 111 ( $^{79}\text{BrO}_3^-$  to  $^{79}\text{BrO}_2^-$ ). The following transitions were monitored for confirmation purposes: perchlorate  $m/z$  101 → 85; chlorate  $m/z$  85 → 69; chlorite  $m/z$  69 → 53; bromate  $m/z$  129 → 113. Perchlorate and bromate

were quantified by isotope dilution using labeled perchlorate ( $\text{Cl}^{18}\text{O}_4^-$ ) and bromate ( $\text{Br}^{18}\text{O}_3^-$ ). The precursor/product ion transitions were 107 → 89 and 133 → 115, respectively. Chlorate and chlorite were quantified using the isotope labeled perchlorate as internal standard. Table 1 shows the analytical performance for each oxyhalide.

Free/total chlorine was determined at the sampling site using a pocket colorimetric instrument (Hach, USA).

## RESULTS AND DISCUSSION

### Sample collection and identification

Samples were collected as part of another study related to the formation of DBPs in WTPs using source waters with high sodium content and naturally occurring ammonium. To maintain consistency with publications related to that study, the numbering of the 16 WTPs described herein is the same as in a previous publication (Tugulea *et al.* 2016). Although samples were collected in summer and winter-like conditions, collection of samples from the same WTP and distribution system proved to be challenging for both seasons (Table 2). Complete data for both winter and summer sampling are only available for five WTPs (WTP 4, 5, 12, 13 and 14).

### Bromate

Bromate was found in all of the hypochlorite solutions collected in both summer and winter at concentrations

Table 1 | Analytical performance

	Oxyhalides method			
	Perchlorate µg/L	Chlorate mg/L	Chlorite µg/L	Bromate µg/L
Dynamic range	0.05–100	0.0005–1.00	5–10,000	0.5–1,000
R2 Value	0.9986	0.9944	0.9862	0.9938
MDL	0.05	0.0005	21	0.5
Precision (RSD)	25	19	30	22
Recovery (low)	96%	81%	109%	76%
Recovery (high)	103%	137%	89%	99%

**Table 2** | Bromate ( $\mu\text{g/L}$ ) concentration in samples collected during 2012–2013 (summer/winter)

WTP	Bromate concentration ( $\mu\text{g/L}$ )							
	Raw ( $\mu\text{g/L}$ )		Hypochlorite (mg/L)		Treated ( $\mu\text{g/L}$ )		Distributed ( $\mu\text{g/L}$ )	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
2	NSR	<0.5	NSR	NSR	NSR	1.8	NSR	1.8
3	0.5	2.2	10.2	NSR	0.5	1.9	0.5	2.1
4	<0.5	<0.5	13.6	5.4	2.4	1.7	2.9	1.4
5	<0.5	<0.5	40	26	11.1	7.3	11.2	7.6
6	<0.5	NSR	20.1	NSR	0.8	NSR	0.7	NSR
7	<0.5	<0.5	35.9	NSR	3.6	4.1	NSR	NSR
8	<0.5	NSR	NSR	NSR	0.6	NSR	NSR	NSR
9	<0.5	NSR	47.8	NSR	5.2	NSR	4.2	NSR
10	<0.5	<0.5	NSR	29.4	2.6	2.4	NSR	NSR
11	<0.5	<0.5	NSR	NSR	1.1	1.5	1.3	1.6
12	<0.5	<0.5	6.4	14	0.9	1.7	0.9	1.6
13	<0.5	<0.5	14.4	27.8	1.2	1.5	1.4	1.7
14	<0.5	<0.5	17.7	31.5	1.4	1.7	1.2	1.9
15	NSR	<0.5	NSR	NSR	NSR	3.1	NSR	1.8
16	NSR	<0.5	NSR	10.6	NSR	<0.5	NSR	<0.5

NSR, No samples received.

ranging from 6.4 to 47.8 mg/L in the summer and from 5.4 to 31.5 mg/L in the winter. The results are similar to those reported in the USA (Snyder *et al.* 2009). Bromate was found in one source water (WTP3), at concentrations of 0.5  $\mu\text{g/L}$  in summer and 2.2  $\mu\text{g/L}$  in winter. At this WTP, the bromate concentrations in both treated and distributed water were in the same range as those found in raw water, suggesting that the source of bromate in the treated water was not from the hypochlorite solution used for treatment (Table 2). Bromate does not occur naturally (Gordon *et al.* 1995); therefore, the source of bromate in this particular source water remains unknown.

