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Drivers of Disinfection Byproduct Formation and Speciation in Small, Chlorinated Coastal Groundwater Systems: Relative Roles of Bromide and Organic Matter, and the Need for Improved Source Water Characterization and Monitoring

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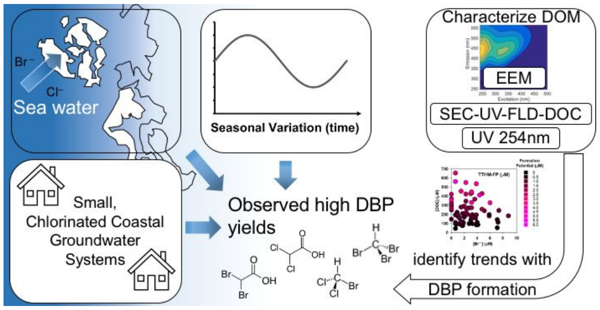

Small, chlorinated coastal groundwater systems are uniquely susceptible to elevated (especially brominated) DBP formation, due to the potential for high bromide and DOM levels, technical and resource constraints, and limited regulatory oversight.

Abstract

Numerous small public groundwater systems on coastal islands in Washington State (WA) that are susceptible to seawater intrusion have reported disproportionately high frequencies of regulatory exceedances for halogenated organic DBPs; especially brominated DBPs. Fifteen such systems spread across a ~1000 km^2 study area were monitored quarterly over a year in a collaboration between the WA Department of Health and University of Washington to identify key drivers of these trends, and to develop operational and regulatory recommendations aimed at minimizing DBP formation in these and similar systems in WA and elsewhere. [Br$^-$] alone was not observed to be a strong predictor of DBP formation potentials (DBP-FPs) or speciation for source waters across the study area, likely due to accompanying large variations in [DOC]. However, bromine substitution factors correlated relatively well with [Br$^-$]/[DOC] ratios, highlighting the importance of both [Br$^-$] and [DOC] in governing DBP formation and speciation in coastal groundwaters. Overall DBP-FPs correlated strongly with [DOC], UV absorbance at 254 nm (A_{254}), and selected size exclusion chromatography (SEC) and fluorescence metrics for each groundwater, with A_{254} a particularly strong surrogate for DOC. This was consistent with high uniformity of DOM properties (confirmed from $SUVA_{254}$, fluorescence index, PARAFAC components, and SEC chromatograms) across the study area. Specific DBP-FPs (e.g., ~72 $\mu g_{TTHM}/mg_C$) for the source waters were quite high compared to typical groundwaters, pointing to inherently high DOM reactivity as an additional factor in the frequent DBP regulatory exceedances observed for the investigated sites. Measurements also revealed seasonal trends (e.g., in [Br$^-$] and [DOC]) correlated with DBP formation, but not captured by routine regulatory monitoring, as well as widespread inconsistencies in chlorination practices at the studied systems. While such factors and correlations are well established for surface waters, this work

provides one of the few examinations incorporating both laboratory and full-scale observations to demonstrate their importance in small, coastal groundwater systems. Based on these findings, WA has adopted a number of changes in its design manual for new groundwater disinfection systems, and is evaluating changes in its disinfection monitoring and DBP programs that may also serve as models for wider implementation.

Water Impact Statement

Laboratory and field investigation of DBPs, bromide, DOM, and other water and operational parameters in small, chlorinated coastal groundwater systems susceptible to seawater intrusion linked frequent regulatory DBP exceedances and brominated DBP yields to highly variable bromide and DOC levels, seasonal trends, and chlorination practices not captured by compliance sampling; highlighting needs/opportunities for better understanding/controlling DBP formation in such systems.

Introduction

In Washington State (WA), 35 out of 571 (6.1%) public groundwater systems have exceeded maximum contaminant levels (MCLs) for halogenated organic disinfection byproducts (DBPs), compared to 12 out of 208 (5.8%) public surface water systems. 27 of the 35 groundwater systems that have reported elevated levels of trihalomethanes (THMs) and/or haloacetic acids (HAAs) are small, chlorinated groundwater systems (population range 28 to 871) concentrated in Island and San Juan Counties (Figure 1). Many of these systems have also reported higher proportions of brominated THMs and HAAs, which are often more harmful than their chlorinated analogues.[1-4] The occurrence of such a high proportion of groundwater systems exceeding DBP MCLs in a distinct geographic area was initially unexpected by the Washington State Department of Health (WA DOH), and indicated that chlorinated groundwater systems within this region are uniquely susceptible to challenges in meeting DBP compliance targets.

It is known that aquifers in these coastal counties may be prone to seawater intrusion.[5, 6] Thus, elevated bromide levels originating from seawater intrusion may represent one possible explanation for the DBP trends observed at some of the Island and San Juan County sites. Prior work has shown that increases in source water bromide accompanying seawater intrusion can have substantial impacts on DBP formation in chlorinated waters.[7-12] This results from the rapid oxidation of bromide by free chlorine (predominantly hypochlorous acid and its conjugate base hypochlorite, or $HOCl/OCl^-$) to form free bromine (i.e., hypobromous acid/hypobromite, or $HOBr/OBr^-$),[13] each of which may then react with DBP precursor moieties in dissolved organic matter (DOM) within a water to generate a mixture of chlorinated and brominated DBPs, with free bromine reacting faster with and more efficiently halogenating DOM and activated aromatic compounds than free chlorine.[13-15] Consequently, higher proportions of brominated DBPs are

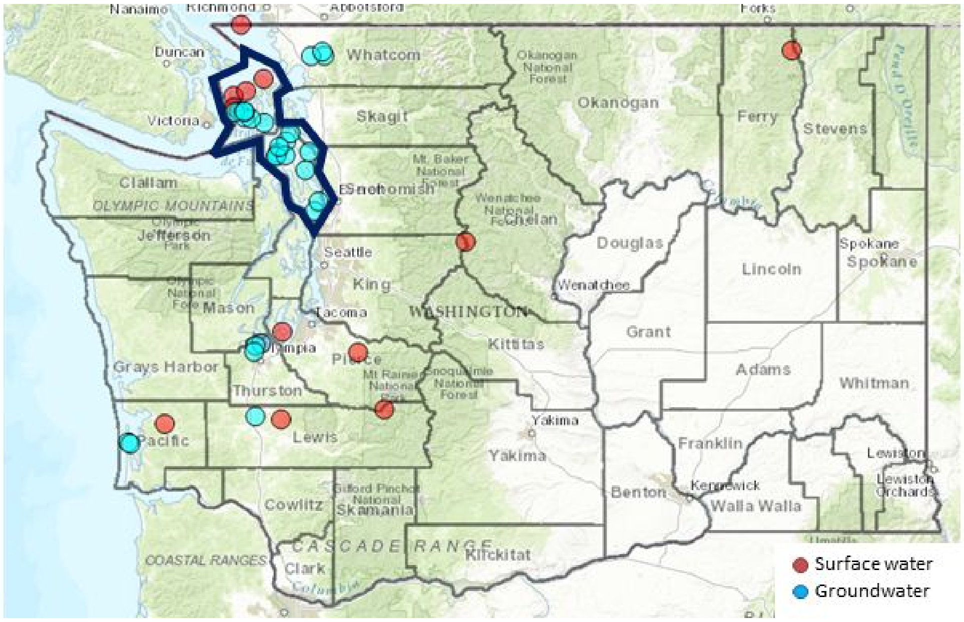

Figure 1. Locations of public water systems that have exceeded DBP MCLs for THMs and/or HAAs. Groundwater sites are indicated by turquoise circles, and surface water sites by red circles. The study area counties (encompassing an overall land area of ~382 mi^2, or 990 km^2) are outlined within the thick, dark blue line.

generally observed as bromide levels increase.[7, 8, 10, 16-24] A number of studies have also reported higher total molar THM and/or HAA yields when bromide levels increase while dissolved organic carbon (DOC) concentrations remain constant.[7, 8, 10, 11, 16, 20-22, 25] In addition to increased regulated THM and/or HAA formation, higher bromide levels may lead to increases in total organic bromine and various unregulated DBPs,[7, 8, 19, 26, 27] with consequent health risks.[1-4, 27, 28]

Another potential factor behind the observed DBP trends at the Island and San Juan County sites may relate to the type and amount of DOM present in their water sources, as DBP formation potentials and speciation can vary widely due to differences in quantities and inherent properties of source water DOM. Although groundwaters are often reported to be less enriched in DBP precursors than surface waters,[23, 29-36] with median specific DBP yields per mg carbon reported to ~10-20% lower for groundwaters than surface waters,[32] specific DBP yields for some groundwaters can be substantially higher than for typical surface waters.[32, 37] A wealth of literature highlights the greater role of hydrophobic, aromatic-enriched fractions of DOM as DBP precursor material compared to less aromatic, hydrophilic DOM fractions,[32, 38-46] where the relative proportions of each can vary substantially depending on water source.[43, 44, 47-53] Groundwater is often depleted in aromatic, hydrophobic fractions relative to surface water,[49, 51, 54-60] though the opposite trend has been reported in some cases.[55, 61] Although overall DOC concentrations are often reported to be higher in surface waters,[23, 32, 36, 56, 58-60] this is also not always the case.[7, 11, 62]

While the literature evaluating relationships of surface water DOM characteristics and quantities to DBP formation is extensive,[33, 38, 40, 43, 46, 50, 53, 56, 60, 62-66] fewer studies have included a substantial focus on the role of groundwater DOM in driving DBP formation.[7, 8, 11, 33, 56, 66, 67] Furthermore, within the very limited subset of studies specifically addressing coastal groundwaters, the potential importance of DOM composition in driving DBP formation does not appear to have been extensively investigated.[7, 8, 11] Thus, in the context of the present work, it was of considerable interest and importance to gain a better understanding of how both quantities (i.e., DOC concentrations) *and* composition of source water DOM may influence the observed trends in DBP formation at each of the Island and San Juan County sites.

In addition to bromide concentrations and DOM quantity/quality, DBP formation and speciation may also be influenced by water quality parameters and operational variables such as pH, temperature, chloride, iodide, and TDS concentrations, ammonia concentrations, and applied chlorine concentration and contact time (amongst others). Unfortunately, routine monitoring of groundwater sources does not typically include many of the key water quality parameters noted above that may influence DBP formation (e.g., bromide, iodide, total organic carbon (TOC), DOC, and ammonia levels),[68, 69] and source water DOM characterization has never been undertaken at the study sites prior to now. Consequently, little information existed prior to the present study that could help confirm the influence of seawater intrusion, elucidate properties of source water DOM pools, or otherwise explain observed trends in the study area; in particular, why DBP yields could exceed regulatory limits in a given coastal groundwater system even while a nearby groundwater system consistently meets regulatory criteria. Additionally, regulatory monitoring of DBPs in such small systems is generally conducted infrequently (often only once per year) and within the distribution system at points temporally and spatially removed from disinfection facilities, complicating direct association of reported DBP levels with variations in source water characteristics. Furthermore, because United States Environmental Protection Agency (US EPA) guidance documents tend to focus on surface water systems, no groundwater– or small system–specific federal guidance on source monitoring or mitigation actions to minimize DBP formation are currently available to WA DOH or other state agencies to provide to such water systems.

In response to the above gaps in knowledge, the WA DOH partnered with the University of Washington (UW) to undertake a comprehensive investigation of source water quality and operational characteristics for a cross section of utilities within the affected areas of WA over a full year, from September, 2015, through August, 2016. A primary aim of the work was to identify water quality and operational characteristics correlated with and potentially responsible for formation of chlorinated and brominated THMs and HAAs at many of the groundwater systems in question, including a variety of raw and treated water quality parameters associated with inorganic constituents and DOM. An additional major aim was to develop a knowledge base that could be used to inform general guidelines for regulatory, design, and operational personnel in minimizing DBP formation at similar small, coastal groundwater systems – not only in WA, but also in other regions of the US and other nations.

The sample sites selected for the study included 18 groundwater sources supplying 15 public community water systems (each serving less than 900 consumers) located in San Juan and Island Counties, distributed across ~1000 km^2 of land surface area within the Puget Sound region of WA (Figure 1). All of the systems practice continuous free chlorination treatment, with twelve utilizing only chlorination, and three also practicing more extensive treatment for water softening and/or removal of iron and manganese – including pre-oxidation with free chlorine and/or permanganate, greensand filtration, ion exchange, and/or aeration. Treatment descriptions are included in Table S1. Ten of the selected systems have exceeded the MCL for total trihalomethanes (TTHMs) during routine regulatory sampling, with six of these having primarily brominated byproducts. Three of the selected systems also exceeded the MCL for HAA5 (the sum of 5 regulated HAAs: mono-, di-, and trichloroacetic acid, and mono- and dibromoacetic acid). Five of the selected systems (here designated as IC02, IC03, IC04, SJC05, and SJC07, with the prefixes IC and SJC representing Island County and San Juan County, respectively) have not exceeded the MCL for TTHMs or HAAs, and were included to enable comparisons of systems reporting low DBP levels with systems reporting high DBP levels. In Figure 2, the averaged results of historical DBP regulatory compliance samples (spanning 2010–2016) are shown for each site. Regulatory sampling frequency during that period ranged from triennial to quarterly, and a majority of the systems in the study collected DBP regulatory compliance samples from only one location in the distribution system.

