Suitability of Organic Matter Surrogates to Predict Trihalomethane Formation in Drinking Water Sources

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Abstract

Broadly applicable disinfection by-product (DBP) precursor surrogate parameters could be leveraged at drinking water treatment plants (DWTPs) to curb formation of regulated DBPs, such as trihalomethanes (THMs). In this study, dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), fluorescence excitation/emission wavelength pairs ($I_{Ex/Em}$), and the maximum fluorescence intensities (F_{MAX}) of components from parallel factor (PARAFAC) analysis were evaluated as total THM formation potential (TTHMFP) precursor surrogate parameters. A diverse set of source waters from eleven DWTPs located within watersheds underlain by six different soil orders were coagulated with alum at pH 6, 7, and 8, resulting in 44 sample waters. DOC, UV_{254} , $I_{Ex/Em}$, and F_{MAX} values were measured to characterize dissolved organic matter in raw and treated waters and THMs were quantified following formation potential tests with free chlorine. For the 44 sample waters, the linear TTHMFP correlation with UV_{254} was stronger ($r^2=0.89$) than $I_{240/562}$ ($r^2=0.81$, the strongest surrogate parameter from excitation/emission matrix pair picking), F_{MAX} from a humic/fulvic acid-like PARAFAC component ($r^2=0.78$), and DOC ($r^2=0.75$). Results indicate that UV_{254} was the most accurate TTHMFP precursor surrogate parameter assessed for a diverse group of raw and alum-coagulated waters.

Key words: alum coagulation; disinfection by-products; fluorescence spectroscopy; natural organic matter; surrogate parameters

Introduction

IT HAS LONG been known that disinfection by-products (DBPs) form by reactions between disinfectants (e.g., free chlorine) and natural organic matter (NOM), the primary pool of DBP precursors. DBPs have been associated with adverse pregnancy outcomes (Jeong *et al.*, 2012) and 11 DBPs, including 4 trihalomethanes (THMs), are regulated by the United States Environmental Protection Agency in treated drinking water. As a result, much DBP research has focused on NOM characterization and removal strategies that can be integrated into unit processes at drinking water treatment plants (DWTPs). Aquatic NOM is a complex mixture of organic compounds (e.g., humic acids, fulvic acids, and proteins) derived from terrestrial and aquatic sources (Huguet *et al.*, 2009). In natural waters, NOM can undergo biotic and abiotic transformations, resulting in spatial (Stedmon *et al.*, 2003) and temporal (Miller and McKnight, 2010) variability. These transformations further complicate NOM characterization efforts and create difficulties relating physicochemical NOM properties to DBP formation (Bond *et*

al., 2010). The complexity of NOM has resulted in the development of various surrogate parameters to assess its properties related to DBP formation and control. Reliable DBP precursor surrogate parameters are critical to improving the effectiveness of NOM removal processes at DWTPs, such as enhanced coagulation (Krasner and Amy, 1995). An ideal surrogate parameter would be capable of tracking DBP precursor concentrations in real time over a range of raw and treated water quality characteristics to optimize, for example, alum dose and pH for enhanced coagulation.

Many techniques have been employed to characterize NOM and relate various properties to DBP formation. In terms of physical properties, size distributions of NOM in raw and alum-coagulated waters have been assessed using size exclusion chromatography (Chow *et al.*, 2008) and asymmetric flow-field flow fractionation (AF4) (Pifer and Fairey, 2012). Whereas these analyses have yielded insights into relationships between the NOM size and treatment, strong DBP precursor surrogate parameters have not been derived from physical NOM characteristics. In contrast, chemical characteristics, such as total organic carbon (TOC) and dissolved organic carbon (DOC, the portion of TOC passing a 0.45- μ m filter), have been correlated to DBP formation. However, DBP correlations with TOC and DOC are inconsistent, in part because the diversity of the various

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organic carbon fractions impacts the formation of specific DBPs (Beggs and Summers, 2011). On the other hand, ultraviolet absorbance at 254 nm (UV_{254}), a bulk chemical characterization technique, has long been known to be a strong precursor surrogate parameter of THMs (Edzwald *et al.*, 1985; Singer and Chang, 1989) and total organic halide for raw and coagulated waters (Archer and Singer, 2006). Normalizing UV_{254} by DOC results in specific UV_{254} ($SUVA_{254}$), an intensive parameter that can provide insight into the effectiveness of treatment processes such as enhanced coagulation for DBP control. $SUVA_{254}$ is a measure of the aromatic content of chromophoric dissolved organic matter (CDOM) (Korshin *et al.*, 2009), and these aromatic, double bond-containing moieties have been demonstrated to participate in DBP formation reactions (Lavonen *et al.*, 2013). However, THM- UV_{254} correlations may be less effective for waters treated with chlorine dioxide (Granderson *et al.*, 2013), a common DBP control measure, and waters impacted by heavy rainfall events (Pifer *et al.*, 2013).

