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A systematic examination of the relationships between CDOM and DOC in inland waters in China

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Abstract: Chromophoric dissolved organic matter (CDOM) plays a vital role in the biogeochemical cycle in aquatic ecosystems. The relationship between CDOM and dissolved organic carbon (DOC) has been investigated, and the significant relationship lays the foundation for the estimation of DOC using remotely sensed imagery data. An algorithm has been developed to retrieve DOC via CDOM absorption (a_{CDOM}) at 275 and 295 nm for coastal waters, but it is still unclear for the relationship between DOC and a_{CDOM} in other types of waters. The current study examined the samples from freshwater lakes, saline lakes, rivers and streams, urban water bodies, and ice-covered lakes in China. The regression model slopes for DOC versus $a_{CDOM}(275)$ ranged from extreme low 0.33 (highly saline lakes) to 1.03 (urban waters) and 3.13 (river waters). The low values were observed in saline lake waters and waters from semi-arid or arid regions where strong photo-bleaching is expected due to thin ozone layers, less cloud cover, longer water residence time and daylight hours. In contrast, high values were found in waters developed in wetlands or forest in Northeast China, where massive organic matter was transported from catchment to

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waters. The study also demonstrated that stronger relationships between CDOM and DOC were revealed when $a_{CDOM}(275)$ were sorted by the ratio of $a_{CDOM}(250)$ to $a_{CDOM}(365)$, which is a tracer for the CDOM absorption with respect to its composition, and the determination of coefficient of the regression models ranged from 0.78 to 0.99 for different groups of waters. Our results indicated the relationships between CDOM and DOC are variable for different inland waters, and therefore remote sensing models for DOC estimation through linking with CDOM absorption need to be tailored according to water types.

Keywords: Absorption, CDOM, DOC, regression slope, saline water, fresh water

1. Introduction

Compared with other terrestrial ecosystems, e.g., forest and grassland, inland waters only occupy a small fraction (3.5%) of the earth surface (Verpoorter et al., 2014). However, they play a disproportional role for the global carbon cycling with respect to carbon transportation, transformation and carbon storage (Tranvik et al., 2009; Verpoorter et al., 2014; Yang et al., 2015). According to Tranvik et al. (2009), 2.9 Pg C was transported from terrestrial ecosystems to inland waters every year, of which about 0.6 Pg C was buried in the lake sediment, 1.4 Pg C was released into the air as CO_2 or CH_4, and the rest of 0.9 Pg C was exported to the ocean via river channels. However, the amount of dissolved organic carbon (DOC) stored in the inland waters is still unclear or the uncertainty is still needed to be evaluated (Tranvik et al., 2009). Determination DOC concentration is straightforward through field sampling and laboratory analysis (Findlay and Sinsabaugh, 2003). However, there are millions of lakes in the world, and many of them are remote and inaccessible, making it impossible to evaluate DOC concentration using routine approach (Cardille et al., 2013; Brezonik et al., 2015). Researchers have found that remote sensing might provide a promising tool for quantification of DOC of inland waters at large scale through linking DOC with chromophoric dissolved organic matter (CDOM), particularly for these inland waters situating in remote region with less accessibility (Cole et al., 2007; Tranvik et al., 2009; Kutser et al., 2015; Brezonik et al., 2015).

CDOM is one of the largest bioactive reservoirs of organic matter on the earth (Para et al., 2010), influencing light transmittance in aquatic ecosystems (Vodacek et

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al., 1997; Williamson and Rose, 2010). As one of the optically active constituents (OACs) in waters, CDOM can be estimated through remotely sensed signals (Yu et al., 2010; Kutser et al., 2015), and is acted as a proxy in many regions for the amount of DOC in the water column. As shown in Fig.1, CDOM and DOC in the aquatic ecosystems are mainly originated from external (allochthonous) and internal (autochthonous) sources, in addition to directly discharge from anthropogenic activities (Zhou et al., 2016). Generally, the autochthonous CDOM is essentially originated from algae and macrophytes, and mainly consists of various compounds of low molecular weights (Findlay and Sinsabaugh, 2003; Zhang et al., 2009). While, the allochthonous CDOM is mainly derived from the surrounding terrestrial ecosystems, and it comprises a continuum of small organic molecules to highly polymeric humic substances with compounds typically ranging from 100 to 100,000 Da. In terms of CDOM originates from anthropogenic, it contains fatty acid, amino acid and sugar, thus the composition of CDOM is more complex than that from natural systems (Zhou et al., 2016; Zhao et al., 2016). Hydrological factor also affects the DOC and CDOM characteristic. The concentrations of and the relationship between CDOM and DOC in river waters depend on many factors, in which the water type, the seasonality and climatology, the typology of the water, the surrounding landscapes. Particularly, the discharge and catchment area are the most important ones (Neff et al., 2006; Spencer et al., 2012; Alvarez-Cobelas et al., 2012).

[Insert Fig.1 about here]

CDOM is a major light-absorbing substance, which is responsible for much of the

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color in waters (Reche et al., 1999). The chemical structure and origin of CDOM can be characterized by its absorption coefficients ($a_{CDOM}(\lambda)$) and spectral slopes (De Haan and De Boer, 1987; Helms et al., 2008). Weishaar et al. (2003) has proven that the carbon specific absorption coefficient at 254 nm, e.g., $SUVA_{254}$ is a good tracer for the aromaticity of humic acid in CDOM, while the ratio of CDOM absorption at 250 to 365 nm ($a_{CDOM}(250/365)$, herein, M values) has been successfully used to track the changes in DOM molecule weight (De Haan and De Boer, 1987; Zhang et al., 2010) and absorption intensity (Song et al., 2013). Biodegradation and photodegradation are the major processes to determine the transformation and composition of CDOM (Findlay and Sinsabaugh, 2003). With prolonged sunlight absorbed by CDOM, some of the colored fraction is lost by the photobleaching processes (Miller et al., 1995; Zhang et al., 2010), which can be measured by the light absorbance decreasing at some specific (diagnostic) wavelength, e.g., 250, 254, 275, 295, 365 or 440 nm. It should be noted that $a_{CDOM}(440)$ is usually used by remote sensing community due to this wavelength is less affected by phytoplankton (Lee et al., 2002). Under this circumstance, the relationship between CDOM and DOC varies since CDOM loses color while the variation of DOC concentration is almost negligible. Saline or brackish lakes in the arid or semi-arid regions generally expose to longer sunlight radiation, thus CDOM absorbance decreases, while DOC is accumulated due to the longer residence time (Curtis et al., 1997; Song et al., 2013; Wen et al., 2016). Compared to photodegradation on CDOM, the biodegradation processes by microbes are much complicated, and extracellular enzymes are the key

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substance required to decompose the high-molecular-weight CDOM into low-molecular-weight substrates (Findlay and Sinsabaugh, 2003; Romera-Castillo et al., 2012). With compositional change, the absorption feature of CDOM and its relation to DOC varies correspondingly, but the relationship between CDOM and DOC is far from solved (Gonnelli et al., 2013). In addition, the $SUVA_{254}$ and $a_{CDOM}(250/365)$ may be used to classify CDOM into different groups and enhance the relationship with DOC based on CDOM absorption grouping.

