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Influence of environmental factors on spectral characteristic of chromophoric dissolved organic matter (CDOM) in Inner Mongolia Plateau, China

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Abstract

Spectral characteristics of chromophoric dissolved organic matter (CDOM) were examined in conjunction with environmental factors in the waters of 22 rivers and 26 terminal waters in Hulun Buir plateau, northeast China. Dissolved organic carbon (DOC), total nitrogen (TN), and total phosphorous (TP) were significantly higher in terminal waters than rivers waters ($p < 0.01$). Principal component analysis (PCA) indicated that non-water light absorption and anthropogenic nutrient disturbances might be the causes of the diversity of water quality parameters in Hulun Buir plateau. CDOM absorption in river waters was significantly lower than terminal waters ($p <$ 0.01). Analysis of ratio of absorption at 250–365 nm ($E_{250:365}$), specific UV absorbance ($SUVA_{254}$), and spectral slope ratio (S_r) indicated that CDOM in river waters had higher aromaticity, molecular weight, and vascular plant contribution than in terminal waters. Furthermore, results showed that DOC concentration, CDOM light absorption, and the proportion of autochthonous sources of CDOM in plateau waters were all higher than in other freshwater rivers reported in the literature. The strong evapoconcentration, intense ultraviolet irradiance and landscape features of Hulun Buir plateau may be responsible for the above phenomenon. Redundancy analysis (RDA) indicated that the environmental variables TSM, TN, and EC had a strong correlation with light absorption characteristics, followed by TDS and chlorophyll *a*. In most sampling locations, CDOM was the dominant non-water light-absorbing substance. Light absorption by non-algal particles often exceeded that by phytoplankton in the plateau waters. Study of these optical-physicochemical correlations is helpful in the evaluation of the potential influence of water quality factors on non-water light absorption in cold plateau water environments. And the study on organic carbon in plateau lakes had a vital contribution to global carbon balance estimation.

HESSD
12, 5895–5929, 2015

1 Introduction

Chromophoric dissolved organic matter (CDOM) is the colored component of dissolved organic matter (DOM) in the natural waters environment. CDOM is principally contributed by terrestrial inputs and river discharge in coastal waters. Phytoplankton excretion, zooplankton and bacterial metabolism are the major CDOM sources in aquatic ecosystems (Coble, 2007). As an important constituent of DOM, which is the largest reservoir of organic carbon on Earth, CDOM plays a vital role in the global carbon cycle (Gonnelli et al., 2013; Mopper and Kieber, 2002). More importantly, CDOM absorbs solar radiation in the UV and visible ranges of the light spectrum to shield biota from harmful UV radiation, and it is largely responsible for the bio-optical properties of natural water (Organelli et al., 2014). The absorption characteristic of CDOM also influences the inversion accuracy of remote sensing of chlorophyll *a* (chl *a*) and other suspended solids (Siegel et al., 2005; Song et al., 2014).

Spectral analysis of CDOM (absorption and fluorescence) has been used to trace its origin and chemical composition (Stedmon et al., 2000; Vodacek et al., 1997; Xie et al., 2014). Understanding the spectral characteristics of CDOM may help to understand DOM cycling in aquatic ecosystem. According to previous studies, the light absorption of CDOM often decreases in a near-exponential manner with increasing optical wavelength (Coble, 2007; Zhang et al., 2010). In order to characterize the properties of CDOM from absorption spectra, several spectral indices have been developed. The ratio of absorption at 250–365 nm ($E_{250:365}$) was used to track changes in the size of DOM molecules (De Haan and De Boer, 1987); specific UV absorbance ($SUVA_{254}$) was found to have strong correlation with DOM aromaticity as measured by ^{13}CNMR spectroscopy (Weishaar et al., 2003); two optical parameters, the absorption coefficients at specific wavelengths λ nm ($a_{CDOM}\lambda$) and CDOM spectral slopes (S), are universally recognized proxies of CDOM concentration and molecular origin (Helms et al., 2008). Furthermore, S may also correlate with the ratio of fulvic acid (FA) to humic acid (HA). In fact, the use of S is dependent on the calculated wavelength intervals, and

HESSD
12, 5895–5929, 2015

the ratio of the slope (S_r), as a dimensionless parameter, could avoid the limitations of spectral wavelength measurements (Helms et al., 2008; Spencer et al., 2012). The analysis of these spectral indices was useful for understanding spatial and temporal CDOM variations in the aquatic environment.

Recent studies have proven that CDOM in aquatic ecosystems exerts an impact on ecosystem productivity, optical properties of water, and biochemical processes (Zhang et al., 2007). However, regional CDOM characteristics are still not thoroughly understood in diverse aquatic environments because of various physico-chemical parameters of water (Findlay and Sinsabaugh, 2003). Many water quality parameters have been proposed to affect the temporal and spatial variation of CDOM, and some correlations among them have been established; a significant positive correlation was found between dissolved organic carbon (DOC) and CDOM absorption coefficients, and a series of different models were established based on this correlation in Lake Taihu (Zhang et al., 2007), the Yangtze River (Zhang et al., 2005), and the Georgia river in the USA (Yacobi et al., 2003). CDOM strongly absorbs in the blue spectral region, which interferes with the determination of chl *a* concentration by remote image sensing (Siegel et al., 2005), therefore the relationship between the spectral characteristics of CDOM with chl *a* concentration has received widespread attention. A significant linear relationship between a_{CDOM} (300) and chl *a* concentrations was identified in the central eastern Mediterranean Basin (Bracchini et al., 2010), the Atlantic Ocean (Kitidis et al., 2006), and the Baltic Sea (Kowalczuk et al., 2006), but a_{CDOM} (440) was loosely related to pigment concentrations in the 0–400 m depth layer of NW Mediterranean Sea (Organelli et al., 2014). Furthermore, the relationship between $a_{\mathrm{CDOM}}(\lambda)$ and other physico-chemical parameters of water, such as total nitrogen (TN), total phosphorous (TP), salinity, and extracellular enzyme activities (Gonnelli et al., 2013; Kowalczuk et al., 2006; Niu et al., 2014; Phong et al., 2014), were all investigated in different aquatic environments. However, these studies reached different conclusions due to regional variations in water quality.

Studies published to date have focused on the relationship between CDOM properties and environmental factors; results indicate that salinity, solar radiation, and watershed characteristics all have important effects on CDOM optical properties (Graeber et al., 2012; Gueguen et al., 2011; Mavi et al., 2012; Song et al., 2013b). The properties of CDOM in plateau water at high altitude have attracted interest due to the unique natural environmental and climatic features of these waters. The DOM composition intwo Tibetan alpine lakes showed a limited terrigenous DOM and exhibited a high biolability of DOC (Spencer et al., 2014). The analysis of CDOM parameters in three intermontane plateau rivers in western US indicated that autochthonous DOM or DOM derived from anthropogenic sources dominated the DOM pool (Spencer et al., 2012). However, the relationship of CDOM to environmental factors in plateaus area has been less well studied. Analysis of these optical-physicochemical correlations is critical for understanding the source and distribution of CDOM in plateau water environments and evaluating the potential influence of water quality factors on non-water light absorption.

