

## Application of EEM fluorescence spectroscopy for characterizing organic DBP precursors in different water sources: a review

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### ABSTRACT

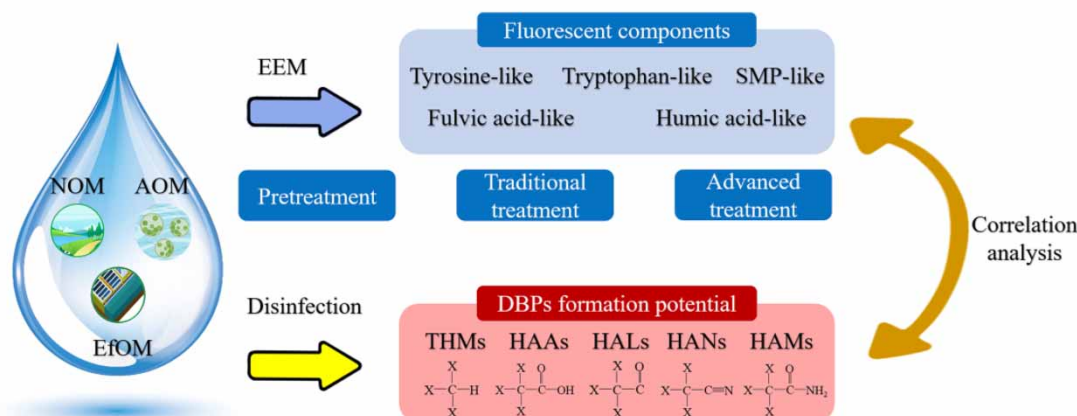
Disinfection by-products (DBPs), generated from the reaction of disinfectants with DBP precursors, have been found to pose unintentional risks to human health. Considering that the concentration and speciation of DBPs formed during disinfection will be affected by the content and composition of dissolved organic matter (DOM), widespread concern about the characteristics of DBP precursors in water sources have been prompted. Three-dimensional excitation–emission matrix (EEM) can quickly and efficiently determine the properties and composition of DOM in water, and thus is generally used to investigate the origin of DBP precursors in water sources. This study overviews the fluorescent properties of different DBP precursors, summarizes the application of different EEM interpretation methods in DBP precursors and analyses the key factors affecting the correlation between the fluorescent components and DBP precursors (e.g., natural organic matter, algal organic matter, effluent organic matter and organic matter derived from other sources). A series of factors, including composition of fluorophores, bromide concentration, spatio-temporal characteristics and disinfectant types, could impact the correlation between DBP formation potential and fluorescent components. As for future research needs, it is of significance to select suitable fluorescence analysis methods and investigate the combination of EEM with other characterization technologies based on different situations.

**Key words:** characterization, correlation analysis, disinfection by-products, excitation–emission matrix, organic matter sources

### HIGHLIGHTS

- The main substances and sources of DBP precursors in water are introduced.
- Fluorescence analysis methods for DBP precursor are summarized.
- The fluorescence properties of DBP precursors from different sources are analyzed.
- The correlation between fluorescent substances and DBP precursors are discussed.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Disinfection of drinking water could effectively control pathogenic microorganisms and prevent the outbreaks of waterborne diseases (Calderon 2000; Chen *et al.* 2021). However, the chemical risks arising from the interaction of disinfectants with organic substances in water have been widely concerned since the first detection of hazardous disinfection by-products (DBPs) in chlorinated drinking water (Bellar *et al.* 1974). Epidemiological studies have shown that DBPs could cause health risks and the related issues include bladder cancer, rectal cancer, colon cancer and unfavorable pregnancy defects (Richardson *et al.* 2007; Bond *et al.* 2012; Postigo *et al.* 2018). So far, more than 700 DBPs have been discovered in drinking water (Richardson *et al.* 2007; Yang & Zhang 2016), and the dominant carbonaceous DBPs (C-DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) have been widely regulated (Richardson 2011). However, relevant research indicated that unregulated nitrogenous DBPs (N-DBPs), including haloacetonitriles (HANs) and haloacetamides (HAMs), exhibited higher toxicity than the regulated C-DBPs (Muellner *et al.* 2007; Wagner & Plewa 2017). In addition, some unregulated phenolic and aromatic DBPs have also been reported to be more toxic (Liu & Zhang 2014; Han *et al.* 2021).

The concentration and speciation of DBPs during disinfection would be influenced by the nature and composition of dissolved organic matter (DOM) in water. Natural organic matter (NOM) is the primary DBP precursors in water sources, leading mainly to the generation of C-DBPs. However, water sources impacted by algal blooms or municipal wastewater discharges have also been utilized in some cases to meet the increasing demand for water resource due to the growth of population. Unlike terrestrial-derived NOM with low organic-nitrogen content (mostly less than 5% of dissolved organic carbon [DOC] by weight), effluent organic matter (EfOM) derived from wastewater treatment plants (WWTPs) and algal organic matter (AOM) produced by cell exudation or lysis are composed of macromolecules and cellular debris with a nitrogen-enriched protein fraction, and could serve as significant N-DBP precursors (Leenheer *et al.* 2007; Shah & Mitch 2012; Liu *et al.* 2022; Wang *et al.* 2023). In addition, some anthropogenic micro-pollutants including pesticides, industrial chemicals, pharmaceuticals and personal care products (PPCPs) could also form DBPs during the disinfection process (Chu *et al.* 2016; Tang *et al.* 2020; Dong *et al.* 2021).

The determination and characterization of DBP precursors could assist in optimizing treatment processes to improve the removal efficiency of DBP precursors (Krasner *et al.* 2007; Chu *et al.* 2013; Wang *et al.* 2021b; Luo *et al.* 2022). Methods used for DOM characterization mainly include spectroscopic methods, chromatographic methods, mass spectrometric methods and bulk parameter determination (Matilainen *et al.* 2011). General parameters such as DOC, ultraviolet (UV) absorbance, and specific UV absorbance (SUVA) could be applied to indicate the overall levels of organic DBP precursors (Chowdhury *et al.* 2009). However, the composition and characteristics of DOM, which is a complex mixture of humic substances, carbohydrates, amino acids, as well as other organic fractions, cannot be fully determined by these bulk parameters (Her *et al.* 2003; Peleato & Andrews 2015). Besides, chromatographic methods need select appropriate separation methods and mass spectrometric methods hardly interpret the data due to complexity of NOM (Matilainen *et al.* 2011), whereas fluorescence methods have faster online detection capability and could be more easily explained (Peleato *et al.* 2018).

EEM can show the composition and relative content of organic substances with different properties in water and is very sensitive to the change of chemical properties of organics in water during disinfectant oxidation (Bieroza *et al.* 2012; Pifer & Fairey 2012; Yang *et al.* 2015a, 2015b; Nguyen *et al.* 2023). The information obtained by EEM spectrum is generally interpreted through the following methods including peak picking (Coble 1996), fluorescence indices (McKnight *et al.* 2001), fluorescence regional integration (FRI) (Chen *et al.* 2003), principal component analysis (PCA) (Peiris *et al.* 2010), and parallel factor analysis (PARAFAC) (Stedmon *et al.* 2003; Yang *et al.* 2015a, 2015b). Peak picking and fluorescence indices use the fluorescence intensity and intensity ratio of the representative positions to establish a relationship with DBP precursor (Massalha *et al.* 2018; Roccaro *et al.* 2020), while FRI using large masses of fluorescence data as well as PCA and PARAFAC providing significant dimensionality reduction based on chemometric methods have also been used in different water bodies (Peleato & Andrews 2015; Jutaporn *et al.* 2021). The neural network (NN) approach allowing for non-linear dimensionality reduction of fluorescence spectra without explicit constraints has less use in the DBP field (Bieroza *et al.* 2011; Peleato *et al.* 2018). In general, the development of modern data analysis methods also provides more diversified choices for fluorescence data analysis and is widely applied to characterize DBP precursors in water sources (Fernández-Pascual *et al.* 2023).

A large amount of studies have used EEM to characterize DBP precursors in different water sources and analyze the change of DBP precursors arising from different treatment processes. However, systematical review is still lacking. This paper aims to (1) discuss the principle of EEM application in characterizing DBP precursors, (2) analyze the correlation between DBP precursors and fluorescent components, (3) overview different data analysis methods used for DBP precursor analysis. Besides, future research needs concerning improvement of fluorescence methods for DBP precursor analysis are proposed.

