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Regulated and unregulated halogenated disinfection byproduct formation from chlorination of saline groundwater



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ABSTRACT

Coastal utilities exploiting mildly saline groundwater (<150 mg/L chloride) may be challenged by disinfection byproduct (DBP) formation, a concern likely to increase with sea-level rise. Groundwater from North Carolina coastal aquifers is characterized by large variations in concentrations of halides (bromide up to 10,600 μ g/L) and dissolved organic carbon (up to 5.7 mg-C/L). Formation of 33 regulated and unregulated halogenated DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, haloacetamides, and haloacetaldehydes, was measured after simulated chlorination of 24 coastal North Carolina groundwater samples under typical chlorination conditions. Results of chlorination simulation show that THM levels exceeded the Primary Maximum Contaminant Levels in half of the chlorinated samples. Addition of halides to a low salinity groundwater (110 mg/L chloride) indicated that elevated bromide triggered DBP formation, but chloride was not a critical factor for their formation. DBP speciation, but not overall molar formation, was strongly correlated with bromide variations in the groundwater. THMs and HAAs dominated the measured halogenated DBPs on a mass concentration basis. When measured concentrations were weighted by metrics of toxic potency, haloacetonitriles, and to a lesser degree, haloacetaldehydes and HAAs, were the predominant contributors to calculated DBPassociated toxicity. For some samples exhibiting elevated ammonia concentrations, the addition of chlorine to form chloramines in situ significantly reduced halogenated DBP concentrations and calculated toxicity. HAAs dominated the calculated toxicity of chloraminated waters. Reverse osmosis treatment of saline groundwater (chloride >250 mg/L) can reduce DBP formation by removing halides and organic precursors. However, we show that in a case where reverse osmosis permeate is blended with a separate raw groundwater, the residual bromide level in the permeate could still exceed that in the raw groundwater, and thereby induce DBP formation in the blend. DBP-associated calculated toxicity increased for certain blends in this system due to the DBPs resulting from the combination of the elevated bromide concentration in the permeate and the organic precursors from the raw coastal groundwater.

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1. Introduction

Salinization of water resources is a global phenomenon to which

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utilities must adjust (Vengosh, 2013). Among the communities that address water salinity are those living in coastal areas and those that desalinate brackish groundwater in areas of high fresh water scarcity. Population growth and an increase in the exploitation of coastal aquifers have made them susceptible to saltwater intrusion (Kampioti and Stephanou, 2002; Vengosh, 2013), which in the future may be also exacerbated by sea-level rise (Bear et al., 1999; Werner and Simmons, 2009). For example, research has indicated

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that many public groundwater supply wells in the coastal southeastern United States feature total dissolved solids (TDS) or chloride concentrations that approach or exceed the U.S. EPA's Secondary Maximum Contaminant Levels (MCLs) of 500 mg/L and 250 mg/L, respectively (Morrissey et al., 2010; Saetta et al., 2015), established to avoid salt-associated taste issues (US EPA, 2016). Together with seawater desalination and potable reuse of municipal wastewater, exploitation of brackish groundwater (chloride >250 mg/L) represents an important option to meet growing water demands with local supplies in areas where fresh water is not available. While all three options often employ reverse osmosis (RO) treatment, brackish groundwater may be particularly attractive. The lower salinity of brackish groundwater and municipal wastewater relative to seawater requires less energy for RO treatment (Pearce, 2008). Furthermore, brackish groundwater generally contains lower concentrations of anthropogenic contaminants compared to municipal wastewater (Kolpin et al., 2002; Barnes et al., 2008).

Disinfection byproduct (DBP) formation promotion by the high halide concentrations in these waters may be a more sensitive endpoint than the taste endpoint captured by the U.S. EPA's Secondary MCLs. For example, a laboratory study chlorinated mixtures of a Gulf of Mexico saltwater sample and a Florida groundwater under typical chlorination conditions (sufficient to achieve 1 mg/L total chlorine residual after 24 h at pH 8 and room temperature; Uniform Formation Conditions (UFC)) (Ged and Boyer, 2014) in order to evaluate the potential for DBP formation. At 0.4-2% Gulf of Mexico water, the sum of the four regulated trihalomethanes (THM4: chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM)) exceeded the 80 µg/L Primary MCL, even though the Secondary MCL for Cl⁻ was not exceeded.

Hypobromous acid (HOBr) generated via bromide (Br⁻) oxidation by the hypochlorous acid (HOCl) disinfectant (Equation (1)) forms brominated DBPs via reactions with organic matter precursors. Many laboratory studies have demonstrated that high bromide concentrations shift the speciation of DBP classes towards their bromine-containing analogues, as quantified by the bromine substitution factor (BSF; e.g., Equation (2) for THMs) (Krasner et al., 1989; Richardson et al., 2003, 2008; Hua et al., 2006; Chen and Westerhoff, 2010; Ged and Boyer, 2014; Ged et al., 2015). This shift towards brominated species is important because mammalian cell-based toxicological assays indicate that brominated DBP species can be more than two orders of magnitude more cytotoxic and genotoxic than their chlorinated analogues on a molar basis (Plewa et al., 2004, 2008, 2010; Muellner et al., 2007; Richardson et al., 2008; Jeong et al., 2015). Because the brominated analogues of DBPs weigh more than their chlorinated analogues, this shift in speciation increases the risk for violating weight-based regulatory limits on THMs and haloacetic acids (HAAs) (Ged and Boyer, 2014). However, elevated bromide concentrations can also increase the formation of certain DBP classes, such as THMs, on a molar basis, because HOBr is a more efficient halogenating agent than HOCl (Westerhoff et al., 2004; Ged and Boyer, 2014; Parker et al., 2014). More than 50 studies have sought to develop empirical models to predict DBP formation and changes in speciation (e.g., BSFs), although most studies focused on regulated THMs (Chowdhury et al., 2009; Hua and Reckhow, 2012; Ged et al., 2015).

