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REMOVAL OF DISINFECTION BY-PRODUCT PRECURSORS USING MAGNETIC ION  
EXCHANGE (MIEX<sup>®</sup>): THE EFFECTS OF pH AND SOURCE WATER VARIABILITY

REMOVAL OF DISINFECTION BY-PRODUCT PRECURSORS USING MAGNETIC ION  
EXCHANGE (MIEX<sup>®</sup>): THE EFFECTS OF pH AND SOURCE WATER VARIABILITY

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science in Civil Engineering

By

Sarah L. Cousins  
University of Arkansas  
Bachelor of Science in Biological Engineering, 2009

December 2011  
University of Arkansas

## ABSTRACT

Disinfection by-products (DBPs) form as an unintended result of drinking water disinfection, from chemical reactions between disinfectants (e.g., free chlorine) and naturally occurring dissolved organic matter (DOM). At present, 11 DBPs are regulated in treated drinking waters due to potential adverse health effects, including four trihalomethanes (THMs). Despite nearly 40 years of DBP research, compliance with DBP regulations remains a challenge for many drinking water treatment plants (DWTPs), including the four DWTPs located on the Beaver Lake Reservoir in Northwest Arkansas. Due to the high net negative surface charge on DOM, anion exchange is one potentially viable method for removing DOM from drinking water sources. Here, magnetic ion exchange, or MIEX<sup>®</sup>, was evaluated for removal of DBP precursors. Raw water samples were collected monthly between April-August, 2011 from four DWTPs on Beaver Lake. The waters were adjusted to pH values of 6, 7, and 8 and treated with fresh MIEX<sup>®</sup> resin at a dose of 6 mL/L. After treatment, the samples were dosed with free chlorine and the DBP formation potential (DBFP) was measured. Three DBPs – chloroform (TCM), dichlorobromomethane (DCBM), and dichloroacetonitrile – formed at measurable concentrations which varied by sample location and date, indicating spatial and temporal variability in the DOM throughout the study period. TCM was the predominant DBP formed and was removed to the greatest extent (75-82%) by MIEX<sup>®</sup> treatment, with no apparent trends with source water pH. In an attempt to related DOM properties to DBFP, fluorescence excitation-emission matrices (EEMs) were collected for 200 raw and MIEX<sup>®</sup> treated water samples. A statistical algorithm, parallel factor (PARAFAC) analysis, was used to decompose the EEMs into four principal component fluorophore (three humic-like and one protein-like) groups, each with a maximum intensity,  $F_{MAX}$  value.  $F_{MAX}$  values of two of the humic-like fluorophore groups more were strongly correlated with TCM formation potential ( $r^2$  values of 0.81 and 0.74) than specific

ultraviolet absorbance at 254 nm ( $SUVA_{254}$ , with an  $r^2$  of 0.01). These results highlight for the first time the usefulness of fluorescence-PARAFAC to assess DBP formation and control using MIEX<sup>®</sup> treatment and may be extended to optimize treatment conditions for DBP-precursor removal by ion exchange.

This thesis is approved for recommendation  
to the Graduate Council.

Thesis Director:

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Dr. Julian L. Fairey

Thesis Committee:

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Dr. James C. Young

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Dr. Wen Zhang

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## TABLE OF CONTENTS

1. Introduction and Motivation .....	1
2. Materials and Methods.....	5
2.1. <i>Selected Waters</i> .....	5
2.2. <i>Water Quality Tests</i> .....	5
2.3. <i>MIEX<sup>®</sup> Experiments</i> .....	7
2.4. <i>Disinfection Byproduct Formation Potential Tests</i> .....	7
2.5. <i>Gas Chromatography</i> .....	8
2.6. <i>Fluorescence-PARAFAC Analysis</i> .....	8
3. Results and Discussion .....	9
3.1. <i>Raw Water Parameters</i> .....	9
3.2. <i>Fluorescence-PARAFAC Analysis</i> .....	10
3.3. <i>Disinfection Byproduct Formation Potential</i> .....	11
3.4. <i>Correlations Between DBPs and DBP-Precursor Properties</i> .....	12
4. Conclusions and Future Work .....	13
References.....	24

## LIST OF TABLES

Table 1 – Analytical equipment and methods used to measure the water quality parameters .....	15
Table 2 – Raw water quality parameters for Beaver Lake samples.....	16
Table 3 – Maxima location and characteristics of the fluorescence-PARAFAC components.....	17
Table 4 – Average contribution and percent removal for each fluorescence-PARAFAC component .....	18
Table 5 – Average percent removal of DBPs from MIEX <sup>®</sup> treatment as a function of pH.....	19

## LIST OF FIGURES

- Figure 1** – Fluorescence-PARAFAC component excitation-emission matrices (EEMs) for the array of 200 EEMs consisting of raw and MIEX<sup>®</sup>-treated waters from the four drinking water treatment plants..... 20
- Figure 2** - Fluorescence-PARAFAC component maximums ( $F_{MAX}$ ) by drinking water treatment plant and treatment for sample dates of (a) April 11, 2011, (b) May 13, 2011, (c) June 28, 2011, (d) July 14, 2011, and (e) August 4, 2011. R indicates a raw water sample, and 6, 7, and 8 indicate the target pH for MIEX<sup>®</sup> treatment. BWD is the Beaver Water District, TT is the Benton/Washington Regional Public Water Authority (commonly referred to as Two Ton), CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District. Fluorescence-PARAFAC components are indicated by color as follows: ■ component 1, ■ component 2, ■ component 3, and ■ component 4..... 21
- Figure 3** – Disinfection by products (DBPs) in  $\mu\text{g/L}$  as each DBP formed during free chlorine formation potential tests by DWTP and treatment for the sample dates: (a) April 11, 2011, (b) May 13, 2011, (c) June 28, 2011, (d) July 14, 2011, and (e) August 4, 2011. R indicates a raw water sample, and 6, 7, and 8 indicate the target pH for MIEX<sup>®</sup> treatment. BWD is the Beaver Water District, TT is the Benton/Washington Regional Public Water Authority (commonly referred to as Two Ton), CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District. DBPs are indicated by color as follows: TCM - chloroform (grey), DCAN - dichloroacetonitrile (white), and BDCM - bromodichloromethane (black)..... 22
- Figure 4** – Correlations between chloroform formed during the free chlorine disinfection byproduct formation potential tests and (a)  $SUVA_{254}$ , (b)  $F_{MAX}$  for Component 1, (c)  $F_{MAX}$  for Component 3, and (d)  $F_{MAX}$  for Component 4. The solid lines are the linear model fits to the experimental data. The dashed lines are the upper and low 95% prediction intervals for the linear models..... 23

## **1. Introduction and Motivation**

Despite nearly 40 years since the discovery of disinfection byproducts (DBPs) in treated drinking waters (Rook 1977), their occurrence remains an ongoing challenge at many drinking water treatment plants (DWTPs). DBPs are formed from reactions between dissolved organic matter (DOM), which is ubiquitous in natural waters, and drinking water disinfectants (e.g., chlorine, chloramines, ozone, etc.). Many DBPs have been regulated in finished drinking waters due to suspected links with various carcinogenic (Cantor et al. 1998) and adverse teratogenic outcomes (Nieuwenhuijsen et al. 2000). The United States Environmental Protection Agency (USEPA) currently regulates 11 DBPs (four trihalomethanes (THM4), five of the nine haloacetic acids (HAA5), chlorite, and bromate) in finished drinking waters under the Stage 2 Disinfection/Disinfection By-Product Rule. Other DBPs, including ones containing nitrogen in their structures (N-DBPs), are being considered for regulation due to high toxicities relative to THM4 and HAA5.

