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Absorption features of chromophoric dissolved organic matter (CDOM) and tracing implication for dissolved organic carbon (DOC) in Changjiang Estuary, China

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Abstract

Chromophoric dissolved organic matter (CDOM) represents the light absorbing fraction of dissolved organic carbon (DOC). Studies have shown that the optical properties of CDOM can be used to infer the distribution and diffusion characteristics of DOC in the estuary and coastal zone. The inversion of DOC concentrations from remote sensing has been implemented in certain regions. In this study we investigate the potential of tracing DOC from CDOM by the measurement of DOC, absorption spectrum of CDOM, Chla concentration, suspended sediment (SS), and salinity from cruises in different seasons around the Changjiang estuary. Our results show that around the Changjiang estuary the absorption coefficients of CDOM in general have the similar spatial and temporal characteristics as that of DOC, but the strength of the correlation between CDOM and DOC varies locally and seasonally. The input of pollutants from outside the estuary, the bloom of phytoplankton in spring, re-suspension of deposited sediment, and light bleaching all contribute to the local and seasonal variation of the correlation between DOC and CDOM. An inversion model for the determination of DOC from CDOM is established, but the stability of model parameters and its application in different environments need further study. We find that relative to the absorption coefficient of CDOM, the fitted parameters of the absorption spectrum of DOM are better indictors for the composition of DOC. In addition, it is found that the terrestrial input of DOC to Changjiang estuary is a typical two-stage dilution process instead of a linear diffusion process.

1 Introduction

Chromophoric dissolved organic matter (CDOM), which is often referred to as "yellow matter", is the portion of dissolved organic matter (DOM) that absorbs UV and visible parts of the light spectrum. It has been used as potential index to indicate dissolved organic carbon (DOC), especially for those derived from continental inputs in estuary and

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coastal areas (Vodacek et al., 1995; Ferrari, 2000). However, the routine or near real time monitoring of land source DOC through CDOM remains unsolved due to the great variability and uncertainty of the relationship between CDOM and DOC. The demand for investigating the CDOM characteristics is thus urgent to advance our understanding of the composition and transformation process of DOC (Kowalczuk et al., 2003; Batchelli et al., 2009).

Changjiang is the longest river in China. The annual carbon flux it transports into the East China Sea sums up to 20.4 Mt, and the runoff from Changjiang River into sea accounts for 51 % of the total runoff in China. The interactions between Changjiang River and East China Sea have a great impact on offshore marine hydrology, landform and biogeochemical cycles of the Western Pacific Ocean (Shen et al., 2009). Therefore, acquisition of terrigenous organic inputs in offshore areas carried by Changjiang River is vital for the estimation of carbon flux in this region. DOC concentration and flux in Changjiang River reportedly vary widely, from 3.3 to 11.2 $mg\,L^{-1}$. Furthermore, the extremely complicated hydrodynamic environment in Changjiang estuary leads to the uncertainty in the estimated concentration of DOC in seawater. This uncertainty can significantly affect the ocean carbon cycle because DOC is a major global carbon reservoir (Ogawa et al., 2003). Up to date, the composition and source of CDOM in Changjiang Estuary are largely unknown. To our knowledge, there are only a few available published literatures on tracing DOC with CDOM optical properties in this region.

In this study, water samples were collected and then CDOM absorption parameter, DOC concentration, chlorophyll *a* and salinity were analysed. We discuss the following three main issues: (1) the distribution characteristics of CDOM absorption in surface water in Changjiang estuary and adjacent sea area; (2) the possibility of using CDOM to indicate the source and composition of DOC; (3) factors influencing the inversion relationship between CDOM absorption parameters and DOC concentrations, and the potential possibility for aerospace remote sensing of terrigenous DOC inputs in Changjiang estuary with CDOM.

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2 Hydrodynamic environment, sampling and methods

2.1 Hydrodynamic environment and sampling

The current system of Changjiang estuary is complicated, as shown in Fig. 1. There are three major water masses in the Changjiang Estuary and nearby waters: (1) fresh water from the Changjiang river, usually nominated as Changjiang Diluted Water (CDW); (2) sea water (continental shelf waters) entering the East China Sea, either with the Yellow Sea alongshore current from the north or with the Taiwan Warm Current and its branches from the south; (3) the transition zone between fresh water and sea water that leads to estuarine mixed water. The relative strength of the current system varied with season, climate, tide and so on. Furthermore, during the northward intrusion of Taiwan Warm Current, the left parts of the front meet with the Changjiang Diluted Water (CDW) and then form an upwelling current outside the estuary (Zhao et al., 1992).

The length of the Changjiang estuarine turbidity zone is about 30 km. Its location corresponds to the inward side of the mouth bar, which moves further inward in winter. The surface salinity of the front which shifts from 122°00′ E to 122°25′ E according to survey records is between 5 and 17 ‰ (Chen et al., 1999).

In this study, three sections were chosen for in situ investigation. Xuliujing–Majiagang (XM) section is located in the head of the mouth bar, representing oligohaline environment dominating with CDW, Luchaogang–Shengsi (LS section in summer cruiser and LW section in winter cruiser) is at the mouth of Changjiang Estuary with mixture of fresh water and seaward saline water forming mesohaline water. PN denotes the area of polyhaline water across East China Sea shelf, which is the extension of CDW spindle and is vertical to the Kuroshio spindle (Zhang et al., 2009). The location of sampling station is chosen to reflect the migration of CDW, the intrusion of polyhaline sea water and the mixture process of the two distinct different current.

The field surveys were carried out separately in August 2011 for XM section, in January 2010 and August 2011 for LS section, in April 2011 for PN line. 47 surface

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seawater samples were collected at all stations. Figure 2 shows the study area and sampling stations.

Seawater samples were filtered immediately on-board through 0.2 µm Nuclepore polycarbonate membrane (soaked in 10 % HCl for 15 min and then rinsed with ultra pure Milli-Q water beforehand) for CDOM measurements, through 0.7 µm pre-combusted Whatman GFF glass fibre filter for DOC, and the residue on the filter membrane for Chl *a* measurement (combusted at 450° for 24 h then pre-packaged in the clean aluminium foil beforehand). The filtrate were preserved in pre-combusted (450° for 6 h) 60 mL amber colour glass bottles then stored frozen until analysis. Seawater samples were naturally thawed to room temperature before measurement.