## 2. SOURCE OF DBP PRECURSORS

Humic acid and fulvic acid, accounting for 50–90% of the total DOC, are hydrophobic substances and serve as the main precursors of THMs (Thurman *et al.* 1989). Compared to fulvic acid, humic acids have more active sites that can react with chlorine and thus yield more THMs (Peters *et al.* 1980), and the active sites including reactive phenolic structures and high aromatic carbon content contribute to the formation of organohalides during chlorine disinfection (Singer 1999). Amino acids, an important hydrophilic fraction of NOM, have also been proven to serve as precursors of THMs and HAAs, and their concentrations in treated water varied from a few to several hundred nmol/L (Hureiki *et al.* 1994; Bond *et al.* 2009). The amino acids with side groups, like activated aromatic rings, amino or sulfur, react more easily with chlorine (Hureiki *et al.* 1994). In addition, these nitrogen enriched compounds such as amino acids and amines may also contribute to the formation of highly toxic N-DBPs (Bond *et al.* 2012). Thus, the concentration and speciation of DBPs formed during disinfection will be affected by the composition of DOM, which is related to the source of organic matter. In general, humic acid and fulvic acid accounted for most of NOM and were more likely to generate C-DBPs during disinfection (Shah & Mitch 2012), while soluble microbial products (SMPs) produced by bacteria during wastewater treatment as well as AOM liberated from algae are comprised of nitrogen-enriched compounds and serve as significant N-DBP precursors (Westerhoff & Mash 2002).

A summary of traditional NOM peaks of three main organic sources are shown in Figure 1. In addition, the DBP precursors with the  $\pi$ -electron system like phenolic structures and electron-donating groups like hydroxy and amino tend to emit fluorescence, and different DBP precursors (e.g., humic acid, fulvic acid and amino acids) can be distinguished due to their different fluorescence properties, which make EEM an effective tool to detect the DBP precursors from different sources.

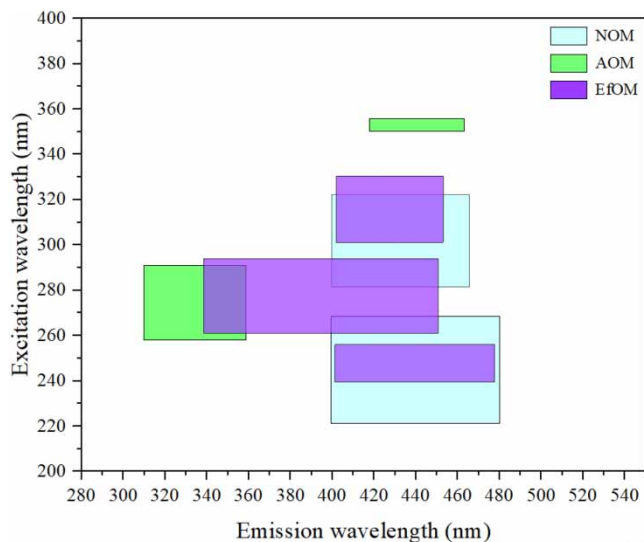
## 3. DATA ANALYSIS METHOD FOR FLUORESCENCE CHARACTERIZATION OF DBP PRECURSORS

Fluorescence data of DOM in different water sources are inconsistent and complex, consisting of hundreds of fluorescence intensities under the different excitation/emission (Ex/Em) pairs. Specific data analysis methods can provide more key information better concerning DBP precursors in water.

### 3.1. Analysis methods based on peak intensity and intensity ratio

#### 3.1.1. Peak picking

Peak picking is a quantitative method based on selecting the fluorescence intensity at a certain excitation/emission wavelength of the regions of interest, and the fluorophore types of the regions in the original data are identified through pre-defined region classification (Coble 1996). The corresponding chemical compositions of different regions are shown in



**Figure 1** | A summary of traditional DOM peaks of three different organic sources: (a) NOM; (b) EfOM; and (c) AOM. Adapted from [Chen et al. \(2017a, 2017b\)](#); [Guo et al. \(2014\)](#); [Wang et al. \(2015\)](#).

Supplementary material, Figure S1. In addition, the ratios between fluorescence intensities are often used to express changes in the composition of organic matter in water. The information of typical fluorescence intensity ratios is listed in Supplementary material, Table S1.

The maximum fluorescence intensity within the peak region was usually applied to connect with DBP formation potential (DBPFP) even though the location of the maximum may vary due to different water quality ([Hao et al. 2012b](#); [Park et al. 2019](#)). Thus, the existence and intensity of some peaks identified by this method can be used as the characteristic factor of DBP precursors in water ([Hua et al. 2007](#); [Hao et al. 2012b](#)). In addition, the differences in peak positions can provide information on the changes in the properties of DBP precursors during the biochemical changes in samples ([Peiris et al. 2011](#); [Luo et al. 2022](#)). Compared to the individual peak intensity, the peak intensity ratio can reflect the relative content of different components in organic matter and reveal changes in the composition of organic matter after different biochemical processes, which can provide an understanding of DBP generation ([Ritson et al. 2014](#); [Hohner et al. 2016](#); [Cai et al. 2020](#)).

### 3.1.2. Fluorescence regional integration

Fluorescence spectra consist of thousands of data points of fluorescence intensity depending on the wavelength, but quantitative technique based on peak picking and other applications use only one to three data points ignoring other available information ([Chen et al. 2003](#); [Peleato & Andrews 2015](#)). FRI is a quantitative technique by integrating all fluorescence intensity of divided region of an EEM. An EEM map is divided into five main regions as shown in Supplementary material, Figure S2. Normalized excitation–emission area volumes beneath each region can express the contents of each region representing the type of substance and percent fluorescence response can show the relative content of each sort of substance in the sample.

The change of integrated intensity in different regions in FRI can provide insight into the location of DBP precursors in EEM ([Johnstone & Miller 2009](#)). Some studies tend to establish regression analysis between the different DBP produced after disinfection and the fluorescence intensity integral of different regions to find the source of DBP precursors and predict the formation of DBPs ([Roccaro et al. 2020](#)). In addition, FRI can reflect the changes of components in different regions during water treatment which can be used to analyze the changes of DBP precursor sources after treatment ([Meng et al. 2016](#); [Fan et al. 2020](#)).

## 3.2. Analysis methods based on data dimensionality reduction

### 3.2.1. Principal component analysis

PCA is a multivariate method that decomposes a data matrix into a series of linear terms and a residual matrix ([Wold et al. 1987](#)). PCA can transform lots of interrelated variables into independent new principal components (PCs) with the directions

of maximum variance of the combined columns of the data matrix to provide significant dimensionality reduction (Persson & Wedborg 2001). The PCs are calculated in order of decreasing variance to contribute to using the first few variables to realize the variance interpretation of a data matrix consisting of a large number of variables. According to the different input variables, the EEM data analysis methods based on PCA are mainly divided into two types, including the fluorescence intensity corresponding to each excitation/emission wavelength and the fluorescence variables obtained by other data analysis methods. The loadings of PCs are directly linked to the fluorophores present and thus provide a basis for interpreting structural differences.

The scores of PCs based on PCA can be applied to predict the formation of DBPs in different source water. Each PC resulting from dimensionality reduction of EEM is composed of different fluorescent substances in water rather than individual component in the fluorescence spectra. However, the high loading values of spectral regions of PCs can be used to identify representative substances of each PC, which can provide insight into the types of DBP precursors (Peleato & Andrews 2015; Peleato *et al.* 2018). In addition, PCA is also applied to track the correlation between some fluorescence parameters like peak intensity and intensity ratio gained by other analysis methods and DBPFP (Nguyen *et al.* 2021).

### 3.2.2. Parallel factor analysis

PARAFAC is also a multivariate analysis technique that decomposes the data matrix into a set of trilinear terms and a residual array (Stedmon *et al.* 2003). Compared with two-way PAC, three-way PARAFAC analysis can obtain more adequate, robust and interpretable models to account for the three-dimensional nature of EEMs by using constraints of unimodality and non-negativity. In PARAFAC models, the overlapping fluorescence signals formed by different organics in water are decomposed into several interpretable components representing a group of fluorophores of similar, specific fluorescence properties (Stedmon & Markager 2005). The tutorials based on different toolboxes for MATLAB have been provided to help practical application of PARAFAC to fluorescence datasets (Stedmon & Bro 2008; Murphy *et al.* 2013). A diagram summarizing the different necessary steps in the fluorescence-PARAFAC analysis was shown in Supplementary material, Figure S3. These analysis methods help provide a reasonable model reflecting the composition of organics in water, but it is worth noting that the fluorescence intensity of the components obtained from the analysis only reflects the relative concentration of organics in the water.

