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Review

Pre-treatments, characteristics, and biogeochemical dynamics of dissolved organic matter in sediments: A review

Meilian Chen, Jin Hur[*]

Department of Environment & Energy, Sejong University, Seoul 143-747, South Korea

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ABSTRACT

Dissolved organic matter (DOM) in sediments, termed here sediment DOM, plays a variety of important roles in global biogeochemical cycling of carbon and nutrients as well as in the fate and transport of xenobiotics. Here we reviewed sediment DOM, including pore waters and water extractable organic matter from inland and coastal sediments, based on recent literature (from 1996 to 2014). Sampling, pre-treatment, and characterization methods for sediment DOM were summarized. The characteristics of sediment DOM have been compared along an inland to coastal ecosystems gradient and also with the overlying DOM in water column to distinguish the unique nature of it. Dissolved organic carbon (DOC) from inland sediment DOM was generally higher than coastal areas, while no notable differences were found for their aromaticity and apparent molecular weight. Fluorescence index (FI) revealed that mixed sources are dominant for inland sediment DOM, but marine end-member prevails for coastal sediment DOM. Many reports showed that sediments operate as a net source of DOC and chromophoric DOM (CDOM) to the water column. Sediment DOM has shown more enrichment of nitrogen- and sulfur-containing compounds in the elemental signature than the overlying DOM. Fluorescent fingerprint investigated by excitation-emission matrix coupled with parallel factor analysis (EEM-PARAFAC) further demonstrated the characteristics of sediment DOM lacking in the photo-oxidized and the intermediate components, which are typically present in the overlying surface water. In addition, the biogeochemical changes in sediment DOM and the subsequent environmental implications were discussed with the focus on the binding and the complexation properties with pollutants.

Contents

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[*] *Corresponding author*. Tel.: +82 2 3408 3826; fax: +82 2 3408 4320.
E-mail address: jinhur@sejong.edu (J. Hur).

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1. Introduction

Sediments refer to the loose particles of sand, clay, silt, and other substances that settle at the bottom of a water body (http://water.epa.gov). They are considered an archive of physical and biogeochemical changes occurring in aquatic environments, and thus often have been used to evaluate lacustrine and oceanic environments as well as the episodic events in paleolimnology and paleooceanography (Xu and Jaffé, 2008; Leeben et al., 2010; Martin et al., 2014). Currents, storms, and hurricanes can act as a physical process to deposit sediments. It has been reported that the Yangtze River carries fine sediments at 480 Mt per year to the sea (Yang et al., 2006). Deltaic sediments account for roughly 45% of global carbon burial (Hedges and Keil, 1995).

Sediments primarily consist of organic and inorganic matters of biogenic origins, and particulate minerals (Wetzel, 2001), bearing a heterogeneous nature in the composition and the characteristics. Humic substances (HS) are the largest component of sedimentary organic matter, constituting 60–90% of the total organic carbon pool in lacustrine sediments (Ishiwatari, 1985). From the operational point of view, sedimentary organic matter can be generally categorized into three different types: pore water organic matter (PWOM), water (neutral or alkaline) extractable organic matter (WEOM), and organic solvents-extractable organic matter. Organic solvents-extractable sedimentary organic matter such as lipid biomarkers (e.g. taraxerol) is typically used for tracing sources sedimentary organic matter (Jaffé et al., 2006; Koch et al., 2011). From here on we refer to PWOM and WEOM as sediment DOM.

Different sampling and pre-treatment protocols, and various types of analytical techniques have been applied in an attempt to unravel the heterogeneous mixture of sediment DOM. Some techniques based on optical sensors such as ultraviolet–visible (UV–Vis) and fluorescence spectroscopy can be directly applied to DOM from sediments, while others usually require extraction and pre-concentration procedures prior to the measurements. Size exclusion chromatography (SEC) is a technique commonly used for estimating the molecular sizes of sediment DOM for decades (Chin and Gschwend, 1991; Chin et al., 1998; O'Loughlin and Chin, 2004). Nuclear magnetic resonance (NMR) is a conventional technique to elucidate sediment DOM structures (Hur et al., 2009). In particular, fluorescence spectroscopy, including single scan and excitation-emission matrix (EEM) has been widely utilized to characterize sediment DOM due to its simplicity, sensitivity, and high throughput (Coble, 1996; Burdige et al., 2004; Fu et al., 2006; Hur et al., 2009; Hur and Kim, 2009; Leeben et al., 2014). EEM fluorescence coupled with parallel factor analysis (EEM-PARAFAC) has opened new windows into sediment DOM in recent years (Santin et al., 2009; Ziegelgruber et al., 2013; Hur et al., 2014; Chen and Jaffé, 2014). Fourier transform ion cyclotron resonance ultra-high resolution mass spectrometry (FT-ICR-MS) has emerged as a promising tool to probe sediment DOM at the molecular level (Tremblay et al., 2007; Schmidt et al., 2009, 2014; Seidel et al., 2014). Among those for analyzing sediment DOM, EEM-PARAFAC and FT-ICR-MS have attracted the most attention in recent years.

The sources of sediment DOM may be allochthonous (terrestrial higher plants-derived) and/or autochthonous (algae, macrophytes, and bacteria-derived). Sediment DOM plays an important role in the global biogeochemical cycling of carbon and nutrients. Once settled into sediments, organic matter undergoes many physical, chemical, and/or biological interactions and transformations in the sedimentary environments (Fig. 1), and the degree is affected by its intrinsic properties as well as external factors such as redox conditions