2.2 Methods

2.2.1 CDOM absorption measurements

25 mL initial aliquot was discarded before the measurements. The CDOM absorption were measured on a UV-visible spectrophotometer (Shimadzu UV-2550) over 200–800 nm with 1 nm increments, using a 10 cm quartz cuvette and referenced to ultra pure Milli-Q water. Each sample was scanned for three times and two absorbance values matching well with each other were selected (Conmy et al., 2004). By subtracting value at 700 nm from each spectrum, we corrected the data to remove the effects of scattering and baseline fluctuations. The CDOM absorption coefficients were obtained by Eq. (1):

$$a_{(\lambda)} = 2.303 \times D_{(\lambda)}/L \quad (1)$$

Where λ is the wavelength and L is the cuvette length in meters.$a_{(\lambda)}$ is the absorption coefficient at wavelength λ, and $D_{(\lambda)}$ is the optical density at wavelength λ.

To remove residual errors from both scattering and instrument noise, CDOM absorption spectrum was simulated using the following non-linear least square regression

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Eq. (2) (Vodacek et al., 1997). k was discarded after regression.

$$a_{(\lambda)} = a_{(\lambda_0)} e^{s(\lambda_0 - \lambda)} + k \quad (2)$$

Where λ_0 is a reference wavelength (nm) with 440 nm chosen in this research, and data were fitted over range of 300–500 nm (Kowalczuk et al., 2003; Han et al., 2005).

2.2.2 DOC concentration measurement

The DOC concentrations were measured by a Shimadzu TOC-VCPH (Shimadzu Co., temperature: 680°). 50 µL were injected automatically per analysis; high temperature catalytic oxidation (HTCO) method was adopted to convert DOC into CO_2, which is then measured quantitatively by non-dispersive infrared detector.

$KHC_8H_4O_4$ was used as a carbon standard. Solutions for the calibration curve were prepared before analysis using the dilution of the stock solution with fresh Milli-Q water. We analysed the solutions by the same procedure as the samples. Instrumental and procedure blanks were determined each day from the analysis of the fresh Milli-Q water.

Analysis was repeated twice per sample with a typical deviation < 2 %. DOC concentration was then determined with the average values. Standard mean ocean water was used as a reference.

2.2.3 Measurements of other parameters

Chl *a* concentration was measured following standard fluorometric protocol (Parsons et al., 1984). The frozen Whatman GFF filters were extracted in 90 % acetone, and the resulting fluorescence was then measured in a Turner Designs Fluorometer, Model 10. This instrument was calibrated with a commercially available Chl *a* standard (Sigma) at an interval of 12 months.

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Salinity was measured with a salimeter (RUIMING InC., Changzhou, China) and suspended sediments (SS) was measured according to Chinese national standard (GB 12763.2-91) (The Oceanographic survey, 1991)

3 Data and Results

3.1 CDOM absorption spectra

Optical absorption of all samples decreases exponentially with increasing wavelength. The curves turn out to be steeper with the decrease of salinity, and distinct blue shift is observed for the bands where obvious decay occurs from 400 nm at XM01 station with salinity of 0.18 ‰ to 300 nm at PN09 station offshore with corresponding salinity of 34.48 ‰. Samples could be divided into three groups according to the slope of curves and bands where maximum attenuation occur, which is in good accordance with the salinity gradient, as shown in Fig. 3.

3.2 Absorption coefficient a(355)

CDOM represents of a variety of mixture and its concentration is difficult to be measured directly. Therefore, the absorption coefficient at a specific wavelength is usually adopted to quantify CDOM. However, selection of waveband of absorption coefficient varied in different studies (Stedmon et al., 2000; Kowalczuk et al., 2003; Chen et al., 2004a; Hoge et al., 1993). a(355) is selected in this research to be comparable with other researches (Hoge et al., 1993; Green and Blough, 1994; Ferrari, 2000; Rochelle-Newall and Fisher, 2002).

a(355) decreases gradually with increasing distance offshore in the salinity range of 0.18–34.48 ‰ (Fig. 4). The abnormally highest value was observed at XM04 station which is located at the upstream of the entrance of Huangpu River. a(355) in LS section fluctuated greatly although it gradually decreases with distance offshore as a whole.

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The mean value in summer is a little higher than that in winter. a(355) significantly reduces in PN section with a minimum value of 0.0461 m^{-1} at PN09 station.

3.3 Slope of fitted absorption spectra

The slope of fitted absorption spectra (Sg) is believed to change basically in relation to the CDOM constitution (Shen et al., 2006), and therefore is suggested as the potential significant index to indicate variation of CDOM composition in varied environment. Relative proportion of humic acid and fulvic acid is the main factor affecting the Sg value. Usually, terrigenous coastal or estuarine seawater with higher humic acid and lower fulvic acid has smaller Sg (Carder et al., 1989) and higher absorption coefficient, indicating greater CDOM molecular weight (Duan et al., 2009). Observed low Sg and high a(355) in coastal water in this study thereby indicate the dominance of land source CDOM.

It's difficult to depict distinct distribution of Sg in this research. Sg exhibits a wide range value of 0.0115–0.0232 nm^{-1} with a mean value of 0.0184 nm^{-1} (Fig. 5). Overall, Sg from saline seawater along PN line exhibits higher values than those from XM and LS section in estuary, showing opposite tendency with that of a(355). The maximum Sg is observed at station PN05. Sg in summer is significantly higher than that in winter from LS section. Minimum Sg is observed at station LW12 in winter. The larger seasonal variation of Sg between summer and winter than that of a(355) could be resulted from the seasonal variation of the composition, but not the concentration of CDOM.

An exponential model of CDOM absorption is then established as described by Eq. (3):

$$a_{(\lambda)} = a_{(440)} e^{0.0184 \times (440-\lambda)} \quad (3)$$

3.4 DOC

DOC decreases gradually with distance offshore (Fig. 6), varying between 0.764–2.644 mg C L^{-1} with average value of 1.308 mg C L^{-1}. The DOC in XM section (with

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mean value of 1.909 mg C L^{-1}) is at the same level with that of mainstream (Wu et al., 2007). XM04 station has a maximum value of 2.644 mg C L^{-1}, which is consistent with the highest vaule of a(355). By comparison, the concentration of DOC in PN section is quite lower with an average value of 0.821 mg C L^{-1} and the minimum appears in PN05 station with a value of 0.764 mg C L^{-1} correspondingly. The surface distribution of DOC in PN section is in good accordance with surveys from Ogawa et al. (2003). DOC in LS section exhibits medium concentration in contrast with that from XM and PN sections.

