

Assessing UV- and fluorescence-based metrics as disinfection byproduct precursor surrogate parameters in a water body influenced by a heavy rainfall event

Ashley D. Pifer, Sarah L. Cousins and Julian L. Fairey

ABSTRACT

Although disinfection byproducts (DBPs) were discovered decades ago and surrogate parameters have been developed to track their precursors, the accuracy of these metrics in waters impacted by heavy rainfall events is largely unknown. We measured DBPs and their precursor surrogate parameters in a water body impacted by 28 cm of rain between 4/24/11 and 4/26/11. Raw waters collected from four locations within the water body from April to August 2011 were treated by coagulation and anion exchange. Ultraviolet absorbance at 254 nm (UV_{254}) and fluorescence excitation-emission pairs ($I_{EX/EM}$) were measured. Excitation-emission matrices (EEMs) were processed with parallel factor (PARAFAC) analysis, which resulted in six component fluorophore groups (C1-C6), each with a maximum intensity (F_{MAX}). DBP formation potential (DBFPF) with free chlorine was used to assess the precursor concentrations. Chloroform (TCM) was the predominant DBP formed, and 37–63% of its precursors were removed by treatment. The trichloromethane formation potential (TCMFP)- UV_{254} correlation was poor ($r^2 = 0.25$) and adversely impacted by the influx of dissolved iron from the heavy rainfall event; in contrast, correlations with fluorescence-based metrics were strong – TCMFP- $I_{278/506}$ ($r^2 = 0.88$) and TCMFP-C1 F_{MAX} ($r^2 = 0.87$) – illustrating the accuracy of these precursor surrogate parameters in waters impacted by a heavy rainfall event.

Key words | anion exchange, chloroform, fluorescence, heavy rainfall event, natural organic matter

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INTRODUCTION

Disinfectants, such as free chlorine, react with natural organic matter (NOM) in drinking water treatment plants (DWTPs) and distribution systems to form disinfection byproducts (DBPs), some of which are suspected carcinogens (Cantor *et al.* 1998) and teratogens (Nieuwenhuijsen *et al.* 2000). The United States Environmental Protection Agency currently regulates 11 DBPs in finished drinking water – four trihalomethanes, five haloacetic acids, chlorite, and bromate – under the Stage 2 Disinfectants and Disinfection By-Product Rule. Despite nearly 40 years of research, DBP control remains a challenge at many DWTPs, primarily because of difficulties associated with removing sufficient NOM, the primary pool of DBP precursors. DWTPs can take a two-pronged approach to curb

DBPs: (1) use alternative disinfectants and/or (2) remove additional DBP precursors. This study focuses on supporting the latter approach, by developing metrics to track trihalomethane (THM) precursors. A unique aspect of this study is the focus on a water body during a period in which an extreme weather event occurred – specifically, 28 cm of rain over a 3-day period (4/24/11 to 4/26/11) in northwest Arkansas.

Although coagulation (Krasner & Amy 1995) is commonly used to remove NOM at DWTPs (Crittenden *et al.* 2012), other processes such as anion exchange have shown promise for DBP-precursor removal (Bolto *et al.* 2002). The Commonwealth Scientific and Industrial Research Organization and Orica Australia Pty Ltd developed magnetic ion

exchange (MIEX[®]) resin, an anion exchange resin that has a high selectivity for NOM and can be used in completely mixed reactors (Drikas *et al.* 2002). While an extensive body of research exists regarding DBP precursor removal with MIEX[®] (Drikas *et al.* 2003; Singer *et al.* 2007; Jarvis *et al.* 2008), no broadly applicable THM precursor surrogate parameters have been developed and evaluated for alum- or MIEX[®]-treated waters that have been impacted by a heavy rainfall event. The availability of robust THM precursor surrogate parameters would allow DWTPs to better adapt THM-control processes during such storm events.

NOM is derived from terrestrial and aquatic sources, is rich in organic carbon, and can have an array of physical and chemical properties which vary temporally (Miller & McKnight 2010) and spatially (Pifer *et al.* 2011). The properties of NOM lend themselves to characterization by spectrophotometric techniques, such as UV absorbance and fluorescence. Edzwald *et al.* (1985) showed that UV₂₅₄ was a strong total THM formation potential (TTHMFP) precursor surrogate parameter (e.g. $r^2 > 0.9$), but the correlations were slightly different for the two waters evaluated. Similarly, Singer & Chang (1989) found a strong TTHMFP-UV₂₅₄ correlation for their study of 12 full-scale DWTPs, but these data were scattered at UV₂₅₄ values greater than 0.4 cm⁻¹. Specific UV₂₅₄ (SUVA₂₅₄), the UV₂₅₄ normalized by the dissolved organic carbon (DOC) concentration, is an intensive parameter that is useful for estimating the proportion of total carbon present as aromatic carbon in aquatic systems (Weishaar *et al.* 2003). Not surprisingly, therefore, DBP-SUVA₂₅₄ correlations are weak in waters over the typical range of SUVA₂₅₄ values (0.5–7 L mg⁻¹ m⁻¹) (Weishaar *et al.* 2003; Ates *et al.* 2007; Pifer & Fairey 2012). However, SUVA₂₅₄ can provide insight into the effectiveness of treatment processes, such as coagulation, by comparison with both UV₂₅₄ and DOC in raw and treated waters.

Fluorescence excitation-emission matrices (EEMs) have been used to characterize NOM in natural waters and identify DBP precursors (Hua *et al.* 2010). Because of the complexity of fluorescence data, parallel factor (PARAFAC) analysis has been used to decompose groups of EEMs into principal fluorophore groups or components (Stedmon *et al.* 2003). For all components within each EEM, PARAFAC analysis determines a maximum fluorescence

intensity (F_{MAX}) value. A recent study of raw and alum coagulated samples (Pifer & Fairey 2012) demonstrated that trichloromethane formation potential (TCMFP) was strongly correlated to F_{MAX} values of a humic-like fluorophore, characterized by an excitation maximum of 238 nm and emission maximum of 430 nm. However, correlations between fluorescence-PARAFAC components and TTHMFP have not been evaluated for MIEX[®]-treated waters. Additionally, data directly from EEMs (e.g. I_{Ex/Em} pairs) have not been compared to PARAFAC F_{MAX} data as THM precursor surrogate parameters. Discrete I_{Ex/Em} pairs could be measured in real-time and with less computational effort relative to PARAFAC, potentially adding to their value as a THM precursor surrogate parameter.