$$HOCl + Br^{-} \leftrightarrow HOBr + Cl^{-}$$
(1)

$$BSF_{THM} = \frac{[BDCM] + 2[DBCM] + 3[TBM]}{3([TCM] + [BDCM] + [DBCM] + [TBM])}$$
(2)

Beyond regulated THMs and HAAs, there has been significant interest in the formation of unregulated DBP classes, including haloacetonitriles. haloacetamides, halonitromethanes, haloacetaldehydes, and iodinated THMs (I-THMs) (Cancho et al., 2000; Krasner et al., 2006; Sharma et al., 2014). Mammalian cell toxicological assays indicate that the cytotoxicity and genotoxicity of these unregulated classes could be orders of magnitude higher than regulated THMs and HAAs (Plewa et al., 2004, 2008, 2010; Muellner et al., 2007; Richardson et al., 2008; Jeong et al., 2015). The formation pathways for some of these DBP classes have been reviewed (Shah and Mitch, 2012). However, their organic precursors in natural waters often are poorly characterized, and different disinfection schemes can favor the formation of one class over others. For example, phenolic structures in natural organic matter may serve as a common precursor pool for haloacetaldehydes and haloacetamides; while chlorination alone favors haloacetaldehydes, chlorination followed by chloramination favors the formation of haloacetamides (Chuang et al., 2015). For regulated DBPs, multiple predictive models using basic water quality parameters (i.e., DOC, SUVA) have been developed; however, the effects of a given parameter are inconsistent between models (for example, THM formation has been both positively and negatively correlated with SUVA values depending on the model), further highlighting the complexity of the factors that influence DBP formation (Chowdhury et al., 2009).

Regardless, as observed in studies measuring regulated THMs and HAAs, the addition of bromide into organic matter isolates or whole waters shifted the speciation of haloacetonitriles (Yang et al., 2007; Chen and Westerhoff, 2010) and halonitromethanes (Hu et al., 2009, 2010) towards brominated analogues, which exhibit higher toxicity. Similarly, the addition of iodide may promote iodinated DBP formation via the generation of hypoiodous acid (HOI), particularly during chloramination (Bichsel and von Gunten, 2000; Jones et al., 2011; Karanfil et al., 2011). While both HOCl and monochloramine (NH₂Cl) can oxidize iodide to HOI, HOCl is significantly more effective at oxidizing HOI to iodate (IO_3^-) (Equations (3)–(5)), hindering iodinated DBP formation. However, research evaluating blends of saline wastewaters from hydraulic fracturing operations with surface waters to mimic the effects of their discharges on downstream drinking water plants demonstrated that the elevated iodide concentrations in these wastewaters can drive the formation of I-THMs (e.g., dichloroiodomethane (DCIM)) even during chlorination (Parker et al., 2014).

$$HOCI + I^{-} \rightarrow HOI + CI^{-}$$
(3)

 $NH_2Cl + I^- + H_2O \rightarrow HOI + Cl^- + NH_3$ (4)

$$HOI + 2 HOCI \rightarrow IO_3^- + 2 CI^- + 3 H^+$$
 (5)

The first objective of this study was to characterize the formation of a broad range of halogenated DBPs, included regulated THMs and HAAs and unregulated HAAs, I-THMs, haloacetonitriles, haloacetamides, haloacetaldehydes, and the halonitromethane, chloropicrin, from chlorination of coastal North Carolina groundwaters used as drinking water supplies that exhibit a range of salinities. Many previous laboratory studies focused on characterizing the formation of a limited array of individual DBP classes after spiking bromide or iodide (but not chloride) into individual source waters (Hu et al., 2009; Jones et al., 2012; Chu et al., 2013). Our assessment of naturally occurring groundwater from North Carolina provides us with an opportunity to evaluate whether DBP speciation trends are robust across water samples with a wide range of organic matter and halide concentrations. Because several of these groundwater samples contain significant ammonia concentrations, chlorination may form chloramines in situ. The second objective was to evaluate whether chloramines formed by

application of chlorine at concentrations below the breakpoint would decrease or increase DBP (e.g., I-THMs) production. Utilities practicing RO treatment of brackish groundwater are expected to blend the RO permeate with other water sources. The third objective was to evaluate the extent to which the halides in RO permeate (Magara et al., 1996; Duranceau, 2010; Watson et al., 2012) could promote DBP formation after blending with other source waters containing organic matter precursors. While the regulated THMs and HAAs (the focus of previous research) dominate DBP formation on a mass basis (Linge et al., 2013; Zeng et al., 2016), the contribution of a DBP to toxicity is a function of both its concentration and its toxic potency. Accordingly, we weighted measured concentrations of regulated and unregulated DBP classes by metrics of toxic potency to clarify which DBP classes may have the greatest potential to contribute significantly to the toxicity of the disinfected waters.