4 Discussion

4.1 Sources of CDOM

Sources of CDOM could be deduced with absorption coefficients and their mutual correlation with environmental factors. Obvious negative correlation between a(355) and salinity in this study regardless of annual seasonal runoff fluctuation (Fig. 7) indicates that the conservative dilution of CDW is a main factor controlling distribution of CDOM absorption. The abnormally highest value at XM04 station may be a result of the organic matter input from the Huangpu River. The weak correlation between absorption and salinity in LS section suggests that some other effects in addition to CDW conservative mixture may also play important roles in the behaviour of CDOM optical properties. Biological decay of vigorous phytoplankton growth in summer and strong sediment re-suspension in winter are the most possible reasons.

The bio-degradation of phytoplankton is recognized as one of important sources for CDOM except riverine terrigenous dissolved organic matter (DOM) input (Hoge et al., 1993). In this study, samples from XM section is characterized with very high a(355) but quite low Chl *a* (from 0.717–0.743 µg L^{-1} with average of 0.729 µg L^{-1}) indicating that phytoplankton output has negligible influence on a(355) value in local river water which is dominated with very high terrigenous DOM. The situation is complicated along LS line: (1) the content of Chl *a* varies seasonally. The average concentration of Chl *a* in

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summer is 1.88 $\mu g\,L^{-1}$ fluctuating from very low 0.127 $\mu g\,L^{-1}$ to very high 6.020 $\mu g\,L^{-1}$. The lowest values occur in station LS12 and LS16 with quite high salinity of 26.5 ‰ and 24.5 ‰ respectively, implying the intrusion of active upwelling current with relatively low phytoplankton concentration. The distinct negative relationship between a(355) and Chl *a* could be observed if the unexpected low phytoplankton in station LS12 and LS16 and abnormally high Chl *a* in station LS04 and LS15 are not considered (Fig. 8a). This suggests that DOM in the mouth of Changjiang Estuary is mainly resulted from the diffusion of terrestrial matter, but the absorption of DOM associated with algal bloom can not be ignored. Vigorous growth of phytoplankton could result in the consumption of DOM and then made a(355) relatively low. However sustainable growth of Chl *a* could induce the increment of DOM, which could be attributed to the metabolites and decomposition of microorganism, therefore resulting in the occurrence of relatively higher a(355) in station LS05 (with Chl *a* 6.020 $\mu g\,L^{-1}$ and 0.998 m^{-1} of a(355)) and LS14 (with Chl *a* 5.450 $\mu g\,L^{-1}$ and 0.725 m^{-1} of a(355)). (2) Chl *a* is relatively stable in winter (range from 0.855 to 1.897 $\mu g\,L^{-1}$ with average of 1.270 $\mu g\,L^{-1}$). The Chl *a* decreases with distance offshore, which could be due to the mixture of CDW with saline water and weak biological processes in winter. The synchronized variation of a(355) and Chl *a* further suggests that the biological effect could be neglected in winter.

Chl *a* has good positive correlation with a(355) in PN section (Fig. 8b), suggesting that in area with low DOM, the metabolites and degradation products of phytoplankton make great contributions to CDOM, controlling the variation of CDOM absorption coefficient. It indicated also that a(355) has close relationship with the content of DOM, but is irrelevant to the composition of CDOM.

There is great difference of suspended sediments concentration between summer and winter surveys in LS section. In summer, suspended sediments decrease with increment of salinity, robust positive relationship between SS and Salinity is observed ($R^2 = 0.89$, $n = 15$). Suspended sediment are steadily high in winter survey with average of 487.8 $mg\,L^{-1}$. The correlation coefficient between SS and salinity is 0.64 ($n = 15$). The high content of SS and the relatively weak relationships with salinity

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could be due to the strong re-suspension during sampling. Huge amount of terrigenous material deposited in this sea area because of the estuary barrier effect. The deposited land source sediment could be re-suspended while disturbed by the high tide, and thereafter organic matter absorbed on the surface of the particle or buried in interstitial water would release, resulting in the higher absorption coefficient of terrigenous CDOM. This could be also proved by correlation analysis between absorption coefficient and suspended sediment (Fig. 9).

In short, the seasonal phytoplankton growth and sediment re-suspension to some extent has impact on CDOM especially in LS section, but terrestrial inputs plays a leading role in general and show basically conservative mixing dilution characteristics.

The very low Sg in LS section in winter indicates that humic acid accounts for a relatively high proportion of CDOM, further indicating the release of deposited land source CDOM in the mouth bar of estuary through re-suspension. The higher Sg values in summer could be attributed to the higher primary production with vigorous biological degradation products in this area in summer, implying seasonal variation of CDOM compositions.

The regional variation of humic acid and fulvic acid proportion could be deduced by the instability of correlation between CDOM absorption coefficient and Sg. Negative relationship between absorption coefficient and Sg was observed in this study excluding Sg in LS section in winter with very low value (Fig. 10), suggesting the unexpected controlling of land source organic matter induced by re-suspension. Absorption coefficients of PN section behave stablaly, while the Sg values fluctuate sharply, indicating that CDOM composition varies significantly in this area. It is suggested that Sg is more sensitive than absorption coefficient to the changes of CDOM composition.

The relatively lower a(355) and higher Sg in this study area compared with data obtained from coastal regions worldwide could also be illustrated by variation of sources and composition of CDOM. With the acceleration of urbanization and long term widely usage of chemical fertilizer instead of organic fertilizer (Chen et al., 2004b), natural humus carried by Changjiang runoff is believed to reduce greatly. Furthermore higher

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suspended sediment in Changjiang river are resulted from the soil erosion, and the original geochemical migration process is changed by the absorption of organic matters on suspended particles (Wang and Zhang, 1998). These factors directly led to the reduction of DOM by the topsoil humification and surface waters chemosynthesis, thereby decreasing the CDOM content in Changjiang runoff. This result is in accordance with previous research conclusions that usually lower absorption coefficient is with higher Sg, and vice verse (Wang et al., 2007), especially for the regions where terrigenous inputs are dominant due to high proportion of humic acid (Duan et al., 2009).

4.2 Sources of DOC

The robust negative relationships between DOC and salinity ($R^2 = 0.89$, $P < 0.001$) indicate that the mixing process of terrigenous organic matter carried by Changjiang runoff is the controlling factor of DOC distribution in this research area. Extremely high value of DOC in XM04 station is induced when water from Huangpu River empties into Changjiang River. Huangpu River is an important potable water source river for nearly 20 million citizens in Shanghai, China, about 114.5 km long with width of about 500–800 m and depth of about 10–20 m, the annually average flux is about 316 $m^3 s^{-1}$. The distance along the Yangtze River to the East Sea is about 80 km (Yang et al., 2007). In recent years, the rapid development of industry and agriculture has led to deterioration of water quality. The average DOC concentration was 6.37 $mg L^{-1}$ (Xu et al., 2007). According to the records from the Datong Hydrometric Station the Changjiang River annually transports a water discharge of about 28 200 $m^3 s^{-1}$ (1951–1990) (Chen et al., 2001) to the estuary. The mixing process quickly weakens the additional input from Huangpu River.