Water quality parameters monitored for each raw water sample collected during this study included Cl^-, Br^-, total iodine (TI), and NH_3-N concentrations; total dissolved solids (TDS) concentration; conductivity; heterotrophic plate count (HPC); adenosine triphosphate (ATP)

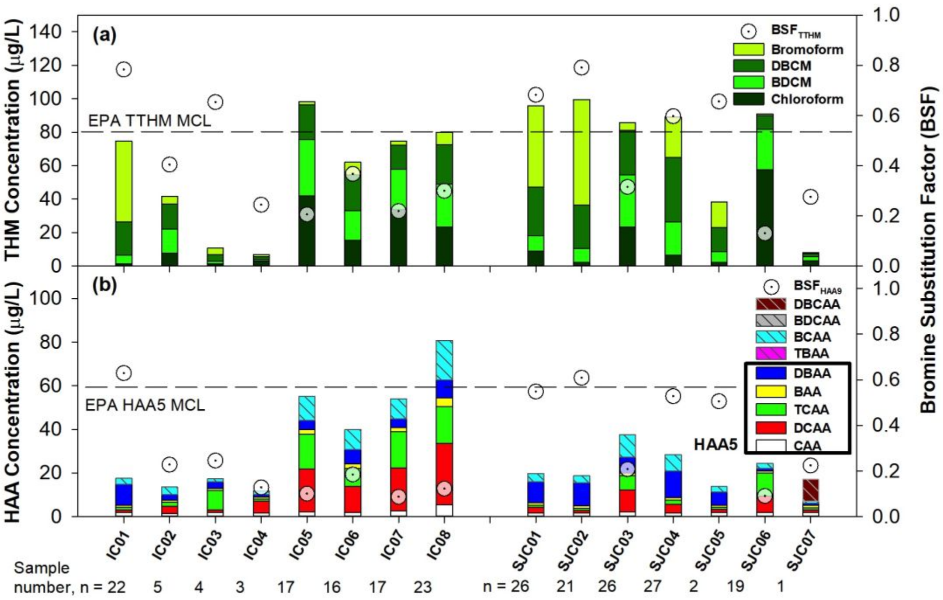

Figure 2. Historical averages from 2010-2016 regulatory measurements of (a) THM; and (b) HAA concentrations in the distribution system (HAA5 species denoted by bold, black borders in bars and legend; remaining HAA species comprising HAA9 denoted by bars with hatched fills). Average BSF_{TTHM} or BSF_{HAA9} values for regulatory measurements are plotted (circles) on the secondary y-axis. Dashed lines represent the US EPA MCLs for TTHMs and HAA5. BDCM – bromodichloromethane, DBCM – dibromochloromethane, CAA – monochloroacetic acid, DCAA – dichloroacetic acid, TCAA – trichloroacetic acid, BAA – monobromoacetic acid, DBAA – dibromoacetic acid, TBAA – tribromoacetic acid, BCAA – bromochloroacetic acid, BDCAA – bromodichloroacetic acid, DBCAA – dibromochloroacetic acid.

concentration; organic carbon (TOC and DOC) concentration; UV absorbance at 254 nm (A_{254}); and 7-day disinfection byproduct formation potentials (DBP-FPs) of chlorinated and brominated THMs and HAAs. In addition, DOM in each water sample was characterized by (a) HPLC/size exclusion chromatography with online UV/visible, fluorescence, and DOC detection (HPLC/SEC-UV/fluor./DOC) – to determine the relative distributions of various molecular weight fractions of DOM present in the samples,[47, 48, 70] and (b) acquisition of fluorescence excitation-emission matrixes (EEM) with subsequent processing by parallel factor analysis (PARAFAC) as a means of identifying characteristic signatures of fluorescent components present in the DOM.[71-73] In treated water samples, all of the above parameters were monitored aside from conductivity and Cl^-, Br^-, TI, NH_3-N, and TDS concentrations. Operational water quality parameters monitored during sampling at each location included free and total chlorine concentrations, pH, and water temperature. Monthly regulatory compliance reports encompassing the sampling dates for each water system were also reviewed to determine average free chlorine residuals and theoretical seasonal water residence times in their distribution systems (ranging from 1.1 to 15.5 days).

Through collection and analysis of the data described above, the WA DOH and UW sought to address a number of specific objectives, including to: (1) identify parameters strongly correlated with DBP formation in chlorinated groundwater systems in San Juan and Island Counties, in particular with formation of brominated byproducts, (2) determine the extent to which observed DBP trends are driven specifically by elevated bromide levels (due to seawater intrusion or other causes) and/or by DOM properties that predispose a site to uniquely high DBP yields, (3) evaluate factors that can result in adjacent water systems with similar well locations exhibiting very different DBP compliance results, (4) establish whether and how variations in DBP yields may vary with season, seawater influence, or other as yet unidentified cause(s), (5) identify readily measurable water quality parameters (and/or surrogates thereof) that could be used by regulators, design engineers, and utility personnel to predict DBP formation potential in these and other coastal groundwater systems, and (6) recommend modifications to current regulatory and/or operational requirements to improve source water characterization and monitoring, and ultimately help minimize DBP formation in such systems. It is important to note that formation of iodinated DBPs (I-DBPs) may also be of concern during chlorination (and moreso chloramination) of coastal groundwaters and other waters containing elevated iodide levels.[8, 74] However, as the principal focus of this work was on better understanding causes of

MCL exceedances associated with regulated DBPs at the study sites, the scope of investigation was limited primarily to evaluation of factors influencing chlorinated and brominated THM and HAA formation.

More broadly, this work was also undertaken with the overarching objectives of (a) providing a bridge between laboratory investigations demonstrating the high susceptibility of coastal groundwaters to regulated and unregulated DBP formation (from prior studies,[7, 8, 11] and within the current work) and practical experiences by full-scale utilities, (b) highlighting widely shared characteristics of small, chlorinated coastal groundwater systems (in WA and elsewhere) that may predispose them to elevated levels of regulated and unregulated DBPs (especially brominated DBPs) – including not only inherent characteristics of their water supplies, but also technical and/or resource limitations that may hinder their abilities to recognize and respond to such challenges, and (c) identifying opportunities for improving source water quality characterization and monitoring practices that simultaneously take into account the unique circumstances of small systems while also ensuring provision of safe water to consumers.

Materials and Methods

Materials. All reagents and solvents used were of at least ACS reagent grade. All aqueous solutions were prepared using Milli-Q® grade water ($\rho \geq 18.2$ MΩ•cm). Calibration and internal standards for analyses of THMs and HAAs were obtained from Sigma-Aldrich. Free chlorine stock solutions were prepared from commercially-available sodium hypochlorite (5%, J.T. Baker) and standardized spectrophotometrically using $\varepsilon = 350\ M^{-1}cm^{-1}$ at 292 nm.[75] BacTiter- Glo™ Microbial Cell Viability Assay kits were obtained from Promega.

Sample Collection and General Analytical Methods. Samples were obtained during four consecutive quarters, with quarter 1 (Q1) samples collected in autumn, quarter 2 (Q2) samples collected in winter, quarter 3 (Q3) samples collected in spring, and quarter 4 (Q4) samples collected in summer. Specific collection dates for each sample site are listed in Table S1. Based on historic rainfall patterns, Q1 and Q4 occurred during the dry season and Q2 and Q3 occurred during the rainy season. The study included 8 water systems on Whidbey and Camano Islands within Island County, WA (labelled here with the prefix IC) and 7 water systems on San Juan Island within San Juan County, WA (labelled here with the prefix SJC). Only raw water samples were collected for the 12 systems using free chlorination treatment alone. Raw and treated water samples were collected for the three systems utilizing more extensive treatment. Free chlorine residuals in treated samples were quenched upon sampling, using 10-fold molar excess $Na_2S_2O_3$. Raw water samples from Source03, Source04, and Source05 of system IC06 were blended in the lab prior to analyses and DBP-FP tests to ensure consistency with water composition at the full-scale, as all three sources are piped separately but blended together on-site before undergoing iron and manganese treatment and chlorination. The blending ratio used in the lab was based on source flow proportions employed at the IC06 treatment facility at the time of sampling.

Prior to sample collection, sample taps were opened and diverted to waste to clear stagnant water. Samples for ATP and HPC analyses were collected following a 30 second flush after heat-sterilizing the sample taps using a portable butane torch. All other water samples were collected directly and stored headspace-free. During on-site sampling, pH, temperature, and free and total chlorine measurements were obtained according to standard methods.[76] Free and total chlorine were measured in the filtered water (where applicable) and/or at the entry to the distribution system. Analyses of Cl^-,[77] Br^-,[77] NH_3-N,[78] TDS,[76] conductivity,[76] and HPC[76] were completed by a certified drinking water laboratory (AmTest Laboratories, Kirkland, WA) in accordance with standard and US EPA methods. TI – comprising the sum of iodide, iodate, and molecular iodine – was also measured by AmTest, using inductively coupled plasma-atomic emission spectroscopy with procedures based on US EPA Method 200.7 (note that TI species could not be quantified individually by this method).[79] Samples used for ATP measurements were stored at 4 °C upon receipt at the UW labs, and processed within 24 hours (see Text S1 for details of ATP measurements). Samples used for DOC, A_{254}, HPLC/SEC, fluorescence EEM analyses, and DBP-FP tests were filtered with Milli-Q-rinsed 0.45 μm polyethersulfone (PES) membranes (Sterlitech) and stored at 4 °C upon receipt at the UW labs. Samples for TOC analyses were likewise stored at 4 °C upon receipt, but omitted the filtration step.

TOC and DOC concentrations were measured using a Shimadzu TOC-L_{CSH} high-temperature catalytic combustion system.[80] Free chlorine measurements during DBP-FP tests were undertaken using DPD colorimetry.[76] An Orion 5 Star meter with Orion ROSS Ultra pH electrode was used to measure pH in the UW labs. Field measurements of free and total chlorine concentrations were undertaken with a Hach Pocket Colorimeter II and DPD Reagent packets (as per manufacturer instructions), and field measurements of pH were obtained using a Hach Sension+ pH1 meter with Sension+ pH Probe 5050T.

UV Absorbance (A_{254}), Fluorescence EEM, and PARAFAC Analyses. Measurements of A_{254} and fluorescence EEMs were obtained for each sample (at native sample pH) on a Horiba Aqualog spectrofluorometer, using a 1 × 1 cm quartz cell. Excitation wavelengths ranged from 240 – 600 nm and emission wavelengths ranged from 245.2 – 826.7 nm. Sample EEMs were processed using Aqualog software to correct for inner filter effects, and Raman and Rayleigh scattering. PARAFAC analyses were performed on the whole set of IC and SJC sample EEMs to deconvolute the aggregate fluorescence for each sample into discrete fluorescent components indicative of DOM composition and reactivity (using tools available at www.models.life.ku.dk/algorithms).[72] PARAFAC analysis and component selection criteria are described in detail in Text S2.

HPLC/SEC-UV/Fluor./DOC Analyses. Size fractions of DOM were characterized by means of online HPLC/SEC-UV/fluor./DOC analyses, using a variation on reported methods (i.e., using pH 6.85, 13.8 mM phosphate buffer as mobile phase).[48, 70] Samples were resolved using a Tosoh Toyopearl HW-50S (250 mm x 20 mm, 3 μm) size exclusion column installed on a Dionex UltiMate 3000 HPLC equipped with a UV diode array detector, fluorescence detector (λ_{ex} = 320 nm/λ_{em} = 450 nm), and GE Sievers 900 Series Turbo online organic carbon detector with an inline inorganic carbon remover. Potassium hydrogen phthalate and polystyrene sulfonate standards were used to develop calibration curves for DOC concentration and molecular weight (MW), respectively. OpenChrom software (Lablicate GmbH and scientific community) was used to integrate peaks.

Disinfection Byproduct Formation Potential Tests and Analyses. Experiments to determine THM and HAA 7-day formation potentials (THM-FP and HAA-FP) were undertaken in accordance with SM 5710B,[76] with minor modifications. In each experiment, 25 mL volumes of filtered and buffered samples (10 mM phosphate, pH 7) contained within headspace-free amber glass vials were dosed with free chlorine concentrations expected to yield a final target residual of 3 – 5 mg/L as Cl_2. After 7 days incubation at 25 ± 2 ºC, two or more experimentally-independent replicate samples with free chlorine concentrations within the target residual range were quenched with sodium thiosulfate ($Na_2S_2O_3$) and analyzed for THMs and HAAs.

Samples were processed for analyses of THMs and HAAs in accordance with US EPA

Method 552.3,[81] with several modifications. Twenty mL of $Na_2S_2O_3$-quenched samples were acidified to pH < 2 with 98% purity H_2SO_4. After adding 2.7 M sodium sulfate, THMs and protonated HAAs were extracted into 4 mL methyl *tert*-butyl ether (MTBE) amended with internal standards (100 µg/L 1,2,3-trichloropropane and 2,3-dibromopropanoic acid) via vigorous mixing. Then, 3 mL of the MTBE layer containing THMs and HAAs was separated from the aqueous phase, and HAAs were esterified via addition of 1 mL acidified methanol (10% volume H_2SO_4) and heating at 50 °C for 2 hours. Control experiments confirmed that THM recoveries were not affected by passage through the HAA esterification step. After esterification, residual acid was neutralized with saturated aqueous $NaHCO_3$, and the mixed organic layer analyzed on a 30 m × 0.25 mm, 1.0 µm HP-1ms Ultra Inert column on a Shimadzu GC-2010 with electron capture detector.

Results and Discussion

Source Water Characteristics and Operational Parameters. Table 1 presents the ranges of general water quality parameters measured in samples of the raw and treated water sources for all studied systems. Descriptions of measured pH, NH_3-N, TDS, conductivity, ATP, and HPC values are provided in Text S3.

Halide Concentrations. All of the study sites are located near coastlines and potentially susceptible to seawater influence or intrusion. Seawater influence can be indicated by elevated (>100 mg/L) chloride concentrations and molar ratios of $[Br^-]/[Cl^-]$ close to the value for natural seawater of $\sim 1.5 \times 10^{-3}$.[5-8, 82, 83] Over the study year, IC01, IC05 Source02, IC07, SJC01, and SJC02 exhibited levels of chloride near or above the 100 mg/L threshold often associated with risk of seawater intrusion, with SJC02 exhibiting concentrations in excess of 150 mg/L (Table 1).