The DBPs formed and their respective concentrations depend on a number of factors, including the quantity and nature of the DOM and the type of disinfectant. DOM is comprised largely of organic carbon and is derived from many sources including decay leaf litter and aquatic fauna secretions. Because of the numerous sources for DOM, its physical and chemical properties can vary temporally (Miller and McKnight 2010) and spatially (Pifer et al. 2011). Additionally, once in a water body, DOM can be altered further biotically (e.g., biological degradation) and abiotically (e.g., photolysis). As such, DOM exists as a dynamic carbon pool, which presents many challenges in terms of curbing DBP formation in finished drinking waters.

DWTPs can draw from a two-pronged approach to curb DBPs: 1) change the disinfectant, or 2) remove more of the DBP precursors. Changing disinfectants can cause a variety of problems including forming different, possibly more dangerous DBPs, such as chloropicrin and haloacetonitriles (HANs) (Krasner et al. 2006). Notably, the Washington, D.C. lead crisis between 2001-2004 was attributed to switching the disinfectant from free chlorine to chloramines, causing elevated lead levels in the drinking water distribution system (Zhang et al. 2008; Zhang et al. 2009). As such, enhanced DBP-precursor removal has received renewed interest in recent years, and was the focus of this study.

One method used to remove DOM from drinking water is anion exchange (Bolto et al. 2002). Typical ion exchange processes are operated in pressurized columns which require the water to be pre-filtered to prevent the column from becoming plugged (Drikas et al. 2002). A more practical and flexible approach to ion exchange for the removal of DOM was developed by the Commonwealth Scientific & Industrial Research Organization (CSIRO) and Orica Australia Pty Ltd as a result of the Australian Water Quality Center (AWQC) prioritizing research on the removal of DOM (Drikas et al. 2002). The method developed was a completely mixed anion exchange process using a novel technology known as magnetic ion exchange, or MIEX<sup>®</sup>. The MIEX<sup>®</sup> treatment process uses small, slightly magnetic resin beads to remove negatively charged compounds from water. MIEX<sup>®</sup> beads consist of a polymer shell with quaternary amide functional groups surrounding a magnetic iron oxide core (Lee et al. 2003). MIEX<sup>®</sup> resin can have a high selectivity for dissolved organic carbon (DOC) (Martin 2009) which largely makes up the DOM pool that drinking water treatment processes aim to remove. This makes MIEX<sup>®</sup> a potentially attractive option for removing DBP precursors. Additional information on the

MIEX<sup>®</sup> treatment process can be found in *Removal of natural organic matter—a fresh approach* (Drikas et al. 2002).

An extensive body of research exists regarding the ability of MIEX<sup>®</sup> to reduce THM formation potential (Drikas et al. 2003; Fearing et al. 2004; Morran et al. 2004; Shorrock and Drage 2006; Jarvis et al. 2008), or both THM and HAA formation potentials (Singer and Bilyk 2002; Boyer and Singer 2005; Singer et al. 2007). However, due to the novelty of MIEX<sup>®</sup>, much research is needed to fully understand its capabilities and limitations. In particular, the impact of source water pH during MIEX<sup>®</sup> treatment has not been extensively documented. DOM is comprised of macromolecules with carboxylic and phenolic acid/base functional groups that have pK<sub>a</sub>'s in the range relevant to drinking water treatment (pH 5-9). While some have speculated that pH has an effect on the removal of DBP-precursors by MIEX<sup>®</sup> because of the changes in the protonation state of the acid/base DOM functional groups (Neale and Schafer 2009), there remains a significant research gap regarding the optimum operating pH for MIEX<sup>®</sup> treatment. Additionally, little is known about how MIEX<sup>®</sup> will affect the formation potentials of N-DBPs, in particular HANs.

This work also attempts to improve on existing methods for predicting DBP formation. Currently, the most common parameter used to predict DBP formation is specific ultraviolet absorbance, or SUVA<sub>254</sub>, which is calculated by dividing the UV<sub>254</sub> absorbance by the product of the dissolved organic carbon concentration (DOC) and the UV cell path length (Ates et al. 2007). This is a fairly simple parameter to obtain, as most DWTPs have the analytical equipment to measure UV<sub>254</sub> and DOC. Unfortunately, not all DOM is sensitive to UV<sub>254</sub> (Kitis et al. 2001) and the relationships between DBPs and SUVA<sub>254</sub> are often inconsistent and unreliable. Here, fluorescence excitation-emission matrices (EEMs) were collected and decomposed with parallel

factor analysis (PARAFAC) and correlated with DBP formation. PARAFAC is a statistical algorithm that decomposes a group of EEMs into its principal components. The excitation-emission maxima of the principal components are their maximum intensity ( $F_{MAX}$ ) values and can provide insight into DBP formation and control. See Anderson's Journal of Chemometrics and Stedmon's Limnology and Oceanography-Methods articles for more in-depth descriptions of the PARAFAC theory (Andersen and Bro 2003; Stedmon and Bro 2008). Comparing the abundance of the PARAFAC-components to the formation of specific DBPs may provide a more reliable method for predicting DBP formation.

The research objective of this study was to test the hypothesis that removal of disinfection by-product (DBP) precursors with magnetic ion exchange (MIEX<sup>®</sup>) resin increases with source water operating pH. The specific steps needed to meet the objective of this research included: 1) method development for MIEX<sup>®</sup> experiments, 2) DBP formation potential tests with MIEX<sup>®</sup> treated waters at pH values of 6.0, 7.0, and 8.0, and 3) correlating fluorescence  $F_{MAX}$  values to DBP formation potential. Raw source waters were collected monthly between April-August, 2011 from four DWTPs located on Beaver Lake reservoir in northwest Arkansas. After MIEX<sup>®</sup> treatment (6 mL/L), the water was filtered and chlorinated to form DBPs. Fluorescence-PARAFAC was used to characterize the DOM in the raw and MIEX<sup>®</sup> treated waters and the resultant  $F_{MAX}$  values were compared to  $SUVA_{254}$  for predicting DBP formation.

