



Characteristics of dissolved organic matter (DOM) and relationship with dissolved mercury in Xiaoqing River-Laizhou Bay estuary, Bohai Sea, China[☆]



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ARTICLE INFO

Article history:

Received 23 August 2016

Received in revised form

30 November 2016

Accepted 3 December 2016

Available online 26 January 2017

Keywords:

Dissolved organic matter

Fluorescence

UV–Vis absorption

Bohai Sea

Laizhou Bay

Mercury

ABSTRACT

Because of heterogeneous properties, dissolved organic matter (DOM) is known to control the environmental fate of a variety of organic pollutants and trace metals in aquatic systems. Here we report absorptive and fluorescence properties of DOM, in concurrence with concentrations of dissolved mercury (Hg), along the Xiaoqing River-Laizhou Bay estuary system located in the Bohai Sea of China. A mixing model consisting of the two end-members terrestrial and aquatic DOM demonstrated that terrestrial signatures decreased significantly from the river into the estuary. Quasi-conservative mixing behavior of DOM sources suggests that the variations in the average DOM composition were governed by physical processes (e.g., dilution) rather than by new production and/or degradation processes. In contrast to some previous studies of river-estuary systems, the Xiaoqing River-Laizhou Bay estuary system displayed a non-significant correlation between DOM and Hg quantities. Based on this and the variation of Hg concentration along the salinity gradient, we concluded that Hg showed a non-conservative mixing behavior of suggested end-member sources. Thus, rather than mixing, Hg concentration variations seemed to be controlled by biogeochemical processes.

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1. Introduction

Environmental pollution and ecological deterioration of river-estuary systems occur due to rapid population growth and industrial development, threatening these vital ecosystems. The fate of environmental pollutants within river-estuary systems is linked to dissolved organic matter (DOM). It is therefore critical to understand the biogeochemical characteristics and reactivities of DOM functionalities in these environments (Bianchi, 2007). This may be

achieved by quantifying the concentration and functionalities of DOM in parallel with pollutants along river-estuary systems. Further, the techniques for analyzing DOM have advanced over the last few decades, which provide deeper insight into the heterogeneous properties of DOM (Leenheer and Croué, 2003). Among these techniques, the low-cost and fast measurements by UV-Vis absorption and fluorescence spectroscopies have resulted in extensive use in DOM investigations. The techniques provide important tools for studies of temporal-spatial distribution, sources, and dynamics of DOM in a range of aquatic environments, including freshwater and coastal ecosystems (Yang et al., 2013; Helms et al., 2008; Fichot and Benner, 2012; Xie et al., 2012; Spencer et al., 2012; Li et al., 2015). Furthermore, the chemical reactivity of DOM mostly depends upon its intrinsic chemical structure such as its aromatic components, molecular weight, and degree of humification. The correlation between “structure and reactivity” may be

[☆] This paper has been recommended for acceptance by Dr. Harmon Sarah Michele.

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useful to elucidate the role of DOM in a number of reactions of importance for the environmental fate of pollutants (Weishaar et al., 2003; Dittman et al., 2009; Burns et al., 2013). Environmental studies to an increasing extent rely upon spectrophotometric analyses to reveal, through optical properties, spatial and temporal variability in the composition of DOM in aquatic systems. Therefore, based upon the optical characterization of DOM, an improved understanding of the causal relationships between DOM composition and pollutants may be obtained for river-estuary system.

Mercury (Hg) pollution has been recognized globally as a problem in many aquatic systems and its harmful health effects are an impetus for studying Hg fate in various environments (Ullrich et al., 2001). Methylmercury (MeHg), which is formed through biotic methylation of inorganic Hg, is especially problematic for aquatic organisms and humans due to its high toxicity and bioaccumulation. Across various aquatic systems, river-estuary systems are important ecological environments. In recent years, Hg cycling in estuarine and coastal marine environments have been widely studied (Merritt and Amirbahamn, 2009; Pan and Wang, 2012; Mason et al., 1999; Laurier et al., 2003; Lawson et al., 2001; Han et al., 2006; Canário et al., 2008; Choe et al., 2004; Conaway et al., 2003). There are only a few reports on the Hg contamination in Chinese estuaries, where high levels of Hg commonly are encountered, caused by the rapid industrial developments (Wang et al., 2009; Luo et al., 2012; Gao et al., 2014; Ci et al., 2011). It is well known that DOM regulates Hg dynamics in aquatic environments through its chemical bonding to reduced sulfur groups (Ravichandran, 2004; Skjellberg et al., 2006), by its induction of photoreactions (Jeremiason et al., 2015), and by its control of dark redox transformations (Gu et al., 2011; Jiang et al., 2015). Additionally, DOM plays a dual role (i.e., enhancement or inhibition) in the production of MeHg due to its effect on Hg speciation and bioavailability (Graham et al., 2012; Zhang et al., 2014; Hsu-Kim et al., 2013). Although a number of studies have suggested that DOM composition is a critical factor for Hg reactivity and bioavailability in estuaries, and offshore areas (Bergamaschi et al. 2012; Schartup et al., 2013; 2015), the relationship between Hg and DOM properties has not been frequently studied along river-estuary systems. To our knowledge, only a few studies have determined absorptive and fluorescent characteristics of DOM in parallel to Hg quantities along river-estuary gradients (Bergamaschi et al. 2012; Schartup et al., 2015).

Optical properties of DOM originating from different environmental sources have been studied freshwater systems (Dittman et al., 2009; Burns et al., 2013). Dissolved organic carbon (DOC) and DOM quality parameters, derived from the UV-Vis absorption spectrum (e.g., specific UV absorbance, spectral slope), were used to explain the relationship between DOM and Hg (Dittman et al. 2009; Burns et al., 2013). Although a strong positive correlation between Hg and DOC concentration have been observed, suggesting Hg mobility in aquatic systems to be associated with DOM (Mierle and Ingram 1991; Dittman et al., 2009; Bergamaschi et al. 2012), across aquatic systems with diverse geochemical processes and sources of DOM, the positive correlation between Hg and DOC is not always consistent. Furthermore, some studies even have arbitrarily concluded that no effect of DOM exists, merely because no significant correlation between DOC and Hg was found. Thus, studying DOM characteristics and dynamics is important for advancing our understanding of the role DOM plays in the river-estuary system with respect to Hg. In this study, we use the optical properties of DOM to help us reveal how human activities' may influence on the Hg distribution in an river-estuary system. Thus, the DOM sources of terrestrial and anthropogenic or microbial/algal origin were used to identify areas with high anthropogenic input signatures, influencing the Hg distribution in a manner that can be identified.

The Xiaoqing River-Laizhou Bay estuary system in Bohai Sea, China, was the object of this study. The aims were to: (1) elucidate the DOM spectroscopic characteristics and understand the reasons for the variation of DOM properties along the river-estuary system; (2) validate the hypothesis that the variations in concentrations of dissolved Hg can be explained by DOM properties; (3) further test whether optical indices (e.g. SUVA₂₅₄) could be reasonable predictors of dissolved Hg concentrations in Xiaoqing River-Laizhou Bay estuary area. As part of a research project on the biogeochemical processes of DOM in river-estuary systems of China, results from this study may explain spatial variations and environmental implications of DOM, and also give insights into the close relationship between DOM and Hg in the estuary environment.

2. Materials and methods

2.1. Study sites

Laizhou Bay is the southernmost of three bays in the Bohai Sea, a semi-enclosed inner sea of China. The shallow coastal bay, less than 10-m in depth, covers approximately 10% of the Bohai Sea area. Since the 1970s, the Bohai Sea has experienced heavy anthropogenic impact due to the rapidly developing urbanization and economy in the area. Laizhou Bay is heavily polluted by anthropogenic pollutants imported from more than fifteen rivers and numerous waste water pipelines discharging into the bay. In 2013, more than one-fourth of its area failed to meet the Grade IV national sea water quality standard (SOA, 2014). Among the rivers draining into Laizhou Bay, the artificial Xiaoqing River is the most important with respect to pollution and runoff (Pan et al., 2010; Heydebreck et al., 2015). It is the second largest freshwater input to Laizhou Bay, following the Yellow River, and it drains an area of 10,340 km² along its 223 km length starting in the north of the Taiyi Mountains. It passes through heavily urbanized and industrialized areas of Shandong Province, including Jinan, Zibo, Weifang, and Dongying, and finally discharges into Laizhou Bay. High levels of trace heavy metals have been a concern in the Bohai Sea with respect to its environmental quality and risk (Gao et al., 2014).

