Water Research 158 (2019) 227–236

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Control wildfire-induced *Microcystis aeruginosa* blooms by copper sulfate: Trade-offs between reducing algal organic matter and promoting disinfection byproduct formation

Kuo-Pei Tsai [a, b], Habibullah Uzun [c, d, 1], Huan Chen [a], Tanju Karanfil [d], Alex T. Chow [a, d, *]

[a] Biogeochemistry & Environmental Quality Research Group, Clemson University, South Carolina, 29440, USA
[b] Department of Agricultural Chemistry, National Taiwan University, Taipei, 10617, Taiwan
[c] Department of Environmental Engineering, Marmara University, Istanbul, 34722, Turkey
[d] Department of Environmental Engineering and Earth Sciences, Clemson University, South Carolina, 29634, USA

ARTICLE INFO

Article history:
Received 14 December 2018
Received in revised form
5 April 2019
Accepted 7 April 2019
Available online 10 April 2019

Keywords:
Wildfire ash
Algal bloom
Microcystis aeruginosa
Copper algaecide
Disinfection byproducts

ABSTRACT

Elevated levels of nutrients due to wildfire ash input into stream waters will likely cause algal blooms. When source water is impeded by algae and requires immediate restoration, copper algaecides are usually applied. Previous studies indicate that Cu^{2+} can promote reactivity of dissolved organic matter in forming disinfection byproducts (DBPs). However, it is unclear that how DBP formation is changed after the treatment of post-fire algal bloom by copper algaecide. In this study *Microcystis aeruginosa* was cultured in the medium containing black and white ash water extracts (BE and WE) to study DBP concentrations before and after 4-days exposures to low and high copper sulfate (0.5 and 1.0 mg-Cu/L). Dissolved organic matter (DOM) was characterized by UV-VIS absorption and fluorescence spectroscopy and chlorination/chloramination-based DBP formation potential (FP) experiments. DOM concentrations and algal population in the treatments were lower than that in control, regardless of types of water extract. *N*-nitrosodimethylamine FP in the treatments were 4–6 times higher than the control (0.23–0.34 vs. 0.05–0.06 μg/L), while haloacetonitrile FP revealed no significant difference (132–191 vs. 167–185 μg/L). Trade-offs between reducing algal population and promoting DBP-FP were more pronounced for the solutions containing BE than WE. Low copper concentration was as effective as high concentration in inhibiting algal growth while minimizing promotion of DBP formation. The results can serve to support risk evaluations of algal population and DBP concentration when wildfire-induced algal bloom is left untreated and treated by copper algaecides.

1. Introduction

Elevated levels of nutrients (e.g., organic carbon, phosphorous, nitrogen) and dissolved organic matter (DOM) due to inputs of wildfire ash in stream waters may cause excessive growth of algae, creating great challenges to downstream drinking water treatment utilities (Bladon et al., 2014; Smith et al., 2011). DOMs released from wildfire ash and algae are precursors of potentially carcinogenic disinfection byproducts (DBPs) [e.g., trihalomethanes (THMs) and haloacetic acids (HAAs)] formed during water treatment disinfection processes such as chlorination and chloramination (Goslan et al., 2017; Gough et al., 2015; Henderson et al., 2008; Tsai and Chow, 2016; Wang et al., 2015a, 2015b). In addition, toxic algal blooms can exacerbate postfire drinking water quality. For example, blue-green alga *Microcystis aeruginosa* commonly occurs in eutrophic reservoirs and often produces microcystins, which are potent hepatotoxins and tumor promoters, causing serious problems to public health (Otten and Paerl, 2015). In order to control abundance of noxious algae in drinking water resources, copper-based algaecides are extensively applied because of its effectiveness (Hoko and Makado, 2011; Le Jeune et al., 2006; McKnight et al., 1983). The amount of algae-produced organic matter (AOM) usually increases with increasing algal population. On the other hand, following exposure of algae to copper algaecides, concentration of AOM and associated DBP precursors may not increase due to

---

* Corresponding author. 177 Hobcaw Road, Georgetown, SC, 29440, USA.
E-mail address: achow@clemson.edu (A.T. Chow).

[1] Current address: Department of Environmental Engineering, Marmara University, Istanbul, 34722, Turkey.

https://doi.org/10.1016/j.watres.2019.04.013

inhibition of algal growth (Tsai, 2015).

Application of copper sulfate ($CuSO_4$) for controlling noxious algae has been practiced for decades (Haughey et al., 2000). In the US, copper sulfate has been widely used to control algae in water supply reservoirs and lakes in Ohio and Michigan States (Song and Wang, 2015; Williams et al., 2015). The amount of copper required for controlling problematic algae varies, and the maximum label recommended concentration of copper sulfate as an algaecide is 2 mg-Cu/L (Tsai, 2016). A maximum contaminant level goal of 1.3 mg/L has been set for copper in drinking water supplies in the US (Drinking Water Contaminants - Standards and Regulations). Previous studies have showed that soluble copper may enhance DOM chlorine/chloramine reactivities in DBP formation potential (DBP-FP) by complexing with DOM and catalyzing haloform formation (Blatchley et al., 2003; Fu et al., 2009; Zhang and Andrews, 2013; Zhao et al., 2016). Thus, persistence of copper in the water column following application of copper sulfate may lead to increases in DBP-FP during water disinfection. In order to ensure drinking water safety after wildfires, minimizing AOM level and associated DBP precursors is particularly important in situations where algal bloom is ongoing. However, it is unclear whether controlling wildfire-induced algal blooms by copper sulfate would face the trade-offs between reduction of AOM associated DBP precursors versus promotion of DBP formation. Therefore, it is needed to investigate alterations of DOM and DBP concentration following exposures of algae to copper sulfate during postfire algal blooms.

DBP formation potential is correlated with DOM quality and quantity (Hua et al., 2015; Hua and Reckhow, 2007). During wildfire-induced algal blooms, bulk DOM chemistry in a reservoir can be influenced by algal population and characteristics of DOMs released from ash and algae (Revchuk and Suffet, 2014; Tsai et al., 2017). Black and white ashes are commonly observed in burned forested watersheds. Compared to white ash, black ash is usually produced at relatively lower burning temperature ($\leq$250 °C) and contains higher amount of organic compounds (Bodí et al., 2014; Pereira et al., 2012). In addition, black ash derived DOM usually contains less aromatic carbon and higher amounts of aliphatic carbohydrate and polysaccharide compounds (Quill et al., 2010; Wang et al., 2015b). After wildfire events, exposures of algae to black and white ash solutions may elicit different responses in terms of algal populations as well as quantity and quality of AOM (Chen et al., 2018; Tsai et al., 2017).

Both autochthonous and allochthonous DOMs exhibit different characteristics and contain diverse metal-binding functional groups in their molecular structures (e.g., carbonyl, carboxyl, phenolic, amino, and sulfidic groups) (Aiken et al., 2011). Measurements of DOM UV–visible absorption and fluorescence characteristics [e.g., excitation-emission matrix (EEM) spectroscopy] have been extensively adopted in previous studies to understand DOM properties such as optical characteristics and compound classes (Maizel and Remucal, 2017; Minor et al., 2014). Importantly, binding capacity of DOM and copper ions relates to DOM functional group and copper concentration, which are critical for copper acting as a catalyst for DBP formation (Liu et al., 2013; Zhang and Andrews, 2012).

Regarding catalytic effect of copper on DBP-FP, Zhang and Andrews (2013) found that during DOM chloramination, as Cu^{2+} concentrations increased from 0 to 1 mg/L, *N*-nitrosodimethylamine (NDMA) concentrations proportionally increased from 31 to 104 ng/L. In addition, previous studies showed that effects of Cu^{2+} on DOM chlorine/chloramine reactivities in DBP formation were related to DOM properties. For example, Blatchley et al. (2003) reported that addition of 1 mg-Cu/L as $CuSO_4$ in the citric acid solution resulted in a significant increase in chloroform formation; however, it was not observed when 2,6-dihydroxybenzoic acid was used. Liu et al. (2013) also found that during Cu-catalytic chlorination reactions, THMs and HAAs formations from carboxylic acids was more enhanced than from carbohydrates. During chloramination of a series of concentrations of Suwannee River DOM (SR-DOM) spiked with 1 mg-Cu/L as $CuSO_4$, Zhang and Andrews (2013) found that NDMA-FP significantly decreased as SR-DOM concentration increased. On the contrary, Barnes et al. (1989) reported that concentrations of chloroform formed during chlorination were positively correlated with humic acid as well as chlorine concentrations. Moreover, it was documented that influence of Cu^{2+} on promoting THMs formation was more remarkable than HAAs during the chlorination of humic acid (Liu et al., 2013). It suggests that catalytic effect of copper on DBP-FP is also DBP species dependent. Exposures of algae to copper can significantly impact algal populations as well as AOM quantity and quality (Tsai, 2015), which would consequently affect Cu-AOM complexation. Hence, it is expected that controlling wildfire-induced noxious algal blooms by copper sulfate affects DBP formation with different degrees during subsequent water disinfection process.

In this study, *M. aeruginosa* was cultured in the medium containing black and white ash water extracts separately in order to simulate fire-induced algal blooms in source water impacted by wildfire ash. Additionally, we investigated alterations of DOM quantity and quality as well as DBP formation following exposures of *M. aeruginosa* to copper algaecide. The specific objectives of this study were to: (1) measure DOM concentrations and *M. aeruginosa* populations following 4-days exposures of *M. aeruginosa* to low and high copper concentrations (0.5 and 1.0 mg-Cu/L) as copper sulfate ($CuSO_4 \cdot 5H_2O$); (2) assess DOM spectroscopic characteristics ($SUVA_{254}$, Humification index, E2/E3, Fluorescence index, Fluorescence excitation-emission matrices); and (3) compare DOM reactivities in DBP formation (Trihalomethanes, Haloacetic acids, Haloacetonitriles, *N*-nitrosodimethylamine, Chloral hydrate, Haloketones) in the absence and presence of copper algaecide.

