



Seasonal Variations of CDOM Optical Properties in Rivers Across the Liaohe Delta

Tiantian Shao · Kaishan Song · Jia Du · Ying Zhao · Zhi Ding · Ying Guan · Lei Liu · Bai Zhang

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Abstract Absorption and fluorescence properties of chromophoric dissolved organic matter (CDOM) in rivers across the Liaohe River Delta, a large estuary located in the southern region of northeast China, were investigated using spectroscopy and fluorescence to analyze CDOM characteristics, composition and sources in winter (January), spring (April and May) and autumn (September) 2013. Results indicated that CDOM absorption of ice samples was lower compared to water samples. CDOM absorption also showed significant spatial variation but not temporal variation. In contrast, dissolved organic carbon (DOC) concentrations showed obvious temporal characteristics. A stronger linear relationship was found between CDOM absorption and DOC concentration in winter (water, $R^2=0.95$, $p<0.001$; ice, $R^2=0.85$, $p<0.001$) compared to samples from other seasons (April, $R^2=0.51$, $p<0.01$; May, $R^2=0.34$, $p<0.05$; September, $R^2=0.45$, $p<0.01$). CDOM fluorescence varied over a large range across seasons, with the highest levels observed in January at the Xisha River (XSR). Moreover, strong linear relationships were also observed between CDOM absorption and fluorescence intensity at 355 nm [Fn(355)] in January ($R^2=0.87$, $p<0.001$), May ($R^2=0.76$, $p<0.001$) and September ($R^2=0.94$, $p<0.001$). Also based on study findings, CDOM fluorophores identified by 3-D excitation-emission matrices (EEMs) illustrated that the rivers across the Liaohe Delta were

seriously polluted by anthropogenic disturbances, exhibiting strong protein-like fluorescence of CDOM in the water column. In addition, the results also confirm that absorption and EEMs would be useful tools for tracing the sources and characteristics of CDOM and monitoring riverine water quality.

Keywords Liaohe Delta · CDOM · 3-D EEMs · Water quality

Introduction

Chromophoric dissolved organic matter (CDOM), the light absorbing fraction of dissolved organic matter (DOC), consists of a varied mixture of aliphatic and aromatic polymers (Kirk 1994; Stedmon et al. 2000). As a major light absorbing constituent in the water column, CDOM influences light attenuation in waters (Markager and Vincent 2000; Foden et al. 2008; Para et al. 2013) and affects the transport and bioavailability of materials such as trace metals and organic substances (Schlesinger et al. 2011). It also has a fundamental link with DOC composition, which provides an effective way for export of DOC flux (Sobek et al. 2007; Webster et al. 2008).

CDOM absorption and fluorescence spectroscopy are useful approaches in examining CDOM characteristics and sources in bays, estuaries, rivers, coastal and marine waters (Chen et al. 2007; Siegel et al. 2009; Singh et al. 2010a). Changes in the CDOM absorption and fluorescence reflect the variations in CDOM composition from several autochthonous or allochthonous sources, resulting from physical, chemical and biological processes that occur in the water column (Coble 1996). The absorption of CDOM at a special wavelength is commonly used to quantify the CDOM concentration (Bricaud et al. 1981; Babin et al. 2003), which can greatly influence the underwater light field due to its optical activity (Laurion et al.

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T. Shao · K. Song (✉) · J. Du · Y. Zhao · Z. Ding · Y. Guan · L. Liu · B. Zhang
Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun, China
e-mail: songks@iga.ac.cn

T. Shao · Z. Ding
University of Chinese Academy of Sciences, Beijing, China

2000; Stedmon et al. 2000). Fluorescence spectroscopy using excitation-emission matrices (EEMs) is a simple, effective method to characterize CDOM in various water masses, differentiate fluorophores and trace different sources of CDOM (Cole 1996; Stedmon and Markager 2005; Zhang et al. 2011).

In spite of the importance of CDOM, most researches to date have been limited to coastal and shelf waters as well as inland lakes and rivers in the arctic and subtropical regions in North American, Europe and China (Stedmon et al. 2000; Singh et al. 2010a, b; Fichot and Benner 2011; Zhang et al. 2011; Spencer et al. 2012; Chen et al. 2013). Few studies have been focused on the rivers of temperate and semiarid zones (Guo et al. 2011; Song et al. 2013). Recent studies have documented variations in riverine dissolved organic matter (DOM) characteristics in relation to both seasons and land uses in surrounding landscapes (Singh et al. 2010b; Piirsoo et al. 2012). For arctic rivers, DOC concentrations are markedly higher during the spring freshet and summer discharge but lower in autumn (Holmes et al. 2012; Griffin et al. 2011). Soil types and other characteristics also greatly influence DOC concentrations (Ågren et al. 2007; Wilson and Xenopoulos 2008). Rivers pass through different landscapes, such as forests or wetlands, carrying higher concentration of CDOM (Griffin et al. 2011). The study area on the rivers across the Liaohe Delta provides unique and diverse environments to investigate the characteristics and sources of DOC and CDOM. Rivers pass through several key types of land use, such as agricultural land (paddy fields and cropland), residential and wetlands. Furthermore, due to excessive population growth, expansion of the cities and industrial and agricultural developments, the rivers in the Liaohe River Basin are greatly affected by localized pollution (Li et al. 1999; Wen et al. 2011; Hu et al. 2012). Each year, large amounts of heavy oil-polluted effluents from oil extraction in the Liaohe oilfield, the third largest in China, are discharged into the rivers across the delta (Ji et al. 2002; Lin et al. 2013) which may affect the CDOM sources and compositions.

The objectives of this study were to (1) characterize the temporal and spatial distribution of CDOM optical absorption and fluorescence, (2) examine the compositions and sources of CDOM in the rivers across Liaohe River Delta based on 3-D EEMs and (3) identify the environmental factors influencing CDOM characteristics.

Material and Methods

Study Area

The Liaohe River Delta is located in the Liaohe River Basin of northeast China (40°39′–41°27′N, 121°25′–122°31′E), adjacent to the Liaohe Bay of the Bohai Sea (Fig. 1). The region is typical temperate monsoon climate, with a frozen period of

about 150 days (Li et al. 1999). The second largest reed marsh in the world (Li et al. 1999) is distributed around the delta. Rivers across the Liaohe River Delta that flow into the Bohai Sea include Big Liaohe River (BLR), Dalinghe River (DLR) and Shuangtaizihe River (STR). BLR includes Hunhe River (HHR) and Taizihe River (TZR), flushing into the Bohai Sea at Yingkou City, with a length of 94 km. STR, also known as the Liaohe River (LHR), is composed of the East and the West Liaohe rivers, with a total length of 1.39×10^3 km (Ren et al. 2002).