2.2. Sampling collection

Surface water samples were collected along the river Xiaoqing River into the Laizhou Bay estuary in April 2014 (Fig. 1). More detailed sample information is found in the reference (Heydebreck et al., 2015). Briefly, the study area was divided into two parts, with respect to the salinity changes along the river-estuary system, including the freshwater river (upstream of the Xiaoqing River mouth, with salinity < 5 psu) and the outer estuary (beyond Xiaoqing River mouth, with salinity > 5 psu). As shown in Fig. 1, a total of 31 sites were selected for surface water collection, including 18 sites (sampling No.1–18) from the Xiaoqing River and 13 sites (sampling No.19–31) from the Laizhou Bay estuary. The river samples were collected below bridges or dams, while the estuarine samples were collected off a fishing boat. A stainless steel bucket was filled with water from the surface along the channel line of the river. Three to five buckets of water were mixed in a pre-cleaned brown glass bottle. An aliquot (approximately 200 mL) of water was used for DOM and Hg chemical analysis. The sampling buckets and glass bottles were rinsed *in situ* with river water three times before use. In the field, *in situ* water quality parameters including pH, dissolved oxygen (DO), salinity and conductivity were measured using a portable multi-parameter water quality meter (YSI ProPlus, YSI Inc., USA).

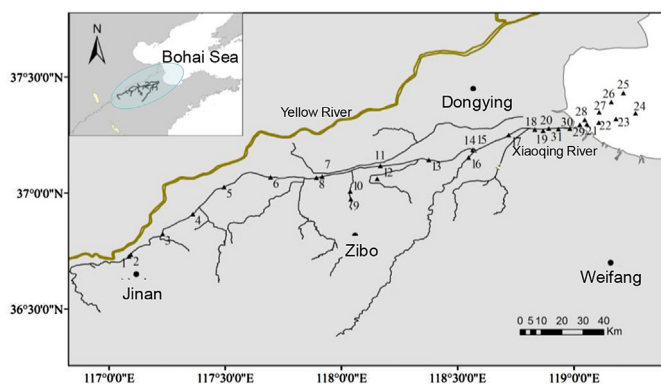


Fig. 1. Sampling sites in Xiaqing River-Laizhou Bay estuary system.

2.3. DOC and spectroscopy measurement

Water samples were filtered through a 0.45 μm cellulose acetate membrane previously rinsed twice with ultrapure Milli-Q water. The filtrate was kept in high-density polyethylene (HDPE) bottles under a dark condition at 4 $^{\circ}\text{C}$ until analysis. DOM concentration was represented by dissolved organic carbon (DOC) (mg L^{-1}), which was measured by a Vario MACRO TOC analyzer (Elementar, Germany) and was calculated as the difference between the total and inorganic carbon concentrations. We also measured the hydrophobic fraction of DOC (expressed as mg L^{-1}) after passing acidified DOM samples ($\text{pH} = 2$) through an Amberlite[®] XAD-8 macroporous resin column, based on the IHSS aquatic humic substance extraction method. The hydrophobic fraction was calculated as the difference between the total DOC and the non-hydrophobic DOC passing through the column. UV–vis and fluorescence spectral measurements were done on an Aqualog[®] (Horiba, Japan) absorption-fluorescence spectrometer equipped with a 150 W ozone-free xenon lamp at a constant 20 ± 3 $^{\circ}\text{C}$ in a temperature-control room. All works, including sampling and spectrophotometric measurements, were completed within less than two weeks.

Briefly, UV–vis absorption spectra of samples in a 10 cm quartz cuvette were determined against a Milli-Q water blank over a 230–800 nm range with 1 nm intervals. The CDOM abundance was represented by decadic absorptivity, $a(355)$ (Guo et al., 2007; Guéguen et al., 2012; Li et al., 2015). For emission-excitation matrices (EEMs) of fluorescence spectra, the emission spectra were scanned every 3.18 nm interval at wavelengths from 250 to 620 nm, with excitation wavelengths ranging from 230 to 450 nm in 5 nm interval. The bandpass of excitation and emission was 5 nm. Scan integration time was 3 s. The EEMs of DOM samples were corrected for Raman scattering by subtraction from a Raman-normalized Milli-Q water. The absorption spectra were used to correct for inner-filter effects. EEMs were not subjected to parallel factor analysis (PARAFAC) due to the small and diverse sample dataset. Instead, fluorescent components were identified according to Coble (1996) by a traditional “peak-pick” method. The abundance of bulk fluorescence DOM (FDOM) was represented by $F_n(355)$ (Chen et al., 2004; Bergamaschi et al., 2012), which is acquired at excitation wavelength of 355 nm and emission wavelength of 450 nm. All DOM samples were processed in triplicates for all measurements unless otherwise specified.

2.4. Determination of dissolved total mercury (THg) and methylmercury (MeHg)

Dissolved THg and MeHg, denoted THg_d and MeHg_d , were

determined in filtered (0.45 μm , Millipore[®] polyvinylidene fluoride filter) acid-treated (0.5% HCl) water samples. A procedure of purging and trapping, followed by cold vapor atomic fluorescence spectroscopy (CVAFS) (Model III, Brooks Rand, USA) was used to determine the samples concentration with THg_d detected after pre-concentration according to EPA method 1631. For MeHg_d , samples were distilled and ethylated according to EPA method 1630 and measured by GC-CVAFS. Method blanks were done for both quality assurance and control (QA/QC). All results here were reported as mean values.

More details of measurement and QA/QC procedure were shown in Support Information S11. Statistical analyses were performed in OriginPro[®] 2015 and SPSS 19.0 by results cross-check. A *t*-test was used to determine whether the means of two independent groups different. Statistical significances (*p* value) were all noted at 0.05 or 0.01, unless otherwise specified.

3. Results and discussion

3.1. DOM quantity

Ranges of DOC, CDOM, and FDOM properties for the Xiaqing River-Laizhou Bay estuary system are shown in Table 1. The range of DOC concentrations in the river was 6.7–32 mg L^{-1} and in the estuary 2.8–11 mg L^{-1} for the collected samples. For both the river and estuary samples, the coefficient of variation averaged 48%, but in spite of this large variance the average means of the DOC concentrations of these two end-members were different ($p < 0.05$). The parameters $a(355)$ and $F_n(355)$ were taken as proxies for the quantities of CDOM and FDOM, respectively. The $a(355)$ ranged from 0.22 to 17 m^{-1} and the FDOM ranged from 1.1×10^3 to 75×10^3 a.u. Both $a(355)$ and FDOM were significantly higher in the Xiaqing River than in the Laizhou estuary ($p < 0.05$). This matched the pattern of CDOM and DOC in other river-estuaries, with lower values in the estuary/coastal water than in the upstream freshwater (Seritti et al., 1998; Rochelle-Newall and Fisher, 2002; Asmala et al., 2013, 2016). Compared with other studies (Support Information S12, Table S1), DOC and CDOM in this study was most similar to river-estuary systems influenced by anthropogenic effluences, such as Yangtze River estuary (Wang et al., 2014), and at the southern and western coasts of Florida (Green and Blough, 1994). Our concentrations of DOC and CDOM was lower than in the more pristine (terrestrial dominated) river-estuary systems in the Baltics (Asmala et al., 2013, 2016) and in the Arno River-Tyrrhenian Sea estuary system (Seritti et al., 1998), but higher than in Cádiz Bay, Spain (Catalá et al., 2013), a similar semi-enclosed system located in the southwest of the Iberian Peninsula. Interestingly, in the Pearl River estuary, in southern China, which is also heavily influenced by anthropogenic effluences, the CDOM was not as high as in the Laizhou Bay estuary (Chen et al., 2004; Hong et al., 2005).

