

# Fluorescent Dissolved Organic Matter Components as Surrogates for Disinfection Byproduct Formation in Drinking Water: A Critical Review

Elena Fernández-Pascual,<sup>○</sup> Boris Droz,<sup>\*○</sup> Jean O'Dwyer, Connie O'Driscoll, Emma H. Goslan, Simon Harrison, and John Weatherill<sup>\*</sup>



Cite This: <https://doi.org/10.1021/acsestwater.2c00583>



Read Online

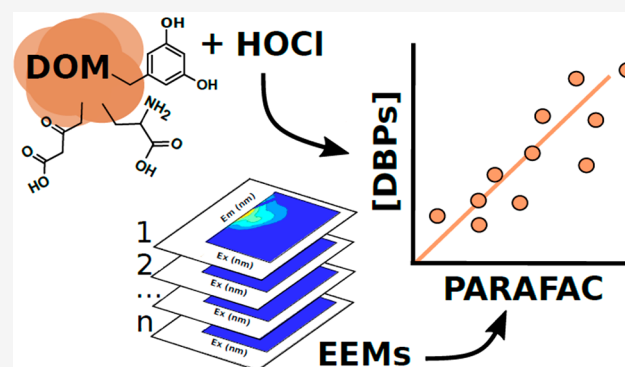
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Disinfection byproduct (DBP) formation, prediction, and minimization are critical challenges facing the drinking water treatment industry worldwide where chemical disinfection is required to inactivate pathogenic microorganisms. Fluorescence excitation–emission matrices-parallel factor analysis (EEM-PARAFAC) is used to characterize and quantify fluorescent dissolved organic matter (FDOM) components in aquatic systems and may offer considerable promise as a low-cost optical surrogate for DBP formation in treated drinking waters. However, the global utility of this approach for quantification and prediction of specific DBP classes or species has not been widely explored to date. Hence, this critical review aims to elucidate recurring empirical relationships between common environmental fluorophores (identified by PARAFAC) and DBP concentrations produced during water disinfection. From 45 selected peer-reviewed articles, 218 statistically significant linear relationships ( $R^2 \geq 0.5$ ) with one or more DBP classes or species were established. Trihalomethanes (THMs) and haloacetic acids (HAAs), as key regulated classes, were extensively investigated and exhibited strong, recurrent relationships with ubiquitous humic/fulvic-like FDOM components, highlighting their potential as surrogates for carbonaceous DBP formation. Conversely, observed relationships between nitrogenous DBP classes, such as haloacetonitriles (HANs), halonitromethanes (HNMs), and *N*-nitrosamines (NAs), and PARAFAC fluorophores were more ambiguous, but preferential relationships with protein-like components in the case of algal/microbial FDOM sources were noted. This review highlights the challenges of transposing site-specific or FDOM source-specific empirical relationships between PARAFAC component and DBP formation potential to a global model.



## INTRODUCTION

The use of chlorine and other chemical disinfection methods (such as ozonation or chloramination) for drinking water disinfection can lead to the unintentional formation of potentially harmful disinfection byproducts (DBPs), through reactions with dissolved organic matter (DOM) precursors present in the raw water source.<sup>1</sup> Consequently, nine organohalide DBPs including four trihalomethanes (THM4) and five haloacetic acids (HAAs) are regulated by drinking water authorities in the European Union (EU)<sup>2</sup> and United States (US).<sup>3</sup> However, in excess of 700 DBPs have been identified to date, the vast majority of which are unregulated with many thoughts of being potentially carcinogenic.<sup>4</sup> Moreover, a recent study estimated that 32–81% of total organic halogen (TOX) loads, produced during chemical disinfection, are attributable to as yet unidentified DBPs, highlighting the likely importance of new and emerging classes over the coming years.<sup>5</sup>

DOM in freshwaters is composed of a multitude of soluble, reduced organic carbon compounds, which may be derived from autochthonous sources, such as in situ primary production (e.g., algae and microbial biomass), and allochthonous watershed sources, such as leaf litter and soil organic matter leachates<sup>6</sup> whose hydrological export varies spatially and temporally within river basins around the world.<sup>7</sup> Humic and fulvic acids (typically originating from allochthonous terrestrial sources) comprise high molecular weight and aromaticity humic substances, which are thought to be important DOM precursors for carbonaceous DBP (C-DBP)

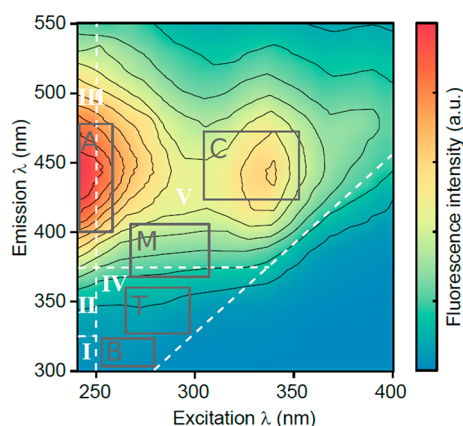
**Received:** November 16, 2022

**Revised:** May 26, 2023

**Accepted:** May 26, 2023

classes.<sup>8,9</sup> In contrast, autochthonous DOM derived from algal and microbial sources, as well as wastewater DOM, may play a role in the formation of nitrogenous DBPs (N-DBPs),<sup>10,11</sup> which are believed to be potentially more harmful to human health than C-DBPs.<sup>12</sup> A global increase in terrestrial DOM export is forecast over the coming decades as a consequence of climate and environmental change.<sup>13,14</sup> Increasing DOM concentrations in raw water sources derived from surface water will pose significant challenges for safe and sustainable production of drinking water, over the coming decades.

Modern advances in fluorescence excitation–emission matrix (EEM) spectroscopy have offered a unique perspective on fluorescent dissolved organic matter (FDOM) characterization and quantification in freshwater environments. Fluorescence spectroscopy is a low-cost, nondestructive, sensitive, and selective technique that can provide critical information on the molecular properties of complex FDOM admixtures.<sup>15</sup> The technique also offers considerable promise for quantification of intrinsic environmental fluorophores, which may be associated with DBP formation.<sup>16–22</sup> Various methods have been developed to extract qualitative and quantitative information from EEM spectra such as “peak picking”<sup>23</sup> and fluorescence regional integration (FRI) (Figure 1).<sup>24</sup> More recently, principal component analysis (PCA) or



**Figure 1.** Classical emission–excitation matrix (EEM) of riverine dissolved organic matter showing fluorescence mainly in the fulvic and humic regions (River Bunsheelin, Ireland; 4th July 2021). White dashed lines delimit the five common environmental fluorescence regions.<sup>24</sup> Gray boxes refer to local wavelength pair regions at which fluorophore maximum intensities are generally “picked”.<sup>23</sup>

parallel factor analysis (PARAFAC) have been applied to reduce the dimensionality of large EEM data sets into a small number of independent components.<sup>25,26</sup> Whereas PCA decomposes EEMs into components which are not physically meaningful, PARAFAC is capable of “unmixing” complex EEM spectra to resolve the underlying independent fluorophores present and has become the EEM decomposition and interpretation tool of choice. Machine learning (ML) approaches, such as artificial neural networks (ANNs) and self-organizing maps (SOMs) are becoming more available for applications with fluorescence spectroscopy data.<sup>27–29</sup> ML approaches complement EEM-PARAFAC outputs and offer pathways toward greater automation in classification<sup>30–32</sup> and regression analysis<sup>33</sup> of large and complex EEM data sets.

**Scope of the Critical Review.** Previous reviews of EEM-PARAFAC have included: a general overview of the

technique,<sup>26</sup> applications in drinking water and wastewater treatment plants,<sup>34,35</sup> critical evaluation of commonly used fluorescence metrics,<sup>36</sup> potential pitfalls of oversimplification of EEM interpretations,<sup>37</sup> application of SOMs for EEM data analysis,<sup>28,38</sup> new approaches for similarity metrics,<sup>39</sup> and the practical challenges for continuous, online monitoring applications.<sup>40,41</sup> However, to date, no article has critically reviewed the potential of ubiquitous environmental fluorophores as low cost optical surrogates for DBP formation potential at a global scale. Hence, the present critical review aims to identify statistically significant and recurrent empirical relationships between FDOM components (identified by PARAFAC) and DBP formation reported in the available literature. Consideration is given to the potential advantages of PARAFAC components for continuous online monitoring applications and early warning detection of DBP formation risk in drinking water, with the overarching goal of protecting consumer health.

## LITERATURE REVIEW

Out of 378 identified articles, 45 were selected for inclusion (hereafter referred to as the “selected articles”) which matched the scope and search criteria of the present study (procedure fully detailed in Supporting Information, Figure S1 and Table S1). Data from the selected articles were extracted into categories such as raw water sources, EEM acquisition procedures, FDOM components, chemical disinfection method, and DBP formation potential parameters (temperature and contact time). Relevant data fields arising from the selected articles are collated in SI, Extracted Data (TXT file).

**PARAFAC Components.** PARAFAC components identified in the selected articles were classified according to their wavelength pairs into the five environmental fluorescence regions (following the established nomenclature) and are summarized in Table 1. Statistically distinct emission values (pairwise Wilcoxon test;  $p$ -value:  $<0.01$ ) are reported between the fluorophore regions except between humic- and fulvic-like components, which can be considered as one group containing similar chemical structures with different degrees of oxidation, molecular size, and solubility at low pH.<sup>42</sup> Moreover, according to the carbon mass fraction, fulvic substances are estimated to be more abundant than humic<sup>43</sup> and exhibit higher fluorescence intensities.<sup>23</sup>

**DBP Classes.** DBP classes have been previously classified as follows:<sup>3</sup> (i) carbonaceous DBPs (C-DBPs), i.e., trihalomethanes (THMs), haloacetic acids (HAAs), halo ketones (HKs), haloacetaldehydes (HALs), halogenated furanones (X-furanones), and iodinated THMs (I-THMs), and (ii) nitrogenous DBPs (N-DBPs), i.e., halonitromethanes (HNMs), haloacetonitriles (HANs), haloacetamides (HAMs), *N*-nitrosamines (NAs), and cyanide (CNX). In total, 41 individual DBP species (4 THMs, 9 HAAs, 2 HKs, 1 HAL, 1 X-furanone, 6 I-THMs, 1 nonclassified C-DBP, 1 HNM, 4 HANs, 2 HAMs, 9 NAs, and 1 CNX) were evaluated.