The objective of this study is to evaluate and compare UV- and fluorescence-based metrics as THMFP precursor surrogate parameters in a water body influenced by a heavy rainfall event. Raw waters were sampled from four DWTP intakes on Beaver Lake (Lowell, AR) between 4/11/11 and 8/4/11 to capture the impact of the 28 cm rainfall event that occurred between 4/24/11 and 4/26/11. Raw waters underwent treatment in the laboratory at pH 6, 7, and 8 with alum and MIEX[®], and UV- and fluorescence-based metrics were measured and calculated. The raw and treated waters were chlorinated in formation potential tests and DBPs were quantified. Correlations were sought between spectrophotometric surrogate parameters and TCMFP using the group of raw and treated waters, a portion of which were impacted by a heavy rainfall event.

METHODS

Sampling locations

Raw water samples (18 L each) were collected in pre-cleaned high-density polyethylene carboys on 4/11/11, 5/13/11, 5/31/11, 6/28/11, 7/14/11, and 8/4/11 at the intakes of the four DWTPs on Beaver Lake: Beaver Water District (BWD), Benton-Washington Regional Public Water Authority, referred to as Two Ton (TT), Carroll Boone Water District (CB), and Madison County Regional Water District (MC). An additional sample was taken at BWD on 5/6/11 to help capture the major rainfall event.

These sampling locations were selected to assess the spatial variability of DBP-precursors within Beaver Lake and determine the impact of this variability on MIEX[®] treatment and DBP formation.

Water quality tests

All glassware, with the exception of volumetric flasks, was washed with a solution of tap water and Alconox detergent, rinsed multiple times with Milli-Q water (18.2 MΩ-cm), and baked for 30 min at 400 °C. Volumetric flasks and plasticware were washed with an Alconox and tap water solution, rinsed with Milli-Q water and air-dried at room temperature. For vacuum filtration, 0.7 μm glass fiber filters (GFFs) were pre-combusted (400 °C for 30 min) and pre-rinsed with 1 L of Milli-Q water (Cory *et al.* 2011). Therefore, in this work, dissolved natural organic matter (DOM) is operationally defined as the portion of NOM passing a 0.7 μm GFF. These filters were used instead of the more common 0.45 μm membrane filters to reduce leaching and/or sorption of organic carbon that could interfere with the UV₂₅₄ measurements (Karanfil *et al.* 2003). Other researchers have used these GFFs in recent DOM-fluorescence studies (Cory *et al.* 2011; Goldman *et al.* 2012), presumably to ensure adequate particle removal while not leaching or sorbing organics that could introduce artifacts to the fluorescence measurements.

Raw water quality parameters, i.e. pH, alkalinity, turbidity, DOC, total dissolved nitrogen, ammonia, and total phosphorus, were measured as part of an alum coagulation study (Pifer & Fairey 2012), and a description of the methods can be found in its Supplementary Data. UV₂₅₄ was measured on filtered samples following Standard Methods 5910-B (Eaton *et al.* 2005) using a Shimadzu UV-Vis 2450 (Kyoto, Japan) spectrophotometer with a 1 cm path length quartz cell. The instrument was blanked with Milli-Q water before the first sample and after every six samples thereafter. SUVA₂₅₄ was calculated by dividing the UV₂₅₄ absorbance by the product of the UV cell path length (0.01 m) and the DOC concentration (mg/L). Total dissolved iron was measured daily at the BWD following Hach Method 8146. Samples were filtered using 1.1 μm GFFs and diluted, as required, with deionized water such that dissolved iron concentrations were less than 3 mg/L.

MIEX[®] experiments

MIEX[®] resin (Orica Watercare, Watkins, CO) was obtained in a 5% brine solution. The resin was prepared by decanting with glass Pasteur pipettes and rinsing with Milli-Q water until the conductivity of the supernatant, measured with a four-cell conductivity probe (Accumet), was less than or equal to 1 mS/cm. The MIEX[®] resin-Milli-Q water slurry was transferred to a 10 mL graduated cylinder and allowed to settle for approximately 10 min before use. A resin dose of 6 mL/L was chosen for all MIEX[®] treatments based on preliminary experiments that showed DOC reduction greater than 50%.

MIEX[®] experiments were conducted at pH 6, 7, and 8. To control pH, 10 mL of phosphate buffer (68.1 g/L KH₂PO₄ and 11.7 g/L NaOH) was added to each 490 mL raw water sample. The pH of the samples was further adjusted using HCl or NaOH. The samples were transferred to 500 mL amber glass bottles, and glass pipettes were used to deliver settled resin to the pH-buffered raw water samples. The samples were tumbled end-over-end at 45 revolutions per minute for approximately 18 hours, a time sufficient to ensure equilibrium was achieved based on preliminary experiments (data not shown). The samples were filtered with 0.7 μm GFFs prior to further analyses.

Disinfection byproduct formation potential tests

DBPFP tests were conducted on 250 mL portions of raw and MIEX[®]-treated water samples collected on 5/13/11, 6/28/11, 7/14/11, and 8/04/11 according to Standard Methods 5710-B with modifications. The samples were adjusted to pH 7.0 with phosphate buffer and spiked with NaOCl solution such that the chlorine residual was between 3 and 7 mg/L as Cl₂ after storage for 7 days in the dark at 25 °C. Chlorine residuals were measured using DPD total chlorine powder pillows (Hach Company) with a Shimadzu UV-Vis 2450 spectrophotometer at a wavelength of 552 nm, calibrated with standard curve between 1.0 and 7.0 mg/L as Cl₂. Precisely 30 mL of each chlorinated sample was taken for DBP analysis, and the remainder was quenched by sodium sulfite and reserved for further analyses. The 30 mL portions were quenched using ammonium chloride to preserve haloacetonitriles, and DBPs were extracted by

liquid–liquid extraction following EPA 551.1 with modifications detailed in Pifer & Fairey (2012). The extraction solvent and internal standard were combined as 0.5 mg/L 1,1,1-trichloroethane in pentane (Wahman 2006). A GC-2010 with an electron capture detector (Shimadzu Corp.) was used to quantify DBPs. A standard curve (1, 2, 5, 10, 20, 40, 60, 80, and 100 µg/L) containing eight DBPs (chloroform, dichlorobromomethane, dibromochloromethane, bromoform, 1,1,1-trichloro-2-propanone, dichloroacetonitrile, trichloroacetonitrile, and dibromoacetonitrile) was run prior to the samples. Blanks and 10 µg/L check standards were run after every twelfth injection, and 90% of checks were within ±20% of the standard concentration and all check standards were within ±25%, which is considered to be acceptable based on EPA 551.1.