Fluorescence excitation/emission matrices (EEMs) have been used to characterize NOM, referred to as fluorescent dissolved organic matter (FDOM), as related to DBP formation. Because EEMs are data-rich, statistical algorithms, such as parallel factor (PARAFAC) analysis, have been used to resolve fluorophore groups (or components) from EEMs (Andersen and Bro, 2003). Each EEM is characterized by a set of PARAFAC components, each with a fluorescence maximum intensity value, F_{MAX} , an extensive property. In a previous study (Pifer and Fairey, 2012), four locations within a single water body were sampled temporally over the spring and summer months to capture the peak THM formation period. Fluorescence PARAFAC was used to characterize FDOM and strong correlations ($r^2=0.84$) were found between F_{MAX} values of a humic acid-like PARAFAC component and chloroform (TCM) formation potential (FP). Other researchers have also used PARAFAC to characterize DBP precursors (Johnstone and Miller, 2009; Johnstone *et al.*, 2009). As such, F_{MAX} could be a significant improvement over metrics like DOC and UV_{254} as a total THM formation potential (TTHMFP) precursor surrogate parameter, but its applicability to a variety of source waters remains untested.

A drawback to the PARAFAC modeling routine is that it is time-consuming and computationally intensive, and it may not be suitable for real-time measurements of DBP precursor properties. To this end, Murphy *et al.* (2011) used discrete excitation/emission intensity pairs ($I_{Ex/Em}$) to approximate PARAFAC components in wastewater effluents, but did not investigate relationships with DBP formation. Pair picking is a viable, near real time, analysis technique, which can be integrated into custom sensors available today (Goldman *et al.*, 2012). However, it is not yet known which fluorescence pairs, if any, could be reliable surrogates of DBP precursors.

The primary objective of this research is to assess DOC, UV_{254} , $I_{Ex/Em}$, and PARAFAC F_{MAX} values as TTHMFP precursor surrogate parameters for a diverse group of raw and alum-coagulated waters. Raw water samples were collected from the intakes of 11 DWTPs located throughout the United States, representing sources from rivers, reservoirs, and 1 surface water-influenced aquifer. Because aquatic NOM properties are influenced by nearby soils (Eswaran *et al.*, 1993; Aiken and Cotsaris, 1995), the sampling locations were chosen such that six soil orders were included. This unique

group of raw waters was alum coagulated at pH 6, 7, and 8 and NOM properties from each of the 44 samples were assessed before chlorination with sodium hypochlorite and measurement of TTHMFP. Linear regression models were developed to assess and compare the various TTHMFP precursor surrogate parameters. A secondary objective of this research was to evaluate the impact of PARAFAC model size (e.g., the number of EEMs used to fit the model) on the quality of F_{MAX} values as TTHMFP precursor surrogate parameters. Two PARAFAC models were fit and compared—one was made using only the 44 EEMs measured in this study, and the other created by combining these 44 EEMs with 378 EEMs collected as part of two previously published reports (Pifer *et al.*, 2011; Pifer and Fairey, 2012).

Experimental Protocols

Sample collection and handling

One raw water sample (18 L) was collected from the intake of each of the 11 DWTPs (Supplementary Fig. S1; Supplementary Data are available online at www.liebertpub.com/ees) between February and April 2012. Sampling locations were chosen based on the dominant soil order (Supplementary Table S1) within each watershed and the type of water source (i.e., river, lake, or groundwater under the direct influence of surface water). At each DWTP, two precleaned 9-L HDPE carboys were filled headspace free with raw water and overnight shipped on ice to the University of Arkansas where they were stored at 4°C in the dark until analysis. The majority of the jar tests were conducted the day after the samples arrived, although inadequate pH control or chlorine dosing necessitated that a handful of jar tests be redone within a few days of the original analyses.

Glassware and reagents

Cleaning and preparation procedures for glassware and plasticware are detailed in the Supplementary Data. Whatman glass fiber filters (GFFs) with a nominal pore size of 0.7 μ m were used for vacuum filtration, similar to other research groups measuring fluorescence EEMs (Cory *et al.*, 2011; Goldman *et al.*, 2012). As such, DOM and DOC were operationally defined as the organic matter or carbon, respectively, which passed through 0.7- μ m GFFs. These filters were used instead of the more common 0.45- μ m membrane filters because their large nominal pore size permits passage of a larger fraction of the NOM, while still retaining particles. Before use, GFFs were precombusted at 400°C for 30 min and prerinsed with 1 L of Milli-Q water, as recommended by Karanfil *et al.* (2003). All chemicals were ACS grade and all aqueous solutions were prepared in 18.2 M Ω -cm Milli-Q water, produced by a Milli-Q Integral 3 (Millipore).

Water quality tests

Raw water pH, alkalinity, and turbidity were measured as described by Pifer *et al.* (2011). Following sample filtration with 0.7- μ m GFFs as described in the Glassware and Reagents section, conductivity was measured using a Malvern Zetasizer Nano ZS90. For raw and alum-treated samples, UV_{254} was measured on a Shimadzu UV-Vis 2450 spectrophotometer with a 1-cm path length low volume quartz cell

following Standard Methods 5910-B (Eaton and Franson, 2005). UV spectra were collected from 200 to 600 nm for selected raw waters (HMO, LNE, MMN, and UNY) to assess the impact of inner filter effects on fluorescence measurements. DOC was measured on a Sievers 900 Portable TOC Analyzer with a limit of quantitation (LOQ) of 26 $\mu\text{g/L}$ ($n=21$). SUVA_{254} was calculated as $\text{UV}_{254} (\text{m}^{-1})$ divided by DOC (mg/L). Bromide (practical quantitation limit [PQL] = 60 $\mu\text{g/L}$) and sulfate (PQL = 160 $\mu\text{g/L}$) were measured on a Dionex DX-120 ion chromatograph with an IonPac AS4A-SC column following USEPA 300.0.