Inner Mongolia Plateau in China is located in an arid and cold climate zone with sparse annual rainfall. The plateau is covered with numerous lakes surrounded by vast grasslands and forest. These lakes are located far away from the ocean and are supplied with water by precipitation and river runoff, and most of them are noncontributing lakes (Tao et al., 2015). The unique geographical environment and climatic factor in arid and cold plateau regions may lead to alterations in CDOM properties compared with the bulk of inland water. Moreover, over 80 % of the lakes are saline, which allows higher carbon storages levels than fresh water lakes (Duarte et al., 2008; Song et al., 2013b). The plateau lakes therefore play an important role in global carbon balance estimation.

In this study, we investigated CDOM in lakes and rivers in Inner Mongolia plateau with the following objectives: (1) characterization of the distribution and spectral characteristic variations of CDOM in plateau rivers and terminal waters in cold and arid regions; (2) assessing the relationships between CDOM optical properties and relevant physico-chemical parameters of water; and (3) evaluating the contribution of CDOM to the total non-water light absorption. The information obtained in this study enhances our understanding of CDOM variation with respect to environmental conditions in inland waters in arid and cold plateau region. The optical-physicochemical correlation analysis could contribute to improved understanding and allow the use of satellite remote sensing imagery in this area.

2 Material and methods

2.1 Study sites

Inner Mongolia Autonomous Region is located in the north of China with an area of about 1.18 million km^2 (37°24′–53°23′ N, 97°12′–126°4′ E). The average altitude of the whole region is over 1000 m, and it is basically a plateau landform composed of Hulun Buir, XilinGol, Ulanqab, Bayannur, Alxa, and Erdos plateaus. Rivers, lakes, reservoirs and other surface water areas account for 0.8 % of the whole area. All the collected water samples were taken from Hulun Buir Plateau (Fig. 1). This plateau is characterized by a typical semi-humid and semi-arid continental monsoon climate with intensive solar radiation throughout the year. Hulun Buir Plateau has distinct seasons with a windy spring, a hot and rainless summer, a windy and short autumn, and a cold dry winter. The plateau is dotted with numerous lakes surrounded by vast grasslands and forests, and the two largest freshwater lakes (Hulun Lake and Buir Lake) of Inner Mongolia are located in this area. Most lakes in this area are inland stagnant lakes filled with terminal waters due to the particular climate and geographic location. Several rivers flow through Hulun Buir Plateau, including the Kerulen, Ergun, Wuerxun, Hailar, and Zhadun Rivers. Wuerxun River originates from Buir Lake's northern shore, flows north and empties into Hulun Lake. Kerulen River flows east through Hulun Lake, and finally into the Ergun River. The Zhadun River flows into the Hailar River, flowing north to join the Ergun River. A total of 22 river waters and 24 terminal waters were

HESSD
12, 5895–5929, 2015

collected in this study with respect to both watershed characteristics and lake size. Because Hulun Lake and Buir Lake are connected with rivers, and the water samples are classified as river water samples in the subsequent analysis in this study.

2.2 Water sampling and water quality measurement

Water samples were taken from 46 sampling sites in Hulun Buir Plateau, China, during September 2012 (Fig. 1). The surface water (0.5–1 m) sample was collected at each site approximately 4 L and carried back to laboratory in a portable refrigerator within 24 h. Chemical and physical parameters, e.g., pH, total dissolved solid (TDS) and EC were determined in sampling situ by a portable multi-parameter water quality analyzer (YSI6600, US). Concentrations of DOC, TN, and TP were measured with unfiltered water samples by a standard procedure (APHA et al., 1998). Total suspended matter (TSM) was determined by gravimetrical analysis (Song et al., 2013a). Water turbidity (Turb) was determined by a UV spectrophotometer in 680 nm (Shangfen, 7230) with Milli-Q water as reference at room temperature ($20 \pm 2\,^{\circ}$C). Chlorophyll *a* (chl *a*) was extracted from water samples by 90 % buffered acetone solution, and the concentrations were determined with a UV spectrophotometer (Shimadzu, UV-2600PC) by the method detailed in Song et al. (2013a).

2.3 Non-water light absorption analysis

CDOM was extracted from the collected water samples by filtering through a 0.7 µm glass fiber membrane (Whatman, GF/F 1825-047) and then was further filtered through 0.22 µm polycarbonate membrane (Whatman, 110606). The filtering process was finished with 2 days in order to avoid alteration by microbial activity. CDOM absorption was analyzed within 12 h throughout UV-2600 spectrophotometer quipped using 1 cm quartz cuvette. Absorbance scans were performed from 200 to 800 nm, and Milli-Q water was used as reference. In order to eliminate the internal backscattering, the absorbance at 700 nm was used to correct absorption coefficients (Bricaud et al.,

HESSD
12, 5895–5929, 2015

1981). The absorption coefficient (a_{CDOM}) was calculated from the measured water optical density (OD) following the Eq. (1).

$$a_{CDOM}(\lambda') = 2.303 \cdot OD_\lambda / L \quad (1)$$

where L is the cuvette path length (0.01 m) and 2.303 is the conversion factor. OD_λ is the average optical density. The absorption coefficients at wavelengths 335 nm (a_{CDOM}335) and 440 nm (a_{CDOM}440) were selected to express the CDOM concentration (Miller, 1998). CDOM absorption ratio ($E_{250:365}$) was calculated using absorbance at 250 nm and 365 nm. $SUVA_{254}$ values were calculated by dividing the UV absorbance at 254 nm by the DOC concentration (mg L^{-1}) (Weishaar et al., 2003).

CDOM spectral slopes ($S_{275–295}$ and $S_{350–400}$) between wavelengths 275–295 nm and 350–400 nm were both calculated using a nonlinear fit of an exponential function to the absorption spectrum according to the Eq. (2) (Bricaud et al., 1981; Jerlov, 1968).

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0) \cdot e^{S(\lambda_0-\lambda)} \quad (2)$$

Where a_{CDOM} (λ) is the CDOM absorption at a given wavelength, and a_{CDOM} (λ_0) is the absorption at a reference wavelength (440 nm). The spectral slope ratio (S_r) was calculated as the ratio of $S_{275-295}$ to $S_{350-400}$.

Particulate absorption was determined by quantitative membrane filter technique (QFT) (Cleveland and Weidemann, 1993). A certain volume of water was filtered through 0.7 µm glass fiber membrane (Whatman, GF/F 1825–047), and the light absorption of total particulate trapped on the filter membrane was determined by UV spectrophotometer (Shimadzu, 2660) with virgin wet membrane as reference. After correction of the path length with path length amplification factor (β), the measured optical densities were transformed into total particulate absorption coefficients according to the Eq. (3) (Bricaud and Stramski, 1990).

$$a_{PB}(\lambda) = 2.303 \cdot \frac{S}{V} \cdot OD_S(\lambda) \quad (3)$$

HESSD
12, 5895–5929, 2015

Where a_{PB} (λ) is the total particulate absorption at a given wavelength (nm), S is the effective area of the deposited particle on the fiber membrane (m^2), and V is the volume of the filtered water (m^3).