Fluorescence-PARAFAC analysis

Fluorescence EEMs of 200 raw and MIEX[®]-treated waters were collected using a dual monochromator fluorescence detector (Agilent Technologies, Model G1321A) at excitation wavelengths from 200 to 400 nm and emission wavelengths from 270 to 600 nm, each in 1 nm increments. The scan speed was 28 ms per data point and the fluorescence cuvette had an inner diameter of 0.5 mm, as opposed to the more common 1 cm cuvette. EEMs were corrected for Rayleigh and Raman scattering using *Cleanscan* in MATLAB[®] (Zepp *et al.* 2004). To facilitate comparison to alum coagulation or MIEX[®]-treatment, 190 EEMs were added to the PARAFAC model from a previously reported alum coagulation study (Pifer & Fairey 2012). Following removal of outliers, the final PARAFAC model contained 378 EEMs. PARAFAC modeling was done in MATLAB[®] using the *DOM-Fluor toolbox* (available for download at www.models.life.ku.kd/algorithms). The function, *Split-Data*, divided the EEM dataset into two pairs of halves. These halves were used in the functions *SplitHalfAnalysis* and *SplitHalfValidation*, which compared the shape of the components. When component shapes from each half were identical, the corresponding model and number of PARAFAC components was considered robust. Stedmon & Bro (2008) suggested that the component plots have a single emission peak at wavelengths that slightly overlap the excitation peaks. Additional details of the PARAFAC

procedure are provided elsewhere (Pifer *et al.* 2011; Pifer & Fairey 2012). The PARAFAC algorithm decomposed the EEM dataset into its principal fluorophore groups (called components) and reported the F_{MAX} values for each component in each sample.

RESULTS AND DISCUSSION

Raw water parameters

The inset of Figure 1 shows a map of Beaver Lake, with the locations of the four DWTPs and the dam noted. The water flows in a northerly direction in this water body, which has a surface area of 103 km² and a hydraulic catchment area of 310,000 ha of mostly forest and agricultural lands (Sen *et al.* 2007). Select raw water parameters (e.g. pH, conductivity, alkalinity, total dissolved nitrogen, total phosphorus, and trophic state index) were collected from 5/13/11 to 8/4/11 and are presented in Pifer & Fairey (2012). Additional raw water parameters are shown in Table 1 for sampling dates before and after the heavy rainfall event (28 cm from April 24–26, 2011, NOAA Satellite and Information Service). Specifically, Table 1 shows values for raw water turbidity, UV₂₅₄, DOC, and SUVA₂₅₄ on 4/11/11, 5/6/13, 5/13/11, 5/31/11, 6/28/11, 7/14/11, and 8/4/11. The impact of the heavy rainfall event was apparent at BWD and TT (at the upstream end of the lake, see inset of Figure 1), where the raw water turbidity spiked (>120 NTU) for the samples collected on 5/6/11 and 5/13/11. In contrast, at CB (adjacent to the dam, see inset of Figure 1), the turbidity was less than 11 NTU for the three sampling dates after the heavy rainfall event and, at MC, only as high as 36 NTU on 5/13/11. In terms of organic indicators, DOC ranged from 1.4 to 9.4 mg L⁻¹ as C and peaked on 5/31/11 in all four sampling locations, with no apparent impact from the heavy rainfall event. Interestingly, raw water DOC was uncorrelated with UV₂₅₄ ($r^2 = 0.01$). SUVA₂₅₄ ranged from 0.3 to 12.4 L mg⁻¹ m⁻¹, with a mean of 4.8 L mg⁻¹ m⁻¹. The data in Table 1 show the SUVA₂₅₄ values were atypically large for BWD on 5/6/11 and 5/13/11 and for TT on 5/13/11 and 6/28/11. For these samples, high UV₂₅₄ absorbance produced the high SUVA₂₅₄, as

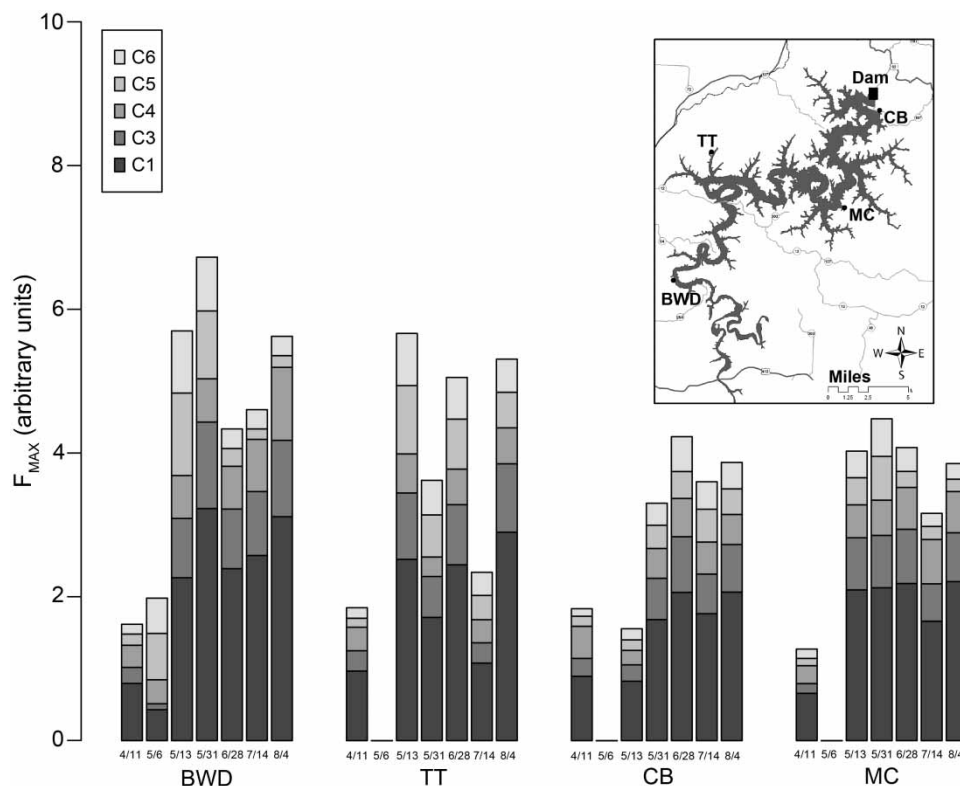


Figure 1 | Fluorescence-PARAFAC component maxima (F_{MAX}) of the five components (C1, C3, C4, C5, and C6) for the raw water samples collected on each sampling date (noted under each bar) and location. BWD is the Beaver Water District, TT is Two Ton, CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District. The inset shows the Beaver Lake watershed and the locations of the dam and the four drinking water plants.