Jar tests

Jar tests were conducted on each of the 11 raw waters at pH 6, 7, and 8 following Pifer and Fairey (2012), resulting in 33 alum-coagulated samples and 44 samples in total. In brief, 1-L aliquots were pH adjusted using 1 N HCl or 1 N NaOH and were coagulated with alum (aluminum sulfate octadecahydrate) at 60 mg/L on an eight-position magnetic stir plate (Challenge Technology). This relatively high alum dose was selected to achieve substantial removal of the DBP precursors, permitting assessment of the accuracy of the DBP precursor surrogate parameters at low concentrations. To maintain the coagulation pH, 1–6 mL of 10.6 g/L Na_2CO_3 was added simultaneously with alum. After settling, the supernatant was filtered and stored in amber glass bottles in the dark at 4°C.

Disinfection by-products

DBPFP was measured following Pifer and Fairey (2012), which was modified based on Standard Methods 5710-B (Eaton and Franson, 2005). Briefly, one 250 mL portion of sample water was chlorinated at $\text{pH } 7.0 \pm 0.2$ using a 5,000-mg/L as Cl_2 sodium hypochlorite stock solution added with a micropipette. Chlorine doses between 7 and 16 mg/L as Cl_2 were chosen to provide a residual of at least 3 mg/L as Cl_2 after 7 days in the dark at room temperature. After the hold time, chlorine residual was measured using Hach DPD total chlorine reagent packs and the UV-Vis spectrophotometer. Thirty milliliters of each chlorinated sample was quenched with ammonium chloride, and DBPs were extracted by liquid–liquid extraction into pentane with 1,1,1-trichloroethane as an internal standard (Wahman, 2006). Concentrations of TCM, bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform, dichloroacetonitrile, trichloroacetonitrile, and 1,1,1-trichloro-2-propanone were measured by gas chromatography with an electron capture detector following USEPA 551.1. Eleven-point standard curves from 2 to 200 $\mu\text{g/L}$ as each DBP were used to quantify DBPs, and blanks and check standards were included after every 12th injection.

Size characterizations of CDOM

AF4-UV₂₅₄ fractograms were collected in duplicate following Pifer and Fairey (2012) using a 1,000-Da polyethersulfone membrane, a cross-flow rate of 4 mL/min, and an elution time of 30 min. Filtered raw waters were fractionated at pH 6 and 8 for comparison with samples coagulated at pH 6 and 8, respectively. The fractionation pH was controlled by the eluent, a phosphate carbonate buffer, pH adjusted with 1 N HCl. The conductivity of the pH 8 eluent

was adjusted with 1 M NaCl to match that of the pH 6 eluent (470 $\mu\text{S/cm}$).

Fluorescence EEM collection and analysis

Fluorescence EEMs were collected using a dual monochromator fluorescence detector (Model G1321A; Agilent Technologies) in ratio mode with excitation and emission bandwidths of 20 nm, a scan speed of 28 ms per datapoint, and a cuvette with an inner diameter of 0.5 mm. EEMs were collected from each filtered raw and alum-coagulated sample at excitation wavelengths of 200–400 nm and emission wavelengths of 270–600 nm with 1 nm step sizes. Based on the inner filter correction described by Ohno (2002), the inner diameter of the cuvette (0.5 mm, as opposed to the more common 1 cm), and the UV spectra (Supplementary Fig. S2), error due to inner filter effects was less than 5% for wavelengths above 225 nm. As such, excitation spectra for 200–224 nm were removed from the EEMs. The EEMs were corrected for Rayleigh and Raman scattering in MATLAB® with Cleanscan (Zepp *et al.*, 2004) and fluorescence intensities, $I_{\text{Ex/Em}}$, were collected and reported in arbitrary units.

The fluorescence index (FI) was developed to distinguish between microbially and terrestrially derived DOM and is calculated by dividing the fluorescence intensity at excitation/emission wavelengths of 370/450 by the fluorescence intensity at 370/500 (McKnight *et al.*, 2001). The humification index (HIX) has been used to ascertain the extent of humification of NOM and was calculated for each sample by dividing the sum of emission intensities from 435 to 480 nm by the sum of emission intensities from 300 to 345 nm and 435 to 480 nm, all from an excitation wavelength of 254 nm (Ohno, 2002).

Two PARAFAC models were fit following Stedmon and Bro (2008) using the DOM-Fluor toolbox (available for download at www.models.life.ku.dk/algorithms). Model 1, a three-component model, was fit using the 44 sample EEMs (11 raw waters, 33 coagulated waters) and the resulting components were named C1.1, C1.2, and C1.3. The model was validated using the Split Half Analysis and Split Half Validation functions, and the least squares model was chosen using the RandInitAnal function (all three functions contained in the DOM-Fluor toolbox). For Model 2, the 44 EEMs were added to a dataset containing 378 EEMs consisting of raw, alum-coagulated, and magnetic ion exchange (MIEX®)-treated waters from three Arkansas lakes. Six outliers were identified and removed from the 422 EEM dataset using the function Outlier Test. The remaining 416 EEMs were resolved into six components, named C2.1, C2.2, C2.3, C2.4, C2.5, and C2.6. Model 2 was validated and the least squares model chosen in the same manner as Model 1. Each EEM in the PARAFAC model comprised differing amounts of each component fluorophore, expressed quantitatively by F_{MAX} values.