Some studies have researched the spatial and seasonal variations of CDOM and DOC in ice free season in lakes, rivers and oceans (Vodacek et al., 1997; Neff et al., 2006; Stedmon et al., 2011; Brezonik et al., 2015), but less is known about saline lakes (Song et al., 2013; Wen et al., 2016), particularly urban waters influenced by sewage effluent and waters with ice cover in winter (Belzile et al., 2000, 2002; Zhao et alb., 2016). The relationship between DOC and CDOM lays the foundation for the remote sensing estimation of DOC in both inland waters (Yu et al., 2010; Griffin et al., 2011; Zhu et al., 2014; Brezonik et al., 2015) and marine (Hoge et al., 1996; Bricaud et al., 2012; Nelson et al., 2012). The significant relationship between CDOM and DOC was observed in the Gulf of Mexico, and stable regression model was established between DOC and $a_{CDOM}(275)$ and $a_{CDOM}(295)$ (Fichot and Benner 2011). Similar results were also found in other estuaries along a salinity gradient, for example the Finish Gulf (Kowalczuk et al., 2006) and the Chesapeake Bay (Le et al., 2013). However, Chen et al. (2004) found that the relationship between CDOM and DOC was not conservative due to estuarine mixing or photo-degradation. Similar arguments were raised for Congo River (Spencer et al. 2009) and waters across mainland USA (Spencer et al., 2012). The study on the relationship between DOC and CDOM in Lake Taihu found a relatively stable relationship for water samples collected in different seasons except winter (Jiang et al. 2012). However, seasonal variations were observed in some studies due to the mixing of various endmembers of CDOM from different terrestrial ecosystems and internal source (Zhang et al., 2010; Spencer et al., 2012; Zhou et al., 2016). Along with laboratory measurements, portable instruments deployed in river or streams provide great potential to quantify DOC and CDOM at very dynamic manner (Lee et al., 2015; Yu et al., 2016).

According to Fig.1, the proposed hypothesis suggests that the main source of CDOM and DOC in different waters vary, coupled with biogeochemical processes (photobleaching and microbial degradation), resulting in the compositional differences, and ultimately affects CDOM absorption and its relationship with DOC. Hydrological feature and anthropogenic processes further cause the relationship between CDOM and DOC varies both in time and space. Remote sensing technology has increasingly played a vital role in quantifying carbon cycling in inland waters (Tranvik et al., 2009; Raymond et al., 2013). However, the prerequisite is to systematically examine the relationship between CDOM and DOC. In this study, the characteristics of DOC and CDOM in different inland waters across China were examined to determine the spatial feature associated with landscape variations, hydrologic conditions and saline gradients. The objectives of this study are to: 1) examine the relationship between CDOM and DOC concentrations across a wide range of waters with various physical, chemical and biological conditions, and 2) develop a model for the relationship between DOC and CDOM based on the sorted CDOM absorption feature, e.g., the ratio of a_{CDOM}(250/365) with aiming to improve the regression modeling accuracy.

2. Materials and Methods

The dataset is composed of five subsets of samples collected from various types of waters across China (Table 1, Fig.2), which encompassed a wide range of DOC and CDOM. The first dataset (n = 288; from early spring 2009 to late October 2014) includes samples collected in freshwater lakes and reservoirs during the growing season with various landscape types. The second dataset (n = 345; from early spring 2010 to late mid-September 2014) includes samples collected in brackish to saline water bodies. The third dataset (n =322; from early May 2012 to late October 2014) includes samples collected in rivers and streams across different basins in China. In addition, 69 samples were collected from three sections along the Songhua Rive, the Yalu and the Hunjiang River during the ice free period in 2015 to examine the impact of river flow on the relationship between DOC and CDOM (see Fig.S1 for location). The fourth dataset (n = 328; from 2011 to 2014 in the ice frozen season) includes samples collected in Northeast China in winter from both lake ice and underlying waters. The fifth dataset (n = 221; from early May 2013 to mid-October 2014) collects samples in urban water bodies, including lakes, ponds, rivers and streams, which were severely polluted by sewage effluents. City maps and Landat imagery data acquired in 2014 or 2015 were used to delineate urban boundaries with ArcGIS

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10.0 (ESRI Inc., Redlands, California, USA), and water bodies in these investigated cities constrained by urban boundaries were considered as urban water bodies. Except river samples, the sampling dates, water body names and locations of other types of water bodies were provided in supplementary Table S1-3.

[Insert Fig.2 about here]

2.1 Water quality determination

Water samples were collected approximately 0.5m below the water surface at each station, generally locating in the middle of water bodies. Water samples were collected in two 1 L amber HDPE bottles, and kept in coolers with ice packs in the field and kept in refrigerator at 4℃ after shipping back to the laboratory; all samples were preprocessed (e.g., filtration, pH and electrical conductivity (EC) determination) within two days in the laboratory. Water salinity was measured using DDS-307 EC meter (μS/cm) at room temperature (20±2℃) and converted to *in situ* salinity units (PSU) in the laboratory. Water samples were filtered using Whatman cellulose acetone filter with pore size of 0.45 μm. Chlorophyll-a (Chl-a) was extracted and concentration was measured using a Shimadzu UV-2050PC spectrophotometer (Song et al., 2013). Total suspended matter (TSM) was determined gravimetrically using pre-combusted Whatman GF/F filters with 0.7μm pore size, details can be found in Song et al. (2013). DOC concentrations were measured by high temperature combustion (HTC) with water samples filtered through 0.45 μm Whatman cellulose acetone filters (Song et al., 2013; Zhao et al., 2016a). The standards for dissolved total carbon (DTC) were prepared from reagent grade potassium hydrogen phthalate in ultra-pure water, while dissolved inorganic carbon (DIC) were determined using a mixture of anhydrous sodium carbonate and sodium hydrogen carbonate. DOC was calculated by subtracting DIC from DTC, both of which were measured using a Total Organic Carbon Analyzer (TOC-VCPN, Shimadzu, Japan). Total nitrogen (TN) was measured based on the absorption levels at 146 nm of water samples decomposed with alkaline potassium peroxydisulfate. Total phosphorus (TP) was determined using the molybdenum blue method after the samples were digested with potassium peroxydisulfate (APHA, 1998). pH was measured using aPHS-3C pH meter at room temperature (20±2℃).

2.2 CDOM absorption measurement

All water samples were filtered at low pressure at two steps: 1) filtered at low pressure through a pre-combusted Whatman GF/F filter (0.7μm), and 2) further filtered through pre-rinsed 25 mm Millipore membrane cellulose filter (0.22 μm). Absorption spectra were obtained between 200 and 800 nm at 1 nm increment using a Shimadzu UV-2600PC UV-Vis dual beam spectrophotometer (Shimadzu Inc., Japan) through a 1 cm quartz cuvette (or 5 cm cuvette for ice melted water samples). Milli-Q water was used as reference for CDOM absorption measurements. The Napierian absorption coefficient (a_{CDOM}) was calculated from the measured optical density (OD) of samples using Eq. (1):

$$a_{CDOM}(\lambda) = 2.303[OD_{S(\lambda)} - OD_{(null)}]/\beta \quad (1)$$

where β is the cuvette path length (0.01 or 0.05m) and 2.303 is the conversion factor of base 10 to base e logarithms. To remove the scattering effect from the limited fine particles remained in the filtered solutions, a necessitated correction was implemented by assuming the average optical density over 740–750 nm to be zero (Babinet al., 2003). All absorption measurements were conducted within 48 h after the samples were shipped back to the laboratory. In addition, $SUVA_{254}$ and $a_{CDOM}(250/365)$ were calculated to characterize and group CDOM with respect to their compositional features and try to link DOC based on CDOM grouping.