2. Materials and methods

2.1. Ash collection and ash water extract preparation

Black and white ash samples were collected on October 2nd from the 2013 Rim Fire in California. Detailed descriptions in sampling location and collection approach were published previously (Wang et al., 2015b) and are presented in the Supporting Information. All ash samples were air-dried at room temperature (22 ± 1 °C) and passed through a 2 mm screen. To obtain black and white ash extracts, 50 g of each type of ash was mixed with 200 mL Milli-Q water in a 250 mL Erlenmeyer flask. The water-ash mixtures were shaken for 24 h using an orbital shaker at 250 rpm. Extracts were filtered using Millipore 0.45 μm filters rinsed three times with 20 mL of Milli-Q water. Black ash water extract (BE) and white ash water extract (WE) were used for further algal bioassay.

2.2. Algal culture and bioassay

The blue-green alga *Microcystis aeruginosa* UTEX 2385 (University of Texas at Austin, Austin, TX) was cultured non-axenically in the medium. Composition of cultural medium substantially affects algal growth as well as the chemistry of algal solution (Huang et al., 2012; Kilham et al., 1998). Noticeably, BG11 medium has been extensively used to culture *M. aeruginosa* for studying DBP formation from algal organic matters (Fang et al., 2010; Liao et al., 2015; Zhou et al., 2014). However, original BG11 medium consists of 6 mg/L of citric acid and 6 mg/L ferric ammonium citrate (Stanier et al., 1971). Citric acid has been identified as a precursor for the formations of trihalomethanes and haloacetic acids during water chlorination (Chowdhury et al., 2014; Kanan and Karanfil, 2011). In order to prevent uncertainty in the analyses of algae-produced organic matters and related DBP formation potential, in this study we minimized DOC concentration in the cultural medium. The medium composition is provided in Table S1.

Algal cultures were maintained at a temperature of 24 ± 2 °C and a 12:12-h light-dark photoperiod illuminated by cool white fluorescent lighting at an intensity of 2100 lux (Tsai and Chow, 2016). The algal bioassay conditions were the same as for algal cultures, where algal population was monitored at the beginning and end of experiment (day 0 and 4) by measuring optical density at 680 nm (OD_{680}) using UV-VIS spectrophotometer (Shimadzu UV-1800). Four-days exposure time was chosen because significant decrease in *M. aeruginosa* population after exposure to copper algaecide was often observed within 4 days in laboratory studies (Tsai, 2016, 2015).

To simulate postfire algal bloom in downstream receiving water, the initial OD_{680} values for algal bioassays were adjusted to 0.1 by adding algal stock solution into 1 L volumetric flasks containing culture medium and ash water extract (BE or WE) (Tsai et al., 2017). In the algal bioassays, dissolved organic carbon (DOC) concentrations derived from BE and WE were adjusted to 5 mg/L, which is within the range of DOM concentrations across the U.S. lakes as well as pre- and post-fire DOM concentrations documented in previous studies (Hohner et al., 2016; Wetzel, 2001). A stock solution (1000 mg-Cu/L) of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, Sigma Chemical Co., St. Louis, MO) was prepared within 1 h prior to experiment initiation using Milli-Q water. To study effects of controlling *M. aeruginosa* blooms by copper sulfate on the changes of DOM and DBP formation, algal bioassays were conducted using three replicates of treatments of 0.5 and 1.0 mg-Cu/L as nominal concentrations and an untreated control. Experimental chambers consisted of 250 mL of treated and untreated *M. aeruginosa* in the mixtures of culture medium and wildfire ash solutions in 1000 mL acid washed Erlenmeyer flasks. Subsamples from the control and treatments were collected at the beginning and end of experiment (day 0 and day 4) for further chemical analysis.

2.3. Chemical and statistical analyses

Subsamples collected in the algal bioassay were filtered using pre-washed Millipore 0.45 μm filters for chemical analyses, which contained extracellular AOM and ash-derived DOM. Methods of all analyses including water chemistry and DBP-FP were published previously (Murray-Gulde et al., 2005; Wang et al., 2015b). Detailed descriptions are presented in the Supporting Information. Spectroscopic characteristics of dissolved organic matter were analyzed, including specific UV absorbance at 254 nm ($SUVA_{254}$), humification index (HIX), E2/E3, and fluorescence index (FI). $SUVA_{254}$ was calculated by normalizing UV absorbance at 254 nm to DOC concentration. Fluorescence excitation-emission matrices (EEMs) from spectrofluorometry were analyzed by fluorescence regional integration (FRI) (Wang et al., 2015b).

Six DBP species were analyzed, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), *N*-nitrosodimethylamine (NDMA), chloral hydrate (CHD), and haloketones (HKs). Most DBP formation potentials were examined under DOM chlorination condition, except that for HANs and NDMA where chloramination was used instead. Yu and Reckhow (2015) showed that hypochlorite can react with HANs via nucleophilic attack on the nitrile carbon, and the products might be transformed or degraded to other DBPs or intermediate forms. It has been reported that chloramines could enhance HAN formation (Bond et al., 2011; Yu and Reckhow, 2015). Therefore, we tested HAN formation potential under chloramination condition. The DOM reactivities for DBP formation were expressed as specific DBP formation potential (specific DBP-FP), which was calculated as DBP concentration divided by DOC concentration (mmol/mol-C). Statistically significant differences between the control and treatments were determined using one-way ANOVA with Tukey's test. Significance was considered as $P < 0.05$. Additional details about materials and methods used in this study can be found in the Supporting Information section.

3. Results and discussion

3.1. M. aeruginosa population and DOM concentration

Characteristics of solutions for *M. aeruginosa* growing in the presence of ash extracts, and nominal and measured soluble copper concentrations (Cu^{2+}) are reported in Table 1. Throughout the experiment, OD_{680} values for *M. aeruginosa* growing in the presence of BE significantly increased ($p < 0.05$) from 0.09 ± 0.00 to 0.18 ± 0.03 in the control (Fig. 1A1). On the contrary, after 4-days exposures to 0.5 and 1.0 mg-Cu/L, OD_{680} values (0.03 ± 0.00 and 0.03 ± 0.00) were significantly lower than the initial value, and there was no significant difference in the values between two treatments. Regarding changes of DOC concentration, it significantly increased from 6.2 ± 0.3 to 8.9 ± 0.4 in the control (Fig. 1A2). Increases in DOC were also observed for both treatments (7.5 ± 0.6 and 6.9 ± 0.1 mg/L for the treatments of 0.5 and 1.0 mg-Cu/L), but the increments in the treatments (about 21% and 11%) were less than the control (30%). Similar patterns of the changes in OD_{680} values and DOC concentrations were also observed in the treatments with WE (Fig. 1B1 and 1B2). The increment of DOC in the treatment at 1.0 mg/L was only about 4% (increase from 5.3 ± 0.7 to 5.5 ± 0.2 mg/L). The results suggest that postfire algal population and DOM concentration in source water may increase over time if no algaecide is applied for inhibiting algal growth. In contrast, as copper sulfate is applied, algal population can be significantly decreased with a minimal increase in DOM concentration. Besides, postfire water quality would affect effectiveness of copper sulfate. Previous studies also suggest that as *M. aeruginosa* bloom is initiated, total microcystin concentration will increase along with cell density; applying copper algaecide can not only inhibit algal population but also decrease microcystin concentration in water bodies (Iwinski et al., 2016; Tsai, 2015).

3.2. DOM spectroscopic properties

$SUVA_{254}$ has been showed as an indicator for DOM aromatic carbon content (Weishaar et al., 2003). The $SUVA_{254}$ value was 2.6 ± 0.1, 4.0 ± 0.3, and 5.2 ± 0.1 L/mg/m for *M. aeruginosa* growing in BE following 4-days exposures to 0 (control), 0.5, and 1.0 mg-Cu/L, respectively (Fig. 2A1). For *M. aeruginosa* growing in the presence of WE, it also proportionally increased with increasing copper exposure concentration (Fig. 2B1). In the current study, we found that black ash from the 2013 Rim Fire in California contained higher amount of US EPA regulated polycyclic aromatic hydrocarbons (PAHs) than white ash (Chen et al., 2018). Those toxic PAHs are likely released into waters eliciting negative impacts to algal cells (Cody and Radike, 1984; Zhang et al., 2018). When *M. aeruginosa* grew in the presence of BE, the decrease in $SUVA_{254}$ observed in control (Fig. 2A1) could be attributed to destruction of algal cells, causing increases of aliphatic and hydrophilic algal organic matters in the solution (Gough et al., 2015; Ly et al., 2017; Yang et al., 2011). Kikuchi et al. (2017) found a positive correlation between $SUVA_{254}$ and copper-to-DOC ratio in the Sagami River Basin, Japan, which is in accordance with our findings (Table S2). $SUVA_{254}$ was found

Table 1
(A) Water quality and optical properties of initial algal solutions containing black ash and white ash extracts (BE and WE). (B) Nominal and measured soluble copper concentrations on day 0 and day 4. OD_{680}, optical density at 680 nm; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; DON, dissolved organic nitrogen; $SUVA_{254}$, specific ultraviolet absorbance at 254 nm; HIX, humification index; E2/E3 ratio, UVA at 254 nm divided by UVA at 365 nm; FI, fluorescence index. (average ± standard deviation, n = 3).

