

Review

Characterization of aquatic organic matter: Assessment, perspectives and research priorities

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ABSTRACT

Organic matter (OM) refers to the largest reactive reservoir of carbon-based compounds on Earth. Aside of its role as a source of carbon, OM is also actively involved in a wide range of ecological functions. It also plays an important role in the solubility, toxicity, bioavailability, mobility and distribution of pollutants. Therefore, OM is a key component in the local and global carbon cycle. About 12,000 articles containing organic matter in the title were published during the past decade, with a continuous increasing number each year (ISI Web of Science). Although this topic was widely explored and its interest has significantly increased, some limitations remain. These limitations can be technical (e.g., pre-treatment processes, low-resolution instrument, data handling) and can be related to the current approach. In this review, we first present the current strategies and tools to characterize the organic matter in the aquatic environment, then we tackle several aspects of current characterization limitations. Finally, we suggest new perspectives and priorities of research to improve the current limitations. From our point of view, simultaneous studies of particulate and dissolved OM fractions should be prioritized and multi-disciplinary approach, creation of databases, controlled experiments and collaborative works should be the next targets for future OM research priorities.

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1. Introduction

Organic matter (OM) refers to the largest reactive reservoir of carbon-based compounds on Earth, with a total amount of carbon of ~3200 PgC through the 3 environments e.g., soils (1600 PgC), sediments (1000 PgC), and the ocean (685 PgC) (Bianchi, 2011; Hedges, 1992). OM present in the environment is introduced either naturally or anthropogenically. Natural OM is generated by the breakdown and degradation of organisms through various biological and physical natural processes involving hydrosphere, biosphere, and geosphere (Sillanpää, 2014). Anthropogenic OM, on the other hand, is introduced in the environment through human activities and by-products, e.g., sewage (Guo et al., 2010) and, litter and through degradation of microplastics (Romera-Castillo et al., 2018). Aside of its role as a source of carbon, OM is also actively involved in a wide range of ecological functions being a source of energy for microbes in soil and aquatic food web and a byproduct of biological metabolism (Jiao et al., 2010; Thurman, 1985). It also plays important roles in the solubility, toxicity, bioavailability, mobility and the distribution of pollutants via binding with heavy metals and/or persistent organic pollutants (POPs) (Deb and Shukla, 2011; Farrington and Takada, 2014; Hedges, 2002; Romera-Castillo et al., 2018). Therefore, OM is a key component in local and global carbon cycle and small changes in its size, proportion and dynamics can potentially impact a large number of biogeochemical processes and/or systems such as carbon storage, CO₂ release and coupling of terrestrial and marine systems (Cole et al., 2007; Tranvik et al., 2009) with several consequences on climate, aquatic life and global habitability (Folger, 2008; Lal et al., 2008; Lehmann and Kleber, 2015; Schuur et al., 2015; York, 2018). In this sense, the understanding of the carbon cycle from local to global scale is currently one of the major conundrums in the fields of environmental sciences and biogeochemistry.

In aquatic environments, OM is defined as a heterogeneous mixture of particles and molecules having variable physical (e.g. size and porosity) and chemical (e.g. functional group content and solubility) properties (Baldock et al., 2004). It is operationally divided into 2 fractions based on filter pore size: dissolved organic matter (DOM: <0.2/0.45/0.7 µm) and particulate organic matter (POM: >0.2/0.45/0.7 µm). Exchanges between both forms are easy and regulated by mechanisms such as adsorption/desorption, aggregation/dissolution, dissolution/precipitation, etc.; and can be mediated by photochemical processes and biological activity (He et al., 2016a, 2016b; Perdue and Ritchie, 2003; Zimmermann-Timm, 2002). Moreover, the amounts and the characteristics of the OM are greatly influenced by biogeochemical processes such as photochemical and biological degradation. Understanding the OM dynamics in aquatic environments and its role in local and global carbon cycles implies a study at various structural level and from diverse perspectives (Summons, 1993). A wide range of techniques are used to characterize the OM based on bulk chemical properties with general parameters (e.g., measurement of dissolved and particulate organic carbon concentration, DOC, and POC) to deep

insights into the molecular setup of DOM via advanced tools (e.g. the characterization via Fourier-transform ion cyclotron mass spectrometry) (Dittmar and Stubbins, 2014). The OM can be studied by using two different approaches: source tracking, which gives information on sources, and molecular characterization, which gives detailed structural information (e.g., class compounds, functional groups, and elemental formula). Within the first approach we can find techniques such as stable isotopes ratios (Lambert et al., 2011), biomarkers (Derrien et al., 2017c), compound-specific isotopes analysis (Schmidt et al., 2004), and spectroscopic characterization by measuring UV-absorption (Helms et al., 2008) and fluorescence (Coble, 1996; Murphy et al., 2014a, 2013; Stedmon et al., 2003). Within the molecular characterization techniques, we can find size exclusion chromatography coupled with organic and/or nitrogen organic detector(s) (Huber et al., 2011), pyrolysis gas chromatography mass spectrometry (Jeanneau et al., 2015), homo and hetero-correlated multidimensional nuclear magnetic resonance spectroscopy (Hertkorn et al., 2013), and Fourier-transform ion cyclotron mass spectrometry (Sleighter and Hatcher, 2007).

Despite numerous studies in the last decades, the OM dynamics in aquatic environments and the DOM-POM interactions as well as, at a bigger scale, its role in local and global carbon cycles are still poorly understood. Various reasons can be found to justify this gap in understanding/knowledge. One of these is related to inherent problems affecting the analysis due to the nature of the sample (low concentration, salt occurrence, heterogeneity, complexity, sensitivity to physical and chemical properties) and/or to the limitations of the techniques (price, accessibility, sample preparation, sensitivity, fraction targeted, etc.). Another critical point is that DOM and POM fractions are mostly investigated separately and only a few studies consider both (Dhillon and Inamdar, 2013; He et al., 2016c; Lambert et al., 2017; Osburn et al., 2015, 2012; Roebuck Jr. et al., 2018; Thibault et al., 2019). Lastly, it can also be explained by the difficulties in linking the results of the OM characterization to the mechanisms and dynamics of the OM. More effort should be made to improve the current strategy for the characterization of the OM and its dynamics. In this framework, the aims of this paper were: 1) to present the current strategies and briefly summarize the tools used to characterize the OM in aquatic environment (i.e., source tracking and molecular characterization techniques), 2) to raise the current issues limiting our ability to clearly understand the dynamics of the OM at local and global scales and, 3) to suggest new perspectives and priorities of research to improve the current limitations.