When CDOM was normalized to DOC (CDOM/DOC , $\text{L mg}^{-1} \text{m}^{-1}$) we observed a decrease from 0.83 in the river to 0.40 in the estuary. Thus the chromophoric DOM decreased approximately 50%. This change can be attributed to an increase in the proportion of non-chromophoric DOM, either through the degradation of CDOM or additional input of non-absorbing DOM in the estuary. Urban (including industrial) developments near estuaries have been reported to add non-chromophoric DOM (Pan et al., 2010; Heydebreck et al., 2015).

Both CDOM and FDOM correlated positively with DOC in the Xiaqing River-Laizhou Bay estuary (Fig. 2), suggesting that these two measures could be used as proxies for DOC concentrations through remote or *in situ* measurements in this system. Similar observations have been reported in other rivers, estuaries and coastal waters (Blough and Del Vecchio, 2002; Kowalczyk et al.,

Table 1
Variations in DOC, decadic $a(355)$ and $F_n(355)$ along the Xiaoqing River-Laizhou Bay estuary transect.

Sampling sites	$a(355)/m^{-1}$			$F_n(355) \times 10^3/a.u$			DOC/mg L ⁻¹		
	Range	Mean	VC(%) ^a	Range	Mean	VC(%)	Range	Mean	VC(%)
Xiaoqing River	3.82–17.24	9.71 ± 4.17	42.96	6.56–75.42	24.67 ± 20.31	82.36	6.69–31.51	12.63 ± 6.35	50.31
Laizhou Bay estuary	0.22–6.53	2.55 ± 2.13	83.33	1.12–16.92	5.72 ± 5.65	98.78	2.75–11.08	5.62 ± 2.71	48.25

^a VC (Variation Coefficient (%)) = standard deviation*100/mean.

2010; Spencer et al., 2012; Hong et al., 2005; Bergamaschi et al., 2012; Yang et al., 2013). The linear relationship between DOC and CDOM in Laizhou Bay estuary: $DOC = 1.1158 \times CDOM + 2.7777$ ($r^2 = 0.76$, $p < 0.01$) suggests that more than 70% of DOC variability among the stations in the estuary can be explained by similar spatial variations in the quantity of CDOM. This co-variation is similar to reports from eutrophic estuarine and coastal waters in the Tyrrhenian Sea (Seritti et al., 1998), but higher than in estuaries of the Baltic Sea (Ferrari et al., 1996; Ferrari, 2000; Kowalczyk et al., 2010), Chesapeake Bay and Delaware Bay (Del Vecchio and Blough, 2004). Furthermore, Oliveira et al. (2006) also reported similarly strong relationships between CDOM and DOC in nearshore areas predominated by riverine inputs. Maie et al. (2005) explained an increase in the non-chromophoric fraction of DOM from 35% to 77% along a river discharge into the coastal bay by DOM sources shifting from mainly terrestrial inputs (e.g., vascular plants) to autochthonous sources of microbial and algal production. The fact that our study did not observe a similar phenomenon highlights that the Laizhou Bay estuary area was more inclined to be influenced by the river rather than by marine DOM sources. Furthermore, less significant correlations (Fig. 2) suggest a greater heterogeneity of DOM in the Xiaoqing River than in the Laizhou Bay estuary, which might be explained by a significant contribution from urban and industrial developments along the river.

3.2. DOM absorption properties

There were no distinct absorption peaks in the UV–vis spectra (Support information S13, Fig. S1), similar to previous studies (Yang et al., 2013; Helms et al., 2008; Fichot and Benner, 2012). Only slight shoulder peaks were observed in the range of 250–290 nm, which may be related to conjugated molecular structures in DOM, such as conjugated diolefin or unsaturated α , β -ketone. With increasing wavelength in the UV range (230–400 nm), absorption coefficients varied more in the Xiaoqing River waters than in the Laizhou Bay estuary (Fig. S1). The greater variance suggests that the DOM characteristics of river samples were more heterogeneous than

the coastal samples.

After correction for the iron background-absorbance, specific UV absorbance at 254 nm ($SUVA_{254}$) was calculated by dividing the absorbance at 254 nm with the corresponding DOC concentration. $SUVA_{254}$ is used as an estimate of DOM aromaticity, due to the absorbance at 254 nm by conjugated rings (Weishaar et al., 2003). Samples collected at the Xiaoqing River (mean value 3.4 ± 1.4 L mg⁻¹ m⁻¹) were clearly higher than at the Laizhou Bay estuary (mean value 2.8 ± 0.82 L mg⁻¹ m⁻¹), demonstrating higher aromaticity of DOM in the river rather than in the estuary. Moreover, along the river to estuary gradient, hydrophobic fractions of DOM (reported as DOC in mg L⁻¹) decreased on average from 5.2 ± 1.3 mg L⁻¹ to 2.7 ± 1.2 mg L⁻¹. Still the hydrophobic DOC made up the same fraction of DOC (49% in the river and 50% in the estuary). The similar trend along the gradient for hydrophobic DOC and $SUVA_{254}$ (Fig. 3a) suggests that aromatic moieties absorbing at 254 nm were associated with mainly the hydrophobic fraction of DOC, likely derived from allochthonous, terrestrial sources (e.g., lignin). Selective removal of the DOM hydrophobic fraction during the transport process may be implied, possibly by processes such as photochemical degradation, microbial respiration, or selective adsorption onto suspended particulate. Alternatively, quasi-conservative mixing of the endmembers could contribute to a decrease in hydrophobic content along the estuary from physical dilution, as observed by the salinity increase, and is discussed more extensively below (in Section 3.4).

The absorption curve of DOM decreases exponentially from the UV region to the visible wavelength region. The determined values on the absorption coefficients were fitted in the spectral interval 275–295 nm (Fichot and Benner, 2012; Asmala et al., 2013, 2016) with the exponential function: $a(\lambda) = a(\lambda_r) * \exp[-S(\lambda - \lambda_r)]$, where λ_r is a reference wavelength and $S_{275-295}$ is the spectral slope. The $S_{275-295}$ is known to correlate negatively with the molecular mass of CDOM, and is sensitive to photochemical and microbial degradation (Helms et al., 2008; Xie et al., 2012; Asmala et al., 2013, 2016). Recent studies also use $S_{275-295}$ as a proxy for the fraction of terrigenous DOC in rivers and oceans (Fichot and Benner, 2012;

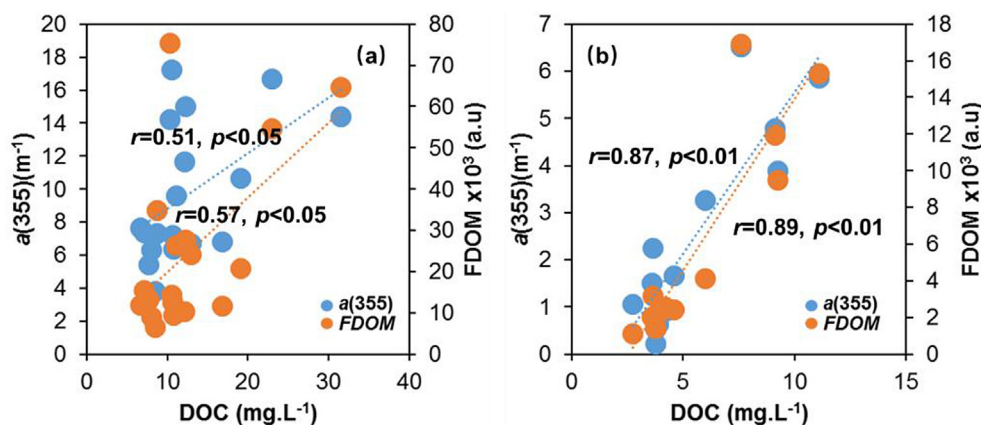


Fig. 2. Relationships between DOC concentrations and CDOM (blue), and FDOM (orange), respectively, in Xiaoqing River, $n = 18$, (a) and Laizhou Bay estuary, $n = 13$, (b). All correlations were significant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