(A)

Parameter	Initial Algal solution + BE	Initial Algal solution + WE
pH	10.0 ± 0.0	9.7 ± 0.0
OD_{680}	0.1 ± 0.0	0.1 ± 0.0
Conductivity (μS/cm)	252 ± 0	259 ± 0
DOC (mg/L)	6.2 ± 0.3	5.3 ± 0.7
TDN (mg/L)	9.1 ± 0.1	8.1 ± 0.3
NH_4^+-N (mg/L)	0.1 ± 0.0	0.0 ± 0.0
NO_x^--N (mg/L)	2.1 ± 0.5	2.0 ± 0.1
DON (mg/L)	6.9 ± 0.6	6.0 ± 0.2
$SUVA_{254}$ (L/mg/m)	3.5 ± 0.4	2.7 ± 0.2
HIX	9.4 ± 0.0	8.0 ± 0.2
E2/E3	5.3 ± 0.4	4.8 ± 1.5
FI	1.7 ± 0.0	1.8 ± 0.0

(B)

	Algal solution + BE			Algal solution + WE		
	Initial/Control	Treatment		Initial/Control	Treatment	
Nominal Cu^{2+}, day 0 (mg/L)	0	0.5	1.0	0	0.5	1.0
Measured Cu^{2+}, day 0 (mg/L)	0.1 ± 0.0	0.4 ± 0.0	0.6 ± 0.0	0.1 ± 0.0	0.3 ± 0.0	0.4 ± 0.0
Measured Cu^{2+}, day 4 (mg/L)	0.0 ± 0.0	0.5 ± 0.1	0.9 ± 0.0	0.0 ± 0.0	0.6 ± 0.0	0.8 ± 0.0

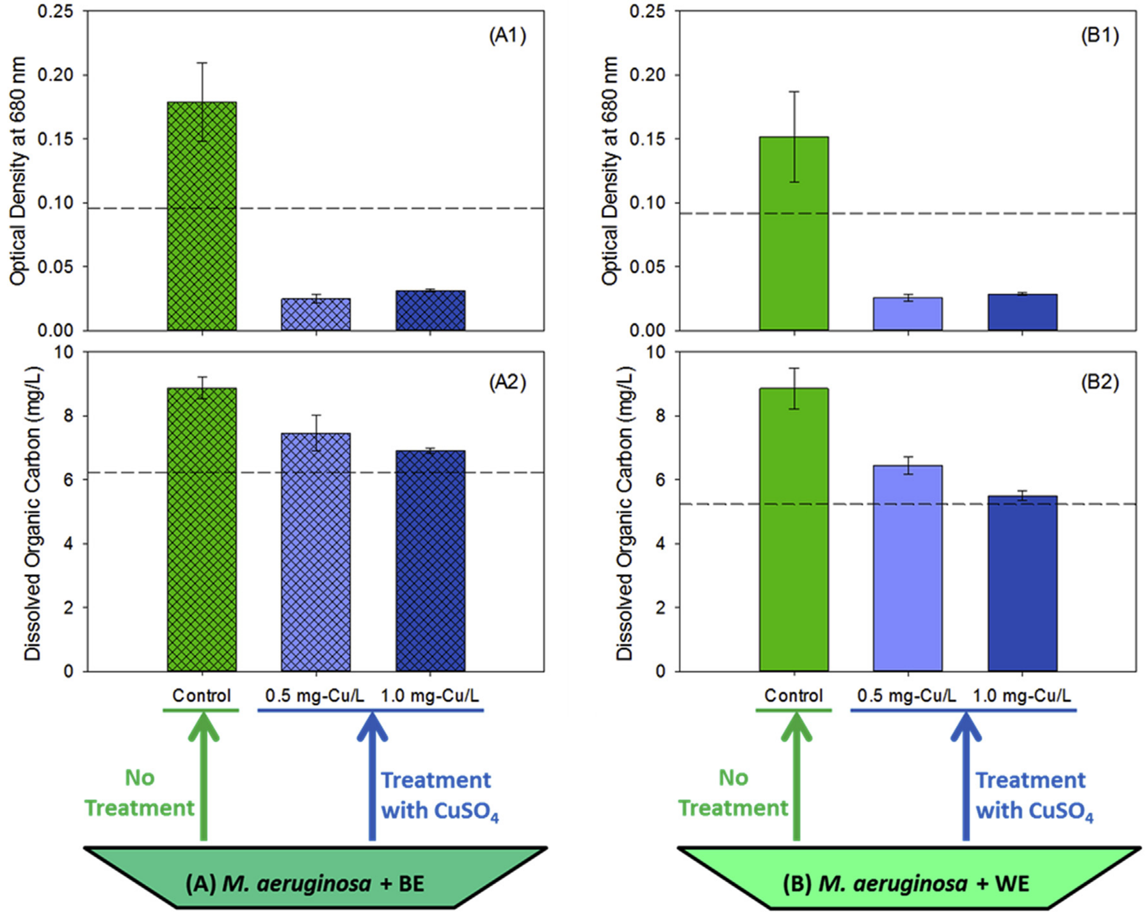

Fig. 1. Optical density at 680 nm (OD_{680}) and dissolved organic carbon (DOC) for *M. aeruginosa* growing in the presence of (A) black ash extract (BE, A1 and A2) and (B) white ash extract (WE, B1 and B2) without (control) and with 4-days exposures to copper sulfate (0.5 and 1.0 mg-Cu/L). Dash lines represent initial (day 0) values of OD_{680} and DOC. Error bars represent the standard deviation (n = 3).

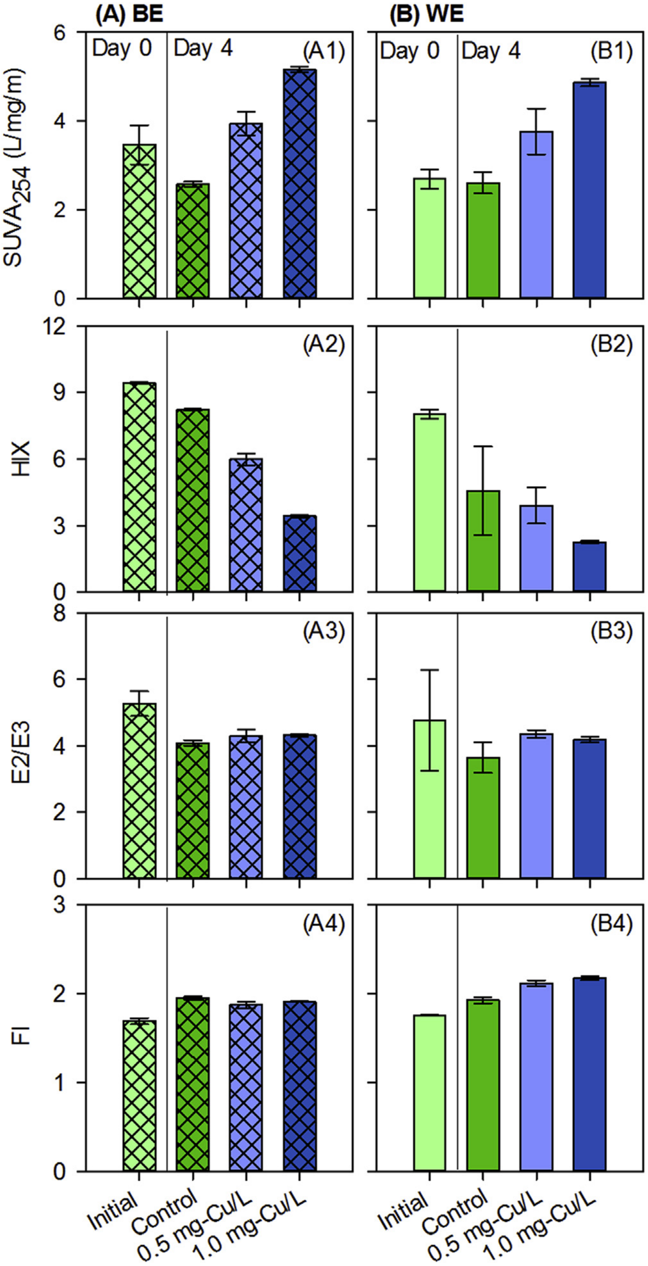

Fig. 2. Spectroscopic characteristics of DOM for *M. aeruginosa* growing in the presence of (A) black ash extract (BE, A1-A4) and (B) white ash extract (WE, B1-B4) before (day 0, initial) and after 4-days exposures to copper sulfate (0.5 and 1.0 mg-Cu/L). SUVA$_{254}$, specific ultraviolet absorbance at 254 nm; HIX, humification index; E2/E3 ratio, UVA at 254 nm divided by UVA at 365 nm; FI, fluorescence index. Error bars represent the standard deviation (n = 3).