The 45 selected articles were published between 2009 and 2022 (Figure 2). Significant growth in the awareness of DBPs and potential associations with EEM-PARAFAC components is noteworthy from 2017 onward (Figure 2). Selected articles focus mainly on drinking water treatment plant optimization or upgrades (47%), tracking the spatiotemporal dynamics of DOM in surface water (15%), and evaluating issues of biofilm algae (17%) or species-specific leaf leachates (9%). Additionally, some articles investigated the photoirradiation impact on

Table 1. PARAFAC Components Identified and Classified by Wavelength Pair from the Selected Articles

fluorophore region <sup>a</sup>	<i>n</i>	range (min–max) <sup>b</sup> $\lambda$ maximum (nm)		peak label <sup>a</sup>	environmental sources <sup>c</sup>
		excitation	emission		
humic-like (V)	299 (188)	250–375 (255–410)	300–520	C	Terrestrial or river source containing polyhydroxylated aromatics such as those found in lignin, as well as phenols, hydroquinones, and indoles. Generally insoluble fraction at neutral pH.
fulvic-like (III)	41 (33)	250–265 (238–360)	400–475	A	Terrestrial and marine source of aromatic species, such quinones or other oxidized aromatics. Generally smaller molecules, more polar and soluble than humic-like.
microbial humic-like (V)	55 (33)	250–346 (285–374)	300–459	M	Originally identified in marine environments associated with biodegradation of humic-like or with specific proteins or metabolic byproducts.
tyrosine-like (IV)	103 (49)	250–280 (270–285)	300–328	B	Free or bound amino acids associated with microbial activity, autochthonous source.
tryptophan-like (IV)	135 (58)	250–300 (255–300)	300–390	T	Soluble protein or byproduct associated with microbial activity, autochthonous source.

<sup>a</sup>Follows the traditional assignment and peak label made elsewhere.<sup>23,24,44,45</sup> Roman numerals delimit the common environmental fluorescence regions where components were identified (Figure 1). Secondary excitation maxima are shown in parentheses. *n* indicates the number of components described in the selected articles used to calculate the range of excitation maxima with the secondary maxima in parentheses. <sup>b</sup>Range of excitation and emission wavelengths were not considered below 240 and 300 nm, respectively, due to potentially deteriorating signal-to-noise ratios. <sup>c</sup>Potential environmental sources are described elsewhere.<sup>23,24,46–52</sup>

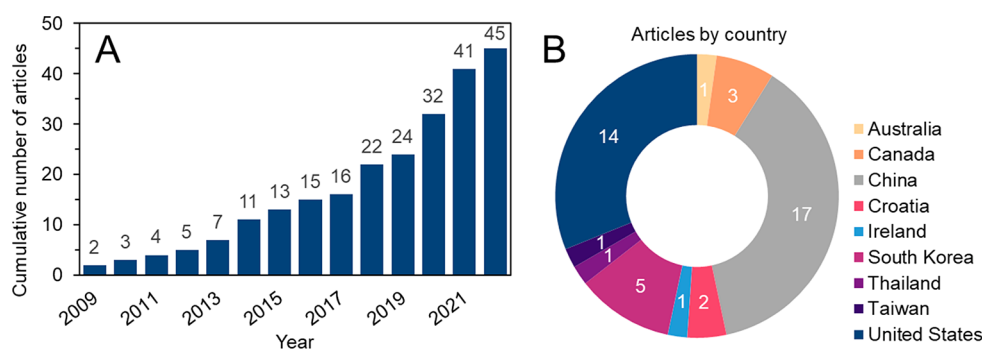


Figure 2. (A) Cumulative number of selected articles ( $n_{\text{articles}} = 45$ ) from 2009 to 2022 included in this critical review. The cumulative number is indicated above the bars. (B) Country of origin and number of selected articles published by each country.

DOM (10%) and a comparison of methods of DOM characterization (3%). A large diversity of DOM sources, e.g., surface water (71%), algal/microbial DOM (24%) and leaf leachate (10%), were investigated and are summarized in the SI. Dissolved organic carbon (DOC) concentrations reported within the selected articles ranged from 0.03 to 1,000 mg C L<sup>-1</sup>.

## EXPERIMENTAL APPROACHES

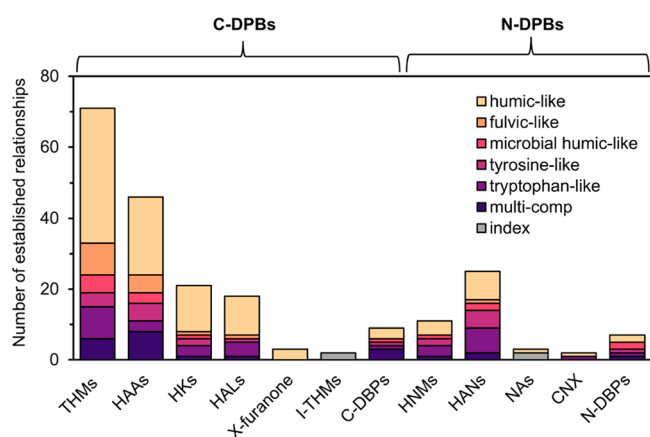
**EEM-PARAFAC Sample Preparation.** PARAFAC methodologies for EEM decomposition have been reviewed elsewhere.<sup>26,53</sup> Sample preparation methods prior to EEM acquisition included filtration, dilution, and/or pH adjustment of various aqueous matrices. EEM spectra were typically recorded for excitation and emission wavelength pairs higher than 240 and 300 nm, respectively, where shorter wavelengths are thought to be associated with deteriorating signal-to-noise ratios.<sup>37</sup> Commonly represented PARAFAC toolboxes included DOMFluor<sup>54</sup> and drEEM,<sup>26</sup> present in 62% and 17% of the selected articles, respectively, with other toolboxes also noted (detailed in SI, Extracted Data).

**Disinfection Byproduct (DBP) Formation Potential.** Two approaches were described in the selected articles to evaluate DBP formation, which are fully reported in SI, Extracted Data. The first and most common approach (employed in 84% of the selected articles) was a collection

of composite samples from the water treatment plant with EEM acquisition and DBP formation evaluated under controlled conditions (e.g., pH, temperature, disinfectant dose and contact time).<sup>55</sup> The second approach, employed in 16% of studies (such as in refs 56 and 57), involved acquisition of EEMs from the raw water source followed by postchlorination sampling for DBPs at points within the distribution network. This second approach may have some limitations as DBP yield is generally a function of residence time within water distribution networks which varies between 1 and 3 days from chlorination to the consumer tap.<sup>58</sup> All DBP formation reactions were arrested using an appropriate quenching agent with ascorbic acid being the most popular (SI, Table S2). Ascorbic acid is shown to have good compatibility with a broad spectrum of DBPs including THMs, HAAs, HKs, HALs, and HANs.<sup>59</sup>

## RECURRENT ASSOCIATIONS BETWEEN FDOM COMPONENTS AND DBP FORMATION

From the 45 selected articles, 218 empirical relationships between PARAFAC component intensities and DBP concentrations (Figure 3) were observed within the selected articles, of which 135 had strong linear relationships (e.g., Pearson correlation coefficient,  $R^2 \geq 0.7$ ; SI, Extracted Data) and 83 had moderate linear relationships (e.g.,  $R^2 \geq 0.5$ –0.7), hereafter referred to as “established relationships”. Overall, a



**Figure 3.** Number of moderate to strong established relationships ( $R^2 \geq 0.5$ ) described in the 45 selected articles as a function of DBP class and PARAFAC component ( $n_{\text{total}} = 218$ ). “Multicomp” and “index” refer to relationships derived from multiple linear regression models (MLR) or the sum of PARAFAC components and PARAFAC component indices (e.g., humic-like divided by tryptophan-like, respectively).

larger proportion of relationships between C-DBP classes (Figure 3) and humic/fulvic-like components compared to other FDOM components were found in the selected articles as follows: 74%, 67%, 71%, and 76% for THMs, HAAs, HKs, and HALs, respectively. In contrast, a similar proportion of relationships between N-DBP classes and humic/fulvic-like versus protein-like, i.e., tyrosine/tryptophan-like components, were observed. Direct comparisons between the selected articles were not always straightforward as EEM-PARAFAC and DBP formation potential methodologies were not uniform and model performance parameters rarely reported. Most established relationships were generally derived from the entire data set using the Pearson correlation coefficient ( $R^2$ ) which constituted a satisfactory metric of the variance for a single model but not a transferable metric to compare two or more models.<sup>60</sup> Error metrics, e.g., root-mean-square error, slope, and intercept, which may aid in intercomparison between models and for model performance evaluation were never discussed in the selected articles. In addition, models trained on a random subset of the data set where the remaining data are used to cross-validate the model performance were absent in the selected articles. Therefore, some caution is warranted in the transferability of the reported established relationships to predict DBP formation, where occasionally strong relationships may be coincidental<sup>61</sup> or site-specific for a single DOM source.<sup>62,63</sup>

**THM and HAA Classes.** THM and HAA classes reported in the selected articles contained 11 regulated DBPs (SI, Table S3) including four THMs (THM4, i.e., trichloro- (TCM), bromodichloro- (BDCM), dibromochloro- (DBCM), and tribromomethane (TBM), and five HAAs (HAA5, i.e., monochloro-, dichloro-, trichloro-, monobromo-, and dibromoacetic acid, with four additional unregulated HAAs, i.e., bromochloro-, bromodichloro-, dibromochloro-, and tribromoacetic acid.<sup>64,65</sup> It is noteworthy that trichloromethane was the dominant DBP, with up to 92% of THM4 and up to 47% of the TOX load,<sup>66</sup> observed from chlorination/chloramination in drinking water treatment plants when bromide concentrations were low.<sup>16,56,67–70</sup> THMs and HAAs were investigated in 88% and 51% of the selected articles (SI, Table S4), respectively,

which together accounted for 53% of the total established linear relationships with PARAFAC components (Figure 3).

