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Characterization of chromophoric dissolved organic matter in lakes on the Tibet Plateau, China, using spectroscopic analysis

Kaishan Song[1#*], Sijia Li[2#], Zhidan Wen[1], Lili Lyu[1], Yingxin Shang[1]

[1] Northeast Institute of Geography and Agroecology, CAS, Changchun, 130102, China

[2] School of Environmental, Northeast Normal University, Changchun, 136000, China

first co-authors

*authors correspondence should be addressed: songkaishan@neigae.ac.cn

Abstract Spatiotemporal variations in the characteristics of fluorescent dissolved organic matter (FDOM) components from 63 lakes across the Tibet Plateau, China, are examined using excitation-emission matrix spectra (EEM) and fluorescence regional integration (FRI) from 2014 to 2017. Freshwater (N=135) and brackish water (N=109) samples from 63 lakes were grouped according to salinity or electrical conductivity. In order to compare results between the lakes, cumulative volumes beneath the EEM values (φ_i, i=I, II, III, IV, V) were normalized to a DOC concentration of 1 mg/L. EEM-FRI identified tyrosine-like (φ_I), tryptophan-like (φ_{II}), fulvic-like (φ_{III}), microbial protein-like (φ_{IV}), and humic-like (φ_V) fluorescence regions, as well as their proportions (P_i). Chromophoric dissolved organic matter (CDOM) absorption parameters, fluorescence indices, average fluorescence intensities of the five fluorescent components and total fluorescence intensities (φ_T) differed under spatial variation among brackish and freshwater lakes (ANOVA, p<0.05). Principal component analysis (PCA) was used to assess and group five normalized FDOM components for all of the water samples. These results show that microbial protein-like (φ_{IV}), fulvic-like (φ_{III}) and humic-like (φ_V) have positive correlations (R^2>0.79, t-test, p<0.01), indicating that these FDOM components may originate from similar sources. A correlation also exists

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between normalized φ_i (i=I, II, III, IV, V) and DOC concentrations with a salinity >19‰ (averaged EC, 23764μs cm^{-1}) (t-test, p<0.01), of which R^2 f regression analysis showed a decreasing tendency with EC. Similar correlations between a(254) and DOC concentrations (t-test, p<0.01) are also evident for sunshine hours > 2900 h. Redundancy analysis (RDA) indicates that a(254) and a(350) have a correlation with CDOM in brackish lakes. a(254), *HIX* and a(350) were also correlated with water quality. Strong evapoconcentration, intense ultraviolet irradiance and landscape features of the Tibet Plateau may be responsible for the FDOM characteristics identified in this study.

Keywords: CDOM; Tibet Plateau; Fluorescence; Brackish lakes; FRI

1. Introduction

Inland lakes are a direct link between the land and atmospheric CO_2 pools and rivers, and they are an indirect link between the oceans (via rivers). Inland lakes play an important role in the transportation, transformation and storage of carbon from terrestrially imported substances (Cole et al., 2007; Tranvik et al., 2009). Carbon flux and biogeochemical processes of lakes have a significant influence on the global carbon cycle, on the aquatic ecosystem, and they confer regional effects on climate (Battin et al., 2009; Jiao et al., 2010; Ran et al., 2013; Carlson et al., 2011). However, anthropogenic activities (i.e., industrial, agricultural and domestic sewage) can alter the carbon balance and interfere with biogeochemical cycling of lakes, effects which can be recorded in spatiotemporal variations of dissolved carbon within the catchment. It is therefore important to investigate biogeochemical cycling of carbon in lakes in different regions that have distinct properties (Cole et al., 2007; Falkowski et al., 2000).

The Tibet Plateau, commonly known as the 'Third Pole' or the 'Asian water tower', possesses an average elevation over 4500 m, and contains the largest ice mass outside the polar regions (Song et al., 2016). This region also contains the greatest number of large-scale lakes and glaciers in the world. The total area of lakes on the Tibet Plateau account for about 49% of the total lake area in China (Zhang et al., 2011). As of 2011, there were 312, 104, 7 and 3 lakes with surface areas greater than 10 km^2, 100 km^2, 500 km^2 and 1000 km^2, respectively (Zhang et al., 2011). In addition, due to dry and thin air with a low concentration of ozone in this area, there are strong Ultraviolet-B (UV-B) radiation-penetration inhibiting properties (Ren et al., 1997). Prolonged sunshine and the arid environment has resulted in a high number of lakes in this region having a high salt content, or having a significant accumulation of dissolved organic carbon

(DOC). DOC and dissolved organic matter (DOM) contents contained in brackish or saline lakes, particularly in arid and semi-arid regions, contribute to the relatively high average DOC concentrations and carbon budget of inland waters (Song et al., 2013; Tranvik et al., 2009; Wen et al., 2016). Due to its high altitude, arid environment, low population density, urbanization, and economic development, the Tibet Plateau is therefore of particular interest for climate change, environmental evolution and the carbon cycle. There is also significant interest to investigate total DOM in brackish and saline lakes across the Tibet Plateau.

DOM (typically <0.45 μm) represents one of the largest pools of organic carbon on Earth (Hedges et al., 1992; McKnight et al., 2001). Chromophoric DOM (CDOM, typically <0.22 μm), light-absorbing DOM in aquatic environments, originates from the decomposition of algal by microorganisms (autochthonous), as well as through the transport of the surrounding allochthonous environment (Singh et al., 2010; Zhang et al., 2010). Chemical properties cause CDOM to absorb energy and re-emit it as fluorescence (FDOM) (Helms et al., 2008; Stedmon et al., 2003; Zhang et al., 2010). Due to the high selectivity and sensitivity of FDOM, absorption and fluorescence spectroscopy has provided detailed insights into its composition and components (Stedmon et al., 2003; Zhang et al., 2010). Multivariate statistical parameters and tools, i.e., spectroscopic characterization (specific ultraviolet absorbance and spectral slope ratio), excitation-emission matrix (EEM), humification index (*HIX*), fluorescence index (*FI*), parallel factor analysis (PARAFAC) and fluorescence regional integration (FRI), have been utilized to identify bio-geochemically meaningful components of CDOM (Coble, 1996; Helms et al., 2008; Stedmon et al., 2003). EEM-PARAFAC and EEM-FRI techniques can show dynamic and detailed components of FCDOM for each EEM, techniques which have been widely used in aquatic environmental dynamics (source

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and fate) (Chen et al., 2003; Zhang et al., 2010; Zhao et al., 2017). Compared to other fluorescence tools, EEM-FRI (a quantitative technique) can integrate the volumes beneath defined by regions of EEM largely based on supporting literature (Chen et al., 2003). This is related to all of the wavelength ranges of different fluorescence peaks in each EEM, and covers continuous fluorescence intensity at excitation-emission wavelength of divided regions for further analysis (Chen et al., 2003).