positively correlated with copper binding affinity of DOM in natural waters (Baken et al., 2011). With further consideration in DOM protonation-active sites, Yan et al. (2017) found that the amount of high metal ion affinity sites (phenolic-type functional groups) increased with SUVA$_{254}$ values, while amount of low metal ion affinity sites (carboxylic-type functional groups) revealed opposite trend. According to those studies, our findings imply that applying copper sulfate to control postfire algal bloom would lead to increases in the aromatic carbon content and copper-DOM affinity. Humification index (HIX) describes the degree of aromatic structure polycondensation (Kalbitz, 2001). We found HIX was significantly higher in the control (8.2 ± 0.0) than treatments of 0.5 and 1.0 mg-Cu/L (6.0 ± 0.3 and 3.4 ± 0.1) for *M. aeruginosa* growing in the presence of BE (Fig. 2A2). For the *M. aeruginosa* growing in the presence of WE, changes of HIX revealed the similar pattern to that with BE, but there was no significant difference ($p \geq 0.05$) in the control (4.6 ± 2.0) and treatment of 0.5 mg-Cu/L (3.9 ± 0.8) (Fig. 2B2). HIX values also represent characteristics of DOM source. HIX <4 indicates that biological or aquatic bacterial origin is the dominant source, while HIX >6 implies that terrestrial DOM is the major source (Huguet et al., 2009). In this study, HIX values after exposures of *M. aeruginosa* to 1.0 mg-Cu/L were lower compared to the control and treatment with 0.5 mg-Cu/L, implying that amount of intracellular compounds released from algal cells following exposures to copper sulfate could be related to copper concentration (Tsai, 2015). E2/E3 ratio is an index inversely correlated with DOM molecular weight (MW) (Peuravuori and Pihlaja, 1997). It was 4.3 ± 0.2 and 4.3 ± 0.0 in the treatment of 0.5 and 1.0 mg-Cu/L for *M. aeruginosa* growing in the presence of BE, which was slightly higher than that in the control (4.1 ± 0.1) (Fig. 2A3). Similar pattern for the changes in E2/E3 was also observed for *M. aeruginosa* growing in the presence of WE (Fig. 2B3). These results suggest that application of copper sulfate for controlling postfire algal bloom may result in decreases in humification extent and MW of bulk DOM, which is likely attributed to the presence of aliphatic compounds with low MW released from algal cells into surrounding water (Fuentes et al., 2007; Huguet et al., 2009; Tsai, 2015). Fluorescence index (FI) provides information on relative contribution of autochthonous and allochthonous DOM sources (i.e., higher values represent more autochthonous origins). Regarding changes of FI values in the control and treatments, there was no significant difference for the *M. aeruginosa* growing in the presence of BE (Fig. 2A4), while FI values in both treatments (2.1 ± 0.0 and 2.2 ± 0.0) were significantly higher than the control (1.9 ± 0.0) for the *M. aeruginosa* growing in the presence of WE (Fig. 2B4). These findings imply that *M. aeruginosa* growing with white ash solution tends to release fluorescent components following exposure of copper sulfate, while the tendency might be minimal for growing with black ash solution. These results provide fundamental information about water characteristics during the treatment of postfire algal bloom by copper sulfate. Further investigations are still needed to understand effects of ash solution and copper algaecide on algal physiology and subsequent water chemistry.

Changes of fluorescence in DOM components in the control and treatments after 4-days exposures of *M. aeruginosa* to copper sulfate were observed through 3D excitation emission matrices (Fig. 3A1-A4 and 3B1-B4). The proportions of tyrosine- and tryptophan-like compounds in the treatment of 1.0 mg-Cu/L were significantly higher ($p < 0.05$) than that in the control and treatment of 0.5 mg-Cu/L, regardless of type of ash extract in the culture medium (Regions I and II in Fig. 3A5 and 3B5). On the contrary, proportions of fulvic acid- and humic acid-like compounds (regions III and V) in the treatment of 1.0 mg-Cu/L were significantly lower than that in the control and treatment of 0.5 mg-Cu/L. For example, the proportion of tyrosine-like compound for the *M. aeruginosa* growing in the presence of BE was 4.1 ± 0.1, 5.0 ± 0.2, and $10.3 \pm 0.1\%$ in the control and treatments of 0.5 and 1.0 mg-Cu/L (Fig. 3A5, region I), where the proportion of fulvic acid-like compound was 27.3 ± 0.1, 26.3 ± 0.3, and $21.1 \pm 0.2\%$, respectively (Fig. 3A5, region III). These results indicate that controlling wildfire-induced algal bloom by copper sulfate would lead to increases in fluorescence of protein-like compounds. Enhancement in DOM fluorescence intensity for the protein-like compounds has also been observed in the mangrove-related DOM with the addition of cupric ion (Yamashita and Jaffe, 2008). Studying the metal binding capacity with DOM fluorescent components in a eutrophic algae-rich lake, Xu et al. (2013) noticed that tyrosine-like substance in

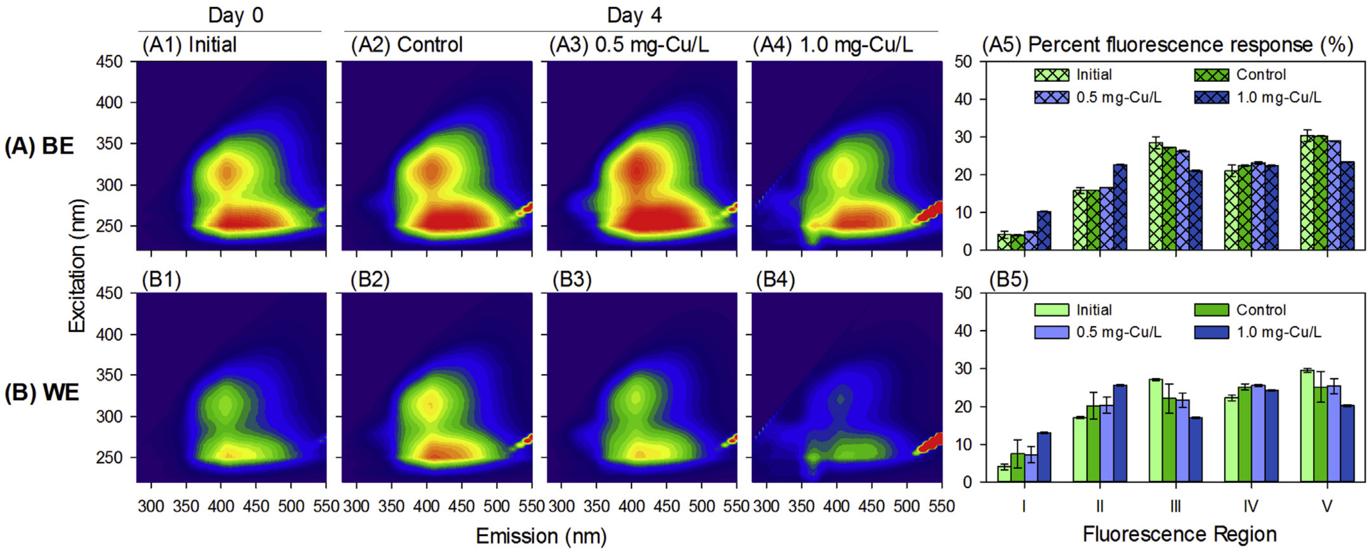

Fig. 3. 3D excitation and emission matrices (EEM) and fluorescence regional integration for *M. aeruginosa* growing in the presence of (A) black ash extract (BE, A1-A5) and (B) white ash extract (WE, B1-B5) before (day 0, initial) and after 4-days exposures to copper sulfate (0.5 and 1.0 mg-Cu/L). Roman numerals I, II, III, IV, and V represent proportion of tyrosine-like, tryptophan-like, fulvic acid-like, soluble microbial byproduct-like, and humic acid-like components analyzed by fluorescence EEM, respectively. Error bars represent the standard deviation (n = 3).

DOM fraction and tryptophan-like substance in algal extracellular polymeric substance exhibited higher copper binding capacity than other component. Fluorescence of humic and fulvic substances could be quenched upon complexation to cupric ion followed by the change of molecular binding structure (Cabaniss and Shuman, 1988; Heibati et al., 2017; Ryan and Weber, 1982; Xu et al., 2013; Yan et al., 2013). It was reported that the quenching of fluorescent humic-like moieties by cupric ion occurs with a vibrational change of the related functionalities, such as phenolic and aryl carboxylic groups (Chen et al., 2015). In the present study, observed decreases in the fluorescence of fulvic and humic substances were likely due to quenching effects of copper on those compounds.

Toxicity of copper sulfate to algae may result from production of reactive oxygen species through the redox cycling of copper ions in the cells, causing suppression of mitosis and loss of cell membrane integrity (Qian et al., 2010; Stauber and Florence, 1987; Stevenson et al., 2013). Generally, protein-like compounds are major constituent in algal cells, followed by carbohydrate, lipid, and relatively low amount of humic substance (Huang et al., 2012; Myklestad, 2000; Pivokonsky et al., 2014). In addition to those compounds, intracellular organic compounds such as toxins (e.g., microcystins) would be released into surrounding water during algal cell lysis. A positive correlation between extracellular microcystin and soluble copper concentration has been reported (Iwinski et al., 2016; Tsai, 2015). In addition, applying minimum amount of copper required for controlling *M. aeruginosa* bloom can not only reduce cell density but also not compromise cell membranes, resulting in minimal release of microcystin. Those studies support our findings that controlling *M. aeruginosa* by applying low concentration of copper (0.5 mg-Cu/L) was as effective as high amount of copper (1.0 mg-Cu/L) (Fig. 1A1 and 1B1), where treatment of 1.0 mg-Cu/L led to higher proportions of protein-like compounds in the solution compared to that in the treatment of 0.5 mg-Cu/L (Regions I and II in Fig. 3A5 and 3B5).

3.3. DOM reactivity for DBP formation potential

DBP formation potential (DBP-FP) and specific disinfection byproduct formation potential (SDBP-FP) for *M. aeruginosa* growing in the presence of BE or WE varied with different extents in the untreated control and treatments (Fig. 4). In terms of DBP-FP, for *M. aeruginosa* growing in the presence of BE, most DBP concentrations in the control were similar to or higher than the initial values, except for the HKs concentration (Fig. 4A6, 10.5 ± 0.7 and 21.3 ± 2.1 μg/L for the control and initial). CHD concentrations increased with increasing copper concentration (Fig. 4A5). In addition to CHD concentration, formations of THMs, HAAs, NDMA, and HKs in the treatments were also higher than the control for *M. aeruginosa* growing in the presence of BE, and it revealed no significant difference for the treatment of 0.5 and 1.0 mg-Cu/L. For example, NDMA concentrations in the treatments with 0.5 and 1 mg-Cu/L were 326.1 ± 16.6 and 342.2 ± 15.1 ng/L, approximately 6 times higher than that in the control (50.8 ± 13.5 ng/L) (Fig. 4A4). For *M. aeruginosa* growing in the presence of WE, the promotion effect of cupric ion on DBP-FP was only observed for NDMA and CHD (Fig. 4B1-B6). There were no significant differences for the formations of THMs, HAAs, HANs, and CHD in the control and treatment of 0.5 mg-Cu/L. Concentrations of THMs, HAAs, and HKs in the treatment of 1.0 mg-Cu/L were lower than that in the control.

