

Characterization and biogeochemical implications of dissolved organic matter in aquatic environments

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ABSTRACT

Dissolved organic matter (DOM) is viewed as one of the most chemically active organic substances on earth. It plays vital roles in the fate, bioavailability and toxicity of aquatic exogenous chemical species (e.g., heavy metals, organic pollutants, and nanomaterials). The characteristics of DOM such low concentrations, salt interference and complexity in aquatic environments and limitations of pretreatment for sample preparation and application of characterization techniques severely limit understanding of its nature and environmental roles. This review provides a characterization continuum of aquatic DOM, and demonstrate its biogeochemical implications, enabling in-depth insight into its nature and environmental roles. A synthesis of the effective DOM pretreatment strategies, comprising extraction and fractionation methods, and characterization techniques is presented. Additionally, the biogeochemical dynamics of aquatic DOM and its environmental implications are discussed. The findings indicate the collection of representative DOM samples from water as the first and critical step for characterizing its properties, dynamics, and environmental implications. However, various pretreatment procedures may alter DOM composition and structure, producing highly variable recoveries and even influencing its subsequent characterization. Therefore, complimentary use of various characterization techniques is highly recommended to obtain as much information on DOM as possible, as each characterization technique exhibits various advantages and limitations. Moreover, DOM could markedly change the physical and chemical properties of exogenous chemical species, influencing their transformation and mobility, and finally altering their potential bioavailability and toxicity. Several research gaps to be addressed include the impact of pretreatment on the composition and structure of aquatic DOM, molecular-level structural elucidation for DOM, and assessment of the effects of DOM dynamics on the fate, bioavailability and toxicity of exogenous chemical species.

1. Introduction

Dissolved organic matter (DOM) is a class of complex and heterogeneous mixture of various active organic species (e.g., polysaccharides, proteins, and lignin) (Aiken et al., 2011a). It is also composed of miscellaneous functional groups including aldehyde, amino, carboxyl, ester, hydroxyl, ketone, phenol, and other functional groups (Wang and Chen, 2018). Owing to the diverse organic species and abundant chemical structures, DOM is recognized as one of the most chemically active organic substances on earth.

DOM exerts enormous influences on a series of biogeochemical processes in aquatic environments (Chen et al., 2018b, 2019). DOM is involved in a spectrum of biological, physical and chemical processes such as complexation, phototransformation, and biodegradation (Dutta Majumdar et al., 2017). These DOM-mediated processes have a profound influence on the biogeochemistry of aquatic systems (Chen et al., 2019; McDonough et al., 2020). For instance, it is reported that the decomposition of DOM could deplete oxygen and produce anoxic or even anaerobic conditions in aquatic environments, leading to the deterioration of water quality and secondary pollution (Song et al., 2020).

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Lists of abbreviations

2D-COS	Two-dimensional Correlation Spectroscopy	IHSS	International Humic Substances Society
AFM	Atomic Force Microscopy	LLE	Liquid-Liquid Extraction
AOC	Assimilable Organic Carbon	MF	Membrane Filtration
APPI	Atmospheric Pressure Photoionization	NCDOM	non-chromophoric DOM
ATR	Attenuated Total Reflection	NMR	Nuclear Magnetic Resonance spectroscopy
BDOC	Biodegradable Dissolved Organic Carbon	PCA	Principal Component Analysis
CSIA	Compound-Specific Isotopes Analysis	Py-GC-MS	Pyrolysis-Gas Chromatography-Mass Spectrometry
DOC	Dissolved Organic Carbon	RO	Reverse Osmosis
DOM	Dissolved Organic Matter	RO-ED	Reverse Osmosis-Electrodialysis
DON	Dissolved Organic Nitrogen	ROS	Reactive oxygen species
EEM	Excitation-Emission Matrix	RP-HPLC	Reversed-Phase High-Performance Liquid Chromatography
EEM-PARAFAC	Excitation-Emission Matrix integrated with parallel factor analysis	POM	Particulate Organic Matter
ESI	Electrospray Ionization	PWOM	Pore Water Organic Matter
FTIR	Fourier Transform Infrared Spectroscopy	SEC	Size Exclusion Chromatography
FT-ICR MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometer	SPE	Solid-Phase Extraction
HILIC	Hydrophilic Interaction Liquid Chromatography	TOM	Total Organic Matter
HPLC	High-Performance Liquid Chromatography	UF	Ultrafiltration
		UV	Ultraviolet
		WEOM	Water Extractable Organic Matter

Moreover, as a significant available carbon source for aquatic organisms, DOM could markedly influence ecological functions in aquatic environments (Minor et al., 2014). DOM plays a crucial role in controlling the migration, transformation, distribution, bioavailability, and toxicity of exogenous chemical species (e.g., heavy metals, organic contaminants, and nanomaterials) (Artifon et al., 2019; Ishii and Boyer, 2012; Jiang et al., 2017; Yamada and Katoh, 2020). The interaction of DOM with these species may significantly alter their physicochemical properties, eventually influencing their bioavailability and toxicity to biota (Al-Reasi et al., 2011; Derrien et al., 2019a). Therefore, considering the integral roles of DOM in aquatic environments, an in-depth understanding of its nature, reactivity and environmental implications is of great importance in the field of environment and ecological chemistry (Chen et al., 2015).

A series of detailed investigation related to DOM has been carried out in the last decades and a wealth of literature is burgeoning around this theme. Fig. 1 presents the number of papers published annually, based on the Web of science core collection database using the keywords “dissolved organic matter.”

Hitherto, a battery of techniques has been developed and/or applied to characterize aquatic DOM for a thorough understanding of its properties and roles in aquatic environments (Derrien et al., 2019a; Pan et al., 2016; Reyes and Crisosto, 2016). Generally, these characterization techniques can be classified into two categories: general parameters

measurement of bulk properties (e.g., dissolved organic carbon (DOC)), ultraviolet absorbance, and fluorescence) and more sophisticated methods providing molecular structure information on DOM (e.g., Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and Nuclear magnetic resonance spectroscopy (NMR)) (Derrien et al., 2019a; Pan et al., 2016; Sandron et al., 2015). For molecular-level structure information, there is an increasing trend in the exploration of aquatic DOM using NMR and FT-ICR MS tools (Hertkorn et al., 2007, 2008, 2015; Minor et al., 2014; Zhang et al., 2019a).

Nonetheless, despite considerable progress on DOM investigation in recent years, a thorough understanding of its exact nature and environmental roles is still lacking (Derrien et al., 2019a; Minor et al., 2014; Sandron et al., 2015). One major reason relates to the characteristics of DOM in aquatic environments (Derrien et al., 2019a; Minor et al., 2014; Reyes and Crisosto, 2016). First of all, the inorganic salt concentration in waters is an influencing factor, especially in seawater (Derrien et al., 2019a). For example, halide ions (e.g., Cl^-) could notably affect the UV–Vis absorption spectra of aquatic DOM (Li and Hur, 2017). Also, the complexity and heterogeneity of DOM often make it challenging to evaluate the elemental composition and chemical structure through various characterization techniques (Chen et al., 2018b; Tran et al., 2015). Although NMR and FT-ICR MS can achieve molecular-level structural characterization of DOM (e.g., chemical bonds and empirical formulae), these characterization techniques often require a pre-treatment procedure (e.g., solid-phase extraction (SPE)) prior to instrument characterization (Minor et al., 2014; Song et al., 2020). These characteristics of DOM pose a great challenge for its characterization.

Currently, various DOM extraction methods (referring to the combination of isolation and concentration) have emerged for the isolation of DOM from aqueous solutions and increasing its concentration. The main objective of isolation protocols is to separate the organics from the inorganics since the inorganics interfere with many characterization techniques. These methods mainly including reverse osmosis, SPE and freeze-drying (Nebbioso and Piccolo, 2013; Pan et al., 2016).

Furthermore, following the extraction procedures as mentioned above, a variety of fractionation techniques have been widely utilized to reduce the complexity and heterogeneity of extracted DOM. Through fractionation procedures, the extracted DOM can be separated into individual fractions based on shared physicochemical properties (e.g., polarity and molecular weight) of DOM molecules (Pan et al., 2016;

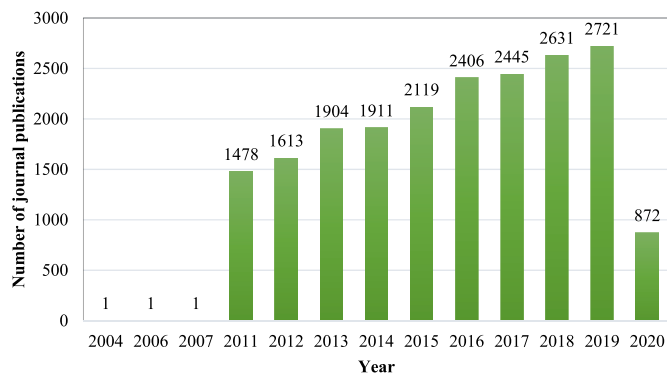


Fig. 1. Number of publications on dissolved organic matter. Data originated from the Thomson Reuters Web of Science (2020/04).

Sandron et al., 2015). Fractionation methods mainly include size exclusion chromatography, membrane filtration, resin fractionation, and high-performance liquid chromatography (HPLC) (Chen et al., 2015; Khundzhua et al., 2017). Overall, the fractionation reduces the complexity of DOM by separating the intact heterogeneous DOM into relatively homogenous fractions (He and Hur, 2015a). The complexity reduction of DOM provides great potential and opportunity to obtain a better and more reliable understanding of its chemical composition and structure (Li et al., 2016; Sandron et al., 2015). In this sense, the efficient extraction and fractionation of aquatic DOM is the premise and foundation for characterizing its properties, environmental behavior and implications (Pan et al., 2016; Reyes and Crisosto, 2016).

Improved pretreatment methods, including reverse osmosis-electrodialysis system (RO-ED), have enabled efficient and simple desalting and enrichment of DOM with high recoveries, thereby complementing subsequent characterization processes (Nebbioso and Piccolo, 2013). However, systematic information on the pretreatment methods for aquatic DOM is still limited. This review tries to offer a characterization continuum for the DOM in aquatic environments.