Results and Discussion

Raw water parameters

Raw water turbidity, conductivity, pH, alkalinity, and sulfate are summarized in Supplementary Table S1. The 11 raw waters encompassed a range of characteristics known to impact DBP formation and control. Raw water turbidities

ranged from <0.1 to 110 NTU, with seven raw waters below 5 NTU and two waters in excess of 50 NTU (COH=60 NTU and YAZ=110 NTU). UNY had the lowest alkalinity (10 mg/L-CaCO₃) and conductivity (42 μ S/cm), likely due to an undeveloped, forested watershed (Mohawk Valley Water Authority, 2011) underlain by granite bedrock, which has been shown to be resistant to weathering (Clow *et al.*, 1996). In contrast, conductivities were the highest for YAZ (1,097 μ S/cm) and LNV (973 μ S/cm), likely due to watershed

characteristics (e.g., sedimentary rock) (Apodaca *et al.*, 1996) and human activities (e.g., irrigation) (Butler and von Guerard, 1996). Raw water DOC (Table 1) was lowest at PPA (0.7 mg/L-C) and highest at MMN (4.1 mg/L-C), the latter of which was an unexpected result because runoff from Molli-sols is typically a neutral solution with little organic matter (Butcher, 1992). However, raw water SUVA₂₅₄ (Table 1) was lowest at RNC (3.10 L/[mg·m]) and highest at COH (7.39 L/[mg·m]). Taken together, the DOC and SUVA₂₅₄

TABLE 1. RAW AND TREATED WATER PARAMETERS

Sample location ^a	Treatment	UV ₂₅₄ (cm ⁻¹)	DOC (mg/L)	SUVA ₂₅₄ (L/[mg·m])	I _{240/562} (-)	HIX (-)	FI (-)	TCM (μ M)	BDCM (μ M)	DBCM (μ M)	BIF (-)
BNY	Raw	0.05	1.0	5.27	0.18	0.88	1.49	0.84	0.02	0.00	0.02
	Alum, pH 6	0.01	0.3	4.01	0.10	0.70	1.56	0.33	0.01	0.00	0.03
	Alum, pH 7	0.02	0.4	4.88	0.11	0.76	1.54	0.43	0.01	0.00	0.02
	Alum, pH 8	0.03	0.6	4.48	0.14	0.79	1.58	0.58	0.01	0.00	0.02
COH	Raw	0.09	1.2	7.39	0.22	0.88	1.53	1.06	0.07	0.00	0.06
	Alum, pH 6	0.02	0.6	2.98	0.11	0.72	1.52	0.47	0.06	0.00	0.11
	Alum, pH 7	0.02	0.7	3.59	0.12	0.76	1.56	0.53	0.05	0.00	0.09
	Alum, pH 8	0.04	0.9	4.47	0.15	0.82	1.60	0.78	0.06	0.00	0.08
HMO	Raw	0.15	3.5	4.25	0.44	0.89	1.60	2.03	0.19	0.00	0.09
	Alum, pH 6	0.05	1.2	4.29	0.14	0.81	1.73	0.80	0.12	0.00	0.13
	Alum, pH 7	0.07	1.6	4.32	0.19	0.83	1.69	0.95	0.15	0.00	0.13
	Alum, pH 8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
LNE	Raw	0.05	1.2	4.39	0.17	0.89	1.68	1.17	0.28	0.07	0.27
	Alum, pH 6	0.02	0.6	3.46	0.10	0.78	1.63	0.60	0.31	0.07	0.45
	Alum, pH 7	0.03	0.9	3.40	0.14	0.83	1.68	0.50	0.14	0.04	0.33
	Alum, pH 8	0.05	1.5	3.14	0.17	0.86	1.69	0.44	0.12	0.06	0.39
LNV	Raw	0.05	1.3	4.24	0.19	0.84	1.58	0.80	0.17	0.03	0.23
	Alum, pH 6	0.02	0.6	4.12	0.10	0.73	1.58	0.33	0.10	0.03	0.34
	Alum, pH 7	0.03	0.9	3.60	0.12	0.76	1.60	0.39	0.11	0.03	0.31
	Alum, pH 8	0.05	1.1	4.09	0.16	0.80	1.59	0.66	0.14	0.03	0.24
MMN	Raw	0.13	4.1	3.27	0.47	0.89	1.67	1.86	0.12	0.00	0.06
	Alum, pH 6	0.05	1.4	3.55	0.09	0.80	1.43	0.81	0.02	0.00	0.03
	Alum, pH 7	0.07	1.9	3.63	0.24	0.83	1.72	1.18	0.04	0.00	0.03
	Alum, pH 8	0.11	3.7	3.04	0.30	0.89	1.66	1.88	0.13	0.00	0.06
PPA	Raw	0.03	0.7	4.90	0.12	0.80	1.56	0.67	0.12	0.01	0.19
	Alum, pH 6	0.02	0.5	3.30	0.07	0.67	1.55	0.43	0.12	0.01	0.26
	Alum, pH 7	0.02	0.4	4.01	0.09	0.68	1.62	0.33	0.09	0.01	0.28
	Alum, pH 8	0.02	0.5	4.09	0.10	0.75	1.62	0.37	0.08	0.01	0.23
RNC	Raw	0.09	3.0	3.10	0.38	0.85	1.57	1.52	0.06	0.00	0.04
	Alum, pH 6	0.05	1.6	2.90	0.20	0.76	1.70	0.78	0.04	0.00	0.05
	Alum, pH 7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Alum, pH 8	0.07	2.0	3.51	0.27	0.80	1.66	1.35	0.06	0.00	0.05
RVA	Raw	0.05	1.0	5.33	0.24	0.87	1.44	1.22	0.04	0.00	0.03
	Alum, pH 6	0.01	0.4	3.33	0.10	0.67	1.52	0.53	0.02	0.00	0.04
	Alum, pH 7	0.02	0.4	3.82	0.14	0.63	1.82	0.43	0.02	0.00	0.03
	Alum, pH 8	0.03	0.7	3.99	0.17	0.76	1.52	0.63	0.02	0.00	0.03
UNY	Raw	0.11	2.1	5.36	0.34	0.93	1.36	2.03	0.00	0.00	0.00
	Alum, pH 6	0.01	0.4	3.04	0.10	0.63	1.64	0.44	0.00	0.00	0.00
	Alum, pH 7	0.02	0.5	4.05	0.10	0.76	1.52	0.60	0.00	0.00	0.00
	Alum, pH 8	0.09	1.5	6.07	0.25	0.88	1.45	1.53	0.00	0.00	0.00
YAZ	Raw	0.05	1.4	3.54	0.18	0.83	1.56	0.58	0.17	0.04	0.33
	Alum, pH 6	0.03	1.0	2.52	0.11	0.75	1.57	0.34	0.11	0.03	0.38
	Alum, pH 7	0.03	1.2	2.77	0.13	0.77	1.60	0.49	0.16	0.04	0.34
	Alum, pH 8	0.04	1.3	3.05	0.16	0.79	1.56	0.49	0.14	0.04	0.32