Water Sampling and In-Situ Data Collection

In total, 50 samples were collected from 10 sites in rivers across the Liaohe Delta including 40 water samples collected during 4 months (January, April, May and September 2013) and 10 ice samples collected in January at the same sites. Surface water samples were collected at each site approximately 0.1 m below the water surface; in January, ice samples were collected with an ice auger, while water samples were subsequently collected by drilling through the ice. In-situ data, including water temperature (thermometer), water depth (sonar sounder, Speedtech Instruments, United States), GPS (G350, UniStrong, China) and water transparency (Secchi disc depth), were determined with portable instruments. An approximate 2500 mL water sample was collected at each site for determining water physical and chemical parameters, e.g., total N (TN), total P (TP), chlorophyll-a (Chla), DOC concentration, as well as CDOM absorption and fluorescence at each site. Water samples were collected in acid-washed HDPE bottles and held in thermoelectric coolers while in the field. In the laboratory, these samples were kept in the dark at 4 °C until analyzing within 2 days.

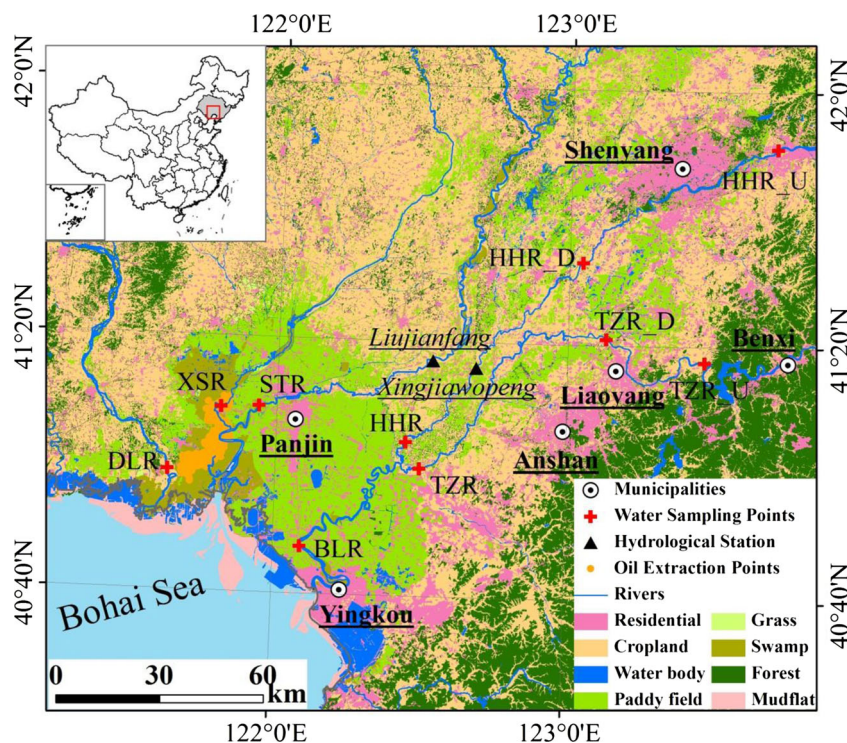
CDOM Absorption Measurement

Samples, filtered with 0.7 µm glass fiber filters (precombusted at 400 °C for 2 h with a Muffle furnace, Millipore) and 0.22 µm nuclepore filters (Whatman) successively, were used to measure CDOM absorption and fluorescence. CDOM absorption spectra were measured using a Shimadzu UV-2600 PC UV–VIS dual beam spectrophotometer with a 1-cm quartz cuvette between 200 and 800 at 1 nm intervals. Milli-Q water was used in the reference cuvette for CDOM absorption measurements. Absorption coefficients of CDOM were calculated as:

$$a_{CDOM}(\lambda') = 2.303OD(\lambda)/l \quad (1)$$

where $a_{CDOM}(\lambda')$ is the uncorrected CDOM absorption coefficient at a given λ , $OD(\lambda)$ is the optical density at the same wavelength, and l is the cuvette path length in meters. Because of the influence of backscattering by small particles and

Fig. 1 Distribution of sampling sites along the rivers across the Liaohe Delta, located in northeast China. Six rivers (10 sections) were investigated during 4 months (January, April, May and September). Specifically, the sections are BLR (Big Liaohe River), DLR (Dalinghe River), HHR (Hunhe River), HHR_U (Upper reaches of Taizihe River), HHR_D (Lower reaches of Hunhe River), STZ (Shuangtaizi River), TZR (Taizihe River), TZR_D (Lower reaches of Taizihe River), TZR_U (Upper reaches of Taizihe River) and XSR (Xishahe River). Eight main types of land use/cover in the Liaohe Delta are present: paddy field, residential, cropland, forest, grassland, mudflat, water body and swamp, respectively



colloids that pass through filters, absorption coefficients were corrected based on the following equation (Bricaud et al. 1981):

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda') - a_{CDOM}(750')(\lambda/750) \quad (2)$$

where $a_{CDOM}(\lambda)$ is the absorption coefficient at wavelength λ corrected for scattering, $a_{CDOM}(750')$ is the uncorrected absorption coefficient at 750 nm, and $a_{CDOM}(\lambda')$ is the uncorrected CDOM absorption coefficient at a wavelength λ .

DOC Concentration Measurement

Water samples were filtered through pre-combusted 0.45 μm GF/F filters. The standards for total dissolved carbon (TDC) were prepared from reagent-grade potassium hydrogen phthalate in ultra-pure water, while dissolved inorganic carbon (DIC) concentrations were determined using a mixture of anhydrous sodium carbonate and sodium hydrogen carbonate. Dissolved organic carbon (DOC) was calculated by subtracting DIC from TDC, both of which were measured by high-temperature catalytic oxidation (680 $^{\circ}\text{C}$) using a total organic carbon analyzer (Shimadzu, TOC-VCN).

Three-Dimensional Fluorescence Measurement

Fluorescence was measured by a Hitachi F-7000 fluorescence spectrometer (Hitachi High-Technologies) with a 700 voltage xenon lamp. The scanning ranges were 200–450 nm for excitation with 5-nm intervals, and 250–600 nm for emission with 1-nm intervals, with a scanning speed of 2400 nm/min.