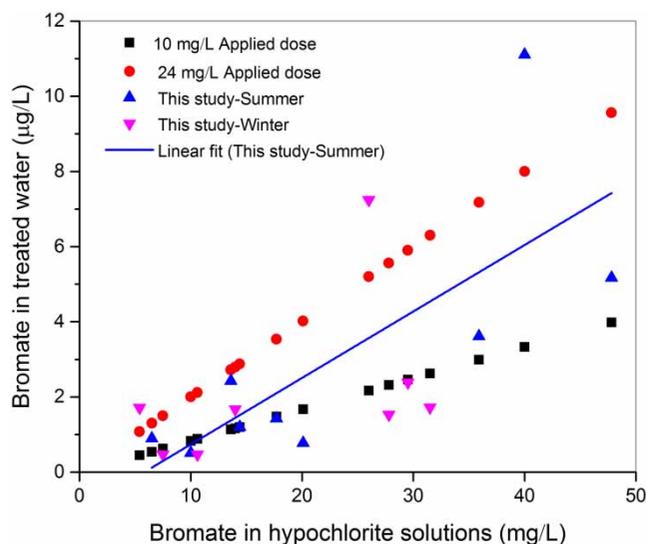
Bromate was detected in all treated and distributed water at concentrations ranging from 0.5 to 11.2  $\mu\text{g/L}$  in summer and from 1.5 to 7.6  $\mu\text{g/L}$  in winter. Bromate levels were very similar immediately after treatment and in the distribution system, confirming that once bromate is produced in the hypochlorite solutions, there is no further formation in the distribution systems. Therefore, it can be concluded that bromate levels in the treated water depend on the concentration of bromate in the hypochlorite solution and the

applied dose of chlorine. However, bromate concentrations may subsequently increase during re-chlorination in the distribution system if using a bromate-contaminated hypochlorite solution.

Only one treatment plant (WTP5) exceeded the Health Canada MAC of 10  $\mu\text{g/L}$  during the summer sampling period in both the treated and distributed water (11.1  $\mu\text{g/L}$  and 11.2  $\mu\text{g/L}$ , respectively). This WTP also had the highest values in the winter (7.3–7.6  $\mu\text{g/L}$ ). It is believed that large amounts of chlorine were used to achieve a free chlorine residual of 2.5 mg/L in the treated water. The second highest concentration of bromate was seen at WTP9 (5.2  $\mu\text{g/L}$  and 4.2  $\mu\text{g/L}$  in T and D, respectively). Hypochlorite solutions used at WTP5 and WTP9 also had the highest bromate concentrations (>40 mg/L). It is known that the dosing of chlorine to achieve a disinfection residual is highly dependent on the source water characteristics, oxidant demand and treatment efficacy. The source water used in many of the WTPs included in the study contained natural ammonium (0.87–2.7 mg/L N). Hypochlorite doses required in order to achieve breakpoint chlorination and the required

chlorine residual in the treated waters are typically higher than in waters without ammonium. Not surprisingly some WTPs in this study reported a high applied dose of hypochlorite, ranging between 10 and 24 mg/L. The use of high doses of hypochlorite to achieve free chlorine concentrations could lead to an exceedance of the MAC if bromate is present.