2. Materials and methods

2.1. Sample collection and characterization

Grab samples were collected from 24 coastal North Carolina groundwater supply wells prior to disinfectant addition and stored at 4 °C prior to analysis. For the RO blending experiments, grab samples were collected at two utilities that blend permeate from RO-treated brackish groundwater (>250 mg/L chloride) with lower salinity groundwater. The first utility is in the Outer Banks of coastal North Carolina that blends brackish groundwater (2900 mg/L chloride) after RO treatment with a lower salinity groundwater (110 mg/L chloride) containing relatively high dissolved organic carbon (DOC) concentrations. The second utility is located in the arid region of Texas and blends brackish groundwater (1230 mg/L chloride) after RO treatment with another groundwater containing low DOC and lower salinity (420 mg/L chloride).

Total organic carbon (TOC) concentrations were measured using a Shimadzu TOC-VCSH total organic carbon analyzer. UV absorbance at 254 nm was measured with an Agilent Cary 60 UV-Vis spectrophotometer and divided by the TOC to calculate the specific UV absorbance (SUVA₂₅₄). Ammonia, nitrate and nitrite concentrations were determined by colorimetric methods using standard methods (Hach methods 10,023, 8171, 8507, respectively). Chloride and bromide concentrations were measured using a Dionex ICS-2100 ion chromatograph (IC). Total iodine was measured with a 0.5 µg/L detection limit by inductively coupled plasma mass spectrometry (ICP-MS) using a VG PlasmaQuad-3 instrument, and spiking of ¹²⁹I-labeled iodide for isotope dilution analysis, as described previously (Parker et al., 2014). Although the total iodine is likely to be predominantly iodide, total iodine concentrations were below the 3 mg/L detection limit for iodide on the IC, preventing further speciation.

2.2. Chlorination conditions and DBP analyses

Free chlorine stock solutions (20 mM) constituted by diluting sodium hypochlorite into deionized water were standardized by UV spectroscopy at 292 nm ($\epsilon_{292} = 365 \text{ M}^{-1} \text{ cm}^{-1}$) (Feng et al., 2007). Water samples were placed in 60 mL borosilicate vials and capped with Teflon-lined septa. Samples were treated with free chlorine at doses found in initial tests to yield a 1 mg/L as Cl₂ free chlorine residual, measured by the DPD colorimetric method (APHA, 1998), after 24 h without pH adjustment (i.e., Simulated Distribution System (SDS) assay (Koch et al., 1991)). For samples containing ammonia, the chlorine dose was sufficient to exceed the breakpoint and achieve the 1 mg/L as Cl₂ free chlorine residual. In separate experiments, we also formed chloramines *in situ* for the subset of these samples where it was possible to add free chlorine at doses below the breakpoint and still achieve a 1 mg/L as Cl_2 chloramine residual after 24 h. After the 24 h treatment, the total chlorine residual was quenched by addition of 33 mg/L ascorbic acid, and the samples were immediately extracted for DBP analyses as described below. All treatments were conducted in triplicate, except for the experiments involving spiking of bromide and chloride, which were conducted in duplicate.

Analytical methods for 33 halogenated DBPs were described previously (Zeng and Mitch, 2016), and are summarized below. A modified USEPA Method 551.1 was used to measure 23 DBPs, including the four regulated THMs, six I-THMs (dichloroiodomethane (DCIM), bromochloroiodomethane (BCIM), dibromoiodomethane (DBIM), chlorodiiodomethane (CDIM), bromodiiodomethane (BDIM), and iodoform (TIM)), four haloacetonitriles (HANs: dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), and trichloroacetonitrile (TCAN)), four haloacetamides (HAMs: dichloroacetamide (DCAM), bromochloroacetamide (BCAM), dibromoacetamide (DBAM), and trichloroacetamide (TCAM)), four haloacetaldehydes (HALs: trichloroacetaldehyde (TCAL), bromodichloroacetaldehyde (BDCAL), dibromochloroacetaldehyde (DBCAL), and tribromoacetaldehyde (TBAL)) and chloropicrin (TCNM). Aliquots (50 mL) of the samples were treated with 12 g of anhydrous sodium sulfate and then extracted by manual shaking for 2 min with 3 mL methyl tert-butyl ether (MtBE) containing 1,2dibromopropane as an internal standard. Two mL of the MtBE extract were concentrated under nitrogen blowdown to 0.5 mL and then analyzed by gas chromatography mass spectrometry (GC-MS). Most analytes were measured in the electron impact (EI) mode. However, haloacetamides were measured using methanol chemical ionization (CI) and tandem mass spectrometry.

A modified USEPA Method 552.3 was used to measure 10 haloacetic acids (HAAs: chloroacetic acid (CAA), bromoacetic acid (BAA), iodoacetic acid (IAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA)). Aliquots (50 mL) were spiked with 10 $\mu g/L$ of 2bromobutyric acid to test for derivatization efficiency, and the pH was adjusted to <0.5 using concentrated sulfuric acid. The aliquots were treated with 12 g anhydrous sodium sulfate and extracted with 3 mL MtBE containing 1,2-dibromopropane as an internal standard. The MtBE extracts were mixed with 2.5 mL methanol containing concentrated sulfuric acid (10% sulfuric acid by volume), and incubated at 55 °C in a water bath for 2 h. The treated extracts were then vortexed with 5 mL of 150 g/L sodium sulfate. After discarding the aqueous phase, the MtBE extract was neutralized by treatment with 2 mL of saturated sodium bicarbonate. The MtBE extract was retrieved, concentrated to 0.5 mL under nitrogen blowdown and analyzed by GC-MS in the EI mode. Method reporting limits for all DBPs varied from 0.14 to 0.33 μ g/L; details on GC-MS parameters and method reporting limits for all analytes were provided previously (Zeng and Mitch, 2016).