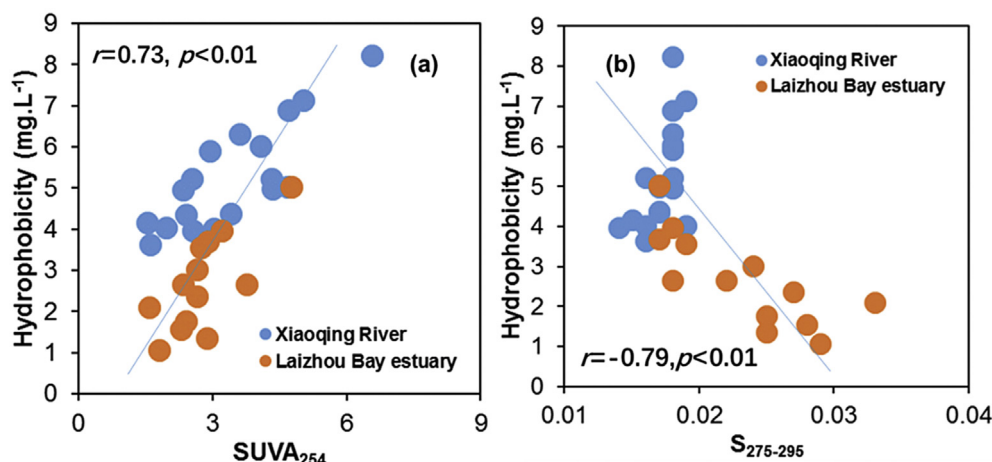


Fig. 3. Relationships between hydrophobic DOC and $SUVA_{254}$ (a), and $S_{275-295}$ (b) in Xiaoqing River, $n = 18$, (blue) and Laizhou Bay estuary, $n = 13$, (orange). Relationships shown represent all data, $n = 31$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fichot et al., 2013). In this study, the $S_{275-295}$ ranged from 0.014 to 0.033 nm^{-1} along the Xiaoqing River-Laizhou Bay estuary gradient. Similar ranges were reported in boreal rivers (Asmala et al., 2012, 2013, 2016; Guéguen et al., 2012) and estuaries (Asmala et al., 2012; Guo et al., 2007; Helms et al., 2008). Fairly constant $S_{275-295}$ values (range of 0.014–0.019 nm^{-1}) were found in the river region, increasing to higher $S_{275-295}$ values (range of 0.017–0.033 nm^{-1}) in the estuary area. This suggests that DOM in the Xiaoqing River had higher aromaticity and molecular mass than in the Laizhou Bay estuary. Spencer et al. (2012) found the spectral slope to correlate negatively with the DOM hydrophobic fraction, which represented the high molecular weight DOM and aromaticity of DOM. We observed a similar pattern for our river-estuary system (Fig. 3b). Importantly, the Xiaoqing River-Laizhou Bay estuary experiences seasonal desalting and flooding from the upstream Yellow River. Elevated levels of suspended particles, caused by the estuarine turbidity maxima (ETM) may preferential remove high molecular mass DOM by adsorption to particles (Guo et al., 2007), further increasing $S_{275-295}$. While in other estuary systems the removal of CDOM was dominated by photochemical and microbial degradation (Vodacek et al., 1997; Blough and Del Vecchio, 2002), the high turbidity and short residence times relative to other estuaries might cause adsorption of on suspended particulates to be an important removal process of hydrophobic DOM along the river-estuary gradient.

3.3. DOM fluorescence property

3.3.1. Fluorescence peaks

Typical DOM EEM spectra are shown in Fig. 4 for the Xiaoqing River-Laizhou Bay estuary system. Four fluorescent components were identified, following the interpretations made by Coble (1996). Three humic-like components were represented by A ($E_x/E_m = 250-260 \text{ nm}/380-480 \text{ nm}$), C ($E_x/E_m = 330-350 \text{ nm}/420-480 \text{ nm}$) and M ($E_x/E_m = 310-320 \text{ nm}/380-420 \text{ nm}$), and one protein-like component represented by T ($E_x/E_m = 270-280 \text{ nm}/320-350 \text{ nm}$). Peak B ($E_x/E_m = 270-280 \text{ nm}/300-320 \text{ nm}$), reported by Coble (1996), was not observed. Peaks A and C are interpreted to be related primarily to vascular plant sources having highly aromatic, conjugated, and mainly high molecular mass components typical for terrestrial sources. The marine, humic-like (M) peak, which has been attributed to marine sources and microbially-altered DOM, was slightly blue-shifted in emission, so it possessed less aromatic character and lower molecular mass than A and C. For identification of protein-like components, tyrosine-like (peak B) and tryptophan-like (peak T) peaks have been important. These components are readily linked to DOM lability (Fellman et al., 2009), trace DOM microbial sources (Coble, 1996) and anthropogenic perturbation (Baker, 2001, 2002; Galapate et al., 1998). The tryptophan-like (peak T) components represents freshly produced proteins and are less degraded compared to the more degraded tyrosine-like component (peak B). Therefore, the lack of peak B in

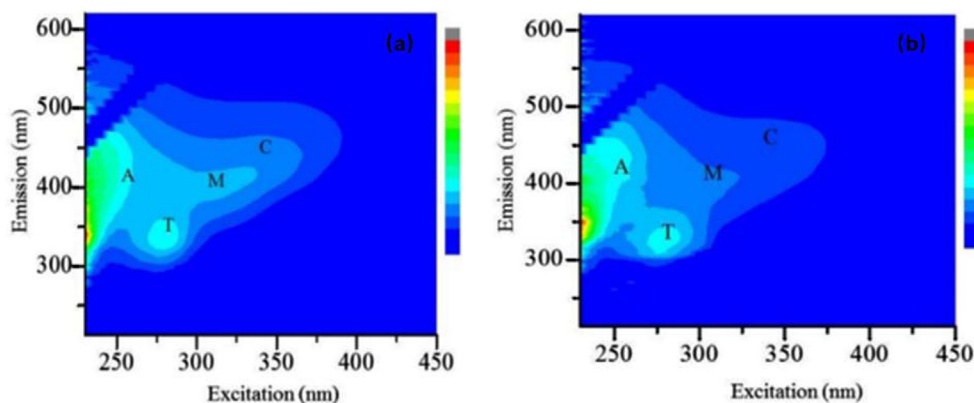


Fig. 4. Typical 3D-EEM spectra of DOM samples from Xiaoqing River (a) and Laizhou Bay estuary (b). Four fluorescent components were identified following the methodology of Coble (1996), including humic-like components (A, C, and M) and protein-like component (T).

the Xiaoqing River-Laizhou Bay estuary may suggest that proteinaceous DOM in the study area may be represented primarily by freshly produced proteins. Furthermore, peak T could also be associated with biological oxygen demand (BOD) and microbial activity in wastewater, and thus be used to identify anthropogenic wastewater effluences (Baker, 2002; Henderson et al., 2009; Carstea et al., 2016). Therefore, the more prominent peak T signatures of DOM in the Xiaoqing River, than in the Laizhou Bay estuary ($p < 0.05$), may suggest that anthropogenic effluences were more significantly influencing the characteristics of DOM in the upstream area. The Xiaoqing River is originally an artificially dug river channel that once was an important waterway and more recently has been closed because of decreased water flows and heavy pollution from domestic sewage and industrial wastewater (Heydebreck et al., 2015).

3.3.2. Fluorescence parameters

Two-dimensional fluorescence index (FI) is calculated as the ratio of the fluorescence intensities at emission 450 and 500 nm, respectively (excitation was kept at 370 nm), and has been widely used to distinguish DOM fractions such as autochthonous (microbially and/or algal-derived DOM with $FI > 1.9$) and allochthonous sources (terrestrially-derived DOM with $FI < 1.4$) (McKnight et al., 2001; Huguet et al., 2009). Overall, two DOM sources could be distinguished by FI values (Fig. 5a). When FI values of the Xiaoqing River-Laizhou Bay estuary were between 1.4 and 1.9, it is suggested that the DOM contained contributions from both terrestrial and microbially-derived DOM. Clearly, a “mixture” was more predominant in the Laizhou Bay estuary than in the Xiaoqing River. Some samples of the river showed FI values of less than 1.4, which indicated a greater terrestrial signature. Yet, it should be noted that 5 sampling sites of the Xiaoqing River, and some estuary samples, showed FI values slightly higher than 1.9, which may be attributed to direct anthropogenic influences resulting in an increase of protein-like components. Also, excess nutrients (e.g., phosphorus and nitrogen) from agricultural runoff due to overuse of fertilizers might have induced higher production of autochthonous DOM in the Xiaoqing River.