Usually it is believed that the bacterial degradation of refractory DOM is responsible partly for the accumulation of DOC in summer, especially for estuarine and coastal zone (Zweifel et al., 1995), where DOC increase was largely explained by riverine

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input. In this study, the relatively weak correlation between DOC and Chl *a* indicates that the biogenic DOC plays minor role in contrast with land source DOC.

The *y*-intercept of the theoretically linear regression at salinity = 0 could be used to obtain an estimate of DOC concentrations in fresh waters that flows into sea. It is argued that although this estimate does not represent the actual concentration in river water, it can be used to estimate the terrestrial input of DOC because this estimation could potentially decrease the error caused by the variation in river water samples (Ogawa et al., 2003). This is feasible especially when the DOC concentrations in Changjiang reportedly vary widely (e.g. from 3.3 to 11.2 $mg\,L^{-1}$ by Thurman (1984) and Ogawa et al. (2003); 105u M C in 1997 and 108 u M C in 2003, Wu et al., 2007). However, in this research, the estimated DOC concentration in riverine water with linear equation is found to be nearly twice than that with nonlinear equation and in-situ retrieved data. There are two possible explains for the overestimation of DOC with linear model: (1) before large scale conservative mixture with the intrusion of marine saline water occur, land source DOC keeps nearly constant at the mouth of Changjiang River, but mechanism of this sustainment needs further investigation. (2) a portion of the terrestrial DOC is removed before it is transported to the continental shelf, possibly by estuary physical-chemical effect or photochemical process (Kieber et al., 1990; Miller and Zepp, 1995) and/or microbial degradation (Benner et al., 1995). If the later happens, in seasons when the water column is stratified, photochemical processes would be important for the removal of terrestrial DOC on the shelf before it is transported to the adjacent open ocean.

4.3 DOC inversion model with CDOM absorption

The achievements of using optical active CDOM to obtain a rapid and accurate estimation on DOM input flux in the surface waters in estuarine and coastal zone by remote sensing are successful in some area such as Beaufort Sea (Matsuoka et al., 2013). Shanmugam (2011) developed a new approach for the simulation of absorption spectra of CDOM and deriving information on its composition in global ocean waters. The

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robustness of the model was independently tested against three independent datasets, NOMAD in situ data, NOMAD SeaWiFS match-ups data and IOCCG simulated data. Studies have showed that some factors acting on CDOM proportion in DOM would change the correlation between them (Hochman et al., 1994, 1995; Hoge et al., 1995; Ferrari et al., 1996; Vodacek et al., 1997). For example, for multi-source based organic matters, CDOM accounts for different proportions in DOM of each source (Battin, 1998). Although CDOM and DOC may change synchronously, the CDOM proportions in DOC could be varied. Autochthonous DOC are commonly unstable and easily decomposed while the exogenous CDOM, which is mainly constituted by humic acid and fulvic acid derived from soil leaching, are more stable and resistant to degradation (Spitzy and Ittekott, 1986). Also, it is well known that some portion of DOM are photo-reactive and degraded to low molecular weight (LMW) carbonyl compounds or carbon monoxide photochemical bleach, and the later two compounds are optically non-active (Vodacek et al., 1997). In addition to this direct photo-mineralization, photo-produced LMW compounds are rapidly decomposed by marine bacteria, and then could be absorbed to produce optically active ones (Nelson et al., 1998; Rochelle-Newall, 1999). In general, the land-based sources DOC are rich of colour fractions compared with those produced by phytoplankton self-degradation, which is typical with colourless DOM (Rochelle-Newall and Fisher, 2002).

The study shows a robust positive correlation between a(355) and DOC concentration ($R^2 = 0.89$, $P < 0.001$) on a whole, although less obvious relationships between a(355) and DOC, and distinct seasonal variation are observed locally.

The distinct correlation between a(355) and DOC shows that CDOM absorptive properties are potentially useful index to obtain DOC from airborne or aerospace with remote sensing technique, especially for the estuarine area where terrestrial material is the dominant source of DOC. Diffusion and dilution are the main cause controlling distribution of DOC. However, the stability, usability, and uncertainty of the model in local waters and even the exact content represented by CDOM all need further study.

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5 Conclusions

This study is based on the measurements of absorption spectra of CDOM, concentration of DOC, and environmental parameters such as sea surface salinity, Chl *a*, and sea surface suspended sediment. There are four main purposes of this study: (1) to obtain characteristics of the distribution of CDOM optical properties; (2) to trace the sources of CDOM, (3) to understand the potential factors affecting the variation of CDOM, and (4) to establish a local inversion algorithm for the input flux of terrestrial DOC. We reach the following conclusions based on the results presented in this study:

1. Absorptive coefficient of CDOM in 355 nm exhibit gradual decrease within the salinity range of 0.18–34.48 ‰, suggesting the diffusion of CDW is the controlling factor that affects the distribution of CDOM. Vigorous biological decay in summer and strong sediment re-suspension in winter are the most likely reasons that result in the seasonal and local variation of CDOM in mouth bar. Exogenous DOC input from highly polluted Huangpu River significantly increases absorption coefficient in 355 nm at XM04 station in XM section.

2. The obvious higher values of Sg along PN line than those from XM and LS section indicate the improved relative proportion of autogenous DOC in PN line, while DOC in XM and LS sections are mainly composed of land source matter. Stable Sg during winter cruise along LS section indicates that released DOC from re-suspension of deposited sediment is mainly composed of terrestrial matter. The higher Sg values in summer could be attributed to the higher primary production with vigorous biological degradation products in this area, implying seasonal variation of CDOM compositions.

3. The estimated DOC concentration in riverine water using traditionally linear equation is found to be nearly twice larger than the in-situ retrieved data. A nonlinear regression equation between DOC and salinity is then developed, indicating a two

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stages diffusion model in the research area in this study: a slow diffusion process of CDW followed by a fast mixing process with offshore saline sea water.

4. a(355) was then determined as a good index for tracing and quantifying the land source of DOC. The distinct correlation between a(355) and DOC shows that CDOM optical properties can be used for the DOC inversion monitoring. The stability, usability and uncertainty of the model in local waters and the exact content represented by CDOM all need further study.

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Table 1. Comparison of a(355) and S_g of CDOM from some estuarine and coastal waters in the world.