Moreover, environmental processes can control the biogeochemical dynamics of DOM in aquatic environments, mainly including photochemical and microbial degradation (Garcia et al., 2018; Lee et al., 2018). These processes greatly determine the chemical structure, optical properties and physicochemical properties of DOM in aquatic environments (Jiao et al., 2010). For instance, previous studies have observed the photobleaching of DOM in aquatic systems under the action of solar radiation (Fichot and Benner, 2012; Niu et al., 2014). In addition, the photodegradation of DOM decreases its molecular weight and aromaticity (Fichot and Benner, 2012; Helms et al., 2008; Moran et al., 2000; Zhang et al., 2020b). In this sense, these biogeochemical processes can significantly alter the quantity and quality of DOM in aquatic environments.

Furthermore, variations in the quantity and quality of DOM have a considerable effect on its interactive properties with exogenous chemical species (e.g., heavy metals, organic contaminants, and nanomaterials) (Aiken et al., 2011b; Wang et al., 2019). Besides, this interaction effect of DOM plays an important role in the migration, transformation, bioavailability and toxicity of these species via altering their properties (Ma and Yates, 2018; Philippe and Schumann, 2014). Improved knowledge about the effects of biogeochemical processes on the dynamics of DOM, and consequent effects on the fate, bioavailability and toxicity of exogenous chemical species is critical for the development of water treatment processes (Artifon et al., 2019; Ishii and Boyer, 2012).

Although there have been numerous studies regarding aquatic DOM in recent years, a comprehensive review related to its pretreatments, characterization, biogeochemical dynamics, and environmental implications is still scarce. To the best of our knowledge, the only relevant review was on sediment DOM instead of aquatic DOM (Chen and Hur, 2015). For aquatic environments, recent papers only reviewed or discussed part of this topic, i.e., evaluate single characterization techniques of DOM in aquatic environments (Brezinski and Gorczyca, 2019; Chen et al., 2019; Derrien et al., 2017, 2019a; Li et al., 2020a; Minor et al., 2014; Nebbioso and Piccolo, 2013, 2013, 2013; Pan et al., 2016; Sandron et al., 2015; Tran et al., 2015; Wang and Chen, 2018; Yang et al., 2015b). Few research articles also report on the interaction of DOM with individual exogenous chemical species such as heavy metals (Aiken et al., 2011b; Jiang et al., 2018a; Yamada and Katoh, 2020; Zhu et al., 2020), organic pollutants (Bai et al., 2019; He et al., 2018; Yang et al., 2020), and nanomaterials (Aiken et al., 2011b; Philippe and Schumann, 2014; Yu et al., 2018b). Hence, there is an urgent need to provide a comprehensive review that offers a characterization continuum of DOM in aquatic environments and demonstrate its biogeochemical dynamics and environmental implications.

Therefore, the ultimate goal of this review is to: 1) synthesize current knowledge on the pretreatment methods (i.e. extraction and

fractionation methods) of DOM in aquatic environments; 2) critically review current techniques and strategies for characterizing aquatic DOM; 3) discuss the biogeochemical behavior and environment implications of DOM in aquatic environments; 4) provide future perspectives and research opportunities that are needed to improve knowledge and thorough understanding of the nature, dynamics and environmental implications of aquatic DOM.

2. DOM in aquatic environments

From the operational point of view, the total organic matter (TOM) in aquatic environments can be generally categorized into two defined phases: a): particulate organic matter (POM), which is defined as organic matter that is retained on a given filter (0.45 μm); b): dissolved organic matter (DOM), organic matter fractions in water solution that can pass through 0.45 μm filter (Aiken et al., 2011a; He et al., 2016). However, it should be noted that in some literature, colloidal organic matter (sizes ranging from 1 nm to 1 μm) is also regarded as another type of organic matter (Artifon et al., 2019). Colloidal organic matter plays “bridging” roles in the transformation between POM and DOM, which can aggregate and decompose between POM and DOM phase (Derrien et al., 2019a).

DOM is composed of micro-molecular compounds (e.g., organic acid) and macromolecules (e.g., fulvic acid) with molecular weight ranging from less than 100 to over 300,000 Da (Wagoner et al., 1997). Additionally, based on their polarities, DOM can also be categorized into three fractions: hydrophobic, transphilic, and hydrophilic components. Better insight into the nature of aquatic DOM is key to an improved understanding of DOM-induced biogeochemical processes (Cai et al., 2020; Wu et al., 2020).

It is widely accepted that aquatic DOM originates from diverse sources, resulting in a complex mixture encompassing various classes of organic compounds (Hawkes et al., 2019). DOM in aquatic environments can be introduced via two major sources: either allochthonous or autochthonous (Fig. 2) (Meng et al., 2013). Autochthonous DOM is generated in-situ, originating from aquatic organisms mainly, including microorganisms, algae, plankton, and macrophytes (Derrien et al., 2019a). For instance, phytoplankton is a major source of DOM in the ocean, while other species contribute little to autochthonous DOM (Artifon et al., 2019). In freshwater lakes, the decomposition of plant litter is viewed as an important source of aquatic DOM (Song et al., 2020). The natural allochthonous DOM, introduced from outside aquatic environments, is primarily composed of organic materials that come from land (e.g., plant litter, soil, and stormwater runoff), atmosphere (e.g., rain, dust storm), and leaching via river, groundwater, and seafloor (Artifon et al., 2019).

In addition, anthropogenic activity is also an important source of allochthonous DOM such as domestic sewage, industrial wastewater, and agricultural runoff, which directly or indirectly contributes to the DOM input from human activities (Meng et al., 2013). It is reported that wastewater effluent organic matter might be a major source of DOM to receiving rivers (Wang et al., 2019).

Moreover, the source and its proportion of DOM in aquatic environments is highly variable, in that the contribution of allochthonous and/or autochthonous sources to DOM depends on a variety of factors such as nutritional status, surrounding environments, and hydraulic characteristics (Connolly et al., 2020; Goldberg et al., 2017; Hosen et al., 2018). Generally speaking, the main source of DOM in terrestrial water is allochthonous, while the major source of DOM in marine water is autochthonous (He et al., 2016). It should be noted that in artificial or natural reservoirs, autochthonous DOM can be important at some periods of the year. Seasonal variation can be an important factor governing the origin of DOM in surface water (Jiang et al., 2018b; Cárdenas et al., 2017). In summary, DOM in aquatic environments originates from various sources, which results in its complexity and heterogeneity.

The strategies extensively used to track the origins of DOM mainly

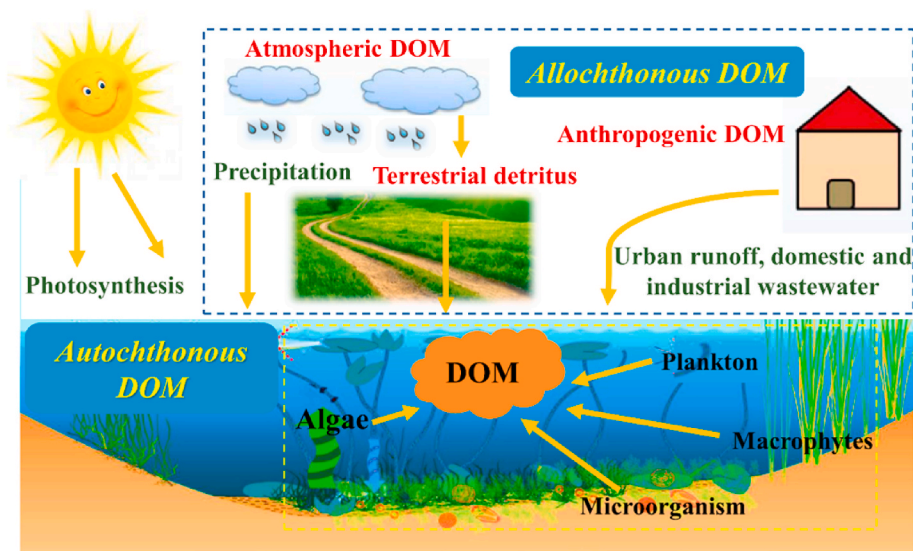


Fig. 2. Schematic diagram of DOM sources in aquatic environments.

include stable isotopes ratios (Lambert et al., 2011), lipid biomarkers (Derrien et al., 2017), compound-specific isotopes analysis (CSIA) (Schmidt et al., 2004), and spectroscopic indices (Murphy et al., 2013; Stedmon et al., 2003). Stable carbon isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) are regarded as one of the most effective methods to determine both the sources (e.g., allochthonous versus autochthonous) and associated biogeochemical processes of DOM in aquatic environment (Toming et al., 2013). Several previous studies have demonstrated the ability of stable isotope ratios to distinguish between allochthonous and autochthonous origins (Lambert et al., 2011; Toming et al., 2013).

Moreover, molecular markers could present a direct and unique link with the given DOM sources under ideal conditions. Currently, lignin-phenol (i.e., lignin), carbohydrates, proteins and lipids have been increasingly popular for identifying DOM origin. Among these, lipids have the highest potential as molecular markers for diverse DOM sources (e.g., allochthonous, autochthonous sources and anthropogenic inputs) (Zimmerman and Canuel, 2001; Parrish et al., 2000). For instance, autochthonous versus allochthonous DOM sources were successfully identified based on the ratios of long-chain (e.g., terrestrial source) to short-chain n-alkanes (e.g., aquatic/marine source) (Poerschmann et al., 2016).

Also, many optical indices derived from spectroscopic spectra are widely utilized to determine DOM sources. Their source identifying capabilities have been tested in many aquatic environments such as wastewater, rivers, groundwater, lakes, rainwater, and oceans (Hur et al., 2006; Fichot et al., 2013). Commonly used indices include the slope ratio (Helms et al., 2008), specific UV absorbance (SUVA_{254} ; Weishaar et al., 2003), fluorescence index (McKnight et al., 2001), humification index, biological index (Huguet et al., 2009), and the relative abundance of different fluorescent components or the ratios (Hur et al., 2011). Derrien et al. (2017) and Derrien et al. (2019a) have recently presented detailed and comprehensive reviews of methods for DOM origin determination and the special characteristics of DOM from certain origins.