3. Results and discussion

3.1. Biological and geochemical characteristics

The biological and geochemical properties in the water bodies are diverse. Chl-a concentrations (46.44±59.71 μg/L) changed from 0.28 to 521.12 μg/L, with the mean of 46.44 μg/L. TN and TP concentration were very high in fresh lake water, saline lake water and particularly urban water bodies (Table 1), indicating that most of the waters are heavily eutrophic. It is worth noting that Chl-a concentration was still high 7.3±19.7 μg/L even in ice-covered lakes in winter from Northeast China, which resulted from high TN (4.3±5.4mg/L) and TP (0.7±0.6mg/L) concentrations even under ice cover. Electric conductivity (EC) and pH were high in the semi-arid and arid regions, and they were 1067-41000 μs/cm and 7.1-11.4, respectively. This is due to specific regional hydro-geologic and climatic conditions. The results are consistent with previous findings (Song et al., 2013; Wen et al., 2016). Overall, waters were highly turbid with high TSM concentrations (119.55 ± 131.37 mg/L), but there were big variation between different types of waters (Table 1). Hydrographic conditions exerted strong impact on water turbidity and TSM concentration, thus these two parameters of river and stream samples were excluded in this study (Table 1). Large variations of water quality parameters in the extensive geographic area, for example in China, provide a more comprehensive dataset for examining the relationship between DOC and CDOM, and the result is very helpful for establishing remote sensing models to estimate DOC through CDOM absorption properties (Cardille et al., 2013; Zhu et al., 2014; Kutser et al., 2015).

[Insert Table 1 about here]

3.2. DOC concentrations in different types of waters

DOC concentrations changed remarkably in the investigated waters (Table 1). DOC concentrations were low in rivers, while they were much lower in ice melting waters sampled in winter, which is consistent with previous findings (Bezilie et al., 2002; Shao et al., 2016). It should be noted that large variations were observed in water samples from rivers and streams (Table 2) (Raymond and Saiers, 2010; Ward et al., 2012), due to the strong connection with hydrological condition and catchment landscape features (Neff et al., 2006; Agren et al., 2007; Lee et al., 2015). Generally, low DOC concentrations were found in rivers or streams in the drainage systems in Tibetan Plateau or arid regions in Northwest China where soil contains relative low level of soil organic carbon, but the high DOC concentrations were found in rivers or streams surrounded by forest or wetlands in Northeast China. The similar findings were reported by Agren et al. (2007, 2010). Among the five types of waters, relatively higher DOC concentrations, ranging from 2.3 to 300.6 mg/L, were found in many saline lakes, in the Songnen Plain, the HulunBuir Plateau and some areas in Tibetan

Plateau (see Fig.2 for location), which is consistent with previous investigations conducted in the semi-arid or arid regions (Curtis et al., 1995; Song et al., 2013; Wen et al., 2016). However, some of saline lakes supplied by snow melt water or ground water exhibited relatively lower DOC concentrations even with high salinity. Compared with samples collected in growing seasons, higher DOC concentrations (7.3-720 mg/L) were observed in ice-covered water bodies, due to the condensed effect caused by the DOC discharged from ice formation (Bezilie et al., 2002; Shao et al., 2016). This condensed effect was particularly marked in these shallow water bodies where ice forming remarkably condensed the DOC in the underlying waters (Zhao et al., 2016a). Even in rivers or saline lakes, the concentrations of DOC demonstrated obvious variations (Table 2). Comparatively, rivers from Qinghai exhibited lower DOC concentration, while these from the Liaohe and Inner Mongolia showed much higher DOC concentration (Table 2). Similarly, large DOC variations were observed in saline lakes in different regions (Table 2). Much higher DOC concentrations were found in saline lakes in Qinghai and Hulunbir, while relative low concentrations were observed in Xilinguole Plateau and the Songnen Plain.

[Insert Table 2 about here]

3.3. DOC versus CDOM for various types of waters

3.3.1 Freshwater lakes and reservoirs

The relationship between DOC and CDOM has been researched based on CDOM absorption spectra at different wavelengths (Fichot and Benner, 2011; Spencer et al., 2012; Song et al., 2013; Brezonik et al., 2015). As suggested by Fichot and Benner

(2011), CDOM absorptions at 275 nm (a_{CDOM}275) and 295 nm (a_{CDOM}295) have stable performances for DOC estimates for coastal waters. In current study, a strong relationship (R^2 = 0.85) between DOC and a_{CDOM}(275) was found in fresh lakes and reservoirs (Fig.3a). However, the participation of a_{CDOM}(295) explains very limited variance, thus it is not considered in the regression models. Regression analyses of water samples collected from different regions indicated that the slopes varied from 1.30 to 3.13 (Table 3). Water samples collected from East China and South China had lower regression slope values (Table 3), and lakes and reservoirs were generally mesotrophic or eutrophic (Huang et al., 2014; Yang et al. 2012, and references therein). Phytoplankton degradation may contribute relative large portion of CDOM and DOC in these water bodies (Zhang et al., 2010), due to the lower molecular weight, its absorption is different from that derived from terrestrial systems (Helms et al., 2008). Comparatively, fresh waters in Northeast and North China revealed larger regression slopes (Table 3).Waters in Northeast China are surrounded by forest, wetlands and grassland and therefore they generally exhibited high proportion of colored fractions, CDOM (Helms et al., 2008). Soils in Northeast China are rich in organic carbon, which may also contribute to high concentration of DOC and CDOM in waters in this region (Jin et al., 2016; Zhao et al., 2016a). Compared with waters in East and South China, waters in Northeast China showed less algal bloom due to low temperature, thus autochthonous CDOM was less presented in waters in Northeast China (Song et al., 2013; Zhao et al., 2016a). As suggested by Brezonik et al. (2015) and Cardille et al. (2013), CDOM in the eutrophic waters or those with very short

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resident time may show seasonal variation due to algal bloom or hydrological variability, while CDOM in some oligotrhopic lakes or those with long resident time may show an opposite pattern.

[Insert Table 3 about here]

[Insert Fig.3 about here]

3.3.2 Saline lakes

A strong relationship between DOC and $a_{CDOM}(275)$ (R^2 = 0.85) was demonstrated for saline lakes (Fig.3b). However, compared to fresh waters, much lower regression slope value (slope = 1.28) was found in saline lakes. Similar to fresh waters, the slopes of most saline lakes exhibited large variations between different regions (Table 3), ranging from 0.86 in Tibetan waters to 2.83 in Songnen Plain waters (see Fig.2 for location). As the extreme case, the slope value was only 0.33 as demonstrated in the embedded diagram in Fig.3b. Saline lakes in semi-arid or arid regions generally exhibit higher regression slope values, for example, west Songnen Plain (2.83), Hulunbir Plateau and East Inner Mongolia Plateau (1.79). Whereas, waters in the west Inner Mongolia Plateau (1.13), the Tibetan Plateau (0.86) exhibited low slope values (Table 3), and the extreme low value was measured in the Lake Qinhai in Tibetan Plateau. Lakes in Tarim Basin were affected by strong photo-bleaching, due to the long resident time and strong solar radiation (Spencer et al., 2012; Song et al., 2013; Wen et al., 2016). Thereby, smaller regression slopes were found and less colored portion of DOC was presented in waters in semi-arid to arid regions, especially for these closed lakes with enhanced photochemical processes (Spencer et al., 2012; Song

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et al., 2013; Wen et al., 2016). The findings highlighted the difference in remote sensing of DOC through CDOM absorption algorithm between saline and fresh lakes, thereby different models should be established to accurately estimate DOC in waters (Cardille et al., 2013; Brezonik et al., 2015).