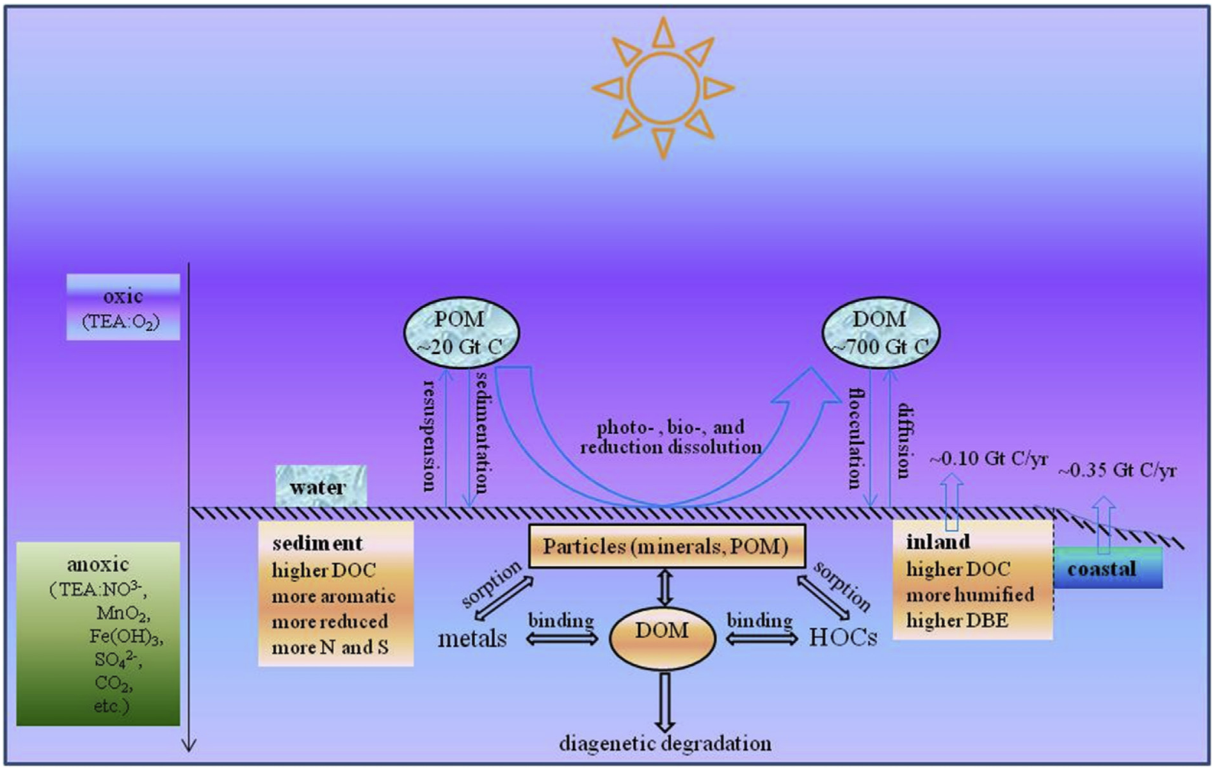

Fig. 1 – Conceptual sketch of DOM flux and biogeochemical interactions in sediments. Carbon stock data regarding particulate and dissolved organic matter (POM and DOM) are from Jiao et al. (2010). Benthic flux estimation data for inland and coastal environments from Yang et al. (2014) and Burdige et al. (1999), respectively. Anoxic status may be above or below sediment depending on different ecosystems' situation. TEA: terminal electron acceptor.

(i.e., oxic, suboxic, anoxic, or mixed-oscillating between different conditions) and the microbial community (Skoog et al., 1996; Burdige, 2007; Shank et al., 2010). For example, microbial enzymatic activity of phenol oxidase is known to be essential for the degradation of phenolic compounds, especially in sediments where sunlight is limited, representing a "latch" on the global carbon store (McLatchey and Reddy, 1998; Freeman et al., 2001). The trophic level and the seasonality are the main factors affecting the oxygen level in inland sediments (Wetzel, 2001). A part of the sediment DOM pool that escapes remineralization is preserved in sediments (Burdige and Komada, 2014), while the turnover rate of sediment DOM is considered to be an important compartment for understanding the global carbon budget from a climate change perspective.

Sediment DOM also plays a pivotal role in the transformations, transport, and environmental fate of inorganic and organic contaminants. Many anthropogenic pollutants including heavy metals and organic chemicals can pose serious threats to the structure and function of ecosystems, and human health (Aiken et al., 2010). Sediments may operate as a reservoir of such contaminants in aquatic environments through sorption and complexation with them. The solubility, bioavailability, mobility, and ecotoxicity of many xenobiotics are closely associated with the quantity and the quality of sediment DOM (Chin, 2003; Aiken et al., 2010; Hur et al., 2014). Therefore, the study of sediment DOM is significant in order to provide better insights into the fate of DOM-mediated pollutants.

The biogeochemical conditions of sediment DOM are unlikely to be the same as those of surface water DOM due to different solar irradiation regime, redox status, and microorganism community, ultimately resulting in dissimilar characteristics and the dynamics between sediment DOM and the overlying water DOM. For example, when oxygen is depleted in the sediments of eutrophic lakes during summer stratifications, only anaerobic respiration can occur in the sediments where the terminal electron acceptor (TEA) is shifted from O_2 to NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-}, CO_2, and etc.

Although there is an abundant literature regarding sediment DOM, comprehensive reviews with respect to its characteristics, the dynamics, and the appropriate analytical methods are surprisingly sparse. To the best of our knowledge, the only relevant review was found in a book chapter on marine sediment pore waters (Burdige and Komada, 2014). Several other reviews primarily discussed the applications of fluorescence, including EEM-PARAFAC, in assessing DOM dynamics (Hudson et al., 2007; Fellman et al., 2010; Jaffé et al., 2014), or characterization methods of DOM in aquatic ecosystems (Leenheer and Croue, 2003; Mopper et al., 2007; Nebbioso and Piccolo, 2013; Minor et al., 2014). These reviews, however, are all about characterization methods in general aquatic ecosystems. To date, an overall review specifically on sediment DOM encompassing inland environments has not been addressed yet. As such, the objectives of this review are four-fold: 1) to provide a broad overview of the pre-treatment and analytical methods for sediment DOM, the unique characteristics, and the dynamics of sediment DOM; 2) to compare sediment DOM between inland and coastal systems; 3) to compare sediment DOM with overlying surface water DOM; 4) to discuss the biogeochemical and environmental roles of sediment DOM so as to provide a profound insight into the uniqueness and the importance of it in aquatic environments.

2. Sampling, pre-treatments, and analytical methods

There is a high risk of oxygen contamination during sampling and pre-treatments for sediment DOM at reduced conditions. To maintain the original redox conditions of the samples, special care should be taken when handling these samplings. Using a nitrogen or inert gas box is a common practice to avoid any potential artifacts caused by contamination.

2.1. *Sampling*

Sediments are usually collected with a corer (e.g. piston corer or gravity corer) or a grab sampler for deep and surface sediments, respectively. As for pore waters, two types of sampling methods have been often employed - squeezer (O'Loughlin and Chin, 2004; Zaccone et al., 2009) or centrifuge (Chin et al., 1998; Hur et al., 2014) ex situ, and Rhizon sampler (Marchand et al., 2006; Schmidt et al., 2014) in situ. It was reported that centrifuge speed might also have considerable effects on the DOM properties (Akkanen et al., 2005). The latter (i.e, Rhizon sampler) was originally used to extract soil seepage water and was introduced later for sampling sediment pore waters (Song et al., 2003). It is a cheap, effective, and convenient method to obtain pore waters directly from sediments with minimum disturbance on sediment structure (Seeberg-Elverfeldt et al., 2005) and no contamination from air (Shotbolt, 2010).