3. DOM pretreatment

Collection of representative DOM samples is the first and most significant step in studying its biogeochemical dynamics and environmental implications (Sandron et al., 2015). The complexity and heterogeneity of DOM molecules and their low concentration in aquatic systems make their characterization challenging (Derrien et al., 2019a; Reyes and Crisosto, 2016). Through DOM pretreatment, highly

concentrated DOM samples with low salt content can be obtained, and then different techniques can be applied for DOM characterization (Reyes and Crisosto, 2016). Currently, various methods have been already proposed and used to isolate and purify DOM extracts prior to its characterization (Fig. 3). Generally, complete pretreatment comprises of three stages: 1) filtration; 2) extraction; 3) fractionation (Chen and Hur, 2015; Pan et al., 2016).

Filtration is the first step in all pretreatment procedures of aquatic DOM. In this step, 0.45 μm filter is often used to remove POM. In some literature, other pore size filters (e.g., 0.2 and 0.7 μm) are also adopted (Artifon et al., 2019; Derrien et al., 2019a; Sosa et al., 2017). Note that the material of a filter is an important consideration. For low to very low DOC water content, scientists like to avoid the use of organic filters and prefer metallic or glass fiber filters.

Following the filtration, various extraction methods are utilized to enrich DOM as well as remove salts. Moreover, it is typically necessary to fractionate extracted DOM into different compound groups based on their shared properties including molecular weight and polarity (Pan et al., 2016). The commonly used fractionation methods contain ultra-filtration, resin fractionation, size exclusion chromatography, and high-performance liquid chromatography (Pan et al., 2016; Reyes and Crisosto, 2016; Sandron et al., 2015).

The DOM fractionation procedures can help to obtain their corresponding structural information involved in individual DOM fractions. Fractionation procedure is a useful strategy to separate complex and heterogeneous DOM into relative homogeneous fractions (He and Hur, 2015a). As such, this characterization continuum is conducive to select optimal DOM pretreatment and characterization methods, enabling an improved understanding of its exact nature, dynamics and roles in aquatic systems.

3.1. Extraction methods

Extraction technologies for aquatic DOM can be categorized into three types: 1) reverse osmosis (RO), 2) solid-phase extraction (SPE), 3) freeze-drying (Broek et al., 2017; Butturini et al., 2020; Li et al., 2016).

3.1.1. Reverse osmosis

RO is generally used following a cation exchange resin (removal of Ca^{2+}) in order to limit scaling problems and this prefiltration can induce the loss of nitrogenous compounds. Nevertheless, considering that the RO system alone usually enriches the inorganic materials including salts during the concentration of DOM, coupling RO with electrodialysis is

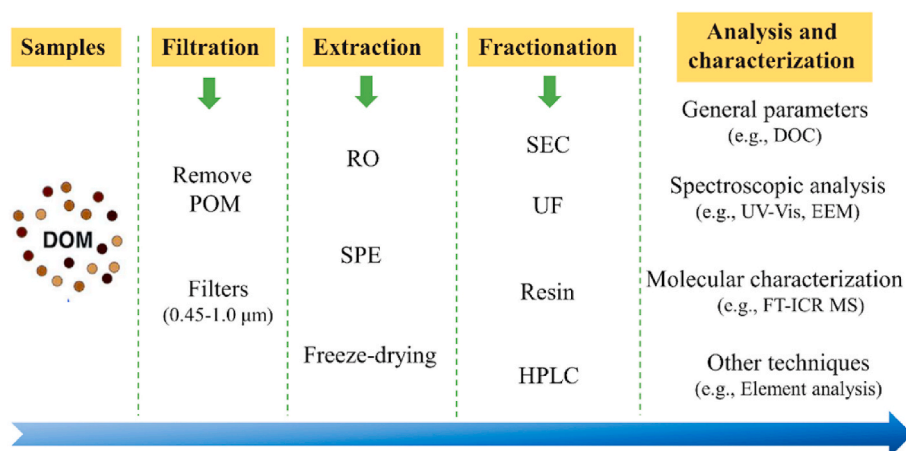


Fig. 3. Flow chart of DOM pretreatment.

proposed and used to isolate and concentrate DOM. Reverse osmosis-electrodialysis (RO-ED) has become a rapidly developed DOM extraction method in the past decades. The RO-ED systems do not only achieve the enrichment of aquatic DOM, but also simultaneously remove inorganic salts in water samples. For instance, Wang et al. (2018a, 2018b) utilized the RO-ED method to extract DOM from agricultural waters and obtained excellent recoveries of marine DOM (66.8%). Similarly, Chen et al. (2014) demonstrated that using RO-ED techniques could achieve an average of 75% of DOM from seawaters. Other previous studies also indicated that RO-ED could effectively desalinate seawater and achieve a high DOM recovery rate of 70–75% (Green et al., 2014). The enriched DOM solution basically meets the core requirements for NMR and FT-ICR MS analysis (Chen et al., 2014). With all these advantages, RO-ED show great potential for DOM extraction from seawater.

3.1.2. Solid-phase extraction

SPE is an enrichment method that is derived from liquid-liquid extraction (LLE). Although it has been used for the separation and enrichment of humus since the 1970s, this technique is still the most commonly used DOM pretreatment method (Li et al., 2016). In SPE approaches, DOM extraction and enrichment are based on the sorption process between organic matter and sorbents (Chen et al., 2016). DOM molecules in solution phase can be adsorbed onto a sorbent packing. Thus, depending on the chemical characteristics of the sorbent, SPE selectively enriches certain DOM components (e.g., hydrophobic fraction), so that the DOM after SPE extraction might not fully represent the original DOM features (Broek et al., 2017).

XAD were used earlier on as SPE adsorbents for DOM extraction, which are a group of non-ionic large pore adsorbents (Broek et al., 2017; Chen et al., 2016). Recently, however, C18 and PPL have been regarded as better options for DOM extraction owing to their high extraction effectiveness (Li et al., 2016; Thorsten Dittmar et al., 2008). PPL is a modified styrene-divinylbenzene polymer, allowing PPL-SPE to simultaneously retain both polar and non-polar compounds (Dittmar et al., 2008). Hence, PPL-SPE usually has a higher DOM recovery rate (up to 89% for terrestrial DOM and 45% for marine DOM) and reproducibility compared to C18-SPE. So, it is viewed as an ideal DOM adsorbent (Li et al., 2016). For C18-SPE, it is generally used to extract non-polar components and low molecular weight DOM from water samples.

However, it is also noteworthy that some drawbacks limit the application of SPE in DOM extraction (Chen et al., 2016). First, DOM extraction with SPE is always complicated and time-consuming (5–120 h per sample) (Broek et al., 2017). Second, SPE may alter the composition and structure of DOM in the sample because of the sample acidification procedure required by SPE (Li et al., 2017). All these limitations could lead to DOM contamination, loss, and transformation. Thus, DOM

extracted by SPE may not represent the “true” DOM in initial samples (Broek et al., 2017; Minor et al., 2014; Sandron et al., 2015).

3.1.3. Freeze-drying

Freeze-drying is usually adopted to prepare DOM samples for subsequent characterization and analysis with the advantage of minimal damage to the composition and structure of DOM (Pan et al., 2016). However, it is worth noting that freeze-drying is capable of concentrating inorganic salts with the enrichment of DOM components in waters, resulting in high ionic strengths in samples. In this case, the samples cannot be used for characterization by means of NMR, FT-ICR-MS, and other characterization techniques (Hernandez-Ruiz et al., 2012; Minor et al., 2014).

Nonetheless, for molecular-level characterization of DOM utilizing NMR and MS, freeze-drying in combination with other DOM extraction methods has been widely used to isolate and concentrate DOM from natural water. After the salt is removed from samples via other extraction methods, freeze-drying can be applied to further concentrate the DOM samples prior to analysis and characterization.

Currently, it is reported that DOM extraction procedures may have a profound influence on the results of DOM characterization (Chen et al., 2016). It is doubtful whether the extracted DOM could adequately represent the initial DOM samples (Broek et al., 2017). Therefore, more efforts should be made to evaluate the effect of DOM extraction on the DOM chemical structure and elemental composition.

3.2. Fractionation methods

When qualitatively describing DOM features, fractionation procedure is typically necessary to obtain an in-depth knowledge on the composition and structure of individual DOM components (Li et al., 2016). DOM molecules can be fractionated into different classes of compounds according to their molecular weight using size exclusion chromatography (SEC) and ultrafiltration (UF), and polarity through resin fractionation and HPLC (De Guardia et al., 2002; Brezinski and Gorczyca, 2019; Haberkamp et al., 2007; Pan et al., 2016; Sandron et al., 2015).

3.2.1. Size exclusion chromatography

Size exclusion chromatography (SEC) is a powerful method that utilizes chromatographic columns to fractionate DOM molecules into different classes of compounds based on their molecular size and weight. However, owing to its poor separation performance, coupled high-performance liquid chromatography-size exclusion chromatography (HPLC-SEC) is developed and applied for DOM fractionation (Pan et al., 2016). The advantage of the HPLC-SEC technique for DOM fractionation

lies in its easy operation, great sensitivity, and reproductivity, and free of an extraction step before instrument analysis (Huber et al., 2011). The combination of HPLC-SEC with multiple detectors provides a great opportunity to qualitatively and quantitatively characterize DOM molecular weight (Brezinski and Gorczyca, 2019).

Currently, various detectors have been coupled with HPLC-SEC for DOM characterization, such as ultraviolet absorption (UV) detectors, fluorescence detectors, organic carbon and organic nitrogen detectors (Brezinski and Gorczyca, 2019; Huber et al., 2011). This technique is one of the most widely used methods for analyzing the molecular weight of DOM fractions from various matrices including natural water, wastewater, and sediments. For instance, the HPLC-SEC method has been widely utilized to characterize the variation of DOM molecular weight during wastewater treatment, as the molecular weight of DOM can be a potential indicator of wastewater treatment performance (Tran et al., 2015). At the same time, this technique is also recognized as an efficient tool to investigate the impact of DOM molecular weight on the binding affinity with heavy metals, organic pollutants, and nanomaterials (Wang et al., 2018a, 2018b; Yu et al., 2018b).