Table 1. Source water physical and inorganic parameters

System Name	Raw Water[a]									Treated Water[a]		
	pH	Temp.	Chloride	Bromide	Total iodine	[Br⁻]/[Cl⁻]	Cond.	TDS	NH_3-N	pH	Free Chlorine Residual	Total Chlorine Residual
	–	ºC	mg/L	mg/L	mg/L	molar ratio × 10^3	µmhos/cm	mg/L	mg/L	–	mg/L as Cl_2	mg/L as Cl_2
IC01	6.96 - 7.64	10.5 - 12.2	84 - 105	0.22 - 0.58	nd	0.93 - 2.91	550 - 620	340 - 390	nd - 0.005	7.13 - 7.83	0.17 - 0.3	0.23 - 0.37
IC02	6.96 - 7.28	10.2 - 12.7	61 - 69	0.14 - 0.26	nd - 0.12	0.95 - 1.67	610 - 950	300 - 450	0.32 - 0.40	7.11 - 7.7	nd - 0.05	nd - 0.83
IC03	7.73 - 7.75	12.0 - 13.0	17 - 18	0.05 - 0.57	nd - 0.12	1.23 - 14.6	390 - 460	240 - 320	nd	7.63 - 8.03	0.33 - 0.34	0.37 - 0.39
IC04	7.32 - 7.71	11.7 - 13	48 - 50	0.1 - 0.14	nd - 0.43	0.89 - 1.26	430 - 490	260 - 330	0.64 - 0.77	7.60 - 7.95	0.05 - 0.16	1.11 - 2.6
IC05 - S02	6.94 - 7.60	11.6 - 12.4	117 -140	0.25 - 0.38	nd - 0.21	0.83 - 1.33	660 - 780	420 - 540	0.33 - 0.39	7.8 - 8.1	0.03 - 0.23	0.47 - 1.22
IC05 - S03	6.80 - 7.40	11.3 - 12.0	61 - 67	0.12 - 0.24	nd - 0.20	0.88 - 1.64	580 - 680	400 - 460	0.23 - 0.92	7.41 - 7.67	nd - 0.03	0.19 - 0.25
IC06	7.0 - 7.35	11.2 - 16.0	57 - 88	0.14 - 0.31	nd - 0.15	1.02 - 2.86	660 - 950	350 - 580	0.06 - 1.06	8.01 - 8.13	0.08 - 0.77	0.14 - 0.94
IC07	7.16 - 7.36	11.7 - 12.4	92 - 145	0.16 - 0.48	nd - 0.25	0.75 - 1.59	840-1200	500 - 730	0.92 - 2.27	7.25 - 7.82	0.03 - 0.23	0.4 - 11.2
IC08	7.20 - 7.72	11.3 - 12.2	89 - 102	0.18 - 0.29	nd - 0.12	0.78 - 1.34	860 - 970	450 - 630	2.70 - 3.20	8.20 - 8.33	0.03 - 0.09	0.3 - 2.9
SJC01	7.36 - 7.7	10.8 - 11.3	130 - 151	0.14 - 0.57	nd	0.41 - 1.70	480 - 890	470 - 490	nd - 0.006	na	0.25 - 0.60	0.4 - 0.81
SJC02	7.66 - 7.82	11.2 - 11.6	176 - 258	0.19 - 0.59	nd	0.39 - 1.19	1100 - 1200	590 - 640	0.15 - 0.19	na	0.06 - 0.64	0.19 - 0.79
SJC03 - S01	7.42 - 7.77	11.3 - 12.2	66 - 114	0.07 - 0.19	nd	0.27 - 1.08	710 - 800	410 - 440	nd - 0.07	na	0.44 - 0.77	0.54 - 0.95
SJC03 - S02	7.48 - 7.75	10.2 - 13.9	32 - 70	nd - 0.10	nd	0.35 - 1.12	420 - 520	220 - 300	nd - 0.03	na	0.38 - 0.77	0.54 - 0.95
SJC04	7.40 - 7.92	8.7 - 12.1	69 - 110	nd - 0.31	nd	1.21 - 2.80	710 - 1110	410 - 510	nd - 0.07	na	0.54 - 1.05	0.68 - 1.24
SJC05	7.56 - 7.72	12 - 13.1	51 - 73	0.06 - 0.15	nd	0.42 - 1.18	560 - 610	300 - 360	0.06-0.11	na	nd - 0.39	0.015 - 0.43
SJC06	7.3 - 7.55	10.5 - 12.1	16 - 40	nd - 0.12	nd	0.55 - 1.40	480 - 510	240 - 350	nd - 0.02	na	0.02 - 0.06	0.02 - 0.21
SJC07	7.71 - 8.21	11.1 - 11.7	34 - 51	0.05 - 0.38	nd	0.46 - 4.95	480 - 550	210 - 300	0.12-0.15	na	0.71 - 1.06	0.71 - 1.29

[a] Data are provided as ranges of measurements obtained for each sample site over the duration of the study. nd = not detected.

Some apparent seasonal trends in chloride levels were also noted, with significantly higher chloride levels observed for several SJC sites (SJC01, SJC02, SJC03 Source01, and SJC07) during Q1 and Q4, and significantly higher levels observed during Q3 and Q4 for two IC sites (IC07 and IC08). Bromide levels ranged from below the detection limit (0.05 mg/L) to as high as 0.71 mg/L (Table 1), and varied widely from Q1-4, with much higher levels measured in Q4 for a number of sites. TI was detectable in only a few samples (LOD = 0.1 mg/L), though in some cases at elevated concentrations, with the highest level (0.43 mg/L) recorded for IC04 in Q3 (Table 1). Since iodine species could not be distinguished in TI analyses, the proportions present as iodide are uncertain; thus, measured TI values can only be taken as upper limits of possible iodide concentrations.

Molar ratios of $[\mathrm{Br}^-]/[\mathrm{Cl}^-]$ measured for each site varied from 0.4×10^{-3}–1.5×10^{-2}, but were more typically within a range of ~$1–2 \times 10^{-3}$ (Table 1). Overall, bromide concentrations were only weakly correlated ($R^2 = 0.32$) with chloride concentrations across the sample set (Figure S1). Although chloride levels in excess of 100 mg/L and $[\mathrm{Br}^-]/[\mathrm{Cl}^-]$ ratios near 1.5×10^{-3} imply the existence of seawater intrusion, they are not definitive, and can be attributed to other sources, such as connate water, sea spray deposition, manure application, or septic field infiltration.[5, 6, 83] Thus, the relatively weak correlation of $[\mathrm{Br}^-]$ with $[\mathrm{Cl}^-]$ could reflect influences from various factors other than or in addition to seawater intrusion.

Nevertheless, the data in Table 1 (including TDS and conductivity values; see Text S3) suggest that seawater intrusion may influence the chemistry of a number of the water supplies investigated – potentially leading to elevated halide levels. Especially notable in this context is that neither bromide nor iodide are part of regulatory source water monitoring in federal or WA regulations. Although beyond the scope of this work, the potential for elevated iodide concentrations (and associated impacts on I-DBP formation) in source waters warrants further study within this context, especially in light of the potential health risks of I-DBPs.[1, 2, 27, 28]

Total and Dissolved Organic Carbon. Across the sample set, DOC concentrations ranged from 0.54 – 7.9 mg_C/L (Figure S3a). TOC and DOC concentrations for individual sites frequently exhibited variation across quarters, with particularly high seasonal variation observed in the case of SJC06, for which DOC varied from 1.3 to 7.9 mg_C/L, with lower values in the dry season (Q1, Q4) and higher values in the rainy season (Q2, Q3). Such trends for SJC06 suggest that heavy precipitation may result in increased percolation of DOC into the aquifer from external sources or DOC-rich soils within the recharge zone, and may in turn result in significant seasonal impacts on the effectiveness of the chlorination process at this site. TOC for each site appeared to be essentially all dissolved, with TOC concentrations exhibiting a nearly 1:1 correlation with the corresponding DOC concentrations for each sample (Figure S3b).

UV Absorbance at 254 nm (A_{254}). Values of A_{254} can provide a measure of the abundance of aromatic DOM constituents in a given sample, and in many cases, a reasonable surrogate of DOC concentration on the whole (provided the relationship of A_{254} to DOC concentration is known, e.g., via determination of specific UV absorbance ($SUVA_{254}$)).[50, 63] Similar to DOC, measurements of A_{254} also varied substantially across the sample set (Figure S4), but generally correlated well with DOC over the study period ($R^2 = 0.95$) (Figure 3a), consistent with previous findings for various other waters.[37, 63, 84] Exceptionally high A_{254} values were noted in the treated IC samples and the Q3 SJC07 sample (Figure S4), and were excluded from the correlation with

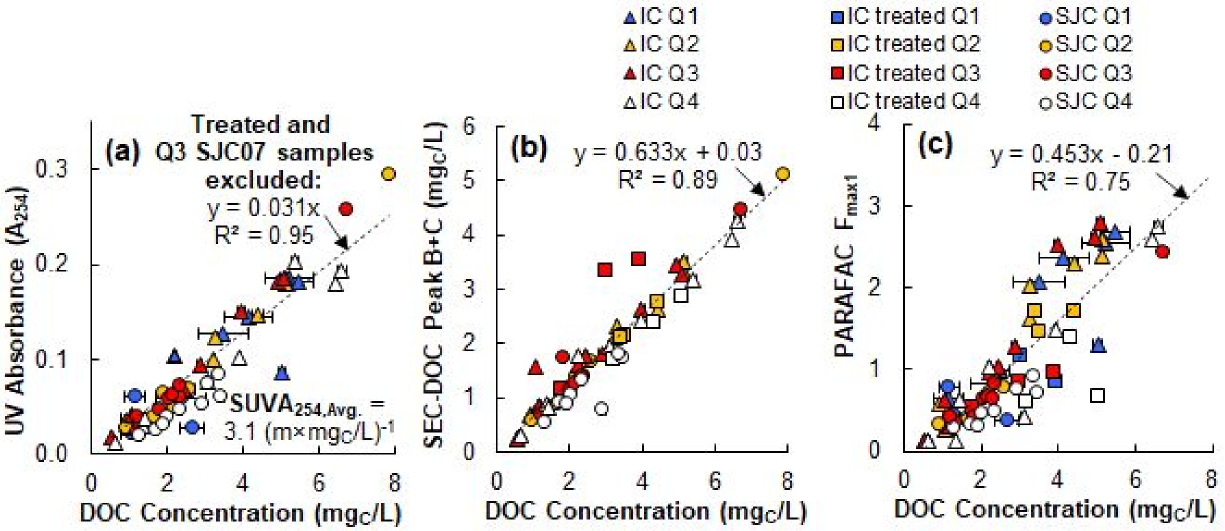

Figure 3. (a) A_{254} versus DOC concentration; (b) SEC-DOC Peak B+C concentration versus DOC concentration; and (c) PARAFAC Fmax1 versus DOC concentration. Spectroscopic measurements (A_{254} and F_{max1}) were obtained at native sample pH. Data points and error bars represent means and standard deviations, respectively, obtained from at least duplicate experimentally-independent measurements.

DOC as outliers. While the origins of the high absorbance within the Q3 SJC07 sample remain unclear, the high A_{254} values observed for the treated IC samples were due to background absorbance from excess $Na_2S_2O_3$ used to quench free chlorine during sampling.

$SUVA_{254}$ values were quite uniform for the aggregate IC and SJC dataset, even across seasons, with an overall $SUVA_{254}$(±95% C.I.) = 3.1(±0.2) $(m\times mg_C/L)^{-1}$ after exclusion of the Q3 SJC07 and IC post-treatment outliers noted above (Figure 3a). This is within the range of typical $SUVA_{254}$ values for groundwaters and surface waters.[7, 8, 18, 32, 53, 80] The relatively low $SUVA_{245}$ variability within the IC and SJC samples suggests similar DOM properties and fairly uniform diagenetic processing within the aquifers at each site.

HPLC/SEC–UV/Fluor./DOC Size Fractions. In accordance with previous studies, HPLC-SEC chromatograms can be resolved into the following regions representing characteristic size fractions of DOM: (A) biopolymers and high MW hydrophilic compounds, (B) humic substances, (C) building blocks (i.e., humic substance sub-constituents), (D) low MW acids, and (E) low MW neutral molecules.[47, 48, 70] An example chromatogram is depicted in Figure S5. The late eluting peak in the DOC chromatogram corresponds to HCO_3^{-}/CO_3^{2-} that was not completely removed by the system's inorganic carbon removal module (due to the high levels of total carbonate in some of the groundwater samples). All sample chromatograms lacked a distinct biopolymer/high MW hydrophilic DOC peak – an important indicator for DOM of recent biological origin (e.g., algal- or wastewater-derived organic matter). This indicates that DOM in the samples is primarily naturally occurring and terrestrial in origin, consistent with relatively pristine groundwaters.[47, 48] This is also consistent with the generally low average HPCs and ATP levels observed across the sample set (Text S3, Table 1).

The SEC peaks corresponding to fractions (B) and (C) (humic substances and building blocks) contain aromatic constituents responsible for much of the fluorescence and A_{254} of bulk DOM in the samples.[47, 48] The DOC signal areas for these peaks (henceforth referred to together as SEC-DOC Peak B+C concentration, in mg_C/L, or [SEC-DOC Peak B+C], in molar units) in turn provided a potential quantitative surrogate measurement of aromatic DOM constituents for each sample (Figure S6), and correlated relatively well with bulk DOC measurements (R^2 = 0.89) (Figure 3b). The relative uniformity of [SEC-DOC Peak B+C]/[DOC] ratios across samples also suggests low seasonal variation in DOM character (as opposed to quantity), even for SJC06; consistent with the noted uniformity in $SUVA_{254}$ values (Figure 3a).