2. DOM and POM in the aquatic environment

Organic matter comprises a large number of molecules belonging to many classes of compounds (e.g., polysaccharides, amino acids, humic substances, lignin, cellulose, peptidoglycan, protein, saturated and unsaturated hydrocarbons, tannins, aromatic compounds), and with different polarity (hydrophobic,

transphilic, and hydrophilic) (Antony et al., 2017; Hawkes et al., 2018; Kellerman et al., 2015; Leenheer and Croué, 2003; Sandron et al., 2015; Volkman and Tanoue, 2002). It represents a complex mixture which also varies widely according to the environment, the geography, the time, and the depth in the water column (McCallister et al., 2018; Mopper et al., 2007). Although the organic matter is commonly divided into the dissolved (DOM) and particulate (POM) size fractions, there is a size continuum where the colloidal forms (marine gels) are the link between the two pools (Orellana and Leck, 2015). These colloidal forms can aggregate and disassemble shifting between the dissolved and particulate form. The size of the molecules is also one of the factors that determine the reactivity and turn over time of OM in the natural environment, e.g. it affects bacterial uptake (Amon and Benner, 1996). The complexity of OM and of the processes affecting it results in a large variability in its reactivity. A reactivity continuum model was proposed by Boudreau and Ruddick (1991) and it is still used to have the most realistic description of OM decomposition in different environments (Aumont et al., 2017; Garcia et al., 2018; Manzoni et al., 2012; Mostovaya et al., 2017). Sources of OM are multiple and diverse, which greatly increases its complexity. These sources are usually classified as allochthonous or autochthonous. The natural allochthonous sources, coming from outside the aquatic environment, include materials from land (e.g., vascular plants, leaves, root exudates and soils) as well as from the atmosphere (e.g., dust storms), and from hydrocarbon seeps at the seafloor. Apart from that, anthropogenic activities play important role as allochthonous OM sources with input from e.g., organic fertilizers, effluents from wastewater treatment facilities, treated ad/or untreated sewage, industrial wastewaters, black carbon from fires and fossil fuel, oil spills and, ultimately, leached from plastic (Carstea et al., 2016; D'Sa et al., 2016; Derrien et al., 2015; Jaffe et al., 2013; Romera-Castillo et al., 2018). Autochthonous OM, produced within water bodies, derives from aquatic biota (e.g., algae, bacteria, plankton, macrophytes, and nekton), and is produced by both autotrophic (Romera Castillo et al., 2010; Thornton, 2014) and heterotrophic organisms at all trophic level (Derrien et al., 2018a; Steinberg et al., 2004; Tulonen, 2004) as well as by viruses through viral lysis. At the same time, both DOM and POM can be removed and/or transformed and can play an important role on the overall biogeochemical cycles and microbial loop within the aquatic environment (Asmala et al., 2018; Ávila et al., 2019). They can be removed by aquatic organisms and used for biomass synthesis or for respiration, the latter producing CO₂. As OM is subject to photochemical processes that can affect DOM and POM properties, it acts as an important photosensitizer, mediating the production of carbon dioxide (CO₂), carbon monoxide (CO) and other dangerous reactive oxygen species causing oxidative stress to living organisms, at the same time that it can also degrade toxic compounds preventing exposure to the biota (Vione et al., 2014). These processes affecting both fractions are variable in time and space and often controlled by environmental parameters (e.g. temperature, pH, salinity), increasing their variability. Moreover, exchanges mechanisms between the two pools (from DOC to POC and vice versa) are highly important and need to be considered. Fig. 1 summarizes the main processes affecting DOM and POM described in this paragraph (Amon and Benner, 1996; Estapa and Mayer, 2010; Grey et al., 2001; Hansell and Carlson, 2015; He et al., 2016a; Hein et al., 2003; Heitmann et al., 2007; Jiao et al., 2010; Jin et al., 2006; McCarthy et al., 2007; Ogawa et al., 2001; Porcal et al., 2015; Romera Castillo et al., 2010; Salonen and Hammar, 1986; Smith et al., 2015; Steinberg et al., 2004; Thornton, 2014; Tulonen, 2004; Weston et al., 2006; Wolf et al., 2018).

3. Source tracking

3.1. Stable isotope ratios

Carbon has two stable naturally-occurring isotopes: ¹²C (98.89%) and ¹³C (1.11%). Physical, chemical or biological processes in natural environments can lead to changes in the isotopic composition due to a difference in atomic mass between ¹²C and ¹³C. For instance, according to the types of plants (e.g., C3, C4 or crassulacean acid metabolism (CAM)) and/or their specific photosynthetic paths, the isotopic ratios may subject to change. C3 plants present values of carbon isotopic composition $\delta^{13}\text{C}$ (ratio of stable isotopes ¹³C/¹²C reported in parts per thousand (per mil, ‰), measured via an elemental analyzer coupled with an isotope ratio mass spectrometer (EA-IRMS)) between −33 to −24‰, while the values range from −16 to −10‰ for C4 and between −20 and −10‰ for CAM. Stable carbon isotope ratios are widely used and considered as one of the most effective ways to track both the sources (e.g., allochthonous versus autochthonous) and the transformation processes of OM in the environment (Amiotte-Suchet et al., 2007; Benner et al., 1997; Lambert et al., 2011; Meyers, 1994; Toming et al., 2013). Previously, most of the studies were focused on $\delta^{13}\text{C}$ analysis. Nowadays, this is often combined with the analysis of stable nitrogen isotope ratios $\delta^{15}\text{N}$ to prevent some existing overlaps with the single use of the $\delta^{13}\text{C}$ tracer (Barros et al., 2010; Berto et al., 2013; Cloern et al., 2002; Derrien et al., 2018a; Gao et al., 2012; Ogrinc et al., 2005). In addition to these measurements, isotopic mixing models, based on isotopic mass balance equation (Phillips et al., 2005; Phillips and Gregg, 2003), can be used to estimate the contributions of OM sources in multi-source watershed context or during storm events (Derrien et al., 2018a; Yang et al., 2015; Yu et al., 2019).

3.2. Biomarkers

Molecular biomarkers (e.g., targeted organic compound analyzed by gas chromatography coupled with mass spectrometry (GC-MS)) provide a powerful tool to identify the origins of OM and the associated biogeochemical processes, and thus to reconstruct environmental changes in the environment. To date, lignin-phenol (i.e., lignin), plant pigments (i.e., chlorophylls and carotenoids), carbohydrates, proteins, and lipids have been most widely used as biomarkers to identify OM sources (Bianchi et al., 1995; Bianchi and Canuel, 2011; Hedges, 1992; Meyers and Ishiwatari, 1993; Saiz-Jimenez and De Leeuw, 1986). Among those, lipids have the highest potential as molecular markers for marine (Berge and Barnathan, 2005; Christodoulou et al., 2009; Prahl et al., 1994; Volkman, 1986), coastal (Canuel, 2001; Wakeham et al., 2002; Wakeham and Beier, 1991; Yoshinaga et al., 2008), estuarine systems (Carreira et al., 2011; Hall et al., 2006; Lauricillard and Saliot, 1993; Mudge and Norris, 1997; Zimmerman and Canuel, 2001), and inland environments (Derrien et al., 2015; Jaffé et al., 1995; Jandl et al., 2005; Pisani et al., 2013), covering diverse OM sources (e.g., allochthonous, autochthonous sources and anthropogenic inputs) (Derrien et al., 2015; Zimmerman and Canuel, 2001), due to the characteristics of ubiquity, diagenetic and chemical stability, and their extreme structural diversity. The accuracy if the assignment of the OM sources via this approach is helped by the use of compounds ratio and the application of multivariate statistical tools. Derrien et al. (2017c) have recently presented a detailed review of the lipid biomarkers and their use.