The above fiber membranes loaded with total particulate were soaked in the sodium hypochlorite solution in order to remove the pigments, and the light absorption coefficient of non-algal particles ($a_{NAP}\lambda$) was determined and calculated as the $a_{PB}(\lambda)$. The phytoplankton light absorption coefficient ($a_{phy}\lambda$) was the difference between $a_{PB}(\lambda)$ and $a_{NAP}(\lambda)$ according to the Eq. (4).

$$a_{phy}(\lambda) = a_{PB}(\lambda) - a_{NAP}(\lambda) \tag{4}$$

2.4 Statistical analysis

The contributions of CDOM, phytoplankton, and non-algal particles (NAP) to non-water light absorption at 440 nm were calculated using Origin 8.0 software (Ortega-Retuerta et al., 2010). The variation of water quality parameters in different sampling locations was assessed by principal component analyses (PCA) using CANOCO 4.5 for Windows with centered and standardized variables. Correlations between water quality parameters and light absorption characteristics were determined by Redundancy analysis (RDA) using CANOCO 4.5, and water quality parameters were selected as explanatory variables. The regression coefficient was calculated using SPSS 5.0. Because the responding variables may exist in the high autocorrelation, they were first screened through Canonical Correspondence Analysis (CCA) to remove the variables with an inflation coefficient greater than 20. A Monte Carlo permutation test was conducted and indicated that the selected environmental variables were significantly related to light absorption characteristics (499 permutations under the reduced model, $p \leq 0.05$).

3 Results

3.1 Water quality

The collected river and terminal water samples exhibited large variations in water quality (Table 1). A significant difference of DOC was also observed between these two water types ($p < 0.001$). The DOC concentration ranged from 8.44 to 39.74 $mg L^{-1}$ in river waters, and exhibited higher values in the terminal waters (23.03–300.5 $mg L^{-1}$). Further, the terminal waters also had higher alkalinity and EC than river waters. The positive relationship between DOC and alkalinity was established in Hulun Buir Plateau waters (Fig. 2a, $R^2 = 0.94$). Regression analyses were also conducted, and a linear relationship between EC and DOC was shown based on the collected data (Fig. 2b; $R^2 = 0.50$). The average nutrient concentrations for TN (1.33 ± 0.63 $mg L^{-1}$) and TP (0.11 ± 0.04 $mg L^{-1}$) in river waters were both lower than in terminal waters, and significant differences were observed for TN ($p < 0.001$) and TP ($p < 0.01$). Strong linear relationships were shown between TN and DOC in Hulun Buir Plateau (Fig. 2c; $R^2 = 0.68$). A positive correlation between DOC and TP was found in surface water in this area (Fig. 2c; $R^2 = 0.82$).

PCA was performed for all the sampling locations with ten water environment variables (Fig. 3a). The first two principal components (PC) of the PCA explained 61.0 % of the variability in all the selected variables (PC1, 36.4 %; PC2, 24.6 %). Relatively high loadings on PC1 were TSM and Turb, whereas DOC and CDOM showed high negative loadings. The second PCA axis revealed gradients of nutrients (TN and TP). These all had positive loadings on PC2. Furthermore, TDS and chl *a* showed high negative loadings on PC2. A clear difference was found between river waters and terminal waters (Fig. 3b). Terminal water samples clustered in close proximity to each other and were distributed on the negative side of PC2 (with the exception of one point) in Fig. 3b, and river waters clustered almost exclusively on the positive side of PC2.

3.2 Spectral characteristics of CDOM

CDOM absorption spectra of the waters collected from Hulun Buir Plateau decreased as the classical near-exponential manner with increasing wavelengths from the ultraviolet to the visible spectral region. This near-exponential CDOM absorption spectra has been observed in many natural waters (Bricaud et al., 1981; Spencer et al., 2009; Xie et al., 2014). The comparative analysis was conducted in two types of sampling waters in the study, and the mean values of a_{CDOM} (335) and a_{CDOM} (440) both showed that the terminal waters exhibited significantly higher CDOM light absorption than river waters (Table 1).

$E_{250:365}$ values in the waters examined ranged from 5.43 to 20.73, and the mean values were 7.80 ± 2.30, and 8.02 ± 3.48 in the river and terminal waters respectively. The majority of the SUVA_{254} values in the river waters ranged from 1.09–3.56 $\mathrm{L\,mg\,C^{-1}\,m^{-1}}$, and the mean SUVA_{254} was clearly higher in river waters ($2.74 \pm 1.08\,\mathrm{L\,mg\,C^{-1}\,m^{-1}}$) than the terminal waters ($1.90 \pm 0.57\,\mathrm{L\ mg\ C^{-1}\,m^{-1}}$), and this was significant ($p < 0.01$). In order to confirm the source and composition of CDOM in different types of waters, the spectral slopes in the 275–295 nm ($\mathrm{S}_{275\text{–}295}$) and 350–400 nm ($\mathrm{S}_{350\text{–}400}$) ranges were both calculated as the indicators (Table 1). $S_{275\text{–}295}$ values showed a wide variation in the river water samples ranging from 14.80×10^{-3} to $26.79 \times 10^{-3}\,\mathrm{nm^{-1}}$ (mean = $19.25 \pm 4.05 \times 10^{-3}\,\mathrm{nm^{-1}}$), and the majority of river waters in the study exhibited $S_{275\text{–}295}$ between $17.11\text{–}17.82 \times 10^{-3}\,\mathrm{nm^{-1}}$. There was not a significant difference when compared with terminal waters. $S_{350\text{–}400}$ values also showed no significant difference between the two types of waters. Furthermore, the mean values of $S_{275\text{–}295}$ and $S_{350\text{–}400}$ in Hulun Lake were both lower than Buir Lake.

3.3 Light absorption of CDOM and particulates

Detailed knowledge regarding the relative contributions of CDOM, phytoplankton and non-algal particles to the total non-water light absorption are essential in bio-optical and biogeochemical models, and the relative contributions at 440 nm are shown in Fig. 4. There was no obvious difference in the relative contributions of CDOM, phytoplankton and non-algal particles between river waters and terminal waters ($p >$ 0.5). At all the sampling locations, the mean contribution of CDOM to the total non-water light absorption was 52.78 % with the range varied from 2.87 to 97.23 %, and the relative contribution of non-algal particles was on mean 39.84 %, ranging from 2.01 up to 97.13 %. Phytoplankton absorption played a minor role in total non-water light absorption with the mean 7.61 %. In most water samples examined in this study, CDOM was the dominant non-water light-absorbing substance.