The humification index (HIX) was calculated as the peak area under the emission spectra 435–480 nm divided by 300–445 nm at constant excitation at 254 nm (Zsolnay et al., 1999; Huguet et al., 2009). All HIX values were in the range of 0.61–2.67 (Fig. 5). Similar to $SUVA_{254}$, the Xiaoqing River showed the highest

HIX values, which suggest DOM of the upstream river had more of a humified and aromatic character than the estuary water. But it must be emphasized that, contrary to expectations, the spatial variability of HIX did not follow $SUVA_{254}$, even though both have been widely used to indicate the humic character and aromaticity of DOM. This inconsistency likely may have been caused by some fluorescent protein-like components and aromatic compounds absorbing UV light at a specific wavelength (e.g., 254 nm) to decouple the HIX and $SUVA$. In the literature, HIX values greater than 10 typically indicate a strong humic character with an important terrigenous contribution (Huguet et al., 2009), however, the HIX in this study was much less than 10, indicating less humification as compared to other river-estuary area (e.g., Gironde estuary) (Huguet et al., 2009). The cause of lower humification of DOM in the Xiaoqing River-Laizhou Bay estuary could be explained by three specific reasons: (1) terrestrial sources in the river system may show an untypically low degree of humification due to land-uses and vegetation composition in the catchment changing the DOM properties; (2) a high microbial production driven by anthropogenic riverine inputs of priming substrate, such as protein and sugar, may cause a “priming effect” (Bianchi, 2011) stimulating the microbial community to degrade recalcitrant (humified) organic matter; (3) a preferential removal of highly humic and aromatic component of DOM due to the adsorption on suspended particulates.

The parameter BIX is an indicator of autochthonous inputs and provides a proxy for the relative contribution of recently microbially-produced DOM (Huguet et al., 2009; Wilson and Xenopoulos, 2009). It was calculated using the ratio of emission intensity at 380 nm divided by the emission intensity maximum value in range of 420–435 nm at excitation of 310 nm (Wilson and Xenopoulos, 2009). The BIX has a high value (>0.8) for DOM with an obvious autochthonous component of freshly produced OM of biological or aquatic bacterial origin (Huguet et al., 2009; Birdwell and Engel, 2010). In this study, all BIX values in the Xiaoqing River-Laizhou Bay estuary were higher than 0.8, and there was no significant difference between the river and estuary (Fig. 5b). Thus, it seems autochthonous DOM sources contributed significantly along the whole river-estuary transect, despite indications from FI values that DOM in the river section was more inclined to terrestrial predominance. Interestingly, only the BIX of DOM in the estuary zone showed significant positive and negative correlations with FI and HIX, respectively ($p < 0.05$). This may suggest that DOM having

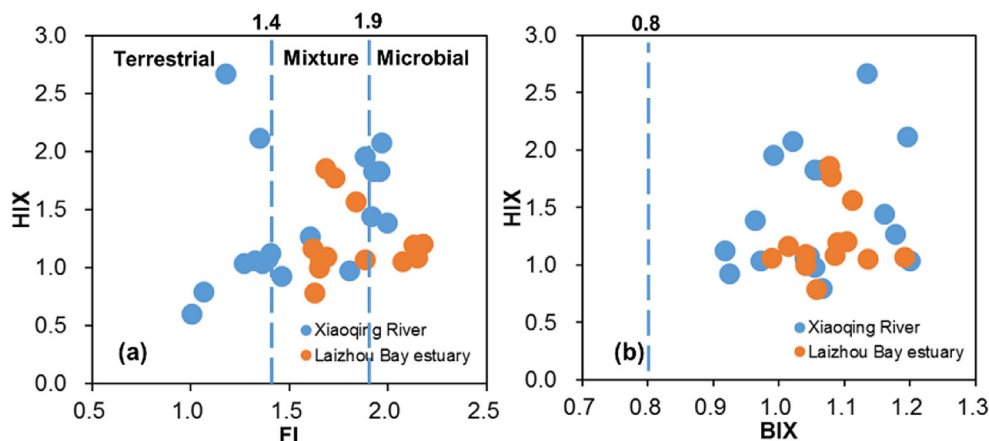


Fig. 5. Correlations plots of FI versus HIX (a), and BIX versus HIX (b) values for Xiaoqing River samples (blue) and Laizhou Bay estuary samples (orange). In plot (a), the region to the left of the dashed line at FI 1.4 indicates terrestrial-dominated CDOM and the region to the right of the dashed line at FI 1.9 indicates microbially-dominated CDOM. In plot (b), the region to the right of the dashed line represents BIX associated with freshly produced DOM from biological sources. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

higher FI values (mainly autochthonous origin) tended to have lower degrees of humification, which can be attributed to the accumulation of biologically-derived organic matter associated with higher BIX values in the estuary.

To further track the modification of fluorescent DOM along the river to the estuary, two intensity ratios of fluorescent peaks, $r(A/C)$ and $r(T/C)$, were calculated. Because Peak C is supposed to be associated with older, more recalcitrant structures, $r(A/C)$ is a parameter to reflect the humification degree of humic-like components in DOM and to distinguish older from relatively less recalcitrant (“younger”) humic structures. Lower $r(A/C)$ values of the Xiaoqing River (2.2 ± 0.37) compared with the Laizhou Bay estuary (2.4 ± 0.20) therefore indicate that the humic-like components of DOM were of more recent nature in the estuary as compared to in the upstream river. Similar observations were done by Huguet et al. (2009). In contrast, $r(T/C)$ was slightly higher in the Xiaoqing River, but not significantly different from in the Laizhou Bay estuary. Therefore, it cannot distinguish between the autochthonous characteristics of DOM in the river and estuary. Additionally, $r(T/C)$ is important for water pollution assessments. Similar to Peak T being used to track wastewater influence on natural waters, $r(T/C)$ was used to assess water quality (Baker, 2001; Galapate et al., 1998). Based on comparisons between natural and polluted waters (Baker, 2001, 2002; Old et al., 2012; Carstea et al., 2016), $r(T/C)$ exceeding approximately 2.0 was proposed to indicate a significant influence from polluted wastewater. In this study, all DOM samples showed $r(T/C)$ higher than 2.0, indicating that anthropogenic pollution in the Xiaoqing River-Laizhou Bay estuary area could not be overlooked. The highest $r(T/C)$ value (4.0) was observed in the Xiaoqing River, highlighting the importance of point-pollution sources along the river with negative impact on the water quality.

3.4. DOM mixing model in river-estuary system

3.4.1. Mixing behavior in estuary

As shown in Fig. 6, eight out of nine different DOM parameters were significantly and negatively correlated with salinity along the river-estuary transect ($r = -0.98$ to -0.61 , $p < 0.01$). The spectral slope $S_{275-295}$ in contrast showed a positive relationship. These relationships suggest that each of these parameters may follow quasi-conservative mixing of two end-members representing the allochthonous/terrestrial/freshwater and autochthonous/non-terrestrial/marine DOM sources along the salinity gradient from the river mouth to the marine end of the Laizhou Bay estuary. Similar observations were reported in estuaries of the Baltic Sea (Kowalczyk et al., 2006; Asmala et al., 2016) and the Yangtze, and Pearl River estuaries (Hong et al., 2005; Guo et al., 2007). In contrast, the Gironde estuary (Huguet et al., 2009), a humic-rich estuary (Tyne estuary) in England (Uher et al., 2001), and a subterranean estuary in the northeastern Gulf of Mexico (Suryaputra et al., 2015) showed no such changes in DOM properties along salinity gradients. It should be emphasized that the apparent quasi-conservative mixing behavior observed (Fig. 6) would not exclude simultaneously ongoing biogeochemical processes altering the DOM along the salinity gradient. The variance of data around the theoretical mixing lines indicated that other processes either removed or produced DOM, especially at low salinity (around 10 PSU). This is not surprising, as the freshwater discharge from the river affects the salinity disproportionately from the river mouth the marine end of the gradient (Asmala et al., 2016). It should be noted that $S_{275-295}$ increased with increasing salinity ($r = 0.84$, $p < 0.01$) (Fig. 6e), similar to the results in the Delaware Estuary (Helms et al., 2008), the St. Lawrence estuarine system (Xie et al., 2012), the estuaries of Taiwan Island (Yang et al., 2013), and the Gulf of Mexico (Fichot and Benner, 2012). This relationship likely suggested a

seaward decrease in the average molecular mass and aromatic content of CDOM (Helms et al., 2008; Spencer et al., 2012; Xie et al., 2012).