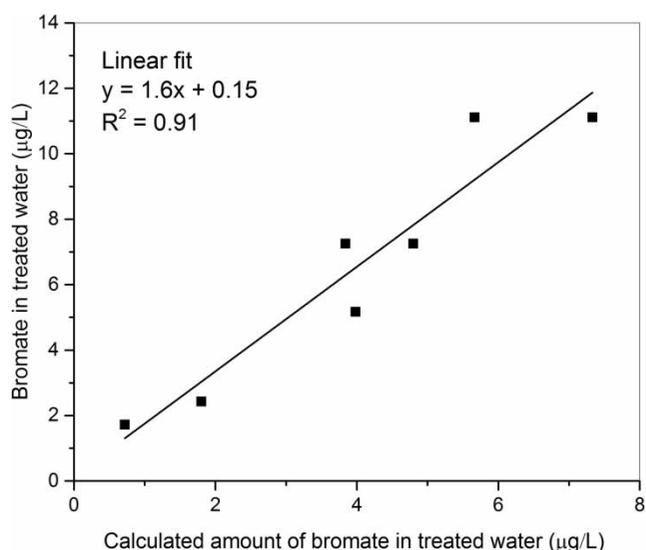
Based on the bromate concentration found in the hypochlorite solutions, one can calculate the amount of bromate theoretically added to the drinking water using the maximum use level (MUL) of 10 mg of chlorine ( $\text{Cl}_2$ ) per liter established through ANSI/NSF 60 (i.e. normalized concentration) or at higher doses. Figure 1 shows the estimated amount of bromate that would be expected to be found in treated water using a hypochlorite solution containing 120 g/L active chlorine with an applied dose of 10 mg or 24 mg of chlorine per litre (applied doses reported by participating WTP range from 10 to 24 mg/L). This estimate is based on the amount of bromate found in nine of the hypochlorite solutions received during the summer and the seven samples received during the winter (Table 2). The amount of bromate measured in the treated water (T) for these same hypochlorite solutions collected in both summer and winter are also shown in Figure 1. WTP 9 had the highest



**Figure 1** | Theoretical levels of bromate in treated water based on the bromate concentration found in the hypochlorite solutions collected in this study at an applied dose of 10 mg (■) and 24 mg (●) for hypochlorite solution (120 g/L active chlorine) vs. bromate concentrations found in treated water (T) during the summer (▲) and winter (▼) sample collection.

amount of bromate measured in the hypochlorite solution (47.8 mg/L) with a reported applied dose of 10 mg/L and the expected concentration of bromate in treated water was 3.98 µg/L but the measured concentration was 5.2 µg/L. WTP5, with the second highest amount of bromate in the hypochlorite solution (40 mg/L), reported a chlorine applied dose of 17 mg/L; however, bromate found in the treated water (11.1 µg/L) far exceeded the theoretical calculated concentration (5.33 µg/L). This treatment plant reported diluting the hypochlorite solutions upon receiving and storing them in a place with controlled temperature.

Although free available chlorine (FAC) for the hypochlorite solutions received was not obtained, chlorine dosages were available for only four treatment plants (for winter and summer). Based on this information and the amount of bromate found in each hypochlorite solution, the theoretical concentration of bromate in the treated water was calculated (Figure 2). Good correlation ( $r^2 = 0.91$ ) was found between the calculated and measured concentration. Although plant operators were asked to fill out a questionnaire, few of them provided details regarding handling and storage conditions of the hypochlorite solutions. Particularly important is time, as longer storage time of the hypochlorite solutions would reduce FAC due to decay, which will result in larger doses of hypochlorite



**Figure 2** | Correlation between the amount of bromate measured in treated water and the expected concentration based on the concentration of bromate in the hypochlorite solution and the reported applied dose.

needed to achieve the required residual chlorine concentration (Asami *et al.* 2009). Knowing the amount of bromate in the hypochlorite solution, FAC and the chlorine dosage applied in the treatment process, a WTP could predict the final bromate concentration in treated water.