3.3. Compound-specific isotope analysis (CSIA)

CSIA refers to the measurement of the isotopic signatures

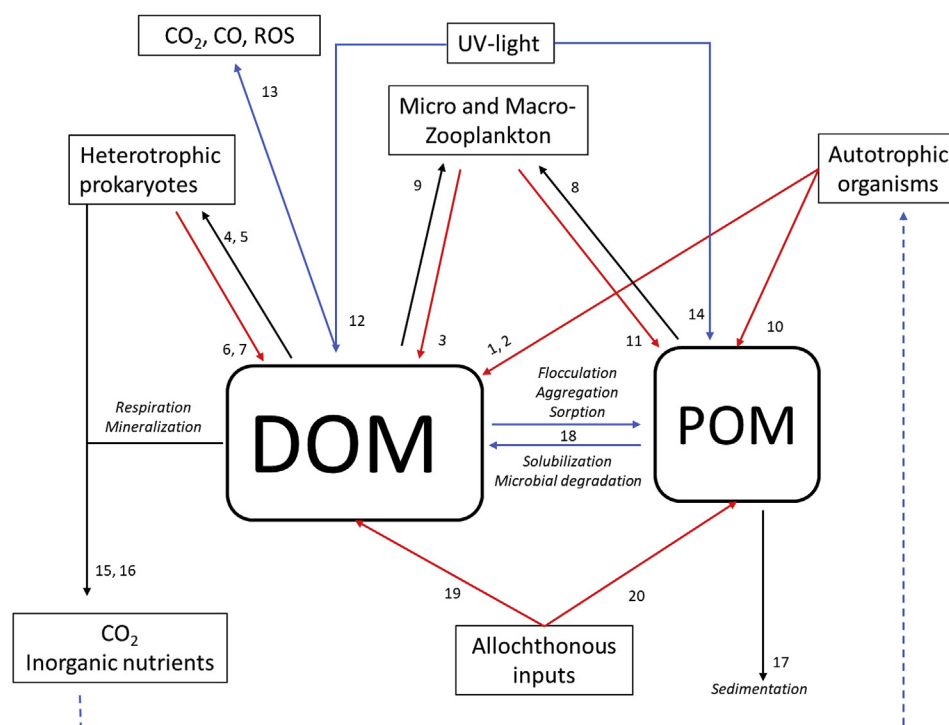


Fig. 1. Scheme showing the processes (e.g. sources, sinks, and transformations) affecting DOM and POM in the aquatic environment (red arrows = sources, black arrows = sinks, blue arrows = transformation processes). The dotted line represents the pathway of the recycled inorganic nutrients back into the cycle. ¹Romera Castillo et al. (2010), ²Thornton (2014), ³Steinberg et al. (2004), ⁴Tulonen (2004), ⁵Amon and Benner (1996), ⁶Ogawa et al. (2001), ⁷Jiao et al. (2010), ⁸Grey et al. (2001), ⁹Salonen and Hammar (1986), ¹⁰Jin et al. (2006), ¹¹McCarthy et al. (2007), ¹²Porcal et al. (2015), ¹³Wolf et al. (2018), ¹⁴Estapa and Mayer (2010), ¹⁵Weston et al. (2006), ¹⁶Heitmann et al. (2007), ¹⁷Smith et al. (2015), ¹⁸He et al. (2016), ¹⁹Hansell and Carlson (2015), ²⁰Hein et al. (2003). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(typically, the stable isotopes of carbon, hydrogen, oxygen, nitrogen or sulfur) of individual compounds from a complex environmental mixture via GC-combustion-isotope ratio mass spectrometry (GC-C-IRMS). This approach can provide information about source differentiation (e.g., origin and fate of organic matter in both extant and fossil environment) (Evershed et al., 2008), reaction pathways in the environment, including biodegradation and abiotic degradation, and help for forensic applications as environmental remediation decision or monitoring remediation processes on polluted sites (Elsner and Imfeld, 2016; Schmidt et al., 2004).

CSIA was first applied to the $\delta^{13}\text{C}$ analysis of hydrocarbons in crude oils and refined products to reduce the variability of source pools and identify the sources of individual compounds or groups of compounds in complex mixtures (Bianchi and Canuel, 2011; Hayes et al., 1990; Simoneit, 1997). Then, it has subsequently been extended to other biogenic elements (e.g., nitrogen and hydrogen) (Batista et al., 2014; Chikaraishi and Naraoka, 2003; Lichtfouse, 2000) and a variety of biochemicals (amino acids, carbohydrates, lipids, and lignin phenols) (Alewell et al., 2016; Pearson et al., 2001) and organic contaminants (e.g., polycyclic aromatic hydrocarbons PAH, polychlorinated biphenyls PCB, benzene, toluene, ethylbenzene BTEX etc.) (Elsner and Imfeld, 2016; Schmidt et al., 2004). The power of this technique lies in the differential fractionation of individual compounds especially when it is used in combination with already known chemical biomarker to identify the origin of the organic matter in all environments (Amelung et al., 2008; Bendle et al., 2007; Cooper et al., 2015; Tolosa et al., 2013).

3.4. Optical properties

The absorbance and fluorescence properties of DOM have been defined as “optical markers” comparable to traditional biomarkers

(Stedmon and Nelson, 2015). UV–visible absorption and fluorescence have been widely used to characterize the colored and fluorescent sub-fractions of DOM: CDOM and FDOM, respectively (Coble, 2007; Helms et al., 2008; Wünsch et al., 2017).

The CDOM component absorbs light mainly in the ultraviolet (UV) and blue regions of the electromagnetic spectrum (Bricaud et al., 1981). The absorption coefficients at selected wavelengths (a_λ), are used for different purposes. The most common is the a_{254} , which is calculated to estimate CDOM content (Del Vecchio and Blough, 2004; Weishaar et al., 2003). The a_{350} and a_{440} are used due to their strong correlation with lignin (Spencer et al., 2009b; Stedmon et al., 2011a) and application to ocean color remote sensing (Siegel et al., 2005), respectively. A series of indices have been also widely applied using absorption coefficients, to gain information on the average molecular weight (the ratio between a_{250} and a_{365} , E2:E3, (Peuravuori and Pihlaja, 1997); the spectral slope ratio— S_r (Helms et al., 2008),) and the aromaticity of the molecules (specific ultraviolet absorption at 254 nm, SUVA_{254} (Weishaar et al., 2003),) and on the tracking of terrestrial compounds (spectral slope between 275 and 295 nm, $S_{275-295}$ (Fichot and Benner, 2012),).

The FDOM is the fraction of CDOM, which can emit fluorescence after absorbing UV–Visible light. The spectral characteristics of FDOM can be investigated by using excitation–emission wavelength pairs (e.g. in situ probes), single emission spectra, synchronous spectra, and three-dimensional excitation–emission matrices (EEMs). Moreover, the combination EEMs with parallel factor analysis (PARAFAC) (Fig. 2) allows to distinguish between different groups of fluorophores (components), such as humic-like, re-elaborated humic-like (also called microbial or marine humic-like) and protein-like (Fellman et al., 2010; Ishii and Boyer, 2012; Murphy et al., 2014a; Stedmon and Bro, 2008). A set of indices have