The loadings at different excitation and emission wavelengths displayed by components separated by PARAFAC can be used to indicate the type and source of DBP precursors and the maximum fluorescence intensity of components can be used to indicate the relative content of DBP precursors. The separated fluorophore signal representing a single substance in water had higher correlation with DBPFPs than the conventional indicators like DOC and SUVA (Jutaporn *et al.* 2021). In addition, combined parameters from different fluorescence components including addition and ratio between components were more flexible and accurate in predicting the formation of DBP (Pifer & Fairey 2014; Xia *et al.* 2018). Compared to other methods, PARAFAC tend to require more data samples to ensure the credibility of the model. The collection of sample data over a long period of time made the application of PARAFAC more accurate and sensitive in the long-term monitoring process (Jutaporn *et al.* 2021; Li *et al.* 2021a, 2021b).

### 3.2.3. Artificial neural networks

An artificial neural network (ANN) is a powerful mathematical model composed of a series of the single processing elements (nodes, neurons) connected with each other. In an active neuron, each input vector is multiplied by its weight and the product is summed with the bias, and the output is generated through the transfer function which is generally a non-linear function (Bieroza *et al.* 2011). Environmental conditions such as pH or temperature, inner filter effects (IFE) and the Rayleigh and Raman scatter can all affect the analysis results of PCA and PARAFAC based on linear dimensionality reduction, while some constraints eliminating these effects may limit the overall precision of reconstruction based on the condensed representation (Peleato 2022). Therefore, an NN approach based on non-linear regression may reduce the dimensionality of fluorescence spectra without explicit constraints, which gradually is used for accounting for fluorescence high-dimensionality and superposition of EEM. In addition, the fluorescence parameters provided by other analytical methods such as PCA and PARAFAC can be used as the input of the ANN model to provide the prediction of DBP precursors. The application of these methods is summarized in Table 1.

The current ANN methods used for DBP analysis include self-organizing maps (SOMs), autoencoder NN and convolutional neural networks (CNNs). SOM is an unsupervised classification algorithm and two-layered ANN, which could

**Table 1** | The principle and drawbacks of different data analysis methods for fluorescence characterization of DBP precursors

Method	Principle	Drawbacks	Critical references/tutorial
Peak picking		<ul style="list-style-type: none"> <li>• Peak shift</li> <li>• Fluorescence quenching</li> </ul>	Coble (1996), Hao <i>et al.</i> (2012a)
FRI	Mathematical integration	<ul style="list-style-type: none"> <li>• Fluorescence overlapping</li> <li>• Non-linear relationship between the component</li> <li>• Concentration and fluorescence intensity</li> </ul>	Chen <i>et al.</i> (2003), Li <i>et al.</i> (2020)
PCA	Alteration of the linear space	<ul style="list-style-type: none"> <li>• Discarding information regarding the three-way structure of the data</li> <li>• Difficult to explain the properties of PC</li> </ul>	Bridgeman <i>et al.</i> (2011), Stedmon <i>et al.</i> (2003)
PARAFAC	Least squares method	<ul style="list-style-type: none"> <li>• High correlation between components separated</li> <li>• Neglections in low concentration components</li> </ul>	Murphy <i>et al.</i> (2013), Peleato & Andrews (2015), Stedmon & Bro (2008)
SOMs	Artificial neural network	<ul style="list-style-type: none"> <li>• Difficult to quantify</li> <li>• High requirement of the raw EEM dataset</li> </ul>	Bieroza <i>et al.</i> (2009), Li <i>et al.</i> (2020)
Autoencoder neural network	Artificial neural network	<ul style="list-style-type: none"> <li>• Difficult to explain components</li> </ul>	Peleato <i>et al.</i> (2018)
CNNs	Artificial neural network	<ul style="list-style-type: none"> <li>• The difference of analysis for single DBP</li> </ul>	Peleato (2022)

provide dominant fluorescence features and the relationship between the sample distribution and the specific excitation-emission wavelengths. The main fluorophores and comparison of relative concentrations of DOM gained by SOMs could provide a reference for the source of DBP precursors (Bieroza *et al.* 2009). Autoencoder NN could obtain the lower dimensional variables representing the characteristics of fluorescence data and use the obtained variables to realize the prediction of the formation of DBP (Peleato *et al.* 2018). Peleato (2022) found that the use of CNNs can significantly improve the accuracy of prediction for all DBP species and the use of heat maps can identify spectral regions associated with DBP precursors without relying on complex dimensionality reduction.

## 4. CHARACTERIZATION OF DBP PRECURSORS FROM DIFFERENT SOURCES

### 4.1. The analysis of DBP precursors in NOM

The most common components in NOM like humic and fulvic acids generally originate from the prolonged degradation of structural polymers lacking nitrogen, like lignin and cellulose, which serve as C-DBP precursors, particularly THMs and HAAs (Shah & Mitch 2012). Therefore, most research has correlated the fluorescence parameters representing humic and fulvic acids with C-DBP formation potential (C-DBPFP). Previous research found that C-DBPFP was more closely associated with the maximum fluorescence intensity of fulvic-like and humic-like components compared to tyrosine-like or tryptophan-like components (Watson *et al.* 2018; Jutaporn *et al.* 2021; Wang *et al.* 2021b; Xu *et al.* 2021). In addition, stronger correlations were also observed between the reduction of C-DBPFP and the removal of humic-like component rather than the protein-like components (Jutaporn *et al.* 2020; Wang *et al.* 2021b). However, both humic-like and protein-like components were used as precursors of THM, thus the correlation between the sum of fluorescence intensity of the two components and THM formation potential (THMFP) was stronger than fluorescence intensity of the single component (Wang *et al.* 2021a). In addition, microbial humic-like substances were also the important N-DBP precursors shown by the higher correlation between dichloroacetonitrile formation potential (DCAN-FP) and microbial humic-like components (Watson *et al.* 2018; Li *et al.* 2021a, 2021b).

Amino acids and protein-like components, accounting for 20–40% in NOM, are also related to N-DBP formation potential (N-DBPFP). Some research found that maximum fluorescence intensity from amino acid-like and protein-like components showed a significant and high correlation with HAN formation potential (HANFP) and NDMA formation potential (NDMAFP) (Yang *et al.* 2008, 2015a, 2015b; Jutaporn *et al.* 2020). However, it is worth noting that humic-like components

sometimes can show a higher correlation with HANFP than amino acid-like or protein-like components, indicating the universality of the sources of HAN precursors (Watson *et al.* 2018; Li *et al.* 2021a, 2021b). In contrast, amino acid-like and protein-like components are the more effective indicators for detecting NDMA precursors than HAN precursors in some polluted surface water (Yang *et al.* 2015a, 2015b). In addition to the correlation with a class of total DBP, the correlation between different halogen substituted DBPs and fluorescent components was related to the amount of substituted bromine. The bromide ion can be oxidized to hypobromous acid (HOBr) competing with free chlorine to react with DOM, therefore, some research found that chlorine substituted DBP had a positive correlation with the fluorescence parameters, but gradually became a negative correlation with the increase of the amount of substituted bromine (Watson *et al.* 2018; Li *et al.* 2021a, 2021b). Jutaporn *et al.* (2021) also found that the presence of bromide ions in water will weaken the predictive power of organic surrogate parameters, indicating that the correlations from fluorescent DOM fractions should be used with caution. In addition, the NOM in surface water is very vulnerable to seasonal climate changes, and the formation of DBP also fluctuates greatly under its influence. Li *et al.* (2021a, 2021b) found that the enhanced microbial activity in autumn resulted in the higher concentrations of C-DBP precursors and the increased discharges of organic matter from industrial and municipal wastewater in autumn brought the higher concentrations of N-DBP precursors, which resulted in non-significant correlation between fluorescence components and THMFP for the overall data for one year. Yang *et al.* (2015a, 2015b) also found that the relationship between THMFP and humic-like components was much strengthened by examining separately for each month compared with the overall data for one year because of the exclusion of the temporal variations in the chemical composition of DOM. In addition, compared with the untreated surface water, the reduced fluorescence intensity after primary and secondary water treatment is more conducive to express the high correlation with the DBPFPs (Watson *et al.* 2018; Li *et al.* 2021a, 2021b). Thus, the correlations between the same type of fluorescent substances and DBPs are sometimes inconsistent in different studies. The low concentration of a certain type of DBP or the low concentration of related fluorescent substances and the concentration of bromine ions in water will affect the correlation between fluorescence parameters and DBPFP (Pifer & Fairey 2012; Watson *et al.* 2018; Jutaporn *et al.* 2021; Li *et al.* 2021a, 2021b; Wang *et al.* 2021b; Xu *et al.* 2021). Several representative studies are summarized in Table 2 and Supplementary material, Table S2.