3.3.3 Streams and rivers

Although some of the samples scattered from the regression line (Fig.3c), close relationship between DOC and $a_{CDOM}(275)$ was found for samples collected in rivers and streams. Compared with the other water types (Fig.3), rivers and streams exhibited the highest regression slope value (slope = 3.13). Further regression analysis with water samples sub-datasets collected in different regions indicated that slope values presented large variability, ranging from 1.07 to 8.49. The lower regression slope values were recorded in water samples collected in rivers and stream in semi-arid and arid regions, such as the Tibetan Plateau, Mongolia Plateau and Tarim Basin, while the higher values were found in samples collected in streams originated from wetland and forest in Northeast China (Table 3). Rivers and streams in North, East and South China generally exhibited intermediate values. In addition, water samples in large river generally presented relatively low slope value; streams, especially head water originating from forest and wetland dominated regions show higher regression slope values (e.g., Branches from the Nenjiang and the Songhua River in Table 3), which is consistent with the findings from Helm et al. (2008) and Spencer et al. (2012). In fact, landscape pattern and soil organic carbon in the catchment are important factors governing the terrestrial DOC and CDOM characteristics in rivers and streams (Wilson and Xenopoulos, 2008; Jaffe et al., 2008; Agren et al., 2010; Lai et al., 2016).

DOC concentration is strongly associated with hydrological conditions (Neff et al. 2006; Agren et al. 2007). Thereby, the relationships between CDOM and DOC in river and stream waters are very variable (Lee et al., 2015) due to the hydrological variability and catchment features (Agren et al., 2010; Spencer et al., 2009; 2012). To investigate the dynamics of CDOM absorption and DOC concentrations, three sections were investigated in three major rivers in Northeast China (see Figure S1 for location). River flow exerted obvious effect on DOC and CDOM (Fig.4) and flood impulse brought large amount of DOC and CDOM into river channels, which is consistent with previous findings (Neff et al., 2006; Larson et al., 2007). As shown in Fig.4, the relationship between river flows and DOC is rather complicated, which is mainly caused by the land use, soil properties, relief, slope, the proportion of wetlands and forest, climate and hydrology of the catchments (Neff et al., 2006; Sobek et al., 2007; Spencer et al., 2012; Zhou et al., 2016), with additional influence by sewage discharge into rivers. The relationships between DOC and $a_{CDOM}(275)$ in sections along three rivers in Northeast China were demonstrated in Fig.5. The sampling point in the Yalu River is near the river head source, thus strong relationship was exhibited with large slope (Fig.5a), due to that the DOC and CDOM were fresh and less disturbed by pollution from anthropogenic activities (Spencer et al., 2012; Shao et al., 2016). The relationship between DOC and $a_{CDOM}(275)$ in the Songhua River at Harbin City section was much scattered (Fig.5c) and this is mainly attributed to both point

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and non-point source pollution that cause the composition and colored fractions of DOC and DOM much varied comparing to river head waters with less human disturbance. Similar mechanisms are further detailed in section 3.3.4 with urban waters. With respect to Fig.5b, it is an in-between case. The sampling point was affected by effluent from Baishan City, thus the coefficient of determination (R^2= 0.822) and the regression slope (3.72) were lower than that from the Yalu River at Changbai point, while higher than that from the Songhua River at Harbin point. Thereby, both spatial and temporal changes of the relationships between DOC and CDOM were observed, and anthropogenic activities further complicated the relationship.

[Insert Fig.4 and Fig.5 about here]

3.3.4 Urban waters

Relative close relationship between DOC and $a_{CDOM}(275)$ was revealed in urban waters (Fig.3d, R^2= 0.71), where it was much scattered compared with other water types (Fig.3), particularly for water samples with DOC concentration less than 60 mg/L. Similarly, regression slope values changed remarkably, ranging from 0.87 to 2.45. It is apparent that urban waters are severely impacted by human activities, particularly sewage, effluents and runoff from urban impervious surface containing large amount of DOM (Yang et al. 2008; Zhao et al., 2016b, and references therein). High nutrients also usually result in algal bloom in most urban water bodies (Chl-a range: 1.0-521.1 μg/L; average: 38.9 μg/L). Thereby, DOC and CDOM derived from phytoplankton may also contribute a portion that should not be neglected (Xing et al.

2006; Zhang et al., 2010; Zhao et al., 2016b). More or less affected by sewage effluent, the DOM in urban waters is much complex than those from natural water bodies. Thus, a large variation of the relationship between DOC and $a_{CDOM}(275)$ was found in urban waters.

3.3.5 Ice covered lakes and reservoirs

The closest relationship (R^2 = 0.93) between DOC and $a_{CDOM}(275)$ was recorded in waters beneath ice covered lakes and reservoirs in Northeast China (Fig.3e). It was argued that the close relationship indicated the concurrent processes taken place for DOC accumulation and CDOM biogeochemical activities (Finlay et al., 2003; Stedmon et al., 2011). The strong positive correlations between DOC and $a_{CDOM}275$ is probably due to ice formation condensed these two parameters. The other possible explanation was that ice and snow cover shielded out most of the solar radiation that might cause a series of biochemical process for CDOM contained in water; further, the inflows and direct rainfall over lakes or reservoirs also diminished, thus causing limited effect on DOC and CDOM composition (Uusikiv et al., 2010; Belzile et al., 2002). Further, the autochthonous DOC and CDOM in ice covered waters were also limited due to the relatively weak primary production in winter (Chl-a = 7.3 μg/L), resulting in much close relationship in winter waters.

Comparatively, a weak relationship between DOC and $a_{CDOM}(275)$ was demonstrated in ice melting waters (Fig.3f), which was probably due to the ice/water depth ratio causing variation of dissolved components expelled during ice formation. The other reason is the biologically derived DOC in the ice matrix, which changes with the variation of light and nutrient (Arrigo et al., 2010; Zhang et al., 2010). Apparently, CDOM from ice melting waters were mainly originated from maternal water during the ice formation, also from algal biological processes (Stedmon et al., 2011; Arrigo et al., 2010). Similarly, snow cover, and nutrients in the ice also causes the variation of biochemical processes that ultimately complicate the relationship between DOC and CDOM (Bezilie et al., 2002; Spencer et al., 2009). Interestingly, the regression slopes for ice samples (1.35) and under lying water sample (1.27) are very close. In addition, there was a significant relationship between DOC in ice and underlying waters (R^2 = 0.86), indicating the dominant components of CDOM and DOC in the ice are from maternal underlying waters.

3.3.6 DOC versus $a_{CDOM}(440)$

CDOM absorption at 440 nm, i.e., $a_{CDOM}(440)$, is usually used as a surrogate to represent its concentration (Bricaud et al., 1981; Babin et al., 2003), and widely used in remote sensing community to quantify CDOM in waters (Lee et al., 2002; Binding et al., 2008; Zhu et al., 2014). Significant relationships between DOC and $a_{CDOM}(440)$ were found in different types of waters (Fig.5). Compared to DOC versus $a_{CDOM}(275)$, the relationships were more scattered due to the weak CDOM absorption at longer wavelength (Bricaud et al., 1981; Binding et al., 2008). Through comparing Fig.3with Fig.6, it can be found that the overall relationships between DOC and CDOM at 440 nm resemble that at 275 nm for different types of waters. This has important implication for remote sensing of DOC through the CDOM absorption as a bridge (Zhu et al., 2014; Kuster et al., 2015; Brezonik et al., 2015). It is also worth noting that most of the streams and rivers, including some of the urban water bodies, are not suitable to quantify DOC through remote sensing imagery, and this is due to that medium or even coarse resolution imagery cannot effectively capture the change of signals from these small water bodies. However, the systematic examination for the relationship between DOC and CDOM may help to quantify DOC through CDOM absorption for deploying portable sensors in streams or rivers that can measure CDOM absorption more accurately with dynamic manner (Spencer et al., 2012; Lee et al., 2015; Ruhala and Zarnetske, 2016).