Strong, recurring relationships between humic- and fulvic-like FDOM components and THM and HAA formation (e.g.,  $R^2 \geq 0.7$ ) indicate these ubiquitous environmental fluorophores may be significantly associated with THM and HAA formation globally. On the other hand, established relationships between THMs and HAAs with UV absorbance at 254 nm ( $A_{254}$ ), especially specific ultraviolet absorbance at 254 nm ( $SUVA_{254}$ ), were made in 35% of cases, for both classes.  $SUVA_{254}$  is directly proportional to the aromaticity of DOM,<sup>71</sup> which is consistent with aromatic DOM as a precursor for THM and HAA formation.<sup>8</sup> In addition, the relationship between THMs and HAAs with UV absorbance demonstrate that, although PARAFAC components are a stronger surrogate for prediction of THMs and HAAs, UV absorbance may be a technically simpler approach and should be considered depending on the purpose and extent of prediction desired.<sup>55</sup>

Humic and fulvic acid compounds form a complex mixture of aromatic and aliphatic hydrocarbon structures with functional groups including amide, carboxyl, hydroxyl, and ketone,<sup>6</sup> which were postulated within the selected articles as important precursors of THMs and HAAs,<sup>8</sup> originating in surface water from fresh plant or leaf litter leachate (Table 1). This observation is consistent with electrophilic attack on carbonyl functional groups such as aldehydes, ketones, and carboxylic acids, which is thought to be one of the major pathways in the production of THMs and HAAs.<sup>72</sup> In addition, changes in EEM spectra may indicate a change in DOM molecular structure, where a decrease in fluorescence intensity over all components during chlorination was widely observed.<sup>17,22,73,74</sup> Decreases in fluorescence intensity tend to support a hypothesis that degradation of aromatic DOM accompanied by the release of DBPs may occur simultaneously with chlorination.<sup>74,75</sup> Finally, to account for the additive and linear contribution of PARAFAC components, multiple linear regression (MLR) models or the sum of PARAFAC components showed substantial relationship improvement in comparison to individual PARAFAC component models.<sup>18,73,76–78</sup> This suggests that several DOM compounds with different fluorescence regions may be associated with precursors for THMs and HAAs.

**Brominated (Br-DBPs) and Iodinated DBPs (I-DBPs).** Br-DBPs and I-DBPs are formed when bromide ( $\text{Br}^-$ ) and iodide ( $\text{I}^-$ ) ions are present in source waters. These species react quickly with hypochlorous acid (HOCl) to form hypobromous (HOBr) or hypoiodous acid (HOI), which may further react with DOM under the same pathway as HOCl.<sup>79,80</sup> However, HOBr reacts typically up to 3 orders of magnitude quicker than HOCl and has a very high reactivity with phenol functional groups.<sup>79</sup> Therefore, the incorporation yield of  $\text{Br}^-$  into THMs is around 50% compared to 5–10% for  $\text{Cl}^-$ .<sup>81</sup> From Table 2, it can be seen that there are a large number of moderate to strong relationships between humic- and fulvic-like fluorophores and Br-DBP formation. Interestingly, the observed ratio between the variation of bromide and PARAFAC components ( $\Delta\text{Br}/\Delta\text{C}_{\text{PARAFAC}}$ ) before and after chlorination exhibit a strong relationship with Br-DBP formation potential, e.g., Br-THMs, Br-HAAs, and Br-HANs. Conversely, weak relationships have been observed with an individual PARAFAC component model in the same study.<sup>82</sup> Similar to Br-DBP formation, PARAFAC component indices (Table 2) derive a stronger linear relationship with I-DBP

**Table 2. Established Relationships between DBP Species and PARAFAC Components per Disinfection Method and DBP Class<sup>a</sup>**

DBP formation potential <sup>b</sup>	PARAFAC component(s) <sup>c</sup>	correlation coefficients ( $R^2$ ) <sup>d</sup>	ref
	Chlorine – Trihalomethanes (THMs)		
trichloromethane (TCM)	hum/ful/m-hum/ tyr/tryp/multi	$\geq 0.71^{**}(5)$ , $\geq 0.52^{**}(3)$ / $\geq 0.70^{**}(2)$ / $0.70^*$ , $\geq 0.61^*(2)$ / $0.61^*/0.82^*$ , $0.57^{**}/\geq 0.77^*(2)$	16, 18, 68, 69, 73, 84, 85
dibromochloromethane (DBCM)	tyr/tryp	$0.54^{**}/0.50^{**}$	86
TCM, bromodichloromethane (BDCM), DBCM	hum/ful	$0.96^*/0.92^*$	87
TCM, BDCM, DBCM, tribromomethane	hum/ful/m-hum/ tyr/tryp/multi	$\geq 0.71^{**}(15)$ , $\geq 0.52^*(9)$ / $\geq 0.70^*(4)$ / $0.82^*$ , $0.66^*/$ $0.95$ , $0.67^{**}/0.84^{**}$ , $\geq 0.52(5)$ / $0.95$ , $0.69^{**}$	51, 63, 67, 69, 84, 88 –95
	Chlorine Dioxide – THMs		
TCM	hum	$\geq 0.92(4)$	96
	Ozone – THMs		
TCM	multi	$0.91^{**}$	97
BDCM	multi	$0.90^{**}$	97
	Chlorine – Haloacetic Acids (HAAs)		
dichloroacetic acid (DCAA)	hum/ful/multi	$0.58^{**}/\geq 0.53^{**}(2)$ / $0.61^{**}$	18, 98
trichloroacetic acid (TCAA)	hum/ful/multi	$0.73^{**}$ , $0.52^{**}/0.68^{**}(2)$ / $0.70^{**}$	18, 98
monochloroacetic acid (MCAA), DCAA, TCAA	hum/m-hum/ tyr/tryp/multi	$\geq 0.73^*(4)$ , $\geq 0.51(2)$ / $0.64^*/0.71^*/0.87^*/0.91^*$	73, 93
DCAA, TCAA, bromochloroacetic acid (BCAA)	hum/ful	$0.93^*/0.89^*$	87
DCAA, TCAA, dibromoacetic acid (DBAA)	hum/multi	$0.72^{**}$ , $0.67^{**}/\geq 0.69^{**}(2)$	78
MCAA, DCAA, TCAA, monobromoacetic acid (MBAA), DBAA	hum/tyr/tryp/ multi	$\geq 0.81^{**}(4)$ , $\geq 0.55(2)$ / $\geq 0.82(2)$ / $0.74/\geq 0.83(2)$	17, 76, 88, 92, 94
MCAA, DCAA, TCAA, BCAA, MBAA, DBAA	hum/m-hum/ tryp	$\geq 0.71^{**}(2)$ , $0.65^*/\geq 0.56^*(2)$ / $0.54^*$	91, 99
MCAA, DCAA, TCAA, MBAA, DBAA, tribromoacetic acid, BCAA, bromodichloroacetic acid, dibromochloroacetic acid	hum	0.71	92
	Ozone – HAAs		
DCAA	multi	$0.90^{**}$	97
	UV + Chlorine – HAAs		
DCAA	tyr	$0.57^{**}$	100
TCAA	tyr	$0.64^{**}$	100
	Chlorine – Haloketones (HKs)		
1,1-dichloro-2-propanone (DCP)	hum/tyr/tryp	$\geq 0.86^{**}(2)$ , $\geq 0.52^{**}/0.54^{**}/0.60^{**}$	101, 102
1,1,1-trichloro-2-propanone (TCP)	hum/ful/tryp	$\geq 0.71^*(5)$ , $\geq 0.56(3)$ / $0.81^*/0.72^{**}$	87, 93, 102
DCP, TCP	hum/m-hum/ tyr/tryp/multi	$\geq 0.72^*(2)$ / $0.71^*/0.71^*/0.76^*/0.86^*$	63, 73
	Chlorine – Haloacetaldehydes (HALs)		
2,2,2-trichloroethane-1,1-diol (chloral hydrate)	hum/ful/tyr/ multi	$\geq 0.72^*(6)$ , $\geq 0.50^{**}(2)$ / $0.52^{**}/0.77^{**}/0.78^{**}$	51, 93, 94, 98
	UV + Chlorine – HALs		
chloral hydrate	hum/tryp	$\geq 0.96(4)$ / $\geq 0.95(4)$	22
	Chlorine – Halogenated Furanones (X-Furanones)		
4-chloro-3-dichloromethyl-2H-furan-5-one	hum	$\geq 0.70^*(3)$	103
	Monochloramine – Iodinated DBPs (I-DBPs)		
dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane, triiodomethane	index	$\geq 0.96(2)$	62
	Chlorine – Carbonaceous Disinfection Byproducts (C-DBPs)		
monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, TCM, DCP, TCP	hum/m-hum/ tyr/tryp/multi	$0.78^*/0.70^{**}/0.72^*/0.88^*/0.92^*$	73
TCM, BDCM, DBCM, TBM, dichloroacetic acid, trichloroacetic acid, dibromoacetic acid	hum/multi	$\geq 0.62^{**}(2)$ / $\geq 0.62^{**}(2)$	78
	Chlorine – Halonitromethanes (HNMs)		
trichloronitromethane (chloropicrin)	hum/m-hum/ tyr/tryp/multi	$\geq 0.73^*(4)$ / $0.75^*/\geq 0.71^*(2)$ / $\geq 0.80^*(2)$ , $0.65^{**}/$ $0.85^*$	51, 63, 73, 99
	Chlorine – Haloacetonitriles (HANs)		
bromochloroacetonitrile	hum/m-hum/ tyr/tryp	$0.76^{**}/0.79^{**}/0.59^{**}/0.57^{**}$	86
dichloroacetonitrile	hum/tyr/tryp	$\geq 0.83^*(3)$ , $0.60/0.52^{**}/0.66^{**}$	93, 102
dichloroacetonitrile, bromochloroacetonitrile	hum/ful	$0.90^*/0.85^*$	87
dichloroacetonitrile, trichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile	hum/tyr/tryp/ multi	$0.55/\geq 0.6(2)$ / $\geq 0.85^{**}(3)$ , $0.64/0.73^{**}$	51, 63, 89, 94