^aSee Supplementary Figure S1 for definitions of the sample location abbreviations.

UV₂₅₄, ultraviolet absorbance at 254 nm; DOC, dissolved organic carbon; SUVA₂₅₄, specific ultraviolet absorbance at 254 nm; I_{240/562}, fluorescence intensity at an excitation of 240 nm and emission of 562 nm; HIX, humification index; FI, fluorescence index; TCM, chloroform; BDCM, bromodichloromethane; DBCM, dibromochloromethane; BIF, bromine incorporation factor; ND, no data.

results indicate that the DOM quantity and aromatic content varied across the sampling locations. In terms of water quality parameters that impact DBP speciation, bromide was detectable only in raw waters from LNE, LNV, PPA, and YAZ at concentrations of 100, 60, 60, and 80 $\mu\text{g/L}$, respectively.

Size characterizations of CDOM

AF4-UV₂₅₄ fractograms of CDOM in the raw and treated waters are shown in Supplementary Figure S3 and discussed in detail in the Supplementary Data. AF4-UV₂₅₄ fractograms indicated that hydrodynamic diameters of CDOM increased with coagulation pH, and alum coagulation removed on average 91% of CDOM at pH 6, but only 34% of CDOM at pH 8. Furthermore, preferential removal of larger sized CDOM occurred at pH 6, similar to our previously reported findings (Pifer and Fairey, 2012).

Absorbance and fluorescence measurements

UV₂₅₄ was measured for all raw and alum-coagulated samples and decreased after alum coagulation at pH 6, 7, and 8 (Table 1). Although SUVA₂₅₄ decreased after alum coagulation at pH 6, 7, and 8 for seven waters (Table 1), it was unchanged or even increased after coagulation for four waters (HMO and MMN at pH 6 and 7; RNC and UNY at pH 8). Taken together, the UV₂₅₄ and SUVA₂₅₄ results indicate that alum coagulation predominantly targeted aromatic CDOM, which is generally considered to be the fraction with the highest THM yield (Edzwald *et al.*, 1985; Singer and Chang, 1989).

Raw water FI ranged from 1.36 for UNY to 1.68 for LNE (Table 1). The FI values for BNY, COH, RVA, and UNY (1.36–1.53) were similar to those reported for terrestrially derived fulvic acids isolated from river water (McKnight *et al.*, 2001). The raw water DOM in the remaining samples had higher FI values (1.56–1.68) indicating that the DOM was microbially influenced. Although DOM from LNE, the sole groundwater source, had the highest raw water FI, it was low relative to the reported FI value of 1.9 of a fulvic acid isolate from a groundwater source (McKnight *et al.*, 2001). This re-

sult may reflect the fact that the LNE aquifer is under the direct influence of surface water and that its DOM may not be completely microbially derived, as was hypothesized for the groundwater sample discussed in McKnight *et al.* (2001).

FI in alum-coagulated samples ranged from 1.43 for MMN to 1.82 for RVA (Table 1). A change in FI of more than 0.1 has been reported to indicate a change in source material, for example, from terrestrial to microbial sources (McKnight *et al.*, 2001). Under this guideline, the FI increased after alum coagulation for HMO, RNC, and UNY at pH 6, and RVA and UNY at pH 7, indicating preferential removal of terrestrially derived DOM. This result was similar to the findings reported by Beggs and Summers (2011). Conversely, the FI for MMN decreased after coagulation at pH 6, indicating preferential removal of microbially derived DOM.