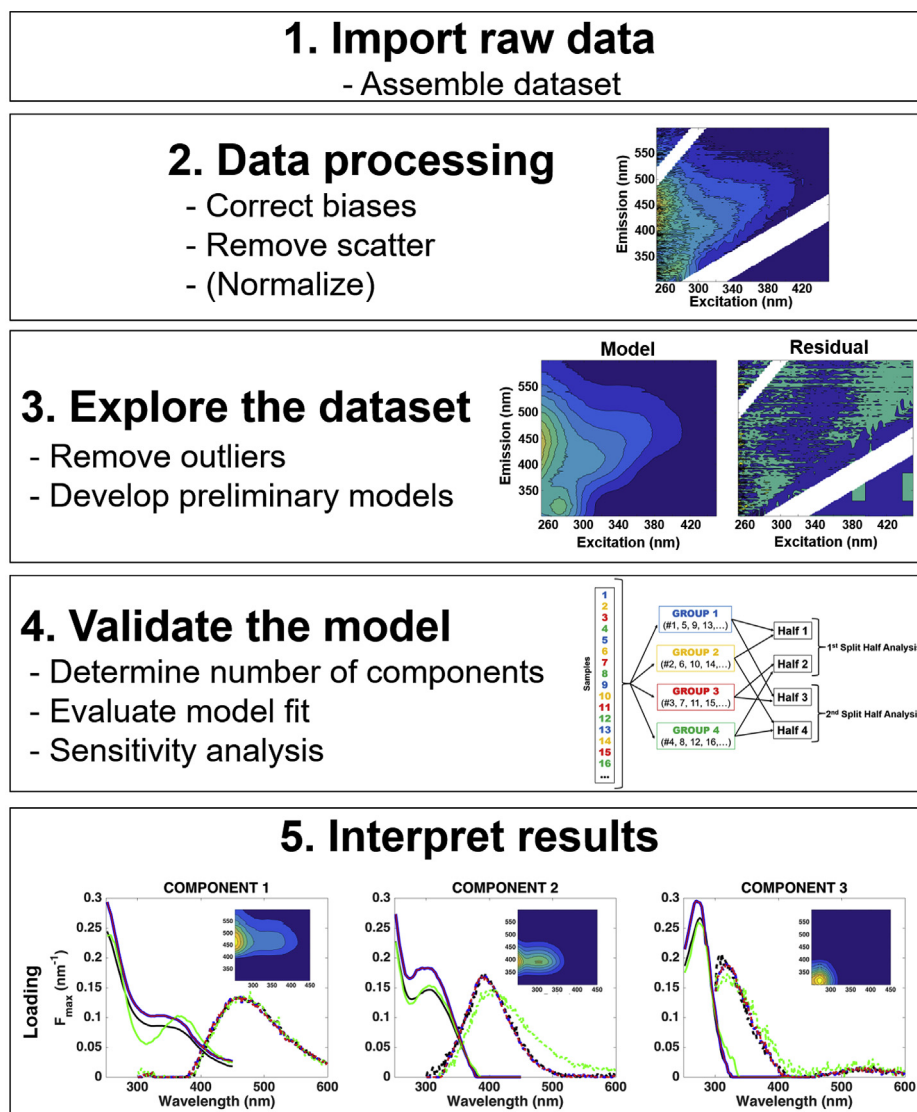


Fig. 2. Scheme presenting the procedure for the PARAFAC analysis of fluorescence EEMs. Modified from Gonçalves-Araujo et al. (2016); Murphy et al. (2013); Stedmon and Bro (2008).

been also developed by using the ratio of the fluorescence intensity at specific wavelengths, or wavelength ranges, mainly to distinguish between autochthonous and allochthonous DOM sources, and to assess the degree of humification of DOM (Gabor et al., 2014; Huguet et al., 2009; McKnight et al., 2001; Zsolnay et al., 1999).

Both, fluorescence component distribution and optical indices have successfully been applied to investigate the chemical composition, identify the sources of DOM and track the involved biogeochemical processes in many aquatic environments such as wastewaters, rivers, groundwaters, lakes, seas, and oceans (Fichot et al., 2013; Gonçalves-Araujo et al., 2016, 2015; Inamdar et al., 2011; Jaffé et al., 2014; Lambert et al., 2016; Retelletti Brogi et al., 2019, 2018; Stedmon et al., 2011b; Yamashita et al., 2013; Yang et al., 2014). Due to their low cost, rapidity, and sensitivity, the very limited sample pre-treatment required, and thanks to the development of user-friendly tools to treat the data (Murphy et al., 2013), these techniques are now considered as a popular, powerful, and standard tool for DOM characterization. Their wide application on an exponentially increasing number of studies allowed for gaining information on OM composition and its related

environmental processes on a global scale, which would take much longer time and effort if done with more complex and time-consuming techniques.

4. Structural characterization

4.1. Size exclusion chromatography techniques

The liquid chromatography coupled to organic carbon and nitrogen detectors (LC-OCD-OND) is basically a size exclusion chromatography coupled to 2 online detectors (OCD and OND) (Huber et al., 2011). This method uses a purified mobile phase (a phosphate buffer) and a chromatographic column (a weak cation exchange column on polymethacrylate basis) able to separate the OM according to the molecular weight (Huber et al., 2011). Nowadays, it is recognized to be an attractive technique providing for direct qualitative and quantitative information on the OM (molecular weight fractionation and DOC and DON concentrations) (Allpike et al., 2007; Her et al., 2003, 2002; Huber et al., 2011; Retelletti Brogi et al., 2018; So et al., 2017; Yan et al., 2012). Five defined

size fractions can be identified and quantified including biopolymers (BP, >10 kDa), humic substances (HS, approximately 1 kDa), building blocks (BB, 300–500 Da), low molecular weight acid and neutrals (LMWA/N, <350 Da) (Huber et al., 2011; Maqbool et al., 2017). Nowadays, this technique is mainly applied to track the natural organic matter in drinking water and/or to study membrane fouling issues (Baghoth et al., 2011; Kennedy et al., 2005; Rosenberger et al., 2006; Zheng et al., 2014). It is also becoming a preferred choice to characterize organic matter from natural environments (Dittmar and Kattner, 2003; Hutchins et al., 2017; Penru et al., 2013; Retelletti Brogi et al., 2018; Villacorte et al., 2015) as the molecular weight of the organic matter strongly affects reactivity in the natural ecosystems (Yan et al., 2012). It has also been suggested that, since it detects the a_{254} coupled with the different size fractions, it can give a hint on the chemical composition of CDOM (Stedmon and Nelson, 2015). One advantage of this method is that the samples do not need any pre-treatment and its strength is enhanced when coupled with other techniques (e.g. optical properties (Baghoth et al., 2008; Penru et al., 2013);) allowing to investigate the properties of the specific size fractions.

4.2. Pyrolysis–gas chromatography-mass spectrometry (Py-GC-MS)

Py-GC-MS is a method of chemical analysis in which natural and synthetic biopolymers present in the sample are heated to decomposition to produce sub-units, i.e. low-molecular-weight molecules that are then separated by gas chromatography and detected using mass spectrometry (Leenheer and Croué, 2003; Matilainen et al., 2011).

This technique is not the most used for the characterization of the molecular composition of the OM, however it represents an interesting option for obtaining detailed structural information on the components of natural organic matter, as well as on humic substances for both DOM and POM and also to assess the preservation/diagenesis and provenance of sediment organic matter (Carr et al., 2010; Derenne and Nguyen, 2014; Greenwood et al., 2012; Iwai et al., 2013). Lately, Jeanneau et al. (2018) demonstrated the suitability of this molecular analysis to apportion the sources of POM in river.