These results imply that controlling fire-induced algal bloom by copper sulfate may promote subsequent DOM chlorine/chloramine reactivities for DBP formation, and the promotion effect of cupric ion on DBP formation is more significant for lower burning temperature (≤250 °C, black ash is formed) compared to higher burning temperature (≥400 °C, white ash is formed). Using FTIR spectroscopy to examine chemical functionality of thermally-altered DOM, Quill et al. (2010) found that DOM derived from plant materials burnt at a lower temperature (150 °C, black ash solution) contained more aliphatic carboxylate groups. Wei et al. (2018) showed that the DOM derived from lower temperature (300 °C) biochar had larger copper complexation capacities than its higher temperature (500 and 700 °C) counterparts as a result of having more carboxyl groups. Zhao et al. (2016) found that catalytic effect of cupric ions on aliphatic DBP precursors was more significant than that on aromatic precursors. In the present study, as *M. aeruginosa* grew in the presence of BE, bulk DOM might exhibit more carboxylic DBP precursors compared to the bulk DOM in WE, leading to more pronounced promotion effect of copper sulfate on

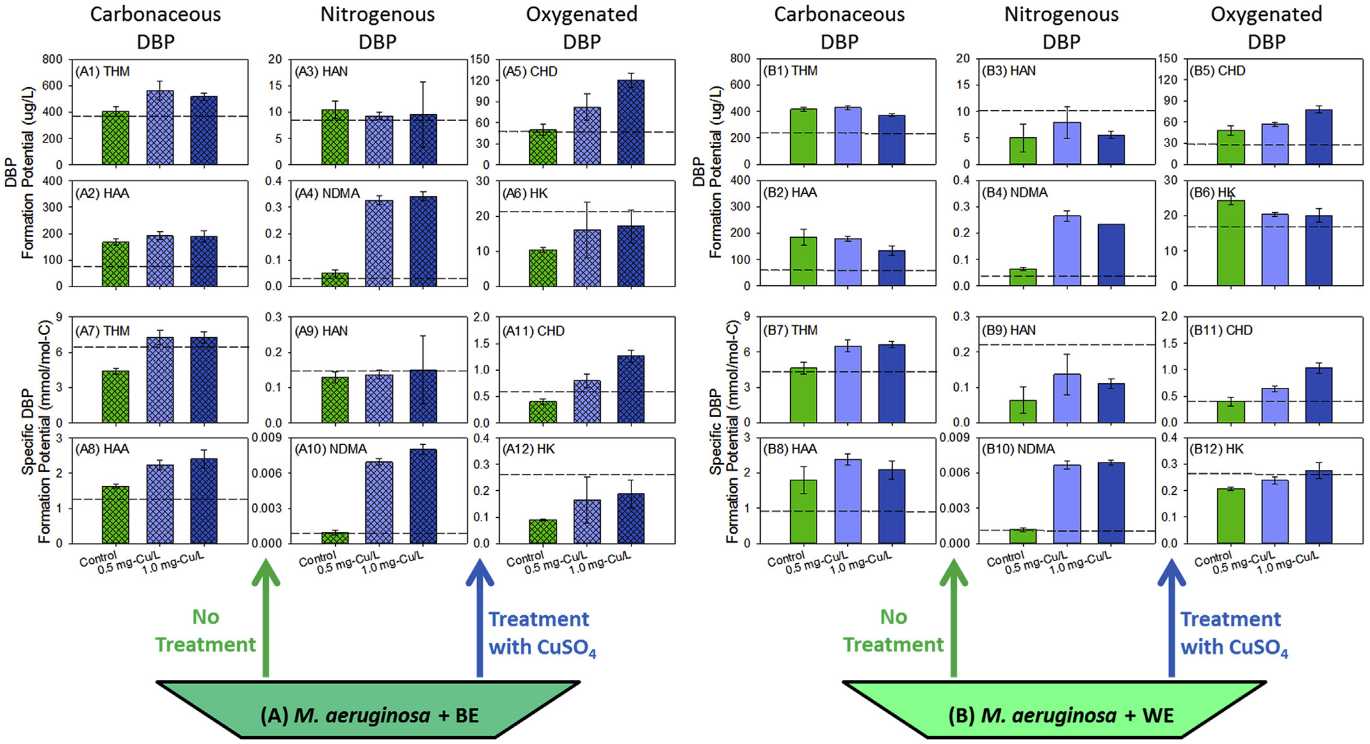

Fig. 4. DBP formation potential (DBP-FP) and specific formation potential (SDBP-FP) for *M. aeruginosa* growing in the presence of (A) black ash extract (BE, A1 – A12) and (B) white ash extract (WE, B1 – B12) without (control) and with 4-days exposures to copper sulfate (0.5 and 1.0 mg-Cu/L). THM, trihalomethanes; HAA, haloacetic acids; HAN, haloacetonitriles; NDMA, *N*-nitrosodimethylamine; CHD, chloral hydrate; HK, haloketones. Dash lines represent initial (day 0) values of DBP-FP and SDBP-FP. Error bars represent the standard deviation (n = 3).

DBP formation.

In terms of DOM reactivity for DBP formation, specific HAA-FP for *M. aeruginosa* growing in the control (1.6 ± 0.1 and 1.8 ± 0.4 mmol/mol-C for BE and WE) was significantly higher than the initial value (1.3 ± 0.2 and 1.0 ± 0.1 mmol/mol-C for BE and WE) (Fig. 4A8 and 4B8). For the other DBP species, their SDBP-FP values in the control were similar to or lower than the initial values. Most specific DBP-FPs in the treatments were higher than the control, except for specific HAN-FP for *M. aeruginosa* growing in the presence of BE. For example, for *M. aeruginosa* growing in the presence of BE, specific THM-FP values in the control and treatment of 0.5 and 1.0 mg-Cu/L were 4.4 ± 0.2, 7.3 ± 0.6 and 7.3 ± 0.5 mmol/mol-C (Fig. 4A7); and SHAN-FP values were 0.1 ± 0.0, 0.1 ± 0.0, and 0.2 ± 0.1 mmol/mol-C, respectively (Fig. 4A9). Regardless of type of ash extract, specific CHD-FP proportionally increased with increasing copper concentration (Fig. 4A11 and 4B11). Obviously, trade-offs between reducing algal organic matter (Fig. 1) and promoting DBP-FP (Fig. 4) were observed in this study. The results in this study can serve to support risk evaluations of algal population and DBP concentration when wildfire-induced algal bloom is left untreated and when it is treated by copper sulfate.

In addition to the characteristics of post-fire source water quality, the amount of copper applied is also a key factor influencing the level of DBP formation promotion. When *M. aeruginosa* is exposed to different amounts of copper, effect of copper on the alteration of DBP formation is related to the quantity and quality of AOM, because it can alter Cu-AOM chelating compounds and associated chlorine/chloramine reactivities. Blue-green algae are able to excrete copper chelators as a defense mechanism to detoxify elevated cupric ion concentration (Gouvêa et al., 2005; Mcknight and Morel, 1979; Tonietto et al., 2014), and a positive relationship in copper concentration and amount of copper complexing ligands released by blue-green algae has been reported (Jardim and December 1984). Previous studies indicated that copper is preferentially complexed by DOM acidic and aromatic moieties with high SUVA$_{254}$ (e.g., carboxylic, phenolic, and aminopolycarboxylate ligands) (Baken et al., 2011; Lu and Allen, 2002). In this study as copper concentration increased from 0.5 to 1.0 mg/L, increases in tyrosine- and tryptophan-like compounds were observed (regions I and II in Fig. 3A5 and 3B5). Both protein-like compounds have been found exhibiting high copper binding capacity during algal blooms (Li et al., 2017; Lorenzo et al., 2007; Xu et al., 2013). Compared to untreated control, elevated DBP formation in the treatments could be also ascribed to larger amounts of protein-like DBP precursors and copper complexing ligands released from *M. aeruginosa*, such as glutathione, *N*-acetylglucosamine, and hydroxamic acids (Gouvêa et al., 2005; Hsu-Kim, 2007; Mcknight and Morel, 1979). During the development of algal bloom in Taihu Lake, China, Li et al. (2017) found that nitrogenous functional groups in fulvic acid revealed strong binding reactivity with cupric ions. For the *M. aeruginosa* growing in the presence of WE, as copper exposure concentration increased from 0.5 to 1.0 mg/L, decreases in carbonaceous and nitrogenous DBP concentrations (Fig. 4B1–4B4) were likely caused by the lower levels of fulvic-like compounds (region III in Fig. 3B5) and nitrogen-containing DBP precursors in the treatment of 1.0 mg/L compared to 0.5 mg/L (Chang et al., 2011; Yang and Shang, 2004).

Functional groups on DOM play a critical role for cupric ion acting as a catalyst for promoting DBP formation. Blatchley et al. (2003) found that cupric ions promoted THM formation during chlorination of citric acid, possibly through complexing with carboxylic and hydroxyl groups, enhancing the oxidative decarboxylation of citric acid. Based on Fourier transform infrared spectra, Fu et al. (2009) confirmed that carboxylate and hydroxyl groups in humic acid were active sites for cupric ion complexation. Besides, Liu et al. (2012) found that catalytic effect of cupric ion on HAA formation was related to the generation of hydroxyl radical caused by the presence of cupric ion. Potential reaction mechanisms for copper-catalyzed THM and HAA formations during chlorination and chloramination of humic acid were proposed in their studies (Fu et al., 2009; Liu et al., 2012). Importantly, cupric ion binding capacity to DOM is limited. Once functional groups or binding sites of DOM are fully occupied, catalytic effect of copper on DBP formation may not be significant (Zhang and Andrews, 2012). In this study, while *M. aeruginosa* grew in the presence of BE, DBP concentrations (except CHD) in the treatments of 1.0 mg-Cu/L were similar to that in the treatment of 0.5 mg-Cu/L, which could be attributed to saturated copper-DOM complexation by 0.5 mg-Cu/L. Chen et al. (2015) found that during copper and DOM binding process, carboxyl and polysaccharide groups revealed the fastest responses to copper binding followed by amide and aliphatic groups.