opposed to low DOC. Weishaar *et al.* (2003) showed that UV_{254} increased linearly with dissolved ferric iron and that $3 \text{ mg Fe}^{3+}/\text{L}$ produced a UV_{254} absorbance of approximately 0.2 cm^{-1} . Figure 2 shows the total dissolved iron concentration in the raw water at BWD between April and August 2011 (data for the other DWTPs were not available). These data show a spike in total dissolved iron, beginning in late April and subsiding in late May, with a maximum in excess of 30 mg/L in early May. Therefore, we concluded that the heavy rainfall event (4/24/11–4/26/11) temporarily increased dissolved iron at BWD and TT and caused high UV_{254} measurements, and, in turn, high $SUVA_{254}$ values. This contention is advanced further in the discussion of the MIEX[®]-treated samples in the ‘Specific ultraviolet absorbance’ section. On balance, the data in Table 1 indicate that the heavy rainfall event impacted the turbidity, UV_{254} , and $SUVA_{254}$ of the raw waters from BWD and TT more so than those at CB and MC.

Fluorescence-PARAFAC analysis

The 378 EEMs in the dataset resulted in a six-component PARAFAC model, which was validated by the *SplitHalf-Analysis* function. The six components were numbered consecutively and referred to as C1–C6. C2 was identified as fluorometer instrument noise (excitation maximum $<225 \text{ nm}$, EEM not shown) based on a previous study (Pifer *et al.* 2011), leaving five meaningful components. The locations of the excitation and emission maxima for these components are listed in Table 2. Based on the location of these maxima and the fluorophore identifications determined by Santin *et al.* (2009), the following component assignments were made: C1 – fulvic acid-like, C3 and C5 – humic acid-like, C4 – tryptophan-like, and C6 – microbial humic-like.

Figure 1 contains the F_{MAX} values of the five PARAFAC components for the raw waters as a function of sampling date and location. On balance, total F_{MAX} values

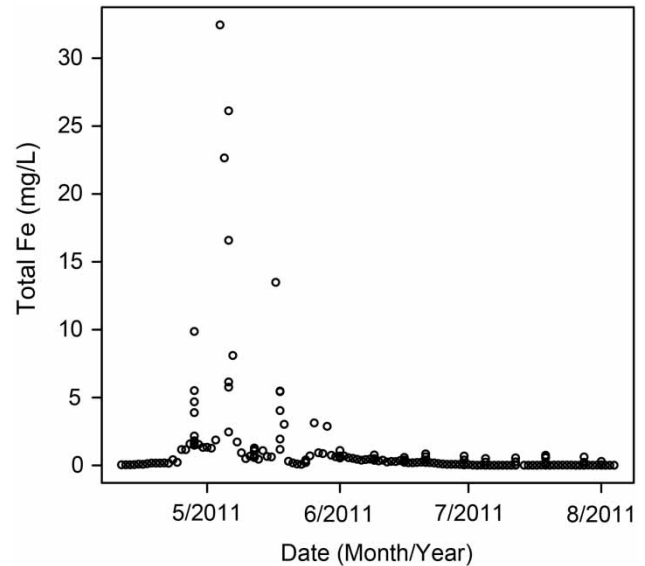
Table 1 | Raw water parameters for the Beaver Lake samples

Location	Date	Turbidity (NTU)	UV ₂₅₄ (cm ⁻¹)	DOC (mg L ⁻¹)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)
BWD	4/11/11	13	0.049	4.8	1.0
	5/6/11	180	0.203	2.7	7.6
	5/13/11 ^a	125	0.367	3.2	11.6
	5/31/11 ^a	81	0.287	5.9	4.9
	6/28/11 ^a	4	0.077	2.2	3.4
	7/14/11 ^a	2	0.072	2.0	3.6
	8/4/11 ^a	2	0.072	2.8	2.6
TT	4/11/11	2	0.056	4.8	1.2
	5/6/11	143	NM	NM	NM
	5/13/11 ^a	120	0.452	3.6	12.4
	5/31/11 ^a	37	0.174	5.9	3.0
	6/28/11 ^a	60	0.265	2.4	11.1
	7/14/11 ^a	12	0.097	1.4	6.8
	8/4/11 ^a	14	0.149	2.2	6.8
CB	4/11/11	<1	0.040	6.6	0.6
	5/6/11	1	NM	NM	NM
	5/13/11 ^a	3	0.034	2.2	1.6
	5/31/11 ^a	11	0.097	6.7	1.4
	6/28/11 ^a	12	0.113	2.0	5.6
	7/14/11 ^a	12	0.131	2.3	5.6
	8/4/11 ^a	10	0.105	2.0	5.4
MC	4/11/11	<1	0.022	6.2	0.4
	5/6/11	6	NM	NM	NM
	5/13/11 ^a	36	0.137	2.9	4.8
	5/31/11 ^a	33	0.209	9.4	2.2
	6/28/11 ^a	4	0.066	1.8	3.6
	7/14/11 ^a	1	0.056	2.1	2.7
	8/4/11 ^a	1	0.059	2.2	2.6

BWD – Beaver Water District; CB – Carroll Boone; DOC – dissolved organic carbon; MC – Madison County; NM – not measured; SUVA₂₅₄ – specific ultraviolet absorbance at 254 nm; TT – Two Ton.

^aReported in Pifer & Fairey (2012), with the exception of the turbidity data.

(the sum of the five components at a given location and date) were higher for BWD and TT compared to those for CB and MC. At each sampling location, total F_{MAX} generally increased in May and remained high through August. Unlike the SUVA₂₅₄ data, there was no apparent impact of

**Figure 2** | Total dissolved iron (Fe) concentrations in raw water samples at the Beaver Water District between April and August 2011.**Table 2** | Maxima location and characteristics of the fluorescence-PARAFAC components

Component	Excitation maxima (nm)	Emission maxima (nm)	Identification ^a
C1	238 (329)	428	Fulvic acid-like
C3	271 (371, 212)	456	Humic acid-like
C4	229	359	Tryptophan-like
C5	371 (229)	481	Humic acid-like
C6	322 (209)	396	Microbial humic-like

Values in parentheses are secondary and tertiary Excitation Maxima.