The HIX for raw water samples ranged from 0.80 for PPA to 0.93 for UNY (Table 1). These values are in the range reported by Ohno (2002) for soil DOM and soil fulvic acid. The HIX for all samples decreased after alum coagulation, similar to results reported by Beggs and Summers (2011). This indicates that alum coagulation preferentially removed aromatic, humic acid-like DOM, in agreement with the UV₂₅₄ data for the majority of the samples and the results of previous research (Liang and Singer, 2003).

Fluorescence PARAFAC analysis

One of the objectives of this article was to determine if the number of EEMs in a PARAFAC model impacted the suitability of its components as DBP precursor surrogates. PARAFAC component EEMs from Model 1 (consisting of 44 EEMs from this study) and Model 2 (consisting of 416 EEMs, including 372 EEMs from previous studies) (Pifer *et al.*, 2011; Pifer and Fairey, 2012) are shown in Supplementary Figure S4 and the locations of their excitation and emission peak maxima are presented in Table 2. In terms of identifying these PARAFAC components, fluorophore groups in DOM samples of unknown composition have traditionally been categorized as humic like, fulvic like, or protein like based on comparisons of their excitation and emission maxima to

TABLE 2. MAXIMA LOCATIONS AND CHARACTERISTICS OF THE FLUORESCENCE PARALLEL FACTOR COMPONENTS

Model 1			Model 2			Identification
Component number	Excitation maxima (nm)	Emission maxima (nm)	Component number	Excitation maxima (nm)	Emission maxima (nm)	
C1.1	238 (328)	426	C2.1	231 (339)	429	Fulvic acid-like ^a
			C2.4	343	427	Humic acid-like ^b
			C2.3	234 (311)	404	Fulvic acid-like ^a
C1.2	374 (268)	467	C2.2	264 (358)	456	Humic acid-like ^{c,d}
C1.3	< 225 (294)	358	C2.5	395 (< 225, 276)	484	Microbial humic-like ^a
			C2.6	< 225 (270)	338	Humic acid-like ^d
						Humic acid-like ^{a,d}
						Tryptophan-like ^c

Values in parentheses are secondary and tertiary excitation maxima.

^aSantin *et al.* (2009).

^bStedmon and Markager (2005).

^cDubnick *et al.* (2010).

^dCoble (1996).

those reported in the literature. This practice facilitates discussion of PARAFAC components, but is not a true identification of DOM constituents. In this study, C1.3 and C2.6 resembled a tryptophan-like component reported by Dubnick *et al.* (2010), and the remaining components resembled various humic- and fulvic-like components reported previously (Coble, 1996; Stedmon and Markager, 2005; Santin *et al.*, 2009; Dubnick *et al.*, 2010).

Increasing the number of EEMs fit from 44 to 416 between Models 1 and 2 increased the number of PARAFAC components from 3 to 6, respectively. For both PARAFAC models, the samples were dominated by the fulvic- and humic-like components (Fig. 1 and Table 2). The sums of these F_{MAX} values for each sample in Models 1 and 2 were linearly correlated ($r^2=0.99$) with a slope of 0.64. The strong linear correlation indicated that the models were similar, but the slope less than unity indicated the potential for an increased resolution with the larger model. As expected, based on previous research (Pifer and Fairey, 2012), the fulvic acid- and humic acid-like components were removed by alum coagulation (Fig. 1). F_{MAX} values decreased following alum coagulation for all sampling locations, but the fraction re-

maining increased with coagulation pH. For the fulvic acid- and humic acid-like components, C1.1 and C2.2 (Fig. 1 and Table 2) were removed to the greatest extent (42–100% at pH 6). In contrast, C1.3 and C2.6 (tryptophan like) were poorly removed by alum coagulation (0–35% at pH 6) for all sampling locations except MMN (84% and 62% for C1.3 and C2.6, respectively).

Disinfection by-products

Of the seven DBPs assessed (see Disinfection By-products section), only three THMs—TCM, BDCM, and DBCM—were detected at quantifiable levels ($>0.01 \mu\text{M}$) in the chlorinated raw and alum-coagulated samples. Check standards were within $\pm 16\%$ for TCM, $\pm 12\%$ for BDCM, and $\pm 8\%$ for DBCM. These checks were within EPA 551.1 requirements, that is, 90% of checks within $\pm 20\%$ and all checks within $\pm 25\%$. The concentrations of each DBP are presented in Table 1 with the exception of two treated samples (HMO pH 8 and RNC pH 7), which were lost during extraction.