Fluorescence. Prior work has demonstrated that DOM source can be distinguished via characteristic regions of excitation-emission maxima and ratios of fluorescence intensity obtained at specific excitation-emission wavelength pairs.[39, 47, 51, 85-93] In all IC and SJC samples, local excitation/emission maxima were observed within the ranges of 250-270/400-450 nm and

320-340/400-450 nm (see Figure S7a for a representative fluorescence EEM), which are typical for humic-like constituents associated with terrestrial DOM.[39, 44, 71, 90, 93, 94] By comparison, DOM constituents characteristic of microbial activity (e.g., bacteria in wastewaters, algae in surface waters) exhibit excitation/emission maxima attributed to amino acids/proteins and soluble microbial products in the region 250-300/330-380 nm.[39, 44, 47, 86-88, 93] PARAFAC modeling of the full sample set identified 4 components that together could account for the observed EEMs (Table S2, Figure S7b-e), with Component 1 representing the dominant contribution to bulk DOM fluorescence in the IC and SJC samples (based on magnitudes of fluorescence intensity, F_{max}), followed by Components 2, 4, and 3 (Text S2). Literature analogues to Components 1-3 are typically attributed to humic-like constituents of DOM, whereas analogues to Component 4 have been attributed to protein-like (possibly microbially-derived) constituents (see Table S2 for comparisons to analogous components reported by other investigators).[60, 64, 71, 93, 95, 96] The relative dominance of humic-like constituents in comparison to protein-like constituents provides additional evidence that the DOM at each site is predominantly terrestrial in origin. In general, of the four PARAFAC components, F_{max} values for Component 1 (F_{max1}, summarized in Figure S7f) were found to correlate most strongly with DOC concentrations ($R^2 = 0.75$) (Figure 3c), though correlations were weaker than for A_{254} or SEC-DOC Peak B+C concentrations (Figure 3a,b). The increased variability in fluorescence characteristics could be due to a variety of factors, including differences in relative fluorophore and UV chromophore abundance (e.g., due to differences in extents or types of light-absorbing aromatic group substitution),[51, 94] effects of metal-DOM complexes,[97] or higher susceptibility of fluorophores (compared to UV chromophores) to variations in pH (as samples were analyzed at their native pH values, averaging 7.4(±0.3) for IC sites and 7.6(±0.2) for SJC sites).[51, 94, 98-100]

Calculation of the fluorescence index (FI) (i.e., the ratio of emission intensities at λ = 470 nm ($I_{\mathrm{Ex370/Em470}}$) and λ = 520 nm ($I_{\mathrm{Ex370/Em520}}$) for excitation at λ = 370 nm[51, 91, 101]) yields an average FI(±95% C.I.) = 1.6(±0.1) across the study area (Figure S8). This FI value – intermediate between the bounds of ~1.2 and ~1.8 typically attributed to purely terrestrial and purely microbial character, respectively [91, 102] – suggests a contribution of microbial processing to the DOM fluorescence signature, and when taken together with the SUVA_{254}, SEC, and PARAFAC data noted above, is generally consistent with soil-derived, terrestrial DOM subject to heterotrophic metabolism and/or physical-chemical fractionation in shallow aquifers, peatlands, and wetlands.[54, 102, 103] The relative constancy of the FI (Figure S8) also further affirms the high spatial and temporal homogeneity of DOM character across the study area.

Disinfection Byproducts. *Formation Potentials and Bromine Substitution Factors.* Seven-day DBP-FP tests are designed to enable standardized measurements of the concentrations in a given water sample of DBP precursors that react when continuously exposed to an elevated chlorine residual over an extended time.[16, 62, 76, 104, 105] While DBP-FP values may not directly reflect the DBP concentrations that can be expected to form under the operating conditions within the treatment facility or distribution system for a given site (as they do not account for variations in pH, temperature, or free chlorine exposure likely to be encountered in practice),[104] the holding time (7 days) specified for the DBP-FP test is within ranges of theoretical maximum distribution residence times for most of these small systems (Table S1). Thus, DBP-FP measurements can provide valuable insight into the “worst-case” conditions that can be anticipated at each site. Standardization of the conditions used for the formation potential tests also facilitates intercomparison of results amongst sites, and can help to identify trends in the inherent characteristics of DBP precursors amongst the full sample set.

As a complement to DBP-FP measurements, bromine substitution factors (BSFs) can provide a measure of the molar proportion of bromine incorporation relative to overall halogen content of the THMs or HAAs. BSFs for TTHM (BSF_{TTHM}), HAA5 (BSF_{HAA5}), and HAA9 (BSF_{HAA9}) were calculated according to Equations 1-3,[106]

$$BSF_{TTHM} = \frac{[BDCM] + 2 \times [DBCM] + 3 \times [Bromoform]}{3 \times [TTHM]} \tag{2}$$

$$BSF_{HAA5} = \frac{[BAA] + 2 \times [DBAA]}{([CAA] + [BAA]) + 2 \times [DCAA] + [DBAA]) + 3 \times [TCAA]} \tag{3}$$

$$BSF_{HAA9} = \frac{[BAA] + [BDCAA] + [BCAA] + 2 \times ([DBAA] + [DBCAA]) + 3 \times [TBAA]}{[CAA] + [BAA] + 2 \times ([DCAA] + [BCAA] + [DBAA]) + 3 \times ([TCAA] + [BDCAA] + [DBCAA] + [TBAA])} \tag{4}$$

where BSF values range from 0 to 1, with the minimum and maximum signifying exclusively chlorinated or brominated THMs or HAAs, respectively.

Figure 4 shows measured THM-FPs and HAA-FPs, in addition to corresponding BSF values, for each sample site over the four study quarters, as well as the historical six-year average (2010–2016) of distribution system DBP concentrations reported for regulatory compliance purposes (also depicted in Figure 2). For most of the water systems, DBP-FPs did not correlate directly with the six-year averages of regulatory distribution sampling; typically, DBP-FPs were higher, consistent with differences between conditions used in the formation potential tests and those encountered in the field.[104] However, sites with historically elevated DBP concentrations or BSFs did consistently yield high DBP-FPs or associated BSFs; aside from IC01 and SJC01, for which Q1-Q3 TTHM-FP levels were below their historical averages. Of the five study sites with historically low regulatory DBP yields, DBP-FP results for two (IC03 and SJC05) were consistent with the regulatory monitoring results, while DBP-FPs for the other three systems

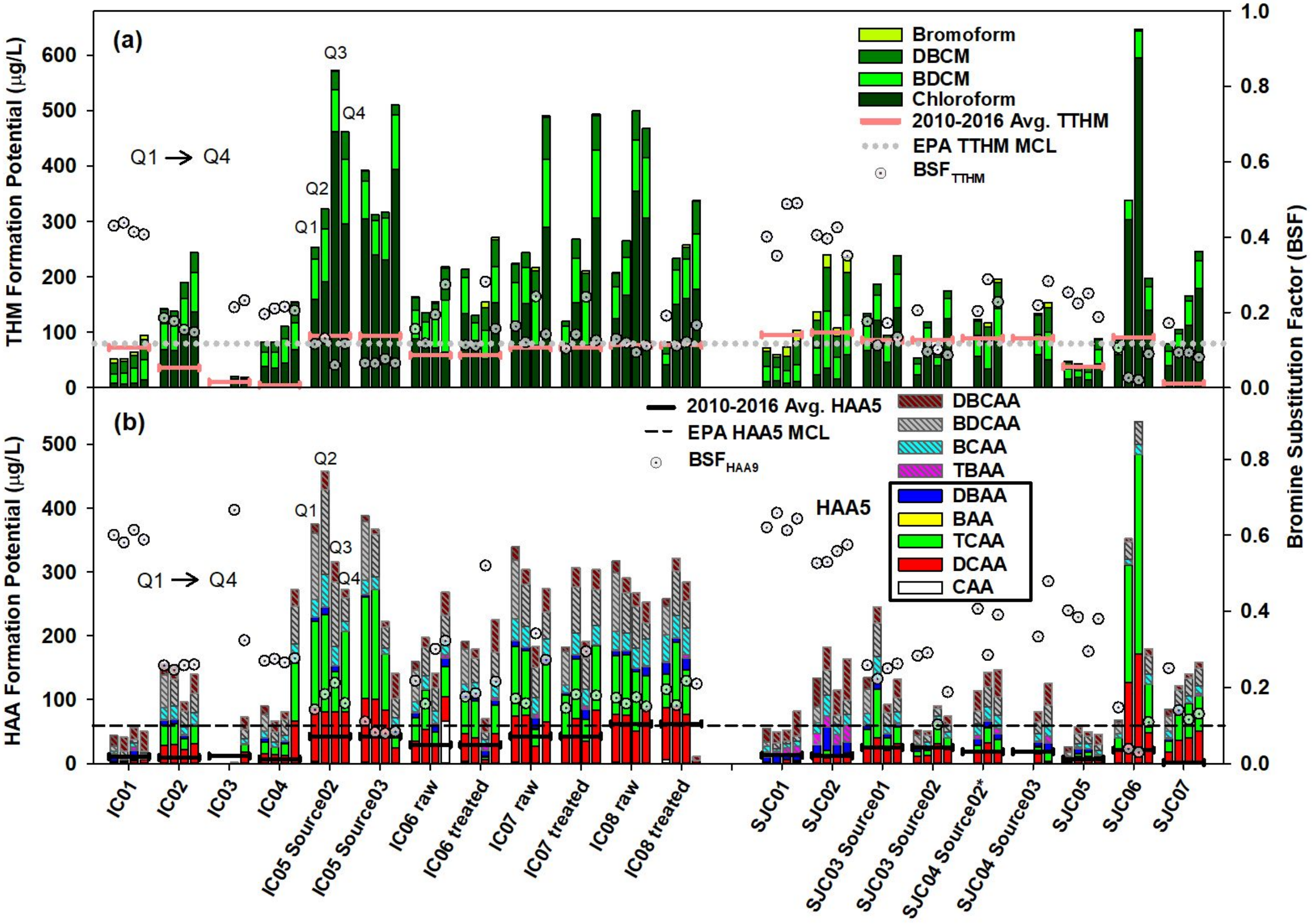

Figure 4. (a) Average THM-FP; and (b) average HAA-FP, plotted with measured historical TTHM and HAA5 averages between 2010-2016. Species included in HAA5 are denoted by bold, black bordered bars; remaining HAA species comprising HAA9 are denoted by bars with hatched fills. BSF_{TTHM} or BSF_{HAA9} for each sample is also plotted (circles) on the secondary y-axis. *Q2 samples plotted for SJC04 Source02 are the operating blend of Source02 and Source03. Average DBP-FP values from at least duplicate (and typically triplicate) experimentally-independent measurements. Dotted/Dashed lines represent the US EPA MCLs for TTHMs/HAA5.

(IC02, IC04, and SJC07) exceeded the historical average.

As evident from the DBP-FP data in Figure 4, nearly every site included in the study (with the exception of IC03) exhibited TTHM-FP levels in excess of the TTHM MCL, indicating that they could each potentially exceed the TTHM MCL under chlorination conditions sufficient to ensure complete consumption of THM precursor groups. Furthermore, only 5 sites (IC01, IC03, SJC01, SJC02, and SJC05) consistently yielded HAA5-FP values below the HAA5 MCL, illustrating that the majority are also at potential risk of exceeding the HAA5 MCL. Whether or not sites exceed MCLs in practice must therefore be primarily a function of the operational parameters at each site (e.g., pH, temperature, and free chlorine exposure); noting that sites IC02, IC04, SJC05, and SJC07 were included in the study as historically compliant DBP sites, yet each was found to yield TTHM-FP and HAA5-FP values in excess of the MCLs.

IC samples generally yielded higher TTHM-FPs and HAA9-FPs when compared to SJC samples. The higher TTHM-FP results for IC samples were initially surprising, given that the regulatory sample results for DBPs are similar between the two counties (Figure 2). Sites with the highest TTHM-FPs and HAA9-FPs also yielded mainly chlorinated DBP species, whereas BSF values were higher for many samples with lower DBP-FPs (e.g., IC01, SJC01, SJC02).

In a number of systems, DBP-FPs varied significantly over the four sampling quarters, consistent with seasonal variations observed for DOC concentrations (Figure S3a). For example, TTHM-FPs for SJC03 Source02 and SJC07 varied from low concentrations in Q1 (54 µg/L and 80 µg/L, respectively) to levels three times higher in Q4, and TTHM-FPs for IC07 and IC08 treated samples quadrupled from Q1 to Q4. Additionally, SJC06 exhibited substantially higher TTHM-FP and HAA-FP in the rainy season (Q2 and Q3) compared to the dry season (Q1 and Q4), ranging from a low of 92 µg/L in Q1 to a high of 646 µg/L TTHM in Q3. Furthermore, TTHM-FP for IC05 Source02 more than doubled between Q1 and Q3, from 253 to 573 μg/L.

The correlations of variations in DBP-FP for such sites (Figure 4) with seasonal variations in source water DOC concentrations (Figure S3a) suggest that such trends may likewise contribute to substantial seasonal variations in DBP yields during full-scale treatment, though this would often not be captured under current regulatory monitoring regimens.

Correlations of DBP Formation Potentials and BSFs with Source Water Characteristics.

General Water Quality Parameters. No clear correlations were observed of TTHM-FP, HAA5-FP, HAA9-FP, or corresponding BSF values with Cl^-, Br^-, TI, or TDS concentrations; conductivity; NH_3-N concentrations; HPCs; or ATP concentrations.