An observed trend was the decrease in the FI with salinity, which indicated the dilution of fluorescent DOM outwards from the river mouth. On the other hand, high and low fluorescence levels of the A, C, M, and T fluorescence components were usually found at low- and high-salinity sites, respectively. This also indicated that the majority of these components in the bay area would be derived from riverine inputs, which strengthens the aforementioned view that the Laizhou Bay estuary is mainly a river-dominated estuary, rather than a marine-influenced one. Importantly, some studies have suggested that photo-degradation occurs mainly in the high-salinity region (Li et al., 2015; Sun et al., 2014; Wang et al., 2014), which could induce non-conservative behavior of fluorescence peaks in the coastal environments (Vodacek et al., 1997). However, in the Laizhou Bay estuary the apparent quasi-conservative mixing behavior of properties reflected by the four fluorescence peaks (Fig. 6f-i) confirmed that photodegradation had a minor effect, as compared to the influence of physical processes (e.g., dilution). Also, because of the high turbidity, which will scatter and attenuate light, the increase in $S_{275-295}$ from the Xiaoqing River into the Laizhou Bay estuary may be caused by selective sorption of high molecular mass DOM to suspended particulates rather than photodegradation.

3.4.2. $SUVA_{254}$ mixing model

The carbon/nitrogen ratio (C/N) and $SUVA_{254}$ differ between terrigenous and aquatic sources of organic matter, and can thus be used in two end-member mixing models (Tan and Strain, 1979; Thornton and McManus, 1994). Following this approach, we used $SUVA_{254}$ to separate the terrigenous and non-terrestrial (aquatic and anthropogenically derived) end-members to differentiate between these two sources along our river-estuary transect. The following equations were used in our model:

$$SUVA_{254} = \frac{A_{254}}{DOC} = f_T \times \left(\frac{A_{254}}{DOC} \right)_T + f_{Non-T} \times \left(\frac{A_{254}}{DOC} \right)_{Non-T} \quad (1)$$

where f_T and f_{Non-T} are the fractions of terrestrial and non-terrestrial organic carbon, respectively. Mass balance requires $f_T + f_{Non-T} = 1$. The A_{254} is the specific absorbance at 254 nm. Equation (1) may be transformed into Equation (2) as follows:

$$f_T = \frac{[A_{254}/DOC] - [A_{254}/DOC]_{Non-T}}{[A_{254}/DOC]_T - [A_{254}/DOC]_{Non-T}}; \quad (2)$$

$$f_{Non-T} = \frac{[A_{254}/DOC]_T - [A_{254}/DOC]}{[A_{254}/DOC]_T - [A_{254}/DOC]_{Non-T}}$$

Finally, Equation (2) can be re-written to Equation (3):

$$f_T = \frac{(SUVA_{254})_{Sample} - (SUVA_{254})_{Non-T}}{(SUVA_{254})_T - (SUVA_{254})_{Non-T}}; \quad (3)$$

$$f_{Non-T} = \frac{(SUVA_{254})_{Sample} - (SUVA_{254})_{Non-T}}{(SUVA_{254})_T - (SUVA_{254})_{Non-T}}$$

Referring to previous studies on light absorptive properties of algal-derived DOM (Tsai and Chow, 2016) and terrestrial DOM (Jaffe et al., 2008; Gabor et al., 2015), we set the value of decadic $SUVA_{254}$ for typical terrestrial sources to $7.0 \text{ L mg}^{-1} \text{ m}^{-1}$, and the value of decadic $SUVA_{254}$ for the expected non-terrestrial sources (e.g., microbial/algal and urban/anthropogenic effluent) to $1.0 \text{ L mg}^{-1} \text{ m}^{-1}$. A clear difference was displayed between the two end-members (terrestrial versus non-terrestrial) and the terrigenous contribution decreased (and thus the non-terrestrial

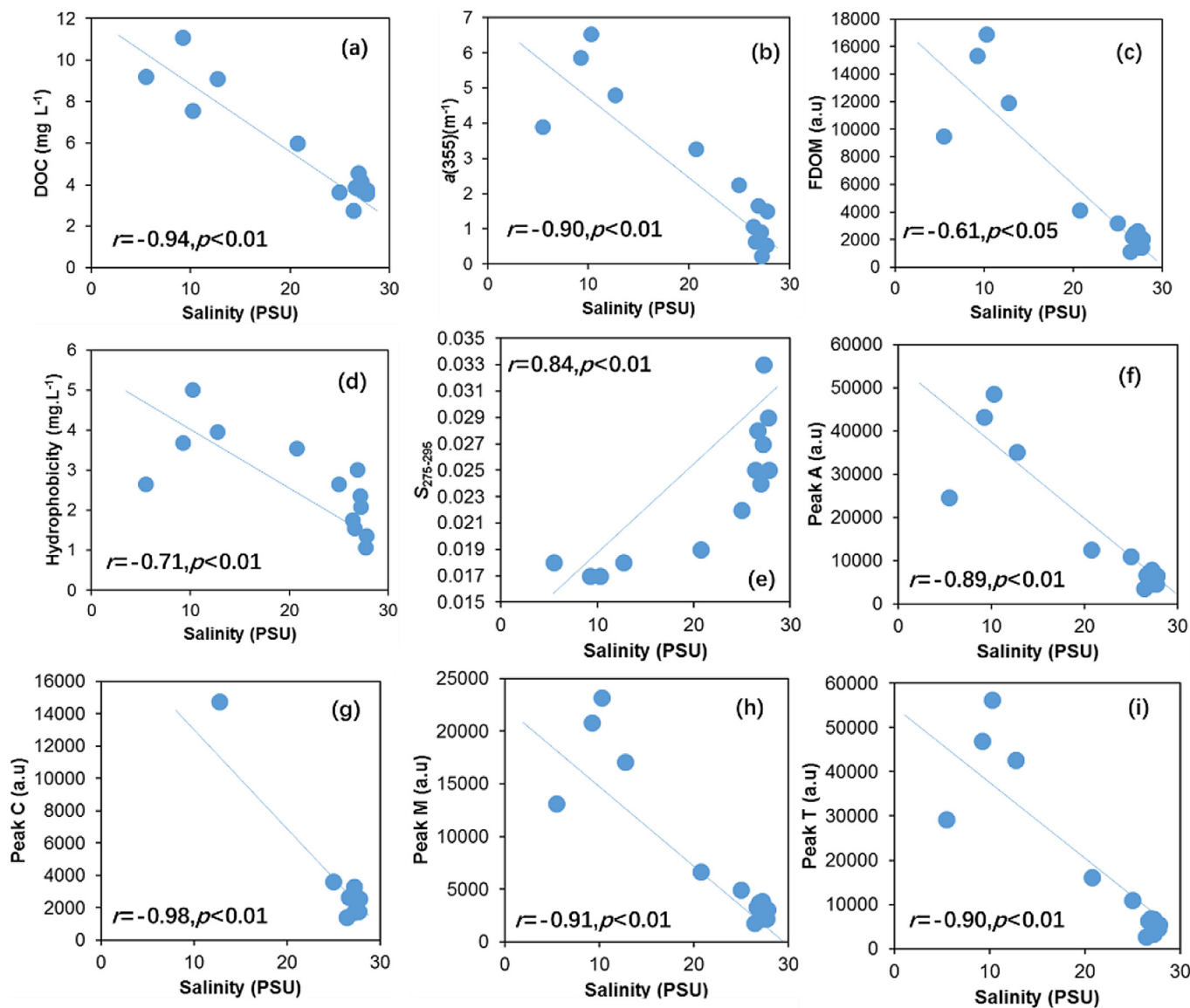


Fig. 6. Relationships between salinity and (a)DOC, (b) $a(355)$ (CDOM), (c)FDOM, (d)hydrophobicity, (e) $S_{275-295}$, (f)peak A, (g)peak C, (h)peak M, (i)peak T in the Laizhou Bay estuary. The significant correlations suggest that conservative mixing of the freshwater and marine water end-members may explain much of the DOM composition in the Laizhou Bay estuary. $n = 13$.