## **2. Materials and Methods**

### ***2.1. Selected Waters***

Raw water samples were collected during Summer 2011, on 04/11/11, 05/13/11, 06/28/11, 07/14/11, and 08/04/11, at the intake of the following drinking water treatment plants (DWTPs) on the Beaver Lake reservoir: (1) Beaver Water District (BWD), (2) Benton-Washington Regional Public Water Authority, commonly referred to as Two Ton (TT), (3) Carroll Boone Water District (CB), and (4) Madison County Regional Water District (MC). These sampling locations were selected to assess the spatial variability of DBP-precursors on Beaver Lake and determine the impact of this variability on MIEX treatment and DBP formation.

Raw water samples from each DWTP intake were collected in pre-rinsed (Milli-Q water) 9-L HDPE carboys and filled headspace-free and sealed with screw-top lids. At the BWD, raw waters were collected with a 6-L Van Dorn bottle (Wildco, Model 1960-H65, Yulee, FL) attached to a rope, and lowered to the level of the intake (approximately 2- to 4-m below the lake surface during the sample collection period). Raw water samples from TT and CB were collected from a tap located within the DWTP, prior to any treatment or chemical addition. At MC, the carboys were filled at the lakeshore adjacent to the DWTP intake structure. All raw water samples were transported to the Water Research Laboratory at the University of Arkansas and stored in a 4°C dark room until use.

### ***2.2. Water Quality Tests***

All glassware used in the water quality tests, 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 M $\Omega$ -cm), and baked for 30 minutes at 400°C in a muffle furnace. Volumetric flasks

and plastic-ware were washed with an Alconox and tap water solution, rinsed with Milli-Q water and air-dried at room temperature. To homogenize the samples, the raw waters were vacuum-filtered with 1-micron nominal glass fiber filters (GFFs), which were pre-combusted (400°C for 30 min) and pre-rinsed (1-L Milli-Q water). The water quality tests performed on the raw water samples are shown in Table 1.

The pH electrode was calibrated daily with standard solutions of pH 4, 7, and 10. For TOC, DOC, and TDN, a blank and 1 mg/L check standard were run between different source waters (typically after every three samples) and were within  $\pm 10\%$ . The ammonia probe was calibrated by diluting a 1,000 mg/L ammonium chloride solution to concentrations between 0.03 and 10 mg-N/L. Nitrate and nitrite were measured with NitraVer<sup>®</sup> 5 and NitriVer<sup>®</sup> 3 powder pillows for 25 mL samples (Hach Company, Loveland, CO). Standard curves for nitrate and nitrite were made according to the respective standard method listed in Table 1. The turbidity meter was calibrated with dilutions of a 4,000 mg/L stock formazin suspension (Ricca Chemical Company, Arlington, TX). For UV<sub>254</sub> measurements, the spectrophotometer was blanked with Milli-Q water at the beginning and then after every six samples. The fluorometer used for both chlorophyll-a and phosphorus testing was calibrated with dilutions of known chlorophyll-a and phosphorus stock solutions (2-60 µg-chlorophyll-a/L and 0.05-0.50 mg-P/L). Specific UV absorbance (SUVA<sub>254</sub>) was calculated by dividing the UV<sub>254</sub> absorbance by the product of the UV cell path length (0.01 m) and the DOC concentration (mg/L). Dissolved organic nitrogen (DON) was determined by subtracting the sum of the inorganic nitrogen species (ammonia, nitrate, and nitrite) from the total dissolved nitrogen. Total phosphorus (TP) was calculated by summing the dissolved and particulate phosphorus.

### **2.3. MIEX<sup>®</sup> Experiments**

To control pH, 10 mL of phosphate buffer (68.1 g/L KH<sub>2</sub>PO<sub>4</sub> and 11.7 g/L NaOH) was added to a 500 mL volumetric flask and filled with a raw water sample. The pH of the sample was then adjusted to 6.0, 7.0, or 8.0 using HCl or NaOH. The pH adjusted, buffered water sample was transferred to a 500 mL amber glass bottle. MIEX<sup>®</sup> resin (Orica Watercare, Watkins, CO) was delivered in a 5% brine solution which was decanted with a glass pasteur pipette before the resin was repeatedly rinsed with Milli-Q water until the conductivity of the supernatant, measured with an Accumet four-cell conductivity probe, was less than or equal to 1 mS/cm. A resin dose of 6 mL/L was chosen for all MIEX<sup>®</sup> treatments based on preliminary experiments that showed significant DOC reduction (greater than 50%). A MIEX<sup>®</sup> resin/Milli-Q water slurry was transferred to a 10 mL graduated cylinder and allowed to separate for approximately 10 minutes. After settling, a glass pipette was used to deliver 3 mL of settled resin to the pH-buffered raw water sample. The water samples dosed with MIEX<sup>®</sup> were tumbled end-over-end at 45 rpm for approximately 18 hours, a time sufficient to ensure equilibrium was achieved.

### **2.4. Disinfection Byproduct Formation Potential Tests**

DBP formation potential (DBFP) tests were conducted on raw and MIEX<sup>®</sup>-treated water samples according to Standard Methods 5710 B with modifications. The water samples were filtered (1  $\mu$ m GFFs) and adjusted to pH 7.0 with phosphate buffer before transfer to 250 mL amber glass bottles with PTFE-lined screw-top lids. These bottles were spiked with a diluted standard NaOCl solution (Fisher Scientific, Fair Lawn, NJ) that resulted in a chlorine residual between 3-7 mg/L (mean residual of 4.7 mg/L) after 7 days in the dark at 25°C. Residuals were measured with Hach DPD powder pillows (Hach Company, Loveland, CO) at 552 nm on a

Shimadzu UV-Vis 2450 spectrophotometer (Kyoto, Japan) calibrated with a total chlorine standard curve (1.0-7.0 mg/L).

### **2.5. Gas Chromatography**

Eight DBPs (trichloromethane (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), tribromomethane (TBM), trichloropropanone (TCP), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and dibromoacetonitrile (DBAN)) were analyzed by liquid-liquid extraction and gas chromatography with an electron capture detector according to the EPA method 551.1 on a Shimadzu GC-2010 (Kyoto, Japan). Pentane was used as the extraction solvent and 1,1,1-trichloroethane for the internal standard. A standard curve (1, 2, 5, 10, 20, 40, 60, 80, and 100  $\mu\text{g/L}$ ) containing the eight DBPs was run prior to the samples and a blank and a 10  $\mu\text{g/L}$  check standard were run after every fourth sample (all check standards were within  $\pm 25\%$  of the standard concentration, considered to be acceptable based on EPA 551.1).