To assess the distribution of light absorption in the waters of Hulun Buir Plateau, levels of light absorption due to CDOM, phytoplankton and non-algal particles were plotted based on the numbers of sampling locations and their contributions to total light absorption at 440 nm using a Pareto–Lorenz curve (Lorenz, 1905). The relative contributions were arranged from high to low. Subsequently, the cumulative sampling points are represented on the abscissa axis, and the cumulative contributions plotted on the vertical axis. The more the curve deviated from the theoretical perfect evenness line (45° diagonal), the more inhomogenous light contributions were observed (Fig. 5). According to the Pareto principle, the value of vertical axis was in accordance with 20 % abscissa axis, being used to interpret the Pareto- Lorenz curves. From the degree of curve deviation (Fig. 5), it was observed that the light absorption of optically active substances in Hulun Buir Plateau area presented inhomogenous phenomena. Among them, CDOM absorption was the most representative relative to other non-water absorption components. CDOM light absorption by 20 % of the samples corresponded with 5.03 % of the cumulative CDOM contributions to non-water absorption. For non-algal particles and phytoplankton, 20 % of the samples corresponded with 1.46 and 0.51 % of cumulative light absorption contributions, respectively. Thus, for all the non-water absorption types, it was observed that CDOM light absorption was numerically dominant compared with non-algal particles and phytoplankton.

HESSD
12, 5895–5929, 2015

3.4 Correlations between water quality parameters and light absorption

The RDA data showed that the forward selected explanatory variables could explain the variability of light absorption characteristics with species-environment correlations of 0.781 (Fig. 6). The first two axes of RDA explained 43.7 % of total variability in light absorption characteristics of all the collected water samples (axis 1, 34.3 %; axis 2, 9.4 %). Coefficients between environmental variables with axes in RDA indicated that TSM, TN, and EC had a strong correlation with light absorption characteristics, followed by TDS and chl *a*. TDS, TP, and DOC were most closely corrected to CDOM light absorption (Fig. 6). TSM, TN, and chl *a* were best correlated to light absorption of phytoplankton, non-algal particulates, and total particulates at 440 nm (Fig. 6). EC and pH were related to the CDOM spectral slope ($S_{275\text{–}295}$) (Fig. 6).

The Pearson correlation coefficients (r_p) between water quality and light absorption characteristics presented in Table 2 indicate that CDOM light absorption ($\alpha_{\text{CDOM}}335$ and $\alpha_{\text{CDOM}}440$) showed a significantly positive correlation with TN, TP, TDS, and DOC ($p < 0.01$), but had no correlation with chl *a* concentration ($p > 0.05$, $n = 46$). There was also no correlation between $S_{275\text{–}295}$ and chl *a* concentration. However, $S_{275\text{–}295}$ presented a significantly positive correlation with DOC, pH, and EC in this plateau water ($p < 0.01$, $n = 46$). Light absorption of pigments at 440 nm showed a significantly positive correlation with TN ($r_p = 0.377$, $p < 0.01$, $n = 46$) and TSM ($r_p = 0.515$, $p < 0.01$, $n = 46$), and there was also no linear relationship with chl *a* concentration. The light absorption at 440 nm of total particulates and non-algal particulates both had a significant positive correlation with TSM ($r_p = 0.985$, $p < 0.01$, $n = 46$).

HESSD
12, 5895–5929, 2015

4 Discussion

4.1 Dissolved organic carbon in river and terminal waters

Previous studies showed that DOC concentrations in inland waters always decrease with the prolongation of water residence times due to biodegradation and photobleaching in humid regions (Curtis and Adams, 1995). However, terminal waters with long water residence times exhibited higher DOC values than the river waters in this study. The most likely explanation for the opposite pattern of DOM concentration is that the most refractory DOC is diluted in humid regions and evapoconcentrated in semi-arid regions (Song et al., 2013b). Further, the higher alkalinity and EC in the terminal waters compared with river waters may explain the inverse pattern (Table 1). The sodicity of water could also increase DOM solubility. Increasing EC (salt concentration) would result in decreased osmotic potential, which has negative effects on microbial activity (Mavi et al., 2012). DOM along with other nutrients come from soil via runoff and leaching, and can accumulate in terminal waters due to lower microbial activity. Furthermore, the average DOC concentration in rivers ($25.99 \pm 6.64\,\mathrm{mg\,L^{-1}}$) is obviously higher than in rivers reported in other studies (Song et al., 2013b; Spencer et al., 2012, 2010). DOC levels in rivers are linked to climate and watershed landscape characteristics (Jiang et al., 2014). The elevated DOC concentrations in these plateau rivers could be attributed to evaporation, which would be expected to be extreme in the arid environment of Inner Mongolia Plateau. Furthermore, Inner Mongolia region is located in semiarid climatic zones with low rainfall, and the impoundment of these plateau waters mainly depended on surface runoff. The land use types around the sampling locations were mainly grassland and forest. The high DOC concentration in the waters highlights the organic-rich nature of these ecosystems.

Many monitoring data indicate that DOC concentration in rivers shows a tendency to increase year by year, potentially due to acid deposition (Evans et al., 2005; Monteith et al., 2007). DOC concentrations in surface water are depressed when acid anion concentrations are high, and increase as acidic anion concentrations decrease (Evans

HESSD
12, 5895–5929, 2015

et al., 2005). The response of water parameters to acid deposition would be apparent in the alkalinity measurements. In this study, the positive relationship between DOC and alkalinity indicated that an empirical model might be established in Hulun Buir Plateau waters for estimating DOC storage based on water alkalinity, with calibration by a comprehensive dataset. Within semi-arid regions, DOC was always related to salinity, which could reflect the water residence times and dissolved organic matter accumulation (Curtis and Adams, 1995; Song et al., 2013b). A positive correlation between DOC and EC was established based on the collected data (Fig. 2b; R^2 = 0.50). A positive correlation between DOC and EC was also reported in semi-arid east-central Alberta, Canada (Curtis and Adams, 1995). More than 80 % of lakes in Inner Mongolia Plateau are saline lakes, and the salinity in the collected waters was generally higher. Prior research has shown that inland saline lakes always contain higher concentrations of DOC in semi-arid region (Arts et al., 2000). Also, concentrations of DOC in various waters were found to increase with salinity in semi-humid/semi-arid regions in China (Song et al., 2013b).

Relationship between CDOM properties and nutrients (TN and TP) may be used to track the plant-derived source. Strong linear relationships were shown between nutrients (TN and TP) and DOC in the surface waters of Hulun Buir Plateau (Fig. 2c, Fig. 2d). The types of land use around the water sampling locations may be a crucial to the nutrition levels in the waters. The main land types in Hulun Buir Plateau were grassland and forest with high nitrogen and organic matter content. A similar relationship between TN and DOC was also shown during rainfall in agricultural and forested wetlands in the Shibetsu watershed, Japan (Jiang et al., 2014). Investigations of 14 boreal and temperate regions of Québec (Canada) with 198 different lakes showed that when TP concentrations were at very low level, DOC and TP fitted linear regressions on log-transformed data ($r^2 = 0.34$, $p < 0.001$) (Lapierre and del Giorgio, 2012). We suspect that these relationships may be connected with the escape of CO_2 from the waters. TN and TP concentrations could affect the respiration and reproduction of microbes and phytoplankton leading to the conversion of DOC to CO_2, which could have a pronounced influence on the relationship between nutrient and organic matter (Findlay and Sinsabaugh, 2003). This speculation needs more data investigation and statistical analysis to verify it further.