2.2. *Pre-treatments: extraction, fractionation, and concentration*

Besides the methods for obtaining pore waters directly from sediments, there are other indirect methods available for sediment DOM extraction, which are feasible by using neutral blank water (Zaccone et al., 2009; Li et al., 2014; Schmidt et al., 2014) or alkaline water (Hur and Kim, 2009; Hur et al., 2009; Santin et al., 2009; Hur et al., 2014). In a previous study, WEOM from an ombrotrophic (rain fed) bog displayed the properties of more humic-like, higher apparent molecular weight (AMW), and a higher degree of aromaticity as compared to those obtained by squeezer (Zaccone et al., 2009). Similarly, another study reported that, in most cases, WEOM was characterized by more aromatic structures and larger molecular sizes than pore waters obtained by centrifugation (Akkanen et al., 2005). A recent study using aqueous Soxhlet extraction followed by FT-ICR-MS measurements revealed that WEOM possessed a larger and more complex pool of sediment DOM than the pore waters (Schmidt et al., 2014). In contrast, alkaline extraction has been widely used to obtain humic substances (e.g. fulvic acids and humic acids) from sediments. More aromatic and terrestrial-derived sediment DOM was found in the alkaline solution from lake and stream sediments, and it has been argued that the alkaline extractable organic matter could be more representative of the bulk properties of the total sediment DOM pool and the sources (Hur et al., 2014).

Extracted sediment DOM can be further fractionated according to size, the polarity/hydrophilicity, or the solubility in acid. Both SEC and ultrafiltration (UF) are commonly used for size-based fractionation methods (Huber et al., 2011; Perminova et al., 1998; Maie et al., 2005, 2007; Benner and Opsahl, 2001; Romera-Castillo et al., 2014; Dang et al., 2014; Leenheer and Croué, 2003). In a study, sediment DOM was classified into four fractions (i.e. hydrophobic bases, hydrophobic acids, hydrophobic neutrals, and hydrophilic matter) with hydrophobic resins and ion exchange (Li et al., 2014). Fulvic and humic acid fractions (i.e., hydrophobic acids) can be further separated through acidification by inducing the precipitation of humic acid fraction from humic substances (Santin et al., 2009).

Depending on the concentration levels of the original sediment DOM and the sensitivity of analyzing instruments, it may be necessary to concentrate the samples before the analyses although this step is usually unnecessary for optical methods. Solid phase extraction (SPE) using silica-C18 sorbents (C18), XAD resins, or styrene divinyl benzene polymer type sorbents (pore size 150 Å, PPL) are commonly applied for the concentration procedures (Aiken et al., 1992; Dittmar et al., 2008; Sleighter and Hatcher, 2008; Koch et al., 2014; Kellerman et al., 2014). C18 sorbents only capture nonpolar compounds from sediment DOM samples while PPL sorbents can retain both highly polar and nonpolar substances and thus a more representative portion of sediment DOM pool (Dittmar et al., 2008; Perminova et al., 2014). Tangential flow (or cross-flow) ultrafiltration is another alternative technique for concentrating samples (Hedges et al., 1994; Benner and Opsahl, 2001; Maie et al., 2005).

2.3. *Analytical measurements and data handling*

As a number of reviews on DOM characterization methods are already available elsewhere (Leenheer and Croue, 2003; Mopper et al., 2007; Nebbioso and Piccolo, 2013; Minor et al., 2014), we only summarized the utilities and the limitations of the frequently used analytical methods in a table (see Table 1). A special aspect that we would like to emphasize is that, due to the complex nature of EEM data, advanced statistical processes such as parallel factor analysis (PARAFAC, Hur et al., 2014; Chen and Jaffé, 2014), principal component analysis (PCA, Chen et al., 2013; Chen and Jaffé, 2014), and self-organising maps (Ejarque-Gonzalez and Butturini, 2014; Cuss et al., 2014) have been employed for the decomposition or the pattern recognition of fluorescence EEM features.

3. Comparisons of sediment DOM quantity and quality

The characteristics and dynamics of sediment DOM are likely to vary along the freshwater to coastal transect, and they are

Table 1 – Comparison of the utilities and the limitations of some popular analytical techniques for sediment DOM.

Measurement	Utility	Limitation
DOC	Bulk analysis, representative of DOM quantity	Lacking detailed structural information
UV–Vis	Representative of bulk CDOM, easy and fast, minimal pre-treatment	Missing information of non-chromophores such as carbohydrates
Fluorescence	Simple, fast, sensitive, solvent-free, small sample volume, (EEMs provide more detailed source and structural information)	Missing information of non-chromophores such as carbohydrates Missing information of colored non-fluolophores Missing molecular level information
EEM-PARAFAC	Decompose set of mixture EEM into individual components	Dismissing the intra- and inter-molecular interactions of optical properties Molecular correspondence and lack of standard
FT-ICR-MS	Provide elemental and formula information at molecular level	High-cost, usually need pre-concentration, need organic solvent Selective ionization, isomers need structural elucidation
SEC	Provide apparent molecular weight information	Potential DOM interaction with stationary phase of column Lack of real standards for calibration
NMR	Provide structural functionalities information	Need extensive pre-treatment such as isolation and concentration

likely to differ from those of DOM in the overlying water due to dissimilar dominant sources and environmental conditions. The previous findings on the characteristics of sediment DOM are summarized (see Table 2). The ranges of some defined values regarding the quantity and quality of sediment DOM such as DOC, specific ultraviolet absorption at 254 nm (SUVA), molecular weight (MW) are listed in Table 3. In the following sub-sections, the ranges of DOC, aromaticity, molecular weights, hydrophobicity, fluorescent EEM-PARAFAC components, and molecular formula information of sediment DOM will be compared between inland and coastal sediments as well as between sediments and the overlying surface water. These comparisons are fundamental for better understanding of the interactions between sediment DOM and overlaying water column and also of the sources and the dynamics of sediment DOM in contrasting environments.

3.1. *Horizontal comparison between inland and coastal sediment DOM*

Coastal areas represent complex ecosystems with tides where the exchange and the mixing of inland water with oceanic water take place. Both terrestrial-transported DOM and marine-derived DOM can contribute to the sources of sediment DOM in these areas. In contrast, sediment DOM in lotic (e.g., rivers and streams) and lentic (e.g., lakes and reservoirs) inland ecosystems is dominated with terrestrial-derived sources. It is well known that terrestrial-derived DOM from freshwaters tend to be more aromatic while marine DOM is more aliphatic (Coble, 1996; McKnight et al., 2001; Maie et al., 2005). Diagenetic history also plays an important role along with different sunlight condition and microbial community between inland and coastal systems. In addition, different water chemistry such as salinity may also be involved in creating dissimilar biogeochemical processes of sediment DOM between freshwater and coastal marine areas.

3.1.1. *Dissolved organic carbon (DOC)*

The values of DOC reported by previous literature are quite extensive, ranging from less than 1 mg C/L to as high as thousands of mg C/L. The lowest and the highest values were observed in a coastal environment and an acidic ombrotrophic bog, respectively (Burdige et al., 2004; Zaccone et al., 2009). Because of the large variability caused by the dilution effect of WEOM and the options of pre-treatments (i.e., fractionation or concentration), only PWOM of whole samples (i.e. nonfractioned) will be compared below.