### **2.6. Fluorescence-PARAFAC Analysis**

Fluorescence excitation-emission matrices (EEMs) of 200 raw and MIEX<sup>®</sup>-treated waters were collected using a dual monochromator fluorescence detector (Agilent Technologies, Model G1321A), at excitation wavelengths between 200 and 400 nm and emission wavelengths between 270 and 600 nm, each at 1-nm step sizes. EEMs were decomposed with fluorescence parallel factor (PARAFAC) analysis to distinguish the principal fluorophore groups (called Components) and their maximum intensities ( $F_{\text{MAX}}$  values). Details of the PARAFAC procedure are provided elsewhere (Pifer et al. 2011).

### 3. Results and Discussion

#### 3.1. Raw Water Parameters

Raw water parameters are summarized in Table 2. The raw water samples were slightly alkaline in pH, with a range of 7.1-8.6, a mean of 7.7, and a median of 7.6. Turbidities were generally less than 20 NTU, with the exception of five samples collected on 5/13/11 and 6/28/11 following a significant rainfall event in Northwest Arkansas (28 cm total, NOAA Satellite and Information Service, 2011). This heavy rainfall occurred between April 24-26, 2011, and resulted in very high turbidities (up to 125 NTU) at the BWD and TT. The conductivity was moderate, with little spatial variation and a mean of 133  $\mu\text{S cm}^{-1}$ ; similarly, alkalinity was moderate, with little temporal or spatial variation. TDN was low throughout the sampling period, with a range of 0.36-1.47  $\text{mg L}^{-1}\text{-N}$  with no noticeable increase following the heavy rainfall event. In contrast, a large spike in TP ( $>100 \mu\text{g L}^{-1}\text{-P}$ ) was observed for the 5/13/11 samples at the BWD, TT, and MC, suggesting that the runoff carried a significant P load that did not reach CB by that date. The lack of correlation between TDN and TP suggests varying sources of N and P throughout Beaver Lake. Attempts were made to characterize the trophic state of the raw waters, as algal primary productivity, driven by N and P enrichments, can impact DBP formation and control. While the opportunity to determine Chl-a became available on the fourth sampling date (and was generally quite low), TSI (based on TP), calculated based on the regression equations developed by Carlson (1977), showed Beaver Lake was mesotrophic (TSI between 32-71, with a mean of 49) throughout the sampling period, with no consistent spatial trends. Lastly,  $\text{SUVA}_{254}$ , often considered the most useful predictor of DBP formation, ranged from 0.3-12.4  $\text{L mg}^{-1} \text{m}^{-1}$ , with a mean of 4.8  $\text{L mg}^{-1} \text{m}^{-1}$ .  $\text{SUVA}_{254}$  spiked following the heavy rainfall event, suggesting the runoff material was rich in organic carbon containing moieties.

### 3.2. Fluorescence-PARAFAC Analysis

A group of 200 EEMs comprised of raw waters and MIEX<sup>®</sup> treated samples from the four DWTPs over the five sampling periods (both chlorinated and unchlorinated) was used as the source data for the PARAFAC analysis, which resulted in a 5-component model. One component was identified as fluorometer instrument noise (EEM not shown) based on a previous study (Pifer et al. 2011), leaving a 4-component model for analysis. The four component EEMs are shown in Fig. 1 and the location of their excitation and emission maxima are listed in Table 3. Based on the location of the excitation and emission maxima, components 1, 2, and 4 were identified as humic-like fluorophore groups (Pifer et al. 2011), which may be important in the formation of THMs. Component 3 had an emission maximum less than 400 nm, and has been identified as a protein-like fluorophore group (Marhaba and Lippincott 2000; Dubnick et al. 2010). The nitrogen that makes up protein moieties suggests that “protein-like” fluorophores may play a role in the formation of N-DBPs.

The  $F_{MAX}$  values for each raw water and MIEX<sup>®</sup> treated sample is shown in Fig. 2 as a function of component and treatment pH (6, 7, and 8). The total  $F_{MAX}$  values for the raw water samples for each DWTP and sampling date were higher than for the corresponding MIEX<sup>®</sup> treated waters. This indicated that MIEX<sup>®</sup> resin removed portions of DOM from raw water. Unexpectedly, based on the net negative surface charge of DOM, there was no apparent impact of treatment pH, indicating operating pH was not an important factor in the removal of fluorophore groups. Table 4 summarizes the average contribution of each fluorophore component relative to the total  $F_{MAX}$  and the average percent removal of each component from raw to treated sample. Components 1 (humic-like) and 3 (protein-like) were the most significant contributors to the overall  $F_{MAX}$  values both before and after treatment. Component 2 was a

much more significant contributor to the total  $F_{MAX}$  of the samples after treatment, indicating MIEX<sup>®</sup> treatment preferentially removed the other components. The average percent removal for component 2 was inconclusive, as noted by the high standard deviations of these values; however, it is worth noting that despite the large deviation, the average percent removal values were negative, indicating no removal. In contrast, components 1 and 4 (both humic-like fluorophore groups) were removed by MIEX<sup>®</sup> to the most significant extents (averages of 78% and 69%). There was no evidence of pH affecting MIEX<sup>®</sup> treatment from the component data in Table 4 and Fig. 2. The absence of a  $F_{MAX}$  removal trend by pH for MIEX<sup>®</sup> treatment may indicate that the portions of DOM removed by ion exchange are relatively insensitive to pH changes between 6 and 8 (Boyer et al. 2008).

### ***3.3. Disinfection Byproduct Formation Potential***

The average concentrations and percent removals for each DBP formed are listed in Table 5. TCM was the dominant DBP formed and was also removed to the greatest extent by MIEX<sup>®</sup> treatment. Similar to the fluorescence-PARAFAC component data (Fig. 2 and Table 4), no trends in DBP formation were apparent as a function pH during MIEX<sup>®</sup> treatment. Of the eight DBPs screened, only three - TCM, DCAN, and DCBM – were found consistently at detectable levels (>1 µg/L) in the raw and MIEX<sup>®</sup> treated samples (Fig. 3). These results indicate temporal and spatial variability of DBP-precursors in Beaver Lake throughout the sampling period. Interestingly, DCBM concentrations *increased* in several instances following MIEX<sup>®</sup> treatment, suggesting the MIEX<sup>®</sup> (or, more specifically, chemicals leached from the resin) was a DCBM precursor. This result was confirmed by the average negative percent removals shown in Table 5. This was a troubling result considering the bromine-substituted DBPs are generally considered to be more toxic than fully chlorinated DBPs.