Table 2. continued

DBP formation potential <sup>b</sup>	PARAFAC component(s) <sup>c</sup>	correlation coefficients ( $R^2$ ) <sup>d</sup>	ref
dichloroacetonitrile, trichloroacetonitrile	Chlorine – Haloacetonitriles (HANs)		
	hum/m-hum/ tyr/tryp/multi	0.56*/0.64*/0.64*/0.78*/0.80*	73
<i>N</i> -nitrosodiphenylamine (NDPhA) <i>N</i> -nitrosomorpholine	Monochloramine – <i>N</i> -Nitrosamines (NAs)		
	hum/index index	0.6/0.6 0.55	104 104
cyanogen chloride	UV + Monochloramine – Cyanide (CNX)		
	hum/tryp	0.91/0.79	22
dichloroacetonitrile, bromochloroacetonitrile trichloronitromethane, trichloroacetonitrile, dichloroacetonitrile	Chlorine – Nitrogenous Disinfection Byproducts (N-DBPs)		
	hum/m-hum/ tyr/tryp/multi	0.50**/0.62** 0.77*/0.80*/0.78*/0.86*/0.94*	86 73

<sup>a</sup>This table is a summary of data extracted from the 45 selected articles (complete data fields are provided in SI, Extracted Data as a TXT file). Established (linear) relationships for similar DBP species and disinfection methods are separated by a forward slash. <sup>b</sup>Reported DBP and chemical disinfection method employed. <sup>c</sup>Identified PARAFAC components classified by excitation–emission wavelength pairs into common environmental fluorescence regions (reported in Table 1), where hum, ful, m-hum, tyr, and tryp refer to humic, fulvic, microbial-humic, tyrosine, and tryptophan-like fluorophores, respectively. In addition, “multi” and “index” refer to relationships derived using multiple linear regression models or sum of PARAFAC components and component indices, e.g., humic-like divide by tryptophan-like, respectively. <sup>d</sup>Strong linear relationships ( $R^2 \geq 0.7$ ) and moderate linear relationships ( $R^2 \geq 0.5$ – $0.7$ ) between similar DBPs species and PARAFAC components are differentiated by a comma. Number of established relationships are expressed in parentheses; \* and \*\* indicate  $p$ -values of  $\leq 0.05$  and  $\leq 0.01$ , respectively. In the case of several significant relationships, only the highest  $p$ -value is reported.

formation compared to individual PARAFAC components.<sup>62</sup> This observation may be consistent to some extent with the variation of the reactivity between HOI and the nature and location of aromatic substituents on the phenolic moieties.<sup>83</sup>

**Other C-DBPs.** Other C-DBPs such as HKs and HALs were investigated in 33% and 20% of the selected articles, respectively (SI, Table S4). Like THMs and HAAs, they exhibited many moderate and strong relationships with humic/fulvic-like components (Figure 3). PARAFAC components were particularly suitable as a surrogate for these DBPs as 75% and 63% of the investigated relationships exhibited moderate or strong relationships (Table 2) for HKs and HALs, respectively. Overall, these other C-DBP classes share similar relationships to THMs and HAAs with humic/fulvic-like fluorophores described above.

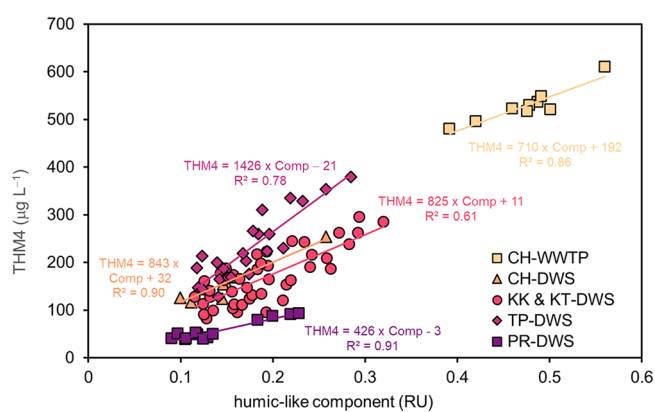
**N-DBP Classes.** N-DBP classes were not as well investigated in the 45 selected articles as C-DBPs. N-DBP classes were represented by HNMs, HANs, NAs, and CNX in 29%, 50%, 5%, and 2% of the selected articles (Figure 3), respectively. Despite the low number of articles for N-DBP classes, noteworthy observations could still be ascertained. Overall, the total number of established relationships with humic/fulvic-like PARAFAC components versus protein-like fluorophores were almost identical across the N-DBP classes (Figure 3 and Table 2). In addition, none of the selected articles reported the PARAFAC component associated with wastewater or nutrient-enriched waters identified in a previous study ( $\lambda_{\text{ex}}/\lambda_{\text{em}}$ : 350/428 nm).<sup>105</sup> This observation is surprising because humic/fulvic DOM generally has a low organic nitrogen mass ratio (e.g.,  $<5\%$  N/C), compared to wastewaters or algal-derived DOM, which can have up to 20% N/C.<sup>106</sup> In addition, protein-like components which contain a high amino acid and *N*-organic compound content<sup>52</sup> may both serve preferentially as N-DBP formation precursors.<sup>10</sup> In the context of identified algal/microbial DOM sources, 72% of the successfully established relationships for chlorination were between protein-like components and HNM and HAN formation potential,<sup>73,89,107,108</sup> which is in agreement with the N-DBP formation precursors described above. In contrast,

other DOM sources, e.g., leaf leachate and natural soil/water organic matter, showed no preferential relationship with humic/fulvic-like or protein-like components and the formation of N-DBPs. These observations support the conclusion that proteinaceous DOM is not necessarily the main precursor of N-DBPs and that their formation pathways may not always involve a similar amine precursor.<sup>10,11</sup> Some N-DBP formation pathways may involve inorganic nitrogen species (e.g.,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  or  $\text{NO}_3^-$ ) or chloramine as a nitrogen source which reacts with humic/fulvic-like DOM to produce N-DBPs,<sup>10</sup> but this cannot be concluded from PARAFAC modeling alone.

## DISCUSSION AND RESEARCH OUTLOOK

**Environmental Implications.** Relationships between THMs and  $\text{SUVA}_{254}$  are well established (see section on THM and HAA classes).<sup>16,68,73,77</sup> From the findings of this review, a majority of the strong, recurring empirical relationships were observed between carbonaceous DBPs and humic/fulvic-like fluorophores (Figure 4) across the selected articles (Table 2) (SI, Extracted Data). Given that EEM-PARAFAC components represent the small number of independent underlying fluorophores present in raw water FDOM admixtures, they offer a much more selective surrogate for quantitative prediction of DBP formation potential in comparison to classical optical parameters such as UV absorbance or fluorescence peak picking.<sup>16,17,51,73,85,89,96</sup> However, some articles were noted where PARAFAC components improve only marginally ( $\Delta R^2 \leq 0.1$ ) the prediction of DBP formation potential.<sup>21,68,77,90</sup> Furthermore, linear models developed with one specific DOM source and/or location with an associated fluorophore intensity are not necessarily transposable to other environments (Figure 4).<sup>62,63</sup>

One possible explanation is that DOM originating from different sources may exhibit contrasting chemical composition but yield similar fluorescence intensities.<sup>111</sup> Additional analytical methods, such as high resolution-mass spectroscopy (HR-MS),<sup>112</sup> size-exclusion chromatography,<sup>113</sup> and size fractionation,<sup>16</sup> may help to better constrain the molecular basis of FDOM components across different environmental



**Figure 4.** Composite of observed relationships between humic-like PARAFAC components (Comp) and total trihalomethane (THM4) formation in a subset of the selected studies. Samples originated from several drinking water sources (DWS) and a wastewater treatment plant (WWTP). The similarity of slopes across all five independent study regions and DOM sources is noteworthy. CH refers to Chapel Hill, North Carolina, US.<sup>63</sup> KK, KT, and TP refer to Kotha, Tapra, and Khon Kaen University in Khon Kaen, Thailand, respectively.<sup>84</sup> PR refers to Pyeongchang river in Korea.<sup>99</sup> Data published in quinine sulfate units (QSUs) were transformed into Raman units (RUs) using the relationship of Lawaetz et al.<sup>109</sup> It should be noted that there is some uncertainty with the RU value positioning along the *x*-axis as instrument-specific conversion factors were not available.<sup>110</sup>

sources. For example, HR-MS undertaken on environmental DOM samples has demonstrated that PARAFAC components can describe up to 59% of nontarget DOM species,<sup>114</sup> which highlights the unique capabilities of EEM-PARAFAC as a low-cost tool in DOM characterization. ML algorithms (such as ANNs) already in use for fluorescence data<sup>33,115</sup> may help to improve the success of DBP formation prediction using PARAFAC components. ML approaches offer distinct advantages by taking into account nonlinear relationships, interaction between variables, and diverse variable types, e.g., continuous and discrete, and do not rely on predetermined physical-based rules or assumptions on a given data set.<sup>60</sup> However, the successful deployment of ML relies on having sufficient contrasting data to train and properly validate an algorithm capable of recognizing subtle differences in FDOM composition.<sup>116</sup> This finding highlights a clear need for community sharing of raw EEM spectra globally to be able to perform unified analysis under the same workflow, in a similar manner to the online repository “OpenFluor” for PARAFAC models.<sup>117</sup> Within the 45 selected articles, no raw EEM spectra were shared. While it is not generally practical to include such large data volumes in publication supporting information, online repositories such as acs.figshare<sup>118</sup> and Zenodo<sup>119</sup> are readily available which embrace FAIR principles of data sharing<sup>120</sup> and are advocated further.