Corrections of original data included water Raman scatter effects, instrument specific variations, inner-filter effects and Rayleigh scatter effects. Water Raman scatter peaks were eliminated by subtracting a Milli-Q water blank from the EEMs. Instrument-specific variations were corrected according to the procedure recommended by Hitachi (Hitachi F-7000 Instruction Manual). Inner-filter effects were removed using the methods detailed in Zhang et al. (2011). The EEMs were corrected for absorbance by multiplying each value in the EEMs with a correction factor, based on the premise that the average path length of the absorption of the excitation and emission light was 1/2 of the cuvette length (McKnight et al. 2001; Zhang et al. 2011). Rayleigh scatter effects were corrected according to Zhang et al. (2011). Fluorescence intensity [Fn(355)], which was the intensity at 355 nm for excitation (Ex) and 450 nm for emission (Em), was calibrated in quinine sulfate units (QSU), where 1 QSU is the maximum fluorescence intensity of 0.01 mg L^{-1} of quinine (qs) in 1 N H_2SO_4 (Hoge et al. 1993; Wada et al. 2007).

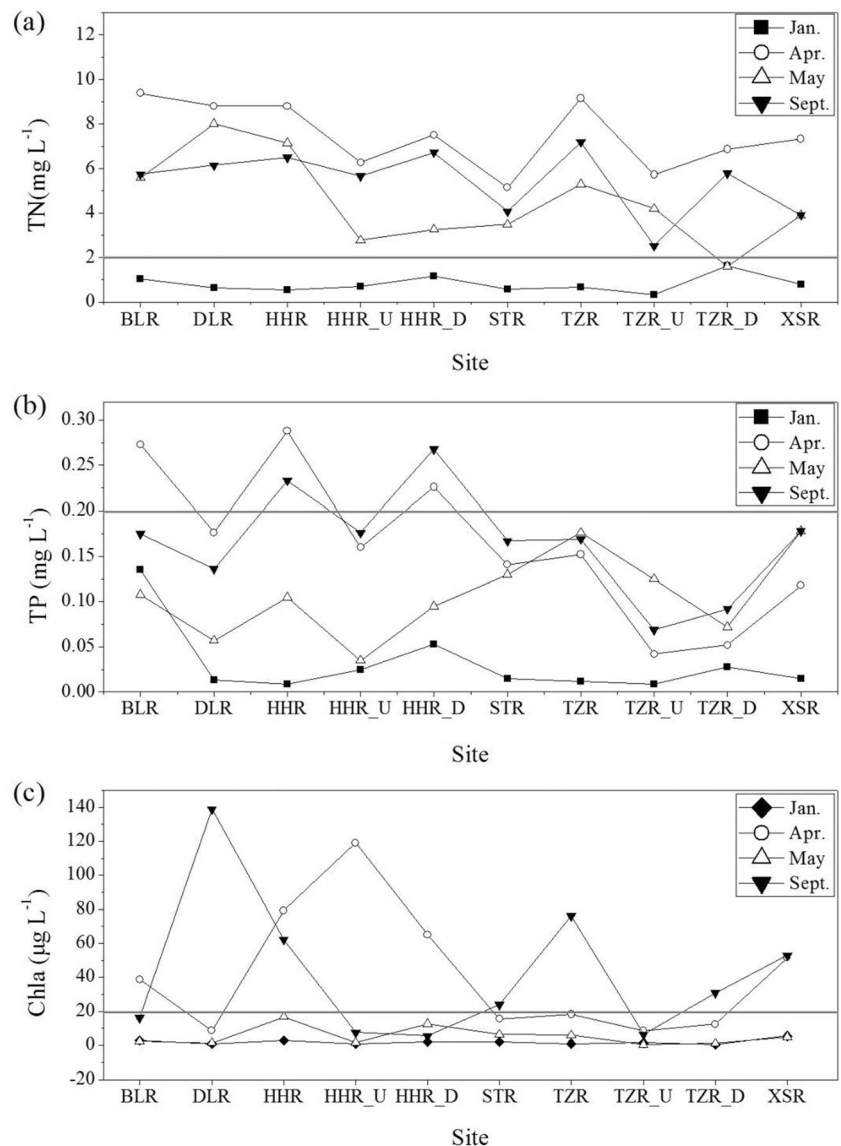
Moreover, CDOM fluorophores can be identified in the 3-D EEMs. According to Coble (1996) and Stedmon et al. (2003), Peak A (Ex/Em: 230–260 nm/ 380–460 nm) and Peak

C (Ex/Em: 320–360 nm/ 420–480 nm) were humic-like components while Peak B (Ex/Em: 220–230 nm/ 300–320 nm nm or Ex/Em: 270–280 nm/ 300–320 nm), Peak T1 and T2 (Ex/Em: 220–230 nm/ 320–360 nm and Ex/Em: 270–280 nm/ 320–360 nm) were both protein-like components.

Determination of Other Parameters

In the laboratory, Chla was extracted using 90 % acetone and measured with a Shimadzu UV-2600 PC spectrophotometer. TN was measured based on the absorption spectrum at 146 nm of water samples decomposed with alkaline potassium peroxydisulfate. TP was analyzed using a molybdenum blue method after the samples were digested with potassium peroxydisulfate (APHA 1998).

Fig. 2 Spatiotemporal characteristics of **a** total N (TN), **b** total P (TP) and **c** chlorophyll-a (Chla) of water samples. The horizontal line in each plot represents the guidelines of parameter concentrations according to GB3838-2002 (national quality standards for surface waters, China). TN: Class V; TP: Class III and Chla: Class III



Results

Water Quality of the Rivers Across the Liaohe Delta

In this study, TP, TN and Chla concentrations which were used to illustrate the general water quality of different tributaries of Liaohe River along the delta region, varied from site to site (Fig. 2). In January, TN concentrations ranged from 0.33 mg L⁻¹ at TZR_U to 1.64 mg L⁻¹ TZR_D while TP concentrations ranged from 0.009 mg L⁻¹ at HHR to 0.14 mg L⁻¹ at BLR. For samples collected in April, TN concentrations ranged from 5.14 to 9.39 mg L⁻¹ and TP ranged from 0.04 to 0.29 mg L⁻¹. In May, ranges of TN and TP concentrations were 1.61–8.02 and 0.035–0.18 mg L⁻¹, with averages of 4.52 and 0.11 mg L⁻¹, respectively. Maxima of TN and TP in September were 7.19 mg L⁻¹ at TZR and

HHR_D, while minima were both located in TZR_U. TN concentrations during April, May and September in the rivers across the Liaohe Delta exceeded the GB3838-2002 (national quality standards for surface waters, China) standard for Class V guidelines of 2.0 mg L^{-1} at all sampling sites (except TZR_D in May). With respect to TP, their concentrations in several sampling sites exceeded 0.2 mg L^{-1} , which is the GB3838-2002 standard for Class III guidelines.