TCM was the dominant DBP formed, with concentrations ranging from 0.58 to $2.03 \mu\text{M}$ in chlorinated raw waters and

FIG. 1. Parallel factor (PARAFAC) component maximum fluorescence intensity (F_{MAX}) values organized by sampling location and treatment for (a) Model 1 and (b) Model 2. Model 1 was fit using excitation/emission matrices (EEMs) for the 11 raw waters and 33 coagulated waters collected as part of this study; Model 2 was fit with these 44 EEMs plus an additional 378 EEMs collectively previously. “R” represents filtered raw water samples, and “6,” “7,” and “8” refer to the pH of coagulation. See Table 2 for a description of the fluorescence PARAFAC components (C1.1–1.3 and C2.1–2.6) and Supplementary Figure S1 for definitions of the sample location abbreviations.

from 0.33 to 1.88 μM in chlorinated alum-treated waters. In general, alum coagulation removed TCM precursors from raw waters with three exceptions (YAZ at pH 7 and 8 and MMN at pH 8). For seven of the waters (BNY, COH, HMO, LNV, MMN, RNC, and UNY), the TCMFP increased with increasing pH of coagulation. BDCM was present in all chlorinated raw waters (0.02–0.28 μM) and alum-coagulated waters (0.01–0.31 μM) except those from UNY, but no removal trends were evident. Similarly, DBCM was present in chlorinated raw and treated waters from HMO, LNE, LNV, PPA, and YAZ at concentrations between 0.01 and 0.07 μM . The bromine incorporation factor (BIF) was calculated following Chang *et al.* (2001) and is shown in Table 1. BIF was highest for the chlorinated raw and coagulated LNE, LNV, PPA, and YAZ samples (0.23–0.45), as expected, based on the relatively high bromide concentrations in the raw waters (see Raw Water Parameters section).

Correlations between TTHMFP and precursor surrogates

Linear regression models were constructed to assess the quality of the various DBP precursor surrogates (e.g., DOC, UV_{254} , $I_{\text{Ex/Em}}$, and PARAFAC component F_{MAX} values) for the group of raw and alum-treated samples (Fig. 2). Of the PARAFAC components, F_{MAX} values for humic- and fulvic-like components C1.1 and C2.2 were most strongly correlated to TTHMFP. Simple linear correlations were developed between TTHMFP and fluorescence intensity at each excitation/emission wavelength pair ($I_{\text{Ex/Em}}$). The correlation coefficients (r^2) between TTHMFP and $I_{\text{Ex/Em}}$ are shown in Supplementary Figure S5a and indicate that the strongest correlations ($r^2 > 0.80$) were in the region approximated by excitation wavelengths of 230–270 nm and emission wavelengths of 510–570 nm. The highest r^2 for this pair-picking process was $I_{240/562}$ ($r^2 = 0.81$); this surrogate was the strongest fluorescence-based predictor for TTHMFP.

Figure 2a–e shows TTHMFP for the group of 11 raw waters and 33 alum-coagulated samples. All five surrogate parameters were good predictors of TTHMFP, with UV_{254}

the strongest ($r^2 = 0.89$) and C1.1 the weakest ($r^2 = 0.73$). This was an unexpected result given the diversity of the raw and alum-coagulated samples and the fact that fluorescence is more sensitive than UV_{254} (Lakowicz, 2006) and more selective than DOC. Notably, F_{MAX} values were weaker TTHMFP precursor surrogate parameters ($r^2 = 0.73$ and 0.78 for the three- and six-component models, respectively) than $I_{240/562}$ ($r^2 = 0.81$), indicating correlations with PARAFAC components were not an improvement over certain $I_{\text{Ex/Em}}$ values taken directly from the EEMs.

To improve the TTHMFP correlations and better understand differences in THM precursors based on watershed soil order, data from the individual sampling locations were compared to the entire dataset. Linear correlations between TTHMFP and the five DBP surrogates were identified for all sampling locations except LNE, a groundwater sample from a Mollisol-underlain watershed ($r^2 < 0.1$ for all five surrogates). Analysis of covariance (ANCOVA) was performed to determine if there were statistically significant differences between the regression line slopes and intercepts for samples collected from watersheds of varying soil order. For MMN, the other sample from a Mollisol-underlain watershed (Supplementary Table S1), ANCOVA indicated that the regression line for TTHMFP and the five DBP surrogates could be better modeled with a unique intercept ($p < 0.1$). Similarly, linear correlations for UNY samples required a unique slope ($p < 0.05$). As shown by the water quality data presented in Supplementary Table S1, the UNY raw water had the lowest pH, alkalinity, conductivity, and sulfate concentration of the 11 waters tested. The unique slope of the TTHMFP correlations implies that the precursors were also different than those in the other waters. This may stem from the fact that the UNY watershed is underlain by Spodosols, characterized by a layer of decomposing organic material above the soil that has been shown to contribute acidic DOM (i.e., humic and fulvic acids) to Adirondack lakes (Cronan and Aiken, 1985), which may be different in provenance and character than DOM in the other waters evaluated.

Based on these results, samples from LNE, MMN, and UNY were excluded from the linear models, which improved

FIG. 2. Correlations between total trihalomethane formation potential (TTHMFP) and (a) dissolved organic carbon (DOC), (b) ultraviolet absorbance at 254 nm (UV_{254}), (c) $I_{240/562}$, (d) F_{MAX} for PARAFAC component 1.1, and (e) F_{MAX} for PARAFAC component 2.2. Linear best-fit models were determined based on least squares analyses of raw and alum-coagulated waters from all 11 sampling locations. Open squares represent data from MMN, UNY, and LNE sampling locations and closed squares represent data from the other eight sampling locations. See Supplementary Figure S1 for definitions of the sample location abbreviations and Table 2 for description of the fluorescence PARAFAC components. Gray-shaded regions encompass the upper and lower 95% prediction intervals for the linear models.