PCA was performed in order to explain the variations in water quality in the different sampling waters (Fig. 3). From the locations of the variables in Fig. 3a, PC1 could be involved in the non-water light absorption, which may be one important factor that distinguishes particulate light absorption from CDOM light absorption. TN and TP with positive loadings on PC2 indicated that PC2 may be related to anthropogenic nutrient disturbance. The close juxtaposition of TDS and chl *a* shown in Fig. 3a indicated that TDS concentration may be linked to phytoplankton metabolism. The PCA also indicated that non-water light absorption and anthropogenic nutrient disturbance might be the causes of the diversity of water quality in different sampling locations.

4.2 Analysis of CDOM spectral characteristic

Terminal waters exhibited significantly higher CDOM light absorption than river waters (Table 1). Terminal waters in the study were almost brackish water with high EC value ($> 1000\,\mu s\,cm^{-1}$) (Song et al., 2013b). Researchers reported that the structure and composition of DOM alters obviously after flowing into saline lakes (Waiser and Robarts, 2000). The use of $E_{250:365}$ for the tracking of changes in CDOM molecule size has been practically demonstrated by many researchers (Helms et al., 2008; Song et al., 2013b). Increasing $E_{250:365}$ values indicate a decrease in aromaticity and molecular weight (MW) of CDOM, and the results of this study showed that CDOM in river waters had higher aromaticity and MW than terminal waters. The relatively low CDOM MW in terminal waters implied that chromophores associated with high MW CDOM were destroyed by photolysis with the prolongation of hydraulic retention time and irradiation. In terminal waters, the change of molecular structure in high MW CDOM caused by bond cleavage, resulted in its transformation to a low MW pool. Furthermore, previous studies showed that the bulk of $E_{250:365}$ mean values in 30 US rivers ranged from 5.00 to 6.50 (Spencer et al., 2012), and in the Elizabeth River and

HESSD
12, 5895–5929, 2015

Chesapeake Bay estuary ranged from 4.33 to 6.23 (Helms et al., 2008). Compared with the reported river waters, the plateau rivers in the study presented significantly higher mean $E_{250:365}$ values. The intense solar irradiance in this region potentially enhances the photochemical degradation of allochthonous DOM and high MW CDOM, causing an increase in the $E_{250:365}$ values with the production of low MW CDOM. Two rivers in the intermontane plateaus of the western US with intense solar irradiance also presented higher $E_{250:365}$ values (9.05 ± 1.47, 7.38 ± 0.84) than other plain rivers (Spencer et al., 2012).

$SUVA_{254}$ values in the river waters in this study were lower than the following rivers: mean $SUVA_{254}$ values in 30 US rivers examined ranged from 1.31 to 4.56 $\mathrm{L\,mg\,C^{-1}\,m^{-1}}$ (Spencer et al., 2012), while $SUVA_{254}$ in the Songnen Plain waters ranged from 2.3 (±0.14 SD) to 8.7 (±2.8 SD) (Song et al., 2013b), in the tropical Epulu river ranged from 3.08 to 3.57 $\mathrm{L\ mg\ C^{-1}\ m^{-1}}$ (Spencer et al., 2010). A possible driver of this CDOM characteristic in these plateau rivers is coupled evapoconcentration, photo-degradation and photobleaching with strong plateau ultraviolet radiation (Spencer et al., 2014, 2009). $SUVA_{254}$ values have been proven to have a correlation with DOM aromaticity as determined by ^{13}C-NMR (Weishaar et al., 2003). In this study, the lower $SUVA_{254}$ measurements in terminal waters indicated that the aromatic moieties of CDOM in this environment were lower compared within river waters due to the effect of photodegradation and microbial degradation with prolonged water residence times. From the conclusions of some studies on $SUVA_{254}$ and hydrophobic organic acid fraction (HPOA), the $SUVA_{254}$ values were always comparable to HPOA, and the conjecture could be reached that low $SUVA_{254}$ values indicate that the aquatic systems with little vascular plant input, and the autochthonous sources (algal or microbial) dominated the organic matter content (Spencer et al., 2008; Weishaar et al., 2003). Conversely, high $SUVA_{254}$ values indicated that the organic matter in aquatic systems was dominated by allochthonous sources with significant vascular plant inputs (Cory et al., 2007; Spencer et al., 2012). In this study, the $SUVA_{254}$ revealed that the contribution of vascular plant matter to DOM in rivers might be greater than the terminal

HESSD
12, 5895–5929, 2015

waters, and the high MW DOM was more abundant in fresh waters than terminal waters. Shorter residence time of DOM in river waters and the quick exchange rates of flow water shortened the photo-oxidation of DOM, which could be responsible for the phenomenon (Song et al., 2013b; Spencer et al., 2012).

The majority of river waters in the study exhibited significantly higher $S_{275-295}$ values than allochthonous-dominated fresh waters which include the majority of US rivers (13.00–$16.50 \times 10^{-3}\,\text{nm}^{-1}$) (Spencer et al., 2012), and the Congo River ($12.34 \times 10^{-3}\,\text{nm}^{-1}$) (Spencer et al., 2009), which indicated the proportion of autochthonous sources CDOM and photolysis of allochthonous CDOM in plateau waters was higher than freshwater rivers. The ratio of spectral slopes (S_R), an indicator of CDOM molecular weight and source (Helms et al., 2008; Spencer et al., 2010), indicated that river water samples with lower S_R values contained greater allochthonous and higher MW DOM than terminal waters. Previous studies have proven that S values were inversely proportional to CDOM MW, with a steeper spectral slope signifing decreasing aromaticity, and a shallower spectral slope signifing an increasing aromatic content (Gonnelli et al., 2013; Helms et al., 2008). S values in this study indicated that the percentage of high MW humic acid in CDOM in Hulun Lake was greater than in Buir Lake, whereas the proportion of fulvic acid and aromatic compounds showed the reverse trend. Furthermore, $S_{275-295}$ could be used as indicator for terrigenous DOC percentage in bodies of water (Gonnelli et al., 2013). Our results indicate that the percentage of terrigenous DOC is higher in Hulun Lake than Buir Lake. From the known geological history of the region, Buir Lake is a throughput lake with inflow from the Halaha river and outflow from the Wuerxun river to Hulun Lake. Also, the land use pattern in Buir Lake watersheds shows potential desertification. Hulun Lake not only accepts the Wuerxun River flowing from Buir Lake, but also receives the water from the Kerulun River. Natural grassland with the fresh organic rich layers was dominant in Hulun Lake watersheds. The geographical location and land use pattern together account for the larger percentage of terrigenous DOM in Hulun Lake.