It is believed that the high altitude and arid environment of the Tibet Plateau could have an influence on CDOM in brackish and saline lakes. These influences may affect DOC accumuation, result in a high photochemical degradation rate due to prolonged sunshine, decrease anthropogenic CDOM inputs, and result in an accumulation of nutrients in lake catchment areas (Spencer et al. 2012; Yao et al., 2011; Song et al., 2017). Although CDOM optical characteristics and their effect on carbon budget contribution have been reported in plateaus and high-mountain lakes (Wen et al., 2016; Zhang et al., 2010), little is currently known about CDOM in the Tibet Plateau. Analysis in this area could reveal a natural state of composition, sources, dynamics, and fate of CDOM by comparing results with other brackish and saline lakes with high eutrophication rates due to increased terrestrial nutrient input. Based on previous studies, our investigation examines sources and fate of CDOM in brackish (31 lakes) and saline lakes (32 lakes) across the Tibet Plateau using EEM-FRI. The study objectives are to: (1) characterize the similarities and differences in CDOM absorption and components among the 63 lakes with similar climatic, hydrologic and geological conditions using EEM-FRI technology; (2) investigate and evaluate spatial dynamics of each fluorescence component using EEM-FRI; (3) link FDOM by EEM-FRI to CDOM absorption and fluorescence parameters, and to water quality; and (4) assess the effects on FDOM by EEM-FRI caused by salinity, solar radiation and land cover.

2. Materials and Methods

2.1 Overview of the Tibet lakes

As the largest and most extensive plateau in the world, the Tibet Plateau covers an area in China of about 2.5 million km^2, having an average elevation of more than 4500 m above sea level (Zhang et al., 2011). Lakes on the Tibeta Plateau are typically formed due to erosion and melting of glaciers, geological tectonic activity (fault and depression), barriers present on the land-surface, or due to melting on hot spots etc. The majority of these lakes are sensitive to global climate change (Liu and Chen, 2000; Qin et al., 2009). Due to the diverse climate (some airflows of tropospheric tropical easterly, subtropical westerly, and southwestern monsoon from the Indian Ocean) and complex topography (numerous different broad basins or valleys with high mountain ranges) in this area, annual precipitation ranges from 100 to 1300 mm. The majority of precipitation occurs during the summer period (June to September). Solar UV radiation in this area is strong due to dry and thin air, having a low ozone concentration (Ren et al., 1997). In the winter the climate is dominated by cold and dry westerly winds which are more pronounced with elevation. During the winter, the northwestern area of the plateau (where average elevation exceeds 5000 m) is the coldest, having average temperatures around −40 °C (Song et al., 2016). Owing to diverse climatic patterns, topographical patterns and few anthropogenic activities, the carbon cycle, climate change and environment evolution over the Tibet Plateau has seen an increase in interest recently (Zhao et al., 2017; Song et al., 2017).

[Insert Figure 1 about here]

2.2 Field sampling

A total of 244 water samples were collected from 63 lakes across the Tibet Plateau from

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2014 to 2017. Sample locations for each lake were recorded using a GPS receiver (Table S1 and Fig. 1). Water samples were collected from lake surfaces (0-50 cm) in 1 L acid-cleaned plastic bottles. The collected water samples were filtered through a pre-combusted Whatman GF/F filter (0.7 μm) and then further filtered through a pre-rinsed 25 mm Millipore membrane cellulose filter (0.22 μm) into brown plastic bottles. Samples were prepared for DOC analysis by being filtered through a pre-combusted Whatman GF/F filter (0.45 μm) under a low vacuum. The filtered samples were stored at 4°C and transported to the laboratory for CDOM absorption and fluorescence analysis within 2 days.

2.3 Water quality measurements

Electrical conductivity (EC) and pH were measured using a portable multi-parameter water quality analyzer (YSI EXO1, US). DOC concentrations were determined by high-temperature catalytic oxidation (680 ℃) using a total organic carbon analyzer (TOC-VCPN, Shimadzu, Japan). Potassium hydrogen phthalate was used in this analysis as a reference. Chlorophyll a (Chl-a) analysis was undertaken by initially filtering the water samples through Whatman cellulose acetone filters (0.45μm) before being extracted with 90% acetone and measured at 664, 647, 630 and 750 nm wavelengths using a Shimadzu UV-2006 PC spectrophotometer. Total nitrogen (TN) and Total phosphorus (TP) were measured following methods highlighted in standard methods (APHA/AWWA/WEF, 1998).

2.4 CDOM absorption measurements

Absorption spectra of filtered samples were measured between 200 and 800 nm at 1 nm increments using a Shimadzu UV-2006 PC spectrophotometer with a 1 cm (or 5 cm) quartz cuvette and Milli-Q water as a reference. The absorption coefficient a_{CDOM} was calculated from the measured sample optical absorption $a(\lambda)$:

$$a_{\text{CDOM}}(\lambda)=2.303\text{OD}(\lambda)/\gamma \quad (1)$$

where, OD(λ) is the corrected optical density at wavelength λ; γ is the cuvette path length (0.01 or 0.05 m); and the factor of 2.303 converts the results from a base 10 to a base natural logarithm (Zhang et al., 2011). The $SUVA_{254}$, $S_{275-295}$ and M (E_{250}:E_{365}) were used to characterize CDOM features (Helms et al., 2008).

2.5 Excitation-emission matrix (EEM) fluorescence

Three-dimensional excitation-emission matrix (EEM) spectra of CDOM were measured at room temperature (20±2 °C) using a Hitachi F-7000 fluorescence spectrometer with a 700 volt xenon lamp. Scanning band pass widths of excitation and emission spectra were obtained using wavelengths of 220-450 nm (with intervals of 5 nm) and 250-600 nm (1 nm intervals), respectively, with a scanning speed of 2400 $nm \cdot min^{-1}$. A Milli-Q water blank was analyzed, the result of which was subtracted from the resulting EEM of the water sample spectrum to eliminate Raman scatter peaks. In order to eliminate the inner filter effect, the EEMs were normalized by subtracting the integral area under the curve of the Milli-Q water Raman peak according to the methods recommended by Zhang et al. (2010) and Zhou et al. (2016). These EEM spectra were then calibrated in quinine sulfate units (QSU) (Lawaetz and Stedmon, 2009).