Research areas		a(355) / m^{-1}	S_g / nm^{-1}	Salinity / ‰	References
Changjiang estuary (2008.8)		0.20 ~ 0.73	/	0.2 ~ 25.3	(Wang et al., 2010)
Changjiang estuary (2009.5)		0.20 ~ 0.77	/	0.3 ~ 29.5	
Changjiang estuary (2006.3)		1.152 ~ 8.715	0.0034 ~ 0.014	/	(Kong et al., 2008)
Pearl River estuary(November)		0.24 ~ 1.93	0.0138 ~ 0.0184	0 ~ 32.49	(Hong et al., 2005)
Pearl River estuary (June)		0.34 ~ 1.40	/	0 ~ 34.96	(Chen et al., 2004b)
South of the	Scheldt estuary	0.97 ~ 4.22a(375)	0.0167 ~ 0.0191	0.7 ~ 29.6	(Astoreca et al., 2009)
North Sea (February)	Belgium coastal sea	0.57 ~ 0.93a(375)	0.0110 ~ 0.0203	29.8 ~ 33.6	
Chesapeake Bay	River end member coast	2.2 ~ 4.1 0.4 ~ 1.1	0.0163 ~ 0.0194 0.0178 ~ 0.0222	0 ~ 35	(Rochelle-Newall and Fisher, 2002)
The Mississippi (in summer)		1.2 ~ 4.2	/	/	(Blough et al., 1993)
The Amazon (in winter)		0.14 ~ 3.12	/	/	(Green and Blough, 1994)
Georgia coast		0.06 ~ 1.20	/	/	(Hoge et al., 1993)
Changjiang intraoral (2011.8)		2.476 ~ 3.742	0.0176 ~ 0.0181	0.18–0.20	In this study
Luchaogang-Shengsi (2008.8)		0.427 ~ 1.440	0.0192 ~ 0.0216	8.40–26.50	
Luchaogang-Shengsi (2009.12)		0.269 ~ 1.154	0.0115 ~ 0.0175	18.96–28.00	
PN section in the East China Sea (2011.3)		0.046 ~ 0.207	0.0143 ~ 0.0232	31.31–34.48	
The whole		0.046 ~ 3.742	0.0115 ~ 0.0232	0.18 ~ 34.48	

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Table 2. Comparison of relationships between DOC and CDOM from estuaries and coastal waters worldwide.

The study area	DOC / mg L^{-1}	CDOM / m^{-1}	Correlation between CDOM and DOC	season/flow	References
South Baltic	5.688–7.392	1.2–12 1.2–6.5	correlated	spring/high autumn/low	(Ferrari et al., 1996) (Ferrari and Dowell, 1998)
Pearl River estuary	1.032–3.0	0.34–1.40	uncorrelated	summer/high	(Chen et al., 2004b)
West Florida Shelf	1.068–3.660	0.05–2.00 *a*(375)	uncorrelated	spring/high	(Del Castillo et al., 2000)
Middle Atlantic Bay	0.840–1.800	0.05–0.9	correlated	summer/high	(Vodacek et al., 1995)
Changjiang estuary	1.673–2.644	2.476–3.742	correlated	summer/high	In this study
Luchaogang-Shengsi	1.154–1.554	0.269–1.154	obscure correlation	winter/low	
PN section	0.764–0.952	0.046–0.207	correlated	spring/low	

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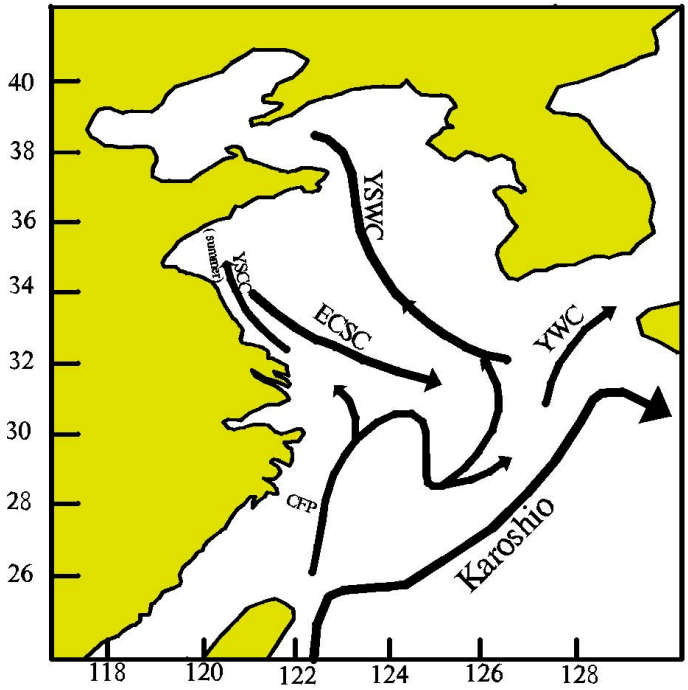

Fig. 1. Schematic diagram of regional hydrodynamic environment (Yuan and Hsueh, 2010).

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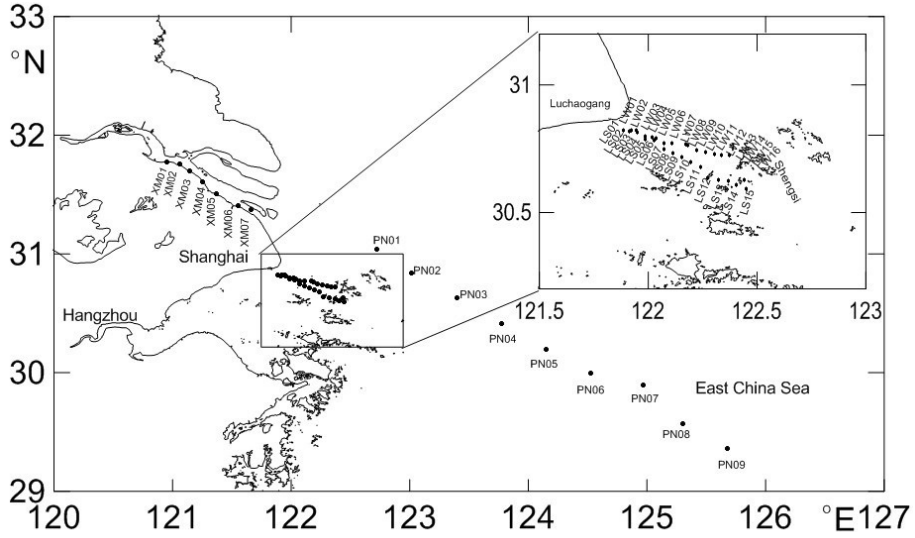

Fig. 2. Schematic diagram of study area and sampling station locations.