[Insert Fig.6 about here]

3.4 CDOM molecular weight and aromacity versus DOC

3.4.1 CDOM versus SUVA254 and $a_{CDOM}(250/365)$

The large variations of the slope of regression of DOC and $a_{CDOM}(275)$ in different types of waters are probably due to the aromacity and colored fractions in DOC component (Spencer et al., 2009, 2012; Lee et al., 2015). $SUVA_{254}$ is an effective indicator to characterize CDOM molecular weight. It may reflect the regression slope value between DOC and CDOM absorption at 275 nm. It is obvious that $SUVA_{254}$ had high values in fresh lakes, and waters from rivers or streams as well (Fig.7a). Saline water and ice covered waters in Northeast China showed intermediate $SUVA_{254}$ values, while urban water and ice melting water exhibited lower values. The M value, i.e., $a_{CDOM}(250/365)$ is another indicator to demonstrate the variation of molecular weight and aromacity of CDOM components (De Haan, 1993). Fresh lake water, river and stream water, and urban water exhibited low M values (Fig.7b), which indicated that larger aromacity dominant for these three types of waters. Saline water, ice covered water in Northeast China and ice melting water showed higher M values. Since $SUVA_{254}$ is a proxy based on the ratio to DOC, it is inappropriate to establish the relationship between CDOM and DOC based on the $SUVA_{254}$ classification. Thereby, only M values, which reveal molecular weight and aromacity, might help to estimate DOC through CDOM absorption based on M threshold values for various types of waters.

[Insert Fig.7 about here]

3.4.2 Regression based on M values

Regression models between DOC and $a_{CDOM}(275)$ were established based on M threshold values, which were determined through trial test with respect to the concentrations of DOC versus $a_{CDOM}(275)$. A relative weaker relationship between DOC and $a_{CDOM}(275)$ was revealed in dataset where M values were less than 5 (Fig.8a). It should be noted that the high regression slope values appeared indifferent groups of subset data (Fig.8a-h). The large range of M value (0<M<4.0) may explain the scattered data pairs in Fig.8a and this is also the reason for the group with M values ranging from 4 to 6 (Fig.8b). Better regression models appeared in groups with intermediate M values (Fig.8c-f), with small range of regression slope values (1.15 - 1.38) and high determination of coefficients (R^2> 0.88). Regression slope values decreased with the increasing of M values (Fig.8g-h). Weak relationship between DOC and $a_{CDOM}275$ appeared with relative lower or higher M values (Fig.8g). Very significant relationship (R^2 = 0.99) was found with extremely high M values (Fig.8h). Most of samples collected from these groups were presented in the embedded diagram in Fig.3b, and the limited water bodies in the group may explain this coincidently high R^2 value. With more samples collected from different water bodies in this extreme group, a weak relationship between DOC and $a_{CDOM}(275)$ may appear, while future explorations are needed.

As noted in Fig.8c-f, close regression slopes implicate that a comprehensive regression model with intermediate M value groups may be achieved. As expected, a promising regression model (the diagram was not shown) between DOC and $a_{CDOM}275$ was achieved ($y = 1.269x + 6.55$, $R^2 = 0.925$, $N = 998$, $p < 0.001$) with pooled dataset shown in Figs.8c to 8f. Inspired by this idea, the relationship between CDOM and DOC also examined with pooled data. As shown in Fig.9a, a significant relationship between DOC and $a_{CDOM}(275)$ was obtained with the pooled dataset (N = 1504) collected from different types of inland waters. However, it should be noted that the extremely high DOC samples may advantageously contribute the better performance of the regression model. Thus, regression model excluding these eight samples (DOC > 300 mg/L) was still significant (Fig.9b, $R^2 = 0.66$, $p < 0.01$). In addition, regression model based on logarithm transformed data was established (Fig.9c, $R^2 = 0.82$, $p < 0.01$). Most of the paired data sitting close to the regression line except some scattered ones. This also implies that relative accurate regression model for CDOM versus DOC can be achieved with data collected in inland waters at global scale (Sobek et al., 2007), which might be helpful in quantifying DOC through linking with CDOM absorption spectra, and the latter parameter can be estimated from remote sensing data (Zhu et al., 2011; Kuster et al., 2015).

[Insert Fig.8 and Fig.9 about here]

4. Conclusions

As a powerful technology, remote sensing plays a crucial role in assessing CDOM and DOC in water environment. In order to get accurate estimates of CDOM and DOC in waters, it is necessary to get insight into the regional water optical properties for developing semi-analytical or analytical models with remotely sensed data. Based on the measurement of CDOM absorption spectral and DOC laboratory analysis, we have systematically examined the relationships between CDOM and DOC in various types of waters in China. This investigation showed that CDOM absorption varied significantly. River waters and fresh lake waters exhibited high CDOM absorption values and specific CDOM absorption ($SUVA_{254}$). On the contrast, saline lakes illustrated low $SUVA_{254}$ values due to the long residence time and strong photo-bleaching effects on waters in the semi-arid regions. Influenced by effluents and sewage waters, CDOM from urban water bodies showed much complex absorption feature. $SUVA_{254}$ for CDOM was lowest in ice melting water samples.

The current investigation indicated that the relationships between CDOM absorption and DOC varied remarkably by showing very varied slope values of regression models in various types of waters. The slope values of saline lakes and urban waters were close to unity, slope values of river water were highest (~ 3.1), and slope values of other water types were in between. It should also be highlighted that head river water generally exhibit larger regression slope values, while rivers affected by anthropogenic activities show lower slope values. When all the data set were pooled together, the slope for regression model was about 1.3, but with much bigger uncertainty (R^2 = 0.66). The accuracy of regression model between $a_{CDOM}(275)$ and DOC was improved when CDOM absorptions were divided into different sub-groups according to M values. Our finding highlights that remote sensing models for DOC estimation based on the relationship between CDOM and DOC should consider water types or cluster waters into several groups according to their absorption features. More researches are still needed to further improved model accuracy.

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Figures

Fig.1. the diagram shows the regulating factors that influence the relationship between CDOM and DOC.

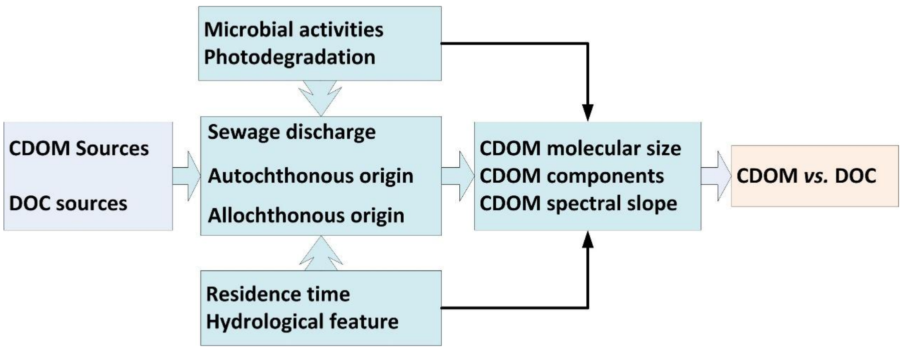

Fig.2. Water types and sample distributions across the mainland China. The dash line shows the boundary of some typical geographic units.