#### 4.2. The analysis of DBP precursors in AOM

Different from terrestrial NOM precursors that are highly aromatic and more hydrophobic, AOM produced by algal cells mainly consists of low aromatic and high hydrophilic components with high nitrogenous content, which are the important sources of C-DBP and N-DBP precursors (Hua & Reckhow 2007; Huang *et al.* 2009). The molecular weight (MW) distribution of AOM is mainly distributed in a range from <1 to >100 kDa and the hydrophilic part with less aromatic content usually has a smaller MW, which serves as the precursor having relatively high formation potential for both C-DBPs and N-DBPs (Fang *et al.* 2010b; Hua *et al.* 2019). Unlike the UV absorbance responding poorly to AOM samples, EEM has been gradually used to characterize DBP precursors in AOM to obtain more comprehensive information (Hua *et al.* 2018).

Different from NOM that mainly contain fulvic acid-like fluorescence and humic acid-like fluorescence, protein-like and amino acid-like fluorophores accounted for a larger proportion of AOM, which had stronger correlation with N-DBPFP and C-DBPFP (Yang *et al.* 2011; Chen *et al.* 2017a, 2017b; Ma *et al.* 2018). Previous research mainly focused on two types of samples including organic matter extracted from cultured algal cells and algal-rich natural water. EEM can distinguish the source of fluorophores from algal-rich natural water and analyze their impact on the formation of DBP. Visentin *et al.* (2020) found that SMP-like and aromatic protein-like components produced by algae growth had stronger correlation with THM and HAA compared with humic acid-like fluorophores from nature water. The DBP precursors of cultured algae derived organics are mainly determined by analyzing the types of main fluorescent substances and DBPFP at different algae growth stages. AOM-containing organic nitrogen-like SMP-like and aromatic protein-like components will react with chlorine to produce organic chloramine, a crucial middle intermediate that promotes the formation of N-DBPs like NDMA and HAN (Zhang *et al.* 2016; Liu *et al.* 2022). It is worth noting that the release of extracellular protein in exponential phase and stationary phase may result in the increase of HANs formation (Yang *et al.* 2011; Zhang *et al.* 2016). In addition, the formation of DBPs during the chlorination process was studied in some research to investigate the effects of Br<sup>-</sup> concentrations, higher concentrations and bromine incorporation factor (BIF) of total DBPs including THMs, HANs, and HNMs were observed in the presence of Br<sup>-</sup> because the substitution reaction efficiency of HOBr/OBr<sup>-</sup> with the fluorescent precursors was higher than that of HOCl/OCl<sup>-</sup> (Yang *et al.* 2011; Zhang *et al.* 2016; Chen *et al.* 2017a, 2017b).

**Table 2** | Applications of EEM for analyzing the NOM from different source waters and various DBPs

Source water of NOM	Fluorescence measurement method	Main fluorescent substances	Correlation analysis and key conclusion	Reference
Huangpu River, China	PARAFAC	Tyrosine-like Tryptophan-like Terrestrial humic-like Microbial humic-like	<ul style="list-style-type: none"> <li>The spatio-temporal variations of DOM resulted in the insignificant correlations for THMFP</li> <li>The level of bromide would influence the correlation for DBP with bromine substituted</li> <li>Microbial humic-like components were the important N-DBPs precursors</li> </ul>	Li <i>et al.</i> (2021a, 2021b)
Dongjiang River, China Roosevelt lake, USA Suwannee River, USA	FRI	Tryptophan-like SMP-like	<ul style="list-style-type: none"> <li>The EEM volume in tryptophan-like and SMP-like (<math>\Phi</math>II + IV) showed relationships with the formation of 1,1-DCP, DCAA, chloroform and DCAN</li> <li>The negative relationships between <math>\Phi</math>II + IV and yields of TOX may be due to the formation of organic chloramines</li> </ul>	Yang <i>et al.</i> (2008)
Missouri Lake, USA	PARAFAC	Terrestrial humic-like	<ul style="list-style-type: none"> <li>Terrestrial humic-like components were better indicators for predicting THMFP than SUVA</li> </ul>	Hua <i>et al.</i> (2010)
Suwannee River, USA	Picking peak	Humic-like Tyrosine-like Tryptophan-like	<ul style="list-style-type: none"> <li>Correcting the fluorescence intensity of a protein-like component can enhance the accuracy of THM prediction</li> </ul>	Saipetch & Yoshimura (2019)
Iowa River, USA	FRI	Five regions difference	<ul style="list-style-type: none"> <li>Compared to intensity, DBP was more closely linked to changes in cumulative regional intensity of EEM than intensity</li> <li>Chlorine consumption was added to the model to provide better predictive power for DBP</li> </ul>	Johnstone & Miller (2009)
Manas River, China	PARAFAC	Terrestrial humic-like Tryptophan-like	<ul style="list-style-type: none"> <li>Humic-like and protein-like fluorophores were important THMs precursors</li> <li>The correlation between the sum of humic-like and tryptophan-like and THMFP was more stable and accurate than that of SUVA for different months</li> </ul>	Wang <i>et al.</i> (2021a)
Northern China reservoir	PARAFAC	Fulvic-like and humic-like UV/visible humic-like Ubiquitous soil fulvic-like	<ul style="list-style-type: none"> <li>The yields of THMFP and TCAA were best correlated with humic-like components</li> <li>The accumulation of humic acid in autumn and winter resulted in the higher DBPFP</li> </ul>	Xu <i>et al.</i> (2021)
DWTPs from South Carolina, USA	PARAFAC	Fulvic acids-like Humic-like Tryptophan-like	<ul style="list-style-type: none"> <li>Humic-like and tryptophan-like components were important parameters for evaluating THM and NDMA respectively</li> <li>The correlation of a single month is higher than that of the entire season and year</li> </ul>	Yang <i>et al.</i> (2015a, 2015b)
DWTPs from Shanghai (China)	PARAFAC	Tryptophan-like Protein-bound-like Tyrosine-like Humic-like	<ul style="list-style-type: none"> <li>The reduction of C-DBPFP had a stronger correlation with humic-like component</li> <li>The correlation between THM and protein-like components improved with the increase of substituted bromine</li> </ul>	Wang <i>et al.</i> (2021b)
Lu Jhu Reservoir, Southern Taiwan	PARAFAC	Fulvic acid-like Humic-like Humic-like	<ul style="list-style-type: none"> <li>Humic-like components were the important precursors of THM and HAA</li> <li>The formation of THMs and HAAs could be primarily attributed to humic acid-like components</li> </ul>	Hidayah <i>et al.</i> (2017)

(Continued.)



Table 2 | Continued

Source water of NOM	Fluorescence measurement method	Main fluorescent substances	Correlation analysis and key conclusion	Reference
Chapel Hill DWTP, USA	PARAFAC	Anthropogenic humic-like Terrestrial humic-like Protein-like	<ul style="list-style-type: none"> <li>Fluorescence parameters were better indicators for evaluating DBPFP from different water sources than DOC and SUVA</li> </ul>	Jutaporn <i>et al.</i> (2020)
Pong River, reservoir rainwater, Thailand	PARAFAC	Microbial humic-like	<ul style="list-style-type: none"> <li>Anthropogenic and terrestrial humic-like components were strongly correlated to long-term THM formation</li> <li>The concentration of Br<sup>-</sup> rather than organic precursors concentration influenced the distribution of THM species</li> </ul>	Jutaporn <i>et al.</i> (2021)
Suwannee River, USA	PARAFAC	Terrestrial humic-like Anthropogenic humic-like Protein-like	<ul style="list-style-type: none"> <li>The correlation between humic-like components and DBPFP was stronger than that of DOC, UV254 or protein-like components</li> </ul>	Watson <i>et al.</i> (2018)
Otonabee River, Ontario, Canada	PARAFAC	Terrestrial humic-like	<ul style="list-style-type: none"> <li>Humic-like components were moderately related to the formation of MX</li> <li>Combined analysis with LC-OCD suggested that polysaccharides may be precursors of MX</li> </ul>	Peleato <i>et al.</i> (2016)

DWTP, drinking water treatment plants; DCAN, dichloroacetonitrile; DCAA, dichloroacetic acid; TOX, total organic halogen; TCM, trichloromethane; TCAA, trichloroacetic acid; CH, chloral hydrate; NDMA, N-nitrosodimethylamine; HK, haloketones; 1,1-DCP, 1,1-dichloropropanone; 1,1,1-TCP, 1,1,1-trichloropropanone; BDCM, bromodichloromethane; DBCM, dibromochloromethane; MX, halofuranones.