### Chlorate and chlorite

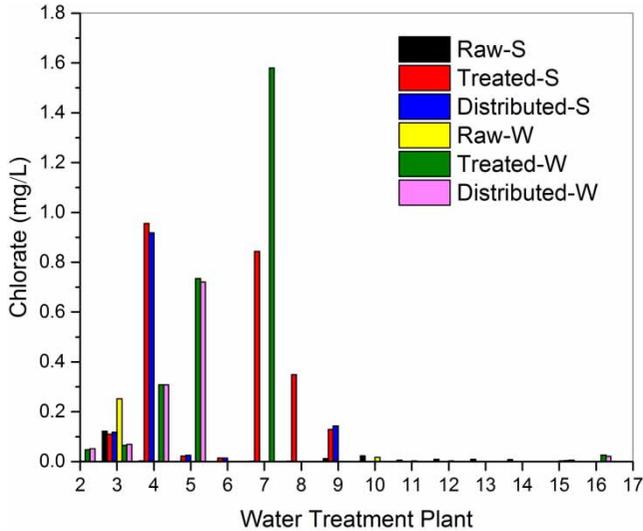
Chlorite was not found in any of the samples collected. Chlorate was found in the majority (83–92%, summer-winter) of source waters at concentrations between 0.002 and 0.12 mg/L in the summer and between 0.001 and 0.25 mg/L in the winter. Chlorate was found in all hypochlorite solutions received, with concentrations between 79 and 8,626 mg/L in the summer and between 1,316 and 4,038 mg/L in the winter (Table 3). The levels found in hypochlorite solutions are in the same orders of magnitude as those reported in the USA (Snyder *et al.* 2009). Although the majority of source water contained chlorate, concentrations were 5 to 500 times higher in treated water except for two treatment plants (WTPs 3 and 11) where the chlorate concentrations measured

in source and treated waters were the same. Chlorate was found in all the treated waters (T) at levels between 0.005 and 0.96 mg/L in the summer and between 0.002 and 1.58 mg/L in the winter. WTPs 4 and 7 had the highest concentrations in the summer (0.96 and 0.84 mg/L, respectively) and WTPs 5 and 7 had the highest concentrations in the winter (0.74 and 1.58, respectively). Only WTP7 (winter) exceeded the Health Canada MAC of 1 mg/L; in this particular case, however, a correlation with hypochlorite solutions cannot be drawn since hypochlorite solution sample was not received in the winter sampling cycle for this particular WTP. The hypochlorite solutions received in the summer from WTPs 4 and 7 contained the highest levels of chlorate (>8,500 mg/L). In WTP5, chlorate concentration was 0.74 mg/L (winter) but concentration found in the hypochlorite was 2,893 mg/L. The concentration of chlorate measured in the distributed water was similar to that found at the treatment plant (Figure 3). Unlike bromate, chlorate levels in the hypochlorite solutions generally increase with time of storage and temperature. WTP7 reported using the hypochlorite solutions after 3 months of storage.