Dissolved Organic Carbon Concentrations. As seen in Figure 5, TTHM-FPs, HAA5-FPs, and HAA9-FPs generally correlated well with DOC concentrations (with $R^2 \geq 0.72$), consistent with observations from numerous prior investigations,[18, 32, 63, 66, 67, 84, 107] with slopes of the linear regressions for each plot representing rough estimates of the average moles of DBPs formed per mol of untreated DOC (i.e., specific DBP formation potentials) for the IC and SJC samples. The value of 6.9×10^{-3} mol_{TTHM}/mol_C (Figure 5a) corresponds to a mass-based specific TTHM-FP of 72 $\mu g_{TTHM}/mg_C$, which is much higher (>90th percentile for groundwaters) than respective median values of ~40 $\mu g_{TTHM}/mg_C$ and ~50 $\mu g_{TTHM}/mg_C$ reported for a large groundwater and surface water dataset,[32] suggesting that DOM in the IC and SJC source waters is particularly rich in DBP precursors compared to DOM pools in many other waters. Furthermore, the strength of the correlations also indicates that DOM quality and reactivity toward free chlorine were fairly consistent across the sample set (i.e., that DBP-FPs across the study area were mainly a function of DOC concentration, rather than differences in DOM character from site to site or seasonally),

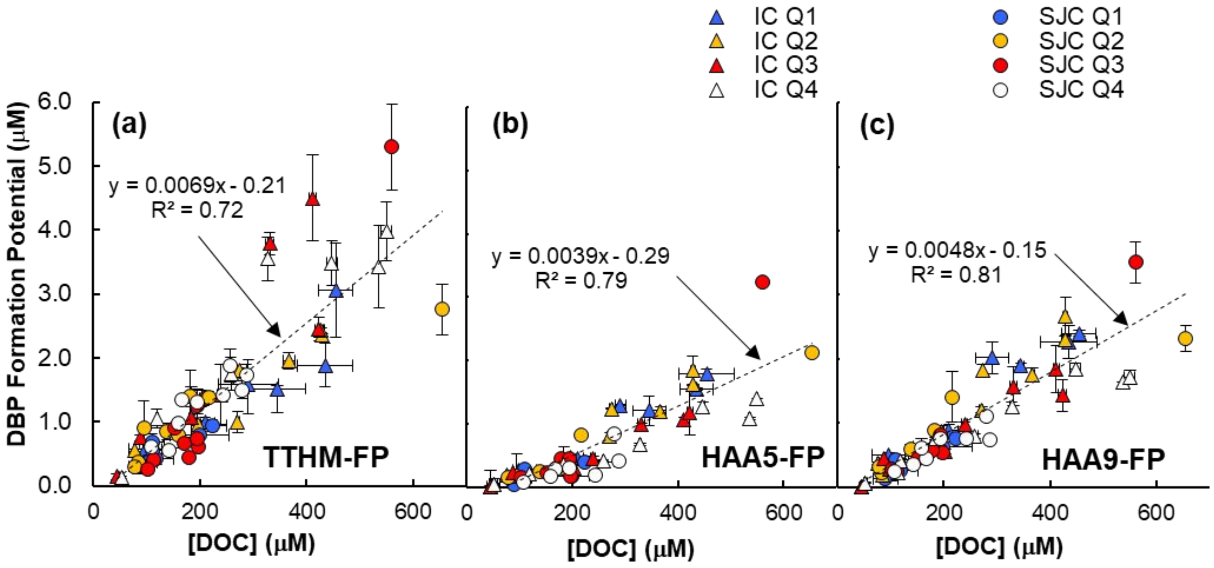

Figure 5. (a) TTHM-FP; (b) HAA5-FP; and (c) HAA9-FP plotted versus [DOC]. Treated samples were excluded because of limited differences in [DOC] (and DBP precursors) before and after treatment processes applied at each site. Data points and error bars represent means and standard deviations, respectively, obtained from at least duplicate (and typically triplicate) experimentally-independent measurements.

consistent with the relatively constant $SUVA_{254}$ and FI values noted above.

UV absorbance (A_{254}). When samples exhibiting extraneous absorbance (i.e., the treated IC samples and the Q3 SJC07 sample) were excluded, correlations of TTHM-FP, HAA5-FP, and HAA9-FP with A_{254} were fairly strong (with $R^2 \geq 0.73$ in all three cases; Figure 6), consistent with the strong correlations of A_{254} with DOC (Figure 3a), and in good agreement with many prior observations.[33, 53, 63, 66, 84, 96, 108, 109] In contrast, no clear correlations of DBP-FPs with $SUVA_{254}$ were observed (Figure S9), primarily on account of the minimal variability in $SUVA_{254}$ values across the sample set (note the clustering of data around the mean $SUVA_{254} = 3.1(\pm0.2)$ $(m\times mg_C/L)^{-1}$ in Figure S9). This further highlights that variations in DBP-FPs within the study area arise primarily from differences in quantity rather than character of source water DOM.

HPLC/SEC–UV/Fluor./DOC Size Fractions. As shown in Figure S10, TTHM-FP, HAA5-FP, and HAA9-FP correlated fairly well with [SEC-DOC Peak B+C], though the

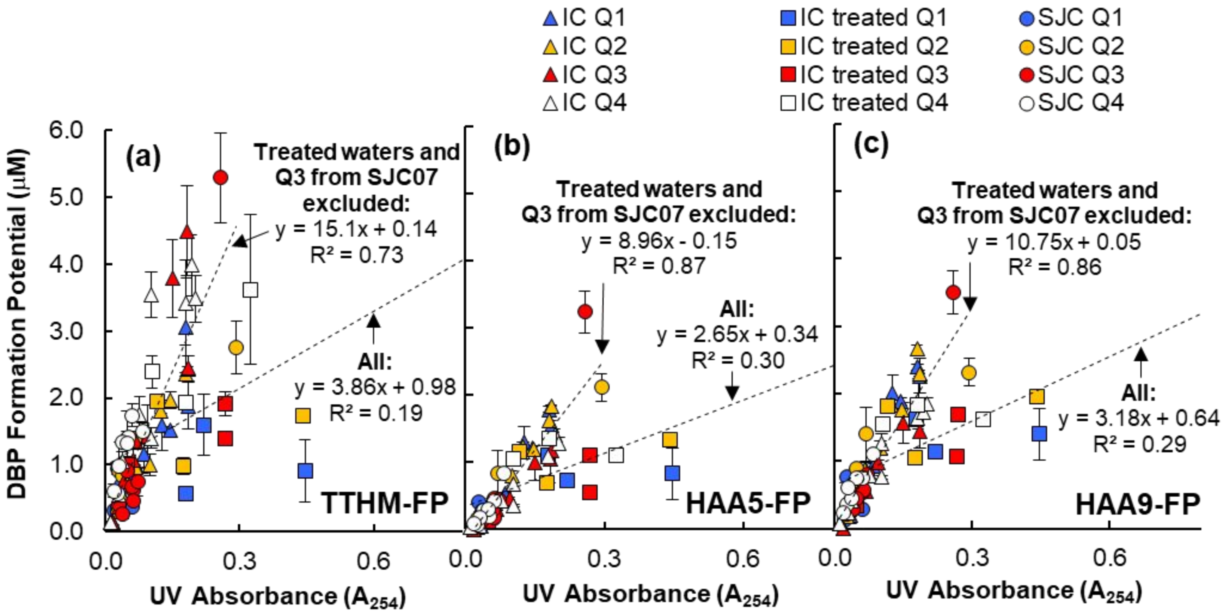

Figure 6. (a) TTHM-FP; (b) HAA5-FP and; (c) HAA9-FP plotted versus A_{254}. Regression lines were obtained with and without outlier samples exhibiting extraneous absorbance due to background matrix constituents (i.e., treated samples and the Q3 sample of SJC07). Measurements of A_{254} were obtained at native sample pH. Data points and error bars represent means and standard deviations, respectively, obtained from at least duplicate (and typically triplicate) experimentally-independent measurements.

coefficients of determination for regressions of DBP-FP versus [SEC-DOC Peak B+C] ($R^2 \geq 0.69$) were lower than those versus bulk DOC concentrations ($R^2 \geq 0.72$) or A_{254} ($R^2 \geq 0.73$).

Fluorescence. In previous studies, PARAFAC components having similar excitation/emission characteristics as Components 1, 2, and 3 (as defined in this model), have been positively correlated with THM and HAA formation potentials.[53, 60, 64, 71, 96, 110] The fluorophore groups comprising these components are likely to include pools of activated aromatic molecules that exhibit relatively high reactivity toward free chlorine, and may hence serve as precursors for DBP formation.[71] The present work found that F_{max} for Component 1 (F_{max1}) correlated strongly with F_{max2} and F_{max3} (with $R^2 \geq 0.97$); therefore, F_{max1} was evaluated as a general surrogate for such DBP precursors. Figure S7f depicts the F_{max1} values derived for each site. As shown in Figure S11, TTHM-FP, HAA5-FP, and HAA9-FP each correlated with

F_{max1} ($R^2 \geq 0.60$), though with lower coefficients of determination than for DOC, A_{254}, or [SEC-DOC Peak B+C] (consistent with the greater variability of F_{max1} across the sample set).

Relative Concentrations of Bromide and DOC. Neither DBP-FPs nor BSFs correlated well with concentrations of bromide alone ($R^2 < 0.20$), as shown in Figures S12 and S13. When considering that speciation of HAAs and THMs involves competition of free bromine and free chlorine for the same DBP precursor sites in DOM, and that free bromine generally reacts faster with organic compounds (leading to more brominated DBPs for equivalent levels of free bromine and chlorine),[7, 13, 15, 16, 18, 22, 111] it is clear that bromination of DBP precursor sites will depend on available concentrations of free bromine *and* DBP precursor sites. In a system containing excess free bromine, DBP precursor sites would be predominantly brominated (with BSF approaching 1 as free bromine concentration increases relative to DBP precursor sites), whereas in a system limited by free bromine, DBP precursor sites that are not rapidly brominated could instead react with excess free chlorine, leading to lower BSFs. Thus, BSF should depend on the ratio of $[Br^-]$ to DBP precursor site concentrations (assuming stoichiometric conversion of bromide to free bromine by molar excess free chlorine). Provided DBP precursor concentrations are proportional to DOC concentrations, BSF should increase to an asymptotic maximum with increasing $[Br^-]/[DOC]$ ratios as more free bromine becomes available to react with precursor sites in lieu of free chlorine, consistent with prior observations.[7, 8, 11, 18-20, 112] To investigate this, BSF_{TTHM}, BSF_{HAA5}, and BSF_{HAA9} data obtained for IC and SJC samples were fit to a model of the form, $[BSF] = 1 - e^{-m([Br-]/[DOC])}$, where, *m* represents an empirical constant dependent on properties of the DOM subjected to halogenation. As shown in Figure 7a,c, regression of the data according to this model yielded reasonably good correlations ($R^2 \geq 0.65$) for BSF_{TTHM} and BSF_{HAA9} when IC03 samples were excluded (as BSFs for the IC03 site were biased by very low

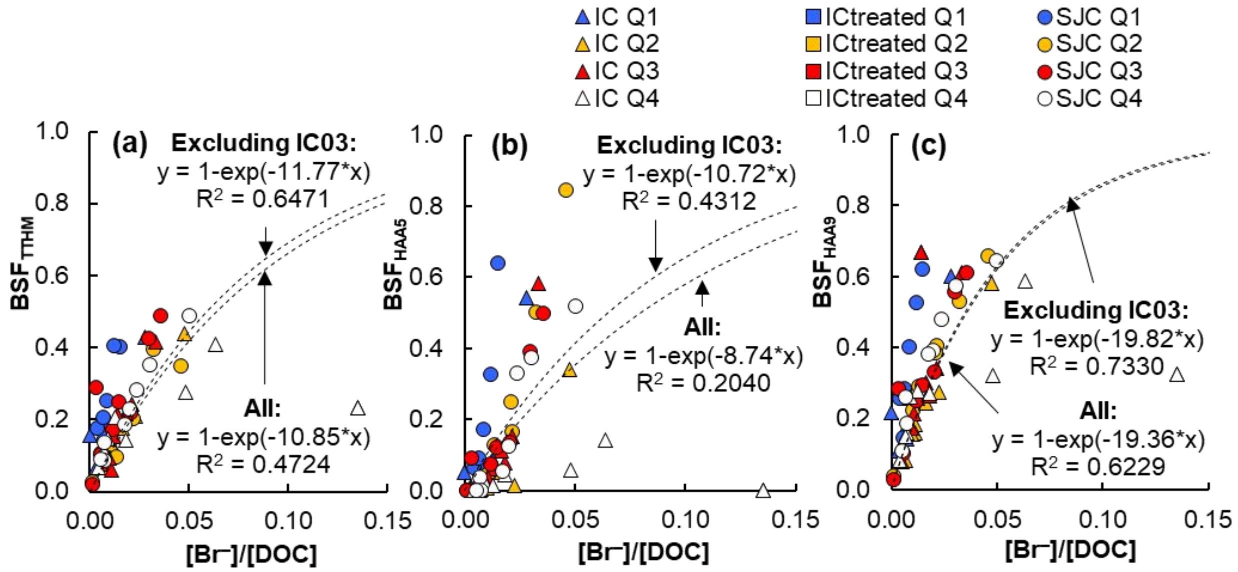

Figure 7. (a) $\mathrm{BSF}_{\mathrm{TTHM}}$; (b) $\mathrm{BSF}_{\mathrm{HAA5}}$; and (c) $\mathrm{BSF}_{\mathrm{HAA9}}$ plotted versus the molar ratio of bromide to dissolved organic carbon (DOC) concentrations.

total HAA and THM values in the denominators of the BSF expressions). In contrast, only a weak correlation was observed for $\mathrm{BSF}_{\mathrm{HAA5}}$ (Figure 7b) – likely because only a subset of the brominated HAAs are included in HAA5. A recent study has also shown strong correlations of BSF with $[\mathrm{Br}^-]/A_{254}$ ratios.[112] Accordingly, the IC and SJC data could also be fit to the model $[\mathrm{BSF}] = 1 - e^{-m([\mathrm{Br}-]/\mathrm{A254})}$, though correlations were not as strong as for $[\mathrm{Br}^-]/[\mathrm{DOC}]$ (with R^2 = 0.46, 0.48, and 0.65 for $\mathrm{BSF}_{\mathrm{TTHM}}$, $\mathrm{BSF}_{\mathrm{HAA5}}$, and $\mathrm{BSF}_{\mathrm{HAA9}}$, respectively, when excluding IC03 and Q3 SJC07 sample data for reasons noted above and in the discussion of Figure 3a).