The fluorescence indices FI_{370} and FI_{310}, defined as Ex/Em=(370/450 nm)/(370/500 nm) and Ex/Em=(310/380 nm)/(310/430 nm), introduced by McKnight et al. (2001), were used to characterize CDOM source. FI_{370} is used to distinguish fulvic acids derived from terrestrial (FI_{370}<1.4) and microbial (FI_{370}>1.9) sources, and FI_{310} is used to distinguish autochthonous (FI_{310}<0.7), autochthonous biological activity (FI_{310}>0.8) and intermediate autochthonous (0.7<FI_{310}<0.8) (Zhang et al., 2010). The humification index (*HIX*) was calculated from fluorescence EEMs, as indices for the

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humification degree and DOM sources (Huguet et al., 2009). Further details of these methods are provided in Zhang et al. (2010).

2.6 EEM fluorescence regional integration

EEM Fluorescence Regional Integration (EEM-FRI) divides EEM boundaries into five regions associated with humic-like, tyrosine-like, tryptophan-like or phenol-like organic compounds, based on the findings of Chen et al. (2003). Fluorescence peaks at Ex<250 nm and Em<350, defined as Regions I and II, relate to aromatic proteins such as tyrosine. Peaks at shorter Ex<250 nm and longer Em>350 nm are fulvic acid-like materials, deemed as Region III. Peaks at intermediate 250 nm <Ex<280 nm and Em<380 nm are microbial protein-like, defined as Region IV. Peaks at longer Ex>280 nm and Em>380 nm are related to humic acid-like organics, denoted as Region V. The integrated area beneath the EEM spectra can be calculated using:

$$\varphi_i = \int_{ex} \int_{em} I(\lambda_{ex}\lambda_{em})\Delta\lambda_{ex}\Delta\lambda_{em} \quad (2)$$

where, $\Delta\lambda_{ex}$ is Ex (interval 5 nm); $\Delta\lambda_{em}$ is Em (interval 1 nm); $I(\lambda_{ex}, \lambda_{em})$ is fluorescence intensity at each EEM pair; and *i* represents the regions of EEM divided by EEM-FRI. The cumulative volume in the five regions beneath the EEM can be calculated using φ_T (*i*= I, II, II, IV, V; unit: nm):

$$\varphi_{T,n} = \sum_{i=1}^{5} \varphi_{i,n} \quad (3)$$

where, *n* represents the numbers of cumulative regions in the five regions. The cumulative volume beneath the EEM (φ_i and φ_T) values were normalized to per unit of DOC concentration (in mg/L) for comparison of EEMs from different sources. The unit of DOC-normalized EEM-FRI is QSU-nm^2-[mg/LC]$^{-1}$. The percent fluorescence response in a specific region ($P_{i,n}$, *i*= I, II, II, IV, V) was calculated as:

$$P_{i,n} = \varphi_{i,n} / \varphi_{T,n} \times 100\% \quad (4)$$

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2.7 Statistical analysis

Statistical analyses, regression and correlation analyses were performed using SPSS 16.0 (Statistical Program for Social Sciences) to examine the relationships between variations (CDOM absorption and fluorescence parameters) among lakes. Significance levels are reported as non-significant (NS) (p>0.05), significant (*, 0.05>p>0.01) or highly significant (**, p<0.01). Redundancy analysis (RDA) and principal components analysis (PCA) was undertaken using CANOCO 4.5 from two principal components analyses (Microcomputer Power, Ithaca, NY, USA).

3. Results

3.1 Biogeochemical characteristics

Water quality parameters (TN, TP, Chl-a, TSM, pH, EC, turbidity and salinity) for the 63 lakes (244 water samples) are shown in Table 1. Thirty one lakes were classified as brackish (N=109; 35‰>salinity >1‰) and 32 lakes were classified as freshwater (N=135; salinity <1‰). The average values of all water quality parameters in each lake were calculated and selected to represent overall water quality of the lake. Concentrations of TN (average, 2.31 ± 2.64 mg L^{-1}), TP (average, 0.04 ± 0.03 mg L^{-1}) and Chl-a (average, 1.45 ± 2.65 μg L^{-1}) were relatively low in fresh lakes (N=135), coinciding with low turbidity. Brackish lakes, having a eutrophic state, recorded high Chl-a (average, 2.57 ± 5.73 μg L^{-1}), TN (average, 4.54 ± 4.32 mg L^{-1}) and TP (average, 0.45 ± 1.35 mg L^{-1}), results related to their high salt (average, 6.01 ± 5.59 ‰) and EC (average, 8880.24 ± 8235.9 μS cm^{-1}) contents. The water quality parameters of the trophic states were slightly higher than the average values for brackish lakes in northeastern China (average, TP=0.11 mg $L^{-1}$and TN=4.07 mg L^{-1};) in Northeast of China (Zhao et al., 2017), and lakes (average, TP=0.033 mg L^{-1} and TN=0.59 mg L^{-1};)

in Yungui Plateau of China (Zhang et al., 2010), and lower than those in Hulun Lake (average, TP=1.52 mg $L^{-1}$and TN=4.58 mg L^{-1}; Wen et al., 2016). Zhang et al. (2010) found that, with an increase in altitude (> 4000 m), oligotrophic lakes increased due to the natural changes in catchment properties and low human activities. However, for terminal lakes with less anthropogenic density, there is an accumulation of nutrients generally derived from allochthonous substances.

[Insert Table 1 about here]

High concentrations of DOC in brackish waters were found to accumulate in lakes with high salinity concentrations (Fig. 2a). DOC values for the brackish lakes were also found to be variable, ranging from 0.27 mg L^{-1} in Lake XRC to 164.8 mg L^{-1} in Lake CCL, with a mean DOC of 35.69 (± 43.52) mg L^{-1} (Fig. S1). Mean DOC concentrations in the fresh lakes were 7.94 ± 12.05 mg L^{-1}, recording lower values than those in brackish lakes. These results are in agreement with the findings of Song et al. (2013), Zhao et al., (2016) and Wen et al (2016) for brackish lakes in arid and semi-arid regions. Although brackish lakes have high spatial heterogeneity, our results indicate that decreasing salinity generally coincides with DOC concentrations (Fig. 2b). In addition, owing to UV-B radiation-penetration inhibiting properties in the Tibet Plateau (Ren et al., 1997), the tendency linear equation of average DOC concentration showed a decreased trend with increasing elevation (Fig. 2a). However, variations in DOC concentrations can also be explained by DOC flux related to physical/chemical properties, hydrology, and land use/land cover within a specific drainage watershed for each lake (Heinz et al., 2015; Wen et al., 2016).