2.3. Toxicity calculations

For metrics of toxic potency, we used literature concentrations that were found to result in a 50% reduction in growth of Chinese hamster ovary (CHO) cells compared to untreated controls (LC_{50} cytotoxicity values; Table S1). We employed the cytotoxicity endpoint as a broad measure of toxicity since many modes of action can result in reduced growth. Importantly, the LC_{50} values for all of the DBPs measured in this study were obtained by the same research group using the same CHO assay (Plewa et al., 2004, 2008,

2010; Plewa and Wagner, 2009; Muellner et al., 2007; Richardson et al., 2008; Jeong et al., 2015). Measured concentrations were divided by LC_{50} concentrations. We assumed the toxicity of individual DBPs was additive.

3. Results and discussion

3.1. Basic water quality

Among the 24 coastal North Carolina groundwater samples that had not been treated by RO, the median chloride (11 mg/L) and bromide (69 μ g/L) concentrations were relatively low, but the range was wide at 2.9–1470 mg/L and 27–10,600 μ g/L, respectively (Table 1). Two of the 24 samples exceeded the U.S. EPA's Secondary MCL of 250 mg/L for chloride. For 6 samples bromide concentrations were >400 μ g/L. The concentrations of chloride and bromide were highly correlated (Fig. 1A), and their median ratio (210 weight ratio) was similar to the ratio observed in seawater (290 weight ratio), suggesting the influence of seawater intrusion. In contrast, the total iodine concentrations (8.3 μ g/L median; 1.4–19 μ g/L range) were less variable, and did not correlate with chloride concentrations (Fig. 1B). We observed similar results for samples of saline produced waters from oil and gas operations (Harkness et al., 2015), and in both cases, this lack of correlation with total iodine suggests that iodine did not originate from seawater intrusion, but rather from organic matter in the aquifer rocks (Harkness et al., 2015). The two groundwater samples collected from the utility in Texas exhibited high concentrations of both chloride and bromide, but total iodine was not measureable. The weight ratios of chloride to bromide (2000 for TX_A_Conventional Water and 420 for TX_A_RO_Source) were also higher than the ratio observed in seawater.

The pH of the North Carolina groundwater samples (7.4–8.4) was higher than those of the Texas samples (6.9 and 7.2). The DOC concentrations from the North Carolina samples were relatively high for groundwater samples (3.2 mg-C/L median; 1.1–5.9 mg-C/L range), while the DOC was <0.3 mg-C/L for the Texas samples. The SUVA₂₅₄ values fall within those previously reported for groundwater (Chapelle et al., 2012). Lastly, while the ammonia concentrations were low for the Texas samples and most of the North Carolina samples, levels were >0.1 mg-N/L in 9 of the 24 North Carolina samples. Four North Carolina samples had >0.5 mg-N/L ammonia. At this ammonia concentration, addition of a typical chlorine dose (2.5 mg/L as Cl₂) would form chloramines *in situ*, while addition of >3.8 mg/L as Cl₂ would be needed to exceed the breakpoint and achieve a free chlorine residual.

Table 1

Basic water quality parameters.^a

Sample	рН (—)	Chloride mg/L	Bromide μg/L	Iodine μg/L	Chloride Bromide g _{Cl} /g _{Br}	DOC mg-C/L	NH3 mg-N/L	$\begin{array}{c} UV_{254\ nm}\\ cm^{-1} \end{array}$	$\begin{array}{c} \text{SUVA}_{254 \text{ nm}} \\ \text{L mg}^{-1} \text{ m}^{-1} \end{array}$
Reference Seawater* NC Groundwater	_	19900	69000	-	290	_	-	_	-
NC A 1	7.6	9.2	59	2.9	150	5.4	0.12	0.10	1.9
NC A 2	7.6	10	60	5.4	170	4.0	0.13	0.14	3.5
NC A 3	8.4	6.0	68	3.2	89	2.3	< 0.01	0.04	1.9
NC_A_4	8.4	8.9	69	3.0	130	2.1	<0.01	0.04	2.0
NC_B_1	7.4	2.9	39	4.4	73	1.2	<0.01	0.02	1.6
NC_B_2	7.4	14	60	6.1	230	1.4	< 0.01	0.02	1.7
NC_B_3	7.9	41	200	8.3	210	1.1	0.05	0.05	4.9
NC_C_1	8.2	16	77	6.3	200	2.0	0.01	0.03	1.3
NC_C_2	8.0	230	960	6.6	240	2.1	0.02	0.02	0.9
NC_D_1	8.0	12	48	7.6	250	2.2	0.01	0.04	2.0
NC_D_2	7.9	9.2	54	6.3	170	3.2	0.01	0.07	2.4
NC_D_3	8.4	23	66	1.4	350	2.2	0.01	0.07	3.3
NC_E_1	7.8	197	790	8.3	250	2.2	0.01	0.04	2.0
NC_E_2	8.0	1470	6400	11	230	2.5	0.09	0.05	2.0
NC_E_3	8.0	1430	10600	15	140	2.3	0.12	0.05	2.0
NC_F_1	8.0	8.5	26	9.8	320	5.2	0.50	0.14	2.6
NC_F_2	8.0	9.4	32	11	290	5.5	0.58	0.12	2.3
NC_F_3	7.6	8.7	83	14	110	5.5	0.24	0.12	2.3
NC_F_4	8.0	11	93	15	120	5.7	0.54	0.13	2.2
NC_G_1	8.2	46	110	4.5	420	2.9	<0.01	0.10	3.4
NC_H_1	8.0	150	560	15	270	3.7	0.56	0.08	2.3
NC_H_2	7.7	180	840	16	210	3.3	0.01	0.10	2.9
NC_I_1	8.0	10	43	19	240	3.9	0.70	0.11	2.9
NC_I_2	7.5	7.5	49	14	150	3.6	0.06	0.10	2.9
Blending Samples									
NC_Conventional	7.4	110	160	17	690	1.4	0.30	0.06	4.3
NC_RO_Source	7.9	2900	9600	170	302	3.1	5.5	0.11	3.6
NC_RO_Permeate	5.5	56	310	3.0	180	<0.3	0.33	<0.01	N/A
TX Conventional	7.6	420	210	250	2000	<0.3	0.02	<0.01	N/A
TX_RO_Source	7.6	1230	2930	500	420	<0.3	0.01	< 0.01	N/A
TX_RO_Permeate	5.5	180	72	13	2500	<0.3	<0.01	<0.01	N/A