contribution decreased) from the river to the estuary (Fig. 7). The fraction of terrigenous contributions was in average 40% in the river and 29% in the estuary DOM. It should be noted that within the estuary, sampling station 31 was very close to the river mouth and stations 24 and 25 were the ones in the marine end of the estuary (Fig. 1). We compared our results with data reported from in three Finnish river-estuary systems of the Baltic Sea (i.e., Karjaanjoki, Kyrönjoki, and Kiiminkijoki), Asmala et al. (2013, 2016). The trend was quite similar trend to ours, with the fraction of the non-terrestrial contributions increasing significantly from the river to the estuary. Karjaanjoki is an urbanized river-estuary system, with similarities to the Xiaoqing River-Laizhou Bay estuary, except with a much colder climate. Both estuaries had relatively smaller terrestrial contributions in the river as compared to in environments that are more heavily influenced by agricultural activities (i.e., Kyrönjoki) or by natural peatlands and forests (i.e., Kiiminkijoki). Usually DOM in pristine areas with low anthropogenic influence are highly affected by forest land or wetland inputs and

show stronger terrestrial signatures with DOM having a greater degree of humification and aromaticity. The $SUVA_{254}$ mixing model varied among different estuaries, implying that the end-member contribution might also be dependent on specific land-uses in a given river-estuary system. Thus, further studies are needed for understanding the impacts of given land-uses on the DOM quality in river-estuary systems.

3.5. Relationships between DOM and Hg

3.5.1. Dissolved Hg species

In most natural aquatic environments, inorganic Hg concentrations are less than 5 ng L⁻¹ and MeHg concentrations are in the range of 0.02–0.30 ng L⁻¹ (Ullrich et al., 2001). Thus, THg_d and MeHg_d concentrations were somewhat higher in our study area. Concentrations of THg_d and MeHg_d in Xiaoqing River ranged from 3.1 to 61 ng L⁻¹ and 0.02–2.0 ng L⁻¹, respectively. In contrast, THg_d and MeHg_d in the estuary were in the ranges of 3.9–45 ng L⁻¹ and

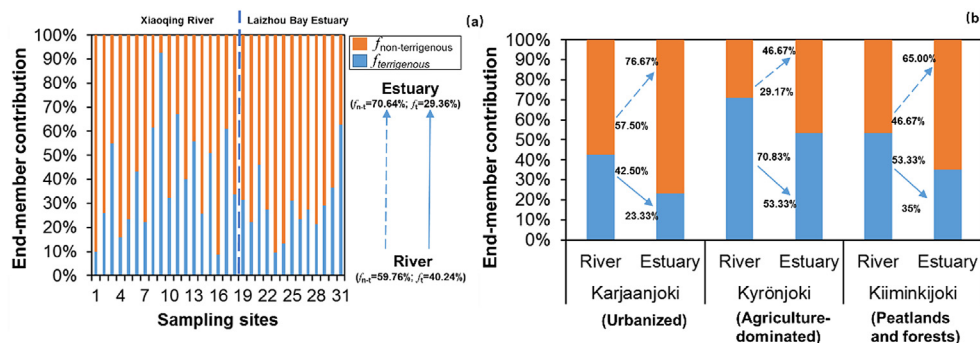


Fig. 7. Two end-member mixing model based on $SUVA_{254}$ measured at 31 sampling sites along the Xiaoqing River-Lai Zhou Bay estuary transect (a), and for comparison, three Finnish river-estuary systems in the Baltic Sea (b). The blue bars (f_t) represent terrigenous contribution and orange bars (f_{n-t}) non-terrigenous contribution. The end-member $SUVA_{254}$ values were set to 7.0 for terrestrial sources and 1.0 for the sum of non-terrigenous sources (e.g., microbial/algal, and anthropogenic effluent). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.12–0.75 ng L^{-1} , respectively. Overall, these results showed that concentrations of dissolved Hg and MeHg in freshwater exceeded concentrations in estuarine waters. Although the study area is heavily influenced by pollution because of the urban and industrial activities (Pan et al., 2010; Heydebreck et al., 2015), the Hg levels were below the Chinese National Surface Water guideline of 50 ng L^{-1} for I and II type water (GB3838-2002) and Chinese National Ocean water guideline of 50 ng L^{-1} for I type water (GB3097-1997). The only exception was sampling station XQ2 (60 ng L^{-1}) obviously influenced by Hg pollution. Additionally, in both river and estuary water, concentrations of Hg showed a high coefficient of variation (>38%), reflecting high spatial variations.

The Bohai Sea is a typical continental shelf, semi-closed sea with a predominant reversing current tide. So, its self-purification capacity is poor due to limited water exchanges with the open ocean. As shown in Table S2 of Support Information SI4, Wang et al. (2009) reported concentrations of THg_d and MeHg_d in three upstream rivers of Jinzhou Bay estuary of Bohai Sea in the range between 84 and 2700 ng L^{-1} and in between 0.12 and 3.0 ng L^{-1} , respectively, which are 1–2 orders of magnitude greater than values observed in this study of the Xiaoqing River. One reason may be locally heavy pollution of Hg from the long-term Zn smelting and chlor-alkali production. Consequently, concentrations of THg_d and MeHg_d were in the ranges of 39–2500 ng L^{-1} and 46–640 ng L^{-1} , respectively, in the Jinzhou Bay estuary showing significantly higher Hg pollution level than in the Laizhou Bay estuary. Similarly, Gao et al. (2014) in a review showed that the Hg levels in the Bohai Sea as a whole varied tremendously (4–2590 ng L^{-1}), with the highest concentrations observed in Dongying Harbour. In comparison with other river-estuary areas, our study showed much lower concentrations of THg_d and MeHg_d than in areas with known contamination by mining, chlor-alkali industry or historical residues (e.g., Thur River of France; Hissier and Probst, 2006; Tagus estuary of Portugal; Canário et al., 2008; and San Francisco Bay estuary of US; Conaway et al., 2003; Choe et al., 2004). Yet our values were still higher than some other estuaries (e.g., New York/New Jersey harbor estuary of US; Balcom et al., 2008; and Seine estuary of France; Laurier et al., 2003). Additionally, the Xiaoqing River showed a higher concentrations of dissolved Hg than the tributaries of the Chesapeake Bay, US (Lawson et al., 2001).

3.5.2. Decoupling between spatial distributions of DOM and Hg

The Hg and DOM concentrations (i.e., DOC) often show a positive correlation in aquatic environments, such as estuaries (Han et al., 2006), either on spatial or temporal scales (Mierle and Ingram, 1991; Dittman et al., 2009; Bergamaschi et al., 2012). This

may suggest Hg is mobilized from soil and transported with DOM in surface waters. However, our results didn't show a similarly strong correlation between concentrations of dissolved Hg species and DOC concentrations (Fig. 8a). This was attributed partially to the complexity of this river-estuary system, which is vastly different from lakes or streams. Our observations were closer to studies in the Everglades of Florida, where a diversity of DOM sources and complicated biogeochemical processes obscured likely weak associations between Hg and DOC concentrations (Aiken et al., 2011). Within such system, predictions of Hg fate and quantity based on DOC concentrations are unreliable.