The sediment depths are different (surface to ~100 cm) for the individual studies, thus it should be noted that our comparison is rough, and attention needs to be paid primarily to general trends rather than to the absolute values. The previously reported DOC concentrations varied widely from 4 to 2201 mg C/L for inland ecosystems and from 0.6 to 448 mg C/L for coastal systems. Similar to surface waters, the DOC ranges of sediments were found to be generally higher for inland systems than for coastal environments. This is reasonable considering the active exchange between surface water and sedimentary pore waters for the inland environments. Most of the studies (both inland and coastal environments) showed an increasing DOC profile with a depth, except for the cases

Table 2 – Summary of recent findings on sediment DOM characteristics.

Ecosystem	Pre-treatment	Sample type	Findings	References
Inland:				
Streams	Alkaline extraction Centrifuge	Whole	Alkaline solution extracted more aromatic and terrestrial-derived DOM Highly representative of bulk properties and sources Significant correlation between terrestrial humic-like and phenanthrene binding affinity	Hur et al. (2014)
Prairie pothole lakes	Centrifuge	Whole	3 humic-like components explained ~90% of total fluorescence More non-humic-like in surface sediments in early autumn	Ziegelgruber et al. (2013)
Stream and reservoir	Alkaline extraction	Humic substances (HS)	SUVA and HIX correlated with AMW	Hur and Kim (2009)
2 Eutrophic lakes	Alkaline extraction	Humic acids (HA)	Higher H/C,N/C,(N + O)/C, than soil HA Aromaticity correlated with phenanthrene binding	Hur et al. (2009)
Erhai lake	Centrifuge	Whole	Highest aromaticity at redox interface	Fu et al. (2006)
Estuarine and coastal:				
Estuary	Alkaline extraction	FA and HA	FA: more fulvic acid-type and microbial humic-like components HA: more humic acid type and protein-like components	Santin et al. (2009)
Coastal	Centrifuge	Whole	Preferentially preserved humic-like in pore waters under anoxic conditions	Burdige et al. (2004)
Coastal Toulon Bay	Alkaline extraction	Whole	Sediments represent a source of CDOM to coastal waters High proportion of low-molecular-weight DOM and the high-molecular-weight DOM (<3 kDa) primarily protein-like fluorophores	Dang et al. (2014)
Coastal mangrove estuaries	C18 SPE for concentration	SPE-PWOM	More condensed hydrocarbons and higher AMW than estuary water	Tremblay et al. (2007)
Coastal sea	PPL SPE for concentration	SPE-PWOM	Highly unsaturated compounds; enriched in N and S elements	Seidel et al. (2014)
Continental shelf	PPL SPE for concentration	SPE-PWOM	Aromatic compounds; N and S compounds; high lignin phenols	Schmidt et al. (2009)

*All HS, HA and FA in the "Sample type" column were based on extraction and fractionation.

Table 3 – Summary of dissolved organic carbon (DOC), specific UV absorbance (SUVA), apparent molecular weight (AMW), and other values for sediment DOM.

Ecosystem	Sediment DOM type	DOC (mg C/L)	Depth profile[a]	SUVA (L/mgC-m)	AMW[b] (Dalton)	Poly-dispersity	FI	HIX	DBE	Reference
Inland:										
Stream	WEOM (alkaline)	27–168	Surface	0.3–2.8	–	–	1.4–2.2	0.8–46.8		Hur et al. (2014)
Prairie pothole lakes	PWOM	26–183	↓ (27 cm)	~0.5–3.5	Mw < 3 kD	~1.3–1.5	–	–	–	Ziegelgruber et al. (2013)
Erhai lake	PWOM	~5–58	U-shaped (30 cm)	0.5–3	Mn < 1 kD, Mw < 2 kD	~2.0–3.0	1.5–1.6	–	–	Fu et al. (2006)
10 Estonian lakes	PWOM	4–121	n/a (60 cm)	–	Mn < 3 kD, Mw < 5 kD	–	~1.4–2.3	–	–	Leeben et al. (2014)
Well-mixed lakes	PWOM	–	n/a (~40 cm)	~0.2–3.3	Mn < 3 kD, Mw < 5 kD	~1.5–5.5	–	–	–	Lepane et al. (2004)
Freshwater wetland	PWOM	–	↓ (33 cm)	–	Mn < 800 D, Mw < 1.3 kD	~1.38–2.00	–	–	–	Chin et al. (1998)
Lake	PWOM	7.0–14.0	↓ (33 cm)	–	Mn < 2 kD, Mw < 3.8 kD	~2.1–2.7	–	–	–	O'Loughlin and Chin (2004)
Eutrophic lakes	HA	–	Surface	1.2–3.7	–	–	–	1.4–1.7		Hur et al. (2009)
Ombrotrophic bog	PWOM, WEOM	225–2201	U-shaped (~100 cm)	–	–	–	–	–	–	Zaccone et al. (2009)
Bog	PPL-PWOM	–	n/a (17 cm)	–	–	–	–	–	~7–31	D'Andrilli et al. (2010)
Estuarine and coastal:										
Yangtze Estuary	PWOM	72.8–81.5	Surface	2.0–2.7	–	–	–	3.1–5.1	–	Wang et al. (2014)
Yangtze Estuary	PWOM	20–448	↓ (25 cm)	0.4–5.0	Mw < 3 kD	–	1.7–2.2	–	–	Wang et al. (2013)
Estuary	FA and HA	–	–	–	–	–	–	–	–	Santin et al. (2009)
Coastal	PWOM	0.6–49.2	↓ (~20 cm)	–	–	–	–	–	–	Burdige et al. (2004)
Coastal mangroves	C18-PWOM	–	n/a (150 cm)	–	–	–	–	–	9.4	Koch et al. (2005)

n/a: not analyzed.

[a] Stands for DOC except for those otherwise indicated. ↓ means values increase with depth; while ↑ represents the opposite trend.

[b] M_n and M_w represent number-averaged molecular weight and weight-averaged molecular weight, respectively.

where a U-shaped trend was displayed with the lowest value at the redox interface approximately 7 cm below water–sediment interface (Fu et al., 2006) and also a similar trend was found in an acidic bog (pH 3.4–3.9, Zaccone et al., 2009). The accumulation of DOC in deeper anoxic sediments were explained by abiotic polymerization of low molecular DOM, anaerobic degradation of particulate organic matter, and/or the reductive dissolution of Fe- and Mn-oxides in the anoxic conditions and the subsequent release of the adsorbed organic matter to pore waters (Sierra et al., 2001; Deflandre et al., 2002; O'Loughlin and Chin, 2004). Nevertheless, sediment DOC levels tend to remain relatively constant below a certain depth (Chin et al., 1998).