^a Samples NC_X_# indicate the North Carolina groundwater samples, with letters A through I corresponding to different water treatment utilities; the last section is RO treated water from North Carolina and Texas. The first line corresponds to reference seawater (Millero et al., 2008).



Fig. 1. A) Bromide and B) total iodine concentrations vs. chloride concentrations in coastal North Carolina groundwater. The dotted line in panel A represents the theoretical bromide concentration at a given chloride concentration in seawater.

3.2. DBP formation from chlorination of North Carolina groundwater

The sum of the measured halogenated DBP concentrations formed during chlorination of North Carolina groundwater samples ranged from 38 μ g/L to 340 μ g/L (Fig. 2); Tables S2-S12 provide the

concentrations for individual DBPs for all of the experiments for this study. DBP concentrations were dominated by HAAs and THM4. THM4 ranged from 20 to 270 μ g/L, with 12 of the 24 samples exceeding the 80 μ g/L primary MCL. For the five regulated HAAs (HAA5), concentrations ranged from 5 to 140 μ g/L, with 5 of 24 samples exceeding the 60 μ g/L MCL. Unregulated HAAs ranged



Fig. 2. Total THM4, HAA9, haloacetaldehyde (HAL), haloacetonitrile (HAN), haloacetamide (HAM) and iodinated THM (I-THM) concentrations formed in chlorinated North Carolina groundwater A) on a mass concentration basis, and C) after weighting measured concentrations by metrics of toxic potency. Each stacked bar represents one groundwater, and they are organized in order of increasing bromide concentrations, provided above the bars (µg/L). Panels B and D provide the percent contribution of each DBP class to the stacked bars for panels A and C, respectively. The dotted line in panel A represents the 80 µg/L primary MCL for THM4.

from 1.3 to 22 µg/L. Other unregulated DBP classes occurred at lower concentrations than regulated DBPs, including haloacetaldehydes (HALs; $0.8-40 \mu g/L$), haloacetonitriles (HANs; $0.7-17 \mu g/L$), haloacetamides (HAMs; $<0.2-4.8 \mu g/L$), and iodinated THMs (I-THMs; $<0.2-5.2 \mu g/L$). Overall, these unregulated halogenated DBP classes accounted for 4.5%-40% of the halogenated DBPs on a mass concentration basis. The highest concentration of unregulated DBPs formed in sample NC_F_3 (67 µg/L), which had a bromide concentration of 83 µg/L. Unregulated DBPs in sample NC_C_1 (40\%).

The total halogenated DBP formation did not correlate with bromide concentration (Fig. 3). Samples NC_E_2 and NC_E_3 had both the highest bromide concentrations ($6400 \mu g/L$ and $10,600 \mu g/L$, respectively) and some of the highest total halogenated DBP concentrations. However, several samples featuring relatively high bromide concentrations ($560-960 \mu g/L$) exhibited lower total halogenated DBP concentrations than samples with lower bromide concentrations (Fig. 2). The total concentration of DBPs within individual compound classes (e.g., haloacetonitriles) also did not correlate with bromide concentrations.

However, the bromine substitution factors (BSFs) for THM4, dihalogenated HAAs (DXAAs), trihalogenated HAAs (TXAAs), haloacetonitriles and haloacetaldehydes demonstrated the conversion to brominated analogues within each class with increasing bromide concentrations (Fig. 4). This trend was strongest for THM4 and HAAs, as observed in previous studies (Hua and Reckhow, 2012; Bond et al., 2014). The BSFs approached 1 (complete bromination) in chlorinated samples containing the highest bromide concentrations for THM4, HAAs and haloacetonitriles. For haloacetaldehydes, the BSF was low at the lowest bromide concentrations, but leveled out near 0.6 at the highest bromide concentrations, potentially due to tribromoacetaldehyde degradation via hydrolysis (Xie and Reckhow, 1996). Concentrations for iodinated THMs and haloacetamides were too close to detection limits to permit such an evaluation. Iodinated THMs also did not exhibit a significant correlation with total iodine concentrations (Fig. S1).