Moreover, HPLC-SEC in combination with other characterization methods (e.g., spectroscopy methods, mass spectrometry) has been extensively used to study the relationship between DOM molecular weight and its structure, composition, and spectral characteristics (Cai et al., 2020; Hawkes et al., 2019). For instance, Yu et al. employed reversed-phase high-performance liquid chromatography (RP-HPLC) and SEC to investigate the molecular weight and polarity evolution characteristics of humic acid, fulvic acid, and the hydrophilic fractions during composting (Yu et al., 2018a).

3.2.2. Ultrafiltration

Membrane filtration (MF) provides an alternative technique for DOM extraction and fractionation, mainly including ultrafiltration (UF) and reverse osmosis (RO) (Li et al., 2019; Minor et al., 2014). MF is a physical process based on molecular size exclusion, which forces water to pass through a membrane via physical means (De Guardia et al., 2002). Therefore, MF is capable of extracting and fractionating DOM without chemical manipulation, thereby posing minimal effects on its chemical composition and structure (Chen et al., 2015; Minor et al., 2014).

In UF, DOM molecules are separated by diafiltration via ultrapure water, which can be classified into two main configuration systems used for isolating samples: tangential flow ultrafiltration and stirred cell ultrafiltration (De Guardia et al., 2002; Minor et al., 2014; Xu et al., 2006). Stirred ultrafiltration is usually suitable for DOM separation and enrichment of small volume water samples, while tangential flow ultrafiltration is used to process large volume water samples (>10 L). Currently, UF has been broadly used to separate DOM into different molecular size series (e.g., 0.5, 1, 3, 5, 10, 30, 100 kDa) (Sandron et al., 2015; Xu et al., 2006). However, it is noteworthy that UF has certain selectivity for DOM with different molecular weights. Generally speaking, DOM recoveries show an elevated tendency along with the increase of molecular size (Sandron et al., 2015). Moreover, membrane fouling is a major obstacle to the wide application of UF for DOM fractionation (Pan et al., 2016).

3.2.3. Resin fractionation

Resin fractionation is applied to separate DOM into different compound groups according to its hydrophobicity. It is one of the standard separation methods recommended by the International Humic Substances Society (IHSS). After resin fractionation, DOM can be fractionated into hydrophobic, transphilic, and hydrophilic components (Aiken and Leenheer, 1993; Aiken et al., 1992; Malcolm and MacCarthy, 1992). Among various resin sorbents, Amberlite XAD resin including XAD-8 is most widely used (Jerry A. Leenheer and Jean-Philippe Croué, 2003). However, the widely used Amberlite XAD-8 resin is no longer commercially available and has been replaced by DAX-8 in recent years

(Chow, 2006). Other resins such as cation and anion exchange resins are often used in series with XAD resins to reduce DOM molecular complexity (He and Hur, 2015b).

However, the complexity of DOM makes it nearly impossible to fractionate them into hydrophobic, neutral, and hydrophilic components only using one type of resin. As a result, a combination of different types of XAD resins is proposed, such as the XAD-4 in combination with XAD-8 (Rho et al., 2019). Nowadays, this combined technique has been extensively applied to characterize the composition of DOM from natural water, drinking water and wastewater effluent (Rho et al., 2019). Additionally, it is also becoming a preferred method to study the interaction of DOM fractions with heavy metals and organic pollutants, allowing to facilitate the understanding of its role in the transport and fate of heavy metals and organic pollutants (Li et al., 2019).

3.2.4. High-performance liquid chromatography

Reversed-phase high-performance liquid chromatography (RP-HPLC) can fractionate DOM into hydrophobic or hydrophilic class of compounds (He et al., 2015). Hence, RP-HPLC has been applied to compare the difference between hydrophobic and hydrophilic fractions in their physicochemical properties (Yu et al., 2018a). The separated fractions from RP-HPLC are often analyzed and characterized by UV absorbance, fluorescence intensity and organic content (He et al., 2015; Li et al., 2013). For example, RP-HPLC with UV and/or fluorescence detection was utilized to investigate the transport of terrestrial organic matter and compare the dissimilarity of DOM from difference sources (Li et al., 2013; Lombardi and Jardim, 1999). The RP-HPLC system adopts relatively strong mobile phase gradients (i.e., polar phase) to elute DOM fractions from the stationary phase (i.e., non-polar phase) (Pan et al., 2016).

Moreover, coupling of RP-HPLC with mass spectroscopy play a vital role in analyzing accurate molecular composition and structure of DOM (He et al., 2015; Koch et al., 2008). With the aid of mass spectroscopy, the empirical formula for DOM fractions can be obtained according to corresponding m/z values, which can help determine molecular composition for individual DOM fractions (Koch et al., 2008). For instance, He et al. (2015) utilized RP-HPLC in combination with FTIR and NMR to examine the differences among size- and hydrophobicity-distinguished fractions in the composition and evolution. In addition to RP-HPLC, hydrophilic interaction liquid chromatography (HILIC) has also been applied for DOM fractionation (Woods et al., 2012). For example, highly-oxidized sterols have been proved to be dominant components of DOM by means of HILIC (Woods et al., 2012).

4. Analysis and characterization of DOM in aquatic environments

A variety of techniques has been proposed and applied for DOM characterization (Jiang et al., 2017). These techniques can be classified into two different categories: source tracking and molecular characterization (Derrien et al., 2019a). The former methods, used to identify the sources and the fate of DOM in aquatic environments, mainly include stable isotopes ratios, lipid biomarkers, and compound-specific isotopes analysis (Derrien et al., 2017, 2019a). Detailed information related to source tracking is discussed elsewhere (Derrien et al., 2017, 2019a). The latter can provide useful information on DOM structure and composition, and mainly include UV-Vis, fluorescence, FTIR, NMR, and FT-ICR MS (Wang et al., 2018a, 2018b; Ishii and Boyer, 2012; Li et al., 2016; Minor et al., 2014).

Understanding the DOM constitution is one of the major scientific conundrums for the investigation related to DOM-mediated biogeochemical processes (Derrien et al., 2019a). As such, more attention is focused on the molecular characterization of DOM in this review (Fig. 4). Current techniques to characterize DOM can be categorized into four aspects: 1) general parameters (e.g., DOC); 2) spectroscopic

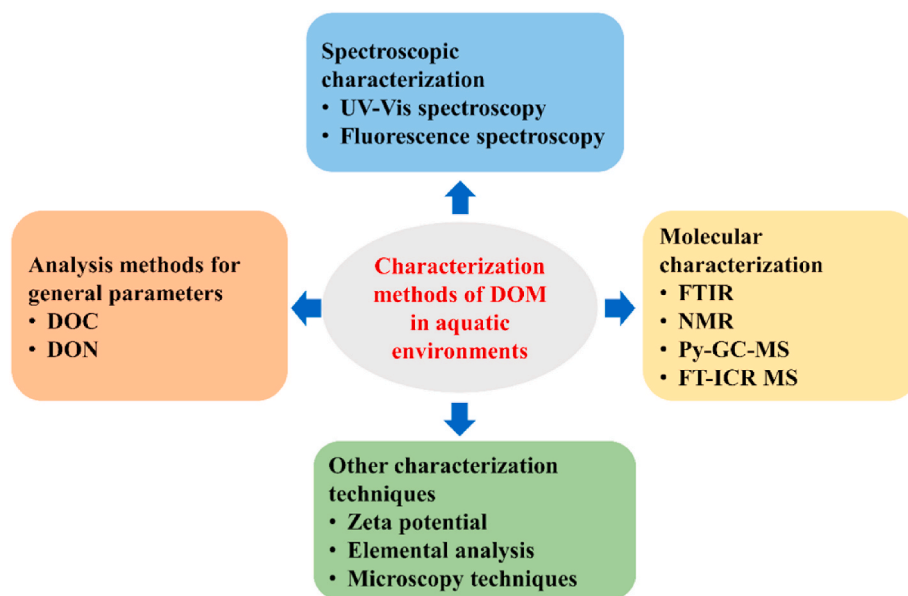


Fig. 4. Characterization methods of DOM in aquatic environments.

characterization (e.g., UV–Vis absorption and fluorescent spectroscopy); 3) molecular characterization (e.g., FTIR, NMR, and FT-ICR MS); 4) other characterization techniques (e.g., Zeta potential).

4.1. Analysis methods for general parameters

DOC is usually used as a surrogate parameter to assess the concentration of DOM in aquatic environments (Tran et al., 2015). In addition to DOC, dissolved organic nitrogen (DON) is also a significant index in drinking water treatment, which is determined by total nitrogen concentration minus ammonia, nitrate, and nitrite concentrations (Pan et al., 2016). However, the major drawback of adopting DOC to evaluate the DOM in aquatic environments is that it covers both biodegradable and non-biodegradable compounds (Tran et al., 2015).

Therefore, it is very challenging to assess the concentration of biodegradable DOC (BDOC) in aquatic environments. As a solution to this problem, there has been increasing focus on the analysis and measurement of BDOC in natural systems. BDOC represents the fractions of DOC that can be utilized as a primary substrate to support microorganism growth in the form of carbon source and energy (Guillemette and Giorgio, 2012; Tran et al., 2015). Thus, BDOC is usually an important indicator that can reflect the development and growth of indigenous microorganisms (Mermillod-Blondin et al., 2015). A more detailed characterization based on biodegradability can provide an improved understanding of the composition and properties of aquatic DOM. In addition to BDOC, assimilable organic carbon (AOC) is also an important parameter, which represents the most easily assimilated BDOC fractions by bacteria (Kamjunke et al., 2019).

Moreover, DOC is often combined with fractionation operation to evaluate the contents of individual DOM fractions (Brezinski and Gorczyca, 2019; He and Hur, 2015a). For example, DOC in combination with SEC was used to investigate the impact of coagulation and adsorption on individual DOC fractions (i.e., biopolymers, humic substances, low-molecular-weight acids, and low-molecular-weight neutrals) (Haberkamp et al., 2007).