3.1.2. *Aromaticity*

Aromaticity is an important indicator reflecting sources and diagenetic status of sediment DOM. It is believed that autochthonous DOM is smaller in size and less aromatic than that of allochthonous origin (McKnight et al., 2001). The aromaticity of DOM closely relates to its photo-reactivity (Helms et al., 2013). SUVA and aromatic index (AI) are two common proxies of aromaticity of DOM measured by UV–Visible spectroscopy and FT-ICR-MS, respectively (Weishaar et al., 2003; Koch and Dittmar, 2006). The latter (AI) will be discussed in later section (3.1.6). Again, the comparison below is rough due to the different depths of the sediment samples reported. Similar to DOC, SUVA values of sediment DOM exhibited a broad range from ~0.2 to 3.5 L/mgC-m for inland ecosystems and 0.4–5.0 L/mgC-m for coastal environments. The lowest and the highest values were reported in a well-mixed lake (Lepane et al., 2004) and an anthropogenically impacted estuary (Wang et al., 2013), respectively. The SUVA values of inland systems were not obviously different from those of the coastal areas, where lower values would be expected considering the marine input. This observation may be attributed to either the possibility that the sediments in some estuarine and coastal areas were primarily remobilized from terrestrial sources, or the preferential preservation of aromatic DOM in coastal sediments, or a combination of both. A common observation is that the SUVA values increased with sediment's depths (Wang et al., 2013; Ziegelgruber et al., 2013), implying preferential preservation of aromatic compounds in the deep sediments. The highest aromaticity (SUVA = 3.0 L/mgC-m) was found at a redox interface of lake sediments where the lowest level of DOC (~5 mgC/L) was shown (Fu et al., 2006). The observation was explained by higher biotic degradation activities in the oxic layer and preferential preservation of aromatic organic matter during the early diagenetic processes (Qualls and Richardson, 2003; Herlemann et al., 2014; Chen and Jaffé, 2014). It is also notable that low sediment DOM aromaticity, with SUVA<1 L/mgC-m, was reported at the peak of growing season when autochthonous DOM with low aromaticity is produced and probably interacts with the pore waters. The value was switched up to ~3.5 L/mgC-m in a different season (Ziegelgruber et al., 2013).

3.1.3. *Apparent molecular weight (AMW)*

It has been suggested that HS, the majority (~60–90%) of sediment DOM, are supramolecular associations of relatively small (<1 kDa) molecules, which are held together in only apparently large molecular sizes by weak linkages such as hydrogen and hydrophobic bonds (Piccolo, 2001). AMW distribution is strongly affected by a variety of factors such as pH, ionic strength, membrane type, pressure, calibration standards, and the measurement techniques (Leenheer and Croué, 2003; Koch et al., 2005). The smaller average MW determined by FT-ICR-MS versus SEC was explained by either disaggregation of weak non-covalent bonds or preferential ionization of lower MW fraction of DOM by electrospray ionization source (Mopper et al., 2007). AMW was found to be correlated with SUVA and humification index (HIX) in stream and reservoir systems (Hur and Kim, 2009).

In most cases, the reported number-averaged MW (M_n) and weight-averaged MW (M_w) were less than 3 kDa and 5 kDa, respectively, with a polydispersity (M_w/M_n) between ~1.3 and 3 for both inland and coastal ecosystems. AMW information of sediment DOM for coastal environments is relatively sparse compared to inland ecosystems although no obvious differences of AMW can be observed from the limited data (see Table 3). Some other factors such as depth and seasonal trends have been found to affect AMW of sediment DOM. An estuary study showed that the MW increased with depth from ~2.5 kDa (M_w) at the water–sediment interface to ~3.2 kDa at a depth of 26 cm (Wang et al., 2013). There was a small shift in MW from 2.3 to 2.8 kDa in June to 1.7–2.7 kDa in September in lacustrine pore waters, indicative of a seasonal variation. The polydispersity was relatively low for most of the ecosystems studied, suggesting a relatively narrow size distribution of sediment DOM. An exception was found for a well-mixed lake exhibiting a much wider polydispersity (~1.5 to 5.5) (Lepane et al., 2004).

3.1.4. *Hydrophobicity*

Hydrophobicity is a relative term for DOM because all soluble organic matter in water refers to DOM (Aitkenhead-Peterson et al., 2003). A recent fractionation study using XAD-8 resin revealed that hydrophobic fractions (acids, bases, and neutrals) were the major pool of WEOM (61.8% as a basis of DOC) in a lacustrine environment (Li et al., 2014). Hydrophobic contents were reported to become enriched with the depth in a mangrove estuary (Marchand et al., 2006). Hydrophobic sediment DOM retained by silica-C18 columns exhibited more condensed hydrocarbon molecules and higher AMW in comparison with the counterpart of water column in coastal mangrove estuaries (Fig.2 c and d). Taken together, hydrophobic fraction appears to be a substantial fraction of sediment DOM, having a relatively high AMW associated with condensed hydrocarbon structure and refractory nature. Detailed comparison of hydrophobicity between inland and coastal sediment DOM needs further research involving its fractionation procedures.

3.1.5. *Fluorescent fingerprint of sediment DOM*

Fluorescent DOM (FDOM) primarily consists of some humic substances and aromatic amino acids/proteins. Anthropogenic inputs such as sewage and oil spills can add additional FDOM pools. HS constitute approximately 50% of DOC in freshwater systems, and the ratio of humic to fuvic acids is typically much higher in interstitial solutions than in surface waters (Aitkenhead-Peterson et al., 2003). FDOM in pore water