THM4 and HAAs predominated among the measured DBP classes on a mass concentration basis, the conventional metric for DBP studies. However, the contribution of a DBP class to the DBP-associated toxicity of a water is a function of both its

concentration and its toxic potency. Unfortunately, current whole water toxicity assays require significant sample concentration, during which the volatile DBPs of interest are lost (Pressman et al., 2010). Pending development of improved concentration techniques that retain volatile DBPs, the weighting of measured DBP concentrations by metrics of toxic potency provides an initial indication of which contaminant classes could contribute significantly to toxicity. Specifically, measured concentrations of individual DBPs were divided by concentrations found to reduce the growth of Chinese hamster ovary cells by 50% (i.e., LC₅₀ cytotoxicity values), as described in the Materials and Methods section. Although the exact values determined from the toxicity-weighted DBP concentrations can not be used directly to quantify toxic risk, the importance of an individual DBP or DBP class relative to all of the measured DBPs could be estimated by comparing its toxicity-weighted concentration to the sum of the toxicity-weighted concentrations; this analysis assumes toxicity is additive, an assumption suggested in previous studies (Stork et al., 2007; Yeatts et al., 2010). Similarly, the sum of the toxicity-weighted concentrations for different waters could be used to compare their calculated DBP-associated toxicity.

The additive toxicity did not correlate with bromide concentration (Figs. 2B and 3B), although the samples with the highest bromide concentrations also exhibited the highest additive toxicity. While THM4 and HAA9 predominated among DBP classes on a mass concentration basis (Fig. 2A and B), haloacetonitriles dominated on an additive toxicity basis (Fig. 2B and D). Haloacetaldehydes and HAA9 were the next most significant contributors to additive toxicity. Together, haloacetonitriles and haloacetaldehydes accounted for >50% of the additive toxicity for 22 of the 24 samples, highlighting the importance of these unregulated DBP classes. Samples NC_A_3 and NC_D_2 were the exceptions, showing relatively low contributions from haloacetonitriles and higher contributions from HAA9.

A few of the samples were noticeable outliers within these trends. For example, samples NC_H_1 (560 μ g/L Br⁻), NC_H_2 (840 μ g/L Br⁻), and NC_C_2 (960 μ g/L Br⁻), frequently exhibited lower BSF values (Fig. 4) and low total halogenated DBP concentrations and additive toxicity (Fig. 3). In terms of basic water quality parameters (Table 1), there was no clear factor to explain these deviations. For example, samples NC_H_1 and NC_H_2 exhibited moderate levels of Cl⁻:Br⁻ ratios, DOC concentrations, UV₂₅₄ and SUVA₂₅₄ values. While water quality parameters for sample NC_C_2



Fig. 3. Total halogenated DBP concentrations measured in chlorinated North Carolina groundwaters vs. bromide concentration A) on a mass concentration basis, and B) after weighting measured concentrations by metrics of toxic potency.



Fig. 4. Bromine substitution factors (BSFs) for A) THM4, B) dihalogenated haloacetonitriles (HANs), C) trihalogenated haloacetaldehydes (HALs) and D) dihalogenated HAAs (DXAAs) and trihalogenated HAAs (TXAAs) vs. bromide concentration.

were mostly similar, the SUVA₂₅₄ value (0.9 L mg⁻¹ min⁻¹) was relatively low. The simultaneous variation in these parameters across these water samples contributes to this uncertainty.

3.3. Effect of high chloride concentrations on DBP formation

The objective in this study was to characterize DBP formation in naturally-occurring halide-containing groundwater. Previous research has characterized several factors contributing to DBP formation for specific DBP classes. For example, THM4 formation has been correlated with DOC concentrations (Serodes et al., 2003), SUVA254 and bromide concentrations (Watson, 1993; Nikolaou et al., 2004; Sohn et al., 2004; Hong et al., 2007; Ged et al., 2015). However, previous research often has spiked water samples with increasing bromide concentrations in order to evaluate the effect of bromide on DBP formation (Jones et al., 2012; Chu et al., 2013). Other research has suggested that chloride could promote DBP formation by forming the reactive brominating agent, BrCl (Equation (6); Sivey et al., 2013; Ged and Boyer, 2014), but the importance of chloride for DBP formation has not been explicitly tested. In our samples, the bromide and chloride concentrations co-varied (Fig. 1A). In order to assess the importance of chloride for promoting DBP formation, we evaluated the DBP formation in groundwater with low concentrations of chloride and bromide

(sample NC_Conventional, where "conventional" reflects the fact that the utility blends this shallow aquifer water with RO-treated brackish groundwater as described below) that was spiked with increasing concentrations of bromide alone, and with increasing concentrations of both chloride and bromide with a 290 weight ratio observed in seawater. The DBP formation increased with increasing concentrations of bromide spiked into the sample (Fig. 5A). One factor contributing to this increase was a change in speciation towards the more brominated, higher molecular weight analogues within each class, as exhibited by the increasing BSFs (Fig. 5B). However, spiking chlorine in addition to bromide resulted in little impact on DBP formation (Fig. 5).

$$HOBr + Cl^{-} + H^{+} \leftrightarrow BrCl + H_{2}O$$
(6)

3.4. Chloramination as an option to control DBP formation

Four of the 24 North Carolina groundwater samples featured sufficiently high ammonia concentrations (0.5-0.7 mg-N/L) that it was possible to form chloramines by application of free chlorine, and still achieve at least a 1 mg/L as Cl₂ total chlorine residual after 1 d. Fig. 6 compares halogenated DBP formation during