4.2. Spectroscopic characterization

4.2.1. UV–vis absorption spectroscopy

UV–Vis absorption spectroscopy has been extensively applied as a complement to fluorescence spectroscopy for DOM characterization.

Recently, the application of UV–Vis spectroscopy has been encouraged and popularized by many scholars with the major advantages of simple operation, low cost, and high sensitivity (Li and Hur, 2017). Numerous specific parameters and chemometrics methods derived from UV–Vis absorption spectra have been developed and applied for the characterization of DOM in aquatic environments (Table 1). For instance, SUVA₂₅₄ termed as the ratio of UVA₂₅₄ to DOC is regarded as an effective indicator of the levels of aromatic contents (Weishaar et al., 2003; Wert et al., 2009). Similarly, the indexes SUVA₂₆₀, SUVA₂₈₀, SUVA₃₆₅, and SUVA₄₃₆, defined as the quotient of UV absorbance at the corresponding wavelength divided by its DOC concentration, is corresponding to double bonds, molecular size, and chromophore in DOM (Chen et al., 2018b). In addition to the absorbance at a specific wavelength, the absorbance between two different wavelengths provides an indicative parameter for the characterization of DOM, such as E_2/E_3 , E_2/E_4 , E_4/E_6 (Santos et al., 2016; Wang et al., 2013).

Apart from quantitative parameters generated from UV–Vis spectra, chemometric methods have been attracting increasing interest to help characterize aquatic DOM such as two-dimensional correlation spectroscopy (2D-COS) and principal component analysis (PCA) (Li and Hur, 2017). 2D-COS has gradually been introduced into DOM absorbance data processing, which is a mathematical tool that can improve spectral resolution by spreading spectra over two dimensions (Chen et al., 2019). Moreover, it can provide information about the sequential order upon external changes by the synchronous and asynchronous spectra of 2D-COS (Zhang et al., 2019b). The detailed application of 2D-COS is discussed elsewhere (Chen et al., 2019; Noda, 2009).

Table 1
Characteristic indexes generated from UV–Vis spectra for DOM characterization.

Index	Indication	Reference
SUVA ₂₅₄	Aromaticity	Du et al. (2016)
SUVA ₂₈₀	Double bonds	Valencia et al. (2013)
SUVA ₃₆₅	Molecular size	(Chen et al., 2018a, 2018b)
E_2/E_3	Aromaticity, molecular size	(Wang et al., 2018a, 2018b, 2019)
E_4/E_6	Polarity	Wang et al. (2020)
$S_{275-295}/S_{275-295}/S_{350-400}$	Molecular weight	Kida et al. (2019)
$S_R (S_{275-295}/S_{350-400})$	Molecular weight	Li et al. (2020)
D-Slope ₃₂₅₋₃₇₅	Binding affinity variation	Wang et al. (2018a, 2018b)

Despite the usefulness of UV–Vis spectroscopy in DOM characterization, it can only characterize the chromophoric sub-fraction of DOM. In fact, there exist relatively large amounts of non-chromophoric DOM (NCDOM) in aquatic environments. For example, NCDOM comprised a larger percentage (59%) of the bulk DOM than CDOM (41%) in Lake Tuscaloosa (Vähätalo and Wetzel, 2004). The quantity of NCDOM, defined as the DOC concentration at zero aromaticity or $a_{254} = 0$ (Spencer et al., 2008; DeVilbiss et al., 2016), indicates the DOM fraction that does not absorb UV light (Zhou et al., 2016). As reported in previous studies, the abundance of NCDOM could be derived from the intercept values in the plot of DOC against a_{254} (Spencer et al., 2008; Zhou et al., 2016). For instance, previous study demonstrated that open-water Great Lakes exhibited a larger proportion of non-chromophoric DOC in the bulk DOC than river systems and smaller embayments, and that non-chromophoric DOC was negatively correlated with bulk DOC concentration (Zhou et al., 2016). The author speculated that this might result from the production of non-chromophoric DOM from aromatic DOM and intensive DOM photodegradation. Interestingly, a recent study reported of a significant difference in the abundance of non-chromophoric DOC (33% in June and 47% in August) in seasonally hypoxia-influenced Green Bay, which implies a more aromatic and higher molecular weight DOM pool in June than August (DeVilbiss et al., 2016). The higher amount of non-chromophoric DOC in the Green Bay likely resulted from intensive DOM photodegradation and autochthonous DOM generated in situ (DeVilbiss et al., 2016).

4.2.2. Fluorescence spectroscopy

Fluorescence spectroscopy has been widely used to track and characterize DOM in natural and engineered systems with the advantage of high reliability, great sensitivity, and non-destruction of samples (Jinlan Yu et al., 2020; Sankoda et al., 2018; Yang et al., 2015b). Fluorescence spectroscopy can be categorized into four types: excitation spectra, emission spectra, synchronous fluorescence spectra, and fluorescence excitation-emission matrix (EEM) (Aiken, 2014; Derrien et al., 2017). Among these spectra, EEM has been the most popular technique in characterizing the origins and compositions of DOM in that both excitation and emission signals can be acquired from EEM spectra (He and Hur, 2015a; Song et al., 2019). Particularly, EEM integrated with parallel factor analysis (EEM-PARAFAC) has been developed and utilized as an influential tool for the characterization of aquatic DOM, which offers a semi-quantitative understanding of compositions and behavior of different DOM components in various environments (Ishii and Boyer, 2012; Jinlan Yu et al., 2020; Li et al., 2020a; Murphy et al., 2013; Stedmon and Bro, 2008; Yang et al., 2015a, 2015b).

EEM-PARAFAC has shown great potential for DOM monitoring in natural and engineered systems (Blaen et al., 2016; Sgroi et al., 2017; Yin et al., 2019). From EEM spectra, the individual components of DOM in various aquatic systems are successfully analyzed, and the dominant components are identified in natural systems such as wetland, lake, and river (Bai et al., 2017; Meng et al., 2013; Wilson G. Mendoza and Rod G. Zika, 2014). Furthermore, EEM-PARAFAC has been successfully utilized to identify the sources of different DOM in various aquatic environments (Garcia et al., 2020; Meng et al., 2013). EEM-PARAFAC is also adopted to investigate DOM-induced biogeochemical processes (Queimaliños et al., 2019; Yang et al., 2016). Apart from the application of EEM-PARAFAC in natural systems, it has been extensively utilized in the area of wastewater treatment processes, such as characterization of membrane fouling and disinfection byproduct formation (Ike et al., 2019). Overall, EEM-PARAFAC is a reliable and useful technique for the characterization of DOM in aquatic environments (Li et al., 2013).

Despite the wide applications of fluorescence spectroscopy and EEM-PARAFAC, there remains several deals to be resolved (Carstea et al., 2020). Fluorescence technologies including EEM have their limitations for its inability in tracking the non-fluorescent DOM (Chen et al., 2018b). Therefore, the application of fluorescence spectroscopy to

characterize non-fluorescent DOM is challenging (Chen et al., 2018b). Additionally, fluorescence spectroscopy cannot provide detailed information on the molecular structure of DOM (Li et al., 2016). Thus, it is difficult to obtain an in-depth molecular-level structural elucidation for DOM. Furthermore, there are still some questions in the use of EEM-PARAFAC, such as the selection of EEM data analysis and calibration of EEM data (Mostofa et al., 2018), which also restrain the extensive application of EEM-PARAFAC methods for DOM studies (Li et al., 2020a).

4.3. Molecular characterization

4.3.1. Fourier transform infrared spectroscopy

FTIR has been recognized as one of the most important techniques to characterize DOM (Wang et al., 2018a, 2018b). Adsorption spectra derived from FTIR spectroscopy has been widely used to identify specific functional groups within DOM molecules (Yang et al., 2015a). In addition to transmission FTIR, attenuated total reflection (ATR) FTIR and diffuse reflectance infrared spectroscopy are also extensively utilized for DOM characterization (Derrien et al., 2019a; Minor et al., 2014). However, absorption peaks of multiple functional groups usually coexist, resulting in the overlapping of characteristic peaks. This phenomenon makes it challenging to analyze and characterize the composition and structure of DOM accurately. Thus, it is only used for the qualitative analysis of DOM.

Despite the effectiveness of FTIR in the identification of functional groups, it is rarely applied alone. In fact, the combination of FTIR with other methods (e.g., UV–Vis, fluorescence spectroscopy, NMR, and FT-ICR-MS) has been attracting increasing attention, which can obtain as much information related to DOM composition and structure as possible (Fan et al., 2019; Guo et al., 2019; Yang et al., 2015a). For instance, the quantity, spectroscopic features and biogeochemical reactivity of DOM in treated wastewaters from different industries were characterized by EEM-PARAFAC and FTIR spectroscopy (Yang et al., 2015a). The binding property of copper and lead onto compost-derived DOM was also characterized employing FTIR, UV–vis, and fluorescence spectra (Guo et al., 2019).

4.3.2. Nuclear magnetic resonance spectroscopy

NMR is one of the most effective means of studying the molecular structure of DOM in the past three decades (Benner et al., 1992; Mopper et al., 2007; Hertkorn et al., 2013). Compared with other methods, this technology has the following advantages: can be directly used for solid materials; does not damage the structure of the DOM sample; provide not only qualitative analysis but also quantitative analysis. NMR can be categorized into two types: solution-state NMR for soluble samples and solid-state NMR for solid samples (Pan et al., 2016).

Typically, it is necessary to isolate and concentrate DOM samples and remove inorganic compounds prior to NMR analysis (Jones et al., 2013; Minor et al., 2014). NMR is an analysis method that can distinguish how the functional groups are connected with each other within DOM molecules (Cortés-Francisco et al., 2014). In recent years, NMR in combination with FTIR and FT-ICR MS has been widely used to determine the functional group, compound class, and molecular formula (Franklin et al., 2020; Kamjunke et al., 2019; Li et al., 2016; Woods et al., 2012). Detailed information on the application of NMR to characterize DOM can be found elsewhere (Duarte et al., 2020; Simpson et al., 2011).