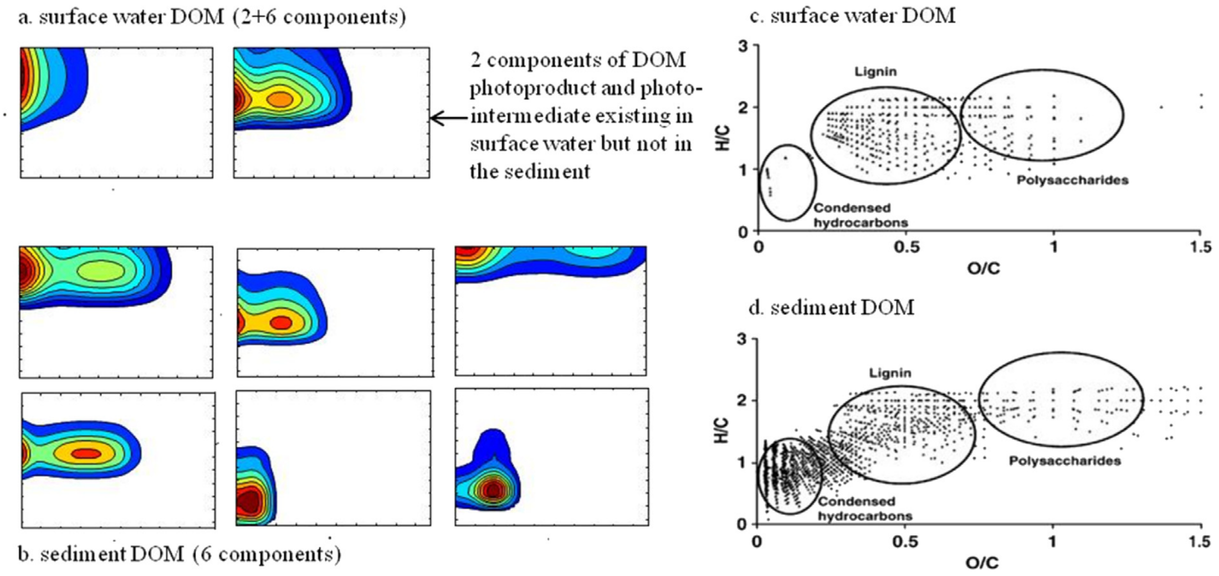

Fig. 2 – **Comparison of sediment DOM with surface water DOM in Florida Bay (a–b, EEM-PARAFAC components' contours taken from Chen et al. (2010) and Brazilian mangrove ecosystems (c–d, van Krevelen plots taken from Tremblay et al. (2007).**

also seems to relate to the trophic levels of lakes because eutrophic lakes showed higher fluorescence intensity than oligotrophic lakes (Leeben et al., 2014).

Fluorescence index (FI) is a ratio of the emission intensity at 450 nm to that at 500 nm at excitation 370 nm (McKnight et al., 2001). It has been used as a proxy to indicate the sources of DOM. FI ranged from ~1.4 to 2.3 for inland ecosystems, indicative of the sources of fulvic acids in sediments from different sources (e.g., higher plants or algae) in various ecosystems. For coastal sediment DOM, a FI of 1.7–2.2 was reported, suggesting more inputs from marine end-member. Humification index (HIX) is defined as a ratio of the area under the emission spectra over 435–480 nm to that over 300–345 nm at excitation 254 nm (Zsolnay et al., 1999). The range of HIX values for inland sediment DOM was from 0.8 to 46.8, exhibiting very different humification degrees in sediments. In contrast, HIX was around 3.1–5.1 for an estuary, which is indicative of low humification status.

Humic-like organic matter has been found to be the majority of sediment DOM in some inland and estuary environments (Ziegelgruber et al., 2013; Wang et al., 2013). Similar to the trend of aromatic sediment DOM, it was found that humic-like fluorescent sediment DOM was preferentially preserved in pore waters under anoxic conditions of coastal systems (Coble, 1996; Burdige et al., 2004). High tyrosine- and tryptophan-like fluorescence intensities were observed in coastal pore waters (Coble, 1996). More protein-like components were found in humic acids than in fuvic acids for estuarine environments, suggesting that the macromolecules like humic acids may protect labile protein-like sediment DOM from microbial degradation through the interactions (Santin et al., 2009).

EEM-PARAFAC is a rather new technique that has a high potential for aiding in better understanding of sediment DOM characteristics and transformations. Several studies have applied this technique to probe sediment DOM in coastal and inland sediments (Table 4). Three to six fluorescence components have been identified from sediment DOM. The maximum number of the components was found from Florida Bay sediments (Chen and Jaffé, 2014). The terrestrial humic-like component is the most dominant for inland sediments while the protein-like component is more pronounced for coastal sediments. This is not surprising, because terrestrial-derived sources are mostly dominant for inland sediments, whereas mixed end-members are more common for coastal environments. A microbial humic-like fluorescence (Ex/Em maximum: 240(320)/410 nm) was reported as one of the most abundant FDOM components (Ziegelgruber et al., 2013), which was previously assigned as marine humic-like fluorescence (Coble, 1996). The sources of the component are still controversial because its presence was also reported for many other environments including terrestrial sources-dominating systems (Stedmon et al., 2003) as well as the ecosystems affected by agricultural and/or anthropogenic activities (Chen and Jaffé, 2014). It should be noted that each EEM-PARAFAC component is, indeed, a mixture of the fluorophores with a wide range of molecular weights, and different structures and sources (Romera-Castillo et al., 2014). Furthermore, water chemistry such as pH, ionic strength, and ions, which is variable in different ecosystems, can affect the revealed DOM fluorescence (Yang and Hur, 2014; Romera-Castillo et al., 2014).

3.1.6. *Molecular level signature provided by FT-ICR-MS*

There were a few reports about the formulas and elemental composition of sediment DOM at molecular level investigated by FT-ICR-MS. Although this technique is only a qualitative method (i.e. the peak intensity cannot be related back to its concentration) with the analytical challenges such as chemical selectivity during ionization, lack of standards, and unknown structural information of isomers, it is widely recognized as one of the most powerful methods available to date due to its high resolution capability to obtain thousands of molecular formulas in a single sample. Nevertheless, there

Table 4 – Summary of EEM-PARAFAC components found in sediment DOM.

Ecosystem	Sample type	Findings					Reference
		Component[a]	Ex/Em maxima (nm)	Assignment	Traditional classification[b]	Relative abundance (%)	
Inland:							
Streams	WEOM (alkaline)	C1	<260(335)/450	Terrestrial humic-like	C, A	7.8–71.6	Hur et al. (2014)
(Affected by algal production, industrial effluent, terrestrial input, respectively)		C2	<260(315)/~400	Marine humic-like	M	14.2–54.2	
		C3	280/350	Protein-like	B, T	0.0–63.9	
Prairie pothole lakes	PWOM	C1	<260(320)/410	Microbial humic-like	M	~20–30	Ziegelgruber et al. (2013)
(Relatively pristine)		C2	<260/446	Terrestrial humic-like	A	~30–40	
		C3	260(355)/470	Terrestrial humic-like	C	~10–20	
		C4	<260(270)/350	Protein-like	T, N	~8–30	
Estuarine and coastal:							
Florida Bay	WEOM	[a]C7	275/326	Tyrosine-like	B	37.1	Chen and Jaffé (2014)
(Carbonate sediment)		[a]C1	<260(345)/462	Terrestrial humic-like	C, A	35.8	
		[a]C8	300/342	Tryptophan-like	T	8.0	
		[a]C5	275(405)/>500	Terrestrial humic-like	–	7.6	
		[a]C4	<260(305)/376	Marine humic-like	M	6.0	
		[a]C6	325/406	Microbial humic-like	M,C	4.5	
Yangtze Estuary	PWOM	C1	<260/425	Terrestrial humic-like	A, C	–	Wang et al. (2014)
(affected by human activities)		C2	<240(280)/340	Protein-like	T	–	
		C3	<260(360)/475	Terrestrial humic-like	A, C	–	
Yangtze Estuary	PWOM	C1	<240(300)/410	Marine humic-like	M	~20–30	Wang et al. (2013)
(affected by human activities)		C2	265(365)/470	Terrestrial humic-like	C, A	~10–20	
		C3	<240(275)/335	Protein-like	T	~20–35	
		C4	<240/450	Terrestrial humic-like	A	~15–25	
Urdaibai and Foz Estuary	FA and HA	C1	<260(305)/439	Fuvic acid -type	C, A	–	Santin et al. (2009)
(affected by human activities)		C2	<260(385)/>500	Humic acid-type	–	–	
		C3	320/388	Marine humic-like	M	–	
		C4	275/304	Tyrosine-like	B	–	
		C5	<260/365	Tryptophan-like	T	–	

[a] The components were named the same as in the references for convenient comparison.