The differences of DOM composition in extracellular organic matter (EOM) and intracellular organic matter (IOM) will also result in the differences in the change of fluorescence intensity and DBPFPs under different chlorine/chloramine doses. Previous studies have reported that the fluorescence intensity of EOM and IOM was mainly attributed to the SMP-like component, which could be a more significant source of NDMA than humic acid-like component, thus, the higher proportion of SMP-like region of EOM led to more NDMA formation and sustained response with increasing chlorine dose (Liu *et al.* 2022). However, another study indicated that the higher organic nitrogen concentrations in IOM were more conducive to the formation of haloacetaldehydes (HALs) and HANs since chlorination of organic nitrogen including free amino acids and aliphatic amines was known to produce HANs and HALs (Fang *et al.* 2010b; Yang *et al.* 2010). The selection of different disinfectant types also has a great impact on the formation of DBP, which may become an important variable in the correlation analysis between fluorescence parameters and DBPFP. Firstly, the concentration of THMs formed during chloramination decreased significantly due to the lower oxidation capacity, whereas the formation potentials of CH, 1,1-DCP, and 1,1,1-TCP increased significantly without the subsequent reactions (Fang *et al.* 2010a; Zhang *et al.* 2016). Secondly, previous studies indicated that both monochloramine and organic nitrogenous compounds contributed to the nitrogen in N-DBPs such as HAN and NDMA (Fang *et al.* 2010b; Yang *et al.* 2011; Liu *et al.* 2022). In addition, the facilitation of bromide on the formation of DBPs is more significant during the chloramination processing (Zhang *et al.* 2016). A few of the studies are summarized in Table 3 and Supplementary material, Table S3.

### 4.3. The analysis of DBP precursors in EfOM

Domestic wastewater from human excreta and other wastes is the source of high dissolved organic nitrogen (DON) and DOC content including proteins and carbohydrates, which usually account for more than 50% of the organics in the raw sewage. Although the biological treatment in WWTPs appeared to be capable of removing some of the DON that could potentially form a nitrogenous class of DBPs, EfOM still had higher DON and DOC contents than NOM in natural water due to some degradation by-products (Krasner *et al.* 2009; Huang *et al.* 2012). In addition, SMPs from bacterial exudates are composed of macromolecules and cellular debris that contain protein (nitrogen-enriched) and polysaccharides, which also serve as the precursors of some N-DBPs like NDMA and HANs (Krasner *et al.* 2009; Shah & Mitch 2012).

**Table 3** | Applications of EEM for analyzing the AOM from different algal sources and various DBPs

Algal sources	Fluorescence measurement method	Main fluorescent substances	Correlation analysis and key conclusion	Reference
Microcystis aeruginosa	FRI	SMP-like	<ul style="list-style-type: none"> <li>The SMP-like components and DBPFP of IOM are higher than those of EOM</li> <li>The fluorophores and DBPFP of EOM and IOM are inconsistent at different growth stages</li> </ul>	Chen <i>et al.</i> (2017a, 2017b)
Microcystis aeruginosa	PARAFAC	Tryptophan-like Amino acid-like Humic-like Fulvic-like	<ul style="list-style-type: none"> <li>Amino acid-like components show a good correlation with THMFP and HANFP</li> <li>The high correlation between BIX and DBPFP indicated the importance of microbial AOM</li> </ul>	Ma <i>et al.</i> (2018)
Cyanobacteria-impacted lakes	PARAFAC	SMP-like Aromatic protein-like	<ul style="list-style-type: none"> <li>Microbial SMP-like and aromatic protein-like components had the highest correlation with THMFP</li> </ul>	Visentin <i>et al.</i> (2020)
Microcystis aeruginosa, Chlorella vulgaris	FRI	SMP-like Aromatic protein-like	<ul style="list-style-type: none"> <li>The proportion of aromatic protein-like components exceeds 60% at all growth stages</li> <li>Bromide can lead to higher DBPFP</li> </ul>	Yang <i>et al.</i> (2011)
Microcystis aeruginosa	FRI	SMP-like Humic-like	<ul style="list-style-type: none"> <li>SMP-like components are the main substances in AOM and more important NDMA precursors than humic-like</li> <li>SMP-like components were more likely to form NDMA during chlorination than chloramination</li> </ul>	Liu <i>et al.</i> (2022)
Cyanobacteria-impacted river	Peak picking	Tryptophan-like Low MW amino acids-like	<ul style="list-style-type: none"> <li>The highest degree of linearity was observed between the three DBPFPs and tryptophan-like components</li> <li>Tryptophan-like components were more likely to be included in the organic matter of 1–700 Da</li> </ul>	Park <i>et al.</i> (2019)
Chlorella sp. HQ	FRI	Tyrosine-like Tryptophan-like SMP-like	<ul style="list-style-type: none"> <li>SMP-like and aromatic protein-like components were the main DBP precursors</li> </ul>	Liu <i>et al.</i> (2017)
Microcystis aeruginosa	FRI Peak picking	Humic-like Protein-like SMP-like	<ul style="list-style-type: none"> <li>Humic-like and protein-like components were most vulnerable to UV treatment, and were most closely related to the formation of UV/Cl induced DBP</li> </ul>	Chen <i>et al.</i> (2018)
Microcystis aeruginosa	Peak picking	Organic nitrogen-like Organic carbon-like	<ul style="list-style-type: none"> <li>The high concentration of org-N in AOM led to the formation of DCA, CH, DCAN, and CNCI</li> <li>The formation of TCNM involved reactions between nitrite and subsequent humic acids</li> </ul>	Fang <i>et al.</i> (2010b)

TCNM, trichloronitromethane; HNMs, halonitromethanes; CNCI, cyanogen chloride; BIX, biological factor; DCA, dichloroacetaldehyde; org-N, organic nitrogen.

Different from protein that can easily be biologically treated, humic acid-like and fulvic acid-like substances were easy to pass through the biological treatment process and were dominant on the spectrogram of the effluent sample due to their non-biodegradable property (Wu *et al.* 2013; Liu *et al.* 2016). However, compared with NOM mainly consisting of humic-like substances in surface water, the proportion of protein-like materials and anthropogenic humic-like DOM in EfOM were higher than NOM, which may become DBP precursors (Cohen *et al.* 2014; Jutaporn *et al.* 2020). During the process of chlorine and chloramine disinfection, humic-like compounds in EfOM usually showed a higher correlation with THM because of the presence of a large number of electron-rich reactive sites that can be easily oxidized (Tungsudjawong *et al.* 2018; Ike *et al.* 2019; Kiattisaksiri *et al.* 2020), while the SMP-like fluorophores in EfOM had the lower reactivity with chlorine than humic-like fluorophores, which resulted in lower DBP yields despite the higher organic content in the effluent (Jutaporn *et al.* 2020; Kiattisaksiri *et al.* 2020). However, the formation of some N-DBPs, including HAN and NDMA, also shows a stronger correlation with the fluorescence parameter of microbial derived proteins or amino acids. Roccaro *et al.* (2020) found that protein-like materials were correlated with the NDMAFP and specific NDMA precursors. Moreover, the reduction of selected EEM peaks

was also correlated with the removal of NDMA precursors. *Kiattisaksiri et al. (2020)* also found that SMP-like peaks showed relatively strong correlation with trichloronitromethane (TCNM) yield compared with other components.

Numerous efforts have been made to understand the main sources of various DBP precursors in EfOM, and some works have tried to link the fractions of DOM in municipal WWTPs gained by resin isolation techniques with the characterization of organics by EEM. *Han & Ma (2012)* found that the more fulvic acid-like and humic acid-like components in the fluorescence spectrogram of hydrophilic acids (HIA) and hydrophobic acids (HOA) fractions were considered to be the main reason for the high generation of THM, while aromatic amino acid-like and SMP-like materials were also important DBP precursors in HOA fraction. In addition, some research has analyzed the main sources of DBP precursors by comparing the DBP formation and main fluorescent components of different fractionation fractions. For instance, *Zhang et al. (2009)* found more aromatic proteins and higher THMFP and HAAFP from HOA fractions, which indicated that aromatic proteins were more responsible for the formation of DBPs than fulvic acids. *Wu et al. (2013)* found that the HOA seemed to have higher THMFP than the hydrophilic neutrals (HON) due to the additional protein-like material. In addition, some research also found that the presence of free or combined aromatic amino acids in the HOA fraction may result in the production of highly genotoxic DBPs during the chlorination of wastewater with high levels of ammonia nitrogen (*Wang et al. 2007; Wu et al. 2013*). Ozone is one of the commonly used disinfectants in the treatment of EfOM (*Du et al. 2020*), but DBPs formed from ozonation disinfection have gradually been concerned in wastewater treatment (*Wert et al. 2008; Liu et al. 2015*). When using ozone disinfection, the changes of integrated fluorescence were applied to establish predictive relationships with different DBPs including bromate and aldehydes and carboxylic acids (ACAs). In addition, *Liu et al. (2015)* achieved a good prediction of the formation of ACA by using relative changes of integrated fluorescence in different peak regions. The removal of total fluorescence was also found to be correlated with the formation of NDMA during ozonation, with a higher regression slope observed in wastewater with higher concentrations of NDMA precursors and TN (*Sgroi et al. 2016*). A few of the studies are summarized in [Table 4](#) and Supplementary material, Table S4.