4.3. Fourier-transform infrared spectroscopy (FTIR)

FTIR is probably one of the most commonly used spectroscopic tool, after fluorescence spectroscopy, for the analysis of either liquid or solid natural OM (NOM) samples (Artz et al., 2008; Derenne and Nguyen, 2014; Dick et al., 2003; Giovanela et al., 2004; Haberhauer et al., 2000; Parolo et al., 2017; Tremblay et al., 2011). This spectroscopy exploits the fact that molecules absorb frequencies that are characteristics of their structure, e.g. vibrational characteristics of their chemical bonds. The resulting absorption is a unique fingerprint of compounds, allowing the identification of functional groups (Matilainen et al., 2011). Transmission spectroscopy through a sample-KBr pellet is the oldest and most commonly used method in NOM studies. Alternatively, reflectance spectroscopy as attenuated total reflectance (ATR) and diffuse reflectance infrared Fourier transform (DRIFT) have been preferentially used as it represents a more robust, reliable and non-destructive technique and generates higher reproducibility than the former one (Simonescu, 2012).

Although this technique presents the advantage of being applicable to both DOM and POM fractions, nowadays, it is rarely used by itself and preferentially combined to other techniques (e.g. NMR, fluorescence) to endorse the interpretation of the results related to changes during biochemical mechanisms and/or to control the quality and efficiency of the water remediation

processes (Maqbool et al., 2017; Rodríguez et al., 2016).

4.4. Nuclear magnetic resonance spectroscopy (NMR)

NMR has been extensively used for decades to characterize the structure of the molecules in OM as it provides a detailed picture of its molecular architecture (Barron and Wilson, 1981; Hertkorn et al., 2016, 2013; Kögel-Knabner, 1997; Konstantinov et al., 2013; Matilainen et al., 2011; Wong et al., 2002; Zhong et al., 2011). Briefly, NMR is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. It can be a very selective technique, distinguishing among many atoms within a molecule or collection of molecules of the same type but which differ only in terms of their local chemical environment. NMR can be done on both solid and liquid-phase samples (Matilainen et al., 2011; Mopper et al., 2007) and commonly performs for the nuclei of atoms ^1H , ^{13}C , and ^{15}N (Minor et al., 2014). Traditionally, 1 dimensional (1D) NMR was used to characterize the OM. However, over the past decade, NMR has been used in two (2D) or multidimensional configuration as they represent a more appropriate technique to characterize complex organic compounds (Hertkorn et al., 2013; Kaiser et al., 2003; Zhong et al., 2011). Detailed information on the use of NMR to characterize OM can be found in Mopper et al. (2007) and Matilainen et al. (2011).

4.5. High-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

FT-ICR MS has emerged as a reliable tool for the in-depth molecular characterization of complex mixtures as DOM. Over the last decade, FT-ICR MS had the prevailing position for the chemical characterization of DOM at the molecular level and for all the environments including lakes, seas/oceans, estuary, wetlands, soils, rivers and even ice cores (Bae et al., 2011; Chen et al., 2011; Derrien et al., 2017a, 2017b; Gonsior et al., 2013; Kujawinski et al., 2002; Li et al., 2019; Lu et al., 2016; Mopper et al., 2007; Retelletti Brogi et al., 2018; Sleighter and Hatcher, 2008).

Coupled with electrospray ionization (ESI), this technique provides the necessary resolution to determine with high accuracy hundreds to several thousand ions with an m/z range typically from 200 to 1000 Da. Furthermore, due to the high mass resolution and accuracy (less than 0.5 ppm), the elemental formulas are assigned with a high level of confidence (Repeta, 2015; Stubbins and Dittmar, 2014). As ESI-FT-ICR-MS analysis generates a large amount of data, the empirical formula data are commonly categorized in 6–8 main class of compounds (e.g., lipids, proteins, carbohydrates, unsaturated hydrocarbons, lignins and/or carboxyl-rich alicyclic molecules (CRAM), tannins, and condensed aromatic compounds) according to their H/C and O/C ratios (e.g., van Krevelen diagram). Some indices related to the degree of unsaturation (DBE: double bond equivalent index) and/or the aromaticity of the formulae (AI or AI_{mod}: modified aromaticity index) have been also developed (Hockaday et al., 2009; Hodgkins et al., 2016; Ohno et al., 2010). Comparison of samples at this molecular specificity scale allowed for the identification of specific classes of compounds according to their sources or ways of production (Koch et al., 2005; Koch and Dittmar, 2006) and also, more recently, to highlight the extreme isomeric complexity in the DOM across aquatic environments (Hawkes et al., 2018). Nowadays, this technique is likely considered as the most powerful tool that can be used to characterize the structures and the molecular properties of the DOM.

5. Limitations of the actual methods and approaches

A large fraction of uncertainty on OM composition is related to

inherent problems affecting its analysis such as (i) low concentration (e.g., seawater $0.4\text{--}1\text{ mg L}^{-1}$): in water with a much higher amount of inorganic compounds that can negatively affect chemical analysis or the low abundance of some compounds (Minor et al., 2014; Stubbins and Dittmar, 2014); ii) extreme diversity and heterogeneity of compounds, of their chemical properties, and of their molecular weights, which complicates isolation and analysis approaches (Hertkorn et al., 2008; Sandron et al., 2015); and (iii) the difficulty in extracting unbiased material during isolation or concentration processes (Matilainen et al., 2011; Mopper et al., 2007). Although notable advances have been done in this last decade to improve the sample pre-treatment, instrument resolution and analytical capabilities of the equipment (McCallister et al., 2018), most of the highly sensitive techniques still present some inconveniences (technical issues and prohibitive cost) in addition to the difficulties related to data handling compared to the elemental techniques. For instance, the analysis of the stable isotope ratios does not require much pre-treatment but it will give only one value which relates to the source of the organic matter while the more advanced techniques such as FT-ICR MS analysis will provide thousands of formulas often not allowing for a full understanding or interpretation of the data.

Besides these issues related to the nature of the samples, it is very important to raise the question related to the representativeness of the studied fraction and/or sub-fractions. Over the past decades, tremendous efforts have been made to quantify, analyze, and characterize the OM, but we are still facing these issues. Bulk, POM, DOM, FDOM or even CDOM are different OM fractions, which can be studied with the techniques previously introduced. CDOM and FDOM are widely investigated since their analyses are cost-effective, relatively quick and non-destructive. However, this optical approach is limited to colored and fluorescent OM. What percentage of bulk OM or even of the DOM does that represent? For example, recently Hawkes et al. (2019) analyzed online the size distribution with HPSEC-UVDAD (high-pressure size exclusion chromatography coupled with UV–Vis diode array detector) and the molecular mass via ESI-MS of different DOM samples. They

observed a clear discrepancy between the two methods and showed that an important pool of organic matter having a strong UV absorbance showed no ESI-MS signal. These results demonstrate that there is a substantial distinction in DOM samples between what is optically active and what is efficiently ionized by ESI. Hence, is targeting only a specific sub-fraction suitable to understand mechanisms at a larger scale? Then, most of the OM studies were focused on DOM or POM fractions separately. This approach is questionable. Is it the most insightful approach to understand the dynamics of the OM in the aquatic environment? The interactions between both fractions happen continuously and sometimes very fast. They also change in time due to the biotic and abiotic factors; it is a dynamic system. Therefore, focusing studies on only one OM fraction has several limits, thus simultaneous studies should be prioritized. Of course, studies integrating simultaneous DOM and POM characterization would induce other issues. As shown in Fig. 3, most of the techniques of OM characterization cannot be directly applied to both fractions. Techniques such as isotopes, biomarkers or Py-GC-MS can be applied on DOM fractions after a process of freeze-drying plus desalination in the case of salted water. These pre-processes require a large amount of sample ($\sim 1\text{ L}$ or more according to the concentration) and may cause OM modification (Repeta, 2015). There are also some techniques (i.e. fluorescence), which can be performed on POM after extracting the DOM from it (i.e. water or solvent extraction), assuming it is representative of the whole POM fraction. However, the representativeness of this extract was never explored or tested. Indeed, this limitation cannot be neglected, especially when recent studies highlight the potential failure of representativeness of these extracts (Derrien et al., 2018a; Yu et al., 2019).