Fig. 5. A) Total THM4, HAA9, haloacetaldehyde (HAL), haloacetonitrile (HAN), haloacetamide (HAM) and iodinated THM (I-THM) concentrations formed from chlorination of a North Carolina groundwater sample (NC_conventional) spiked with either bromide or chloride and bromide held at a 290 weight ratio on a mass concentration basis. The left column in each pair corresponds to a bromide spike and the right column corresponds to a bromide and chloride spike. Panel B shows the BSFs for spiking with bromide (continuous lines) or chloride and bromide (dashed lines). The error bars on the red circle represent the maximum range for the experimental duplicates. (For interpretation of this article.)

chloramination to the formation that occurred when free chlorine was applied at doses sufficient to break out ammonia and leave at least a 1 mg/L as Cl_2 total free chlorine residual after 1 day. The total concentrations of halogenated DBPs formed during chloramination never exceeded 10 μ g/L and were 15–26 times lower on a mass basis than those formed during chlorination. While THM4 and HAA5 concentrations exceeded their MCLs in all 4 samples during chlorination, THM4 and HAA5 concentrations were far below the MCLs during chloramination.

The change in DBP concentrations produced during chloramination relative to DBP concentrations produced during chlorination depends on the DBP class. Concentrations of THM4, HAA9, haloacetonitriles and haloacetaldehydes on a mass basis decreased 15to 82-fold. However, chloramination increased haloacetamides in three of the four samples up to 5-fold (sample NC_I_1 was the exception). Even though chloramination has been associated with iodinated THM formation, this effect was not observed with these water samples. Iodinated THM concentrations were higher during chlorination in two of the four samples, and differed by at most $0.4 \mu g/L$ between chloramination and chlorination. Haloacetamides accounted for up to 36% of the total halogenated DBPs formed during chloramination compared to <0.7% of the total halogenated DBPs formed during chlorination (Fig. 6B). THM4 and HAA9 dominated the rest of total halogenated DBPs on a mass basis, accounting for 19–36% and 31–37% of the total halogenated DBP concentration formed during chloramination, respectively. Although the percentage contributions of THM4 and HAA9 to total halogenated DBPs were similar during chlorination and chloramination, the regulated HAA5 accounted for as low as 46% of total HAAs during chlorination but all of the HAAs during chloramination.

When concentrations were weighted by measures of toxic potency, HAA9 dominated the calculated toxicity for the chloraminated samples (91–93%), but accounted for only 10–22% of the calculated toxicity for the chlorinated samples (Fig. 6D). The low contribution to calculated toxicity from haloacetamides during chloramination, despite their important contribution to total halogenated DBPs on a mass basis, derives from the shift in speciation to the less brominated analogues that feature lower toxic potency (i.e., lower LC_{50} values). For these samples, chloramination by addition of chlorine at doses below the breakpoint reduces both the total halogenated DBPs formed on a mass basis and their calculated halogenated DBP-associated toxicity. However, the benefits of this approach for DBP reduction must be weighed against the reduction in pathogen disinfection associated with the less potent chloramine disinfectant.

3.5. Blending with RO-treated brackish groundwater supplies

Some utilities are adopting RO treatment of higher salinity brackish groundwater to augment water supplies. The RO permeate would be blended with conventional water supplies, potentially including some of the brackish groundwater evaluated above. Because of the significant removal of the DOC and bromide precursors to halogenated DBPs achieved by RO treatment, blending with RO-treated water may be expected to reduce DBP formation by diluting the overall level of precursors in the blend. However, if the feed water to the RO features sufficiently high levels of bromide, the bromide concentrations in the permeate may exceed those in the conventional source water. In this case, it is possible that certain blending ratios may promote DBP formation in the blend water via elevated DOC and bromide concentrations from the conventional source water supply and RO permeate, respectively. For example, an increase in THM4 was observed during blending of desalinated seawater with a conventional drinking water supply, associated with the elevated bromide concentrations in the RO-treated seawater (i.e., up to ~650 μ g/L; Agus et al., 2009).

In order to evaluate the relevance of such effects to systems blending RO-treated brackish groundwater with conventional groundwater, we evaluated DBP formation from different blending ratios for samples collected from two such facilities. For one facility from coastal North Carolina, RO treatment of a saline groundwater (2900 mg/L Cl⁻ and 9600 μ g/L Br⁻) reduced the bromide concentration to 310 µg/L and the DOC to <0.3 mg-C/L (Table 1). However, this Br⁻ concentration still exceeded the 160 μ g/L concentration level in the conventional groundwater (which had a 1.4 mg-C/L DOC). DBP formation during chlorination of the conventional water (Fig. 7) was at the lower end of that observed for the other chlorinated North Carolina groundwater on a mass basis (Fig. 2), but the calculated DBP-associated toxicity was at the higher end. DBP formation during chlorination of the RO permeate alone was very low on both a mass basis and a toxicity-weighted basis, likely reflecting the low level of organic precursors (<0.3 mg-C/L DOC). On a mass basis, total halogenated DBP formation increased with the increasing percentage of conventional water in the blends.