#### 4.4. The analysis of DBP precursors in other organic sources

In addition to the direct study on DOM in surface water, the original DOM formed by the decay of plants is increasingly recognized as an important source of DBP precursors in watersheds (*Mikkelsen et al. 2013*). During the rainy period, the decaying litter and the upper soil horizons in the surface of the watersheds will leach organic matter and inflow into surface water (*Palmer et al. 2001; Ritson et al. 2014*). The quantity and quality of DOM in leachates from decaying litter composed of different types of plants may affect the formation potential and toxicity potency of DBPs of various species (*Reckhow et al. 2004; Jian et al. 2016*). In addition, the chemical composition of DOM in leachates can also be affected by environmental conditions including sunlight, microbial activity, wildfire combustion and anthropogenic activity, resulting in the changes of DBP formation (*Majidzadeh et al. 2015; Lee et al. 2019*). Plant litter is composed of complex mixtures of organic components, including lignin, aliphatic biopolymers and amino sugars having a higher nitrogen content, which are considered the major precursors of C-DBPs and N-DBPs in drinking water disinfection (*Kalbitz et al. 2006; Pellerin et al. 2010; Chow et al. 2011; Jian et al. 2016*). Many studies have applied EEM to characterize the organic matter released from plant litter to explore the types of DBP precursors.

The organic matter leached from plant litter (LLOM) is mainly composed of humic-like and protein-like fluorescent components. Consequently, this index of sole humic or protein fluorescence may not give an accurate picture of DOC characteristic. When both humic and protein-like fluorescence were considered, *Ritson et al. (2014)* found that the ratio of peak C to peak T was correlated with DOC removal efficiency via coagulation, which can provide a reference for the formation of DBP after coagulation. Consistent with surface water, since the formation of C-DBPs including THM and HAA dominated, the humification index (HIX) and humic-like fluorescence parameters could well reflect different characteristics of the total DBP precursors from soil and litter leaf sources (*Lee et al. 2019*). However, different from surface water, protein-like fluorescence from LLOM had a higher proportion than NOM from surface water, resulting in lower C-DBP like THM and higher N-DBP like DCAN and TCNM (*Jian et al. 2016*). In addition to the vegetation type, litter decomposition stage and leaf age also affect the composition of LLOM because of the role of natural processes such as photolysis and microbial biodegradation. The amino acids and proteins as labile materials were preferentially degraded during the initial stages of exposure in the field, while the remaining humic-like materials generated at first and then degraded under solar exposure and biodegradation, which resulted in the reduction of total concentrations of THM, CH, and TCNM from aged leaves (*Chow et al. 2011; Cuss & Gueguen 2015; Jian et al. 2016*).

**Table 4** | Applications of EEM for analyzing the EfOM from different biological treatment and various DBPs

Biological treatment process	Fluorescence measurement method	Main Fluorescent substances	Correlation analysis and key conclusion	Reference
Membrane bioreactor	FRI Peak picking	Protein-like Fulvic-like Humic-like Aromatic protein-like peek	<ul style="list-style-type: none"> <li>The difference in fluorescence integral of humic acid and fulvic acid-like regions was strongly correlated with THMFP and HANFP after chlorine and chloramine</li> </ul>	Ma <i>et al.</i> (2016)
Membrane bioreactor	FRI Peak picking	Aromatic protein-like SMP-like	<ul style="list-style-type: none"> <li>Aromatic protein-like components were associated with overall NDMAFP and specific NDMA precursors (eg., erythromycin, azithromycin, clarithromycin, venlafaxine)</li> </ul>	Roccaro <i>et al.</i> (2020)
Aeration tank	FRI	Tryptophan-like Amino acid-like Humic-like Fulvic-like	<ul style="list-style-type: none"> <li>Relative changes of total integrated EEM fluorescence were associated with ozone by-products (eg., aldehydes and carboxylic acids)</li> </ul>	Liu <i>et al.</i> (2015)
Sequencing batch reactor	Peak picking	Humic-like SMP-like	<ul style="list-style-type: none"> <li>Humic-like components were strongly correlated with THMFP while SMP-like was strongly correlated with TCNM yields</li> </ul>	Wang <i>et al.</i> (2018)
Four WWTPs	FRI	Fulvic acid-like Humic acid-like SMP-like	<ul style="list-style-type: none"> <li>High proportion of fulvic-like and humic-like in HIA fractions and aromatic protein-like and SMP-like in HOA fractions resulted in the formation of THM</li> </ul>	Han & Ma (2012)
Activated sludge treatment	Peak picking	Fulvic-like Humic-like Aromatic protein-like	<ul style="list-style-type: none"> <li>The DBPFP of HOA fractions exceeded HIN due to the high proportion of aromatic protein-like component</li> </ul>	Zhang <i>et al.</i> (2009)
Four WWTPs	FRI	Total fluorescence	<ul style="list-style-type: none"> <li>The removal of total fluorescence was related to the formation of NDMA during ozone oxidation</li> <li>The regression slope of predictive equation was higher in wastewater with higher NDMA precursor concentration</li> </ul>	Sgroi <i>et al.</i> (2016)
Four WWTPs	Peak picking	Tyrosine-like Tryptophan-like SMP-like	<ul style="list-style-type: none"> <li>The ratio of intensity at Ex/Em of 257/277, calculated by dividing the secondary effluent sample by the finished effluent sample, can be used to predict the impact of oxidative treatment on the concentrations of TONO precursors</li> </ul>	Needham <i>et al.</i> (2017)
Membrane bioreactor	FRI Peak picking	Humic-like SMP-like Aromatic protein-like	<ul style="list-style-type: none"> <li>The DOM in the PAC/MBR effluent had a higher composition of aromatic protein-like substances, which led to the reduction of brominated THMs formation and the increase of total THM formation</li> </ul>	Ma <i>et al.</i> (2014)
Four WWTPs	PARAFAC	Tyrosine-like Tryptophan-like Fulvic acid-like	<ul style="list-style-type: none"> <li>Tyrosine-like, tryptophan-like and fulvic acid-like components were correlated with DCAN-FP and BCAN-FP</li> <li>The sunlight photolysis of tryptophan-like and fulvic acid-like components led to a decrease in DCAN-FP and BCAN-FP, and BCAN-FP is more easily reduced than DCAN-FP</li> </ul>	Xu <i>et al.</i> (2020)
Oxidation ditch	Peak picking	Tyrosine-like Tryptophan-like Microbial humic-like	<ul style="list-style-type: none"> <li>Higher microbial humic-like component in HOA and HIN fractions had a high THMFP</li> </ul>	Wu <i>et al.</i> (2013)
Activated sludge process	FRI	Total fluorescence	<ul style="list-style-type: none"> <li>Bromate formation had an exponential relationship with the decrease in total fluorescence (TF)</li> <li>When the decrease in TF exceeded these thresholds, a rapid increase in the formation of bromate can be observed</li> </ul>	Ruffino <i>et al.</i> (2020)

Abbreviations: TONO, total N-nitrosamine; AEA, anti-estrogenic activity.