^aSantin *et al.* (2009).

dissolved iron on the F_{MAX} values. Similarly, Pullin *et al.* (2007) found no general trends between the effect of dissolved iron on various fluorescence peaks of resin-extracted DOM isolates. However, future DOM studies regarding the impact of heavy rainfall events should include the measurement of dissolved iron.

For the raw water F_{MAX} data presented in Figure 1 and those for the MIEX[®] and alum-treated waters, there were no consistent trends with sampling date or location. As such, the following were calculated for the F_{MAX} data and are presented in Table 3: (1) the average contribution of each PARAFAC component to the total F_{MAX} and

Table 3 | Average contribution and percent removal for each fluorescence-PARAFAC component for samples collected on 5/13/11, 6/28/11, 7/14/11, and 8/4/11

Treatment	C1	C3	C4	C5	C6
Average contribution					
Raw	51 ± 5	17 ± 2	13 ± 3	10 ± 5	9 ± 3
MIEX [®] , pH 6	31 ± 7	4 ± 1	21 ± 4	25 ± 6	20 ± 4
MIEX [®] , pH 7	33 ± 8	5 ± 2	21 ± 4	22 ± 7	19 ± 5
MIEX [®] , pH 8	35 ± 7	5 ± 2	22 ± 5	21 ± 7	18 ± 4
Alum, pH 6 ^a	38 ± 3	8 ± 3	25 ± 8	16 ± 6	14 ± 4
Alum, pH 7 ^a	41 ± 3	11 ± 3	24 ± 7	12 ± 4	12 ± 3
Alum, pH 8 ^a	44 ± 3	14 ± 3	23 ± 6	9 ± 4	10 ± 3
Average percent removal					
MIEX [®] , pH 6	82 ± 5	94 ± 3	49 ± 14	10 ± 25	32 ± 14
MIEX [®] , pH 7	76 ± 7	88 ± 5	35 ± 29	− 10 ± 68	11 ± 51
MIEX [®] , pH 8	78 ± 7	90 ± 4	45 ± 18	21 ± 27	36 ± 19
Alum, pH 6 ^a	73 ± 8	83 ± 9	27 ± 34	28 ± 35	40 ± 29
Alum, pH 7 ^a	61 ± 11	67 ± 17	10 ± 35	28 ± 35	32 ± 29
Alum, pH 8 ^a	41 ± 16	42 ± 20	− 22 ± 37	27 ± 31	28 ± 24

Values are averages ± standard deviations.

^aData from Pifer & Fairey (2012).

(2) the average percent removal of each component by treatment. C1 (fulvic acid-like) was the largest contributor to the average overall fluorescence before and after treatment, and was removed by alum and MIEX[®] for all sample locations. Alum treatment at pH 6 performed similarly to MIEX[®] at all three pH values tested. The absence of a pH trend for MIEX[®] treatment may indicate that the portions of NOM removed by anion exchange are relatively insensitive to pH changes between 6 and 8, similar to the findings reported by Boyer *et al.* (2008). C3 (humic acid-like) was largely removed (>80%) by MIEX[®] treatment and alum coagulation at pH 6, and to a lesser extent by alum at pH 7 and 8. C4 (tryptophan-like), C5 (humic acid-like), and C6 (microbial humic-like) were more significant fractional contributors after MIEX[®] treatment, possibly indicating that MIEX[®] preferentially removed C1 and C3 and/or these components were impacted by dissolved iron. The percent removals of C5 and C6 for both alum and MIEX[®] were inconsistent, as noted by the high standard deviations relative to their means. In Table 3, negative values for the average percent removals indicate that the treatments achieved little-to-no removal.

Specific ultraviolet absorbance

UV₂₅₄, DOC, and SUVA₂₅₄ values for the raw and MIEX[®]-treated samples are shown in Figure 3 as a function of sampling date and location. For BWD, SUVA₂₅₄ was highest in the 5/13/11 MIEX[®]-treated samples and decreased from 6/28/11 through the remainder of the study. Similarly, for TT, SUVA₂₅₄ was high for 5/13/11 and 6/28/11 samples before decreasing in the last two sampling dates. For CB and MC, SUVA₂₅₄ was comparatively low throughout the entire study. These data show that SUVA₂₅₄ values in MIEX[®]-treated samples were higher than the corresponding raw waters for BWD on 5/13/11 and TT for 5/13/11 and 6/28/11. Similar to the raw water SUVA₂₅₄ data discussed previously, the presence of dissolved iron (Figure 2) was the likely cause. MIEX[®] is an anion exchange resin, therefore iron (a cation) remains in solution following MIEX[®] treatment. As shown in Figure 3, there was disproportionate removal of DOC relative to UV₂₅₄-absorbing moieties (e.g. DOM and iron), which produced higher SUVA₂₅₄ values following MIEX[®] treatment. This is further evidence that the heavy rainfall event added dissolved iron to the BWD and TT samples and interfered with the UV₂₅₄-based