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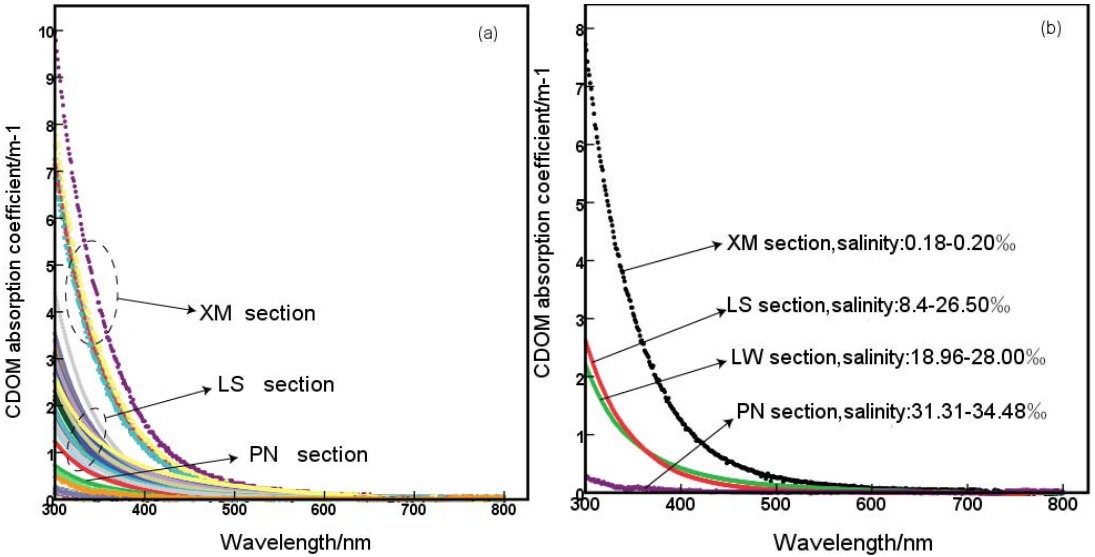

Fig. 3. Absorption curve of CDOM **(a)** represents spectra from all of the stations; **(b)** represents average values of spectra from different sections.

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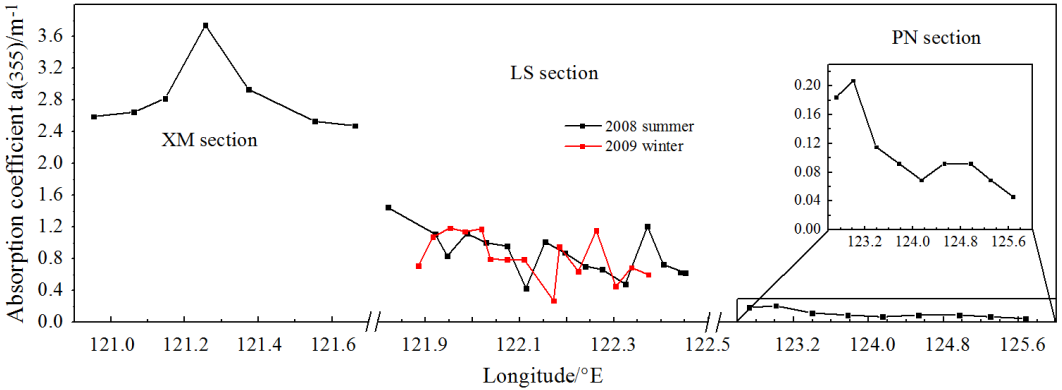

Fig. 4. Variation of a(355) with the distance offshore.

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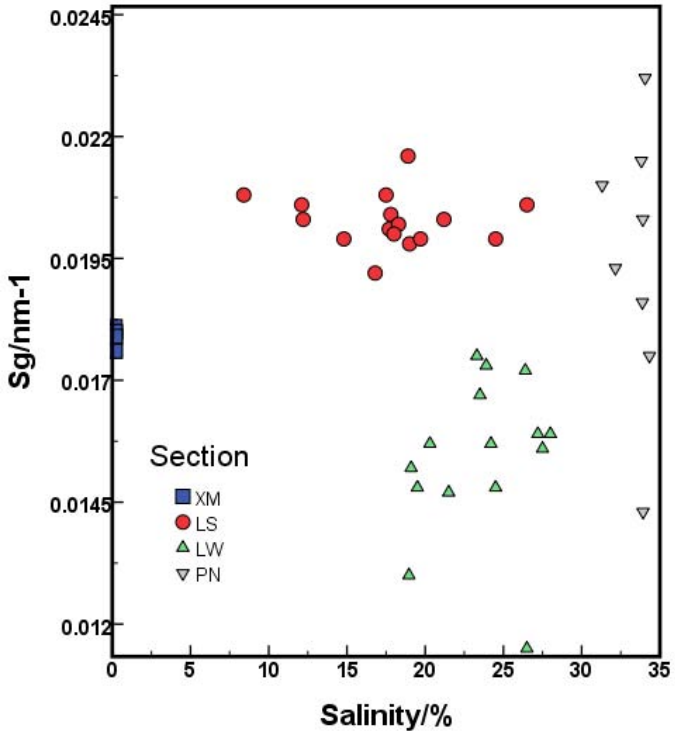

Fig. 5. Variation of Sg with salinity.

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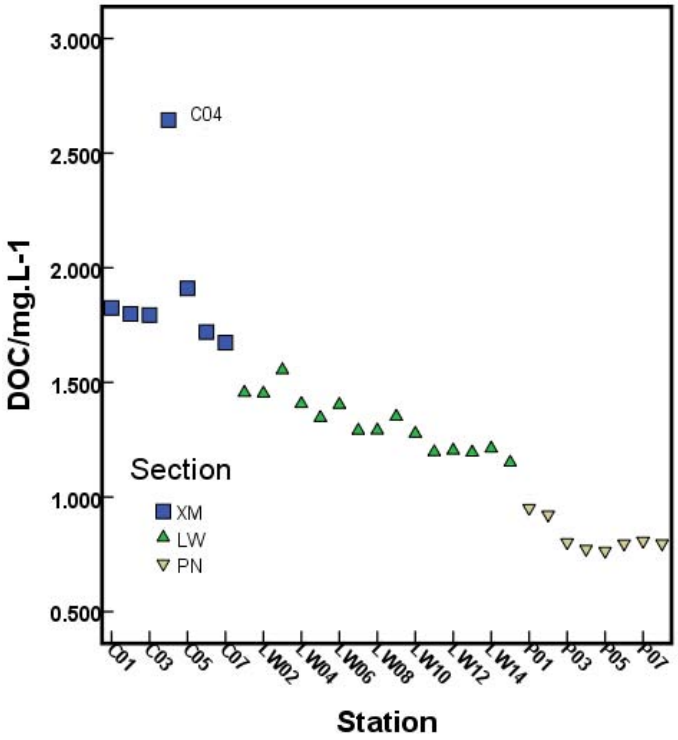

Fig. 6. Variation of DOC with stations offshore.