Due to the occurrence of wildfire events, the changes of organic components of different vegetation types after wildfire combustion were also noticed. Previous research has reported that thermal effects of wildfire on DOM in watersheds may reduce the coagulation efficiency of DOM and increase the DOM reactivity to yield toxic N-DBPs (Cawley *et al.* 2017; Cai *et al.* 2020). The relationship between fluorescence properties of extractable organic matter affected by wildfire and DBPFP was inconsistent in different literatures because of the influence of temperature conditions and vegetation types. Generally, the proportion of tyrosine-like and humic acid-like FRI showed a decreasing trend after wildfires, which indicated the general reduction of the reactivity to form THM (Majidzadeh *et al.* 2015; Wang *et al.* 2015; Uzun *et al.* 2020a, 2020b). In addition, many studies showed that the reactivity of LLOM to form HAN had been enhanced in most wildfire tests, and some research indicated that the polymerization of N into a condensed aromatic structure, resulting in the formation of dissolved black nitrogen compounds, is likely a major factor in the increased reactivity of HAN formation (Knicker 2007; Wang *et al.* 2015; Hohner *et al.* 2016; Cawley *et al.* 2017). According to the change of fluorescence spectrum, the increase of aromatic protein-like fluorescence and SMP-like fluorescence in some literatures can also explain the increase of HAN formation (Wang *et al.* 2015; Uzun *et al.* 2020a). Wang *et al.* (2015) also found the higher reactive NDMA precursors at moderate burning temperatures (200 – 500 °C) and the subsequent degradation of NDMA precursors in higher levels burning (>510 °C). At the same time, it is worth noting that under the influence of different regions, the increase of bromide ions after combustion in some coastal areas will lead to the increase of the proportion of brominated DBP (Wang *et al.* 2015; Uzun *et al.* 2020a). Different from wildfires, Uzun *et al.* (2020b) conducted experiments on specified fires and found that low-intensity and low severity specified fires can consume humic-like substances and SMP-like fluorescent substances, thus reducing the concentration of DBP precursors and not leading to the formation of additional N-DBPs and brominated THMs and HAAs with higher toxicity.

Due to the harm caused by some wildfires, considering the similarity of biochar- and wildfire ash-derived DOM experienced pyrolysis, some studies also focused on the potential hazards of biochar produced by pyrolysis as a soil additive for agricultural management (Lee *et al.* 2018; Cai *et al.* 2020). A laboratory-scale study found that terrestrial or ubiquitous humic-like C1/fulvic-like C2 ratios exhibited a significant positive correlation with specific THMFP, suggesting that condensed aromatic structures released from sludge, corn, and rice biochars may serve as significant precursors for the formation of DBPs (Lee *et al.* 2018). However, Cai *et al.* (2020) studied the two long-term (5 and 11 years) biochar addition experimental farmlands, and the results showed that an increase in aromatic DOM did not result in an increase in the reactivity of DOM in forming DBPs and the toxicity levels of chlorinating soil-derived DOM. In addition to the LLOM from natural watersheds, some DOM released by particles from urban pipelines and streets are more likely to have higher DBPFP because of the humic-like substances having higher degrees of condensation (Lee *et al.* 2021). In addition, atmospheric particulate matter (PM)-derived DOM were composed of aromatic protein-like and SMP-like fluorescent substances, which contributed to the formation of a variety of DBPs and should not be ignored (Lee *et al.* 2021). A few of the studies are summarized in Table 5 and Supplementary material, Table S5. The application of EEMs in correlation between DBPFP and DOM in different water sources is also briefly introduced in Figure 2.

## 5. FUTURE RESEARCH NEEDS OF EEM FOR DBP STUDIES

### 5.1. Further expansion of fluorescence analysis methods

The application of EEM in DBP precursors is mostly limited to establish the correlation between fluorescence intensity and DBPFP. Some unexploited fluorescence parameters like the apparent fluorescence quantum yield, stokes shift and excited energy state could characterize the MW, hydrophilicity and chemical structure of DOM (Xiao *et al.* 2016, 2018b). Therefore, these parameters could be used to explain the distinction of DBPFP from different water sources due to tendency characteristics of different DBP precursors (Mao *et al.* 2016). In addition, common fluorescence analysis methods tend to use a single or all data points of fluorescence intensity to analyze the composition of DBP precursors. Due to the presence of data points unrelated to DBP precursors, selecting more representative DBP precursor related regions contributes to precise analysis of the precursors of different DBPs (Trueman *et al.* 2016). Marhaba *et al.* (2009) also expected to screen out the fluorescence intensity variables that best represent the variation characteristics of DBP precursors by removing the scatter and focusing on peak areas. The development of machine learning may provide a feasible approach for screening out intended data points. Some new analytical methods, such as fluorescence quotient, have been used to divide regions related to the properties of organic matter like hydrophobicity and functional behavior of DOM (Xiao *et al.* 2018a, 2018b). Thus, selecting more

**Table 5** | Applications of EEM for analyzing the DOM from other sources and various DBPs

Water sample source	Fluorescence measurement method	main related fluorescent substances	Correlation analysis and key conclusion	Reference
Postfire soil samples, Tuolumne River Watershed	FRI Peak picking	Tryptophan-like	<ul style="list-style-type: none"> <li>• Tryptophan-like components had a stronger linear correlation with specific THMFP, HAAFP and HANFP</li> <li>• NDMA had a bell shaped relationship with tryptophan-like components</li> <li>• Wildfire burning resulted in the higher tryptophan and SMP-like components</li> <li>• After wildfire burning, DOM exhibited lower reactivity in the formation of THM and HAA, but had higher reactivity in forming HAN and NDMA</li> </ul>	Wang <i>et al.</i> (2015)
Unburned and burned litter, Congaree National Park	FRI	Tyrosine-like Fulvic acid-like Humic acid-like SMP-like	<ul style="list-style-type: none"> <li>• SMP-like had a significant correlation with the formation of specific HAN</li> <li>• Wildfire burning reduced the total amount of DBP formation but increased the reaction of HAN formation</li> </ul>	Majidzadeh <i>et al.</i> (2015)
Surface peat samples, Exmoor National Park, UK	Peak picking	Tyrosine-like Humic-like	<ul style="list-style-type: none"> <li>• Fluorescence peak C/T was more related with DOC</li> </ul>	Ritson <i>et al.</i> (2014)
Soil and leaf litters, Han River basin	PARAFAC	Terrestrial humic-like Tyrosine-like Microbial humic-like	<ul style="list-style-type: none"> <li>• Total DBPFP showed a good correlation with HIX and humic-like components while HAAFP was correlated with tryptophan-like component</li> <li>• The photo-released humic-like components had high THMFP, while photo-dissolved protein-like component had high HANFP</li> </ul>	Lee <i>et al.</i> (2019)
Fresh litter and associated decomposed litter, oak woodland	Intensity ratio	Fluorescence index	<ul style="list-style-type: none"> <li>• Pine litter had significantly lower specific THMFP and higher N-DBPFP than oak and grass</li> </ul>	Chow <i>et al.</i> (2011)
Rain from Postfire area, Northern California Coastal	FRI	Tyrosine-like Tyrosine-like Fulvic-like Humic-like SMP-like	<ul style="list-style-type: none"> <li>• Wildfire caused more DOM consisting of aromatic protein-like component in the watershed in the short term</li> <li>• The increase in bromide led to long-term species transformation of THM and HAA for up to 2 years</li> <li>• Wildfire led to an increase in the concentration of NDMA precursor</li> </ul>	Uzun <i>et al.</i> (2020a)
River samples from Postfire area Cache la Poudre River	Intensity ratio	Fluorescence index	<ul style="list-style-type: none"> <li>• The increase in FI after wildfire also indicated a lower molecular weight which is usually not easily removed by traditional coagulation processes</li> <li>• In the wildfire affected area, N-DBP precursors may be enriched relative to C-DBP precursors after the rainstorm</li> </ul>	Hohner <i>et al.</i> (2016)
Foliage samples	PARAFAC	Tyrosine-like Tryptophan-like Terrestrial humic-like Microbial humic-like	<ul style="list-style-type: none"> <li>• Aromatic protein-like component was an important contributor to fluorescence DOM in fresh leaves and showed a good correlation with TCNM</li> <li>• With the increase of leaf age, the proportion of humic-like substances continued to increase, while the proportion of</li> </ul>	Jian <i>et al.</i> (2016)

(Continued.)