**Implications for Continuous Online Monitoring.** Two approaches for continuous online monitoring applications have recently been explored: (i) selection of specific excitation–emission wavelength pairs from PARAFAC analysis and monitoring of intensities to predict online DBP formation with relatively inexpensive in situ UV light-emitting diodes (LED) fluorescence sensors;<sup>93,121,122</sup> (ii) acquisition of full EEM spectra using a laboratory fluorometer connected to the source water via an in situ fiber-optic sensor in combination with SOMs.<sup>123</sup> New, faster PARAFAC algorithms now available<sup>124,125</sup> will allow continuous online data processing

where EEMs can be acquired at near-real time frequencies. Currently, method (i) is the most cost-effective method where UV-LEDs offer a narrow spectral bandwidth centered on a specific wavelength pair and are commercially available for humic-like ( $\lambda_{\text{ex}}/\lambda_{\text{em}}$ : 320–370 ± 15/450–490 ± 30 nm) and tryptophan-like ( $\lambda_{\text{ex}}/\lambda_{\text{em}}$ : 270–285 ± 30/340–350 ± 30 nm) regions. An exhaustive list of current commercially available sensors and overview of key practical aspects in the use of UV-LEDs have been reviewed elsewhere.<sup>41,126</sup> Custom made UV-LED systems have also been explored by some authors,<sup>121,127</sup> and the field is expected to grow with the rapid development of new UV-LEDs becoming available on the market.<sup>128</sup> In addition, there are several practical challenges reviewed by Henderson<sup>40</sup> for continuous online fluorescence applications in surface water. For example, some distortion of the fluorescence signal will be observed under high suspended sediment loads or rapid changes in temperature, which may require additional in situ instrumentation, postprocessing, and validation with a laboratory fluorometer for continuous monitoring applications.<sup>129,130</sup>

## CONCLUSIONS

To the best of our knowledge, the present study represents the first critical review to collate and extract recurring associations between observed PARAFAC components and the formation of specific DBP classes during chemical disinfection. From the 45 selected articles, we found 218 statistically significant linear relationships between the formation of 10 DBP classes and observed PARAFAC components; of these, 135 were strong ( $R^2 \geq 0.7$ ). From the findings of this review, humic- and fulvic-like fluorophores, typically originating from allochthonous watershed sources demonstrate considerable potential as low-cost fluorescence surrogates ( $R^2 \geq 0.7$ ) for the formation of multiple C-DBP classes including THMs, HAAs, HALs, and HKs. In contrast, the formation of potentially more harmful N-DBP classes exhibited strong linear relationships across all fluorophore regions. However, where algal or microbial autochthonous DOM sources were present, protein-like fluorophores (e.g., tryptophan-like) alone show strong relationships with N-DBP formation. Here, assigning specific components as surrogates for N-DBP formation is more challenging and source-specific than humic- and fulvic-like fluorophores for C-DBPs. Relationships derived from multiple linear regression or sums of PARAFAC components tended to show stronger predictive capability compared to an individual component model. Predicting DBP formation from FDOM components during drinking water treatment presents new opportunities for continuous online monitoring applications where treatment process operation and optimization are informed by source water FDOM composition with a view toward minimizing harmful concentrations of DBPs in consumer tap water.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.2c00583>.

Further information on the literature review (article selection criteria, classification of PARAFAC components, scope of selected articles) (PDF)

Extracted data from the 45 selected articles used in this review (TXT file format with a header directly readable)

in an R environment); metadata file (PDF) explaining the extracted data fields and coding (ZIP)

## AUTHOR INFORMATION

### Corresponding Authors

**John Weatherill** – School of Biological, Earth and Environmental Sciences, University College Cork, Cork T23 TK30, Ireland; Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland; iCRAG Science Foundation Ireland Research Centre in Applied Geosciences, University College Dublin, Dublin D04 V1W8, Ireland; [orcid.org/0000-0001-9803-8397](https://orcid.org/0000-0001-9803-8397); Phone: +353 21 490 4578; Email: [john.weatherill@ucc.ie](mailto:john.weatherill@ucc.ie)

**Boris Droz** – School of Biological, Earth and Environmental Sciences, University College Cork, Cork T23 TK30, Ireland; Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland; [orcid.org/0000-0002-3942-704X](https://orcid.org/0000-0002-3942-704X); Phone: +353 21 490 3000; Email: [bodroz@bluewin.ch](mailto:bodroz@bluewin.ch)

### Authors

**Elena Fernández-Pascual** – School of Biological, Earth and Environmental Sciences, University College Cork, Cork T23 TK30, Ireland; Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland

**Jean O'Dwyer** – School of Biological, Earth and Environmental Sciences, University College Cork, Cork T23 TK30, Ireland; Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland; iCRAG Science Foundation Ireland Research Centre in Applied Geosciences, University College Dublin, Dublin D04 V1W8, Ireland

**Connie O'Driscoll** – Ryan Hanley Ltd., Castlebar F23 E400, Ireland

**Emma H. Goslan** – Cranfield Water Science Institute, Cranfield University, Cranfield MK43 0AL, United Kingdom

**Simon Harrison** – School of Biological, Earth and Environmental Sciences, University College Cork, Cork T23 TK30, Ireland; Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsestwater.2c00583>

### Author Contributions

○E.F.-P. and B.D. contributed equally to the publication.

### Author Contributions

The manuscript was written with the contributions of all authors. CRediT authorship contribution statement: E.F.-P.: Conceptualization, Data curation, Formal Analysis, Writing—original draft. B.D.: Data curation, Conceptualization, Methodology, Writing—original draft. J.W.: Conceptualization, Funding acquisition, Methodology, Supervision, Writing—original draft. J.O.D.: Conceptualization, Formal Analysis. C.O.D., E.H.G., and S.H.: Writing—review and editing. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was carried out as part of the Proactive Optical Monitoring of Catchment Dissolved Organic Matter for Drinking Water Source Protection (PRODOM) project which is entirely funded by the Irish Environmental Protection

Agency (Grant No. 2019-W-MS43) as part of the EPA Research Program 2021-2030. Finally, the authors thank the anonymous reviewer for their helpful and constructive comments.

## REFERENCES

- (1) Sedlak, D. L.; von Gunten, U. The Chlorine dilemma. *Science* **2011**, *331* (6013), 42–43.
- (2) The European Parliament and the Council, Directive (EU) 2020/2184: The quality of water intended for human consumption (recast). *OJEU* **2020**, *63*, (L 435), pp 1–62.
- (3) Environmental Protection Agency (EPA). National primary drinking water regulations: Stage 2 disinfectants and disinfection byproducts rules. *Federal Register*; 71 FR 387; 2006; pp 387–493.
- (4) Richardson, S. D.; Kimura, S. Y. Water analysis: Emerging contaminants and current issues. *Anal. Chem.* **2020**, *92* (1), 473–505.
- (5) Allen, J. M.; Plewa, M. J.; Wagner, E. D.; Wei, X.; Bokenkamp, K.; Hur, K.; Jia, A.; Liberatore, H. K.; Lee, C. T.; Shirkhani, R.; Krasner, S. W.; Richardson, S. D. Feel the burn: Disinfection byproduct formation and cytotoxicity during chlorine burn events. *Environ. Sci. Technol.* **2022**, *56* (12), 8245–8254.
- (6) Leenheer, J. A.; Croué, J.-P. Characterizing aquatic dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37* (1), 18A–26A.
- (7) Battin, T. J.; Kaplan, L. A.; Findlay, S.; Hopkinson, C. S.; Marti, E.; Packman, A. I.; Newbold, J. D.; Sabater, F. Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* **2008**, *1* (2), 95–100.
- (8) Bond, T.; Goslan, E. H.; Parsons, S. A.; Jefferson, B. A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environ. Technol. Rev.* **2012**, *1* (1), 93–113.
- (9) Bond, T.; Henriot, O.; Goslan, E. H.; Parsons, S. A.; Jefferson, B. Disinfection byproduct formation and fractionation behavior of natural organic matter surrogates. *Environ. Sci. Technol.* **2009**, *43* (15), 5982–5989.
- (10) Shah, A. D.; Mitch, W. A. Halonitroalkanes, halonitriles, haloamides, and N-nitrosamines: A critical review of nitrogenous disinfection byproduct formation pathways. *Environ. Sci. Technol.* **2012**, *46* (1), 119–131.
- (11) Bond, T.; Templeton, M. R.; Graham, N. Precursors of nitrogenous disinfection by-products in drinking water—A critical review and analysis. *J. Hazard. Mater.* **2012**, *235–236*, 1–16.
- (12) Allen, J. M.; Plewa, M. J.; Wagner, E. D.; Wei, X.; Bokenkamp, K.; Hur, K.; Jia, A.; Liberatore, H. K.; Lee, C.-F. T.; Shirkhani, R.; Krasner, S. W.; Richardson, S. D. Drivers of disinfection byproduct cytotoxicity in U.S. drinking water: Should other DBPs be considered for regulation? *Environ. Sci. Technol.* **2022**, *56* (1), 392–402.
- (13) McDonough, L. K.; Santos, I. R.; Andersen, M. S.; O'Carroll, D. M.; Rutledge, H.; Meredith, K.; Oudone, P.; Bridgeman, J.; Goody, D. C.; Sorensen, J. P. R.; Lapworth, D. J.; MacDonald, A. M.; Ward, J.; Baker, A. Changes in global groundwater organic carbon driven by climate change and urbanization. *Nat. Commun.* **2020**, *11* (1), 1279.
- (14) Ritson, J. P.; Graham, N. J.; Templeton, M. R.; Clark, J. M.; Gough, R.; Freeman, C. The impact of climate change on the treatability of dissolved organic matter (DOM) in upland water supplies: a UK perspective. *Sci. Total Environ.* **2014**, *473–474*, 714–730.
- (15) Lakowicz, J. R. *Principles of fluorescence spectroscopy*, 3rd ed.; Springer: New York, 2006.
- (16) Pifer, A. D.; Fahey, J. L. Improving on SUVA<sub>254</sub> using fluorescence-PARAFAC analysis and asymmetric flow-field flow fractionation for assessing disinfection byproduct formation and control. *Water Res.* **2012**, *46* (9), 2927–2936.
- (17) Beggs, K. M.; Summers, R. S. Character and chlorine reactivity of dissolved organic matter from a mountain pine beetle impacted watershed. *Environ. Sci. Technol.* **2011**, *45* (13), 5717–5724.
- (18) Johnstone, D.; Sanchez, N.; Miller, C. Parallel factor analysis of excitation–emission matrices to assess drinking water disinfection