Practical Implications. *Dual Impacts of DOC and Bromide on DBP Formation in Coastal Groundwater Systems.* Two of the most significant water quality parameters identified in this study as influencing DBP formation potentials and speciation in the investigated groundwaters are [DOC] and $[\mathrm{Br}^-]$, consistent with prior findings.[7, 11, 16, 18, 22, 32, 63, 67, 113] As noted above, DOM in groundwaters at the studied sites appears to be primarily terrestrial in origin (i.e., soil-derived, and not originating from algae, wastewater, or other anthropogenic sources); therefore source control efforts toward mitigating DBP formation are not practical. The DOM character is also fairly consistent from site to site, with TOC being nearly all dissolved (Figure S3b). The relative invariance of DOM character at the IC and SJC sites suggests that accurate knowledge of DOC (or TOC) concentrations in source waters in the study area can be used to anticipate groundwater systems that are more likely to have HAA and THM compliance issues associated with chlorination. For example, DBP-FPs for the IC and SJC sites suggest that TTHMs would not likely exceed MCLs for source waters with less than ~1.2 mg_C/L of DOC, while HAA5s would not likely exceed MCLs for source waters with less than ~2.1 mg_C/L of DOC (Figure 5a,b). DOC (or TOC) should in turn be considered a critical design and routine monitoring parameter for groundwater systems such as these, as is already the case for surface water systems.[68, 69]

The large seasonal variations observed in DOC concentrations and DBP-FP values for several groundwater sources in the study have significant implications for WA's implementation of the US EPA's Stage 1 and 2 Disinfectants and Disinfection Byproducts Rules (DBPRs). Many groundwater systems that chlorinate are only required to collect a single annual DBP sample to characterize DBP levels in the system (usually during the period of warmest water temperature, such as in the summer/dry season, which is also generally a high demand/lower water age period for these systems).[68, 69] If this sample result is low, no further samples are collected during the rest of the year. This approach for determining potential exposure of water system customers to DBPs is predicated on the assumption that groundwater quality and distribution system residence time do not change throughout the year, which is not the case for some sites included in this study and could likewise be a concern for many other groundwater sources. Regular monitoring of DOC (or TOC) concentrations in the source waters of these and other coastal groundwater sites is therefore highly recommended. In the event that more frequent monitoring is needed, there is also potential for utilizing A_{254} as a surrogate for DOC concentration, considering the widespread availability of lab and field spectrophotometers and the utility of A_{254} as a predictor of DBP-FPs across the investigated sample set, and in many other systems.[53, 56, 63, 84, 96, 108, 109, 114]

In contrast to HAA-FP and THM-FP values, DBP speciation – as quantified by means of BSFs – does not appear to exhibit direct dependence on any single parameter monitored during the study. Rather, because of variations in both $[Br^-]$ and [DOC] across the study area, BSFs appear to depend primarily on *molar ratios* of $[Br^-]$/[DOC], with higher $[Br^-]$/[DOC] values indicative of a higher tendency to form brominated HAAs and THMs (especially the unregulated HAAs included in HAA9, as evident from the bars with hatched fills in Figure 4), as observed in prior studies.[10, 11, 18, 112, 113] Thus, it may be feasible to utilize $[Br^-]$/[DOC] to estimate the extent to which DBPs are likely to be dominated by brominated species at various groundwater sites.

To evaluate variations in DBP yields and speciation across the IC and SJC sites with respect to both $[Br^-]$ and [DOC], measured DBP-FP and BSF values were re-plotted in heat maps versus $[Br^-]$ and [DOC] (Figure 8), akin to matrix diagrams presented by Krasner et al. (1994) for an investigation of seawater intrusion in surface waters of the Sacramento-San Joaquin River Delta.[10] Consistent with Figure 5, Figure 8a-c shows that TTHM-FP, HAA5-FP, and HAA9-FP increased with increasing DOC concentrations, and that there was little dependence of DBP-FPs on $[Br^-]$ alone across the IC and SJC sites (see also Figure S12). Figure 8 also shows that while sites with higher [DOC] levels exhibited higher *absolute yields* of mostly chlorinated DBP species, sites with lower [DOC] levels exhibited higher *proportions* of brominated DBPs at a given $[Br^-]$ level, in agreement with prior studies.[7, 10, 18, 111, 113] Accordingly, the IC and SJC sites at greatest risk for high proportions of brominated DBPs (BSFs > 0.1) appeared to be those with

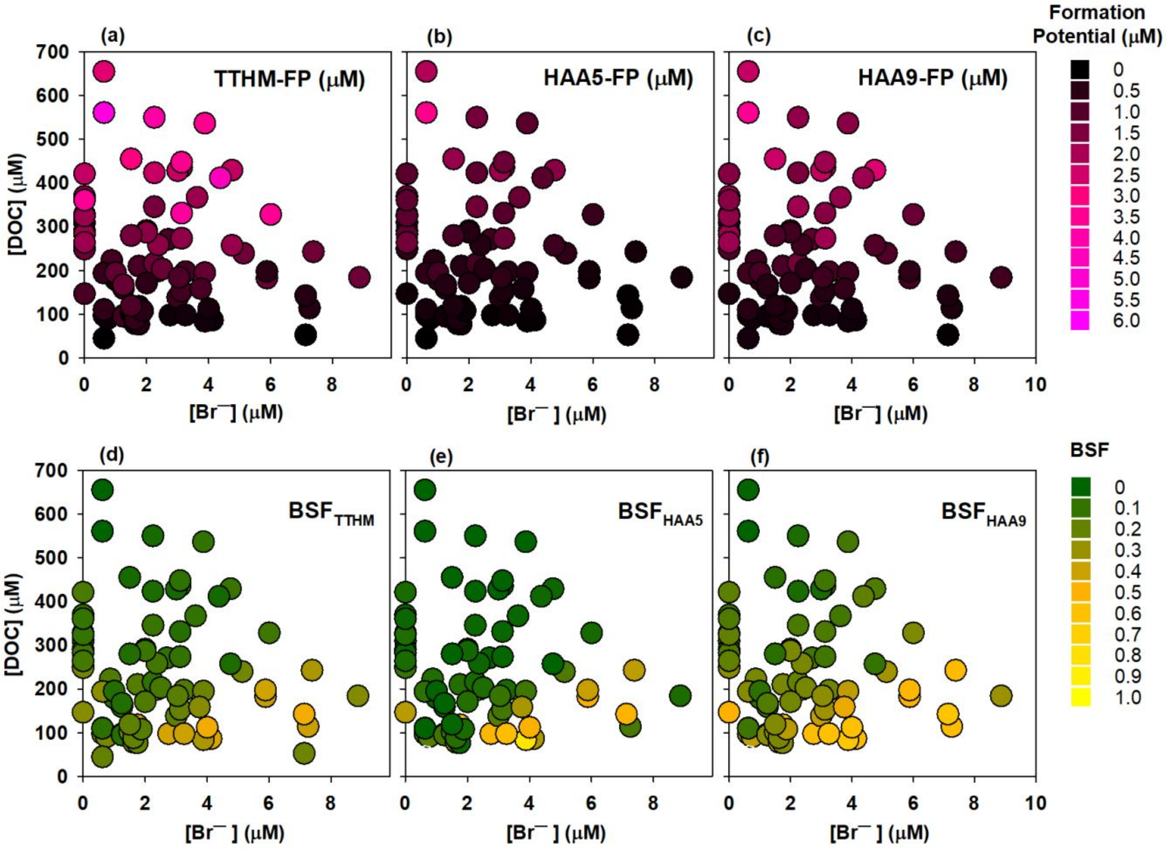

Figure 8. Heat map plots of (a) TTHM-FP); (b) HAA5-FP; (c) HAA9-FP; (d) BSF$_{TTHM}$; (e) BSF$_{HAA5}$; and (f) BSF$_{HAA9}$ plotted versus [DOC] and [Br$^-$].

high [Br$^-$] (above ~2.5 μmol/L, or ~200 μg/L) and low [DOC] (below ~250 μmol/L, or ~3 mg$_C$/L), or [Br$^-$]/[DOC] ratios above ~0.01 (Figure 7). This agrees quite well with findings by Francis et al. (2010) based on Information Collection Rule data.[113]

By combining the DBP-FP and BSF datasets, one can also conclude more generally that groundwater systems with low [Br$^-$] and high [DOC] (e.g., SJC06) are at risk for high absolute levels of DBP formation, but with a predominance of chlorinated DBPs, whereas systems with high [Br$^-$] and low [DOC] (e.g., SJC01) would likely exhibit relatively lower absolute levels of DBP formation, but with the risk of substantial proportions of brominated DBPs, consistent with prior observations.[10, 113] Systems falling into the upper right quadrants of each panel of Figure 8 (i.e., systems with high [Br$^-$] *and* high [DOC]) would likely be of greatest concern from a regulatory and public health perspective, as these would be anticipated to exhibit high levels of DBP formation *and* high BSFs,[9, 10, 17, 20] though additional measurements from systems with such characteristics would be needed to confirm this.

Potential Influence of Seawater Intrusion. [Cl$^-$] in excess of 100 mg/L and [Br$^-$]/[Cl$^-$] ratios approaching or exceeding that of natural seawater ($\sim 1.5 \times 10^{-3}$) suggest that multiple IC and SJC sites may be at risk of seawater intrusion (Table 1). While this risk is well known for the study area, it has thus far been managed as a water resource and taste issue rather than a health concern. However, increased [Br$^-$] due to seawater intrusion could have important consequences for managing DBP formation and speciation in the future.[7, 9] As evident from the data in Table 1 and Figures S3, 4, and 7, unregulated HAA yields are higher with increased [Br$^-$] for a given [DOC] level, yet frequent, comprehensive monitoring of HAA9 levels may not be feasible in many cases. Furthermore, recent studies also suggest that high [Cl$^-$] may favor shifts in free chlorine and bromine species from HOCl and HOBr to the much more reactive Cl_2 and BrCl, which could result in increased DBP formation.[7, 13, 115-117] In light of the above, regular monitoring of [Br$^-$] and [Cl$^-$] is highly recommended for at risk sites, in addition to identification of alternate water sources in the event that seawater intrusion becomes significant enough to preclude compliance with DBP MCLs.

Effects of Iron and Manganese Treatment. Additional treatment steps at systems IC06–IC08 did not substantially influence DOC/TOC or DBP-FP levels (Figures S3a and 4).

Chlorination Practices and Reporting. All of the IC and SJC systems submit monthly compliance reports to WA DOH that typically include water production, chlorine usage, and free chlorine residuals measured 1-5 times/week. Notably, total [NH_3-N] measurements during the study identified significant NH_3-N levels in source waters at a number of sites (Table 1). This appeared to result in maintenance of combined chlorine rather than free chlorine in treated waters at these sites (Figure S14). However, review of compliance reports during the months in which study samples were collected showed that only one system measured both free and total chlorine; the rest reported only free chlorine. Accordingly, monthly reports recorded very low distribution system free chlorine; nearly every water system had at least one quarter with a monthly average free chlorine residual <0.2 mg/L as Cl_2, and six sites never exceeded 0.2 mg/L as Cl_2 in the distribution system. Field measurements of free and total chlorine at entries to the distribution systems also varied significantly at certain sites over time (Figure S14), indicating inconsistent chlorination practices. Low chlorine residuals measured at certain sites, or instances of unintentional chloramination at others, may also indicate vulnerabilities to microbial risks.

The measurement of combined chlorine, as opposed to free chlorine, in IC04 samples is of particular note, as it could provide an explanation for very low HAA and THM levels reported in regulatory compliance samples for this site. This also highlights the possibility of using NH_2Cl as an alternative disinfectant to minimize DBP formation at some sites, though investigation of potential effects on nitrogenous and iodinated DBP formation would be needed beforehand.[8]

In general, free chlorine residuals reported in Island County were also lower than in San Juan County. This could explain why IC systems have historically had DBP levels similar to SJC systems during compliance monitoring (Figure 2), even though average DOC appears higher and laboratory tests yielded higher DBP-FPs for IC systems (Figures S3a and 4) .

The finding that study systems follow inconsistent chlorination operating and reporting practices – resulting in highly variable and unstable distribution system free chlorine residuals – has significant implications for WA's implementation of the DBPRs. This indicates that the public may be intermittently exposed to higher DBP levels – particularly of more harmful brominated DBPs – than regulatory monitoring indicates, due to significant fluctuations in free chlorine residuals (whether caused by operational variation, changes in water quality, or other unidentified factors). It is unlikely that these findings are limited to just the systems included in this study. This suggests that in the future, implementation of the DBPRs for coastal groundwater utilities in WA and other states should include emphasis on chlorination best practices *and* regular monitoring of key indicators for DBP-FPs (e.g., [Br^-], [DOC], or appropriate surrogates), rather than relying solely on limited TTHM/HAA5 sampling to characterize DBP levels.