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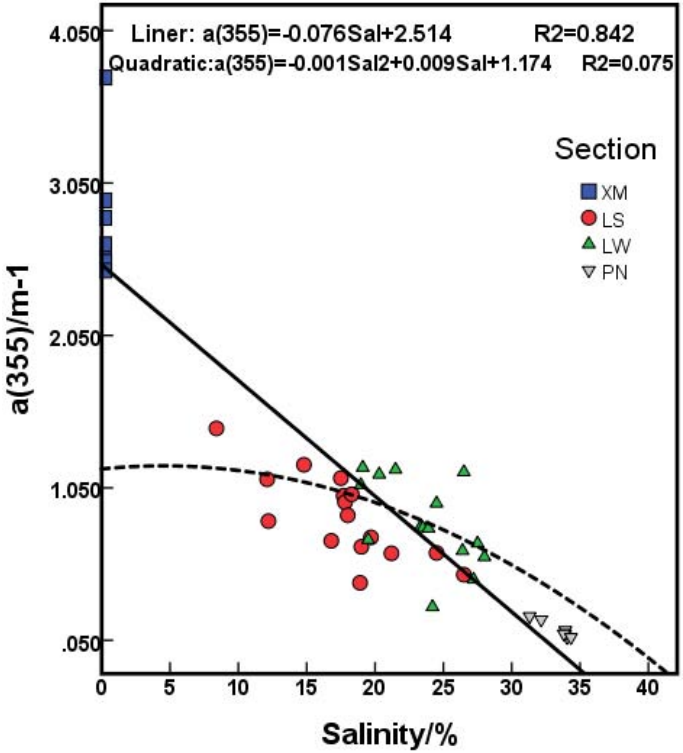

Fig. 7. Relationship between a(355) and salinity.

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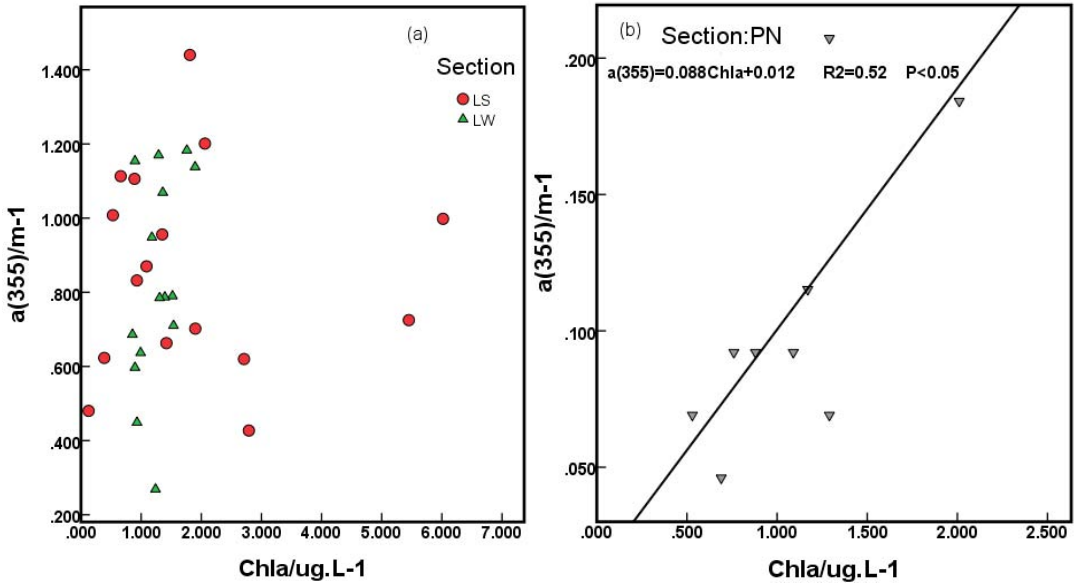

Fig. 8. Relationship between a(355) and Chl *a*.

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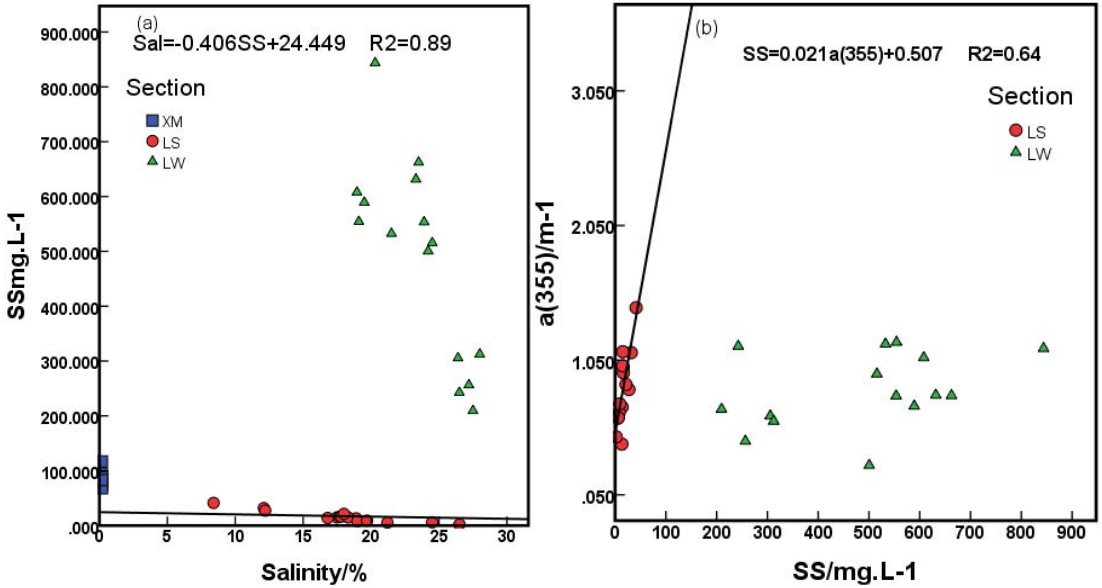

Fig. 9. Relationship between a(355) and SS.