Fig. 6. Total THM4, HAA9, haloacetaldehyde (HAL), haloacetonitrile (HAN), haloacetamide (HAM) and iodinated THM (I-THM) concentrations formed in chlorinated and chloraminated North Carolina groundwaters A) on a mass concentration basis, and C) after weighting measured concentrations by metrics of toxic potency. Panels B and D provide the percent contribution of each DBP class to the stacked bars for panels A and C, respectively. CN = chloramine and FC = free chlorine. Samples 1, 2, 3, and 4 represent NC_F_1, NC_F_2, NC_L_1, and NC_F_3, respectively.

However, the largest percentage increases relative to RO permeate alone were observed at the lowest percentage of conventional water (i.e., 20% and 40%, corresponding to ~0.3 and 0.6 mg/L DOC, respectively), leveling out thereafter. These results suggest that relatively low DOC concentrations are needed to drive significant DBP formation. However, the calculated DBP-associated toxicity was highest for intermediate blends (80% and 60% conventional water) (Fig. 7B), with haloacetonitriles and haloacetaldehydes contributing most to the calculated toxicity. Interestingly, the highest bromine substitution factors (BSFs) were observed for blends with less conventional water (i.e., 20% and 40%) (Fig. 7C), near a 1 mg Br⁻ to 1 mg DOC ratio. Although brominated species tend to exhibit higher toxic potency, the elevated DBP formation for blends featuring higher levels of conventional water offset the somewhat lower BSF to yield higher levels of calculated DBPassociated toxicity.

We also evaluated blends associated with a brackish groundwater desalination system in Texas. The conventional groundwater had 210 mg/L Br⁻ and a much higher Cl⁻:Br⁻ weight ratio (2,000) relative to the North Carolina groundwater samples (Table 1). Total halogenated DBP formation from chlorination of this groundwater was nearly an order of magnitude lower than for the North Carolina conventional groundwater (Fig. 7D), and comparable to levels observed for chloramination of North Carolina groundwater samples (Fig. 6). We suggest that the low DBP formation was driven by the low level of organic precursors in the conventional groundwater (DOC <0.3 mg-C/L). Chlorination of the RO permeate, which exhibited <0.3 mg-C/L DOC and 72 μ g/L Br⁻, produced somewhat lower concentrations of halogenated DBPs. While total halogenated DBPs were highest for 60% and 80% conventional water blends on a mass basis, the calculated DBP-associated toxicity was highest for the 80% and 100% conventional water blends. Although THM4 and HAA9 dominated on a mass basis, haloacetonitriles dominated in terms of contributions to calculated toxicity. Despite the high total iodine concentrations (250 μ g/L and 310 μ g/L for the conventional groundwater and RO permeate, respectively), iodinated THMs were not detected, likely due to the low DOC.

4. Conclusions

Chlorinated groundwaters frequently exhibit lower DBP concentrations than chlorinated surface waters, presumably due to lower levels of organic matter precursors in common groundwater. However, simulated chlorination of groundwater from the coastal aquifer of North Carolina with a wide range of halide levels formed regulated THMs and HAAs at levels that exceeded in some cases their respective MCLs. For a low-halide groundwater spiked with halides, total halogenated DBP formation increased with increasing bromide concentration, but was not strongly impacted by high chloride concentrations. However, total halogenated DBP formation was less strongly correlated with bromide concentration across groundwater samples, indicating that bromide is just one of several factors contributing to DBP formation. On a mass concentration basis, THM4 and HAAs were the predominant DBPs. When



Fig. 7. Total THM4, HAA9, haloacetaldehyde (HAL), haloacetonitrile (HAN), haloacetamide (HAM) and iodinated THM (I-THM) concentrations formed after chlorination of different blends of RO-treated and conventional groundwaters on a mass concentration basis (panels A and D), and after weighting measured concentrations by metrics of toxic potency (panels B and E). Panels C and F provide the BSFs for the water blends. Panels A, B, and C are associated with North Carolina samples and panels D, E, and F are associated with Texas samples. The error bars on the red circle represent the maximum standard deviation for the experimental triplicates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

weighted by measures of toxic potency, unregulated haloacetonitriles and, to a lesser degree, HAAs and unregulated haloacetaldehydes were the important contributors to the calculated DBP-associated toxicity. The potential importance of haloacetonitriles in these chlorinated groundwater samples concurs with the dominance of haloacetonitriles for the calculated DBP-associated toxicity of municipal wastewaters after treatment by either Full Advanced Treatment (i.e., MF/RO/AOP) (Zeng et al., 2016) or ozone followed by biological activated carbon (Chuang and Mitch, 2017). Validation by whole water bioassays of the predicted importance of haloacetonitriles requires improved methods to concentrate the samples without loss of volatile DBPs.

There are several options for reducing high DBP concentrations in chlorinated water, and perhaps more importantly, DBPassociated toxicity. First, chloramination dramatically reduced total halogenated DBP concentrations. Even though chloramination may increase the formation of haloacetamides, which tend to exhibit high toxic potency, calculated DBP-associated toxicity declined overall, and HAAs were the predominant contributors to this DBP-associated toxicity. However, these benefits must be weighed against the lower efficacy of chloramination for pathogen deactivation. Second, RO treatment can dramatically reduce DBP formation by removing both halides and organic precursors. However, bromide concentrations following RO treatment of higher salinity brackish groundwater may exceed the bromide levels in conventional source waters. Blending percentages may need to be optimized to avoid increases in DBP concentrations and calculated toxicity via the combination of the bromide from the RO permeate and the organic precursors in the conventional water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.watres.2017.06.028.

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