4.3.3. Pyrolysis-gas chromatography-mass spectrometry

Py-GC-MS is not the most used technique for the characterization of DOM molecular structures. However, it is a powerful and useful method for the rapid molecular characterization and source tracking of DOM with the advantage of convenient operation and efficient analysis speed (Park et al., 2019). Most techniques only provide information on the general composition of DOM, such as UV–vis spectrophotometry, fluorescence spectroscopy, and nuclear magnetic resonance (NMR)

spectroscopy. However, Py-GC-MS can offer more detailed information on the molecular arrangement of chemical groups (Kaal et al., 2017).

Py-GC-MS is a chemical characterization technique that can decompose macromolecular DOM molecules into a variety of small fragments by heating above 500 °C and then detecting these fragments using GC/MS. The pyrolysis chromatogram of each DOM generated from Py-GC/MS has a certain correspondence with the composition and relative content of various fragments, called fingerprint pyrolysis spectrum, which can be used as a qualitative basis for DOM characterization (Greenwood et al., 2012; Kaal et al., 2016).

4.3.4. Fourier transform ion cyclotron resonance mass spectrometry

FT-ICR MS is the most advanced of all the characterization techniques described above (Derrien et al., 2019a; Zhang et al., 2020a). Currently, FT-ICR MS appears to be the most promising tool that can observe the chemical composition and structure of DOM at molecular level (Derrien et al., 2019a; Liu et al., 2020). Its primary advantages over other techniques lies in sufficiently high-resolution power, thereby providing an in-depth molecular characterization of DOM from various aquatic environments (e.g., wetlands, lakes, rivers, and wastewater effluents) (Minor et al., 2014; Zhang et al., 2020a).

The most commonly used ionization techniques of FT-ICR MS mainly include electrospray ionization (ESI) and atmospheric pressure photo-ionization (APPI) (Butturini et al., 2020; Pan et al., 2016). It is noteworthy that ESI is suitable for polar or semi-polar DOM molecules (Pan et al., 2016). With respect to less polar DOM molecules, the combination of ESI with APPI is proposed and applied for DOM characterization.

FT-ICR MS coupled with ionization techniques has brought unprecedented opportunities for molecular formula determinations (Pan et al., 2016; Riedel et al., 2012). The empirical formula for thousands of individual DOM components can be acquired from a great deal of data originating from FT-ICR-MS analysis (Lavonen et al., 2015; Minor et al., 2014). Molecular compositional information of DOM provides more solid and persuasive support for the investigation on the source, composition, reactivity and environmental behaviors of DOM in aquatic environments (Butturini et al., 2020; Li et al., 2020a).

Although FT-ICR MS is recognized as the most powerful tool for DOM characterization, there is still much room for the development of FT-ICR MS, such as how to assign molecular formulae, how to improve the ionization efficiencies, how to observe more classes of components and how to avoid environmental interference caused by contaminants (Derrien et al., 2019a; Minor et al., 2014).

4.4. Other characterization techniques

Zeta potential analysis is usually employed to track the variation of DOM surface charge in various conditions (Yu et al., 2018b). It is the electrostatic potential difference across phase boundaries between suspended solids and liquids, which can reflect particle-particle repulsion forces in colloidal suspensions. Thus, zeta potential can be used to predict colloid stability against particle aggregation in liquids. The value of zeta potential corresponds to the interaction force of DOM with exogenous chemical species (e.g., nanomaterials and heavy metals) (Yu et al., 2018b). Previous studies demonstrated that the zeta potential of DOM became much more negative after the introduction of certain heavy metals (Yang et al., 2019). Apart from Zeta potential analysis, elemental analysis has been widely used to examine the types of elements (e.g., carbon, hydrogen, nitrogen, halides, and sulfur) and their corresponding amount within DOM molecules (Niu et al., 2018).

Moreover, microscopy techniques have been utilized to visualize the interaction between DOM and mineral surface, such as atomic force microscopy (AFM) and Raman microscopy (Yin et al., 2015; Zhang et al., 2018a, 2018b). These microspectroscopic methods are beneficial to understanding the nature of DOM and its interaction with exogenous chemical species (e.g., nanomaterials) in waters (Sun et al., 2019).

5. Biogeochemical dynamics and environmental implications of DOM in aquatic environments

5.1. Biogeochemical dynamics

The net pool of DOM in aquatic environment is the ultimate results of a variety of biogeochemical processes, leading to a dynamic change between the input and output of organic matter in water bodies (Lee et al., 2018; Zhuang and Yang, 2018). In aquatic environments, various processes play important roles in the alteration and transformation of DOM, mainly including sorption/desorption, aggregation/decomposition, complexation, leaching, biodegradation, and phototransformation (Bolan et al., 2011; Kothawala et al., 2012; Xu and Guo, 2018). Among these processes, photochemical transformation, microbial degradation, and adsorption are the three most important mechanisms that regulate the biogeochemical dynamics of DOM in aquatic environments (Dutta Majumdar et al., 2017; Klapstein et al., 2018; Zhang et al., 2019b). Additionally, as shown in Fig. 5, the biogeochemical dynamics of DOM could exert a wide range of alteration effects on its quantity and quality.

5.1.1. Photochemical degradation

Photodegradation could significantly influence the transformation of DOM in aquatic environments such as lakes, wetlands, and rivers (Carena et al., 2020; Dutta Majumdar et al., 2017; Xue et al., 2016). Previous studies have indicated that UV light from solar light serves a key function in changing chromophoric and fluorescent DOM during solar light irradiation. For instance, UV light can transform aquatic DOM into carbonyl compounds, and the removal efficiency of humic acid and protein in natural waters is negligible under visible light (Andley et al., 1984; Davies, 1987). On the other hand, this might be attributed to the strong photochemical reactivity of DOM molecules, which is closely associated with its chemical groups (Xue et al., 2016). DOM contains a large number of chromophores such as benzene rings, which can absorb sunlight at a certain wavelength (Li and Hur, 2017; Sulzberger and Arey, 2016). As a result, DOM could photochemically produce reactive intermediates (PPRIs) under proper light conditions, mainly including singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($\cdot\text{OH}$), triplet DOM ($^3\text{DOM}^*$), and superoxide ion (O_2^-) (Niu et al., 2014; Rosado-Lausell et al., 2013; Sardana et al., 2019).

Currently, a great deal of studies have been carried out on the photodegradation processes of DOM and underlying mechanisms in natural waters (Mostafa, 2013). Direct and indirect photolysis is viewed as the essential pathways responsible for the alteration and transformation of DOM in aquatic environments (Lee et al., 2014; Song and Jiang, 2020). The difference between direct photolysis and indirect photolysis lies in the object of absorbing photons. Regarding direct photolysis, DOM absorbs photons to decompose directly or undergo other conversions. Conversely, indirect photolysis is initiated by the reactive oxygen species (ROS) (Clark et al., 2009; Garcia et al., 2019), which is generated by the photosensitizers in water, such as DOM, NO_3^- , NO_2^- , Fe^{3+} , and so on (Chiwa et al., 2015; Marchetti et al., 2013; Song and Jiang, 2020). Moreover, the origin, concentration and structure of DOM have a profound influence on the DOM photodegradation (Dutta Majumdar et al., 2017; Zhou et al., 2019). For instance, it has been observed that the apparent quantum yields of hydroxyl radicals ($\cdot\text{OH}$) and singlet oxygen ($^1\text{O}_2$) derived from wastewater effluent DOM is higher than those from NOM (Mostafa and Rosario-Ortiz, 2013).

Photodegradation could change the quality and quantity of aquatic DOM (Fig. 5) (Bodhipaksha et al., 2017; Xue et al., 2016; Zhang et al., 2019b). For instance, photodegradation could lead to the loss of the UV- and visible-light absorbing properties of DOM (Niu et al., 2014). In addition, it is reported that the abundance of aquatic DOM decreased and low-weight DOM components were produced when exposed to sunlight. Certain DOM molecules could even be converted into carbon dioxide under natural solar irradiation (Zhang et al., 2019b). Additionally, photodegradation decreased the binding affinity of DOM with

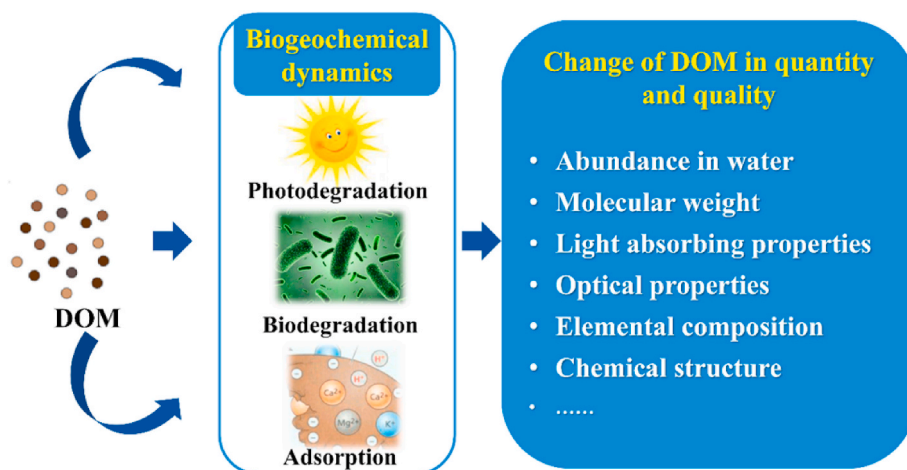


Fig. 5. Effects of DOM dynamics on its quantity and quality.

benzopyrene and altered the toxicity and bioavailability of benzopyrene to aquatic organisms (Du et al., 2016; Zhang et al., 2019b).

As an indispensable photosensitizer in the aquatic environments, DOM also plays an important role in the photochemical transformation of organic pollutants (Cristale et al., 2017; Xue et al., 2019). For example, DOM-induced photochemical transformation has been proved to be an important mechanism to accelerate the photolysis of various micropollutants in water such as drugs and antibiotics (McNeill and Canonica, 2016).

Thus, photodegradation is a significant process that controls the dynamics of DOM in aquatic environments (McNeill and Canonica, 2016). Nonetheless, the DOM photodegradation also greatly affects the migration, transformation, bioavailability and toxicity of exogenous chemical species.