Effect of cupric ion on DBP formation is also influenced by the preference of complexation with DBP precursors. Zhang and Andrews (2012) noticed that catalytic effect of cupric ion on HAAs formation was only observed for dichloroacetic acid (DCAA) but not for trichloroacetic acid (TCAA), suggesting that copper would preferentially complex with DCAA precursors and increase their chlorine reactivity. Similarly to their studies, we found that specific DCAA-FP was significantly higher than specific TCAA-FP for *M. aeruginosa* growing in the presence of BE after 4-days exposures to copper sulfate at 0.5 and 1.0 mg-Cu/L (Fig. S2A). The same patterns were also observed for the treatments with WE, but the differences were not significant (Fig. S2B). For *M. aeruginosa* growing in the presence of WE, it is noted that THM, HAA, and HK-formation potentials decreased with the addition of copper sulfate (Fig. 4B1, 4B2, and 4B6) while their correspondent specific formation potentials increased (Fig. 4B7, 4B8, and 4B12), which may indicate that cupric ion tends to catalyze reactions of those DBP formation by complexing with their precursors. On the other hand, no significant differences for specific HAN-FPs were found in the control and treatments (Fig. 4A9 and 4B9), which may imply that cupric ions prefer complexing with non-HAN precursors.

4. Conclusions and implications for water resources management

Regarding management of drinking water resources impeded by wildfire and subsequent algal blooms, understanding effects of algaecide application on DBP formation is important for making risk-based decisions for drinking water safety. In this bench-scale study, *M. aeruginosa* was cultured in the presence of black and white ash extracts, and we comparatively investigated changes of DBP formation as well as algal population following exposures to copper sulfate. Under these experimental conditions, the results indicated the trade-offs between reducing algal population and organic matter increment, and promoting DBP formation; where the trade-offs were more pronounced for the solution containing BE than WE. Besides, the results demonstrated that low copper concentration (0.5 mg-Cu/L) was as effective as high concentration (1.0 mg-Cu/L) in inhibiting algal growth while minimizing promotion of DBP formation. Importantly, characteristics of source water (DOM properties, pH, and metal concentrations) as well as water disinfection conditions (chlorine/chloramine concentrations and reaction time) could affect the level of trade-off (Fu et al., 2009; Sharma et al., 2017; Zhang and Andrews, 2013, 2012; Zhang et al., 2019; Zhao et al., 2016). Some of those parameters are beyond the scope of this study and therefore are not included into the experimental design. Further investigations (e.g., using real water samples with realistic chlorine dose and spikes of ash extract) are needed to better verify the trade-off.

Post-fire algal populations will likely increase over time due to elevated levels of nutrients and the minimum amount of copper required to inhibit algal growth increases with increasing algal population. Accordingly, after wildfire event, monitoring water chemistry especially nutrient and chlorophyll concentrations in receiving water is important to better predict occurrence of algal bloom. Copper algaecides may need to be applied as early as algal bloom is about to form, and the amount of copper algaecide applied should be carefully determined to minimize copper concentration in source water and reduce promotion of DBP formation during drinking water chlorination/chloramination processes.

In addition to copper salt (e.g., copper sulfate), several chelated copper compounds (e.g., copper-ethanolamine, copper-citrate, copper-gluconate) also have been widely used as formulations for copper-based algaecides (Bishop and Rodgers, 2011; Calomeni et al., 2015). Following a copper sulfate treatment for controlling blue-green algae in channel catfish ponds, Liu et al. (2006) found that over 99% of copper applied was transferred to the bottom sediment within approximately 2 days. Chelated copper algaecides have been reported to be able to provide a higher concentration of copper in the water column for a longer period of time and loss to the sediment is slower than for copper sulfate (Murray-Gulde et al., 2002). Formulation of copper algaecide used for controlling harmful algal blooms can differ from site to site and also likely affect Cu-DOM concentration (Barnes et al., 1989; Murray-Gulde et al., 2002). Future investigations are needed to understand post-fire DBP formation potential following non-chelated and chelated copper algaecide applications. Instead of applying algaecides, other chemical, physical, and biological approaches for controlling post-fire algal bloom and subsequent impacts on drinking water quality should be also studied.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This study was financially supported by Joint Fire Science Program (14-1-06-19 and 14-1-06-11), USDA NIFA (SCN-2013-2784 and SC-17004574), and USEPA (R835864). The authors thank Dr. Randy A. Dahlgren at the University of California, Davis for the ash collection, and Dr. Wayne Chao at the Clemson University for copper analysis. Dr. Alexander M. Ruecker at the Max Planck Institute for Biogeochemistry is also thanked for reviewing the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2019.04.013.

References

Aiken, G.R., Hsu-kim, H., Ryan, J.N., 2011. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. Environ. Sci. Technol. 3196–3201. https://doi.org/10.1021/es103992s.

Baken, S., Degryse, F., Verheyen, L., Merckx, R., Smolders, E., 2011. Metal complexation properties of freshwater dissolved organic matter are explained by its aromaticity and by anthropogenic ligands. Environ. Sci. Technol. 45, 2584–2590. https://doi.org/10.1021/es103532a.

Barnes, D., FitzGerald, P.A., Swan, H.B., 1989. Catalysed formation of chlorinated organic materials in waters. Water Sci. Technol. 21, 59–63.

Bishop, W.M., Rodgers, J.H., 2011. Responses of Lyngbya magnifica Gardner to an algaecide exposure in the laboratory and field. Ecotoxicol. Environ. Saf. 74, 1832–1838. https://doi.org/10.1016/j.ecoenv.2011.06.007.

Bladon, K.D., Emelko, M.B., Silins, U., Stone, M., 2014. Wildfire and the future of water supply. Environ. Sci. Technol. 48, 8936–8943. https://doi.org/10.1021/es500130g.

Blatchley, E.R., Margetas, D., Duggirala, R., 2003. Copper catalysis in chloroform formation during water chlorination. Water Res. 37, 4385–4394. https://doi.org/10.1016/S0043-1354(03)00404-4.

Bodí, M.B., Martin, D.A., Balfour, V.N., Santín, C., Doerr, S.H., Pereira, P., Cerdà, A., Mataix-Solera, J., 2014. Wildland fire ash: production, composition and eco-hydro-geomorphic effects. Earth Sci. Rev. 130, 103–127. https://doi.org/10.1016/j.earscirev.2013.12.007.

Bond, T., Huang, J., Templeton, M.R., Graham, N., 2011. Occurrence and control of nitrogenous disinfection by-products in drinking water - a review. Water Res. 45, 4341–4354. https://doi.org/10.1016/j.watres.2011.05.034.

Cabaniss, S.E., Shuman, M.S., 1988. Fluorescence quenching measurements of copper—fulvic acid binding. Anal. Chem. 60, 2418–2421. https://doi.org/10.1021/ac00172a020.

Calomeni, A.J., Iwinski, K.J., Kinley, C.M., McQueen, A., Rodgers, J.H., 2015. Responses of Lyngbya wollei to algaecide exposures and a risk characterization associated with their use. Ecotoxicol. Environ. Saf. 116, 90–98. https://doi.org/10.1016/j.ecoenv.2015.03.004.

Chang, H., Chen, C., Wang, G., 2011. Identification of potential nitrogenous organic precursors for C-, N-DBPs and characterization of their DBPs formation. Water Res. 45, 3753–3764. https://doi.org/10.1016/j.watres.2011.04.027.

Chen, H., Chow, A.T., Li, X., Ni, H., Dahlgren, R.A., Zeng, H., Wang, J., 2018. Wild fire burn intensity affects the quantity and speciation of polycyclic aromatic hydrocarbons in soils. ACS Earth Space Chem. 2, 1262–1270. https://doi.org/10.1021/acsearthspacechem.8b00101.

Chen, W., Habibul, N., Liu, X.Y., Sheng, G.P., Yu, H.Q., 2015. FTIR and synchronous fluorescence heterospectral two-dimensional correlation analyses on the binding characteristics of copper onto dissolved organic matter. Environ. Sci. Technol. 49, 2052–2058. https://doi.org/10.1021/es5049495.

Chowdhury, S., Al-hooshani, K., Karanfil, T., 2014. Disinfection byproducts in swimming pool: occurrences, implications and future needs. Water Res. 53, 68–109. https://doi.org/10.1016/j.watres.2014.01.017.

Cody, T.E., Radike, M.J., 1984. The phototoxicity of benzo [a] pyrene in the green alga selenastrum capricornutum. Environ. Res. 132, 122–132.

Drinking Water Contaminants - Standards and Regulations [WWW Document], n.d. URL https://www.epa.gov/dwstandardsregulations#List (accessed 3.11.17).

Fang, J., Ma, J., Yang, X., Shang, C., 2010. Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of Microcystis aeruginosa. Water Res. 44, 1934–1940. https://doi.org/10.1016/j.watres.2009.11.046.

Fu, J., Qu, J., Liu, R., Qiang, Z., Liu, H., Zhao, X., 2009. Cu(II)-catalyzed THM formation during water chlorination and monochloramination: a comparison study. J. Hazard Mater. 170, 58–65. https://doi.org/10.1016/j.jhazmat.2009.04.133.

Fuentes, M., Baigorri, R., González-Gaitano, G., García-Mina, J.M., 2007. The complementary use of 1H NMR, 13C NMR, FTIR and size exclusion chromatography to investigate the principal structural changes associated with composting of organic materials with diverse origin. Org. Geochem. 38, 2012–2023. https://doi.org/10.1016/j.orggeochem.2007.08.007.