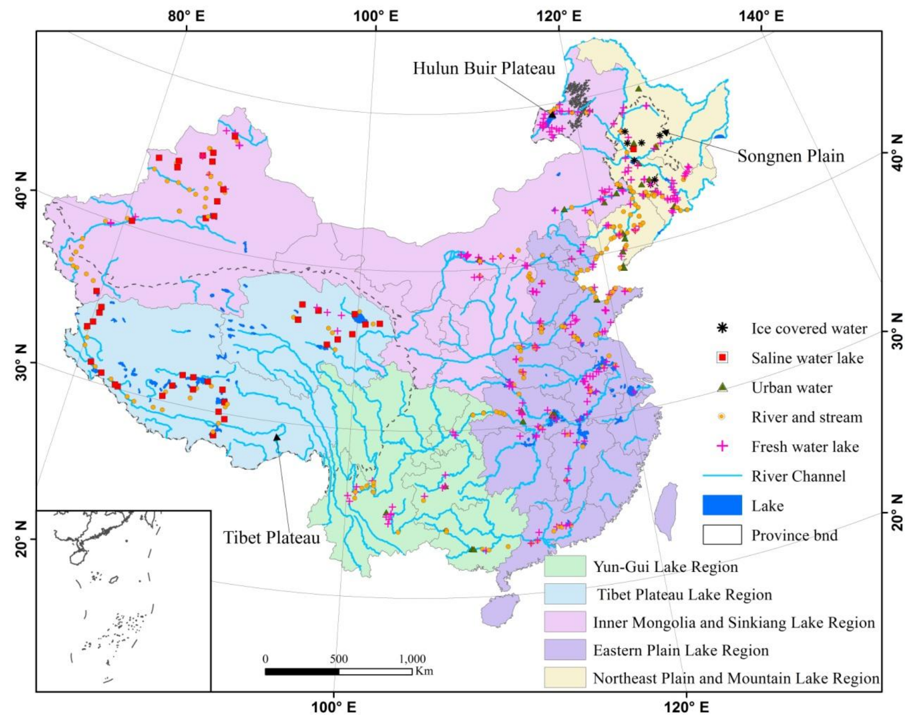

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Fig.3. Relationship between DOC and $a_{CDOM}(275)$in different types of inland waters, (a) fresh water lakes, (b) saline water lakes, (c) river and stream waters, (d) urban waters, (e) ice covered lake underlying waters, and (f) ice melting lake waters.

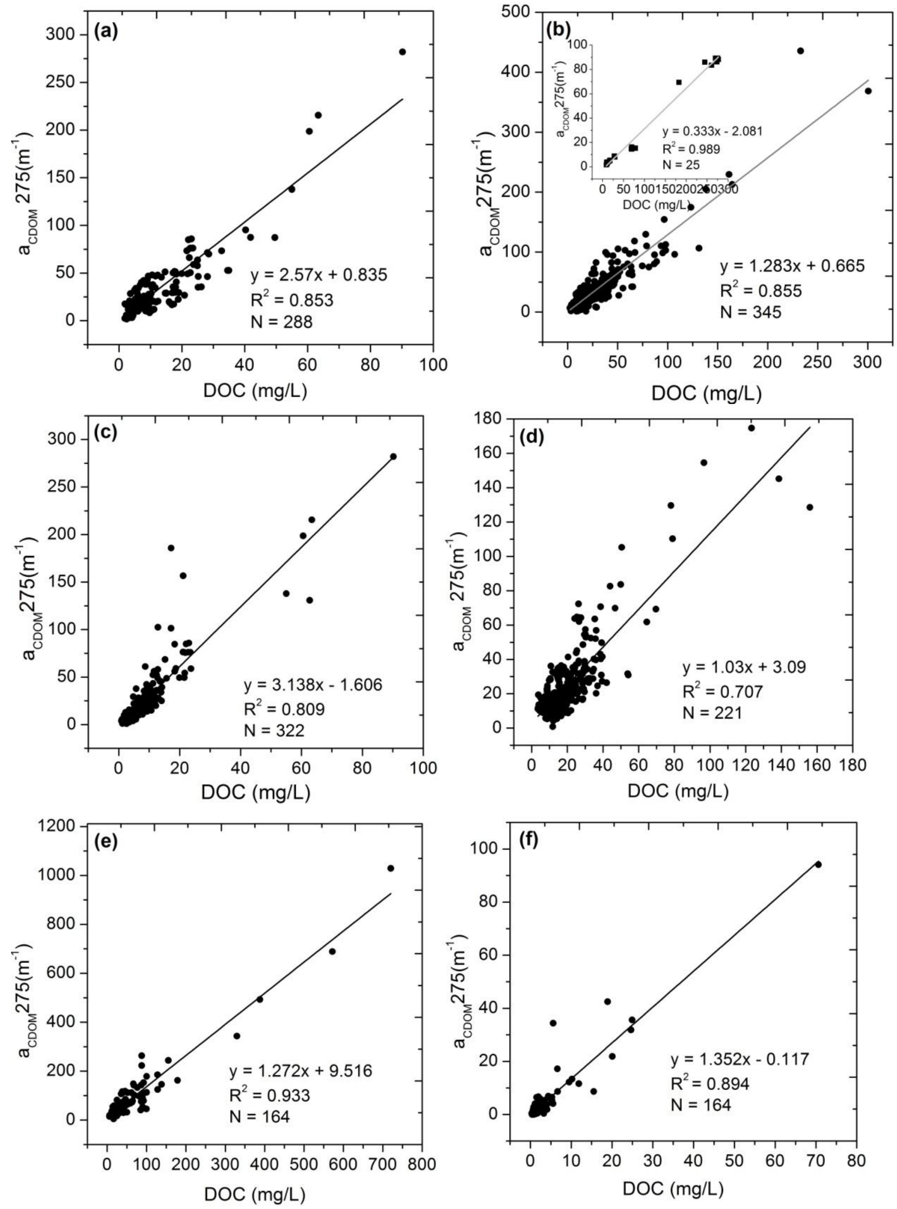

Fig.4. Flow dynamics for three rivers in Northeast China and corresponding DOC and CDOM variations; (a) the Yalu River near Changbai County, (b) the Hunjiang River with DOC and CDOM sampled at Baishan City, while the river flow gauge station is near the Tonghua City, (c) the Songhua River at Harbin City. Note, the flow data for the Yalu River and the Hunjiang River were the average values measured during 1970s, while the Songhua River was measured during 2000-2010.