### ***3.4. Correlations Between DBPs and DBP-Precursor Properties***

Fig. 4 shows correlations between chloroform formed during the DBPFP tests and SUVA<sub>254</sub> (Fig. 4a) and fluorescence-PARAFAC components (Fig. 4b-d). The plot of TCM concentration versus SUVA<sub>254</sub> showed no relationship ( $r^2 = 0.01$ ) indicating that the SUVA<sub>254</sub> data was not a good predictor for TCM formation for raw and MIEX<sup>®</sup> treated water samples. This was an interesting result, considering SUVA<sub>254</sub> is thought to be the most appropriate predictor of DBP formation. Fortunately, significant correlations were found between the F<sub>MAX</sub> data and the individual DBP concentrations. TCM was positively correlated with F<sub>MAX</sub> for Components 1, 3, and 4 with  $r^2$  values of 0.81, 0.40, and 0.74, respectively. These relationships indicated that humic-like fluorophore groups determined by PARAFAC analysis could be strong predictors of TCM formation and could be used in future studies to optimize DBP-precursor removal processes, such as MIEX<sup>®</sup> treatment. The lack of correlation between the protein-like component 3 and any of the nitrogen containing DBPs was unexpected and indicates fluorescence spectroscopy may be inappropriate in assessing formation and control of N-DBPs.

#### 4. Conclusions and Future Work

In this study, fresh MIEX<sup>®</sup> resin was evaluated for removal of DBP precursors during DBPFP tests with free chlorine. Source waters from four DWTPs on Beaver Lake in Northwest Arkansas were sampled from April-August, 2011 and treated with fresh MIEX<sup>®</sup> resin at pH 6, 7, and 8. TCM, DCAN, and DCBM formed during the DBPFP tests at measurable concentrations (> 3 µg/L). Fluorescence-PARAFAC analysis revealed the presence of three humic-like and one protein-like component fluorophore groups. The fluorescence maximum intensity values,  $F_{MAX}$ , of the components were compared to  $SUVA_{254}$  measurements to evaluate their potential as predictors of DBP formation in raw- and MIEX<sup>®</sup> treated waters. The conclusions of this study were:

- Four principal fluorophore components – three humic-like and one protein-like – were found in the water samples. The humic-like component 1 (primary excitation maxima = 237 nm, secondary excitation maxima = 329 nm, and emission maximum = 429 nm) was the predominant fluorophore group in the water samples and was removed to the greatest extent, as determined by  $F_{MAX}$ , by MIEX<sup>®</sup> treatment. Removal of all four PARAFAC components varied, but removal of each component was independent of source water pH.
- TCM was the predominant DBP formed during the DBPFP tests in the raw and MIEX<sup>®</sup> treated waters. MIEX<sup>®</sup> treatment (with fresh resin at 6 mL/L) reduced the TCM formation potential by approximately 50%, with no quantifiable pH effect. On average, DCBM increased following MIEX<sup>®</sup> treatment, indicating the resin or chemicals from its polymer shell may be a source of DCBM precursors.

- $F_{MAX}$  for two humic-like components were more strongly correlated to TCM formation potential ( $r^2 = 0.81$  and  $0.74$ ) than  $SUVA_{254}$  ( $r^2 = 0.01$ ), indicating fluorescence-PARAFAC analysis was a more reliable predictor of DBP formation.

Future work should evaluate the conditions under which the MIEX<sup>®</sup> resin could contribute to the formation of DCBM and possibly other DBPs, such as N-nitrosodimethylamine (NDMA). More in depth characterization of the size distribution of DOM following MIEX<sup>®</sup> treatment, by techniques such as asymmetric flow-field flow fractionation, may enhance understanding of the DOM removal mechanisms through comparison to DOM size distributions following removal by other treatment processes, such as enhanced coagulation.

**Table 1 – Analytical equipment and methods used to measure the water quality parameters**

<b>Water Quality Test</b>	<b>Equipment</b>	<b>Method</b>
pH	8272 pH electrode, Orion Corp., USA	SM 4500-H <sup>+</sup>
TOC and DOC	TOC-5000, Shimadzu Corp., Japan	SM 5310-B
TDN	TOC-V & NHM-1, Shimadzu Corp., Japan	High Temperature Combustion
NH <sub>3</sub>	Thermo Orion 9512 ammonia electrode (Waltham, MA)	SM 4500-NH. D
NO <sub>3</sub> <sup>-</sup>	UV-Vis 2450, Shimadzu Corp., Japan	SM 4500-NO <sub>3</sub> <sup>-</sup> B
NO <sub>2</sub> <sup>-</sup>	UV-Vis 2450, Shimadzu Corp., Japan	SM 4500-NO <sub>2</sub> <sup>-</sup> B
Br <sup>-</sup>	ED 40, Dionex Corp., USA	USEPA Method 300
THM	[GC-2010AFAPC, 115V] GC-ECD, Shimadzu Corp., Japan	USEPA Method 551.1
Other DBPs (HAN, TCP)	[GC-2010AFAPC, 115V] GC-ECD, Shimadzu Corp., Japan	USEPA Method 551.1
Free Chlorine	UV-Vis 2450, Shimadzu Corp., Japan	SM 4500-Cl F
Turbidity	HF Scientific DRT-100 (Fort Myers, FL)	SM 2130-B
UV <sub>254</sub>	UV-Vis 2450, Shimadzu Corp., Japan	SM 5910-B
Chlorophyll-a	Trilogy fluorometer with SIS, Turner Designs (Sunnyvale, CA)	SM 10200-H
Dissolved Phosphorus	Trilogy fluorometer with SIS, Turner Designs (Sunnyvale, CA)	SM 4500-P E
Particulate Phosphorus	Trilogy fluorometer with SIS, Turner Designs (Sunnyvale, CA)	Persulfate Digestion

**Table 2** – Raw water quality parameters for Beaver Lake samples

Sampling Date	Location	pH	Turbidity (NTU)	Conductivity ( $\mu\text{S cm}^{-1}$ )	Alkalinity ( $\text{mg L}^{-1}\text{-CaCO}_3$ )	TDN ( $\text{mg L}^{-1}\text{-N}$ )	TP ( $\mu\text{g L}^{-1}\text{-P}$ )	Chl-a ( $\mu\text{g L}^{-1}$ )	TSI	SUVA <sub>254</sub> ( $\text{L mg}^{-1} \text{m}^{-1}$ )
4/11/11	BWD	7.6	2	191	59	1.17	ND	ND	ND	0.7
	TT	7.7	1	210	73	0.64	ND	ND	ND	0.7
	CB	7.9	2	182	67	0.67	ND	ND	ND	0.3
	MC	7.8	1	ND	72	0.43	ND	ND	ND	3.9
5/13/11	BWD	7.3	125	108	33	0.98	105	ND	71	11.6
	TT	7.6	120	110	34	0.91	100	ND	71	12.4
	CB	7.5	3	174	64	0.52	14	ND	42	1.6
	MC	7.7	36	138	51	0.80	113	ND	72	4.8
6/28/11	BWD	7.6	4	87	49	0.65	7	ND	32	3.4
	TT	7.3	60	79	43	1.07	15	ND	43	11.1
	CB	7.6	12	100	54	0.77	15	ND	43	5.8
	MC	8.6	4	90	52	0.64	4	ND	24	3.6
7/14/11	BWD	8.2	2	144	50	0.36	23	2.5	49	3.6
	TT	7.1	12	145	33	0.85	11	0.1	39	6.8
	CB	7.6	12	162	54	0.67	13	1.2	41	5.6
	MC	8.1	1	154	54	0.29	10	1.1	37	2.7
8/4/11	BWD	8.3	2	141	56	0.58	46	3.4	59	2.6
	TT	7.2	14	135	46	1.11	32	1.2	54	6.8
	CB	7.1	10	161	56	0.99	32	1.1	54	5.4
	MC	8.9	1	150	54	0.54	23	1.4	49	2.6
Mean		7.7	21	133	53	0.73	35	1.5	49	4.8
Median		7.6	4	143	54	0.67	19	1.2	46	3.8