[b] Based on Coble (1996).

are still some robust indices such as double bond equivalent (DBE = 1 + 1/2(2C−H + N + P), i.e. the total number of double bonds and aliphatic rings) and aromatic index (AI=(1+C−O−S-0.5H)/(C−O−S−N−P)) can provide the potential degree of the unsaturation and the aromaticity of sediment DOM samples (Koch and Dittmar, 2006; Tremblay et al., 2007; Schmidt et al., 2009). Most reports were focused on marine environments. Based on the most updated literature, both inland and coastal sediment DOM exhibited highly aromatic compounds and enrichment of N- and S-containing compounds (Fig. 2c and d, Tremblay et al., 2007; Schmidt et al., 2009; D'Andrilli et al., 2010; Seidel et al., 2014). The findings are consistent with the above-stated observation revealed by optical analyses, in which aromatic compounds tend to be preferentially preserved in sediments. Biotic and abiotic degradation of proteinaceous material, and sulfurization of organic matter in sediments may contribute to the enrichment of N and S elements (Schmidt et al., 2009; McKee and Hatcher, 2010; Schmidt et al., 2011). Further FT-ICR-MS investigations based on a wide range of samples are required to reveal more detailed formulas, elements, aromaticity, and compound class information on sediment DOM and the dynamics.

3.2. *Vertical comparison between sediment DOM and overlying surface water DOM*

3.2.1. *Comparison of DOM quantity and carbon flux from sediments to water column*

An elevated level of DOC has been found in sediment pore waters (~61–90 mg C/L) as compared to the overlying surface water (~22–30 mg C/L) in prairie pothole lakes and estuary ecosystems (Chin and Gschwend, 1991; Mozeto et al., 2001; Wang et al., 2014), suggesting a net upward benthic efflux of DOM. The integrated DOC efflux from coastal and continental margin sediments including vegetated sediments was estimated to be 0.35 Gt C/yr (Burdige and Komada, 2014). In addition, there was some evidence that sediments can operate as a source of CDOM and protein-like DOM to the overlying waters in coastal systems (Burdige et al., 2004; Wang et al., 2014). In laboratory benthic chamber experiments, meanwhile, a conservative value for the benthic flux of DOC from inland sediments was estimated to be around 60 mg/m^2/day, and a rough estimate of global benthic flux of 0.10 Gt C/yr was achieved by scaling up the above results to global inland waters areas of 4.6 million km^2 (Yang et al., 2014; Downing et al., 2006). The benthic flux may be affected by a variety of meteorological, geographical, physical, chemical, and biological factors. Higher efflux (~39%) was observed under hypoxic than oxic conditions (Yang et al., 2014).

3.2.2. *Comparison of DOM quality*

Table 5 summarizes a comparison of selected characteristics between sediment DOM and DOM in the overlying waters. Higher SUVA values were also reported for sediment DOM (~2.0 L/mgC-m) versus overlying bottom waters (~1.5 L/mgC-m) in an estuary study (Wang et al., 2014). AMW values of sediment DOM were higher than those of the overlying water in lake and coastal environments (Ziegelgruber et al., 2013; Tremblay et al., 2007). Much higher HIX was also observed in sediment (~3.1) as compared to the water column (~1.5) in an

Table 5 – Comparison of selected characteristics between sediment DOM and DOM in overlying surface waters.

	DOC (mg C/L)		DOC (mg C/L)	SUVA (L/mgC-m)	HIX	EEM-PARAFAC	Carbon# range	Oxygen# range
	Prairie pothole lakes		Yangtze estuary	Yangtze estuary	Yangtze estuary	Florida bay	Amazon estuaries	
	P1	P8						
Sediment DOM:	61 ± 9	90 ± 50	81.5 ± 23.6	2.0 ± 0.9	3.1 ± 0.6	[a]6 components	7~44	1~18
Surface water DOM:	30.1 ± 0.1	22.1 ± 0.2	29.7 ± 1.6	1.5 ± 0.9	1.5 ± 0.3	8 components	7~33	0~15
Reference	Ziegelgruber et al. (2013)		Wang et al. (2014)			Chen and Jaffé (2014)	Tremblay et al. (2007)	

[a] With photo-produced and photo-intermediate components missing.

estuary, suggesting that an enhanced humification progressed in the sediments. These trends are in good agreement with the comparison of SUVA and AMW values between sediment DOM and overlying DOM. In a coastal mangrove estuary, the sediment DOM of pore waters was characterized by more condensed hydrocarbons than in the estuarine water (Tremblay et al., 2007), which is consistent with the SUVA values. In the same report, the pore waters showed broader carbon and oxygen numbers ranges (7–44 and 1–18, respectively) than the surface waters (7–33 and 0–15, respectively).

Significant differences in fluorescence components have been reported between sediments and surface waters. In Florida bay, for example, no photorefractory/photoproduct component (C2: Ex/Em maximum <260/454 nm, traditional peak A in Coble, 1996) and no photo-degradation intermediate component (C3: Ex/Em maximum <260/(305)416 nm) were found in the sediments although both were commonly observed in the surface water (Chen and Jaffé, 2014, Figs. 2a and b). These two components were also sparse in groundwater where the oxygen level was also very low (Chen et al., 2010). It is also notable that reduced and partly reduced forms of quinone and semiquinone fluorophores were observed in Antarctic lake environments. The increase of such reduced forms was concurrent with a decrease of an oxidized counterpart below the oxycline (Cory and McKnight, 2005). Therefore, for the environments where sediments experience reducing condition, highly oxidized components appear to decrease or even disappear, and instead more reduced or partly reduced forms of FDOM are likely to be produced in the sediment DOM although further investigations are needed for the evidence.