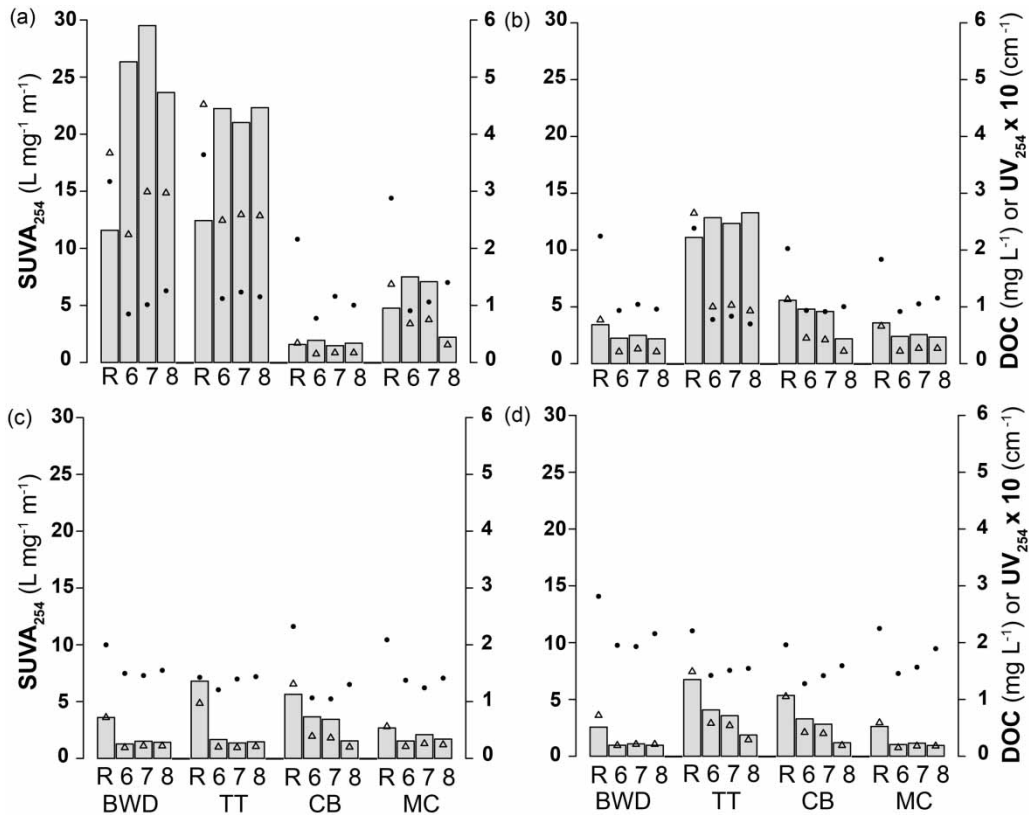


Figure 3 | Ultraviolet absorbance at 254 nm (UV₂₅₄), dissolved organic carbon (DOC), and specific UV₂₅₄ (SUVA₂₅₄) by sampling location and treatment for the waters collected on (a) 5/13/11, (b) 6/28/11, (c) 7/14/11, and (d) 8/4/11. R indicates a raw water sample, and 6, 7, and 8 indicate the target pH for MIEX[®] treatment. The bars represent SUVA₂₅₄, empty triangles represent UV₂₅₄, and the filled circles represent DOC. BWD is the Beaver Water District, TT is Two Ton, CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District.

measurements. These SUVA₂₅₄ data follow the trends observed in turbidity (Table 1), further supporting the assertion that the heavy rainfall event impacted the water quality at BWD and TT more so than CB and MC. Throughout the study, the DOC values in the MIEX[®]-treated samples were between 0.70 and 2.15 mg L⁻¹ as C, indicating MIEX[®] did not remove a portion of the organic carbon. The role of these compounds in DBP formation is explored in the next sections.

Disinfection byproduct formation potential

Of the eight DBPs screened, only three – chloroform (TCM), dichloroacetonitrile, and bromodichloromethane (BDCM) – formed consistently at detectable levels (>1 µg/L) in the raw and MIEX[®]-treated samples. There

were no consistent spatial or temporal trends in DBPFP, so their concentrations and percent reductions were averaged for each DBP and listed in Table 4. As expected, TCM was the dominant DBP formed by chlorination of the raw and treated waters. The TCMFP was reduced by MIEX[®] treatment (58–63% on average) and was insensitive to pH, similar to the fluorescence-PARAFAC component data (Table 3). Interestingly, BDCM concentrations *increased* in several instances following MIEX[®] treatment, suggesting that bromide ion leached from the resin and reacted to form bromine-substituted DBPs. This is a potentially troubling result considering these DBPs are generally considered to be more toxic than fully chlorinated DBPs. Based on the DBP data presented in Table 4, UV- and fluorescence-based correlations were sought with TCM only.

Table 4 | Average formation potential and percent reduction in formation potential as a function of treatment for samples collected on 5/13/11, 6/28/11, 7/14/11, and 8/4/11

	Chloroform	Dichloroacetonitrile	BDCM
Average formation potential ($\mu\text{g/L}$)			
Raw	120 \pm 25	4 \pm 2	8 \pm 1
MIEX [®] , pH 6	44 \pm 10	3 \pm 1	14 \pm 2
MIEX [®] , pH 7	49 \pm 12	3 \pm 1	13 \pm 2
MIEX [®] , pH 8	46 \pm 9	3 \pm 1	15 \pm 3
Alum, pH 6	46 \pm 7	3 \pm 1	6 \pm 1
Alum, pH 7	56 \pm 8	3 \pm 1	6 \pm 1
Alum, pH 8	73 \pm 14	3 \pm 2	6 \pm 1
Average percent reduction			
MIEX [®] , pH 6	63 \pm 9	20 \pm 24	- 86 \pm 31
MIEX [®] , pH 7	58 \pm 11	16 \pm 21	- 76 \pm 38
MIEX [®] , pH 8	61 \pm 9	21 \pm 24	- 97 \pm 29
Alum, pH 6 ^a	62 \pm 8	29 \pm 30	24 \pm 7
Alum, pH 7 ^a	52 \pm 10	25 \pm 33	22 \pm 11
Alum, pH 8 ^a	37 \pm 9	8 \pm 35	17 \pm 11

Values are averages \pm standard deviations; TCM – chloroform; DCAN – dichloroacetonitrile; BDCM – bromodichloromethane.

^aFrom Pifer & Fairey (2012).

Correlations between DBPs and DBP-precursor properties

Figure 4 shows a plot of the correlation coefficients (r^2) between TCMFP and $I_{\text{Ex/Em}}$ for each excitation and emission wavelength pair. This plot was generated using fluorescence and TCM data from the four sampling locations and four sampling dates (5/13/11, 6/28/11, 7/14/11, and 8/4/11). Interestingly, Figure 4 reveals that a large group of $I_{\text{Ex/Em}}$ pairs correlated strongly ($r^2 > 0.8$) with TCMFP. This region is approximated by excitation wavelengths between 225 and 300 nm and emission wavelengths between 430 and 550 nm. Compared to the fluorophore groups identified by PARARAC analysis, this region encompasses the maxima of a fulvic acid-like fluorophore (C1) and two humic acid-like fluorophores (C3 and C5). The highest r^2 value (0.88) occurred at $I_{278/506}$ and is noted in Figure 4 and used in subsequent correlations.

Figure 5 shows correlations between TCMFP and (i) UV_{254} ($r^2 = 0.25$, Figure 5(a)), (ii) C1 F_{MAX} ($r^2 = 0.87$, Figure 5(b)), and (iii) $I_{278/506}$ ($r^2 = 0.88$, Figure 5(c)).