Despite dissolved Hg concentrations being affected by suspended particulates, light irradiation, and microbial processes involving the biogeochemistry of iron and sulfur, some previous studies reported very strong relationships between DOM properties and concentrations of Hg. The relationship was strong enough in some regions for researchers to suggest special spectral characteristics (e.g., $SUVA_{254}$) of DOM as a surrogate for predicting temporal and spatial variation in Hg concentration distributions (Dittman et al., 2009; Burns et al., 2013). We argue that the complicated and diverse biogeochemical factors altered the DOM characteristics in a way that obscures the correlation between dissolved Hg and $SUVA$ along the Xiaoqing River-Lai Zhou Bay estuary transect. It should be noted that often the correlation between Hg and $SUVA$ is stronger in a smaller and more homogeneous region, for example in a watershed or basin where terrestrial inputs heavily influence the DOM composition. In contrast, the Xiaoqing River-Lai Zhou Bay estuary was more heterogeneous. Protein-like components also could contribute to the Hg binding capacity of DOM through –RSH (thiol) ligands, which are not linked to $SUVA$. So we inferred that in river-estuary systems where there are significant impacts from urban and/or microbial/algal DOM sources, like the Xiaoqing River-Lai Zhou Bay estuary, that a significant positive spatial or temporal relationship between the concentrations of DOM and Hg is not expected.

A significant relationship between Hg and CDOM (Mierle and Ingram, 1991) was not observed in this study (Support Information SI5, Table S3). Bergamaschi et al. (2012) successfully used *in situ* FDOM measurements to predict the tidally-driven export of THg_d and MeHg_d in a mangrove-dominated estuary, but for our study areas strong correlations between FDOM and Hg were not observed. Besides, none of the fluorescence parameters BIX, HIX, or FI were significantly correlated with dissolved species of Hg (Support Information SI5, Table S3). Neither were concentrations of THg_d or MeHg_d significantly correlated with the salinity gradient (Fig. 8b). Altogether, this suggests that the concentrations of

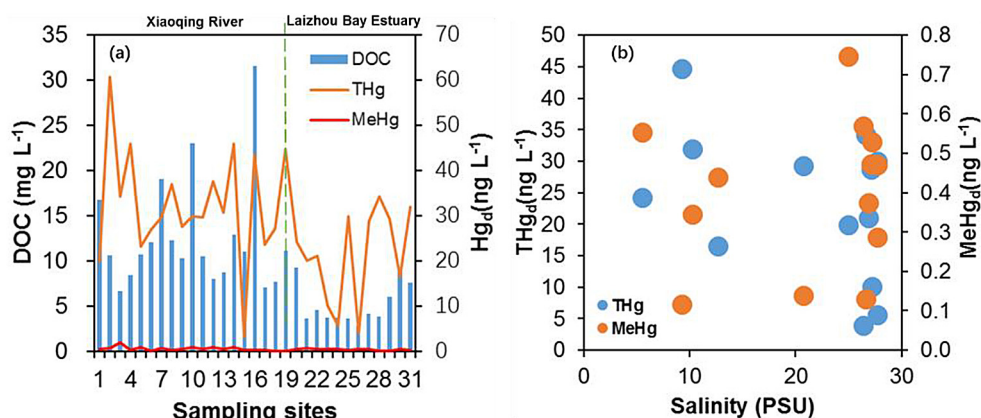


Fig. 8. Variations in DOC, THg_d and MeHg_d measured at 31 sampling sites along the Xiaoqing River-Laizhou Bay estuary transect (a), and the relationship between dissolved Hg and MeHg, and salinity (b).

dissolved Hg could not be explained by a conservative mixing of two end-members: terrestrial/allochthonous and non-terrestrial/urban/atmospheric sources of Hg. Similar non-conservative patterns of Hg changes from freshwater to estuary had also been previously reported (Han et al., 2006; Canário et al., 2008; Laurier et al., 2003; Balcom et al., 2008). Notably, in high salinity water, inorganic ligands (e.g. Cl⁻) may also affect the THg_d distribution by the formation of possibly mixed complexes with chloride and thiol ligands (Skylberg, 2012). Additionally, in some highly turbid river-estuary areas with high sedimentation loads, the effect of suspended particulate matter (SPM) on the Hg distribution may be significant (Mason et al., 1999; Lawson et al., 2001; Han et al., 2006). The Xiaoqing River-Laizhou Bay is influenced seasonally by desilting and flooding discharges from upstream, and thus the selective adsorption of Hg by SPM may be an important factor affecting Hg species mobility. Natural organic matter (NOM)-coated minerals may serve as the predominant sorption components of SPM for binding Hg through forming Hg-NOM complexes (Gu et al., 2014). Theoretically, the fractionation of DOM that occurs between solution (i.e., water) and solid (i.e., suspended particles) phases could result in adsorption of the aromatic component onto the minerals surfaces while leaving aliphatic compounds dissolved in the river-estuary. Therefore, further studies need to consider the DOM fractionation onto particulate NOM in order to fully explain the SPM-Hg relationship.

The quasi-conservative mixing behavior of DOM contrasting with the non-conservative mixing behavior of dissolved Hg species in this river-estuary system seems to be an explanation for the decoupling between spatial distributions of Hg and DOM. Thus, it is likely that the Hg dynamics in this study area was controlled by biogeochemical reactions while the DOM variations were more affected by physical mixing processes (e.g., dilution).

In recent years, there has been an increase in the publication of papers describing the use of spectroscopic methods, such as UV absorbance and fluorescence, to provide information about the composition and reactivity of DOM. In general, the results presented in this paper suggest that caution is warranted in estimating the composition and reactivity of DOM derived from a wide range of environments and source materials when using these methods in a more heterogeneous environment (e.g., river-estuary system), as compared to pristine lakes or streams. Besides using optical parameters to explain the role of DOM behind pollutant fate, other factors, such as hydrology, water residence time, biological activity, solar radiation may influence the DOM dynamics itself, which would further impact the relationship with Hg concentrations. Additionally, we must emphasize that the lack of an apparent

spatial relationship with Hg, which does not mean DOM and its properties did not affect Hg transportation and transformations processes. On the contrary, in an oxidized system we know Hg and MeHg are both entirely complexed by thiol moieties associated with DOM (Skylberg, 2012). Even in the most contaminated areas, thiol groups are most often in excess of both Hg and MeHg concentrations. Mechanistic studies are required to clarify the details of how DOM and its functional groups interact with Hg and MeHg under different environmental conditions. On the other hand, higher Hg levels were clearly observed in some sites impacted by heavy anthropogenic influences, which also were identified by DOM optical properties.

4. Conclusions

Through absorption and fluorescence spectral analysis, DOM characteristics along the Xiaoqing River-Laizhou Bay estuary transect were determined and tied to terrestrial/allochthonous and non-terrestrial/autochthonous end-member sources. The terrestrial signatures decreased along the river-estuary system and in the marine end of the estuary autochthonous DOM dominated. Variations in CDOM properties could explain more than 70% of the spatial variation in DOC. The DOM in the Laizhou Bay estuary was concluded to be mainly river-influenced. The quasi-conservative mixing behavior of DOM suggests that DOM variations in this study were more likely governed by physical mixing processes (e.g., dilution), although production or removal mechanisms might be other factors to alter DOM properties. In the Xiaoqing River-Laizhou Bay estuary system the spatial relationship commonly observed between DOM and Hg was decoupled. Biogeochemical processes may explain the lack of a simple correlation of Hg and DOM and the non-conservative mixing behavior of Hg. Above all, the results from our study demonstrated the difficulties to discern the processes behind the DOM composition and its possible linkages to Hg biogeochemistry by spectral analysis alone, in river-estuary systems. The complex interactions of DOM-Hg in the river-estuary system are not easily modeled or generalized, and thus more mechanistic studies including DOM spectral characterization are advised.

Acknowledgements

This research was financially supported by National Science Foundation of China (41403079), the National Key Basic Research Program of China (973 Program) (2013CB430004) and the Key Research Programs of the Chinese Academy of Sciences (KZZD-EW-

14 and XDA11020402). Dr. Tao Jiang personally gives his appreciation to funding provided by the Swedish Research Council (VR) to US (No. 621-2014-5370), supporting his research position at the Swedish University of Agricultural Sciences.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.12.006>.

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