- byproduct formation during a peak formation period. *Environ. Eng. Sci.* **2009**, *26*, 1551–1559.
- (19) Hao, R.; Ren, H.; Li, J.; Ma, Z.; Wan, H.; Zheng, X.; Cheng, S. Use of three-dimensional excitation and emission matrix fluorescence spectroscopy for predicting the disinfection by-product formation potential of reclaimed water. *Water Res.* **2012**, *46* (17), 5765–5776.
- (20) Jutaporn, P.; Laolertworakul, W.; Armstrong, M. D.; Coronell, O. Fluorescence spectroscopy for assessing trihalomethane precursors removal by MIEX resin. *Water Sci. Technol.* **2019**, *79* (5), 820–832.
- (21) Hua, B.; Veum, K.; Yang, J.; Jones, J.; Deng, B. Parallel factor analysis of fluorescence EEM spectra to identify THM precursors in lake waters. *Environ. Monit. Assess.* **2010**, *161* (1–4), 71–81.
- (22) Lyon, B. A.; Cory, R. M.; Weinberg, H. S. Changes in dissolved organic matter fluorescence and disinfection byproduct formation from UV and subsequent chlorination/chloramination. *J. Hazard. Mater.* **2014**, *264*, 411–419.
- (23) Coble, P. G. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Mar. Chem.* **1996**, *51* (4), 325–346.
- (24) Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K. Fluorescence excitation–emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37* (24), 5701–5710.
- (25) Bro, R. PARAFAC. Tutorial and applications. *Chemometrics Intellig. Lab. Syst.* **1997**, *38* (2), 149–171.
- (26) Murphy, K. R.; Stedmon, C. A.; Graeber, D.; Bro, R. Fluorescence spectroscopy and multi-way techniques. *PARAFAC. Anal. Methods* **2013**, *5* (23), 6557–6566.
- (27) Bieroza, M.; Baker, A.; Bridgeman, J. Classification and calibration of organic matter fluorescence data with multiway analysis methods and artificial neural networks: an operational tool for improved drinking water treatment. *Environmetrics* **2011**, *22* (3), 256–270.
- (28) Cuss, C. W.; Guéguen, C. Analysis of dissolved organic matter fluorescence using self-organizing maps: mini-review and tutorial. *Anal. Methods* **2016**, *8* (4), 716–725.
- (29) Li, L.; Wang, Y.; Zhang, W.; Yu, S.; Wang, X.; Gao, N. New advances in fluorescence excitation–emission matrix spectroscopy for the characterization of dissolved organic matter in drinking water treatment: A review. *Chem. Eng. J.* **2020**, *381*, 122676.
- (30) Harjung, A.; Schweichhart, J.; Rasch, G.; Griebler, C. Large-scale study on groundwater dissolved organic matter reveals a strong heterogeneity and a complex microbial footprint. *Sci. Total Environ.* **2023**, *854*, 158542.
- (31) Xu, R.-Z.; Cao, J.-S.; Feng, G.; Luo, J.-Y.; Feng, Q.; Ni, B.-J.; Fang, F. Fast identification of fluorescent components in three-dimensional excitation–emission matrix fluorescence spectra via deep learning. *Chem. Eng. J.* **2022**, *430*, 132893.
- (32) Cuss, C. W.; Donner, M. W.; Noernberg, T.; Pelletier, R.; Shoty, W. EEM-PARAFAC-SOM for assessing variation in the quality of dissolved organic matter: simultaneous detection of differences by source and season. *Environ. Chem.* **2019**, *16* (5), 360.
- (33) Peleato, N. M. Application of convolutional neural networks for prediction of disinfection by-products. *Sci. Rep.* **2022**, *12* (1), 612.
- (34) Sciscenko, I.; Arques, A.; Micó, P.; Mora, M.; García-Ballesteros, S. Emerging applications of EEM-PARAFAC for water treatment: A concise review. *Chem. Eng. J. Adv.* **2022**, *10*, 100286.
- (35) Yang, L.; Hur, J.; Zhuang, W. Occurrence and behaviors of fluorescence EEM-PARAFAC components in drinking water and wastewater treatment systems and their applications: A review. *Environ. Sci. Pollut. Res. Int.* **2015**, *22* (9), 6500–6510.
- (36) Korak, J. A.; Dotson, A. D.; Summers, R. S.; Rosario-Ortiz, F. L. Critical analysis of commonly used fluorescence metrics to characterize dissolved organic matter. *Water Res.* **2014**, *49*, 327–338.
- (37) Rosario-Ortiz, F. L.; Korak, J. A. Oversimplification of dissolved organic matter fluorescence analysis: Potential pitfalls of current methods. *Environ. Sci. Technol.* **2017**, *51* (2), 759–761.
- (38) Bieroza, M.; Baker, A.; Bridgeman, J. Exploratory analysis of excitation–emission matrix fluorescence spectra with self-organizing maps—A tutorial. *Educ. Chem. Eng.* **2012**, *7* (1), e22–e31.
- (39) Wünsch, U. J.; Bro, R.; Stedmon, C. A.; Wenig, P.; Murphy, K. R. Emerging patterns in the global distribution of dissolved organic matter fluorescence. *Anal. Methods* **2019**, *11* (7), 888–893.
- (40) Henderson, R. K.; Baker, A.; Murphy, K. R.; Hambly, A.; Stuetz, R. M.; Khan, S. J. Fluorescence as a potential monitoring tool for recycled water systems: A review. *Water Res.* **2009**, *43* (4), 863–881.
- (41) Carstea, E. M.; Popa, C. L.; Baker, A.; Bridgeman, J. In situ fluorescence measurements of dissolved organic matter: A review. *Sci. Total Environ.* **2020**, *699*, 134361.
- (42) Leenheer, J. A. Systematic approaches to comprehensive analyses of natural organic matter. *Ann. Environ. Sci.* **2009**, *3*, 1–130.
- (43) Perdue, E. M.; Ritchie, J. D. Dissolved organic matter in freshwaters. In *Treatise on Geochemistry*; Holland, H. D., Turekian, K. K., Eds.; Elsevier: 2009; p 1–46.
- (44) Coble, P. G. Marine optical biogeochemistry: The chemistry of ocean color. *Chem. Rev.* **2007**, *107* (2), 402–418.
- (45) Stedmon, C. A.; Markager, S.; Bro, R. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **2003**, *82* (3–4), 239–254.
- (46) Del Vecchio, R.; Blough, N. V. On the origin of the optical properties of humic substances. *Environ. Sci. Technol.* **2004**, *38* (14), 3885–3891.
- (47) Gabor, R. S.; McKnight, D. M.; Miller, M. P.; Coble, P.; Lead, J.; Baker, A.; Reynolds, D. M.; Spencer, R. G. M. Fluorescence indices and their interpretation. In *Aquatic Organic Matter Fluorescence*; Cambridge University Press: Cambridge, 2014; pp 303–338.
- (48) Coble, P. G.; Green, S. A.; Blough, N. V.; Gagosian, R. B. Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. *Nature* **1990**, *348* (6300), 432–435.
- (49) Coble, P.; Lead, J.; Baker, A.; Reynolds, D. M.; Spencer, R. G. M. Aquatic organic matter fluorescence. In *Aquatic Organic Matter Fluorescence*; Coble, P., Lead, J., Baker, A., Reynolds, D., Spencer, R., Eds.; Cambridge University Press: Cambridge, 2014; pp 75–122.
- (50) Fox, B. G.; Thorn, R. M. S.; Anesio, A. M.; Reynolds, D. M. The in situ bacterial production of fluorescent organic matter: An investigation at a species level. *Water Res.* **2017**, *125*, 350–359.
- (51) Jian, Q.; Boyer, T. H.; Yang, X.; Xia, B.; Yang, X. Characteristics and DBP formation of dissolved organic matter from leachates of fresh and aged leaf litter. *Chemosphere* **2016**, *152*, 335–344.
- (52) Yamashita, Y.; Tanoue, E. Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids. *Mar. Chem.* **2003**, *82* (3), 255–271.
- (53) Pucher, M.; Wünsch, U.; Weigelhofer, G.; Murphy, K.; Hein, T.; Graeber, D. staRdom: Versatile software for analyzing spectroscopic data of dissolved organic matter in R. *Water* **2019**, *11* (11), 2366.
- (54) Stedmon, C. A.; Bro, R. Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial. *Limnol. Oceanogr. Methods* **2008**, *6*, 572–579.
- (55) Sadiq, R.; Rodriguez, M. J. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. *Sci. Total Environ.* **2004**, *321* (1), 21–46.
- (56) Kurajica, L.; Ujevic Bosnjak, M.; Novak Stankov, M.; Kinsela, A. S.; Stiglic, J.; Waite, D. T.; Capak, K. Disinfection by-products in Croatian drinking water supplies with special emphasis on the water supply network in the city of Zagreb. *J. Environ. Manage.* **2020**, *276*, 111360.
- (57) O'Driscoll, C.; McGillicuddy, E.; Croot, P.; Bartley, P.; McMyler, J.; Sheahan, J.; Morrison, L. Tracing sources of natural organic matter, trihalomethanes and metals in groundwater from a karst region. *Environ. Sci. Pollut. Res.* **2020**, *27* (11), 12587–12600.
- (58) Summers, R. S.; Hooper, S. M.; Shukairy, H. M.; Solarik, G.; Owen, D. Assessing DBP yield: Uniform formation conditions. *J. - Am. Water Works Assoc.* **1996**, *88* (6), 80–93.