HESSD
12, 5895–5929, 2015

4.3 Correlations between water quality parameters and light absorption

Strong positive correlations between CDOM absorption coefficients and TN, TP, and DOC concentrations in all water samples indicated that CDOM light absorbance could be explained by variations in nutrients and DOC concentration to a greater extent. Previous studies have shown that CDOM absorption in a range of spectra could be used as an proxy for DOC in many inland water bodies, including the Kolyma river basin (Griffin et al., 2011), the Epulu river (Spencer et al., 2010), as well as many US rivers (Spencer et al., 2012), and our results once again support this relationship in the aquatic environment of Hulun Buir Plateau. $S_{275-295}$ and chl *a* concentration had no correlation; a similar phenomenon has been identified in the Ligurian Sea (BOUSSOLE site) and the Mediterranean Sea (central eastern basin) (Bracchini et al., 2010; Organelli et al., 2014). These results indicated that CDOM in natural waters did not originate entirely from the release and dissociation of the phytoplankton, and that terrestrial input and microbial activities all play an important role in the generation and properties of CDOM (Ogawa et al., 2001; Rochelle-Newall and Fisher, 2002). Furthermore, strong solar radiation in the plateau area and the open ocean enhanced the photobleaching of CDOM, resulting in variation in the structural composition of CDOM. Inner Mongolian Plateau has high levels of wind and dust, and a number of lakes in the region have shrunk remarkably in recent decades (Tao et al., 2015). The shrinkage and resuspension of lakes as a result of climatic conditions may seriously influence the optical characteristics and chl *a* concentration. The significant positive correlation between light absorption with TSM may be related to the unique climate of Hulun Buir Plateau with alternating of windy, rainless, and frigid conditions, which need to be further studied.

4.4 Contribution of CDOM to light absorption

At all the sampling locations, phytoplankton absorption played a minor role on total non-water light absorption (Fig. 4). The low levels of phytoplankton in the Hulun Buir

HESSD
12, 5895–5929, 2015

Plateau lakes with higher salinity may be responsible for this phenomenon. Previous studies also showed that light absorption by non-algal particles often exceeds that of phytoplankton in shallow, inland lakes and coastal waters (Carder et al., 1991; Frenette et al., 2003). In most water samples examined in this study, CDOM was the dominant light-absorbing substance even when the CDOM absorption was minimal due to photobleaching in summer. The large contribution of CDOM to total absorption (approximately 50 % at 440 nm in the surface layer) was also shown in the Sepik River (Parslow et al., 1998). The large contribution of CDOM was also identified in other water environments, such as a fluvial lake (Frenette et al., 2003), the equatorial Pacific area (Bricaud et al., 2002), and the Ligurian Sea (Organelli et al., 2014). The above analysis indicated that the waters in Hulun Buir Plateau were Case-2 water with CDOM present in all the water samples (Morel and Prieur, 1977). According to the optical classification of surface waters (Prieur and Sathyendranath, 1981), the majority of the collected river and terminal water samples in Hulun Buir Plateau could be classified as "CDOM-type" water, and others were "NAP-type". Different catchment properties and water quality parameters could be responsible for the variation in optical classification of these waters. Other studies have shown that CDOM absorption was related to the EC of water (Sieczko and Peduzzi, 2014). EC values in rivers and lakes of Hulun Buir Plateau showed a wide range, which may affect the agglomeration or dissociation of particles and CDOM in the waters and indirectly influence light absorption. In addition, in lakes located near the paddy filed and built-up areas, water quality is greatly influenced by human activities (Graeber et al., 2012).

Pareto–Lorenz curve analysis indicated that in Hulun Buir Plateau and the similar geographical aquatic environment, we could randomly select 20 % of the collected water samples to analyze the light absorption, the contributions of optically active substances might be estimated based on these absorption values and the cumulative contributions in this study. Then the estimated value could be used to identify water type and evaluate regional homogeneity of non-water light absorption.

HESSD
12, 5895–5929, 2015

5 Conclusions

Knowledge of CDOM properties and their relationship to environmental factors in plateaus areas is not well conducted. The unique environmental conditions of plateau areas with dry and cold climates have an important effect on CDOM properties and potential implications for carbon cycling in inland water. An intensive study was conducted in Hulun Buir plateau which includes several freshwater rivers and numerous non-contributing lakes with high salinity. The study primarily provides information on the water quality and CDOM in river and terminal waters in cold and arid plateaus regions. Also it provides insight into CDOM properties linked to water quality and climate in inland water. The following conclusions were obtained: (1) A significant difference in water quality was observed between river and terminal waters in Hulun Buir plateau ($p < 0.01$). The non-water light absorption and anthropogenic nutrient disturbance might be the main causes of the wide range of water quality parameters; (2) CDOM in river waters had higher aromaticity, MW, and vascular plant contribution than in terminal waters in cold and arid plateau regions and other fresh water rivers due to the strong evapoconcentration, intense ultraviolet irradiance and plateau landscape features; (3) Environmental variables TSM, TN, and EC had a strong correlation with light absorption characteristics, followed by TDS and Chl *a* in the waters of Hulun Buir plateau. Study of the optical-physicochemical correlation is helpful for evaluating the potential influence of water quality factors on non-water light absorption in arid and cold plateau water environments, and it is useful for the understanding the satellite remote sensing data of plateau inland water.

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HESSD
12, 5895–5929, 2015

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

References

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Table 1. Water quality and CDOM absorption parameters of water samples collected in Hulun Buir plateau.

	River water (n = 22)		Terminal water (n = 24)	
	Mean	Min–Max	Mean	Min–Max
DOC	25.99 ± 6.64	8.44–39.74	83.83 ± 68.79	23.03–300.50
TN	1.33 ± 0.63	0.64–3.51	4.58 ± 3.80	1.39–19.03
TP	0.11 ± 0.04	0.06–0.23	1.52 ± 1.87	0.12–6.31
TAlk	156.22 ± 53.60	48.00–298.56	652.70 ± 642.15	96.00–2906.40
EC	325.95 ± 141.64	106.70–745.00	5729.69 ± 9715.26	1236–41 000.00
TDS	163.07 ± 70.62	53.40–372.00	743.59 ± 483.34	93.10–1505.00
Turb	20.21 ± 20.80	2.19–83.84	273.79 ± 608.75	1.75–2521.20
Chl *a*	4.62 ± 3.95	0.04–11.06	6.27 ± 11.06	0–41.07
$a_{\mathrm{CDOM}}335$	18.29 ± 9.87	4.71–40.07	36.16 ± 30.27	10.47–158.24
$a_{\mathrm{CDOM}}440$	2.68 ± 1.68	0.60–7.14	5.60 ± 5.10	0.83–26.21
$E_{250:365}$	7.80 ± 2.30	5.43–12.30	8.02 ± 3.48	5.47–20.73
SUVA_{254}	2.74 ± 1.08	1.08–4.79	1.90 ± 0.57	0.79–3.74
$S_{275-295}$	0.019 ± 0.004	0.015–0.027	0.02 ± 0.004	0.015–0.031
S_{R}	1.00 ± 0.17	0.73–1.35	1.05 ± 0.09	0.91–1.25

TN, TP, TDS, TSM, TAlk and DOC represent total nitrogen, total phosphorus, total dissolved solids, total suspended matter, total alkalinity and dissolved organic carbon concentration, respectively (mg L^{-1}). Turb represents water turbidity (NTU), and EC represents the electrical conductivity of water samples (µs cm^{-1}). Chl *a* is chlorophyll *a* concentration (µg L^{-1}). The unit SUVA_{254} was L mg C^{-1} m^{-1}.