The Chla concentrations significantly fluctuated, spanning from $0.40 \text{ } \mu\text{g L}^{-1}$ at TZR_U in January to $138.84 \text{ } \mu\text{g L}^{-1}$ at DLR in September. Averages of Chla concentrations were $2.08 \text{ } \mu\text{g L}^{-1}$ in January, $41.77 \text{ } \mu\text{g L}^{-1}$ in April, $5.41 \text{ } \mu\text{g L}^{-1}$ in May and $42.13 \text{ } \mu\text{g L}^{-1}$ in September. Chla concentrations in most samples from April and September exceeded $20 \text{ } \mu\text{g L}^{-1}$, which is the GB3838-2002 standard for Class III guidelines.

Seasonal Properties of CDOM Absorption

CDOM absorption from various sampling locations across months is used to illustrate the spectral properties of CDOM (Fig. S1). The general spectral curves for CDOM showed near-zero absorption values at the red end of the visible spectral domain (700 nm), which exponentially increased to maximum values in ultraviolet (UV) wavelength regimes (280–

400 nm). CDOM absorption spectra showed significant variations in both temporal and spatial scales.

CDOM is often characterized using the absorption coefficient at a specific wavelength (Weishaar et al. 2003; Zhang et al. 2007; Spencer et al. 2012; Wang et al. 2014). In this study, absorption at 254 nm [$a_{\text{CDOM}}(254)$], widely used in tracing dissolved aromatic carbon content in aquatic systems (Weishaar et al. 2003; Laudon et al. 2004; Helms et al. 2008), was selected to characterize CDOM. Correlations between $a_{\text{CDOM}}(254)$ and DOC concentrations were shown for the rivers across Liaohe River Delta (Fig. 3). The coefficients of determination (R^2) between DOC concentrations and $a_{\text{CDOM}}(254)$ across seasons varied significantly. The most intimate correlations were obtained from both water and ice samples collected in January. Relationship between DOC concentrations and $a_{\text{CDOM}}(254)$ in May was weak. As shown in Fig. 3f, DOC concentrations of water samples in May were higher than those in other months, while the lowest DOC concentrations were recorded in the ice samples collected in January.

Spatiotemporal Characterization of CDOM Fluorescence

Due to significant differences observed in environmental conditions, F_n(355) showed significant variations among sites

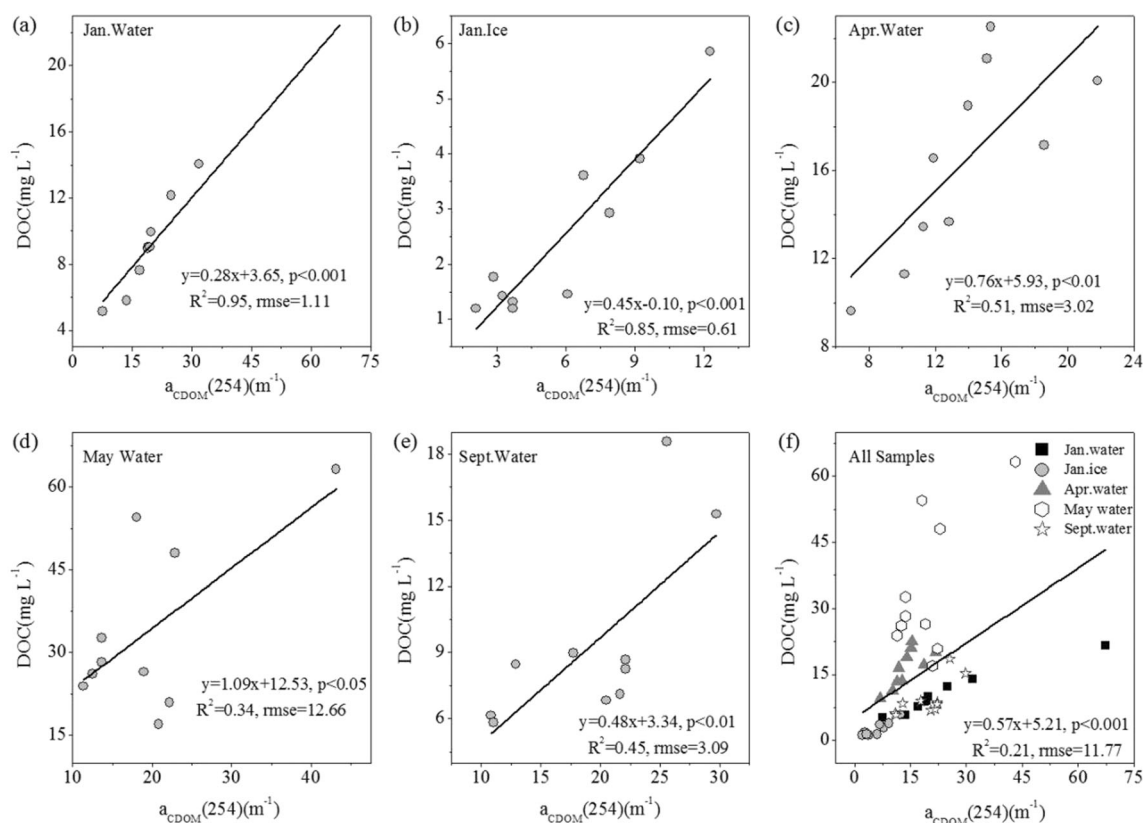


Fig. 3 Relationships between CDOM and DOC concentrations in the ten river sections during different months: **a** water samples obtained in January; **b** ice samples obtained at the same location with water