Goslan, E.H., Seigle, C., Purcell, D., Henderson, R., Parsons, S.A., Jefferson, B., Judd, S.J., 2017. Carbonaceous and nitrogenous disinfection by-product formation from algal organic matter. Chemosphere 170, 1–9. https://doi.org/10.1016/j.chemosphere.2016.11.148.

Gough, R., Holliman, P.J., Cooke, G.M., Freeman, C., 2015. Characterisation of algogenic organic matter during an algal bloom and its implications for trihalomethane formation. Sustain. Water Qual. Ecol. 6, 11–19. https://doi.org/10.1016/j.swaqe.2014.12.008.

Gouvêa, S.P., Vieira, A.A.H., Lombardi, A.T., 2005. Copper and cadmium complexation by high molecular weight materials of dominant microalgae and of water from a eutrophic reservoir. Chemosphere 60, 1332–1339. https://doi.org/10.1016/j.chemosphere.2005.01.061.

Haughey, M.A., Anderson, M.A., Whitney, R.D., Taylor, W.D., Losee, R.F., 2000. Forms and fate of Cu in a source drinking water reservoir following CuSO4 treatment. Water Res. 34, 3440–3452. https://doi.org/10.1016/S0043-1354(00)00054-3.

Heibati, M., Stedmon, C.A., Stenroth, K., Rauch, S., Toljander, J., Säve-Söderbergh, M., Murphy, K.R., 2017. Assessment of drinking water quality at the tap using fluorescence spectroscopy. Water Res. 125, 1–10. https://doi.org/10.1016/j.watres.2017.08.020.

Henderson, R.K., Baker, A., Parsons, S.A., Jefferson, B., 2008. Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. Water Res. 42, 3435–3445. https://doi.org/10.1016/j.watres.2007.10.032.

Hohner, A.K., Cawley, K., Oropeza, J., Summers, R.S., Rosario-Ortiz, F.L., 2016. Drinking water treatment response following a Colorado wildfire. Water Res. 105, 187–198. https://doi.org/10.1016/j.watres.2016.08.034.

Hoko, Z., Makado, P.K., 2011. Optimization of algal removal process at Morton Jaffray water works, Harare, Zimbabwe. Phys. Chem. Earth 36, 1141–1150. https://doi.org/10.1016/j.pce.2011.07.074.

Hsu-Kim, H., 2007. Stability of metal-glutathione complexes during oxidation by hydrogen peroxide and Cu(II)-catalysis. Environ. Sci. Technol. 41, 2338–2342. https://doi.org/10.1021/es062269+.

Hua, G., Reckhow, D.A., 2007. Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. Environ. Sci. Technol. 3309–3315. https://doi.org/10.1021/es062178c.

Hua, G., Reckhow, D.A., Abusallout, I., 2015. Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. Chemosphere 130, 82–89. https://doi.org/10.1016/j.chemosphere.2015.03.039.

Huang, W., Chu, H., Dong, B., 2012. Characteristics of algogenic organic matter generated under different nutrient conditions and subsequent impact on microfiltration membrane fouling. Desalination 293, 104–111. https://doi.org/10.1016/j.desal.2012.03.001.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009. Properties of fluorescent dissolved organic matter in the Gironde Estuary. Org. Geochem. 40, 706–719. https://doi.org/10.1016/j.orggeochem.2009.03.002.

Iwinski, K.J., Calomeni, A.J., Geer, T.D., Rodgers, J.H., 2016. Cellular and aqueous microcystin-LR following laboratory exposures of Microcystis aeruginosa to copper algaecides. Chemosphere 147, 74–81. https://doi.org/10.1016/j.chemosphere.2015.12.070.

Jardim, W.F., December, R., 1984. A study of the copper-complexing compounds released by some species of cyanobacteria. Water Res. 18, 985–989.

Kalbitz, K., 2001. Properties of organic matter in soil solution in a German fen area as dependent on land use and depth. Geoderma 104, 203–214. https://doi.org/10.1016/S0016-7061(01)00081-7.

Kanan, A., Karanfil, T., 2011. Formation of disinfection by-products in indoor swimming pool water: the contribution from filling water natural organic matter and swimmer body fluids. Water Res. 45, 926–932. https://doi.org/10.1016/j.watres.2010.09.031.

Kikuchi, T., Fujii, M., Terao, K., Jiwei, R., Lee, Y.P., Yoshimura, C., 2017. Correlations between aromaticity of dissolved organic matter and trace metal concentrations in natural and effluent waters: a case study in the Sagami River Basin. Jpn. Sci. Total Environ. 576, 36–45. https://doi.org/10.1016/j.scitotenv.2016.10.068.

Kilham, S.S., Kreeger, D.A., Lynn, S.G., Goulden, C.E., Herrera, L., 1998. COMBO: a defined freshwater culture medium for algae and zooplankton. Hydrobiologia 377, 147–159. https://doi.org/10.1023/A:1003231628456.

Le Jeune, A.H., Charpin, M., Deluchat, V., Briand, J.F., Lenain, J.F., Baudu, M., Amblard, C., 2006. Effect of copper sulphate treatment on natural phytoplanktonic communities. Aquat. Toxicol. 80, 267–280. https://doi.org/10.1016/j.aquatox.2006.09.004.

Li, W., Zhang, F., Ye, Q., Wu, D., Wang, L., Yu, Y., Deng, B., Du, J., 2017. Composition and copper binding properties of aquatic fulvic acids in eutrophic Taihu Lake, China. Chemosphere 172, 496–504. https://doi.org/10.1016/j.chemosphere.2017.01.008.

Liao, X., Liu, J., Yang, M., Ma, H., Yuan, B., Huang, C.-H., 2015. Evaluation of disinfection by-product formation potential (DBPFP) during chlorination of two algae species — blue-green Microcystis aeruginosa and diatom Cyclotella meneghiniana. Sci. Total Environ. 532, 540–547. https://doi.org/10.1016/j.scitotenv.2015.06.038.

Liu, R., Zhao, D., Barnett, M.O., 2006. Fate and transport of copper applied in channel catfish ponds. Water, Air, Soil Pollut. 176, 139–162. https://doi.org/10.1007/s11270-006-9155-5.

Liu, S.G., Zhu, Z.L., Tan, X.C., Feng, X.H., Huang, Z.Y., Qiu, Y.L., Zhao, J.F., 2013. The influence of Cu(II) on the formation and distribution of disinfection by-products during the chlorination of drinking water. Water, Air, Soil Pollut. 224 https://doi.org/10.1007/s11270-013-1493-5.

Liu, X., Chen, Z., Wang, L., Shen, J., 2012. Effects of metal ions on THMs and HAAs formation during tannic acid chlorination. Chem. Eng. J. 211–212, 179–185. https://doi.org/10.1016/j.cej.2012.09.014.

Lorenzo, J.I., Nieto-Cid, M., Álvarez-Salgado, X.A., Pérez, P., Beiras, R., 2007. Contrasting complexing capacity of dissolved organic matter produced during the onset, development and decay of a simulated bloom of the marine diatom Skeletonema costatum. Mar. Chem. 103, 61–75. https://doi.org/10.1016/j.marchem.2006.05.009.

Lu, Y., Allen, H.E., 2002. Characterization of copper complexation with natural dissolved organic matter (DOM) - link to acidic moieties of DOM and competition by Ca and Mg. Water Res. 36, 5083–5101. https://doi.org/10.1016/S0043-1354(02)00240-3.

Ly, Q.V., Maqbool, T., Hur, J., 2017. Unique characteristics of algal dissolved organic matter and their association with membrane fouling behavior: a review. Environ. Sci. Pollut. Res. 24, 11192–11205. https://doi.org/10.1007/s11356-017-8683-4.

Maizel, A.C., Remucal, C.K., 2017. Molecular composition and photochemical reactivity of size-fractionated dissolved organic matter. Environ. Sci. Technol. 51, 2113–2123. https://doi.org/10.1021/acs.est.6b05140.

McKnight, D.M., Chisholm, S.W., Harleman, D.R.F., 1983. CuSO4 treatment of nuisance algal blooms in drinking water reservoirs. Environ. Manag. 7, 311–320. https://doi.org/10.1007/BF01866913.

Mcknight, D.M., Morel, F.M.M., 1979. Release of weak and strong copper-complexing agents by algae. Limnol. Oceanogr. 24, 823–837. https://doi.org/10.4319/lo.1979.24.5.0823.

Minor, E.C., Swenson, M.M., Mattson, B.M., Oyler, A.R., 2014. Structural characterization of dissolved organic matter: a review of current techniques for isolation and analysis. Environ. Sci. Process. Impacts 16, 2064–2079. https://doi.org/10.1039/C4EM00062E.

Murray-Gulde, C.L., Bearr, J., Rodgers, J.H., 2005. Evaluation of a constructed wetland treatment system specifically designed to decrease bioavailable copper in a wastestream. Ecotoxicol. Environ. Saf. 61, 60–73. https://doi.org/10.1016/

j.ecoenv.2004.12.020.

Murray-Gulde, C.L., Heatley, J.E., Schwartzman, A.L., Rodgers, J.H., 2002. Algicidal effectiveness of Clearigate, Cutrine-Plus, and copper sulfate and margins of safety associated with their use. Arch. Environ. Contam. Toxicol. 43, 19–27. https://doi.org/10.1007/s00244-002-1135-1.

Myklestad, S.M., 2000. Dissolved organic carbon from phytoplankton. Mar. Chem. 5, 112–144. https://doi.org/10.1016/j.marchem.2009.01.001.

Otten, T.G., Paerl, H.W., 2015. Health effects of toxic cyanobacteria in U.S. Drinking and recreational waters: our current understanding and proposed direction. Curr. Environ. Health Reports 2, 75–84. https://doi.org/10.1007/s40572-014-0041-9.

Pereira, P., Úbeda, X., Martin, D.A., 2012. Fire severity effects on ash chemical composition and water-extractable elements. Geoderma 191, 105–114. https://doi.org/10.1016/j.geoderma.2012.02.005.

Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337, 133–149. https://doi.org/10.1016/S0003-2670(96)00412-6.

Pivokonsky, M., Safarikova, J., Baresova, M., Pivokonska, L., Kopecka, I., 2014. A comparison of the character of algal extracellular versus cellular organic matter produced by cyanobacterium, diatom and green alga. Water Res. 51, 37–46. https://doi.org/10.1016/j.watres.2013.12.022.

Qian, H., Yu, S., Sun, Z., Xie, X., Liu, W., Fu, Z., 2010. Effects of copper sulfate, hydrogen peroxide and N-phenyl-2-naphthylamine on oxidative stress and the expression of genes involved photosynthesis and microcystin disposition in Microcystis aeruginosa. Aquat. Toxicol. 99, 405–412. https://doi.org/10.1016/j.aquatox.2010.05.018.

Quill, E.S., Angove, M.J., Morton, D.W., Johnson, B.B., 2010. Characterisation of dissolved organic matter in water extracts of thermally altered plant species found in boxironbark forests. Aust. J. Soil Res. 48, 693–704. https://doi.org/10.1071/SR09157.

Revchuk, A.D., Suffet, I.H., 2014. Effect of wildfires on physicochemical changes of watershed dissolved organic matter. Water Environ. Res. 86, 372–381. https://doi.org/10.2175/106143013X13736496909671.

Ryan, D.K., Weber, J.H., 1982. Copper(II) complexing capacities of natural waters by fluorescence quenching. Environ. Sci. Technol. 16, 866–872. https://doi.org/10.1021/es00106a009.

Sharma, V.K., Yang, X., Cizmas, L., Mcdonald, T.J., Sayes, C.M., Yuan, B., Dionysiou, D.D., 2017. Impact of metal ions, metal oxides, and nanoparticles on the formation of disinfection byproducts during chlorination. Chem. Eng. J. 317, 777–792. https://doi.org/10.1016/j.cej.2017.02.071.

Smith, H.G., Sheridan, G.J., Lane, P.N.J., Nyman, P., Haydon, S., 2011. Wildfire effects on water quality in forest catchments: a review with implications for water supply. J. Hydrol. 396, 170–192. https://doi.org/10.1016/j.jhydrol.2010.10.043.

Song, L.Y., Wang, Y.Q., 2015. Investigation of microbial community structure of a shallow lake after one season copper sulfate algaecide treatment. Microbiol. Res. 170, 105–113. https://doi.org/10.1016/j.micres.2014.08.008.

Stanier, R.Y., Kunisawa, R., Mandel, M., Cohen-Bazire, G., 1971. Purification and properties of unicellular blue-green algae (order Chroococcales). Bacteriol. Rev. 35, 171–205.

Stauber, J.M., Florence, T.M., 1987. Mechanism of toxicity of ionic copper and copper complexes to algae. Mar. Biol. 94, 511–519.

Stevenson, J., Barwinska-Sendra, A., Tarrant, E., Waldron, K.J., 2013. Mechanism of action and applications of the antimicrobial properties of copper. Formatex 1, 468–479.

Tonietto, A.E., Lombardi, A.T., Henriques Vieira, A.A., Parrish, C.C., Choueri, R.B., 2014. Cylindrospermopsis raciborskii (Cyanobacteria) exudates: chemical characterization and complexation capacity for Cu, Zn, Cd and Pb. Water Res. 49, 381–390. https://doi.org/10.1016/j.watres.2013.10.025.

Tsai, K.-P., 2016. Management of target algae by using copper-based algaecides: effects of algal cell density and sensitivity to copper. Water, Air, Soil Pollut. 227, 238. https://doi.org/10.1007/s11270-016-2926-8.

Tsai, K.-P., 2015. Effects of two copper compounds on Microcystis aeruginosa cell density, membrane integrity, and microcystin release. Ecotoxicol. Environ. Saf. 120, 428–435. https://doi.org/10.1016/j.ecoenv.2015.06.024.

Tsai, K.-P., Chow, A.T., 2016. Growing algae alter spectroscopic characteristics and chlorine reactivity of dissolved organic matter from thermally-altered forest litters. Environ. Sci. Technol. 50, 7991–8000. https://doi.org/10.1021/acs.est.6b01578.

Tsai, K.P., Uzun, H., Karanfil, T., Chow, A.T., 2017. Dynamic changes of disinfection byproduct precursors following exposures of Microcystis aeruginosa to wildfire ash solutions. Environ. Sci. Technol. 51, 8272–8282. https://doi.org/10.1021/acs.est.7b01541.

Wang, J.J., Dahlgren, R.A., Chow, A.T., 2015a. Controlled burning of forest detritus altering spectroscopic characteristics and chlorine reactivity of dissolved organic matter: effects of temperature and oxygen availability. Environ. Sci. Technol. 49, 14019–14027. https://doi.org/10.1021/acs.est.5b03961.

Wang, J.J., Dahlgren, R.A., Ersan, M.S., Karanfil, T., Chow, A.T., 2015b. Wildfire altering terrestrial precursors of disinfection byproducts in forest detritus. Environ. Sci. Technol. 49, 5921–5929. https://doi.org/10.1021/es505836m.

Wei, J., Tu, C., Yuan, G., Bi, D., Wang, H., Zhang, L., Theng, B.K.G., 2018. Pyrolysis temperature-dependent changes in the characteristics of biochar-borne dissolved organic matter and its copper binding properties. Bull. Environ. Contam. Toxicol. 0, 1–6. https://doi.org/10.1007/s00128-018-2392-7.

Weishaar, J., Aiken, G., Bergamaschi, B., Fram, M., Fujii, R., Mopper, K., 2003. Evaluation of specific ultra-violet absorbance as an indicator of the chemical content of dissolved organic carbon. Environ. Sci. Technol. 37, 4702–4708. https://doi.org/10.1021/es030360x.

Wetzel, R.G., 2001. Limnology: lake and river ecosystems. J. Phycol. https://doi.org/10.1046/j.1529-8817.2001.37602.x.

Williams, M.C.W., Conroy, J.D., Miner, J.G., John, R.F., 2015. Indirect effects of copper sulfate addition on zooplankton communities in Ohio upground reservoirs. Ohio J. Sci. 115, 24–31.

Xu, H., Yan, Z., Cai, H., Yu, G., Yang, L., Jiang, H., 2013. Heterogeneity in metal binding by individual fluorescent components in a eutrophic algae-rich lake. Ecotoxicol. Environ. Saf. 98, 266–272. https://doi.org/10.1016/j.ecoenv.2013.09.008.

Yamashita, Y., Jaffé, R., 2008. Characterizing the interactions between trace metals and dissolved organic matter using excitation-emission matrix and parallel factor Analysis. Environ. Sci. Technol. 42, 7374–7379. https://doi.org/10.1021/es801357h.

Yan, M., Dryer, D., Korshin, G.V., Benedetti, M.F., 2013. In situ study of binding of copper by fulvic acid: comparison of differential absorbance data and model predictions. Water Res. 47, 588–596. https://doi.org/10.1016/j.watres.2012.10.020.

Yan, M., Ma, J., Zhang, C., Zhou, Y., Liu, F., Han, X., Li, M., Ni, J., 2017. Optical property of dissolved organic matters (DOMs) and its link to the presence of metal ions in surface freshwaters in China. Chemosphere 188, 502–509. https://doi.org/10.1016/j.chemosphere.2017.09.001.

Yang, X., Guo, W., Shen, Q., 2011. Formation of disinfection byproducts from chlor(am)ination of algal organic matter. J. Hazard Mater. 197, 378–388. https://doi.org/10.1016/j.jhazmat.2011.09.098.

Yang, X., Shang, C., 2004. Chlorination byproduct formation in the presence of humic acid, model nitrogenous organic compounds, ammonia, and bromide. Environ. Sci. Technol. 38, 4995–5001. https://doi.org/10.1021/es049580g.

Yu, Y., Reckhow, D.A., 2015. Kinetic analysis of haloacetonitrile stability in drinking waters. Environ. Sci. Technol. 49, 11028–11036. https://doi.org/10.1021/acs.est.5b02772.

Zhang, H., Andrews, S.A., 2013. Factors affecting catalysis of copper corrosion products in NDMA formation from DMA in simulated premise plumbing. Chemosphere 93, 2683–2689. https://doi.org/10.1016/j.chemosphere.2013.08.067.

Zhang, H., Andrews, S.A., 2012. Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. Water Res. 46, 2665–2673. https://doi.org/10.1016/j.watres.2012.02.028.

Zhang, M., Ma, H., Wang, H., Du, T., Liu, M., Wang, Y., Zhang, T., Li, Y., 2019. Effects of ion species on the disinfection byproduct formation in artificial and real water. Chemosphere 217, 706–714. https://doi.org/10.1016/j.chemosphere.2018.11.066.

Zhang, M., Wang, X., Tao, J., Li, S., Hao, S., Zhu, X., Hong, Y., 2018. PAHs would alter cyanobacterial blooms by affecting the microcystin production and physiological characteristics of Microcystis aeruginosa. Ecotoxicol. Environ. Saf. 157, 134–142. https://doi.org/10.1016/j.ecoenv.2018.03.052.

Zhao, Y., Yang, H., Liu, S., Tang, S., Wang, X., Xie, Y.F., 2016. Effects of metal ions on disinfection byproduct formation during chlorination of natural organic matter and surrogates. Chemosphere 144, 1074–1082. https://doi.org/10.1016/j.chemosphere.2015.09.095.

Zhou, S., Shao, Y., Gao, N., Deng, Y., Li, L., Deng, J., Tan, C., 2014. Characterization of algal organic matters of Microcystis aeruginosa: biodegradability, DBP formation and membrane fouling potential. Water Res. 52, 199–207. https://doi.org/10.1016/j.watres.2014.01.002.