Table 2. Pearson correlation coefficients for general water quality and light absorption properties.

	a_{CDOM} (335)	a_{CDOM} (440)	a_{PB} (440)	a_{phy} (440)	a_{NAP} (440)	$S_{275-2295}$
TN	0.574^b	0.548^b	0.288^a	0.377^b	0.264	0.164
TP	0.508^b	0.401^b	0.078	0.194	0.062	0.151
TDS	0.483^b	0.534^b	−0.048	0.178	−0.068	0.015
DOC	0.527^b	0.411^b	−0.007	0.151	−0.024	0.377^b
pH	0.192	0.129	−0.121	0.026	−0.131	0.567^b
Chl *a*	0.021	0.084	−0.056	0.224	−0.083	0.089
TSM	0.021	0.045	0.985^b	0.515^b	0.985^b	−0.073
EC	−0.024	−0.083	0.055	0.081	0.050	0.506^b

[a] $p < 0.05$; [b] $p < 0.01$.
Units of DOC, TN, TP, TDS, TSM, and DOC concentrations are $mg\,L^{-1}$, chl *a* concentrations unit is $\mu g\,L^{-1}$, EC unit is $\mu s\,cm^{-1}$.

HESSD
12, 5895–5929, 2015

Influence of environmental factors on plateau CDOM characteristic

Z. D. Wen et al.

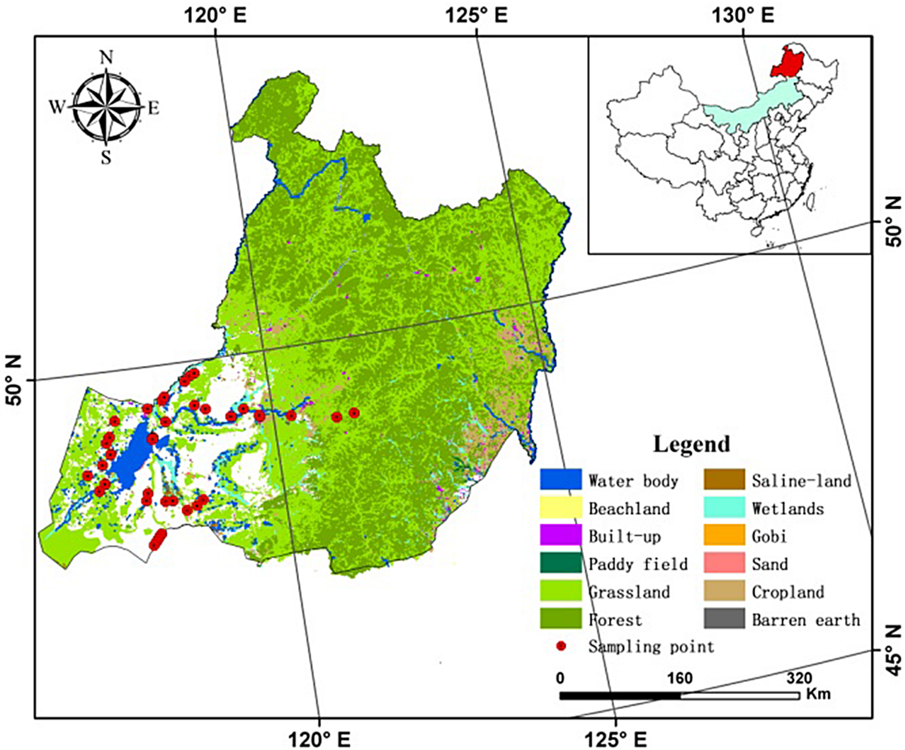

Figure 1. Study area location and sampling station distribution.

HESSD
12, 5895–5929, 2015

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Z. D. Wen et al.

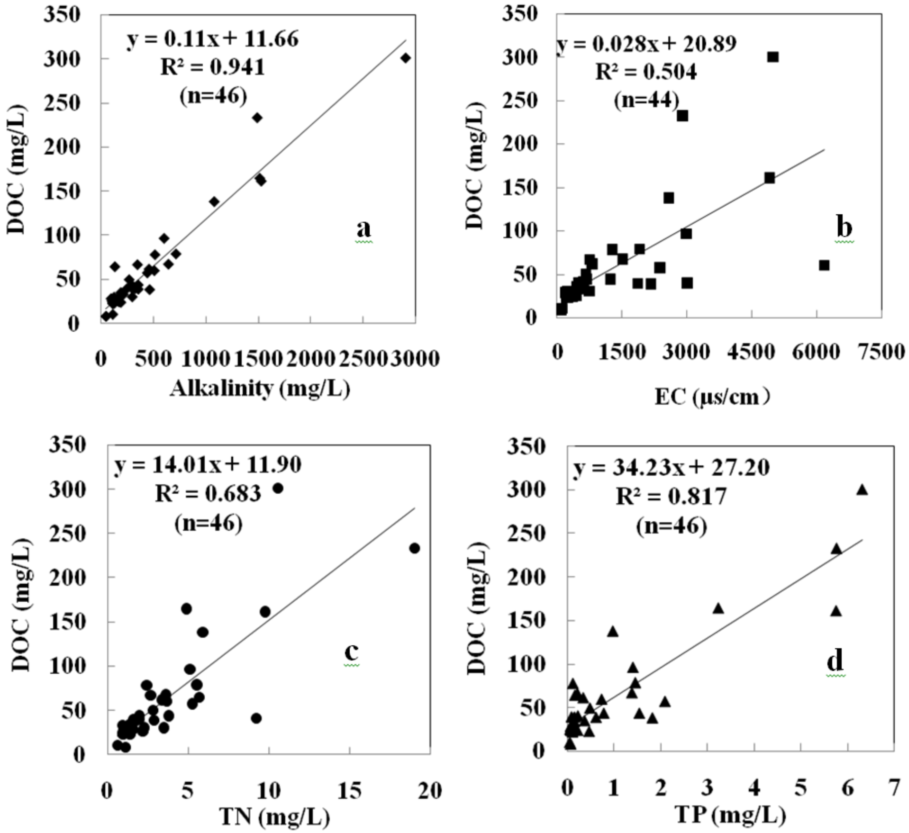

Figure 2. Correlation between DOC and alkalinity, EC, TN, and TP in Hulun Buir plateau water.