- (59) Kristiana, I.; Lethorn, A.; Joll, C.; Heitz, A. To add or not to add: The use of quenching agents for the analysis of disinfection by-products in water samples. *Water Res.* **2014**, *59*, 90–98.
- (60) Zhong, S.; Zhang, K.; Bagheri, M.; Burken, J. G.; Gu, A.; Li, B.; Ma, X.; Marrone, B. L.; Ren, Z. J.; Schrier, J.; Shi, W.; Tan, H.; Wang, T.; Wang, X.; Wong, B. M.; Xiao, X.; Yu, X.; Zhu, J. J.; Zhang, H. Machine learning: New ideas and tools in environmental science and engineering. *Environ. Sci. Technol.* **2021**, *55* (19), 12741–12754.
- (61) Baldwin, D. S.; Valo, W. Exploring the relationship between the optical properties of water and the quality and quantity of dissolved organic carbon in aquatic ecosystems: strong correlations do not always mean strong predictive power. *Environ. Sci. Process. Impacts* **2015**, *17* (3), 619–630.
- (62) Xia, Y.; Lin, Y. L.; Xu, B.; Hu, C. Y.; Gao, Z. C.; Tang, Y. L.; Chu, W. H.; Cao, T. C.; Gao, N. Y. Effect of UV irradiation on iodinated trihalomethane formation during post-chloramination. *Water Res.* **2018**, *147*, 101–111.
- (63) Jutaporn, P.; Armstrong, M. D.; Coronell, O. Assessment of C-DBP and N-DBP formation potential and its reduction by MIEX® DOC and MIEX® GOLD resins using fluorescence spectroscopy and parallel factor analysis. *Water Res.* **2020**, *172*, 115460.
- (64) Munch, D. J.; Munch, J. W.; Pawlecki, A. M. *EPA Method 552.2, Rev. 1.0: Determination of haloacetic acids and dalapon in drinking water by liquid–liquid extraction, derivatization and gas chromatography with electron capture detection*; U.S. EPA: Cincinnati, OH, 1995.
- (65) Kali, S.; Khan, M.; Ghaffar, M. S.; Rasheed, S.; Waseem, A.; Iqbal, M. M.; Bilal Khan Niazi, M.; Zafar, M. I. Occurrence, influencing factors, toxicity, regulations, and abatement approaches for disinfection by-products in chlorinated drinking water: A comprehensive review. *Environ. Pollut.* **2021**, *281*, 116950.
- (66) Kristiana, I.; Gallard, H.; Joll, C.; Croue, J. P. The formation of halogen-specific TOX from chlorination and chloramination of natural organic matter isolates. *Water Res.* **2009**, *43* (17), 4177–4186.
- (67) Kurajica, L.; Ujevic Bosnjak, M.; Kinsela, A. S.; Stiglic, J.; Waite, T. D.; Capak, K.; Pavlic, Z. Effects of changing supply water quality on drinking water distribution networks: Changes in NOM optical properties, disinfection byproduct formation, and Mn deposition and release. *Sci. Total Environ.* **2021**, *762*, 144159.
- (68) Mash, C. A.; Winston, B. A.; Meints II, D. A.; Pifer, A. D.; Scott, J. T.; Zhang, W.; Fairey, J. L. Assessing trichloromethane formation and control in algal-stimulated waters amended with nitrogen and phosphorus. *Environ. Sci. Process. Impacts* **2014**, *16* (6), 1290–1299.
- (69) Yang, L.; Kim, D.; Uzun, H.; Karanfil, T.; Hur, J. Assessing trihalomethanes (THMs) and N-nitrosodimethylamine (NDMA) formation potentials in drinking water treatment plants using fluorescence spectroscopy and parallel factor analysis. *Chemosphere* **2015**, *121*, 84–91.
- (70) Kumari, M.; Gupta, S. K. Occurrence and exposure to trihalomethanes in drinking water: A systematic review and meta-analysis. *Exposure Health* **2022**, *14*, 915–939.
- (71) Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37* (20), 4702–4708.
- (72) Deborde, M.; von Gunten, U. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. *Water Res.* **2008**, *42*, 13–51.
- (73) Li, L.; Jeon, Y.; Ryu, H.; Santo Domingo, J. W.; Seo, Y. Assessing the chemical compositions and disinfection byproduct formation of biofilms: Application of fluorescence excitation-emission spectroscopy coupled with parallel factor analysis. *Chemosphere* **2020**, *246*, 125745.
- (74) Roccaro, P.; Vagliasindi, F. G. A.; Korshin, G. V. Changes in NOM fluorescence caused by chlorination and their associations with disinfection by-products formation. *Environ. Sci. Technol.* **2009**, *43* (3), 724–729.
- (75) Korshin, G. V.; Kumke, M. U.; Li, C.-W.; Frimmel, F. H. Influence of chlorination on chromophores and fluorophores in humic substances. *Environ. Sci. Technol.* **1999**, *33* (8), 1207–1212.
- (76) Beggs, K. M. H.; Summers, R. S.; McKnight, D. M. Characterizing chlorine oxidation of dissolved organic matter and disinfection by-product formation with fluorescence spectroscopy and parallel factor analysis. *J. Geophys. Res.* **2009**, *114*, G04001.
- (77) Lee, H. S.; Hur, J.; Lee, M. H.; Brogi, S. R.; Kim, T. W.; Shin, H. S. Photochemical release of dissolved organic matter from particulate organic matter: Spectroscopic characteristics and disinfection by-product formation potential. *Chemosphere* **2019**, *235*, 586–595.
- (78) Lee, H. S.; Hur, J.; Shin, H. S. Dynamic exchange between particulate and dissolved matter following sequential resuspension of particles from an urban watershed under photo-irradiation. *Environ. Pollut.* **2021**, *283*, 117395.
- (79) Heeb, M. B.; Criquet, J.; Zimmermann-Steffens, S. G.; von Gunten, U. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds - A critical review. *Water Res.* **2014**, *48*, 15–42.
- (80) Bichsel, Y.; von Gunten, U. Oxidation of iodide and hypiodous acid in the disinfection of natural waters. *Environ. Sci. Technol.* **1999**, *33* (22), 4040–4045.
- (81) Amy, G. L.; Tan, L.; Davis, M. K. The effects of ozonation and activated carbon adsorption on trihalomethane speciation. *Water Res.* **1991**, *25* (2), 191–202.
- (82) Hua, L.-C.; Cai, P.; Huang, C.; Huang, C. Tracking Br-DBPs and bromine substitution factors by two-stage differential characterization of water matrix and NOM during chlorination. *Sci. Total Environ.* **2021**, *782*, 146836.
- (83) Zhao, X.; Ma, J.; von Gunten, U. Reactions of hypiodous acid with model compounds and the formation of iodoform in absence/presence of permanganate. *Water Res.* **2017**, *119*, 126–135.
- (84) Jutaporn, P.; Laolertworakul, W.; Tungsudjawong, K.; Khongnakorn, W.; Leungprasert, S. Parallel factor analysis of fluorescence excitation emissions to identify seasonal and watershed differences in trihalomethane precursors. *Chemosphere* **2021**, *282*, 131061.
- (85) Pifer, A. D.; Cousins, S. L.; Fairey, J. L. Assessing UV- and fluorescence-based metrics as disinfection byproduct precursor surrogate parameters in a water body influenced by a heavy rainfall event. *J. Water Supply Res. T.* **2014**, *63* (3), 200–211.
- (86) Li, L.; Liu, T.; Dong, H.; Wang, Y.; Yang, H.; Qiang, Z. Tracking spatio-temporal dynamics of fluorescence characteristics of Huangpu River, China by parallel factor analysis: Correlation with disinfection by-product precursor and pesticide level variations. *Chemosphere* **2021**, *283*, 131198.
- (87) Li, W.; Wang, J.; Xin, H.; Li, T.; Duan, J.; Mulcahy, D. Determination of cost-effective optimum coagulant dosage for removal of disinfection by-product precursors in water treatment based on the theory of elasticity. *J. Water Process. Eng.* **2022**, *47*, 102782.
- (88) Hidayah, E. N.; Chou, Y. C.; Yeh, H. H. Comparison between HPSEC-OCD and F-EEMs for assessing DBPs formation in water. *J. Environ. Sci. Health, Pt. A: Toxic/Hazard. Subst. Environ. Eng.* **2017**, *52* (4), 391–402.
- (89) Ma, C.; Xu, H.; Zhang, L.; Pei, H.; Jin, Y. Use of fluorescence excitation-emission matrices coupled with parallel factor analysis to monitor C- and N-DBPs formation in drinking water recovered from cyanobacteria-laden sludge dewatering. *Sci. Total Environ.* **2018**, *640–641*, 609–618.
- (90) Pifer, A. D.; Fairey, J. L. Suitability of organic matter surrogates to predict trihalomethane formation in drinking water sources. *Environ. Eng. Sci.* **2014**, *31* (3), 117–126.
- (91) Visentin, F.; Bhartia, S.; Mohseni, M.; Peldszus, S.; Dorner, S.; Barbeau, B. Impact of vacuum UV on natural and algal organic matter from cyanobacterial impacted waters. *Environ. Sci.: Water Res. Technol.* **2020**, *6* (3), 829–838.