**Table 3** | Chlorate (mg/L) concentration in samples collected during 2012–2013 (summer/winter)

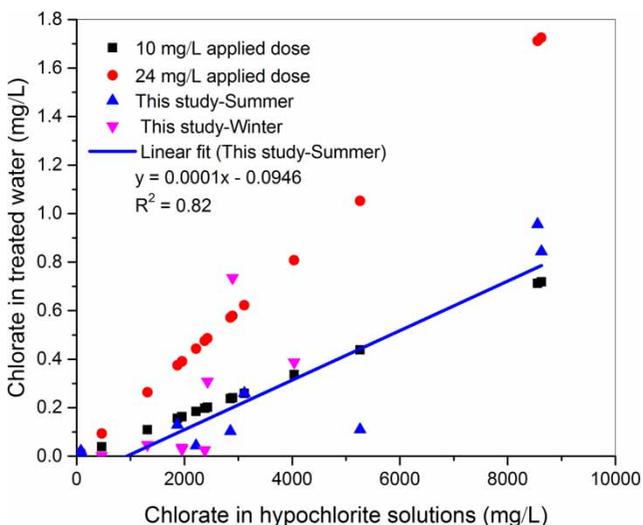
WTP	Chlorate concentration (mg/L)							
	Raw		Hypochlorite		Treated		Distributed	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
2	NSR	0.001	NSR	NSR	NSR	0.05	NSR	0.05
3	0.12	0.2526	5,260	NSR	0.11	0.06	0.12	0.07
4	0.003	0.0017	8,556	2,430	0.96	0.31	0.92	0.31
5	<0.0005	<0.0005	79	2,893	0.02	0.73	0.03	0.72
6	<0.0005	NSR	80	NSR	0.01	NSR	0.01	NSR
7	0.002	0.001	8,626	NSR	0.84	1.58	NSR	NSR
8	0.002	NSR	NSR	NSR	0.35	NSR	NSR	NSR
9	0.011	NSR	1,872	NSR	0.13	NSR	0.14	NSR
10	0.023	0.017	NSR	4,038	0.45	0.39	NSR	NSR
11	0.006	0.003	NSR	NSR	0.01	0.003	0.01	0.003
12	0.009	0.003	3,111	1,316	0.26	0.05	0.32	0.06
13	0.008	0.001	2,217	1,958	0.04	0.03	0.09	0.01
14	0.008	0.001	2,855	1,953	0.10	0.04	0.06	0.04
15	NSR	0.003	NSR	NSR	NSR	0.004	NSR	0.006
16	NSR	<0.0005	NSR	2,378	NSR	0.03	NSR	0.02

NSR, No samples received.



**Figure 3** | Chlorate concentration (mg/L) found in water samples received from 16 WTPs: source water at the treatment plant before distribution (Raw), after treatment before leaving the treatment plant (Treated) and at one point in the distribution system (Distributed) during summer (S) and winter (W).

Similarly to bromate, the expected chlorate concentration in the treated waters are presented in Figure 4, which were calculated based on the applied dose of chlorine (10 and 24 mg/L chlorine) and chlorate concentrations measured in the hypochlorite solutions received. Samples from WTPs that did not provide hypochlorite solutions are excluded in this plot. Figure 4 shows that,



**Figure 4** | Theoretical levels of chlorate in treated water based on the chlorate levels found in the hypochlorite solutions collected during the winter and an applied dose of 10 mg/L (▲) and 24 mg/L (●) for hypochlorite solution (120 g/L active chlorine) vs. levels found in treated water (▲) for summer and (▼) winter.

even at the very high levels of chlorate found in the hypochlorite solutions, the resulting concentration in the treated water would not be expected to exceed the MAC of 1 mg/L at an applied dose of 10 mg/L. The results for the concentrations in treated water samples in the survey showed that indeed none exceeded the MAC. However, there was a strong correlation between the amount of chlorate in the hypochlorite solution and the amount found in treated water ( $r^2 = 0.82$ ) in the summer but no correlation was observed in the winter ( $r^2 = 0.04$ ). It is also observed that for an applied dose of 10 mg/L, hypochlorite solution containing chlorate >2,400 mg/L would have exceeded the SPAC of 0.3 mg/L.