[Insert Figure 2 about here]

3.2 CDOM absorption

Previous studies have indicated that high salinity could have a direct or indirect impact on water quality, and they highlighted different structures and composition of DOM (Waiser and Robarts, 2000; Song et al., 2013; Zhang et al., 2010). Generally, Helms et al. (2008) and Weishaar et al. (2003) showed that the absorption coefficient *a*(350) is seen as a proxy to characterize CDOM concentration. *a*(350) absorption coefficients in our study ranged from 0.09-8.45 m^{-1} and 0-13.49 m^{-1} for brackish and fresh lakes, with mean values of 2.38 (± 3.14 SD) m^{-1} and 1.74 (± 1.99 SD) m^{-1}, respectively (Fig. 3). These values were found to be significantly different from each other (ANOVA, $p<0.05$). *a*(254) represents the optical properties of DOC aromaticity, and $SUVA_{254}$ (the ratio of *a*(254) and DOC) can be used to characterize the optical properties of DOC aromaticity (Helms et al., 2008; Spencer et al., 2012). Higher $SUVA_{254}$ values are related to allochthonous-dominated sources, having a higher percentage of DOC aromaticity and microbial-dominated substances in DOC; lower $SUVA_{254}$ values indicate the opposite (Spencer et al., 2012; Weishaar et al., 2003). Mean $SUVA_{254}$ values ranged from 1.47 (±2.55 SD) mg C^{-1} m^{-1} in brackish lakes to 2.29 (±1.36 SD) mg C^{-1} m^{-1} in fresh lakes (Fig. 2). ANOVA analysis indicated there are significant differences ($p<0.05$) between $SUVA_{254}$ values for brackish and fresh lakes. $SUVA_{254}$ values for brackish lakes recorded lower values than those recorded in terminal water on the Inner Mongolia Plateau (Brackish, $SUVA_{254}$=1.90±0.57 mg C^{-1} m^{-1}; Fresh, $SUVA_{254}$=2.74±1.08 mg C^{-1} m^{-1}) or in brackish lakes of northeastern China (2.8-5.7 mg C^{-1} m^{-1}) (Zhao et al., 2016; Wen et al., 2016). In this study, the lower $SUVA_{254}$ values in the brackish lakes indicated that aromatic moieties of CDOM in this environment were lower than those in fresh lakes, or other brackish environments in China. These differences are due to the effect of photo-degradation and microbial degradation, with prolonged water residence times.

For brackish water lakes, M (E_{250}:E_{365}) ranged from 6.82 in Dajiacuo Lake (DJC)

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to 74.7 in Gemangcuo Lake (GMC), having an average value of 28.3± 20.3 (Fig. 3) across all brackish lakes. Results for M (E_{250}:E_{365}) in fresh lakes ranged from 5.7 in Tongzecuo Lake (TZC) to 89.5 in Lang'angcuo Lake (LAC), having an average value of 16.27 ± 20.6. This suggests a significant difference (ANOVA, p<0.05) between fresh and brackish waters in M (E_{250}:E_{365}). The spectral $S_{275\text{-}295}$ (275–295 nm) was used to represent DOM molecular weight, with higher values signifying lower average molecular weights of DOC (Helms et al., 2008). Then $S_{275\text{-}295}$ can be regarded as an indicator for terrestrial DOC percentage (Gonnelli et al., 2013). As shown in Figure 3, the higher $S_{275\text{-}295}$ values (0.0380 ± 0.009 nm^{-1}) in brackish lakes than those in presented in fresh lakes (0.0324 ± 0.01 nm^{-1}; Fig. 3), indicating lower average molecular weight of DOM. This result showed a significant difference between fresh and brackish lakes (ANOVA, p<0.05). This implies that chromophores associated with high molecular weight were destroyed by chemical bond rupture into low molecular weight pool in the photolysis process with a prolonged hydraulic retention time and irradiation (McKnight et al., 2001). The difference in CDOM absorption parameters is probably associated to spatial variations influencing terrestrial inputs from soil and microbial activities due to plant decay.

[Insert Figure 3 about here]

3.3 EEM-FRI components

EEM spectra of CDOM referred to the major fluorescent components and location information identified using the peak-picking method of Coble (1996) and PARAFAC from previous studies (Stedmon et al. 2003; Kowalczuk et al., 2010). Typical EEM spectra of CDOM for four water samples obtained from brackish and fresh lakes in the Tibet Plateau are shown in Figure 4 (a-d). Traditional EEM fluorescence peaks, i.e., phytoplankton production ('N' peak), tyrosine-like ('B' peak), humic-like ('M' peak) and tryptophan-like ('T' peak) were observed in the 244 EEM spectra (Coble, 1996). According to Chen et al. (2003), EMM-FRI divides the EEM signal into five regions (I, II, III, IV and V; Fig. 3a). In the Tibet Plateau, these regions varied with changes in intensity of the five marked fluorescence fractions between brackish lakes and the fresh lakes. EEM-FRI results from the lakes were used to demonstrate CDOM fluorescence characteristics. The excitation-emission area volumes φ_i (i= I, II, II, IV, V) and their proportion to total fluorescence intensity P_i (i= I, II, III, IV, V) for the five different regions are shown in Figure 4 (e and f), respectively. A significant difference (ANOVA, p<0.05) of total fluorescence intensity φ_T was observed between the brackish and fresh lakes. φ_T ranged from 1.94×10^8 nm to 3.5×10^{10} nm for brackish lakes, having an average of 1.44×10^{10} nm (±8.1×10^9 SD), and it ranged from 3.54×10^8 nm to 3.5×10^{10} nm for freshwater lakes, with an average of 1.38×10^{10} nm (±7.9×10^9 SD). For both lake types, the area volume of φ_i in the five integrated regions identified by EEM-FRI were in the order of: φ_V (Humic-like) > φ_{III} (Fulvic-like) > φ_{IV} (Microbial protein-like) > φ_I (Tyrosine-like)> φ_{II} (Tryptophan-like). This result indicates that the allochthonous humic-like and fulvic-like materials are predominate in these DOM, and the content of protein-like materials and phenolic compounds were low. Furthermore, a significant difference for the fluorescence intensities of humic-like φ_V and fulvic-like φ_{III} was found in brackish lakes and fresh lakes (ANOVA, p<0.05). The fluorescence intensities with φ_V accounting for P_V=62.4% (±14.6 SD) in brackish lakes ranged from 34.1% in Gemangcuo Lake (GMC) to 96.8% in Chuocuolong Lake (CCL). Then fresh lakes recorded a range of 32.8% (Garencuo Lake; GRC-2) to 87.5% (Cuolongque Lake; CLQ), having an average P_V of 53.7% (±13.0 SD). This result indicates that humic-like substances both in brackish and fresh lakes dominated fluorescence intensities. In addition, the φ_{III} (fulvic-like) fluorescence intensities also showed a significant

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difference (ANOVA, p<0.05) between P_{III} in fresh lakes (24.8%; ±7.4 SD) and those in brackish lakes (15.9 %; ±8.8 SD). The fluorescence intensities for φ_{IV} (microbial protein-like) accounted for a greater proportion in brackish lakes (P_{IV} of 15.5%; ±8.2 SD) than in fresh lakes (12.5%; ±6.8 SD). These results demonstrated that the fluorescence intensities of the five components φ_i (i= I, II, II, IV, V) and the relative proportions to the total fluorescence intensities P_i (i= I, II, II, IV, V) differed in brackish and fresh lakes.