Conclusions

Careful examination of correlations amongst THM-FP and HAA-FP values and the suite of water quality parameters monitored during this study showed that neither yields nor speciation patterns of THMs and HAAs at the study sites were clearly associated with Cl^-, TI, or TDS concentrations; conductivities; NH_3-N concentrations; HPCs; or ATP concentrations. In contrast, THM-FP and HAA-FP values exhibited strong positive correlations with DOC concentrations (which in turn correlated extremely well with TOC concentrations) and with A_{254} across the sample set over the full duration of the study. Weaker, but still relatively strong correlations were observed with SEC and fluorescence metrics. DOM characteristics were quite uniform from site to site, indicating that the *concentration* of DOC, rather than variation in DOM *character*, is the primary driver controlling THM-FPs and HAA-FPs within the study area.

These data suggest that regular monitoring of DOC (or TOC) concentrations could provide an important means of evaluating the propensities for THM and HAA formation at these and other small, coastal groundwater systems, though this is not currently required under the

DBPRs.[68, 69] Regular monitoring of DOC (or TOC) concentrations in the source waters of small coastal groundwater utilities is therefore highly recommended as a modification to current regulations. Alternatively, A_{254} can likely serve as a suitable surrogate for DOC, considering the relative simplicity and low cost of monitoring A_{254}, and its strong correlation with [DOC] and DBP-FPs across the investigated sample set and in general.

In contrast to THM-FPs and HAA-FPs, THM and HAA speciation patterns – as quantified by means of BSF values – did not exhibit direct dependence on any single parameter monitored during the study. Rather, they depended strongly on the ratios of $[Br^-]/[DOC]$ in each sample, with higher $[Br^-]/[DOC]$ values indicative of a higher tendency to form brominated THMs and HAAs. Thus, it may also be feasible to utilize $[Br^-]/[DOC]$ ratios as a means of estimating the extent to which THM and HAA formation are likely to be dominated by brominated species at various sites. Regular monitoring of bromide is therefore also highly recommended as a complement to DOC (or TOC) or A_{254} for these and similar systems, especially those potentially susceptible to seawater intrusion, as a modification to current rules.

This work and the accompanying review of IC and SJC system operation and reporting practices also show that some chlorination facilities are operating inconsistently, and that current monitoring requirements do not capture the range of water characteristics or operating conditions at the study sites; most notably with respect to source water [DOC] and $[Br^-]$, and free chlorine within treatment and distribution systems. The observation that a number of the study sites may be prone to maintenance of combined rather than free chlorine residuals, coupled with the possibility of elevated iodide levels in source waters, also highlights the need for future work to assess the potential formation of elevated nitrogenous and iodinated DBP levels under operating conditions typical of these and similar systems. Based on the study findings, WA has adopted changes in its design manual for new groundwater disinfection systems including testing of all groundwater sources for seasonal trends in [DOC] and total [NH_3-N], as well as [Br^-] and [Cl^-] for coastal groundwater sources,[118] and is evaluating changes in its disinfection monitoring and DBP programs that may also serve as models for wider regional and national implementation.

Conflicts of Interest

There are no conflicts of interest to declare.

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References

1. S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny, D. M. DeMarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research, *Mutat. Res. - Rev. Mut. Res.*, 2007, 636(1-3), 178-242.
2. M. J. Plewa, E. D. Wagner, M. G. Muellner, K. M. Hsu, S. D. Richardson. Comparative Mammalian Cell Toxicity of N-DBPs and C-DBPs. In: T. Karanfil, S. W. Krasner, P.

Westerhoff, Y. Xie, editors. Disinfection By-Products in Drinking Water: Occurrence, Formation, Health Effects, and Control. ACS Sym. Ser. 995, 2008. 36-50.

3. S. Regli, J. Chen, M. Messner, M. S. Elovitz, F. J. Letkiewicz, et al., Estimating potential increased bladder cancer risk due to increased bromide concentrations in sources of disinfected drinking waters, *Environ. Sci. Technol.*, 2015, 49(22), 13094-102.
4. C. Kolb, R. A. Francis, J. M. VanBriesen, Disinfection byproduct regulatory compliance surrogates and bromide-associated risk, *J. Environ. Sci.*, 2017, 58(191-207.
5. T. Wixom, B. Snow. San Juan County Water Resources Management Plan WRIA 2. San Juan County Board of County Commissioners, Friday Harbor, WA; 2004.
6. D. Kelly. Island County Water Resource Management Plan: Appendix F - Seawater intrusion topic paper. 2005.
7. E. C. Ged, T. H. Boyer, Effect of seawater intrusion on formation of bromine-containing trihalomethanes and haloacetic acids during chlorination, *Desalination*, 2014, 345(85-93.
8. A. Szczuka, K. Parker, C. Harvey, E. Hayes, A. Vengosh, et al., Regulated and unregulated halogenated disinfection byproduct formation from chlorination of saline groundwater, *Water Res.*, 2017, 122(633-44.
9. C. Kolb, M. Pozzi, C. Samaras, J. M. VanBriesen, Climate change impacts on bromide, trihalomethane formation, and health risks at coastal groundwater utilities, *ASCE-ASME J. Risk Uncertain. Eng. Syst. A*, 2017, 3(3), 04017006.
10. S. W. Krasner, M. J. Sclimenti, E. G. Means, Quality degradation: implications for DBP formation, *J. Am. Water Works Ass.*, 1994, 86(6), 34-47.
11. W. W. Wu, P. A. Chadik, Effect of bromide ion on haloacetic acid formation during chlorination of Biscayne aquifer water, *J. Environ. Eng.*, 1998, 124(10), 932-8.

12. A. A. Kampioti, E. G. Stephanou, The impact of bromide on the formation of neutral and acidic disinfection by-products (DBPs) in Mediterranean chlorinated drinking water, *Water Res.*, 2002, 36(10), 2596-606.

13. M. B. Heeb, J. Criquet, S. G. Zimmermann-Steffens, U. Von Gunten, Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds—a critical review, *Water Res.*, 2014, 48(15-42.

14. P. Westerhoff, P. Chao, H. Mash, Reactivity of natural organic matter with aqueous chlorine and bromine, *Water Res.*, 2004, 38(6), 1502-13.

15. J. Criquet, E. M. Rodriguez, S. Allard, S. Wellauer, E. Salhi, et al., Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts–Electrophilic aromatic substitution and oxidation, *Water Res.*, 2015, 85(476-86.

16. J. M. Symons, S. W. Krasner, L. A. Simms, M. Sclimenti, Measurement of THM and precursor concentrations revisited: the effect of bromide ion, *J. Am. Water Works Ass.*, 1993, 85(1), 51-62.

17. G. A. Cowman, P. C. Singer, Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, *Environ. Sci. Technol.*, 1996, 30(1), 16-24.

18. S. Chellam, S. W. Krasner, Disinfection byproduct relationships and speciation in chlorinated nanofiltered waters, *Environ. Sci. Technol.*, 2001, 35(19), 3988-99.

19. M. S. Ersan, C. Liu, G. Amy, T. Karanfil, The interplay between natural organic matter and bromide on bromine substitution, *Sci. Total Environ.*, 2019, 646(1172-81.

20. G. Hua, D. A. Reckhow, J. Kim, Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination, *Environ. Sci. Technol.*, 2006, 40(9), 3050-6.

21. E. Chang, Y. Lin, P. Chiang, Effects of bromide on the formation of THMs and HAAs, *Chemosphere*, 2001, 43(8), 1029-34.

22. T. Bond, J. Huang, N. J. Graham, M. R. Templeton, Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water—a case study, *Sci. Total Environ.*, 2014, 470(469-79.

23. C. J. Nokes, E. Fenton, C. J. Randall, Modelling the formation of brominated trihalomethanes in chlorinated drinking waters, *Water Res.*, 1999, 33(17), 3557-68.

24. M. Langsa, S. Allard, I. Kristiana, A. Heitz, C. A. Joll, Halogen-specific total organic halogen analysis: Assessment by recovery of total bromine, *J. Environ. Sci.*, 2017, 58(340-8.

25. K. M. Parker, T. Zeng, J. Harkness, A. Vengosh, W. A. Mitch, Enhanced formation of disinfection byproducts in shale gas wastewater-impacted drinking water supplies, *Environ. Sci. Technol.*, 2014, 48(19), 11161-9.

26. J. Tan, S. Allard, Y. Gruchlik, S. McDonald, C. Joll, et al., Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems, *Sci. Total Environ.*, 2016, 541(1572-80.

27. Y. Yang, Y. Komaki, S. Y. Kimura, H.-Y. Hu, E. D. Wagner, et al., Toxic impact of bromide and iodide on drinking water disinfected with chlorine or chloramines, *Environ. Sci. Technol.*, 2014, 48(20), 12362-9.

28. E. D. Wagner, M. J. Plewa, CHO cell cytotoxicity and genotoxicity analyses of disinfection by-products: an updated review, *J. Environ. Sci.*, 2017, 58(64-76.

29. S. Parvez, Z. Rivera-Núñez, A. Meyer, J. M. Wright, Temporal variability in trihalomethane and haloacetic acid concentrations in Massachusetts public drinking water systems, *Environ. Res.*, 2011, 111(4), 499-509.

30. M. J. McGuire, R. G. Meadow, AWWARF trihalomethane survey, *J. Am. Water Works Ass.*, 1988, 80(1), 61-8.

31. M. Varma, A. Balram, H. Katz, Trihalomethanes in groundwater systems, *J. Environ. Sys.*, 1984, 14(2), 115-25.

32. D. Reckhow, P. Rees, K. Nüsslein, G. Makdissy, G. Devine, et al. Long-term variability of BDOM and NOM as precursors in watershed sources: AWWA Research Foundation; 2007.

33. H. Gallard, U. von Gunten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, *Water Res.*, 2002, 36(1), 65-74.

34. Y. Zhang, C. Collins, N. Graham, M. R. Templeton, J. Huang, et al., Speciation and variation in the occurrence of haloacetic acids in three water supply systems in England, *Water Environ. J.*, 2010, 24(3), 237-45.

35. C. Adams, T. Timmons, T. Seitz, J. Lane, S. Levotch, Trihalomethane and haloacetic acid disinfection by-products in full-scale drinking water systems, *J. Environ. Eng.*, 2005, 131(4), 526-34.

36. H. D. Coulibaly, M. J. Rodriguez, Portrait of drinking water quality in small Quebec municipal utilities, *Water Quality Research Journal*, 2003, 38(1), 49-76.

37. D. A. Reckhow, P. C. Singer. Formation and Control of Disinfection By-products. In: J. K. Edzwald, editor. Water Quality and Treatment: A Handbook on Drinking Water. 6th ed. New York, NY: AWWA/McGraw-Hill; 2011.

38. L. Liang, P. C. Singer, Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water, *Environ. Sci. Technol.*, 2003, 37(13), 2920-8.

39. W. Chen, P. Westerhoff, J. A. Leenheer, K. Booksh, Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter, *Environ. Sci. Technol.*, 2003, 37(24), 5701-10.

40. D. A. Reckhow, P. C. Singer, R. L. Malcolm, Chlorination of humic materials: byproduct formation and chemical interpretations, *Environ. Sci. Technol.*, 1990, 24(11), 1655-64.

41. C.-W. Li, M. M. Benjamin, G. V. Korshin, Use of UV spectroscopy to characterize the reaction between NOM and free chlorine, *Environ. Sci. Technol.*, 2000, 34(12), 2570-5.

42. G. V. Korshin, C.-W. Li, M. M. Benjamin, Monitoring the properties of natural organic matter through UV spectroscopy: a consistent theory, *Water Res.*, 1997, 31(7), 1787-95.

43. G. Hua, D. A. Reckhow, I. Abusallout, Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources, *Chemosphere*, 2015, 130(82-9.

44. J. A. Leenheer, J.-P. Croué, Characterizing Aquatic Dissolved Organic Matter, *Environ. Sci. Technol.*, 2003, 37(1), 18A-26A.

45. I. Kristiana, H. Gallard, C. Joll, J.-P. Croué, The formation of halogen-specific TOX from chlorination and chloramination of natural organic matter isolates, *Water Res.*, 2009, 43(17), 4177-86.

46. S. E. Barrett, S. W. Krasner, G. L. Amy. Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water—An Overview. In: S. E. Barrett, S. W. Krasner, G. L. Amy, editors. Natural Organic Matter and Disinfection By-Products. ACS Sym. Ser. 761, 2000. 2-14.

47. N. Her, G. Amy, D. McKnight, J. Sohn, Y. M. Yoon, Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection, *Water Res.*, 2003, 37(17), 4295-303.

48. S. A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND), *Water Res.*, 2011, 45(2), 879-85.

49. Y.-P. Chin, G. Aiken, E. O'Loughlin, Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.*, 1994, 28(11), 1853-8.

50. J. L. Weishaar, G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, et al., Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, 2003, 37(20), 4702-8.

51. D. M. McKnight, E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, et al., Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, *Limnol. Oceanogr.*, 2001, 46(1), 38-48.

52. J.-P. Croue, G. V. Korshin, M. M. Benjamin. Characterization of natural organic matter in drinking water: AWWA Research Foundation; 2000.

53. A. D. Pifer, J. L. Fairey, Suitability of Organic Matter Surrogates to Predict Trihalomethane Formation in Drinking Water Sources, *Environ. Eng. Sci.*, 2014, 31(3), 117-26.

54. S. Inamdar, N. Finger, S. Singh, M. Mitchell, D. Levia, et al., Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA, *Biogeochemistry*, 2012, 108(1-3), 55-76.

55. M. Chen, R. M. Price, Y. Yamashita, R. Jaffé, Comparative study of dissolved organic matter from groundwater and surface water in the Florida coastal Everglades using multi-dimensional spectrofluorometry combined with multivariate statistics, *Appl. Geochem.*, 2010, 25(6), 872-80.