### Perchlorate

Perchlorate was detected in 42% of source waters sampled during the summer at concentrations between 0.08 and 0.28  $\mu\text{g/L}$  (Table 4). In the winter, perchlorate was detected in 54% of source waters at concentrations between 0.06 and 0.26  $\mu\text{g/L}$ . These results are similar to those reported in the US in surface and ground water at levels between 0.06 and 6.4  $\mu\text{g/L}$  (Snyder *et al.* 2005). Higher concentrations have been reported in Japan (Kosaka *et al.* 2007); however, these elevated concentrations have been attributed to industrial effluents. In samples collected at WTP 3, levels remained unchanged (0.08  $\mu\text{g/L}$ ) after treatment (T and D) in both winter and summer. Perchlorate was not detected in any of the water samples collected in WTP9 where perchlorate in the hypochlorite solution was very low. For those treatment plants where perchlorate was not detected in the source water, perchlorate was detected in the treated and distributed water at concentrations between 0.06 and 0.66  $\mu\text{g/L}$  in the summer and between 0.06 and 5.72  $\mu\text{g/L}$  in the winter. Perchlorate was found in all of the hypochlorite solutions tested during the summer at concentrations ranging between 64 and 14,877  $\mu\text{g/L}$  and were significantly higher than levels observed in the winter samples (maximum value of 477  $\mu\text{g/L}$ ). In winter samples, perchlorate was not detected in three hypochlorite solutions from WTPs 12, 13 and 14. Treated water obtained from WTP7 had the highest level of perchlorate in the winter (5.72  $\mu\text{g/L}$ ) and in the summer (0.69  $\mu\text{g/L}$ ). Hypochlorite solution from WTP7 had the highest

**Table 4** | Perchlorate ( $\mu\text{g/L}$ ) concentration in samples collected during 2012–2013 (summer/winter)

WTP	Perchlorate concentration ( $\mu\text{g/L}$ )							
	Hypochlorite		Raw		Treated		Distribution	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
2	NSR	NSR	NSR	<0.05	NSR	<0.05	NSR	0.07
3	1,881	NSR	0.08	0.08	0.07	0.08	0.08	0.08
4	4,466	443	<0.05	<0.05	0.66	0.07	0.64	0.07
5	562	477	<0.05	<0.05	0.22	0.14	0.26	0.19
6	665	NSR	<0.05	NSR	0.06	NSR	0.06	NSR
7	14,877	NSR	<0.05	<0.05	0.69	5.72	NSR	NSR
8	NSR	NSR	<0.05	NSR	0.18	NSR	NSR	NSR
9	64	NSR	<0.05	NSR	<0.05	NSR	<0.05	NSR
10	NSR	356	0.10	0.06	0.40	0.14	NSR	NSR
11	NSR	NSR	0.18	0.25	<0.05	0.26	<0.05	0.24
12	1,711	ND	0.28	0.26	0.33	0.23	0.58	0.23
13	427	ND	0.13	0.17	0.11	0.30	0.09	0.22
14	480	ND	0.12	0.12	0.11	0.16	<0.05	0.17
15	NSR	NSR	NSR	0.06	NSR	0.09	NSR	0.08
16	NSR	466	NSR	<0.05	NSR	<0.05	NSR	<0.05

NSR, No samples received.

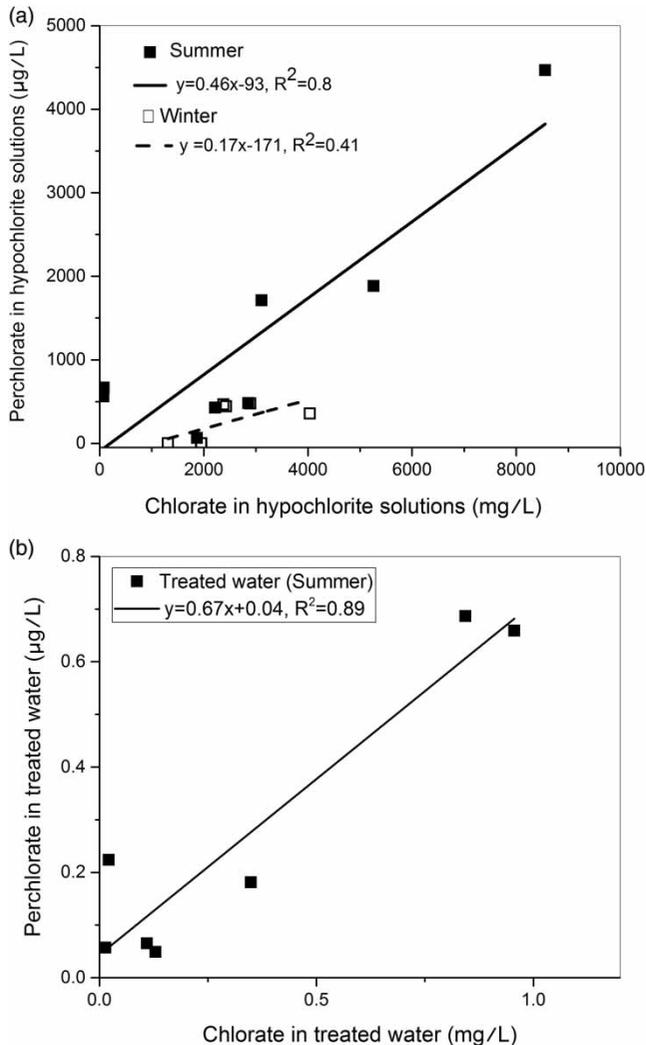
concentration of perchlorate in the summer, but a winter sample was not provided.