4. Biogeochemical changes in sediment DOM and the environmental implications

4.1. *Biogeochemical changes*

Diagenetic processes such as photo- and bio-degradation are expected to change sediment DOM quantity and the quality, ultimately affecting the local and global carbon cycling. Solar irradiation has been reported to result in photo-bleaching of chromophoric DOM (CDOM), or in photo-humification and/or photoproduction of new DOM (Moran and Zepp, 2000; Shank et al., 2010). DOM bioavailability was found to be controlled by its sources. For example, protein-like materials were degraded to a greater extent compared to polyphenols (Scully et al., 2004). There is a general consensus that sunlight has a "priming effect" for bacterial uptake of old, aromatic, terrestrial-derived DOM, while the opposite effect has been observed on fresh, non-aromatic, algae-derived DOM (Moran and Covert, 2003). Solar irradiation can even enhance the photo-dissolution of suspended particulate organic matter to DOM (Shank et al., 2011).

Compared to surface water, sediments are expected to receive much less solar irradiation due to the blocking and the attenuation by the suspended particles and to the CDOM in the overlying water column. Microbial degradation in sediments takes place usually under a low oxygen level or even without oxygen, and thus anaerobic respiration of microorganisms may be more dominant under these conditions. Co-accumulation of sediment DOM together with Fe^{2+} was observed in many pore waters from lake and wetland systems (Chin et al., 1998; O'Loughlin and Chin, 2004). The understanding of transformations, remineralization, preservation, and burial of sediment DOM is crucial for global carbon budget and elemental cycling. The oceanic sediment burial rate is estimated to be approximately 0.16 Gt C/yr (Hedges and Keil, 1995). Furthermore, the carbon burial in the inland sediments can be comparable to that in the ocean (Cole et al., 2007; Tranvik et al., 2009).

Sediment DOM also acts as a driver of aquatic nutrients cycling, especially in the ecosystems (e.g., Florida Everglades) where most of the nitrogen (N) and phosphorous (P) exit in organic forms (Boyer and Fourqurean, 1997; Boyer et al., 2006a). In marine sediments overlain by anoxic bottom waters, the biological and chemical retention of phosphorous driven by sediment DOM may become less efficient than in oxic settings, resulting in a higher extent of P release from the sediments (Steenbergh et al., 2011). Since organic nutrients may be present in sediment DOM and even inorganic nutrients can be bound to it, biogeochemical processes occurring in sediment DOM can ultimately affect global cycling of the nutrients. Production of nutrients (N, P, Si, etc.) was observed in coastal pore waters during sediment DOM diagenetic degradation (Dang et al., 2014). It is known that DOM-bound nutrients can promote phytoplankton blooms, resulting in elevated autochthonous carbon production (Boyer, 2006).

4.2. *Environmental implications*

One of the significant roles of sediment DOM from environmental perspectives can be ascribed to its ability of complexation with metals and binding with HOCs (hydrophobic organic contaminants). The fate, speciation, bioavailability, and transport of these pollutants are intricately associated with its quantity and the quality. In sediments, condensed aromatic structures are usually present in elevated levels as stated above. Such a hydrophobic nature may lead to enhancing the interactions between sediment DOM and xenobiotics (Leenheer et al., 1998; Hur et al., 2009, 2014). It was reported that the extent of DOM-HOCs binding was highest in porewater (up to ~70%) as compared to other sources of DOM such as groundwater and surface water (Chin, 2003). As such, pore water DOM is likely to play more critical roles as adsorbent, carrier, and degradation sensitizer or inhibitor of pollutants in comparison with its counterpart in water column.

There are many factors influencing the extent of the complexation and/or sorption between sediment DOM and pollutants. The binding-site densities and conditional stability constants of DOM-metals/HOCs complexes are affected by the sources and composition of DOM (Chin et al., 1997; Brooks et al., 2007). Overall, DOM harbors a myriad of charged sites to bind trace elements. Aromaticity is an important structural element because aromatic moieties have high molecular electronegativity due to the electron-withdrawing character, enhancing the complexation of positively charged metals (Leenheer et al., 1998). Meanwhile, previous studies have shown that the extent of HOC binding increased with a higher content of aromaticity, more abundance of terrestrial humic-like FDOM, and a higher ratio of humic-to fulvic-like FDOM in sediment DOM (Hur et al., 2014, 2009; Hur and Kim, 2009). Besides this, solution chemistry such as salinity and pH could also influence the interactions between sediment DOM and pollutants (Lu and Jaffé, 2001; Haitzer et al., 2003).

5. Conclusions and future research need

Much more attention has been paid to the DOM in the water column as compared to sediment DOM. Furthermore, marine sediment DOM has been more reviewed than that of freshwater. The information provided here fills this research gap. The general higher DOC quantity and more aromatic and more reduced sediment DOM quality as compared to overlying surface water, as revealed by the vertical comparison, deliver valuable messages to organic geochemists and ecologists. As the amount of estimated inland sediment DOM efflux is of the same magnitude as the riverine DOM fluxes to the oceans (~0.21 Gt C/yr, Ludwig and Probst, 1996), the sediment-derived DOM seems a significant component in the water column. It is suggested that DOM plays a role as an intermediate of carbon flow during sediment particulate organic matter (POM) remineralization (Burdige and Komada, 2014). Further studies are needed to investigate the impact of benthic DOM fluxes on the composition and photo- and bio-reactivity of surface water DOM.

Similar to the gradients in the surface water, the horizontal comparison showed higher DOC and humification index for inland sediment DOM than coastal ecosystems, which most likely due to the active sediment–water interaction (Fig.1). It was suggested that the inland benthic carbon fluxes cannot be negligible and even comparable to that of marine environment as an important part of global carbon cycling (Yang et al., 2014). Considering the high diversity of the global inland waters, the sediment DOM in these ecosystems is much more heterogeneous in quantity and quality than surface water DOM. Furthermore, since inland water systems are usually more affected by anthropogenic activities such as pollution and eutrophication, benthic flux of DOC may be associated with the transport of nutrients and pollutants from the sediment to the surface waters, which is very critical to the structure and function of the freshwater ecosystem. With respect to this, more studies should be warranted for inland sediment DOM.

Due to the inherent heterogeneity of sediment DOM (even more than surface water DOM), its characterization still remains a challenge with approximately 80% yet uncharacterized. With the advance of new techniques such as EEM-PARAFAC and FT-ICR-MS, it is anticipated that better insight into many unanswered questions for biogeochemical and environmental roles of sediment DOM will be provided. Still, there is a need to develop promising sediment DOM analyzing techniques and/or to introduce new methods from other areas to shed fresh light on the characteristics and dynamics of sediment DOM. Re-mineralization, preservation, and the associated nutrients cycling are also important topics of sediment DOM from the perspectives of geochemistry and ecology. Considering that the summed amount of the sediments underlying highly productive coastal waters only accounts for nearly half of the global carbon burial (Hedges and Keil, 1995), it is crucial to evaluate the early diagenetic processes in the sediments so as to fully understand the production and removal processes associated with the sediment DOM carbon budget. In addition, sediment DOM-metals/HOCs complexes and their dynamics in sediments remain an intriguing area of future research as well.

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