TDN – total dissolved nitrogen; TP – total phosphorus; Chl-a – chlorophyll-a; TSI – trophic state index calculated from TP; SUVA<sub>254</sub> – specific ultraviolet absorbance at 254 nm; BWD – Beaver Water District; TT – Two Ton; CB – Carroll Boone; MC – Madison Country; ND – no data.

**Table 3** – Maxima location and characteristics of the fluorescence-PARAFAC components

<b>Component</b>	<b>Excitation Maxima (nm)</b>	<b>Emission Maxima (nm)</b>	<b>Identification</b>
<b>1</b>	237 (329)	429	Humic-like (Pifer et al., 2011)
<b>2</b>	346 (229, 203)	427	Humic-like (Coble 1996)
<b>3</b>	214 (298)	372	Protein-like (Dubnick et al., 2010)
<b>4</b>	398 (270, 212)	474	Humic-like (Pifer et al., 2011)

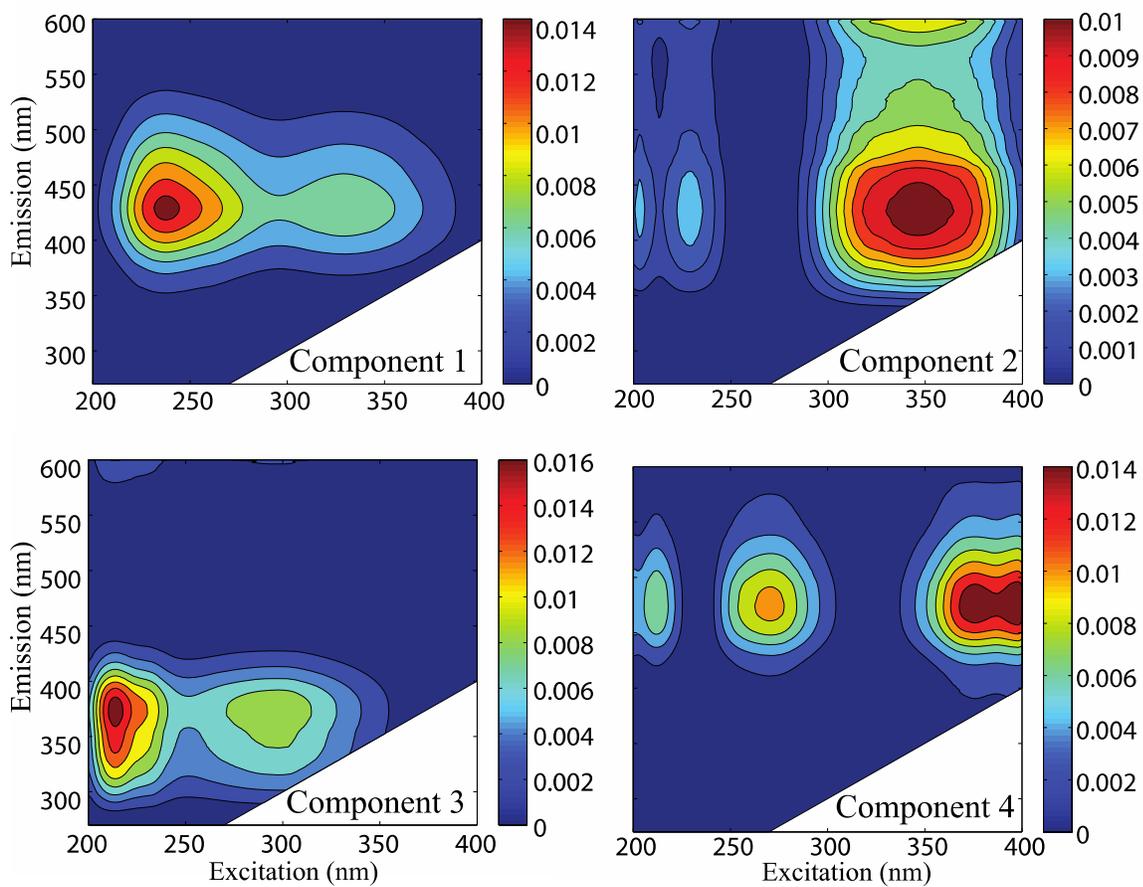
Values in parentheses are secondary and tertiary Excitation Maxima