These observations, finally, lead to an ultimate question. How can we link all the various and diversified collected data to the basic understanding of OM dynamics in the aquatic environment? OM is studied at various structural level and from diverse perspectives (Fig. 4). Elemental analysis as DOC or POC concentrations or stable isotope help estimate the flux of carbon or identify the sources of the organic matter. One can thus understand mechanisms of

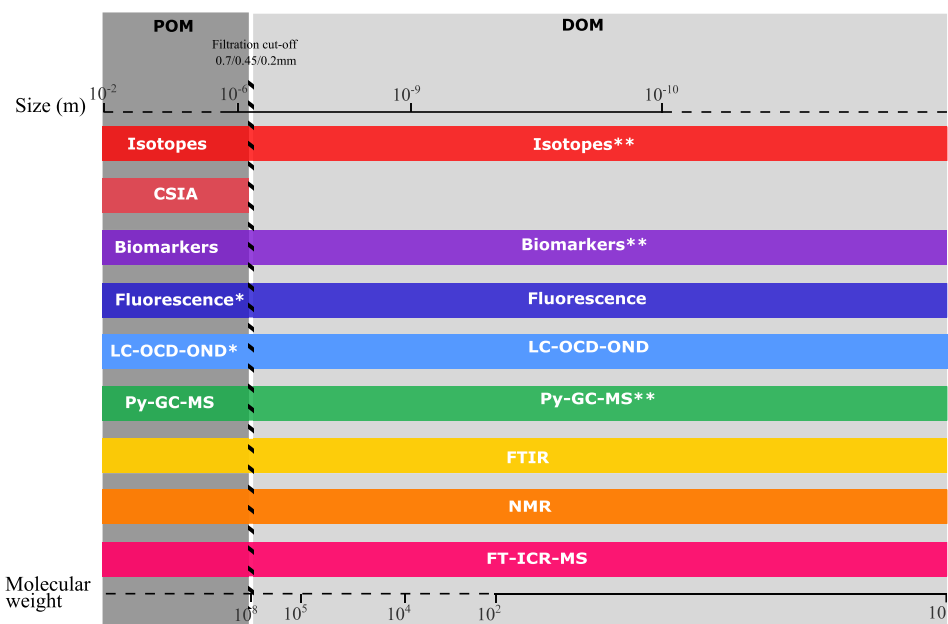


Fig. 3. A diagram presenting the most commonly used analytical tools to characterize organic matter in the aquatic environment and their applicability with respect of the fraction e.g., dissolved and particulate. (*: Analyses of the POM fraction can be performed on the extracted DOM from the POM; **: Analyses of the DOM fraction limited to large amounts of samples and after the freeze-drying process). The dashed line represents a change in size scale.

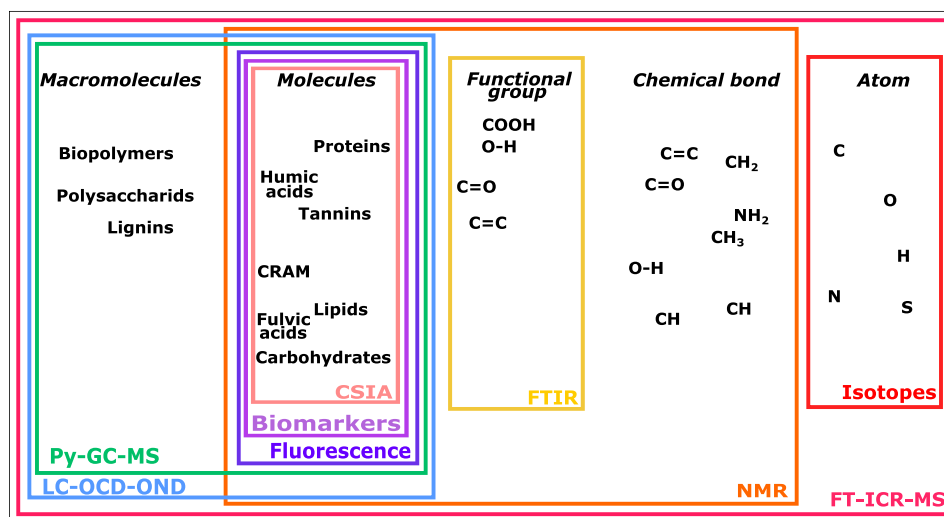


Fig. 4. A representation of the chemical structural level from atomic to macromolecular level and the analytical tools presented in this study.

transport. By contrast, a molecular approach will give information on the state of the material (maturity, lability, aromaticity, freshness, etc ...), diagenetic effects or geological changes (Summons, 1993). It is clear that a complementary approach is necessary, but linking all the information together is probably the biggest challenge we have to solve, in order to achieve a full understanding of the aquatic organic matter dynamics and at a larger scale, the carbon cycle. So far, few recent studies have attempted to combine source tracking methods and molecular characterization techniques with a preference for fluorescence and FT-ICR-MS (Stubbins et al., 2014; Wagner et al., 2015; Wünsch et al., 2018a). Although the work of Wagner et al. (2015) has given a good correlation between the results of both techniques, the question of the representativeness of the fluorescence fraction is still pending. Newly, Thibault et al. (2019) published a multi-compartment (e.g., DOM, POM, and bulk fractions) study in which they applied complementary analytical approaches including bulk (elemental and isotopic composition) and structural (solid state ^{13}C NMR) analyses. This strategy allowed them to irrefutably demonstrate each OM pool has its own properties and dynamics. Challenges are still up but similar approaches need to be preferentially applied for the better understanding.

6. Future directions and new perspectives

After describing the inherent issues related to the techniques applied for characterization of the aquatic OM and/or its nature, in this last paragraph, we attempt to suggest some approaches that would be worthwhile to explore more in the future.

6.1. Standardization and databases

Some of the previously mentioned analytical techniques require the choice of different instrumental settings and samples preparation. However, these different choices may sometimes affect the final measurement of the samples making difficult a comparison of the results between different studies. Two symbolic examples are the processing and data treatment of the fluorescence EEMs and the FT-ICR MS coupled with ESI.

The results of fluorescence measurements depend on several factors such as instrumental settings (slits, scan speed, internal instrument biases) and phenomena like inner filter effect

(exceeding a certain concentration will result in a decrease of the fluorescence signal and the modification of the emission spectrum). These factors can be controlled and normalized to be comparable between different studies during post-measurements data treatment. However, some of these data treatments vary according to different studies. For example, some authors correct the inner-filter effect during data treatment whereas others dilute the samples according to the absorbance at 254 nm (a_{254}), but there is no agreement on the limit of the a_{254} value for the dilution (Hur et al., 2008; Miller et al., 2010; Ohno, 2002). Moreover, some authors present the data in Raman Units (RU) whereas others use Quinine Sulfate Units (QSU). The latter is however doubtful because different studies report different methods or do not give details on the QSU conversion (Ferretto et al., 2017; Lønborg et al., 2010; Romera-Castillo et al., 2014; Yamashita et al., 2010; Yao et al., 2011).