all five models— r^2 values increased from 0.75 to 0.82 for DOC, 0.89 to 0.91 for UV₂₅₄, 0.81 to 0.92 for I_{Ex/Em}, 0.73 to 0.89 for C1.1, and 0.78 to 0.92 for C2.2. The r^2 values between TTHMFP and I_{Ex/Em} (Supplementary Fig. S5b) indicated that there were strong correlations ($r^2 > 0.85$) in the region approximated by excitation wavelengths between 240–290 nm and emission wavelengths of 450–540 nm, with a maximum at I_{266/482}. The best I_{Ex/Em} for the reduced dataset (I_{266/482}) was different than that from the whole dataset (I_{240/562}), which reflects the fact that multiple excitation/emission pairs were strongly correlated with TTHMFP (Supplementary Fig. S5). Compared with the fluorophore groups identified by the PARAFAC analysis (Table 2), I_{240/562} is near the excitation maxima of humic acid- and fulvic acid-like components (C1.1, C2.1, and C2.3). However, the emission maxima (562 nm) is higher than those of any PARAFAC component identified and adjacent to the second-order Raman scattering region. This region was excised and interpolated using a Delaunay interpolation algorithm within the EEM Cleanscan protocol (Zepp *et al.*, 2004; Pifer *et al.*, 2011). Similarly, I_{266/482} is near to the excitation and emission maxima of humic acid-like components (C1.2, C2.2, and C2.5), but near the second-order Rayleigh scattering region. These results point to the value of Cleanscan used for EEM processing related to TTHMFP precursor surrogates. As was the case for the complete dataset, I_{266/482} and PARAFAC F_{MAX} values were equally effective TTHMFP surrogate parameters, providing further evidence that EEM processing using PARAFAC may not strengthen correlations relative to scatter-corrected EEM data. Additionally, metrics from EEM pair-picking (e.g., I_{240/562}, I_{266/482}) could potentially be processed in near real time (Goldman *et al.*, 2012) to monitor THM precursor removal during alum coagulation at DWTPs.

Overall, results in Figure 2 indicate that UV₂₅₄, I_{Ex/Em}, and F_{MAX} values from humic acid- and fulvic acid-like components were strong TTHMFP precursor surrogate parameters for a diverse group of raw and alum-coagulated samples. The fact that UV₂₅₄ was the most highly correlated surrogate parameter was an unexpected result given that similar studies showed fluorescence-based metrics were stronger (Granderson *et al.*, 2013; Pifer *et al.*, 2013). However, in the Granderson *et al.* (2013) study, UV₂₅₄ was shown to be insensitive to chlorine dioxide, a treatment step not assessed in this work. Similarly, in the Pifer *et al.* (2013) study, a heavy rainfall event produced an influx of dissolved iron, which biased the UV₂₅₄ measurements, but not the fluorescence. As such, we conclude that UV₂₅₄ is an excellent TTHMFP precursor surrogate for a diverse group of raw waters and alum-coagulated samples, similar to previous findings (Edzwald *et al.*, 1985; Singer and Chang, 1989), but with notable exceptions (e.g., Granderson *et al.*, 2013; Pifer *et al.*, 2013). In terms of future work, the fact that the Mollisol- and Spodosol-underlain sampling locations required unique linear models indicates that additional investigations should be conducted in watersheds with these soil orders, with particular attention paid to groundwater sources (e.g., LNE). In addition, further research is needed to determine if UV₂₅₄- and fluorescence-based precursor surrogate parameters could accurately predict the formation of other DBPs (e.g., haloacetic acids, haloacetonitriles, and nitrosamines) under various disinfection regimes (e.g., free chlorine, chloramines, and chlorine dioxide).

Summary

DOC, UV₂₅₄, I_{Ex/Em}, and F_{MAX} values of fluorophore components for a diverse group of raw and alum-coagulated samples from 11 drinking water sources resulted in the following insights:

- For the entire dataset consisting of 11 raw waters and 33 alum-coagulated samples, the strongest TTHMFP precursor surrogate parameter was UV₂₅₄ ($r^2 = 0.89$), followed by I_{240/562} ($r^2 = 0.81$), C2.2 ($r^2 = 0.78$), DOC ($r^2 = 0.75$), and C1.1 ($r^2 = 0.73$). This demonstrates the accuracy of UV₂₅₄ for a diverse group of waters treated by alum coagulation alone and that PARAFAC was not an improvement over fluorescence intensity metrics taken directly from the scatter-corrected EEMs.
- For fluorescence PARAFAC, increasing the number of EEMs used to fit the model (from 44 to 416) increased the number of PARAFAC components from 3 to 6 and resulted in an improvement in subsequent correlations with TTHMFP (e.g., for all 11 DWTPs, r^2 increased from 0.73 to 0.78).
- Following exclusion of the groundwater samples (LNE) and samples from MMN and UNY, linear correlations improved between TTHMFP and DOC, UV₂₅₄, I_{Ex/Em}, and PARAFAC F_{MAX} for C1.1 and C2.2 ($r^2 = 0.82$ – 0.92).
- For the reduced dataset (8 raw waters and 24 alum-coagulated samples), I_{266/482}, C1.1, and C2.2 were all similarly strong TTHMFP precursor surrogate parameters ($r^2 = 0.89$ – 0.92). This is further evidence that EEM processing with PARAFAC did not improve correlations. Additionally, I_{Ex/Em} could be measured in near real time using custom sensors, which could permit DWTPs to optimize alum dosing and pH for removal of THM precursors.

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