**Table 4** – Average contribution and percent removal for each fluorescence-PARAFAC component

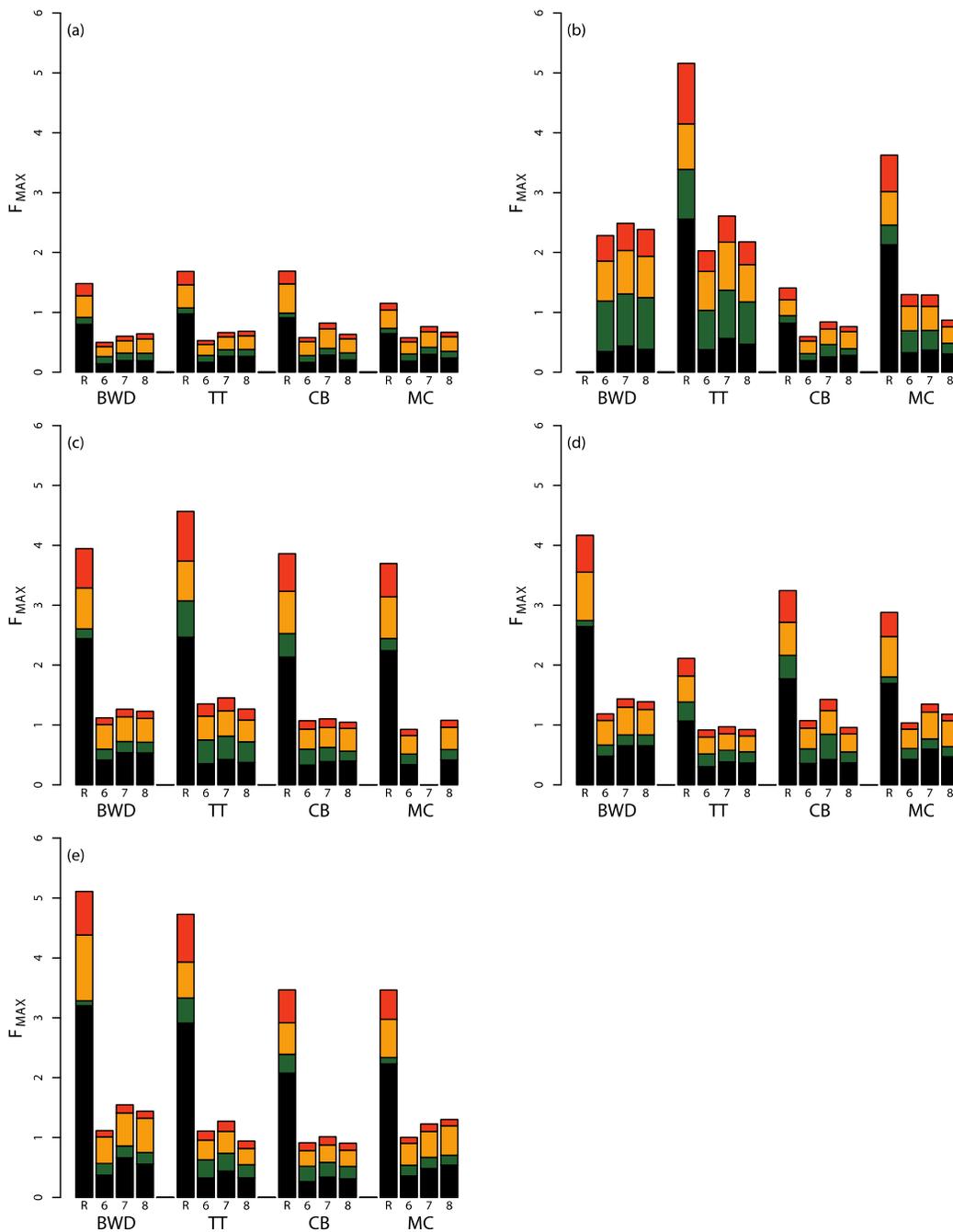
<b>Treatment</b>	<b>Component 1</b>	<b>Component 2</b>	<b>Component 3</b>	<b>Component 4</b>
<b>Average Contribution</b>				
<b>Raw</b>	57 ± 5	8 ± 5	19 ± 4	15 ± 2
<b>pH 6</b>	30 ± 7	24 ± 6	33 ± 3	13 ± 3
<b>pH 7</b>	34 ± 8	21 ± 7	32 ± 3	13 ± 3
<b>pH 8</b>	35 ± 8	20 ± 7	33 ± 4	12 ± 3
<b>Average Percent Removal</b>				
<b>pH 6</b>	82 ± 5	-13 ± 49	42 ± 14	71 ± 12
<b>pH 7</b>	75 ± 8	-22 ± 49	30 ± 20	64 ± 16
<b>pH 8</b>	77 ± 7	-5 ± 52	36 ± 18	71 ± 14
Average values ± standard deviation				

**Table 5** – Average percent removal of DBPs from MIEX<sup>®</sup> treatment as a function of pH

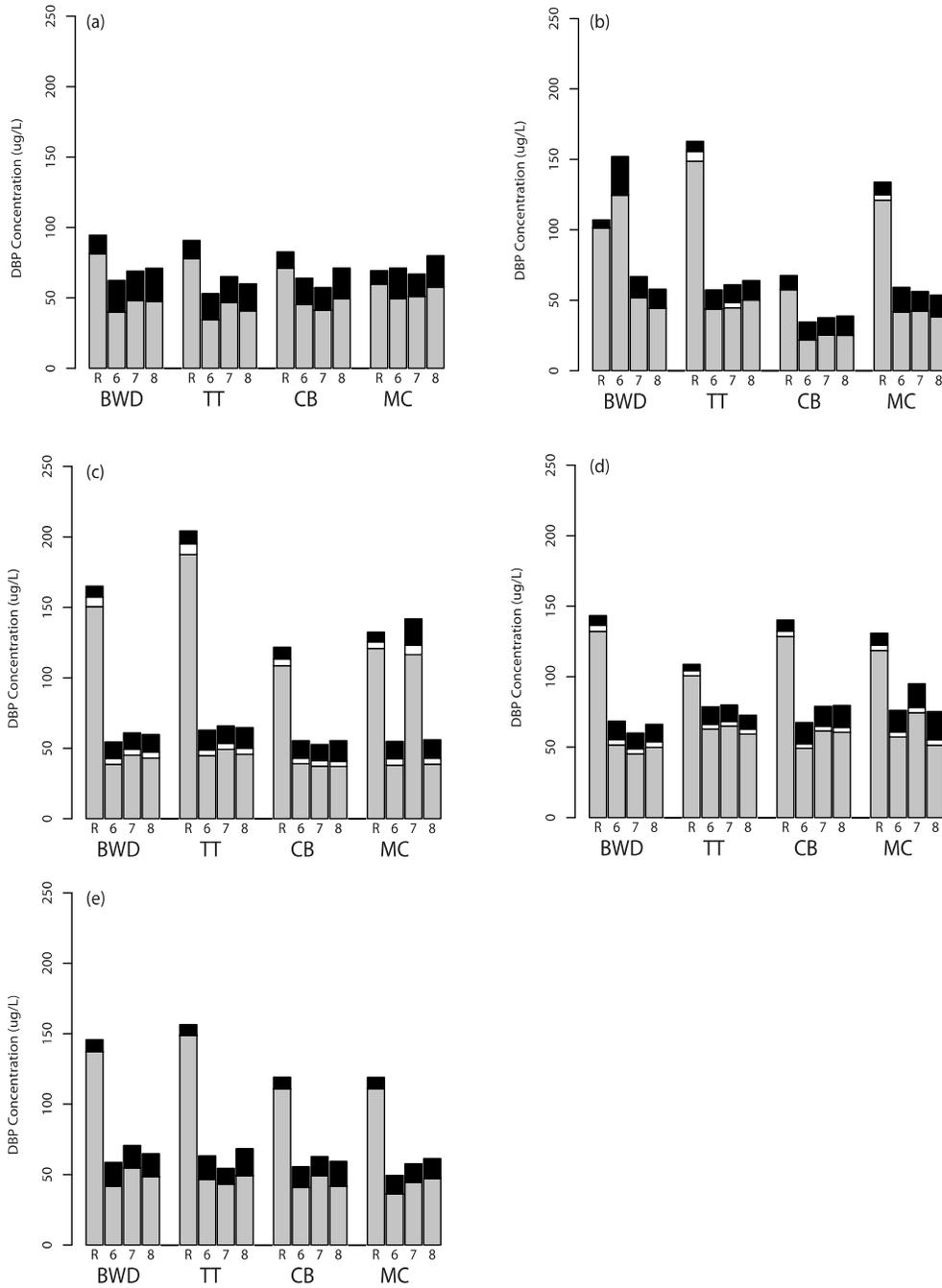
	<b>TCM</b>	<b>DCAN</b>	<b>DCBM</b>
<b>Average Concentration (µg/L)</b>			
<b>Raw</b>	115 ± 33	3.5 ± 2	8 ± 2
<b>pH 6</b>	47 ± 20	2.5 ± 1	16 ± 4
<b>pH 7</b>	51 ± 18	2.7 ± 1	14 ± 3
<b>pH 8</b>	46 ± 8	2.4 ± 1	16 ± 4
<b>Average Percent Removal</b>			
<b>pH 6</b>	56 ± 23	14 ± 52	-98 ± 73
<b>pH 7</b>	52 ± 19	7 ± 54	-74 ± 42
<b>pH 8</b>	57 ± 17	17 ± 42	-96 ± 36
Average values ± standard deviation			