56. B. Chen, P. Westerhoff, Predicting disinfection by-product formation potential in water, *Water Res.*, 2010, 44(13), 3755-62.

57. L. K. McDonough, H. Rutlidge, D. M. O'Carroll, M. S. Andersen, K. Meredith, et al., Characterisation of shallow groundwater dissolved organic matter in aeolian, alluvial and fractured rock aquifers, *Geochim. Cosmochim. Acta*, 2020, 273(163-76.

58. Y. Shen, F. H. Chapelle, E. W. Strom, R. Benner, Origins and bioavailability of dissolved organic matter in groundwater, *Biogeochemistry*, 2015, 122(1), 61-78.

59. S. Singh, S. Inamdar, M. Mitchell, P. McHale, Seasonal pattern of dissolved organic matter (DOM) in watershed sources: influence of hydrologic flow paths and autumn leaf fall, *Biogeochemistry*, 2014, 118(1-3), 321-37.

60. D. W. Johnstone, N. P. Sanchez, C. M. Miller, Parallel Factor Analysis of Excitation-Emission Matrices to Assess Drinking Water Disinfection Byproduct Formation During a Peak Formation Period, *Environ. Eng. Sci.*, 2009, 26(10), 1551-9.

61. S.-b. Huang, Y.-x. Wang, T. Ma, L. Tong, Y.-y. Wang, et al., Linking groundwater dissolved organic matter to sedimentary organic matter from a fluvio-lacustrine aquifer at

Jianghan Plain, China by EEM-PARAFAC and hydrochemical analyses, *Sci. Total Environ.*, 2015, 529(131-9.

62. G. L. Amy, P. A. Chadik, Z. K. Chowdhury, Developing models for predicting trihalomethane formation potential and kinetics, *J. Am. Water Works Ass.*, 1987, 79(7), 89-97.
63. J. K. Edzwald, W. C. Becker, K. L. Wattier, Surrogate parameters for monitoring organic matter and THM precursors, *J. Am. Water Works Ass.*, 1985, 77(4), 122-32.
64. A. D. Pifer, J. L. Fairey, Improving on SUVA(254) using fluorescence-PARAFAC analysis and asymmetric flow-field flow fractionation for assessing disinfection byproduct formation and control, *Water Res.*, 2012, 46(9), 2927-36.
65. D. W. Johnstone, C. M. Miller, Fluorescence excitation–emission matrix regional transformation and chlorine consumption to predict trihalomethane and haloacetic acid formation, *Environ. Eng. Sci.*, 2009, 26(7), 1163-70.
66. D. M. White, D. S. Garland, J. Narr, C. R. Woolard, Natural organic matter and DBP formation potential in Alaskan water supplies, *Water Res.*, 2003, 37(4), 939-47.
67. R. E. Miller, S. J. Randtke, L. R. Hathaway, J. E. Denne, Organic carbon and THM formation potential in Kansas groundwaters, *J. Am. Water Works Ass.*, 1990, 82(3), 49-62.
68. National Primary Drinking Water Regulations; Subpart L - Disinfectant Residuals, Disinfection Byproducts, and Disinfection Byproduct Precursors, 40 CFR 141, 130-135.
69. National Primary Drinking Water Regulations; Subpart V - Stage 2 Disinfection Byproducts Requirements, 40 CFR 141, 620-629.

70. N. Her, G. Amy, D. Foss, J. Cho, Y. Yoon, et al., Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection, *Environ. Sci. Technol.*, 2002, 36(5), 1069-76.

71. S. K. L. Ishii, T. H. Boyer, Behavior of Reoccurring PARAFAC Components in Fluorescent Dissolved Organic Matter in Natural and Engineered Systems: A Critical Review, *Environ. Sci. Technol.*, 2012, 46(4), 2006-17.

72. C. A. Stedmon, R. Bro, Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, *Limnol. Oceanogr.: Methods*, 2008, 6(572-9.

73. R. M. Cory, D. M. McKnight, Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, *Environ. Sci. Technol.*, 2005, 39(21), 8142-9.

74. E. Agus, N. Voutchkov, D. L. Sedlak, Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review, *Desalination*, 2009, 237(1-3), 214-37.

75. K. Kumar, R. A. Day, D. W. Margerum, Atom-Transfer Redox Kinetics - General-Acid-Assisted Oxidation of Iodide by Chloramines and Hypochlorite, *Inorg. Chem.*, 1986, 25(24), 4344-50.

76. APHA/AWWA. Standard Methods for the Examination of Water and Wastewater. 22 ed. Washington D.C.: American Public Health Association; 2012.

77. J. Pfaff. US EPA Method 300.0: Determination of inorganic anions by ion chromatography. 1993.

78. J. O'Dell. US EPA Method 350.1: Determination of Ammonia Nitrogen by Semi-automated Colorimetry. 1993.

79. T. D. Martin, C. A. Brockhoff, J. T. Creed. US EPA Method 200.7: Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry. 1994.

80. B. B. Potter, J. C. Wimsatt. US EPA Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254nm in Source Water and Drinking Water. 2009.

81. D. J. Munch, J. W. Munch, A. M. Pawlecki. EPA Method 552.2: Determination of Haloacetic acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection. 1995.

82. F. J. Millero, R. Feistal, D. G. Wright, T. J. McDougall, The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, *Deep Sea Res. (I Oceanogr. Res. Pap.)*, 2008, 55(1), 50-72.

83. M. Land, E. G. Reichard, S. M. Crawford, R. R. Everett, M. W. Newhouse, et al. Ground-water quality of coastal aquifer systems in the West Coast Basin, Los Angeles County, California, 1999-2002. Sacramento, CA; 2004.

84. P. C. Singer, S. D. Chang, Correlations between trihalomethanes and total organic halides formed during water treatment, *J. Am. Water Works Ass.*, 1989, 81(8), 61-5.

85. R. K. Henderson, A. Baker, K. R. Murphy, A. Hamblya, R. M. Stuetz, et al., Fluorescence as a potential monitoring tool for recycled water systems: A review, *Water Res.*, 2009, 43(4), 863-81.

86. S. N. Nam, S. W. Krasner, G. L. Amy. Differentiating effluent organic matter (EfOM) from natural organic matter (NOM): Impact of EfOM on drinking water sources. In: Y. J. Kim, U. Platt, editors. Advanced Environmental Monitoring2008. 259-70.

87. P. G. Coble, Marine optical biogeochemistry: The chemistry of ocean color, *Chem. Rev.*, 2007, 107(2), 402-18.

88. C. A. Stedmon, S. Markager, R. Bro, Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, *Mar. Chem.*, 2003, 82(3), 239-54.

89. P. G. Coble, Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, *Mar. Chem.*, 1996, 51(4), 325-46.

90. J. A. Korak, A. D. Dotson, R. S. Summers, F. L. Rosario-Ortiz, Critical analysis of commonly used fluorescence metrics to characterize dissolved organic matter, *Water Res.*, 2014, 49(327-38.

91. R. M. Cory, M. P. Miller, D. M. McKnight, J. J. Guerard, P. L. Miller, Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra, *Limnol. Oceanogr.: Methods*, 2010, 8(2), 67-78.

92. M.-H. Lee, C. L. Osburn, K.-H. Shin, J. Hur, New insight into the applicability of spectroscopic indices for dissolved organic matter (DOM) source discrimination in aquatic systems affected by biogeochemical processes, *Water Res.*, 2018, 147(164-76.

93. R. D. Holbrook, J. H. Yen, T. J. Grizzard, Characterizing natural organic material from the Occoquan Watershed (Northern Virginia, US) using fluorescence spectroscopy and PARAFAC, *Sci. Total Environ.*, 2006, 361(1-3), 249-66.

94. J. J. Mobed, S. L. Hemmingsen, J. L. Autry, L. B. McGown, Fluorescence characterization of IHSS humic substances: Total luminescence spectra with absorbance correction, *Environ. Sci. Technol.*, 1996, 30(10), 3061-5.

95. S. A. Baghoth, S. K. Sharma, G. L. Amy, Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC, *Water Res.*, 2011, 45(2), 797-809.

96. K. M. Beggs, R. S. Summers, Character and chlorine reactivity of dissolved organic matter from a mountain pine beetle impacted watershed, *Environ. Sci. Technol.*, 2011, 45(13), 5717-24.

97. S. A. Green, F. M. M. Morel, N. V. Blough, Investigation of the Electrostatic Properties of Humic Substances by Fluorescence Quenching, *Environ. Sci. Technol.*, 1992, 26(2), 294-302.

98. A. Baker, S. Elliott, J. R. Lead, Effects of filtration and pH perturbation on freshwater organic matter fluorescence, *Chemosphere*, 2007, 67(10), 2035-43.

99. R. G. M. Spencer, L. Bolton, A. Baker, Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations, *Water Res.*, 2007, 41(13), 2941-50.

100. N. Patel-Sorrentino, S. Mounier, J. Y. Benaim, Excitation-emission fluorescence matrix to study pH influence on organic matter fluorescence in the Amazon basin rivers, *Water Res.*, 2002, 36(10), 2571-81.

101. R. Jaffé, D. McKnight, N. Maie, R. Cory, W. McDowell, et al., Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties, *J. Geophys. Res.: Biogeosci.*, 2008, 113(G4),

102. A. M. Hansen, T. E. Kraus, B. A. Pellerin, J. A. Fleck, B. D. Downing, et al., Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation, *Limnol. Oceanogr.*, 2016, 61(3), 1015-32.

103. A. J. McCabe, W. A. Arnold, Multiple linear regression models to predict the formation efficiency of triplet excited states of dissolved organic matter in temperate wetlands, *Limnol. Oceanogr.*, 2018, 63(5), 1992-2014.

104. S. R. Summers, S. M. Hooper, H. M. Shukairy, G. Solarik, D. Owen, Assessing DBP Yield: Uniform Formation Conditions, *J. Am. Water Works Ass.*, 1996, 88(6), 80-93.

105. A. A. Stevens, J. M. Symons, Measurement of trihalomethane and precursor concentration changes, *J. Am. Water Works Ass.*, 1977, 546-54.

106. G. H. Hua, D. A. Reckhow, Evaluation of bromine substitution factors of DBPs during chlorination and chloramination, *Water Res.*, 2012, 46(13), 4208-16.

107. S. C. Chapra, R. P. Canale, G. L. Amy, Empirical models for disinfection by-products in lakes and reservoirs, *J. Environ. Eng.*, 1997, 123(7), 714-5.

108. A. Obolensky, P. C. Singer, Development and interpretation of disinfection byproduct formation models using the Information Collection Rule database, *Environ. Sci. Technol.*, 2008, 42(15), 5654-60.

109. J. Sohn, G. Amy, J. W. Cho, Y. Lee, Y. Yoon, Disinfectant decay and disinfection by-products formation model development: chlorination and ozonation by-products, *Water Res.*, 2004, 38(10), 2461-78.

110. P. Jutaporn, M. Armstrong, O. Coronell, Assessment of C-DBP and N-DBP formation potential and its reduction by MIEX® DOC and MIEX® GOLD resins using fluorescence spectroscopy and parallel factor analysis, *Water Res.*, 2020, 172(115460.

111. R. S. Summers, M. A. Benz, H. M. Shukairy, L. Cummings, Effect of separation processes on the formation of brominated THMs, *J. Am. Water Works Ass.*, 1993, 85(1), 88-95.

112. L. Zheng, H. Sun, C. Wu, Y. Wang, Y. Zhang, et al., Precursors for brominated haloacetic acids during chlorination and a new useful indicator for bromine substitution factor, *Sci. Total Environ.*, 2020, 698(134250.

113. R. A. Francis, J. M. VanBriesen, M. J. Small, Bayesian statistical modeling of disinfection byproduct (DBP) bromine incorporation in the ICR database, *Environ. Sci. Technol.*, 2010, 44(4), 1232-9.

114. K. M. Beggs, J. A. Billica, J. A. Korak, F. L. Rosario-Ortiz, D. M. McKnight, et al., Spectral evaluation of watershed DOM and DBP precursors, *J. Am. Water Works Ass.*, 2013, 105(4), E173-E88.

115. M. R. Rose, S. S. Lau, C. Prasse, J. D. Sivey, Exotic Electrophiles in Chlorinated and Chloraminated Water: When Conventional Kinetic Models and Reaction Pathways Fall Short, *Environ. Sci. Technol. Lett.*, 2020,

116. S. S. Lau, S. M. Abraham, A. L. Roberts, Chlorination revisited: does Cl–serve as a catalyst in the chlorination of phenols?, *Environ. Sci. Technol.*, 2016, 50(24), 13291-8.

117. Z.-Q. Liu, A. D. Shah, E. Salhi, J. Bolotin, U. von Gunten, Formation of brominated trihalomethanes during chlorination or ozonation of natural organic matter extracts and model compounds in saline water, *Water Res.*, 2018, 143(492-502.

118. WADOH. Water System Design Manual. DOH Publication 331-123. 4th ed: Washington State Department of Health; 2019.

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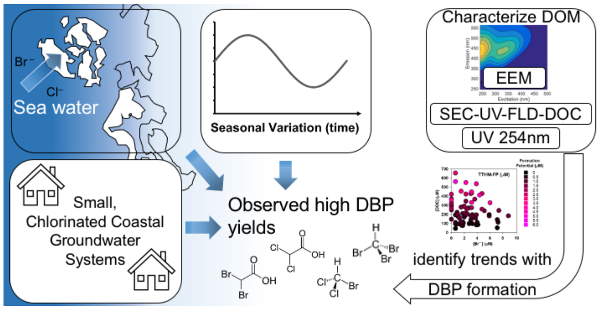

Small, chlorinated coastal groundwater systems are uniquely susceptible to elevated (especially brominated) DBP formation, due to the potential for high bromide and DOM levels, technical and resource constraints, and limited regulatory oversight.