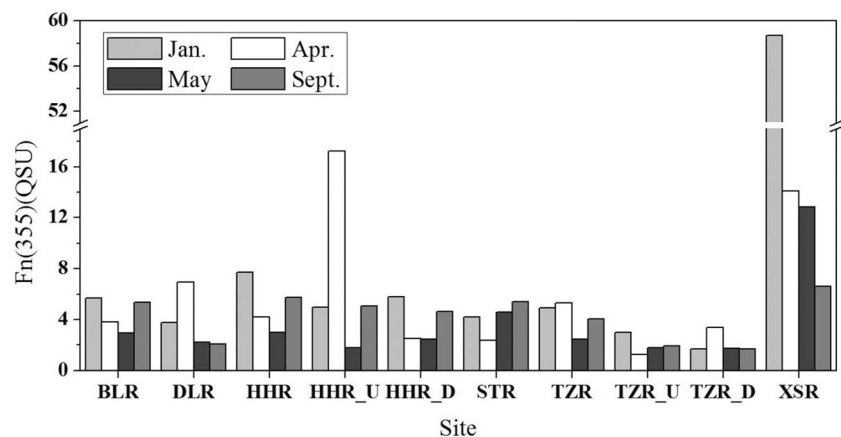
samples in January; **c** water samples collected in April; **d** water samples collected in May; **e** water samples collected in September; and **f** all the 50 samples

and seasons as well (Fig. 4). The highest $F_n(355)$ was found in XSR while the lowest $F_n(355)$ was in TZR_D in January, May and September. In April, the lowest $F_n(355)$ was measured in TZR_U and the highest $F_n(355)$ was found in HHR_U while samples from XSR and TZR_D were the second highest and lowest values, respectively. Half of the samples in January exhibited higher $F_n(355)$ than samples collected in the other months; $F_n(355)$ in May was lower than those in samples collected in January, April and September. Two values were slightly higher than other samples in the same month: HHR_U in April and XSR in January. Moreover, $F_n(355)$ values recorded at Hunhe River (including HHR, HHR_U and HHR_D), which passes through the largest city in Northeast China (i.e., Shenyang City), were higher than that at Taizihe River (including TZH, TZH_U and TZH_D) passing through Liaoyang City.

Table 1 presents the fluorescent data of water samples for all 10 river sections collected in different seasons, focusing on the CDOM fluorophores identified in the 3-D EEMs of rivers across the Liaohe Delta. Clearly, no samples exhibited all five fluorophores (Peak A, B, C T1 and T2) at the same time in this study. However, in April, some samples exhibited four fluorophores including Peak A, Peak B, Peak C and Peak T2 (Table 1). Many water samples showed fluorophore T1 and T2 of protein-like substances while several sites exhibited only fluorophore A and C of fulvic acid-like substances. Samples only in April exhibited strong peak B.

Peak B intensity ranged from 5.89 (TZR_D) to 21.86 QSU (HHR_U) for all river samples, with an average of 12.80 QSU; Peak T1 intensity ranged from 3.00 (TZR_D) to 277.5 QSU (XSR), with an average of 26.04 QSU; Peak T2 intensity ranged from 5.89 (TZR_U) to 247.19 QSU (XSR) for all sites, with an average of 25.67 QSU; Peak A intensity ranged from 4.33 (TZR_U) to 27.28 QSU (HHR_U), with an average of 12.52 QSU; Peak C intensity ranged from 2.53 (TZR_D) to 22.55 QSU (HHR_U) for all sites, with an average of 8.05 QSU.

Fig. 4 Fluorescence intensity at 355 nm [$F_n(355)$] of water samples among different sites across seasons; details on the river section locations are shown as Fig. 1



Relationship Between Water Quality and $a_{CDOM(254)}/DOC$

Correlations between select water quality parameters (TP, TN and Chla) and $a_{CDOM(254)}/DOC$ were analyzed using SPSS 17.0 for data sets of each month and pooled data from all seasons (Table 2). In January, significant correlations were observed between Chla and $a_{CDOM(254)}/DOC$; strong relationships between TP and $a_{CDOM(254)}/DOC$ were recorded in May; significant correlations were obtained for all water samples. There were no strong relationships between water quality and $a_{CDOM(254)}/DOC$ both in April and September.

Relationship Between CDOM Absorption and Fluorescence

Significant linear relationships were found between $F_n(355)$ and $a_{CDOM(254)}$ in different tributaries of Liaohe River across the delta region, except for samples collected in April 2013 (Fig. 5a–d). Despite different seasons and locations, the fluorescence intensity increased linearly with CDOM absorption (Fig. 5e), consistent with previous studies (Kowalczyk et al. 2003; Zhang et al. 2007) except for the April results. A negative correlation between $F_n(355)$ and $a_{CDOM(254)}$ was observed for samples collected in April (Fig. 5b).

Discussion

Correlations Between Water Quality and $a_{CDOM(254)}/DOC$

Correlations observed between water quality parameters and $a_{CDOM(254)}/DOC$ in each month, were highly variable in different seasons. When all the water samples were pooled together, the correlations were improved, especially the relationships between TN and $a_{CDOM(254)}/DOC$. The main reason may lie in the great variation of water quality in different

Table 1 CDOM Fluorophores were identified by 3-D EEMs of water samples in rivers across the Liaohe Delta. Sampling sites were detailed in Fig. 1; Peak A, B, C, T1 and T2 represent different fluorophores, respectively. Ex/Em, excitation/emission; F-Int, fluorescence intensity (Unit: QSU)