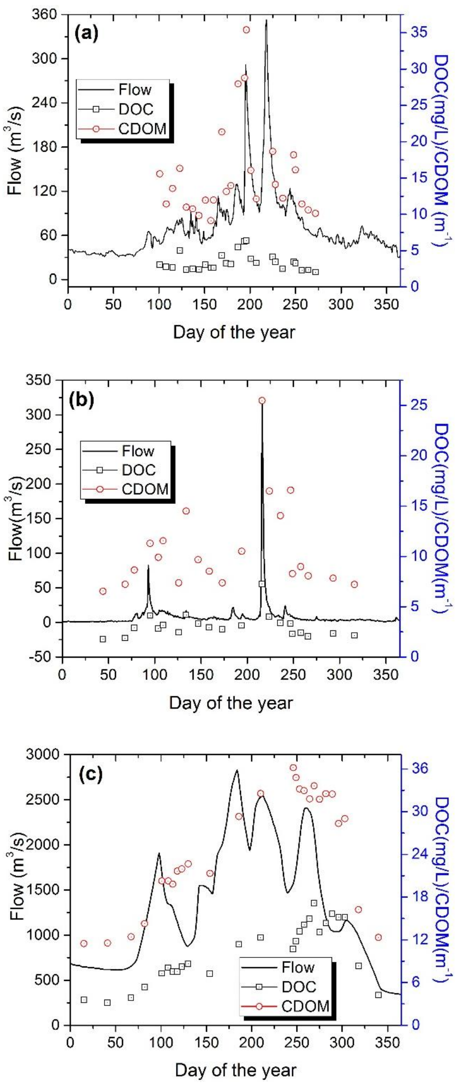

Fig.5. The relationships between $a_{CDOM}275$ and DOC at sections across (a) the Yalu River, (b) the Hunjiang River, and (c) the Songhua River. The samples were collected at each station at about one week or around ten days in ice free season in 2015.

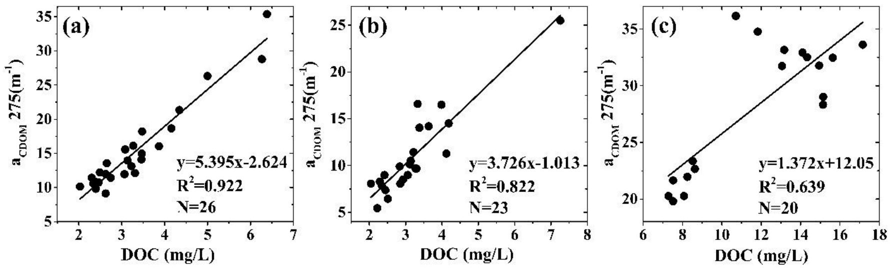

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Fig.6. Relationship between DOC and $a_{CDOM}(440)$ in different types of inland waters, (a) fresh water lakes, (b) saline water lakes, (c) river and stream waters, (d) urban waters, (e) ice covered lake underlying waters, and (f) ice melting waters.

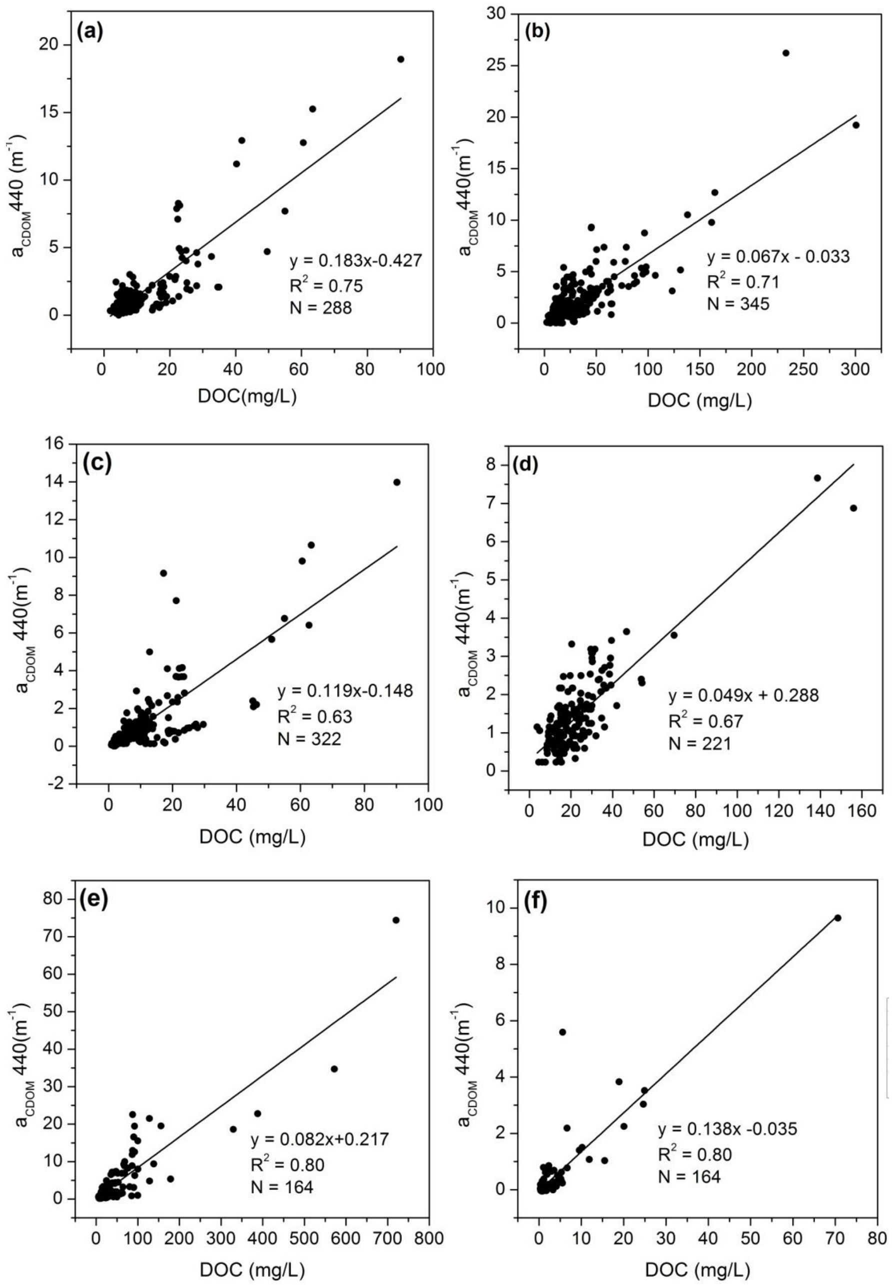

Fig.7. Comparison of (a) SUVA254, and (b) M (a_{250}:a_{365}) values in various types of inland waters. FW, fresh lake water; SW, saline lake water, RW, river or stream water; UW, urban water; WW, ice covered winter water from Northeast China; IMW, ice melt water from Northeast China.

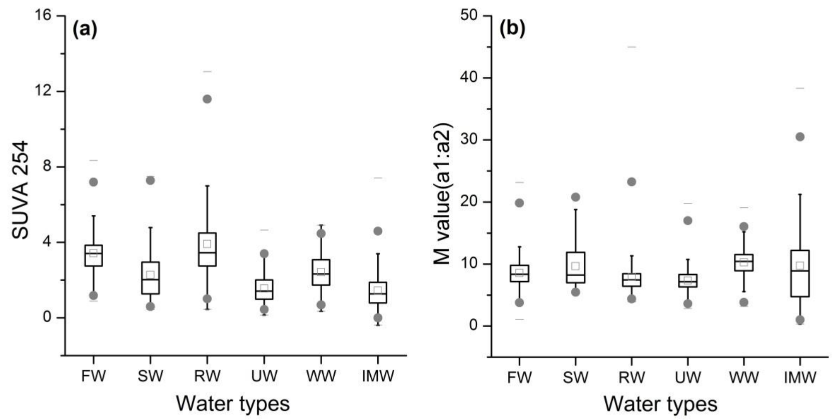

Fig.8. Relationship between DOC and $a_{CDOM}275$ sorted by M ($a_{CDOM}250/365$) values ranges, (a) M <4.0, (b) 4.0< M<6.0, (c) 6.0< M< 7.0, (d) 7.0< M< 8.0, (e) 8.0< M< 10.0, (f) 10.0< M< 12.0, (g) 12.0< M< 20.0, and (h) 20.0< M< 68.0.