- (92) Young, T. R.; Deem, S.; Leslie, J. C.; Salo-Ziemann, V.; He, H.; Dodd, M. C. Drivers of disinfection byproduct formation and speciation in small, chlorinated coastal groundwater systems: relative roles of bromide and organic matter, and the need for improved source water characterization and monitoring. *Environ. Sci.: Water Res. Technol.* **2020**, *6* (12), 3361–3379.
- (93) Zhang, X.; Shen, J.; Huo, X.; Li, J.; Zhou, Y.; Kang, J.; Chen, Z.; Chu, W.; Zhao, S.; Bi, L.; Xu, X.; Wang, B. Variations of disinfection byproduct precursors through conventional drinking water treatment processes and a real-time monitoring method. *Chemosphere* **2021**, *272*, 129930.
- (94) Zhang, Y. X.; Liang, X. Q.; Hua, G. F.; Li, M. R.; Lin, L. M. Disinfection byproduct precursors in paddy fields under swine manure application: Reactivity, origins and interception. *Agric., Ecosyst. Environ.* **2018**, *256*, 173–183.
- (95) Yang, L.; Hur, J.; Lee, S.; Chang, S. W.; Shin, H. S. Dynamics of dissolved organic matter during four storm events in two forest streams: source, export, and implications for harmful disinfection byproduct formation. *Environ. Sci. Pollut. Res.* **2015**, *22* (12), 9173–9183.
- (96) Granderson, C. W.; Pifer, A. D.; Fairey, J. L. An improved chloroform surrogate for chlorine dioxide and alum-treated waters. *J. - Am. Water Works Assoc.* **2013**, *105* (3), E103–E114.
- (97) Siddique, M. S.; Xiong, X.; Yang, H.; Maqbool, T.; Graham, N.; Yu, W. Dynamic variations in DOM and DBPs formation potential during surface water treatment by ozonation-nanofiltration: Using spectroscopic indices approach. *Chem. Eng. J.* **2022**, *427*, 132010.
- (98) Xu, X.; Kang, J.; Shen, J.; Zhao, S.; Wang, B.; Zhang, X.; Chen, Z. EEM-PARAFAC characterization of dissolved organic matter and its relationship with disinfection by-products formation potential in drinking water sources of northeastern China. *Sci. Total Environ.* **2021**, *774*, 145297.
- (99) Nguyen, H. V.-M.; Lee, M.-H.; Hur, J.; Schlautman, M. A. Variations in spectroscopic characteristics and disinfection byproduct formation potentials of dissolved organic matter for two contrasting storm events. *J. Hydrol.* **2013**, *481*, 132–142.
- (100) Huang, X.; Wang, S.; Zhu, S.; Ye, Z. Spectroscopic characteristics and disinfection byproduct formation during UV-assisted photoelectrochemical degradation of humic acid. *J. Cleaner Prod.* **2022**, *375*, 134171.
- (101) Wang, Y.; Li, L.; Sun, Z.; Dong, H.; Yu, J.; Qiang, Z. Removal of disinfection by-product precursors in drinking water treatment processes: Is fluorescence parallel factor analysis a promising indicator? *J. Hazard. Mater.* **2021**, *418*, 126298.
- (102) Watson, K.; Farre, M. J.; Leusch, F. D. L.; Knight, N. Using fluorescence-parallel factor analysis for assessing disinfection by-product formation and natural organic matter removal efficiency in secondary treated synthetic drinking waters. *Sci. Total Environ.* **2018**, *640–641*, 31–40.
- (103) Peleato, N. M.; McKie, M.; Taylor-Edmonds, L.; Andrews, S. A.; Legge, R. L.; Andrews, R. C. Fluorescence spectroscopy for monitoring reduction of natural organic matter and halogenated furanone precursors by biofiltration. *Chemosphere* **2016**, *153*, 155–161.
- (104) Maqbool, T.; Zhang, J.; Qin, Y.; Ly, Q. V.; Asif, M. B.; Zhang, X.; Zhang, Z. Seasonal occurrence of N-nitrosamines and their association with dissolved organic matter in full-scale drinking water systems: Determination by LC-MS and EEM-PARAFAC. *Water Res.* **2020**, *183*, 116096.
- (105) Murphy, K. R.; Hambly, A.; Singh, S.; Henderson, R. K.; Baker, A.; Stuetz, R.; Khan, S. J. Organic matter fluorescence in municipal water recycling schemes: Toward a unified PARAFAC model. *Environ. Sci. Technol.* **2011**, *45* (7), 2909–2916.
- (106) Westerhoff, P.; Mash, H. Dissolved organic nitrogen in drinking water supplies: a review. *J. Water Supply Res. T.* **2002**, *51* (8), 415–448.
- (107) Wang, R.; Wang, T.; Qu, G.; Zhang, Y.; Guo, X.; Jia, H.; Zhu, L. Insights into the underlying mechanisms for integrated inactivation of A. spiroides and depression of disinfection byproducts by plasma oxidation. *Water Res.* **2021**, *196*, 117027.
- (108) Xiong, X.; Siddique, M. S.; Graham, N. J. D.; Yu, W. Towards microplastics contribution for membrane biofouling and disinfection by-products precursors: The effect on microbes. *J. Hazard. Mater.* **2022**, *426*, 127797.
- (109) Lawaetz, A. J.; Stedmon, C. A. Fluorescence intensity calibration using the Raman scatter peak of water. *Appl. Spectrosc.* **2009**, *63* (8), 936–940.
- (110) Murphy, K. R.; Butler, K. D.; Spencer, R. G. M.; Stedmon, C. A.; Boehme, J. R.; Aiken, G. R. Measurement of dissolved organic matter fluorescence in aquatic environments: An interlaboratory comparison. *Environ. Sci. Technol.* **2010**, *44* (24), 9405–9412.
- (111) Rosario-Ortiz, F. L.; Snyder, S. A.; Suffet, I. H. Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. *Water Res.* **2007**, *41* (18), 4115–4128.
- (112) D'Andrilli, J.; Fischer, S. J.; Rosario-Ortiz, F. L. Advancing critical applications of high resolution mass spectrometry for DOM assessments: Re-engaging with mass spectral principles, limitations, and data analysis. *Environ. Sci. Technol.* **2020**, *54* (19), 11654–11656.
- (113) Allpike, B. P.; Heitz, A.; Joll, C. A.; Kagi, R. L.; Abbt-Braun, G.; Frimmel, F. H.; Brinkmann, T.; Her, N.; Amy, G. Size exclusion chromatography to characterize DOC removal in drinking water treatment. *Environ. Sci. Technol.* **2005**, *39* (7), 2334–2342.
- (114) Stubbins, A.; Lapierre, J. F.; Berggren, M.; Prairie, Y. T.; Dittmar, T.; del Giorgio, P. A. What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environ. Sci. Technol.* **2014**, *48* (18), 10598–10606.
- (115) Peleato, N. M.; Legge, R. L.; Andrews, R. C. Neural networks for dimensionality reduction of fluorescence spectra and prediction of drinking water disinfection by-products. *Water Res.* **2018**, *136*, 84–94.
- (116) Artrith, N.; Butler, K. T.; Coudert, F. X.; Han, S.; Isayev, O.; Jain, A.; Walsh, A. Best practices in machine learning for chemistry. *Nat. Chem.* **2021**, *13* (6), 505–508.
- (117) Murphy, K. R.; Stedmon, C. A.; Wenig, P.; Bro, R. OpenFluor— an online spectral library of auto-fluorescence by organic compounds in the environment. *Anal. Methods* **2014**, *6* (3), 658–661.
- (118) American Chemical Society. *figshare*; <https://acs.figshare.com/> (accessed 2023-04-20).
- (119) European Organization For Nuclear Research; OpenAIR. *Zenodo*; <https://www.zenodo.org/> (accessed 2023-04-20).
- (120) Wilkinson, M. D.; Dumontier, M.; Aalbersberg, I. J.; Appleton, G.; Axton, M.; Baak, A.; Blomberg, N.; Boiten, J. W.; de Silva Santos, L. B.; Bourne, P. E.; Bouwman, J.; Brookes, A. J.; Clark, T.; Crosas, M.; Dillo, I.; Dumon, O.; Edmunds, S.; Evelo, C. T.; Finkers, R.; Gonzalez-Beltran, A.; Gray, A. J.; Groth, P.; Goble, C.; Grethe, J. S.; Heringa, J.; t Hoen, P. A.; Hooft, R.; Kuhn, T.; Kok, R.; Kok, J.; Lusher, S. J.; Martone, M. E.; Mons, A.; Packer, A. L.; Persson, B.; Rocca-Serra, P.; Roos, M.; van Schaik, R.; Sansone, S. A.; Schultes, E.; Sengstag, T.; Slater, T.; Strawn, G.; Swertz, M. A.; Thompson, M.; van der Lei, J.; van Mulligen, E.; Velterop, J.; Waagmeester, A.; Wittenburg, P.; Wolstencroft, K.; Zhao, J.; Mons, B. The FAIR guiding principles for scientific data management and stewardship. *Scientific Data* **2016**, *3*, 160018.
- (121) Li, W.-T.; Jin, J.; Li, Q.; Wu, C.-F.; Lu, H.; Zhou, Q.; Li, A.-M. Developing LED UV fluorescence sensors for online monitoring DOM and predicting DBPs formation potential during water treatment. *Water Res.* **2016**, *93*, 1–9.
- (122) Khamis, K.; Bradley, C.; Hannah, D. M. Understanding dissolved organic matter dynamics in urban catchments: insights from in situ fluorescence sensor technology. *WIREs Water* **2018**, *5* (1), e1259.
- (123) Carstea, E. M.; Baker, A.; Bierzoza, M.; Reynolds, D. Continuous fluorescence excitation-emission matrix monitoring of river organic matter. *Water Res.* **2010**, *44* (18), 5356–5366.
- (124) Bro, R.; Kiers, H. A. L. A new efficient method for determining the number of components in PARAFAC models. *J. Chemom.* **2003**, *17* (5), 274–286.

(125) Kiers, H. A. L.; Harshman, R. A. An efficient algorithm for Parafac with uncorrelated mode-A components applied to large  $I \times J \times K$  data sets with  $I \gg JK$ . *J. Chemom.* **2009**, *23* (7–8), 442–447.

(126) Ruhala, S. S.; Zarnetske, J. P. Using in-situ optical sensors to study dissolved organic carbon dynamics of streams and watersheds: A review. *Sci. Total Environ.* **2017**, *575*, 713–723.

(127) Croghan, D.; Khamis, K.; Bradley, C.; Van Loon, A. F.; Sadler, J.; Hannah, D. M. Combining in-situ fluorometry and distributed rainfall data provides new insights into natural organic matter transport dynamics in an urban river. *Sci. Total Environ.* **2021**, 755 (Pt 1), 142731.

(128) Krames, M. The rise of UV-C LEDs. In *LEDs Magazine*, July 24, 2020.

(129) Khamis, K.; Sorensen, J. P.; Bradley, C.; Hannah, D. M.; Lapworth, D. J.; Stevens, R. In situ tryptophan-like fluorometers: assessing turbidity and temperature effects for freshwater applications. *Environ. Sci. Process. Impacts* **2015**, *17* (4), 740–752.

(130) Lee, E. J.; Yoo, G. Y.; Jeong, Y.; Kim, K. U.; Park, J. H.; Oh, N. H. Comparison of UV–VIS and FDOM sensors for in situ monitoring of stream DOC concentrations. *Biogeosciences* **2015**, *12* (10), 3109–3118.

## Recommended by ACS

### Unravelling High-Molecular-Weight DBP Toxicity Drivers in Chlorinated and Chloraminated Drinking Water: Effect-Directed Analysis of Molecular Weight Fractions

Huiyu Dong, Susan D. Richardson, *et al.*

JULY 07, 2023

ENVIRONMENTAL SCIENCE & TECHNOLOGY

READ 

### Toxicity Evaluation and Effect-Based Identification of Chlorine Disinfection Products of the Anti-COVID-19 Drug Chloroquine Phosphate

Shengchao Hu, Huijuan Liu, *et al.*

MAY 15, 2023

ENVIRONMENTAL SCIENCE & TECHNOLOGY

READ 

### Co-Occurrence of Bromine and Iodine Species in US Drinking Water Sources That Can Impact Disinfection Byproduct Formation

Naushita Sharma, Paul Westerhoff, *et al.*

JANUARY 17, 2023

ENVIRONMENTAL SCIENCE & TECHNOLOGY

READ 

### Chlorination for *Microcystis aeruginosa* in the Late Lag Phase: Higher Inactivation Efficiency and Lower Environmental Risk

Xuanxuan Xian, Xin Yu, *et al.*

JANUARY 20, 2023

ACS ES&T WATER

READ 

Get More Suggestions >