Month	Site	Peak A		Peak B		Peak C		Peak T1		Peak T2	
		Ex/Em	F-Int	Ex/Em	F-Int	Ex/Em	F-Int	Ex/Em	F-Int	Ex/Em	F-Int
Jan.	BLR	–	–	–	–	–	–	280/349	16.78	230/359	30.11
	DLR	–	–	–	–	–	–	285/344	14.78	230/348	14.77
	HHR	230/423	20.07	–	–	310/429	14.61	–	–	230/360	21.12
	HHR_U	–	–	–	–	–	–	280/378	10.33	230/363	19.34
	HHR_D	–	–	–	–	–	–	280/349	12.28	230/360	20.59
	STR	235/403	9.85	–	–	305/414	5.97	280/385	6.38	–	–
	TZR	–	–	–	–	–	–	280/348	35.58	230/359	58.53
	TZR_U	–	–	–	–	–	–	275/358	9.18	235/367	20.32
	TZR_D	–	–	–	–	–	–	280/361	4.50	230/368	8.81
	XSR	–	–	–	–	–	–	265/412	277.50	–	–
Apr.	BLR	–	–	270/317	12.91	–	–	–	–	230/361	19.69
	DLR	270/455	10.80	270/314	14.95	335/445	9.81	–	–	235/358	6.44
	HHR	–	–	–	–	–	–	–	–	230/357	14.90
	HHR_U	270/445	27.28	275/317	21.86	340/446	20.36	–	–	225/323	20.85
	HHR_D	–	–	–	–	–	–	–	–	230/356	11.59
	STR	235/398	6.61	270/315	9.74	–	–	–	–	235/388	6.59
	TZR	265/443	9.50	275/335	15.83	330/443	7.58	–	–	230/360	32.00
	TZR_U	–	–	–	–	–	–	–	–	235/375	5.89
	TZR_D	270/444	5.20	270/315	5.89	330/444	4.83	–	–	235/377	6.31
	XSR	270/441	26.98	–	–	330/444	22.55	280/365	15.70	235/365	36.00
May	BLR	–	–	–	–	305/418	4.74	290/373	4.91	230/363	11.36
	DLR	–	–	–	–	315/423	3.47	285/370	4.02	235/370	8.26
	HHR	–	–	–	–	305/422	4.77	290/367	5.17	230/358	14.99
	HHR_U	235/421	4.61	–	–	310/427	2.62	–	–	–	–
	HHR_D	–	–	–	–	–	–	290/367	4.29	230/357	12.36
	STR	–	–	–	–	–	–	290/394	7.44	230/360	18.26
	TZR	–	–	–	–	–	–	285/349	10.53	230/357	27.70
	TZR_U	–	–	–	–	–	–	290/370	3.54	230/366	8.31
	TZR_D	–	–	–	–	–	–	285/364	4.34	230/362	10.39
	XSR	–	–	–	–	–	–	290/369	89.58	230/359	247.19
Sept.	BLR	240/429	14.10	270/320	8.41	315/429	8.51	–	–	–	–
	DLR	–	–	–	–	–	–	–	–	230/359	8.01
	HHR	235/429	14.64	–	–	310/429	9.17	–	–	–	–
	HHR_U	240/429	11.84	–	–	315/427	7.06	–	–	–	–
	HHR_D	240/435	9.95	–	–	320/433	6.16	–	–	–	–
	STR	240/434	12.10	–	–	315/428	7.54	–	–	–	–
	TZR	–	–	–	–	–	–	280/344	15.00	230/357	29.11
	TZR_U	240/436	4.33	–	–	318/430	2.57	–	–	–	–
	TZR_D	–	–	–	–	315/417	2.53	280/372	3.00	235/367	6.12
	XSR	–	–	–	–	–	–	290/377	18.05	235/371	39.81

months. River flow, water temperature, the variation for effluents from industrial activities and domestic discharge, soil erosion and surface runoff would be all the factors influencing the relationship.

The temperature may be the key factor affecting the relationship between $a_{CDOM}(254)/DOC$ and Chla in January, because the growth of phytoplankton was limited, which might lead to the relatively low Chla (Fig. 2c). For the other months,

Table 2 Correlations between water quality parameters (TP, TN and Chla) and $a_{\text{CDOM}(254)}$ /DOC for the water samples in every month and all the water samples

Month	Parameters	TP	TN	Chla
January	$a_{\text{CDOM}(254)}$	-0.11	-0.15	0.79**
	DOC	-0.18	-0.10	0.75*
April	$a_{\text{CDOM}(254)}$	-0.090	-0.012	-0.22
	DOC	-0.081	-0.012	-0.28
May	$a_{\text{CDOM}(254)}$	0.39	0.33	0.10
	DOC	0.61	0.18	-0.15
September	$a_{\text{CDOM}(254)}$	0.17	-0.028	0.07
	DOC	-0.08	-0.003	-0.23
All water samples	$a_{\text{CDOM}(254)}$	-0.43**	-0.30	-0.17
	DOC	-0.30	-0.24	-0.40*

*Significant at the 0.05 level (2-tailed)

**Significant at the 0.01 level (2-tailed)

flow and precipitation would be the main environmental factors affecting the variation of water quality parameters (Singh et al. 2004). Only data for two hydrological stations were acquired for this study. Monthly mean flows from 2003 to 2011 at the Liujianfang hydrological station (located at STR,

Fig. 1) were collected from the River Sediment Report of China (The Ministry of Water Resources of the People's Republic of China), while monthly mean flows from 1970 to 2005 at the Xingjiawopeng hydrological station located at HHR were obtained from Zhou et al. (2014). Although the hydrological data were limited, this information was valuable to explain the effects of flows on the relationship between water quality parameters and $a_{\text{CDOM}(254)}$ /DOC to some extent. There was a great increase in flows during May compared with April (Fig. 6). The increased flow diluted the concentrations of TN, TP and algae, which led to low Chla concentrations. The increased flow in May also caused the temporal variations of TP and TN concentrations to follow a different pattern than those in April and September. In addition, rainfall may have caused notable fluctuations of Chla concentrations in September. As shown in Fig. S2, high precipitation in July and August increased soil erosion and surface runoff; this subsequently increased exogenous input of particulate matter and CDOM, resulting in significant variation in Chla concentrations. Further investigations should be carried out to examine these relationships between water quality parameters and $a_{\text{CDOM}(254)}$ /DOC at larger scale with more sampling stations.