[Insert Figure 4 about here]

3.4 Normalized EEM-FRI components and fluorescence indices

With various hydrological, geographical and climatic characteristics, the fluorescence of CDOM components in different lakes shows spatial heterogeneity. The water samples collected from each lake were combined to examine spatial variation. In order to eliminate the influence of spatial heterogeneity, the cumulative volumes beneath the EEM (φ_i) values were normalized to a DOC concentration of 1 mg L^{-1}. The average normalized total fluorescence intensities φ_T in brackish lakes was 1.1×10^9 QSU-nm^2-[mg L^{-1} C] (±8.8 SD), with a maximum value of 3.3 $\times10^9$ QSU-nm^2-[mg L^{-1} C] in Gongzhucuo Lake (GZC) and a minimum value of 4.8×10^7 QSU-nm^2-[mg L^{-1} C] in Qinghaihu Lake (QHH). Results for the fresh lakes showed that φ_T ranged from 2.1 $\times10^7$ QSU-nm^2-[mg L^{-1} C] in Tongzecuo Lake (TZC) to 9.5×10^9 QSU-nm^2-[mg L^{-1} C] in Wurucuo Lake (WRC), having an average φ_T of 3.3×10^9 QSU-nm^2-[mg L^{-1} C] (±2.6 SD). There was a significant difference of normalized total fluorescence intensities φ_T in brackish and fresh lakes (ANOVA, p<0.001), which is opposite to the non-normalized EEM-FRI result in Figure 4e. This difference may be attributed to DOC accumulation in terminal brackish lakes, having a prolonged hydraulic retention time and irradiation, and the presence of a greater volume of colorless DOC (Table S1). By contrast, it can be seen that the inflow rivers of a certain lake generally showed lower DOC concentrations (Fig. S2). Although photochemistry due to strong UV-B caused the different composition of CDOM, allochthonous substances are important for the accumulation of DOC in brackish lakes.

In addition, the normalized volumes φ_i in the five integrated regions identified by EEM-FRI also presented normalized φ_V (humic-like), φ_{III} (fulvic-like) and φ_{IV} (microbial protein-like), these being more predominate in CDOM than φ_I (tyrosine-like) and φ_{II} (tryptophan-like). Percentage distributions (P_i) of EEM-FRI extracted FDOM in brackish and fresh lakes also showed significant differences (ANOVA, p<0.001). Normalized humic-like (φ_V) and fulvic-like (φ_{III}) were terrestrial sources, accounting for P_{III+V} = 77.7% (±10.1 SD) in brackish lakes and 77.7% (±7.3 SD) in fresh lakes. Protein-like fluorescence, including tyrosine-like and tryptophan-like (φ_{I+II}), recorded a greater proportion in brackish water (P_{I+II} =6.47%; ±2.6 SD) than in fresh lakes (P_{I+II} =22.3%; ±4.0 SD) (Fig. 5c and d). Although autochthonous and microbial occupied small proportions of normalized volumes φ_T, FDOM in brackish lakes generally indicated more allochthonous inputs.

[Insert Figure 5 about here]

As shown in Fig. 6, the average values of the fluorescence indices FI_{370} and FI_{310} introduced by McKnight et al. (2001) were derived to characterize CDOM sources in the Tibet Plateau (Fig. 6). FI_{370} in brackish lakes ranged from 0.11 (Peikucuo Lake; PKC) to 1.93 (Chuocuolong Lake; CCL), with a mean value of 0.64 (±0.51 SD); FI_{310} ranged from 0.58 (PKC) to 1.93 (Gemangcuo Lake; GMC), having a mean value of 1.14 (± 0.36 SD). In contrast, fresh lake results ranged from 0.11 (Taruocuo Lake; TRC) to 2.87 (Weizhi-1 Lake; WZ-1), with a mean value of 0.79 (±0.75 SD) and from 0.57

(WZ-1) to 2.38 (La'angcuo Lake; LAC), with a mean value of 1.04 (± 0.43 SD), for FI_{370} and FI_{310}, respectively. Average FI_{370} (<1.4) and FI_{310} (> 0.8) in most brackish and fresh lakes indicated that CDOM sources were derived from terrestrial humic-like substances and autochthonous biological activity. There may be no differences between FI_{310} and FI_{370}, signifying no difference for CDOM sources between brackish and fresh lakes (ANOVA, p>0.05). However, average *HIX* (3.15 ± 3.5) in fresh lakes showed a higher degree of humification than in brackish lakes (average *HIX* of 1.8 ± 1.7).

[Insert Figure 6 about here]

3.5 PCA of normalized EEM-FRI components

PCA (principal component analysis) was undertaken to calculate the relative scores of normalized cumulative volume φ_i by EEM-FRI, and to assess the spatial distributions of water samples in brackish and fresh lakes. Our results indicate that PCA factor 1 and factor 2 axes (Fig. 7) could explain 92.8% of total variance, and they account for 66.9% and 25.9%, respectively. The Kaiser-Meyer-Olkin result showed that the statistical magnitude was larger than 0.8, and that the five normalized EEM-FRI fluorescent components exhibited positive factor 1 loadings (Fig. 7a). Factor analysis showed PAC factor 1 and factor 2 to be associated with five cumulative volumes φ_i (i=I, II, III, IV, V) in a linear formula. Factor 1 and factor 2 were expressed as:

$$\text{factor 1}= -0.543\varphi_{I}-1.35\varphi_{II}+0.788\varphi_{III}+0.856\varphi_{IV}+0.98\varphi_{V}$$

$$\text{factor 2}= 0.899\varphi_{I}+1.78\varphi_{II}-0.559\varphi_{III}-0.636\varphi_{IV}-0.774\varphi_{V}.$$