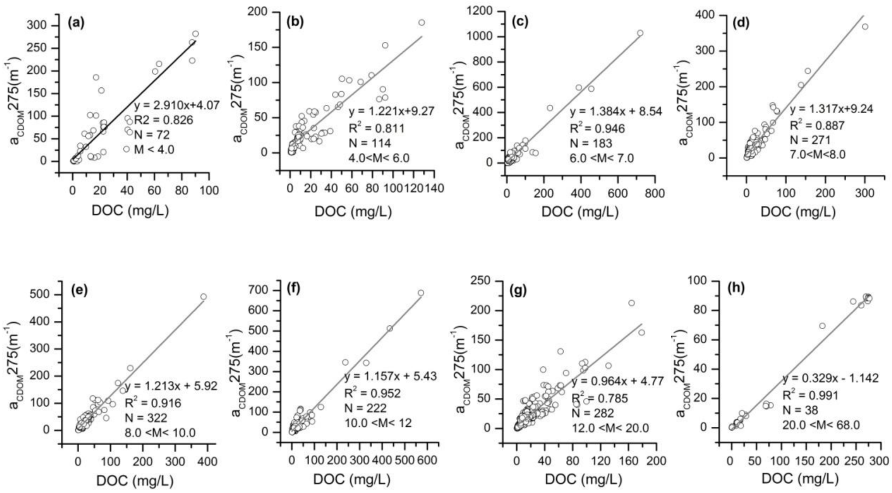

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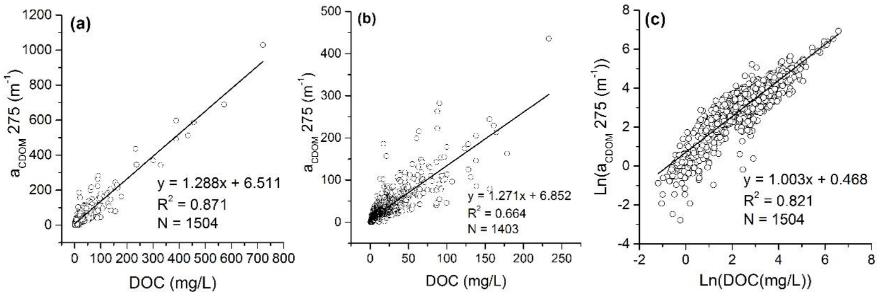
Fig.9. the relationships between $a_{CDOM}275$ and DOC concentrations. (a) regression model with pooled dataset; (b) regression model with DOC concentration less than 300 mg/L; (c) regression model with natural logarithmic transformed data.



Tables

Table 1. Water quality in different types of waters, DOC, dissolved organic carbon; EC, electrical conductivity; TP, total phosphorus; TN, total nitrogen; TSM, total suspended matter; Chl-a, chlorophyll-a concentration.

		DOC (mg/L)	EC μs/cm	pH	TP (mg/L)	TN (mg/L)	TSM (mg/L)	Chl-a (μg/L)
FW	Mean	10.2	434.0	8.2	0.5	1.6	67.8	78.5
	Range	1.9-90.2	72.7-1181.5	6.9-9.3	0.01-10.4	0.001-9.5	0-1615	1.4-338.5
SW	Mean	27.3	4109.4	8.6	0.4	1.4	115.7	9.0
	Range	2.3-300.6	1067-41000	7.1-11.4	0.01-6.3	0.6-11.0	1.4-2188	0-113.7
RW	Mean	8.3	10489.1	7.8-9.5	-	-	-	-
	Range	0.9-90.2	3.7-1000	8.6	-	-	-	-
UW	Mean	19.44	525.4	8.0	3.4	3.5	50.5	38.9
	Range	3.5-123.3	28.6-1525	6.4-9.2	0.03-32.4	0.04-41.9	1-688	1.0-521.1
WW	Mean	67.0	1387.6	8.1	0.7	4.3	181.5	7.3
	Range	7.3-720	139-15080	7.0-9.7	0.1-4.8	0.5-48	9.0-2174	1.0-159.4
IMW	Mean	6.7	242.8	8.3	0.19	1.1	17.4	1.1
	Range	0.3-76.5	1.5-4350	6.7-10	0.02-2.9	0.3-8.6	0.3-254.6	0.28-5.8

Note: FW, fresh water lake; SW, saline water lake, RW, river or stream water; UW, urban water; WW, ice covered winter water from Northeast China; IMW, ice melt water from Northeast China.

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Table 2. Descriptive statistics of dissolved organic carbon (DOC) and $a_{CDOM}(440)$ in various types of waters.

Type	Region	DOC				$a_{CDOM}(440)$			
		Min	Max	Mean	S.D	Min	Max	Mean	S.D
River	Liaohe	3.6	48.2	14.3	9.49	0.46	3.68	0.92	0.58
	Qinghai	1.2	8.5	4.4	1.96	0.13	2.11	0.54	0.63
	Inner M	16.9	90.2	40.4	24.84	0.32	7.46	1.03	2.11
	Songhua	0.9	21.1	8.1	4.96	0.32	18.93	3.2	4.19
Saline	Qinghai	1.7	130.9	67.9	56.7	0.13	0.86	0.36	0.23
	Hulunbir	8.4	300.6	68.5	69.2	0.82	26.21	4.41	4.45
	Xilinguo	3.74	45.4	14.2	8.8	0.36	4.7	1.34	0.88
	Songnen	3.6	32.6	16.4	7.4	0.46	33.80	2.4	3.78

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Table 3. Fitting equations for DOC against $a_{CDOM}(275)$ in different types of waters except ice covered lake underlying water and ice melting waters.

Water types	Region or Basin	Equations	R^2	N
Freshwater lakes	Northeast Lake Zone	y = 3.13x-3.438	0.87	102
	North Lake Zone	y = 2.16x-1.279	0.90	63
	East Lake Zone	y = 1.98x+7.813	0.66	69
	Yungui Lake Zone	y = 1.295x-44.56	0.71	54
Saline lakes	Songnen Plain	y = 2.383x+1.101	0.92	159
	East Mongolia	y = 1.791x+8.560	0.67	57
	West Mongolia	y = 1.133x+3.900	0.81	46
	Tibetan Plateau	y = 0.864x+2.255	0.84	83
Rivers or streams	Branch of the Nenjiang River	y = 7.655x-42.64	0.81	33
	Songhua River stem	y = 3.759x-6.618	0.71	29
	Branch of Songhua River	y = 8.496x-12.14	0.98	33
	Liao River Autumn 2012	y = 1.099x+3.900	0.80	38
	Liao River Autumn 2013	y = 1.073x-4.157	0.88	28
	Liao River Spring 2013	y = 2.262x-10.32	0.85	25
	Rivers from North China	y = 3.154x-1.207	0.87	48
	Rivers from East China	y = 3.037x-2.585	0.88	47
	Rivers from Tibetan	y = 2.345x+2.375	0.87	41
Urban waters	Waters from Changchun	y = 2.471x-2.231	0.54	48
	Waters from Harbin	y = 1.413x-4.521	0.67	31
	Waters from Beijing	y = 0.874x+11.12	0.63	27
	Waters from Tianjin	y = 0.994x + 7.368	0.57	23