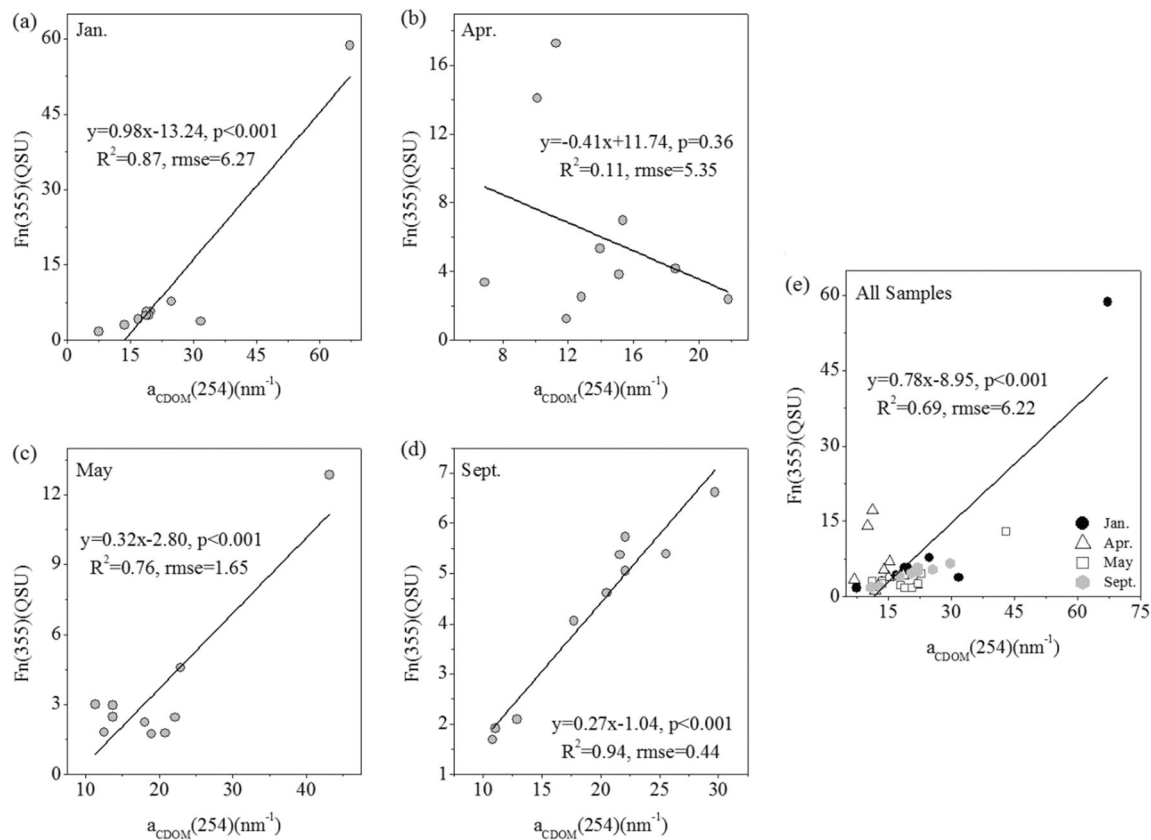


Fig. 5 Relationship between CDOM fluorescence intensity at 355 nm [Fn(355)] and absorption coefficients of 254 nm [$a_{\text{CDOM}(254)}$] of water samples in 4 months: **a** January, **b** April, **c** May, **d** September, and **e** all the water samples

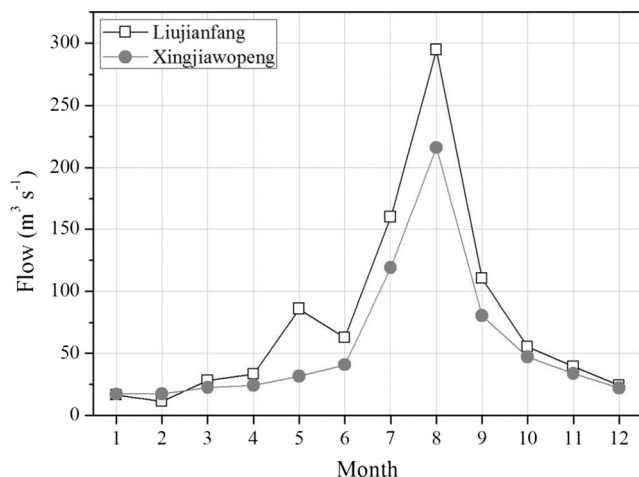


Fig. 6 Flow data at 2 hydrological stations, **a** mean flow at Liujianfang (located at STR) hydrological station from 2003 to 2011 and **b** mean flow at Xingjiawopeng (located at HHR) hydrological station from 1970 to 2005

Temporal Variation of CDOM and DOC Concentration

It is evident that rivers investigated across the Liaohe Delta were highly eutrophic in April and September. Different eutrophication levels affected CDOM concentrations. If the highest mean CDOM concentrations collected in January are excluded, CDOM concentrations in the remaining samples exhibited comparable average levels with respect to samples from other months. Rivers across the Liaohe Delta were frozen in January and did not completely melt until April. Under such condition, more substances as suspended matters remained in the water when ice formed along the rivers in the study region. As a result, CDOM concentrations in the ice samples were lower than the water samples (Belzile et al. 2002; Thomas et al. 2010). Unlike CDOM concentrations, DOC concentrations showed obvious temporal characteristics. Sobek et al. (2007) found that the catchment, soil, and climate significantly affected DOC concentrations, and mean annual runoff and precipitation were negatively correlated with DOC concentrations in large lake data set from 6 continents. Strong positive relationships between DOC concentrations and river discharge in the arctic river basin were found in previous investigations (Neff et al. 2006; Guo et al. 2012). In this study, DOC concentrations measured in April were significantly higher than those previously observed in January and September, as soils began to thaw in the spring and drained into nearby streams through surface runoff. The increased flow accelerated the exogenous input of soil DOC, resulting in further increases in DOC concentrations from April to May. Concentrations observed in May were higher also because there was less precipitation in sub-catchments during that time (Fig. S2), thereby reducing the dilution of DOC concentrations (Wilson and Xenopoulos 2008). In

September, the increased rainfall brought soil DOC into the rivers, but the effects of diluting DOC concentrations due to more precipitation were greater than the input of soil DOC, which led to the comparatively low DOC concentration. Negative correlations between precipitation and $a_{\text{CDOM}(254)}$ were also found in this study (Fig. 7a).