The first step for FT-ICR MS is solid phase extraction (SPE) and, according to the method used, the extraction efficiency can vary (Lv et al., 2016; Repeta, 2015; Stücheli et al., 2018; Wünsch et al., 2018b). Dittmar et al. (2008) summarized the different methods used to extract DOM for FT-ICR MS analysis, highlighting the different retention properties of the most commonly used sorbents. Then, FT-ICR MS is mostly used with electrospray ionization ESI including both negative and positive modes. The results of positive and negative ESI can overlap, but differences are still present (Repeta, 2015). For example, Hertkorn et al. (2013) compared both modes of ESI for FT-ICR MS analysis on ocean DOM samples from the surface to deep depths. The results showed a preferential detection of carbon-rich (62%) and oxygen-depleted (~26%) ions in positive mode compared to the negative mode (~50% and 36–42%, respectively) in the assigned molecular formulas. They generally observed a larger number of assigned molecular compositions in positive mode than in negative mode. On the other hand, negative mode ESI seems to be more sensitive towards acidic functional groups (Solihat et al., 2019). Higher discrepancies are inevitably observed with different ionization sources such as atmospheric pressure ionization (API) or atmospheric pressure chemical ionization (APCI) due to their inherent selectivity for specific types of molecules (Hertkorn et al., 2008; Solihat et al., 2019). Hence, the selectivity and the matrix sensitivity of the ionization sources represent an issue which needs to be considered and refined with a standardization of the method (Derrien et al., 2018b; Mopper et al., 2007).

These examples highlight the need for a standardization of sample preparation, analytical methods, and data treatment. Standardized data processing tools are already available for fluorescence EEMs treatment and were improved during the last few years. The newest drEEM tool developed by [Murphy et al. \(2014a\)](#) allows for the correction of EEMs by doing blank subtraction, Raman (or quinine sulfate) normalization, instrumental bias correction, and inner filter correction producing comparable data from different instruments and instrumental settings ([Murphy et al., 2010](#)). Similarly, a standardized method to prepare and measure the samples and/or treat the data after measurements should be prepared for all the techniques that might have these issues in order to improve the quality of the data and the comparison of different studies.

On top of that, the creation of online databases of published data would allow for a big step forward to improve data comparison and interpretation. For instance, a database of published fluorescence components (obtained by coupling EEMs with parallel factor analysis) has been created ([Murphy et al., 2014b](#)) and allows calculating the percentage of similarities between the published spectra. More recently, [Leefmann et al. \(2019\)](#) developed a new browser-based software tool for processing high resolution mass spectrometry data with the option to export the final data report and to compare with previous datasets. These kinds of databases, similarly to libraries used in chromatography and mass spectra analyses, would help a faster interpretation of the results, if previously reported, and increase the coherence between different studies with similar results.

The standardization of the methods and creation of databases will benefit especially those techniques, such as FT-ICR MS, that produce big datasets that are currently only partially exploited.

6.2. Laboratory experiment in controlled conditions

As previously highlighted, the factors regulating DOM and POM in the aquatic environment are several and variable in time and space. The analysis of samples from natural environments provides a snapshot of the OM in a specific place (either at a small or large scale) at a specific time. However, according to the parameters chosen, it is not always possible to identify the processes that lead to the observed dynamics/characteristics and extending these observations to a larger spatial and/or temporal scale is challenging. Setting up a laboratory experiment can help in identifying the effects that certain factors have on OM dynamics/properties. Experiments carried out under controlled conditions can be split into two categories according to the main purpose: 1) to study a single factor by isolating its effects, and 2) to study the combined effect of multiple factors. Many experiments studying the effect of a single factor have already been carried out for DOM. For instance, incubation experiments to study microbial degradation of OM have been carried out by removing the effect of autotrophic activity (by filtration and dark incubation) and grazers (by filtration) ([Asmala et al., 2014](#); [Logue et al., 2016](#); [Raymond and Bauer, 2000](#); [Retelletti Brogi et al., 2015](#)); photodegradation experiments to study the effect of UV radiation were carried out by removing the microbial communities (by poisoning) ([Porcal et al., 2004](#); [Spencer et al., 2009a](#)). A step forward would be at this point to put more efforts in planning experiments that consider the concurrent effect of more factors. Some good examples can be already found. [Whitehead et al. \(2000\)](#) set up a mesocosm experiment in 1500 L volume tanks and studied the combined effect of phytoplankton, biological activity, irradiation and water mixing on DOM properties. More recently, [Osterholz et al. \(2015\)](#) carried out an experiment, in 10 L volume bottles, to study the microbial production of refractory DOM. For this purpose, the authors took account of phytoplankton

abundance and species, microbial abundance and DNA, and nutrients concentration (simulating an upwelling). Lastly, [D'Andrilli et al. \(2019\)](#) performed a small-scale microcosm incubation experiment to isolate temporal patterns of C processing (i.e., respiration and total C utilization) for 3 different OM sources. The combination of several parameters measured in two recent incubation experiments highlighted the complexity of DOM production and consumption in a coastal environment and in particular showed that the composition of autochthonous DOM was mainly controlled by nutrient availability and the characteristics of the initial bulk DOM rather than the phytoplankton community [[Haraguchi pers. comm.](#)]. These studies demonstrated that the combination of biological and chemical techniques allows for linking the different factors such as time, DOM sources, biological activity, UV radiation, and to have a hint of the effects of these combined factors that is more similar to what is happening in a natural environment. By contrast, few studies were focused on the POM fraction and most of them investigated its degradation under different conditions of bioturbation ([Navel et al., 2012](#); [Sun and Dai, 2005](#)) or mineralization processes ([Guenet et al., 2014](#)). The laboratory experiments should also be realistic and, consequently, resemble as much as possible to the natural environment. Planning an experiment that resembles the natural environment is challenging because it is not possible to reproduce and consider all the factors controlling the OM dynamics. However, when planning an experiment, it is fundamental to think about size and time scale. How much the size of the experiment can be related to the natural environment? If we want to relate the results of a laboratory experiment to the environmental processes, the experiment should have an appropriate size scale. For instance, it could be difficult to relate the results of an experiment conducted in 200 mL bottle to what really happens in the aquatic environment. Big size experiments would be preferable for this purpose. This should be analogously considered for the time scale. For how long the experiment will keep the original conditions? During the experiments, we can observe changes that do not happen in the natural environment. Nutrients get depleted, oxygen is consumed, the biological community can change due to the experimental conditions, and many others. Appropriate measures should be considered to either keep the original conditions (e.g. nutrient supply, aeration) or terminate the experiment once the conditions are too different from those observed in the natural environment.

6.3. Holistic approach

Nowadays, we have at our disposal a wide range of advanced and high-frequency analytical techniques in the field of biogeochemistry to characterize the organic matter. However, because the dynamics and the behavior of the organic matter are intimately linked to the biomass, the topography, the hydrology and the ecology of the environment, a full understanding requires a holistic approach and a collaborative work with all these fields of expertise. Below are presented, from our point of view, the most promising holistic approaches.