φ_{III} (fulvic-like), φ_{V} (humic-like) and φ_{IV} (microbial protein-like) showed a positive factor 1 loading, and concurrently showed negative factor 2 loading. This correlation result indicated that PCA in our study could separate normalized cumulative volume φ_i by EEM-FRI into two groups: Group 1 (φ_{III}, fulvic-like; φ_{V}, humic-like; φ_{IV}, microbial protein-like) and Group 2 (φ_I, tyrosine-like; φ_{II}, tryptophan-like). This finding was contrary to the results of Zhao et al. (2017), Yao et al. (2011) and Yamashita et al., (2010) from other water bodies. Differences in results from our study and previous investigations may be due to the majority of the microbial protein-like fluorescence of CDOM in lakes in our study being derived from terrestrial microbial decomposition. The spatial variation of PCA factors 1 and 2 scores for all water samples is shown in Figure 7b. Water samples from brackish lakes were mainly distributed in the range of -1 to 1 for both PCA factor scores. This finding confirms that the contributions of allochthonous substances (including microbial protein-like) were obvious in brackish lakes. Differences in FDOM results are likely to be due to spatial variations influencing terrestrial inputs from soil and microbial activities from plant decay. However, PCA scores from areas of fresh lakes were sporadic, signifying that normalized cumulative volume φ_i were affected by regional hydrological and geographical lake conditions.

[Insert Figure 7 about here]

3.6 Correlation analysis of CDOM spectroscopic indices

In general, there was strong correlation between tyrosine-like φ_I and tryptophan-like φ_{II} in fresh (R^2=0.86, N=135; t-test, p<0.01) and brackish lakes (R^2=0.80, N=109; t-test, p<0.01), suggesting that they may have similar sources (Fig. 8a). A moderate correlation between φ_I and microbial protein-like φ_{IV} was observed in brackish lakes (R^2=0.70, N=109; t-test, p<0.01), and a weak correlation was recorded in fresh lakes (R^2=0.57, N=135; t-test, p<0.01) (Fig. 8b), demonstrating that parts of the two FRI fluorescent components may have some common sources in brackish lakes. However, strong correlations between tryptophan-like φ_{II} and microbial protein-like φ_{IV} were not observed (Fig. 8c), a finding that is consistent with the results of Chen et al. (2003) and

Zhao et al. (2017). This lack of correlation may be due to the sources of the three protein fluorescence materials (tyrosine-like, tryptophan-like and microbial protein-like) being independent in fresh lakes. Furthermore, EEM can be divided into two groups in the PCA results (Fig. 7), and there was a positive correlation between the total normalized cumulative volume $\varphi_{III\&IV\&V}$ and $\varphi_{I\&II}$ ($R^2 = 0.76$, $N= 109$; t-test, $p<0.01$) in brackish lakes (Fig. 8d). Then a weak correlation in fresh lakes ($R^2 = 0.54$, $N= 135$; t-test, $p < 0.01$). It indicated that the autochthonous substances and they affected by microorganism activity in brackish lakes was not strong. Arts et al. (2000) reported that increasing salinity could limit the microbial activity by reduce the cell permeability. In addition, moderate correlations between the $a(350)$, FI_{370} and HIX were observed in the fresh lakes ($R^2>0.66$, $N= 135$; t-test, $p<0.01$) (Fig. 8 e and f), showing that FI_{370} and HIX represented similar indications in CDOM sources for most fresh lakes. This result was consistent with the findings of Zhang et al. (2010) and Zhao et al. (2016). In brackish lakes, $a(350)$ and HIX showed a more moderate correlation ($R^2=0.65$, $N= 109$; t-test, $p<0.01$).

[Insert Figure 8 about here]

3.7 Correlation between CDOM and water quality

Redundancy analysis (RDA) between water quality parameters for the brackish and fresh lakes (Fig. 9) showed that the forward selected environment explanatory variables (CDOM absorption and fluorescence; $a(254)$, $a(350)$, $S_{275\text{-}295}$, $SUVA_{254}$, M (E_{250}:E_{365}), FI_{310}, FI_{370}, HIX and φ_i (i=I, II, III, IV, V)), could explain the variability of species variables (water quality parameters; DOC, Chl-a, TN, TP, salinity and turbidity). Species–environment correlations of brackish and freshlakes were 0.43 and 0.33, respectively. For brackish lakes (N=109), the first two RDA axes accounted for 86.3%

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of total water quality parameter variability (axis one, 48 %; axis two, 38.3 %). Coefficients between environmental variables with RDA axes indicated that *a*(254), *a*(350) and *HIX* were correlated with CDOM, followed by M(E_{250}:E_{365}) and $S_{275\text{-}295}$. For the fresh lakes (*N*=135), the first two RDA axes accounted for 82.4 % of total variability (axis one, 66.7 %; axis two, 15.7 %). *a*(254), *HIX* and *a*(350) were correlated with water quality, followed by FI_{370} and φ_{IV}. The CDOM absorption *a*(254) can generally characterize DOC aromaticity and CDOM concentration (Baker, 2001).

[Insert Figure 9 about here]

In addition, regression analysis was undertaken between DOC concentration and normalized cumulative volume φ_i (*i*=I, II, III, IV, V) for all water samples (Table 2). Salinity of the brackish lakes was divided into four parts: salinity >19‰ (average EC 23764 μs cm^{-1}), salinity >7‰ (average EC 10945 μs cm^{-1}), salinity >2‰ (average EC 5708 μs cm^{-1}) and salinity <1‰ (average EC 2119 μs cm^{-1}). Salinity <1‰ was consistent with that of fresh lakes (average EC 586 μs cm^{-1}). There were moderately strong negative correlations between the normalized cumulative volume φ_i (*i*=I, II, IV, V) and DOC concentration, with R^2 ranging from 0.51 to 0.73. This result suggests that parts of the FDOM components and DOC potentially derived from common sources in brackish lakes (salinity >19‰ or averaged EC 23764μs cm^{-1}). In particular, R^2 values showed a consistent decreasing tendency with salinity (EC), suggesting that DOC with high salinity (EC) was dominant with allochthonous substances. The link of the five FDOM components to DOC was complicated due to various hydrological, geographical and climatic characteristics.