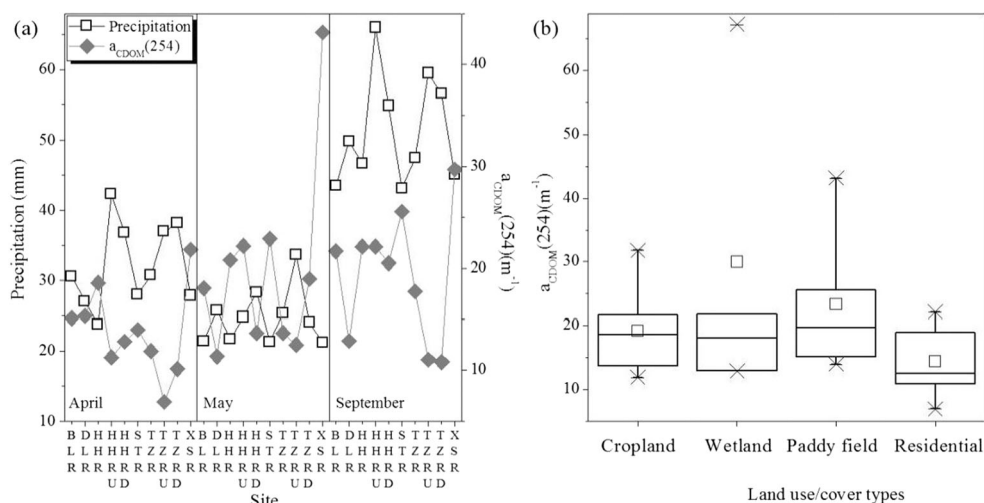
In addition, land-use changes in the sub-catchments could have influenced river CDOM concentrations and characteristics (Wilson and Xenopoulos 2008, 2009; Williams et al. 2010). Unlike arctic rivers which mostly pass through peatland/forest with abundant soil DOC, the rivers investigated in this study flow through paddy field, cropland and residential that are greatly influenced by anthropogenic activities. Thus, the CDOM measured in rivers across the Liaohe Delta is quite different from those in other regions (Neff et al. 2006; Spencer et al. 2012). Samples collected from river sections close to paddy field exhibited high CDOM concentrations because of the abundant soil DOC, while rivers passing through residential had low CDOM concentrations (Fig. 7b).

A strong linear relationship was recorded between CDOM and DOC in winter (January), whereas a weak relationship was observed in spring (May). The main reason may be that DOC and CDOM do not follow the same trends. When CDOM and DOC co-vary, or uncolored dissolved organic matter (UDOM, the other component of DOC) is constant in DOC, a good correlation between CDOM and DOC typically occurs (Chen et al. 2004). However, any factor that influences the two parameters will weaken this correlation (Chen et al. 2004). In winter, the influence of environmental factors reduced (e.g., sealed off by ice cover), which resulted in a strong positive relationship between $a_{\text{CDOM}(254)}$ and DOC concentrations for both the water and ice samples. But in May, many uncertain factors, such as snowmelt discharge, soil thawing, increased flow and recovery of phytoplankton growth, negatively influenced the relationship between CDOM and DOC. Urban pollutants or crude oil of the Liaohe oilfield flushed into nearby rivers might have also further complicated this situation (Ji et al. 2002; Lin et al. 2013).

Temporal Distribution of CDOM Fluorescence

In general, humic-like fluorophore is stronger than any other fluorophore. Furthermore, there is only humic-like fluorophore present, because riverine CDOM is influenced by exogenous input of humic and fulvic acid (Baker 2001; Fu et al. 2004). However, the river water polluted by human activities shows fairly strong protein-like fluorophores in the 3-D EEMs for the living sewage and oil (Fu et al. 2005; Zhang et al. 2011). As shown in Table 1, most samples did not show all the fluorophores (A, B, C, T1 and T2) at the same time, which was likely because the intensity of the stronger fluorophore covered the weaker ones in each sample (Zhang et al. 2011). In fact, only if the values of the fluorophores were

Fig. 7 Environmental factors that affect $a_{\text{CDOM}(254)}$ concentrations, **a** relationships between monthly precipitation and CDOM concentrations; **b** mean CDOM concentrations among different types of land use. Due to the presence of snow and ice covering the water, the influence of total precipitation in January was not analyzed



similar to each other, would all the fluorophores exhibit together (Fu et al. 2005). In this study, water samples had stronger protein-like fluorophores during the study months, except in September. The downstream areas of rivers across the Liaohe River Delta pass through several municipalities including Shengyang City, Liaoyang City, Benxi City and Fuxin City (Fig. 1). Therefore, the rivers received effluents from industrial, agricultural and domestic sources, and were severely polluted by related anthropogenic activities. This is also evident from the strong protein-like fluorophores presented in samples collected in the delta region.

The highest value of fluorophore T (including T1 and T2) was measured at XSR, except in April, which indicated that this area was the most seriously influenced by human activities. Notably, the sampling site of XSR is located in the area of Liaohe oilfield (Fig. 1); therefore, the associated water was easily influenced by crude oil. Crude oil is an extremely complex assemblage of chemicals, mainly consisting of aliphatics, aromatics and polar compounds (Moonkoo et al. 2013). In the study, there were small particles (protein, amino acid and lipid) remaining in the water samples that may have influenced the fluorescence measurements. As a result, XSR exhibited the strongest protein-like fluorophore. Furthermore, samples collected at Taizihe River, including TZR, TZR_U and TZR_D, all exhibited strong protein-like fluorophores during all the study months. The main reason for this phenomenon is because the rivers pass through two industrial cities, Liaoyang City and Benxi City, thereby carrying many pollutants from industries and domestic effluents.

CDOM in September exhibited more humic-like fluorophores (fluorophore A and fluorophore C) due to the legacy effect of dissolved organic matter from the high precipitation in July and August (Fig. 6, Fig. S2). This high precipitation increased erosion of soil and river discharge, resulting in the more exogenous input of humic acid and fulvic acid into the rivers in September. Both humic-like and protein-

like fluorophores were measured in April samples, which demonstrated that the sources of CDOM during this time had various derivations. As a result, the relationship between $\text{Fn}(355)$ and $a_{\text{CDOM}(254)}$ (Fig. 5b) varied inconsistently with those samples collected during the other months.

Conclusion

CDOM absorption and fluorescence of the rivers across the Liaohe Delta examined over an annual cycle revealed large variability in their optical properties. Flows, precipitations and anthropogenic activities were the main factors dominating the seasonal optical properties of CDOM. Our results showed significant linear relationships between CDOM absorption and DOC concentrations, especially for samples collected in January. Snowmelt discharge, soil thawing and recovery of phytoplankton may be the reasons for the poor relationships observed between CDOM and DOC in May. Empirical relationships between CDOM absorption and fluorescence determined during different months (except April) in the Liaohe River Basin could be used to trace organic matter sources using rapid and sensitive fluorescence measurements in comparison to absorption measurements. Tributaries of Liaohe River that cross the Liaohe Delta revealed strong protein-like substances, which are attributed to anthropogenic impacts on these areas. Overall, our results demonstrate that absorption and EEMs may be useful tools for temporal water quality monitoring and CDOM characterization. However, future research is needed to monitor the specific sources and characteristics of CDOM across the Liaohe River Basin. Additionally, more information about basin characteristics, types of land use/cover of the watershed and regional human population needs to be analyzed systematically. New techniques also may be used to trace the sources and characteristics of CDOM in the watershed.

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