Table 5 | Continued

Water sample source	Fluorescence measurement method	main related fluorescent substances	Correlation analysis and key conclusion	Reference
Heated soil samples, Cache la Poudre Watershed	PARAFAC	Terrestrial humic-like Humic-like and Black nitrogen-type moieties	protein-like substances continued to decline, which resulted in the increase of THM formation and the reduction of N-DBP formation • The low-temperature (225°C) leachate forms the highest concentration of C – and N-DBP and humic-like component	Cawley <i>et al.</i> (2017)
Forest materials, Georgetown, South Carolina	FRI	Humic-like SMP-like	• Prescribed fires can significantly reduce humic-like and SMP-like components • Prescribed fires resulted in the reduction of THM and HAA formation • The additional toxic NDMA, brominated THMs and HAAs would not increase	Uzun <i>et al.</i> (2020b)
Biochar, Chuncheon, South Korea	PARAFAC	Terrestrial humic-like Microbial humic-like Tryptophan-like	• Specific THMs were positively correlated with the proportion of terrestrial humic-like components • The DOM of corn and rice biochar had a higher humic carbon structure and THMFP	Lee <i>et al.</i> (2018)
Soil samples from biochar addition	Intensity ratio	HIX FI $\beta/\alpha$	• The addition of biochar in 11 years can increase the humic and aromatic DOM but would not significantly increase additional DBP	Cai <i>et al.</i> (2020)
Surface water and six different PM samples	PARAFAC	Two terrestrial humic-like Autochthonous Tryptophan-like	• Urban-derived pollutants had higher THMFP and correlation with terrestrial humic-like components than particle from river	Lee <i>et al.</i> (2021)
PM2.5, PM10, total PM samples and Rainwater samples	FRI	Tyrosine-like Tryptophan-like SMP-like	• Aromatic protein-like and SMP-like compounds were important DBP precursors	Hou <i>et al.</i> (2018)

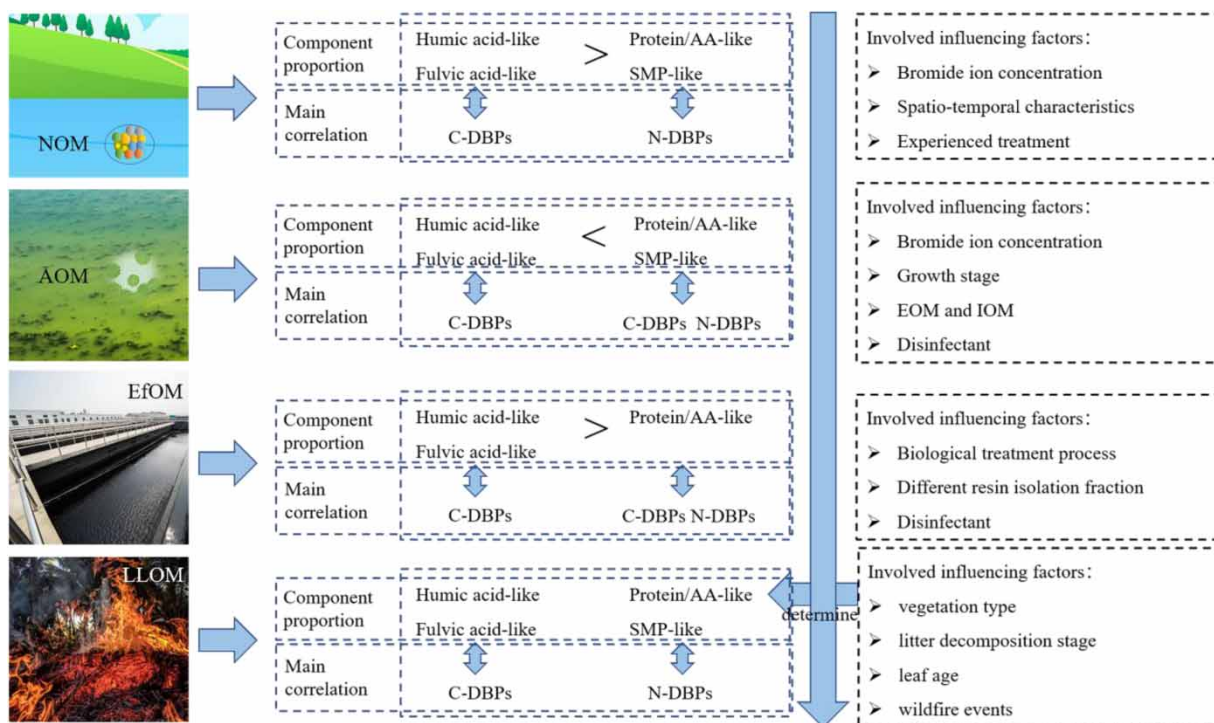
representative DBP precursor related regions on the EEM map based on some new methods like fluorescence quotient also requires further research.

## 5.2. Further expansion of identifying the precursors of emerging DBPs by EEM

Some emerging DBPs, such as iodinated THMs, HAMS, haloanisoles, chlorophenols, and halofuranones, have been found to exhibit high toxicity at extremely low concentrations (Richardson & Postigo 2016; Xie *et al.* 2016; Chen *et al.* 2017a, 2017b; Gilca *et al.* 2020). Previous studies mainly focused on the formation mechanisms and detection methods of emerging DBPs, whereas the use of three-dimensional fluorescence in analyzing potential organic precursors has rarely been considered. Potential fluorescent precursor for emerging DBPs in different water sources also requires further research for comparison with fluorescent precursors of conventional DBPs. In addition, some emerging organic micro-pollutants have been proven to serve as the precursors for many DBPs during chlorine-based disinfection processes (Shao *et al.* 2023), and some water quality parameters like NOM, temperature, pH value, and the type of ions could have an essential impact on DBPs formation during the chlorination of these micro-pollutants (Kali *et al.* 2021). Some organic micro-pollutants also exhibit fluorescence properties (Li *et al.* 2021a, 2021b), and the concentration in water was strongly correlated with specific fluorescence parameters. Thus, the fluorescence properties of micro-pollutants can be linked to the formation of DBP to expand subsequent research.

## 5.3. Further expansion of identifying by-products of other disinfectants by EEM

Disinfectants that produce organic DBPs generally include chlorine, chloramine, and ozone. Similar to ozone, the research on by-products of other oxidants mainly focused on the production of by-products caused by the oxidation of bromine ions or



**Figure 2** | Summary of the application of EEMs in correlation between DBPFP and DOM in different water sources.

iodine ions to produce hypobromic acid or hypoiodic acid (Jiang *et al.* 2016; Yang *et al.* 2019; Wang *et al.* 2020). Currently, the formation of ozone oxidation by-products like bromate and ACA can be predicted by changes in fluorescence intensity (Liu *et al.* 2015), but the research on by-products of other oxidants mainly focused on the reaction mechanism with halogen ions, without involving the analysis of EEM fluorescence spectrum (Huang *et al.* 2016; Wang *et al.* 2020). However, other oxidants like ferrate, persulfate and permanganate have been used to reduce the production of DBPs produced by chlorine, and the influence on the fluorescence properties of DOM has also been revealed in some research. Permanganate had a strong removal effect on humic-like fluorescence to achieve the removal of formation of different DBP including trichloromethane (TCM), DCAN, dichloroacetamide (DCAcAm) and TCNM (Chu *et al.* 2011). UV/H<sub>2</sub>O<sub>2</sub> could break down the fluorescent and aromatic components of DOM like fulvic-like and humic-like fluorophores and transform DOM with high MW into low MW species, which resulted in the increasing THMFP following chlorination or chloramination but the reduction of I-THMs following chlorination (Zhang *et al.* 2018). Ferrate showed the ability to remove humic-like components and thus achieve a reduction in THM formation (Li *et al.* 2021a, 2021b). Overall, the effect of oxidants on fluorescent DOM tends to be positive, which is beneficial for controlling the subsequent production of DBP. The effect of oxidants on fluorescence properties can be combined with other possible by-products to expand subsequent research.

## 6. CONCLUSIONS

The application of EEM for characterizing DBP precursors has developed for a long time and still has more research potential for some information like the apparent quantum yield and fluorescence lifetime with less use. In this review, analytical methods of EEM for characterizing DBP precursors, differences of main fluorescent components and DBP precursors in different water sources have been discussed to help researchers better use EEM for the study of DBP precursors in water. It is necessary to select appropriate fluorescence analysis methods according to different water quality conditions and analysis purposes. The application of ANNs based on non-linear regression is rarely used but has prospects for wider application in the future.

Some discussions and analyses in this paper are expected to further provide insights into the application of EEM in DBP precursors. The content and properties of fluorescent components in different source waters are different, leading to the



inconsistency of the main related DBP precursors. Therefore, it is important to use different methods to more comprehensively evaluate the correlation between DBP precursors and fluorescent components, which contribute to screening out the key fluorescent parameters related to DBP precursors.

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## AUTHOR CONTRIBUTIONS

J.H. conceptualized and wrote the original draft. R.X., R.Z., Z.W., F.J., C.Y., and R.Q. wrote, reviewed, and edited the article. W.C. supervised, wrote, reviewed, and edited the article..

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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