HESSD
12, 5895–5929, 2015

Influence of environmental factors on plateau CDOM characteristic

Z. D. Wen et al.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

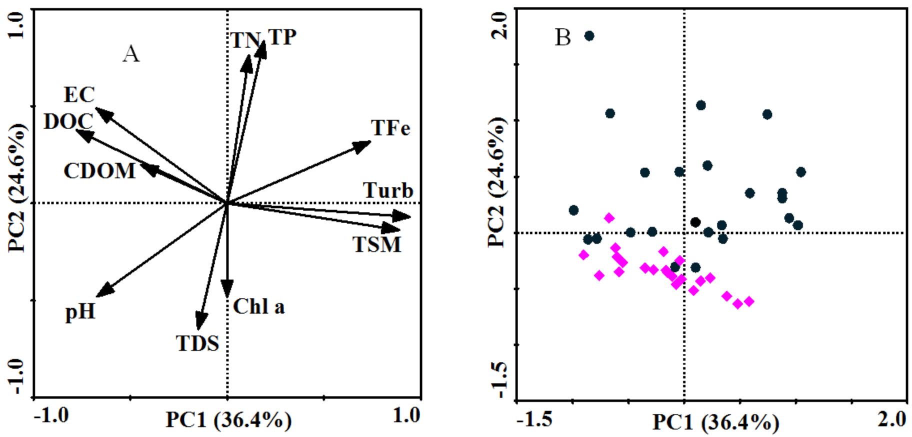

Figure 3. PCA of the physico-chemical characteristics of all collected waters, **(a)** factors loading data, and **(b)** sample scores. • represents terminal waters, and ♦ represents river waters.

HESSD

12, 5895–5929, 2015

Influence of environmental factors on plateau CDOM characteristic

Z. D. Wen et al.

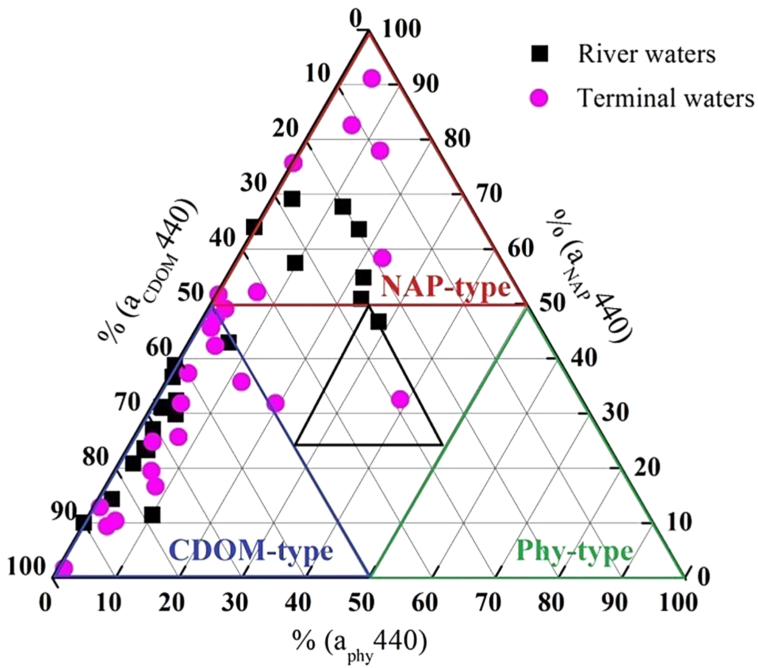

Figure 4. Relative contributions of CDOM, phytoplankton and non-algal particles to total non-water light absorption at 440 nm.

HESSD
12, 5895–5929, 2015

Influence of environmental factors on plateau CDOM characteristic

Z. D. Wen et al.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

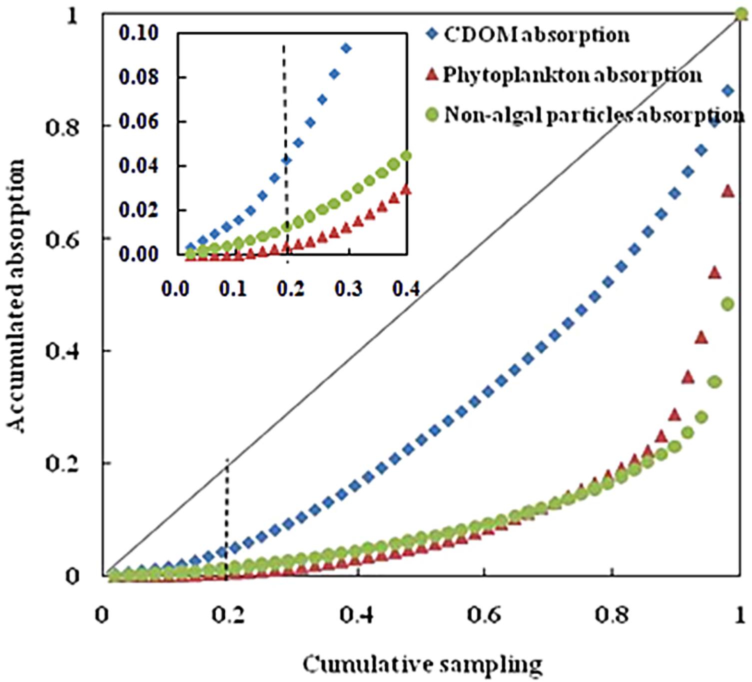

Figure 5. Pareto–Lorenz curves derived from the total non-water light absorption at 440 nm.

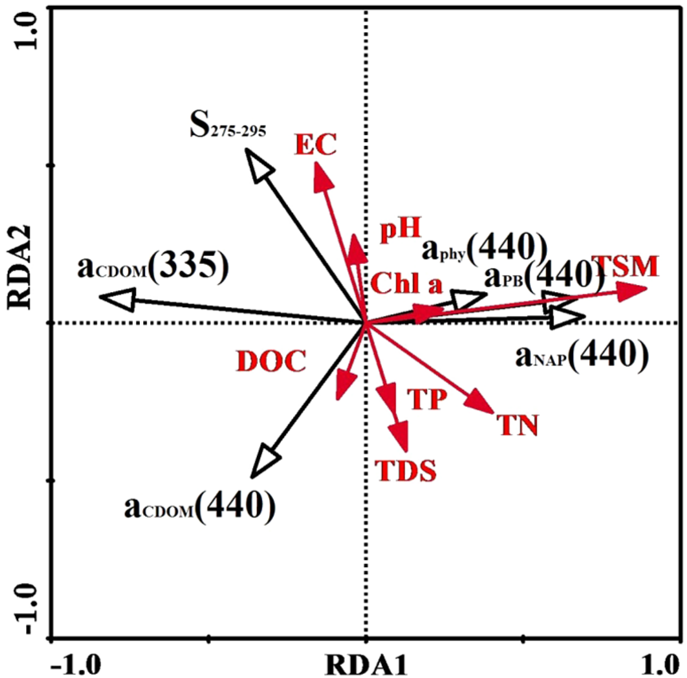

Figure 6. RDA of CDOM adsorption data and water quality parameters (n = 44).

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12, 5895–5929, 2015