6.3.1. Satellite remote sensing and bio-optics

A complementary approach to expand the spatial and time scale of the study of OM distribution is the use of bio-optical sensors designed for applications in remote sensing and autonomous oceanographic platforms. The retrieval of particulate matter (PM) and CDOM at the ocean's surface from satellite observations has been getting more attention in the latest years and allows to have a synoptic view of OM dynamics on a global scale ([Ahn et al., 2001](#); [Cao et al., 2018](#); [Kutser et al., 2015](#); [Le et al., 2018](#); [Loisel et al., 2002](#); [Nelson and Siegel, 2013](#); [Woźniak et al., 2016](#); [Zhu et al., 2014](#)).

However, the currently operating ocean color algorithms for retrieving CDOM and PM have shown poor performances, especially in high-CDOM waters, such as coastal zones and the Arctic Ocean (Aurin and Dierssen, 2012; Gonçalves-Araujo et al., 2018; Siegel et al., 2005). Moreover, it has been recently highlighted the importance of combining satellite remote sensing with numerical hydrodynamic modeling that can, for example, link physical processes and the distribution and transport of water constituents in the coastal environments (D'Sa and Ko, 2008; Joshi et al., 2017). Along with that, the incorporation of bio-optical sensors with channels for CDOM and PM into oceanographic autonomous platforms (gliders, moorings, autonomous underwater vehicles, ice tethered profilers, etc.) has emerged as the state-of-the-art monitoring tools in the past decades as they allow for sampling also over the water column and despite of sun light coverage and weather conditions. Those sensors do not only provide highly resolved spatial CDOM coverage over the water column (Laney et al., 2014; Niewiadomska et al., 2008; Seegers et al., 2017), they also gather large datasets for improving the current ocean color algorithms.

6.3.2. Neural network analysis

Collaborative work with the bioinformatic community can undeniably be of high profit and it should be one of the directions of our future research. Indeed, using computational tools will greatly help the interpretation of the voluminous and complicated datasets. For instance, Longnecker and Kujawinski (2016) applied neural network analysis to their FT-ICR-MS spectra. The combination of both tools helped them identify new potential building blocks of organic compounds in deep sea and to highlight the importance of the dissolved organic sulfur components in this kind of environment. Recently, Zark and Dittmar (2018) have concluded the major component of DOM is molecularly indistinguishable after a meticulous comparison of the structural fingerprint of individual molecular formulae in fresh and sea waters. One of the hypotheses to explain this observation was the results of a cascade of degradation processes or common synthetic pathways, which lead to the formation of a universal pool of molecules regardless of the origin or the history of the material. This novel insight in this study directly affects the understanding of long-term turnover of DOM and ruins the idea of universality of mechanisms. Another example would be Peleato et al. (2018) who applied the neural networks to their PARAFAC data. The combined approach allowed them to identify the relations between fluorescence regions and the disinfection by-product formation facilitating, therefore, the prediction of their formation. A similar approach could be used to predict organic matter reactivity. Combining computational tools like neural networks to this kind of large and similar data set might improve and certainly help interpret what is observed in the aquatic environment. It would also generate new findings and contribute to re-think and re-built our understanding of the OM dynamics as it is illustrated by the few studies that applied this kind of approach.

6.3.3. Numerical modeling

Another approach will consist of coupling analytical approaches and numerical modeling to acquire a more detailed picture of the dynamics of the aquatic OM. Modeling approaches can be performed at different scales: (i) large scale such as catchment to regional scale, (ii) ecosystem scale and (iii) microcosmic scale. They require collaborative and interdisciplinary work with hydrologist/hydrogeologists, ecologists, biologists, and modelers. At catchment scale, developed models are based on a coupling between hydrological and biogeochemical approaches (Fabre et al., 2019; Futter et al., 2007; Kim et al., 2007; Nakayama, 2017a). These kinds of models such as the Integrated Catchments Model for Carbon INCA-

C (Futter et al., 2007) or National Integrated Catchment-based Ecohydrology NICE-BGC (Nakayama, 2017a) or the Soil and Water Assessment Tool hydrological model SWAT (Fabre et al., 2019) mainly simulate the horizontal and vertical organic carbon fluxes in a carbon budget framework. For instance, they were applied to various environment to assess the inter-annual and seasonal DOC dynamics in mixed catchments (Futter et al., 2011; Nakayama, 2017b; Oni et al., 2012), to estimate the lateral DOC exports (de Wit et al., 2016) or even both horizontal and vertical carbon fluxes (Nakayama, 2017a) or to estimate the DOC, POC and sediment transfer at daily timescale (Fabre et al., 2019). Recently, Nakhavali et al. (2018) implemented the Joint UK Environment Simulator JULES (model used to evaluate the global C cycle and its role in the Earth system) (Le Quéré et al., 2015) in order to provide a model able to represent the DOC processes (JULES-DOCM) from the land to the river (e.g., model integrating a representation of DOC production in terrestrial ecosystems based on the incomplete decomposition of organic matter, DOC decomposition within the soil column, and DOC export to the river network via leaching). At the ecosystem scale, the models target the response of the living organisms to the surrounding parameters and they are generally called General Ecosystem Model (GEM) (Fitz et al., 1996). They have been widely applied for terrestrial ecosystems to simulate the soil organic matter cycling (Campbell E. and Paustian, 2015; Li-xia and Jian-jun, 2003; Schmidt et al., 2011). They are also used, to a lesser extent, in the aquatic environment. Most of them were used to simulate vertical dynamics of the biomass, nutrients, detritus, and dynamics of elements including carbon (Fitz et al., 1996; Mann et al., 2014; Prokopenko et al., 2010; Schmittner et al., 2005). Models at the microcosmic scale are commonly used to characterize and simulate the interactions between DOM and POM (He et al., 2016a and references therein). Most of them are only focused on individual DOM-POM exchange mechanisms. One of the options to overcome this limitation will be to develop the exergy theory (Dewulf et al., 2008) in order to establish a unified model that combines all the DOM-POM exchange mechanisms and will fully simulate the exchange behaviors as suggested by He et al. (2016a).

The ideal case would be to simulate any single microcosmic interaction at a global scale, taking account of all the processes involved in the aquatic environment. Therefore, research dedicated to this complementary, multidisciplinary approach should be expanded, in particular with respect to linking processes operating at a molecular scale to those operating at the global scale (Jansen et al., 2014). All the aforementioned modeling approaches presented still require improvements. Two directions could be simultaneously taken to overcome all the limitations related to their processes of elaboration and/or their uses. First, the calibration of the models requires to be supported with a higher amount of field data. Creating a database of the standard measurement in the field including chemical, physical, hydrological and ecological data over the world would greatly facilitate the establishment of accurate models at the global scale. Another direction might be to focus our efforts on the microcosmic scale model supported by laboratory experiments e.g., microcosm and mesocosm experiments to fully characterize the interactions between DOM and POM (see above) and implement this microcosmic/mesocosmic models into models at a larger/global scale.

7. Conclusion

Organic matter is a key component in the local and global carbon cycle and the understanding of this cycle is currently one of the major conundrums in the fields of environmental sciences and biogeochemistry. Although the organic matter topic was

extensively explored over the last decades, several research gaps still need to be filled and improvements and/or new ideas are required. Future studies should be done at various structural levels and from diverse perspectives. Simultaneous studies of both particulate and dissolved OM fractions should be prioritized. Likewise, multi-disciplinary approaches, creation of databases and collaborative works should be the future OM research priorities.

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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