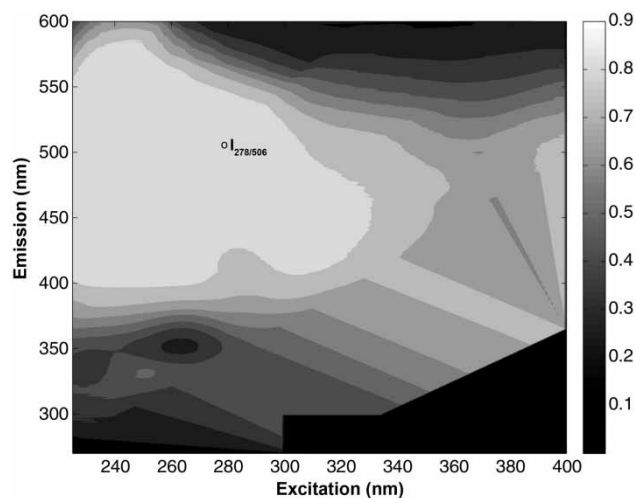


Figure 4 | Correlation coefficients (r^2) between chloroform formation potential (TCMFP) and fluorescence intensity values for each excitation-emission pair ($I_{\text{Ex/Em}}$). These r^2 values were determined with the group of EEMs consisting of raw, MIEX[®]-treated, and alum-treated waters from BWD, TT, CB, and MC collected on 5/13/11, 6/28/11, 7/14/11, and 8/4/11. $I_{278/506}$ is indicated with a circle and is the highest correlated pair ($r^2 = 0.88$). BWD is the Beaver Water District, TT is Two Ton, CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District.

Weak TCMFP correlations were determined for $SUVA_{254}$ ($r^2 = 0.00$) and DOC ($r^2 = 0.23$) and were not shown. It is important to note that data in Figure 5 include samples collected on 5/6/11, 5/13/11, 6/28/11, 7/14/11, and 8/4/11, a portion of which were influenced by the heavy rainfall event. In Figure 5(a), the circled cluster of MIEX[®]-treated samples (on the border of the lower 95% prediction interval) were from BWD and TT sampled on 5/6/11 and 5/13/11, and had UV_{254} values influenced by dissolved iron (Table 1 and Figure 2). In contrast, correlations with fluorescence-based TCMFP surrogate parameters – both from PARAFAC F_{MAX} components and EEM-intensity pairs ($I_{278/506}$) – were not negatively impacted by the presence of dissolved iron. This result demonstrates that fluorescence-based metrics were superior to UV_{254} for tracking TCMFP surrogate parameters in a water body impacted by a heavy rainfall event.

TCMFP was also positively correlated to C3 ($r^2 = 0.83$), a humic acid-like component. In contrast, there was weak correlation with the tryptophan-like C4 ($r^2 = 0.20$); however, fluorophore groups like C4 may be useful surrogate parameters of nitrogen-containing DBPs, a potentially fruitful topic of future research. Similarly, C5 and C6 were

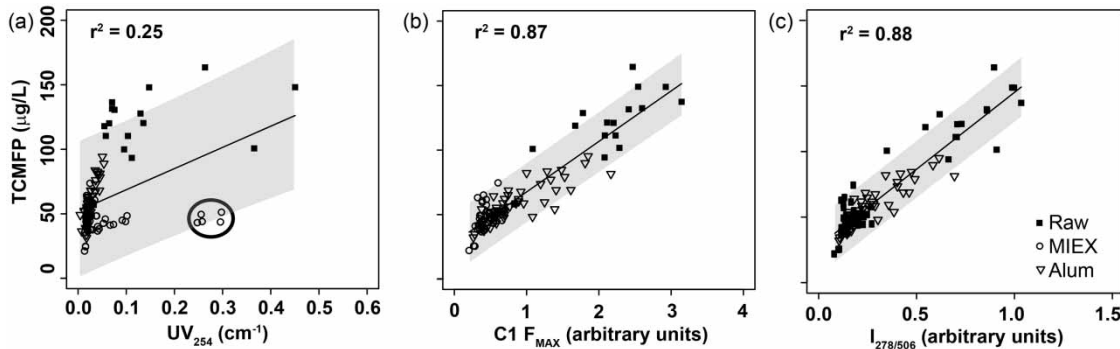


Figure 5 | Correlations between chloroform formation potential (TCMFP) formed during the free chlorine disinfection byproduct formation potential tests and (a) UV_{254} , (b) F_{MAX} for Component 1, and (c) $I_{278/506}$. Linear best-fit models were generated from least-squares analyses of raw waters, MIEX-treated waters, and alum-treated waters from all four sampling locations collected on 5/13/11, 6/28/11, 7/14/11, and 8/4/11. Grey-shaded regions encompass the upper and lower 95% prediction intervals for the linear models.

uncorrelated with TCMFP ($r^2 = 0.10$ and 0.23 , respectively), suggesting they could be impacted by the heavy rainfall event (e.g. dissolved iron). In summary, F_{MAX} values from fluorescence-PARAFAC produced an accurate DBP-precursor surrogate parameter because the algorithm is able to differentiate between components that are strongly correlated to TCMFP (e.g. C1) without significant interferences from dissolved iron which resulted in erroneously high UV_{254} values.

CONCLUSIONS

UV- and fluorescence-based metrics were compared as DBP precursor surrogate parameters at four locations within a water body between April and August 2011, during which a heavy rainfall event occurred (28 cm from April 24–26, 2011). Raw waters were treated at pH 6, 7, and 8 by alum coagulation and ion exchange with MIEX[®]. Based on the results of this study, the following conclusions can be made:

- After the heavy rainfall event, the raw water turbidity increased at BWD and TT more so than at CB and MC, indicating the storm event had a larger impact on the upstream portion of the reservoir.
- High UV_{254} that produced $SUVA_{254}$ values larger than $7 \text{ L mg}^{-1} \text{ m}^{-1}$ were attributed to the presence of dissolved iron from the heavy rainfall event; in contrast, the dissolved iron had no apparent impact on the fluorescence measurements.

- Fluorescence-PARAFAC analysis of the raw and treated waters revealed five meaningful component fluorophore groups: a fulvic acid-like group (C1), two humic acid-like groups (C3 and C5), a tryptophan-like group (C4), and a microbial humic-like group (C6).
- TCM was the predominant DBP formed following chlorination of the raw and treated waters; MIEX[®] removed approximately 60% of TCM precursors, regardless of the treatment pH (between 6 and 8).
- UV_{254} was a poor TCMFP surrogate parameter ($r^2 = 0.25$); this was in part due to interferences in the UV_{254} data produced by dissolved iron at the BWD and TT sampling locations from the heavy rainfall event.
- Fluorescence-based metrics, both from PARAFAC (F_{MAX}) and EEM pairs ($I_{Ex/Em}$), were strong TCM precursor surrogate parameters ($r^2 = 0.87$ for C1 F_{MAX} and $r^2 = 0.88$ for $I_{278/506}$) for the entire dataset and were not negatively impacted by the influx of dissolved iron from the heavy rainfall event.