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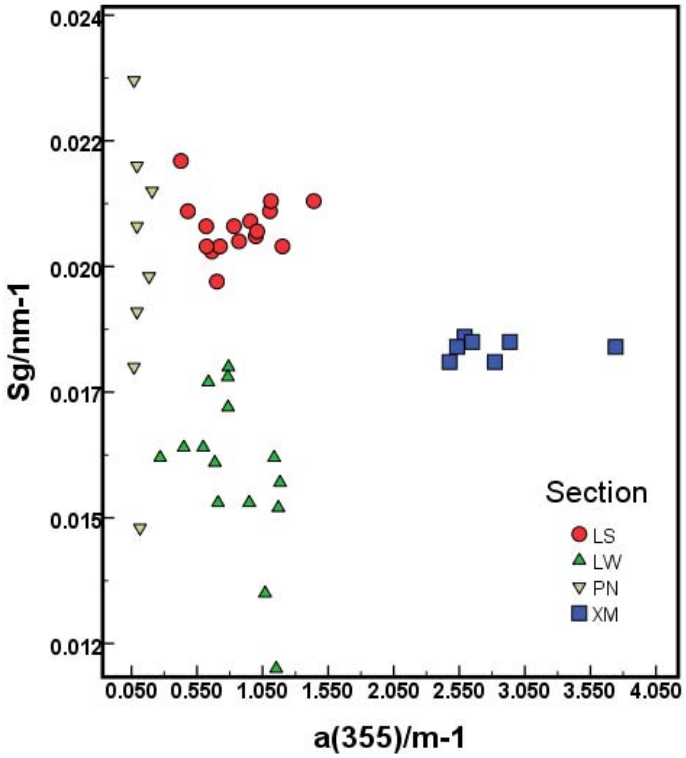

Fig. 10. The relationship between Sg and a(355).

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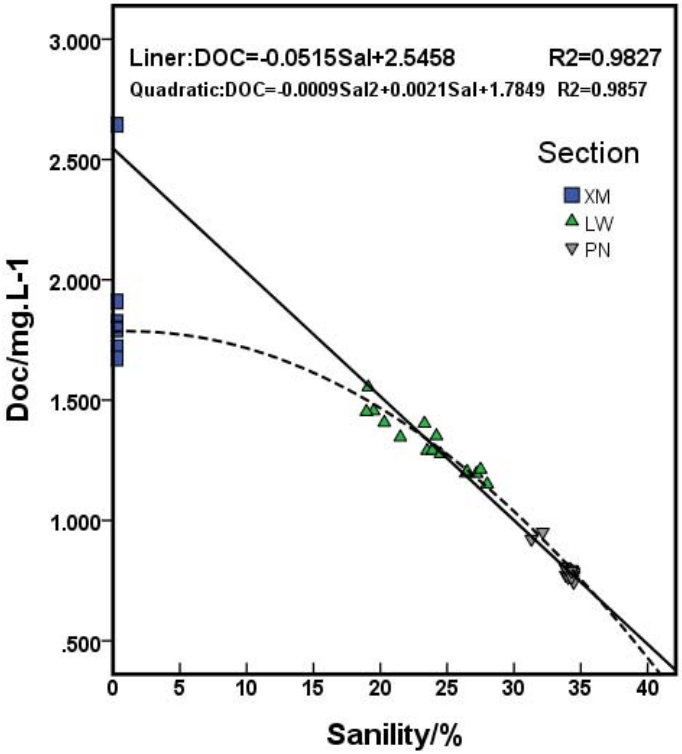

Fig. 11. Relationship between DOC and salinity.

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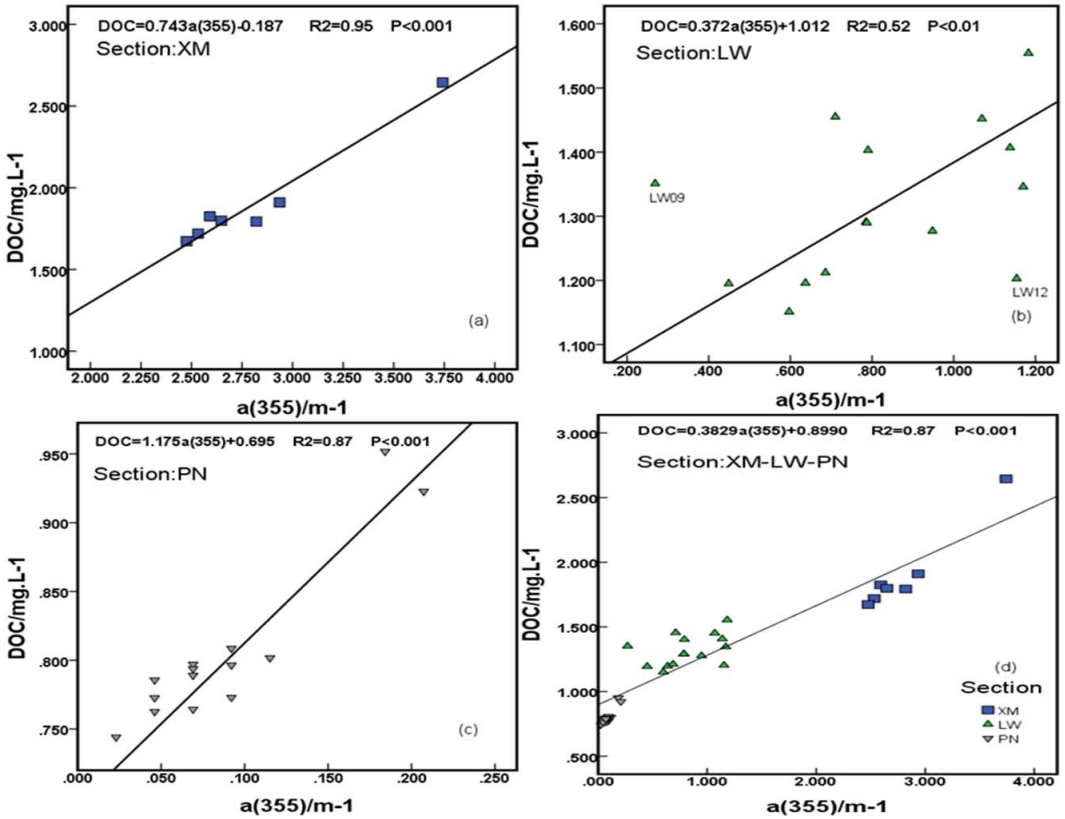

Fig. 12. Relationship between DOC and a(355).

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