5.1.2. Microbial degradation

Biodegradation plays an irreplaceable role in DOM transformation (Derrien et al., 2019b; Xu and Guo, 2018; Zeri et al., 2014). Microbial metabolism contributes significantly to the biogeochemical dynamics of DOM in aquatic environments. The majority of DOM in aquatic environments is transformed into CO₂ via microbial metabolism (Jiao et al., 2010; Ni et al., 2020). However, it is worth noting that although DOM is subject to photochemical and microbial transformation in aquatic environments, the DOM photodegradation is dominant in aquatic environments, particularly in surface water (Chen and Hur, 2015).

DOM is an important carbon source for bacterial growth and reproduction. Microbial degradation and utilization are proved to be one of the critical pathways to affect the environmental fate of DOM (Kisand et al., 2013). The labile DOM components tend to be more readily mineralized or assimilated into microbial biomass (Xu and Guo, 2018). Besides, the DOM derived from algae and plant litter in waters can be microbially decomposed and utilized (Hansen et al., 2016; Klotzbücher et al., 2013; Lee et al., 2018; Song et al., 2020). It is reported that during the biodegradation of plant litter, certain DOM including cellulose, hemicellulose, and lignin can be transformed into intermediate and low weight sized compounds that can be assimilated (Song and Jiang, 2020).

DOM biodegradation is not only dependent on its physicochemical properties and chemical structures (Kalbitz et al., 2003), but also related to various environmental factors such as nutrient, microbial community structure and composition. The biological availability of DOM itself fundamentally determines its lability. It is well-known that DOM is classified into three categories according to biological availability: labile DOM, semi-labile DOM and recalcitrant DOM (Broek et al., 2017; Jiao et al., 2010; O'Connor et al., 2020). The source, composition, and structure significantly influence its microbial lability. Previous studies have indicated that the biodegradation rate of DOM varied among

different sources (Jiao et al., 2010). This variation might be ascribed to the difference in its composition such as elements ratios (e.g., C: N and C: P) within DOM molecules (Xu and Guo, 2018).

In addition to the nature of DOM, nutrients available also regulate the microbial degradation of DOM (Bleyen et al., 2018). In seawaters, the lack of nitrogen, phosphorus, or iron may limit the growth of microorganisms, thereby limiting the degradation of bioavailable DOM (Bleyen et al., 2018). This phenomenon results in the continuous accumulation of DOM in water bodies.

Moreover, a large number of studies have also shown that the difference in microbial abundance and community structure is another important factor that affects the biodegradation rate of DOM (Ávila et al., 2019). One of the major reasons might be due to the fact that the lability of DOM can also be specific to the utilizing microbial communities (Jiao et al., 2010; Letscher et al., 2015). Different microbial communities produce different types of extracellular enzymes, so the capacity to utilize DOM varies among various microorganism communities. Meanwhile, the types of DOM also affect the function and composition of microbial community, such as productivity, respiration and growth rate due to the specific selectivity utilization (Li et al., 2020b).

5.1.3. Adsorption

DOM adsorption onto nanoparticles, colloid surfaces, and mineral surfaces has received increasing attention in recent years (Aiken et al., 2011b; Pan et al., 2020). When sorption processes occur between DOM and nanoparticles, colloid surfaces and mineral surfaces, DOM will be retained, subsequently changing its mobility and transformation. Since DOM is a class of complex and heterogeneous mixture of various active organic species, fractionation of DOM by nanoparticles, colloid surface and mineral surface may occur, potentially changing its physicochemical properties (Philippe and Schaumann, 2014). Previous studies have indicated that certain nanoparticles including carbon nanotubes preferentially adsorbed higher molecular weight fractions of DOM (Engel and Chefetz, 2016a). Similarly, DOM fractionation by colloids has also been reported, indicating DOM with different origins exhibited different adsorption affinities on colloid surfaces (Morales et al., 2011; Pan et al., 2020).

Owing to the extreme complexity and heterogeneity of both DOM and nanoparticles, colloids, and mineral surfaces, many kinds of interaction mechanisms have been proposed to describe the DOM adsorption process, including van der Waals forces, H-bonding, cation bridging, electrostatic interaction, and chelation (Engel and Chefetz, 2016a). For instance, amphiphilic organic matters show various adsorption effects due to the presence of both polar and nonpolar functional groups, such as humic substances and amino acids (Kleber et al., 2007). The

hydrophilic fractions of humic substances can be adsorbed on mineral surfaces via electrostatic forces and/or ligand exchange reactions, while the hydrophobic fractions are absorbed via hydrophobic interactions (He et al., 2016).

These interactions largely dependent on a series of factors including the DOMs chemical structure and elemental composition (e.g., molecular weight and hydrophobicity), the characteristics of nanoparticles, colloids, and minerals (e.g., functional groups and surface area), and environmental factors (e.g., temperature, light irradiation and pH) (Aiken et al., 2011b; Philippe and Schaumann, 2014; Yu et al., 2018b). It is reported that DOM adsorption to soil mineral surfaces is a significant process that controls the dynamics of DOM in soil. The biogeochemical dynamics of DOM is highly associated with the quantity and quality of its functional groups, which largely determine the specific interactions with soil minerals, including ligand exchange with OH groups on metal oxide surfaces (Avneri-Katz et al., 2017). Meanwhile, for a given aquatic system, the most significant influence on the adsorption process should be attributed to the inherent characteristics of DOMs, including molecular weight and size.

5.2. Environmental implications

DOM plays a critical role in the cycling of elements, transport of exogenous chemical pollutants and interaction with microbial communities (Ishii and Boyer, 2012; Khundzhua et al., 2017). Among these roles, the interaction of DOM with exogenous chemical species (e.g., heavy metals, organic pollutants, and nanomaterials) has been attracting an increasing interest due to concern about the ecological and human effects exposed to these species (Al-Reasi et al., 2011; Artifon et al., 2019; Yu et al., 2018b). In recent years, tremendous efforts have been made to obtain an in-depth insight into the nature of DOM interaction with these species, which has become one of the hot topics in the field of environmental science and engineering.

DOM in aquatic environments could change the physical and chemical properties of these species, influencing their occurrence and mobility, and finally significantly altering their potential bioavailability and toxicity (Fig. 6) (Philippe and Schaumann, 2014; Yu et al., 2018b). Considering the complexity and heterogeneity of DOM, it can affect the bioavailability and toxicity of exogenous chemical species in different manners. The main mechanisms of interaction between DOM and these species are hydrophobic interactions, electrostatic and van der Waals forces, complexation and hydrogen bond (Philippe and Schaumann, 2014). Detailed information on the interaction mechanism is discussed

elsewhere (Philippe and Schaumann, 2014; Yu et al., 2018b). Hence, the focus of our review will be on the environmental implications of heavy metals, organic matter and nanomaterials caused by DOM.

DOM in aquatic environments have great effects on the environmental behavior of heavy metals, organic pollutants and nanomaterials, mainly including physical (e.g., sorption, deposition, and transport) and chemical behaviors (e.g., photooxidation and photoreduction) (Carena et al., 2019; Engel and Chefetz, 2016b; Xu et al., 2017; Zhang et al., 2014). DOM is recognized as a significant carrier of heavy metals, which can exert a profound influence on the mobility of trace metals by forming soluble and insoluble DOM complexes with metals. Numerous studies have indicated the mobility of heavy metals is positively correlated with DOM abundance in aquatic environments, suggesting aquatic DOM is an important contributor to the increased mobility of heavy metals (Luo et al., 2020; Zhang et al., 2020c). For the organic micropollutants with hydrophobicity, DOM could alter their sorption onto colloid, suspended solid particles and sediments, photochemical transformation, and mobility in aquatic environments. DOM push forward an immense influence on the elevated mobility of organic pollutants through binding with organic pollutants or competing with organic pollutant for sorption sites (Aschermann et al., 2018; Zhang et al., 2014). Moreover, the presence of DOM in aquatic environments may exert alteration effects on the fate of organic pollutants through DOM-induced photolysis (Wang et al., 2021; Yuan et al., 2018). Up to now, a large number of investigations has been carried out on the impact of DOM derived from different sources on the phototransformation pathway of organic micropollutants (Cristale et al., 2017; Lee et al., 2014; Sornalingam et al., 2016; Wang et al., 2020). DOM from various environmental matrices (e.g., sediments, plant litter, algae, wetland water, and wastewater effluent) has been extracted to investigate their photosensitization mechanism in the phototransformation of various organic micropollutants including pharmaceuticals, endocrine disrupting compound, and pesticides (Bodhipaksha et al., 2015, 2017; Cristale et al., 2017; Lee et al., 2014; Wang et al., 2020).

Generally, DOM could pose two kinds of effects on the photolysis processes of coexisting organic micropollutants: inhibition or promotion effects (Remucal, 2014). On one hand, regarding the inhibitory effect of DOM, two main mechanisms result in the inhibition of pollutants phototransformation: light-shielding effect and quenching effect (Remucal, 2014). Previous studies have also shown that DOM presents an inhibitory effect on the photochemical transformation of certain pollutants due to the quenching effect of DOM (Black et al., 2012; Jiang et al., 2020). On the other hand, it was also observed that the presence of DOM

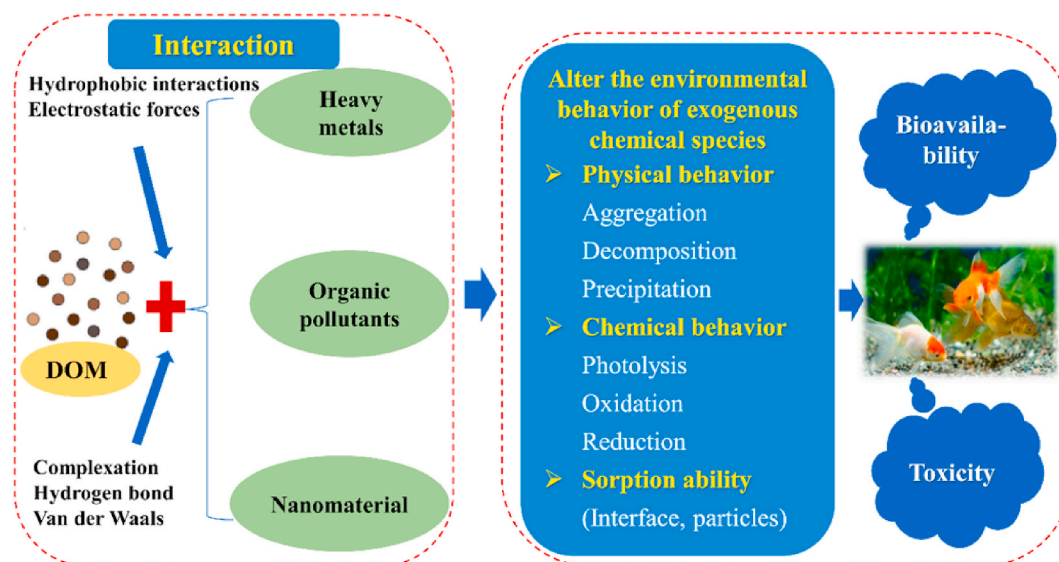


Fig. 6. Impacts of DOM on fate, bioavailability, and toxicity of exogenous chemical species.

promoted the photolysis of organic pollutants in aquatic environments (Koltsakidou et al., 2019; Tian et al., 2019). In fact, there are many different mechanisms responsible for this promotion effect due to the broad origins and complex structure of DOM in a specific photolysis system. The ability of DOM to generate ROS varies among various sources (Garcia et al., 2019). Therefore, it is difficult to find a unified law and mechanism.