[Insert Table 2 about here]

4. Discussion

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4.1 The effect of EC/salinity

Previous studies have reported that DOC concentrations in inland waters showed a decreased tendency with the prolongation of water residence times in humid regions due to prolonged photobleaching and possible dilution (Curtis and Adams, 1995; Spencer et al., 2012). For lakes in the study area having a long retention period (Table S1), brackish lakes were found to have higher DOC concentrations (35.69 ± 43.52 mg L^{-1}) compared with fresh lakes (7.94 ± 12.05 mg L^{-1}) (Table 1). Substantial variations for both DOC and CDOM spectroscopic parameters were also observed between the fresh and brackish lakes (ANOVA, p<0.05) (Table 1 and Fig. 3). Previous investigations have attributed this pattern to evapo-concentrated and accumulation processes in semi-arid regions (Twardowski and Donaghay, 2002; Song et al., 2013; Wen et al., 2016). However, the affined characteristics of brackish lakes in our study area could be due to a weak connection between salinity (EC) and DOC (un-exhibited; R^2=0.3, t-test, p<0.01). Comparably, opposite results from brackish lakes in the northeastern plain (R^2= 0.93, p<0.01; Zhao et al., 2016) and on the Inner Mongolia Plateau (R^2= 0.72, p<0.01; Wen et al., 2016) have been previously noted. Generally, organic carbon with different sources (allochthonous or autochthonous) and composition may result in different relationships existing between DOC and salinity (EC) (Spencer et al., 2012). This indicated that regional hydrogeological and climatic conditions may play an important role in driving DOC variability in brackish lakes.

Although the lakes in the study area have high spatial heterogeneity, decreasing salinity generally showed a consistent tendency of DOC concentrations (Fig. 2b). Furthermore, salinity was divided into four groups (>19‰; >7‰; >2‰; >1‰) in brackish lakes (Table 2). The normalized cumulative volume φ_i (φ_I, φ_{II}, φ_{IV} and φ_V) of water samples with a salinity >19‰ (average EC 23764μs cm $^{-1}$) by EEM-FRI showed moderate correlations with DOC concentrations (R^2 ranged from 0.52 to 0.73). R^2 correlation values showed a consistent decreasing tendency with salinity or EC. Based on previous research which showed brackish lakes to always contain higher concentrations of DOC than freshwater lakes in arid regions, this result may reflect water residence times and DOM accumulation. DOM, along with other nutrients, could accumulate via soil leaching and runoff passing through various landscapes (Song et al., 2013). These DOM could be available for the microorganisms and sink to the bottom, or be transformed into inorganic carbon (including CO^2) (Cole et al., 2007; Tranvik et al., 2009). Increasing salinity (EC) could increase DOM solubility, resulting in an impact on microbial activity due to a decrease of osmotic potential (Mavi et al., 2012). Likewise, saturating small humic-like molecules formed colloidal particles which could continue to form macromolecular structures (globular aggregates and ring-like) in high ionic strength environments (Chin et al., 1998; Myneni et al., 1999; Zhao et al., 2016). Therefore, DOC accumulates in brackish (terminal) waters at significantly higher rates than those in fresh (open) waters (Duarte et al., 2005; Song et al., 2013).

A higher humic-like averaged percentage (P_V 60.2%) by normalized EEM-FRI was presented in brackish lakes compared with freshwater lakes (51.8%) (Fig. 5), signifying a greater formation of macromolecular structures of humic-like substances. These processes could account for DOC and nutrients accumulating in terminal brackish lakes. RDA results also indicated that environmental variables (CDOM absorption and fluorescence) showed a relatively more positive correlation with water quality in brackish lakes than in fresh lakes (Fig. 9). Zhao et al. (2016) reported that the formed macromolecular structures of humic-like substances in brackish aquatic environments can regulate the solubility of heavy metals and organic pollutants in water. For areas of brackish lakes in the study site, elevated DOC concentrations could be attributed to evapo-concentration and accumulation due to long residence times.

4.2 The effect of solar radiation/ elevation

In these synchronous processes (arid environment, terminal lakes and terrestrial inputs), it is also important to highlight that these lakes receive higher levels of ultraviolet radiation due to increasing altitude and a thin atmosphere compared to other studies (Ren et al., 1997) (Fig. 1c). These attributes result in increased exposure to sunlight, an increase in water residence times and strong UV radiation with an increase of altitude. These factors may have an important influence on the photochemical oxidation processes of DOC/CDOM and the mineralization of DOC (Duarte et al., 2005; Tobias and Bohlke, 2011). Among the 63 lakes (*N*=224), the average M(E_{250}:E_{365}) (28.3± 20.3), $S_{275\text{-}295}$ (0.0380 ± 0.009 nm^{-1}) and $SUVA_{254}$ (1.47 ± 2.55 mg C^{-1} m^{-1}) in the brackish lakes (*N*=109) were distinctly different from fresh lake results (*N*=135): *a*(350) (1.74 ± 1.99 m^{-1}), M(E_{250}:E_{365}) (16.27 ± 20.6), $S_{275\text{-}295}$ (0.0324 ± 0.01 nm^{-1}) and $SUVA_{254}$ (2.29 ±1.36), respectively. This pattern is similar to that reported by Boehme et al. (2004) in the Gulf of Mexico. In contrast with previous research indicating that brackish (terminal) lakes always contain terrestrial DOM accumulation, our results show that they were provided with low aromatic moieties of CDOM and average molecular weight of DOC compared within fresh lakes (Helms et al., 2008; Gonnelli et al., 2013). Results also highlighted significant differences in total fluorescence intensities φ_T between brackish lakes (1.44×10^{10}± 8.1×10^9 nm) and fresh lakes (1.38×10^{10} ± 7.9×10^9 nm) (ANOVA, p<0.001) (Fig. 5 and Fig. 6), respectively. However, we found that the average normalized total fluorescence intensities φ_T between brackish lakes (1.1×10^9±8.8 QSU-nm^2-[mg L^{-1} C]) and fresh lakes (3.3×10^9 ±2.6 QSU-nm^2-[mg L^{-1} C]) showed opposite vitiation tendency when the φ_T was normalized to a DOC concentration of 1 mg L^{-1}. This finding may account for relatively higher colorless DOC present in the brackish

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lakes compared with the fresh lakes, a finding linked to solar radiation and prolonged hydraulic retention time (Table S1).