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REFERENCES

- Ates, N., Kitis, M. & Yetis, U. 2007 Formation of chlorination by-products in waters with low SUVA-correlations with SUVA and differential UV spectroscopy. *Water Res.* **41** (18), 4139–4148.
- Bolto, B., Dixon, D., Eldridge, R., King, S. & Linge, K. 2002 Removal of natural organic matter by ion exchange. *Water Res.* **36** (20), 5057–5065.
- Boyer, T. H., Singer, P. C. & Aiken, G. R. 2008 Removal of dissolved organic matter by anion exchange: effect of dissolved organic matter properties. *Environ. Sci. Technol.* **42** (19), 7431–7437.
- Cantor, K. P., Lynch, C. F., Hildesheim, M. E., Dosemeci, M., Lubin, J., Alavanja, M. & Craun, G. 1998 Drinking water source and chlorination byproducts I. Risk of bladder cancer. *Epidemiology* **9** (1), 21–28.
- Cory, R. M., Boyer, E. W. & McKnight, D. M. 2011 Spectral methods to advance understanding of dissolved organic carbon dynamics in forested catchments. In: *Forest Hydrology and Biogeochemistry: Synthesis of Past Research and Future Directions* (D. F. Levia, D. Carlyle-Moses & T. Tanaka, eds). Springer, New York, pp. 117–135.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. 2012 *Water Treatment Principals and Design*. MWH, 3rd edn. John Wiley & Sons, Inc., Hoboken, NJ.
- Drikas, M., Morran, J. Y., Pelekani, C., Hepplewhite, C. & Bursill, D. B. 2002 Removal of natural organic matter – a fresh approach. *Water Sci. Technol. Water Suppl.* **2** (1), 71–79.
- Drikas, M., Chow, C. W. K. & Cook, D. 2003 The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: an evaluation of magnetic ion exchange resin (MIEX (R)) and alum coagulation. *J. Water Suppl. Res. Technol. Aqua* **52** (7), 475–487.
- Eaton, A. D., Franson, M. A. H., American Public Health Association, American Water Works Association & Water Environment Federation 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association, Washington, DC.
- Edzwald, J. K., Becker, W. C. & Wattier, K. L. 1985 Surrogate parameters for monitoring organic matter and THM precursors. *J. Am. Water Works Assoc.* **77** (4), 122–132.
- Goldman, J. H., Rounds, S. A. & Needoba, J. A. 2012 Applications of fluorescence spectroscopy for predicting percent wastewater in an urban stream. *Environ. Sci. Technol.* **46** (8), 4374–4381.
- Hua, B., Veum, K., Yang, J., Jones, J. & Deng, B. L. 2010 Parallel factor analysis of fluorescence EEM spectra to identify THM precursors in lake waters. *Environ. Monit. Assess.* **161** (1–4), 71–81.
- Jarvis, P., Mergen, M., Banks, J., McIntosh, B., Parsons, S. A. & Jefferson, B. 2008 Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. *Environ. Sci. Technol.* **42** (4), 1276–1282.
- Karanfil, T., Erdogan, I. & Schlautman, M. A. 2003 Selecting filter membranes for measuring DOC and UV254. *J. Am. Water Works Assoc.* **95** (3), 86–100.
- Krasner, S. W. & Amy, G. 1995 Jar-test evaluations of enhanced coagulation. *J. Am. Water Works Assoc.* **87** (10), 93–107.
- Miller, M. P. & McKnight, D. M. 2010 Comparison of seasonal changes in fluorescent dissolved organic matter among aquatic lake and stream sites in the Green Lakes Valley. *J. Geophys. Res. Biogeosci.* **115**, G00F12.
- Nieuwenhuijsen, M. J., Toledano, M. B., Eaton, N. E., Fawell, J. & Elliott, P. 2000 Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. *Occup. Environ. Med.* **57** (2), 73–85.
- Pifer, A. D. & Fairey, J. L. 2012 Improving on SUVA₂₅₄ using fluorescence-PARAFAC analysis and asymmetric flow-field flow fractionation for assessing disinfection byproduct formation and control. *Water Res.* **46** (9), 2927–2936.
- Pifer, A. D., Miskin, D. R., Cousins, S. L. & Fairey, J. L. 2011 Coupling asymmetric flow-field flow fractionation and fluorescence parallel factor analysis reveals stratification of dissolved organic matter in a drinking water reservoir. *J. Chromatogr. A* **1218** (27), 4167–4178.
- Pullin, M. J., Anthony, C. & Maurice, P. A. 2007 Effects of iron on the molecular weight distribution, light absorption, and fluorescence properties of natural organic matter. *Environ. Eng. Sci.* **24** (8), 987–997.
- Santin, C., Yamashita, Y., Otero, X. L., Alvarez, M. A. & Jaffe, R. 2009 Characterizing humic substances from estuarine soils and sediments by excitation-emission matrix spectroscopy and parallel factor analysis. *Biogeochemistry* **96** (1–3), 131–147.
- Sen, S., Haggard, B. E., Chaubey, I., Brye, K. R., Costello, T. A. & Matlock, M. D. 2007 Sediment phosphorus release at Beaver Reservoir, northwest Arkansas, USA, 2002–2003: a preliminary investigation. *Water Air Soil Pollut.* **179** (1–4), 67–77.
- Singer, P. C. & Chang, S. D. 1989 Correlations between trihalomethanes and total organic halides formed during water treatment. *J. Am. Water Works Assoc.* **81** (8), 61–65.
- Singer, P. C., Schneider, M., Edwards-Brandt, J. & Budd, G. C. 2007 MIEX for removal of DBP precursors: pilot-plant findings. *J. Am. Water Works Assoc.* **99** (4), 128–139.
- Stedmon, C. A. & Bro, R. 2008 Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. *Limnol. Oceanog.-Meth* **6**, 572–579.
- Stedmon, C. A., Markager, S. & Bro, R. 2003 Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **82** (3–4), 239–254.
- Wahman, D. G. 2006 Cometabolism of Trihalomethanes by Nitrifying Biofilters under Drinking Water Treatment Plant Conditions. Civil, Architectural, and Environmental Engineering. Austin, PhD Dissertation, The University of Texas at Austin.

- Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R. & Mopper, K. 2003 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37** (20), 4702–4708.
- Zepp, R. G., Sheldon, W. M. & Moran, M. A. 2004 Dissolved organic fluorophores in southeastern US coastal waters: correction method for eliminating Rayleigh and Raman scattering peaks in excitation-emission matrices. *Mar. Chem.* **89** (1–4), 15–36.

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