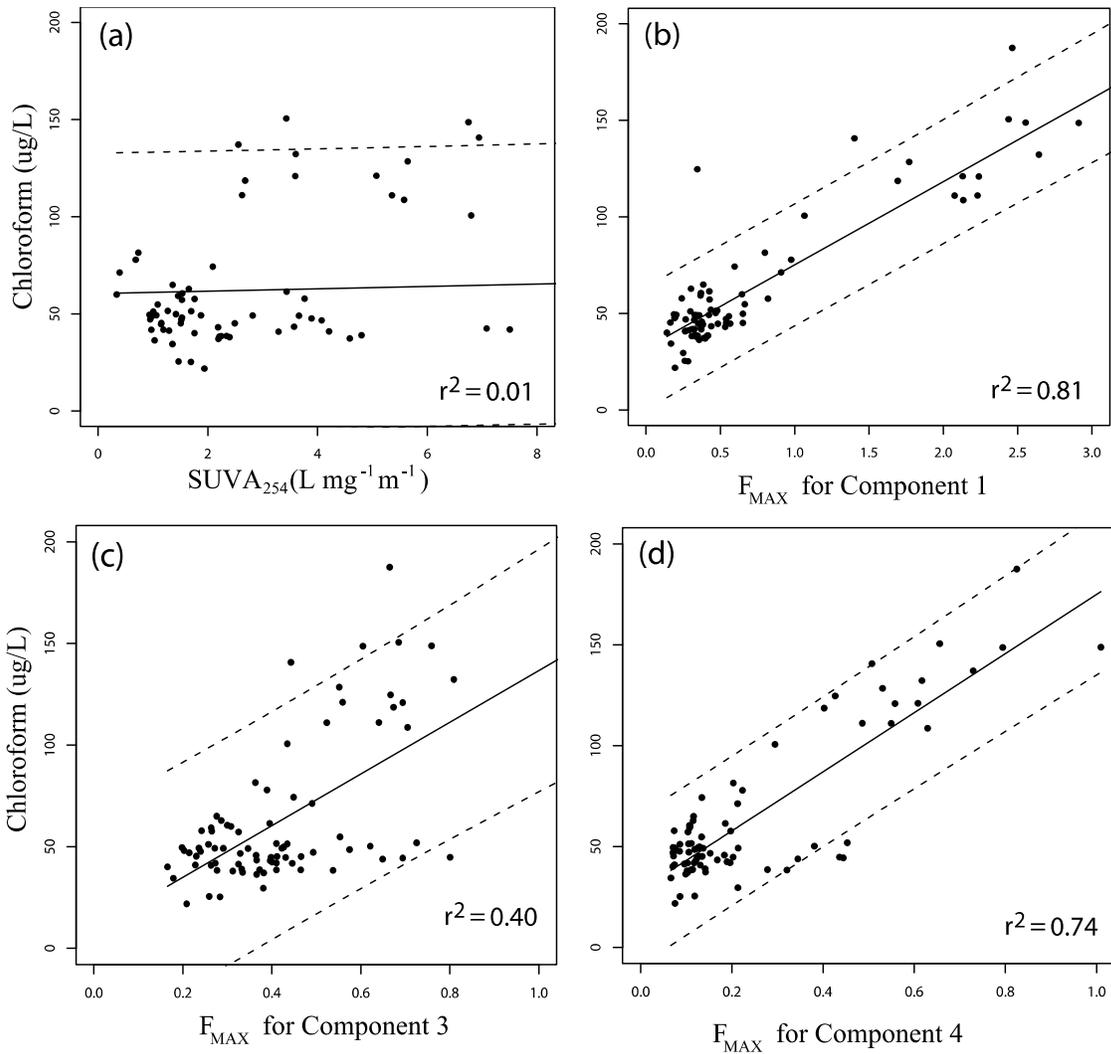
**Figure 1** – Fluorescence-PARAFAC component excitation-emission matrices (EEMs) for the array of 200 EEMs consisting of raw and MIEX<sup>®</sup>-treated waters from the four drinking water treatment plants.



**Figure 2** - Fluorescence-PARAFAC component maximums ( $F_{MAX}$ ) by drinking water treatment plant and treatment for sample dates of (a) April 11, 2011, (b) May 13, 2011, (c) June 28, 2011, (d) July 14, 2011, and (e) August 4, 2011. R indicates a raw water sample, and 6, 7, and 8 indicate the target pH for MIEX<sup>®</sup> treatment. BWD is the Beaver Water District, TT is the Benton/Washington Regional Public Water Authority (commonly referred to as Two Ton), CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District. Fluorescence-PARAFAC components are indicated by color as follows: ■ component 1, ■ component 2, ■ component 3, and ■ component 4.



**Figure 3** – Disinfection by products (DBPs) in  $\mu\text{g/L}$  as each DBP formed during free chlorine formation potential tests by DWTP and treatment for the sample dates: (a) April 11, 2011, (b) May 13, 2011, (c) June 28, 2011, (d) July 14, 2011, and (e) August 4, 2011. R indicates a raw water sample, and 6, 7, and 8 indicate the target pH for MIEX<sup>®</sup> treatment. BWD is the Beaver Water District, TT is the Benton/Washington Regional Public Water Authority (commonly referred to as Two Ton), CB is the Carroll-Boone Water District, and MC is the Madison County Regional Water District. DBPs are indicated by color as follows: TCM - chloroform (grey), DCAN - dichloroacetonitrile (white), and BDCM - bromodichloromethane (black).



**Figure 4** – Correlations between chloroform formed during the free chlorine disinfection byproduct formation potential tests and (a) SUVA<sub>254</sub>, (b) F<sub>MAX</sub> for Component 1, (c) F<sub>MAX</sub> for Component 3, and (d) F<sub>MAX</sub> for Component 4. The solid lines are the linear model fits to the experimental data. The dashed lines are the upper and low 95% prediction intervals for the linear models.

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