DOM in aquatic environment also play significant roles in microplastics photodegradation due to their abundant chromophores. Liu et al. (2019a, 2019b) reported that DOM in the Yangtze River might be a significant factor leading to different photo-aging rates of polypropylene and polystyrene microplastics. Furthermore, DOM has an important influence on the sorption behaviors of microplastics in the aquatic environment. The effect of DOM on the interactions between DOM and microplastics is greatly associated with the quantity and quality of DOM (Zuo et al., 2019). Previous studies indicated that the sorption capacity of phenanthrene on polystyrene microplastics was negatively correlated with DOM concentration. The presence of DOM might result in intermolecular interactions with microplastics or organic compounds due to its functional groups.

Moreover, DOM molecules can inhibit the adsorption of organic compounds on microplastics by entering the pores or covering the surface of microplastics. In a recent study, the effects of two kinds of DOM (humic acid and fulvic acid) on the sorption behaviors of antibiotics oxytetracycline on polystyrene microplastics were investigated (Zhang et al., 2018a, 2018b). The results suggested that the sorption capacity of oxytetracycline first increased and then decreased with increasing humic acid concentration. However, an increasing concentration of fulvic acid resulted in a small increase in sorption capacity. This may be attributed to a large number of benzene rings in humic acid, and could form highly conjugated co-polymers with polystyrene microplastics by carboxyl and carbonyl linkage. As a result, the boosted electron density could lead to the electrostatic attraction to zwitterionic oxytetracycline, thereby enhancing the adsorption opportunities for oxytetracycline on microplastics (Chen et al., 2018a). In comparison with humic acid, fulvic acid has a smaller molecular weight and fewer benzene rings.

After entering the environment, it is possible for microplastics to react with DOM. DOM could serve as heterogeneous sites for the binding of microplastics. Therefore, the transport, transformation, and biotoxicity of microplastics could be affected by the DOM-microplastics interaction (Duan et al., 2021). Additionally, the interaction between microplastics and DOM may also have implications for the transport and transformation of hydrophobic emerging pollutants, such as polychlorinated biphenyls and perfluorooctanoic acids (Besseling et al., 2013; Bakir et al., 2014). Thus, further insights into the DOM-microplastics interaction is essential for understanding the environmental implications of microplastics for aquatic environments.

More importantly, DOM could significantly change the potential bioavailability and toxicity of many chemicals by interfering with their surface properties (Liu et al., 2019a, 2019b; Yu et al., 2018b). Binding between DOM and organic pollutants such as pesticides and endocrine-disrupting compounds may alter their toxicity to microalgae and other organisms (Coquillé et al., 2018). Similarly, the formation of stable complexes between DOM and certain heavy metal ions such as Cu, Hg, and Pb may enhance the movement of toxic metals, thereby resulting in an increased bioavailability (Chen et al., 2020; He et al., 2020). Conversely, it is generally realized that the presence of DOM could mitigate the toxicity of nanomaterials.

Furthermore, it is acknowledged that a myriad of biogeochemical processes could change the quantity and quality of DOM, and subsequently affect its interactive properties with exogenous chemical species (He et al., 2020; Lee et al., 2018). Consequently, these processes may alter the bioavailability and toxicity of these exogenous chemical species to biota through modifying binding affinity. Specifically, once DOM is released into aquatic environments, it undergoes various biogeochemical processes such as photochemical and biological degradation

(Artifon et al., 2019; Lee et al., 2018). These processes could alter the abundance, composition and structure of DOM in aquatic environments (Lee et al., 2018; Xu et al., 2018). Meanwhile, the quantity and quality of aquatic DOM are closely related to the bioavailability and toxicity of exogenous chemical species (Macoustra et al., 2020; Yan et al., 2017). As a result, sunlight incidence might exert much alteration effect on the bioavailability and toxicity of heavy metal in water (Xu et al., 2018). However, current knowledge on the impact of DOM photodegradation on its interaction with exogenous chemical species, and their subsequent transport, bioavailability, and toxicity, have not been investigated.

Undoubtedly, the interaction of DOM with exogenous chemical species is greatly dependent on various factors including (i) abundance, source, elemental composition, and chemical structure of DOM; (ii) physicochemical properties of exogenous chemical species; (iii) solution chemistry (e.g., pH) (iiii) environmental factors (e.g., light radiation, temperature) (Chen and Hur, 2015; Hyung and Kim, 2008; Yu et al., 2018b; Zhu et al., 2020).; For example, Pb(II)-binding affinity of humic acid is significantly related to the solution pH (Habibul and Chen, 2018). Previous studies have also indicated that the charge and functional groups of both DOM and pharmaceuticals have a profound influence on the types of bonds formed between them (Hernandez-Ruiz et al., 2012).

6. Conclusions and future perspectives

DOM exists ubiquitously in aquatic environments and plays a series of critical roles in various biogeochemical processes. As such, understanding its sources, composition, reactivity, dynamics, and environmental implications is vitally important to elucidating its environmental roles. Despite abundant literature with respect to aquatic DOM, several research gaps still exist, including: collection of representative DOM samples, molecular-level structural characterization of DOM, assessment of the dynamics of DOM quantity and quality, and the consequent effects of DOM interaction on the transport, bioavailability, and toxicity of exogenous chemical species. Based on this review, the following conclusions and future perspectives are drawn:

- (1) DOM recoveries are greatly influenced by experimental procedures and external environment factors, which usually results in limited and highly variable DOM recoveries. In this sense, it is questionable if the extracted DOM can be viewed as representative of initial water samples. Additionally, chemical manipulation during DOM pretreatment processes might exert more alteration effect on the composition and structure of DOM. In this context, further efforts should be made to develop more reliable, efficient and gentle pretreatment methods to improve DOM recoveries with minimal damage to the nature of DOM.
- (2) Despite much work on DOM extraction and fractionation techniques, each method exhibits various advantages and limitations. Therefore, we should choose the most appropriate and reliable one among various methods according to research purpose, nature of sample, and laboratory conditions. Additionally, a combination of various extraction and fractionation methods is highly recommended. For instance, considering the high concentration efficiencies of reverse osmosis for DOM, and the fineness of resin separation technology, the combination of these two techniques has become one of the powerful methods for aquatic DOM pretreatment. Specifically, the combined technology of reverse osmosis and XAD resin can be applied in this way: first, use reverse osmosis to pre-concentrate the raw water, and then fractionate extracted DOM into different fractions with the help of XAD resin, therefore, obtaining multiple DOM components with different polarities.
- (3) Although spectroscopy techniques, including UV-Vis and fluorescence, have been most widely used to characterize DOM properties due to their easy operation, low cost and high sensitivity to DOM, it should be thoroughly realized that these

technologies have limitations for its inability in monitoring the non-fluorescent DOM and molecular structure. In fact, only a small portion of DOM is fluorescent, and the representativeness of these fluorescent components for DOM structure is usually challenged. Recently, FT-ICR-MS has attracted considerable attention and widely applied for achieving molecular-level structural characterization of DOM due to its sufficiently high resolving power. In this context, FT-ICR-MS will be an important complementary tool of other DOM characterization methods, and its application can present an in-depth understanding of DOM at the molecular level. Moreover, it must be noted that each characterization techniques can offer different composition and structure information due to the tremendously complex structure of DOM. Therefore, future studies are highly recommended to explore how a broad range of analysis techniques can be intimately and systematically linked together for DOM characterization. This may provide more comprehensive and convincing evidences for the assessment of the composition and structure of DOM. Furthermore, in addition to the application of various characterization techniques, chemometric methods will be of great help to extract more valuable and meaningful information from data obtained from instrument analysis, such as parallel factor analysis (PARAFAC), principal component analysis (PCA), and artificial neural networks (ANN). Thus, it is worth making further efforts to investigate how to utilize these data analytic methods to provide solid support for investigation on DOM.

- (4) DOM can directly or indirectly interact with exogenous chemical species through numerous reactions, such as photo-transformation, adsorption/desorption, and complexation reactions. Currently, numerous experimental and modelling efforts have been dedicated to providing insights into the interaction of DOM with these species. However, the effects of biogeochemical processes (e.g., light-induced transformation) on the dynamics of DOM and its effects on the migration and transformation of exogenous chemical species are not fully understood. Additionally, pilot-scale and even full-scale investigations based on practical natural waters are very scarce due to the more complicated conditions of real aquatic environments. Therefore, further research is needed to determine how DOM influences the transport and transformation of exogenous chemical species under real aquatic conditions at pilot-scale or even full-scale field studies. Such studies will provide more persuasive evidences for understanding the environmental behavior of DOM in aquatic environments. Such investigations also may be of great help to evaluate the ecological risk of heavy metals, organic pollutants, and nanomaterials, which is beneficial for more efficient control of these contaminants.

Declaration of competing interest

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

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