Perchlorate levels in hypochlorite solutions were between three and four orders of magnitude lower than those of chlorate, which was also reported in Japan (Asami *et al.* 2009). Investigations into the factors that influence the formation of perchlorate in hypochlorite solutions have shown that higher chlorate, ionic strength, and hypochlorite concentration result in faster rates of perchlorate formation. Contradictory is the finding that hypochlorite solutions with low FAC had higher chlorate and perchlorate concentration; however, this was attributed to decay of FAC in the solutions (Asami *et al.* 2009) due to longer storage time. Figure 5(a) shows a correlation ( $r^2 = 0.80$ ) between the concentrations of chlorate and perchlorate in the hypochlorite solutions (WTP7 excluded) collected in the summer and there was a weak correlation ( $r^2 = 0.41$ ) in samples collected in the winter. There was a strong correlation (Figure 5(b),  $r^2 = 0.89$ ) between the amount of chlorate and perchlorate found in treated water during the summer sampling. No correlation was

found in the winter or for the distributed water (data not shown).

## CONCLUSIONS

This study looked at concentrations of bromate, chlorate, chlorite and perchlorate from 16 WTPs where the source water contained high sodium concentrations (10–760 mg/L) and where ammonium was either used in the treatment process, or naturally occurring. Due to the presence of ammonium, these WTPs faced challenges in maintaining residual chlorine levels in the distribution system. This study showed additional challenges faced by these treatment plants due to the presence of various impurities in the hypochlorite solutions used for disinfection. Bromate, chlorate and perchlorate were found in the majority of the treated water at these WTPs as a result of their presence in the hypochlorite solutions. In the case of bromate and chlorate, the concentrations found in the treated water correlated well with the amount of contaminants found in the hypochlorite



**Figure 5** | Correlation between chlorate and perchlorate concentration in (a) hypochlorite solutions in summer (■) and winter (□) and (b) treated water collected during the summer sampling.

solutions used. One treated water sample exceeded the MAC for bromate of  $10 \mu\text{g/L}$ , which may be attributed to the amount of chlorine required to meet the free chlorine residual. A water sample obtained from a different WTP exceeded the MAC of  $1 \text{ mg/L}$  for chlorate in the winter only. Chlorate and perchlorate were frequently found in the source water. Perchlorate was found at very low concentrations. There were good correlations between the amount of chlorate and perchlorate in the hypochlorite solutions ( $r^2 = 0.80$ ) in treated water ( $r^2 = 0.87$ ) in the summer. Given that bromate, chlorate and perchlorate may be present in the hypochlorite solutions, which can consequently

affect the treated water quality, staff at WTPs must be aware of this issue and follow best practices for the handling and storing of hypochlorite solutions used in their treatment processes such as: (1) use of treatment chemicals that are certified as meeting NSF/ANSI 60; (2) use of low bromide salt for on-site generation of hypochlorite solutions; (3) follow handling and storage recommendations; and (4) establish a quality control program to verify product quality.

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