In order to evaluate the influence of solar irradiance to CDOM optical characteristics (Fig. 10), solar irradiance was divided into three groups (>2900 h; >2800 h; >2700 h) based on the consistent result of decreasing tendency between elevation (solar radiation) and DOC concentration (Fig. 2). Strong solar radiance and time could accelerate chromophores associated with high molecular weight being destroyed by chemical bond rupture into low molecular weight pools in photolysis processes with a prolonged hydraulic retention time and intensive solar radiation (McKnight et al., 2001). However, for water samples with a solar radiance >2900 h (averaged solar irradiance), DOC recorded a moderate positive correlation with *a*(254) concentrations (R^2=0.73, *t*-test, p<0.01), and a correlation with FI_{370} (R^2=0.50, *t*-test, p<0.01). This indicated that, in areas of the Tibet Plateau with intensive UV-B radiation (solar irradiance, >2900 h), parts of the colored DOM (mainly from allochthonous inputs) have similar sources with DOC. In addition, the PCA result of normalized cumulative volume φ_i by EEM-FRI in this study exhibited that φ_{IV} (microbial protein-like) was consistent with φ_V (humic-like) and φ_{III} (fuvic-like), signifying that they have common sources (Fig. 7). A positive correlation between the total normalized cumulative volume $\varphi_{III\&IV\&V}$ and $\varphi_{I\&II}$ (R^2 = 0.76, N= 109; *t*-test, p<0.01) in brackish lakes also demonstrated that microbial protein-like FDOM in these lakes had high DOC concentrations associated with products from terrestrial microbial decomposition (Fig. 8d). Zhang et al. (2013) identified correlations between total bacterial community structure and altitude in Tibet, and they did not found more microorganism usually dominate in other lake environments, even though a relative high average percentage of P_{IV} (brackish 15.8%; freshwater 13.3%) were identified for normalized cumulative volume (Fig. 5). In the Tibet Plateau, intensive

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solar radiance has the potential to enhance photochemical degradation of allochthonous CDOM and high molecular weight CDOM, resulting in an increase in absorption parameters with the production of low molecular weight CDOM. These findings are contrary to those recorded from rivers in intermontane plateaus in the USA (Spencer et al., 2012), lakes in the Songnen Plain, China (Song et al., 2013), Hulun Lake, China (Wen et al., 2016) and basin rivers in China (Zhao et al., 2016). In arid and semi-arid regions, brackish lakes commonly support highly active biological communities which can actively break down refractory organic matter into DOC and accumulate in waters (Wen et al., 2016). However, due to strong UV-B radiation and terminal lakes in the Tibet Plateau, long sunlight duration may result in photobleaching of CDOM which will limit microbial activities and increase mineralization of DOC (Granéli et al., 1996; Duarte et al., 2005). These Characteristics characters result in CDOM and DOC in brackish lakes in the study area being similar to that in marine environments. Zhang et al. (2013) reported that the majority of lakes in Tibet were affiliated with SAR11-III clade, similar to observations from Chesapeake Bay bacterio plankton. These findings show that solar radiation has a non-negligible effect on CDOM photo-absorption characteristics, and that it contributes to DOC variability and fate. In addition, a comparatively prolonged hydraulic retention time (Duarte et al., 2005) and terrestrial allochthonous inputs could cause higher DOC production and accumulation.

[Insert Figure 10 about here]

4.3 Effects of land-cover variation on lakes

Land-cover types within and around each lake affect soil runoff and leaching, having an important effect on CDOM inputs and nutrient levels. These effects result in obvious differences in physicochemical properties between the lakes (Bai et al., 2008; Heinz et

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al., 2015; Song et al., 2013). In particular, for water samples dominated by allochthonous substances in terminal lakes, spatial variations influenced terrestrial inputs from soil and microbial activities due to plant decay. The land-cover in the basin can also affect CDOM components and FDOM with similar climatic and hydrological conditions. In order to acquire the integrated land-cover area of each basin, 20 basins (B1-B20) were extracted using a 30 m resolution DEM (Digital Elevation Model; http://www.gscloud.cn/). The proportion of different land use types to total basin area is shown in Figure S2. In the Tibet Plateau, grass with plentiful organic-rich ecosystems were the major land-cover types, accounting for amounts of total basin area (Fig. S2). CDOM optical parameters of lake samples in each basin were averaged to analyze the influence of land-cover, results showing a moderate correlation between DOC and normalized humic-like φ_V for 20 basins (R^2=0.54, *t*-test, p<0.01; Fig. 11). Due to the grass area accounting for amounts of basins (Fig. S3), normalized φ_{III}, φ_{IV} and φ_V in basins with large grass areas (average area 14876 km^2; N=10 basins) exhibited higher values than in basins with small grass areas (averaged area 1976 km^2; N=10 basins) (ANOVA, p<0.05). Similar results were also found for forest and unused land, although they accounted for small proportions of total area (Fig. 11). The Tibet Plateau is located in an arid climatic zone with low rainfall, and the impoundment of lakes mainly depends on surface runoff. Grasslands and forests where characterized by high nitrogen and organic matter export rates (Bai et al., 2008; Heinz et al., 2015). High DOC concentrations in the lake waters highlights the organic-rich nature of these ecosystems (Zheng et al., 2015). As a result of climatic and geographical conditions, these environment factors may change the optical characteristic of CDOM and water quality in the Tibet Plateau.

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5. Conclusions

Little is currently known about CDOM fluorescence and its relationship with water quality in lakes across the Tibet Plateau. This area has a unique environmental condition with strong ultraviolet radiation and low anthropogenic impact. In this study, EEM-FRI was applied to characterize CDOM from 63 lakes (N=244) under spatial variation between brackish lakes (salinity>1‰) and fresh lakes (salinity<1‰). Significant differences of CDOM absorption parameters, normalized φ_T and DOC concentrations were found between the two lake types (ANOVA, p<0.05), indicating lower average molecular weight of DOM in brackish lakes.

Although the terrestrial component (φ_{III} and φ_V) accounted for large amounts of fluorescence, PCA results indicated that the majority of microbial protein-like fluorescence φ_{IV} of CDOM in the lakes derived from terrestrial microbial decomposition products. This was attributed to DOC accumulation in terminal brackish lakes having a prolonged hydraulic retention time and solar radiation. In addition, correlations between average DOC concentrations and a(254) in annual total sunshine hours > 2900 h or salinity >19‰ (averaged EC, 23764μs cm $^{-1}$) were identified, while R^2 values of regression analysis had a decreasing tendency with sunshine hours and salinity, respectively. Findings from our study also demonstrated that CDOM components were affected by spatial variation in land-cover (mainly grass) (ANOVA, p<0.05), with a moderate relationship between average normalized φ_V and DOC concentration from 20 basins (R^2=0.54, t-test, p<0.01). These results demonstrate that salinity, solar hours and land–cover may contribute to CDOM and DOC properties. The EEM-FRI method was also shown to be very useful for evaluating the spatial dynamics of FDOM components.

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858 **Figure 1 (a)** Map of sampling locations from lakes in Tibet Plateau with various land
859 use/land cover types; (b) the elevation (m) of Tibet Plateau; (c) sunshine duration
860 characteristics for the Tibet Plateau. The total sunshine hours in 2016 were from China
861 meteorological data sharing service system.

862

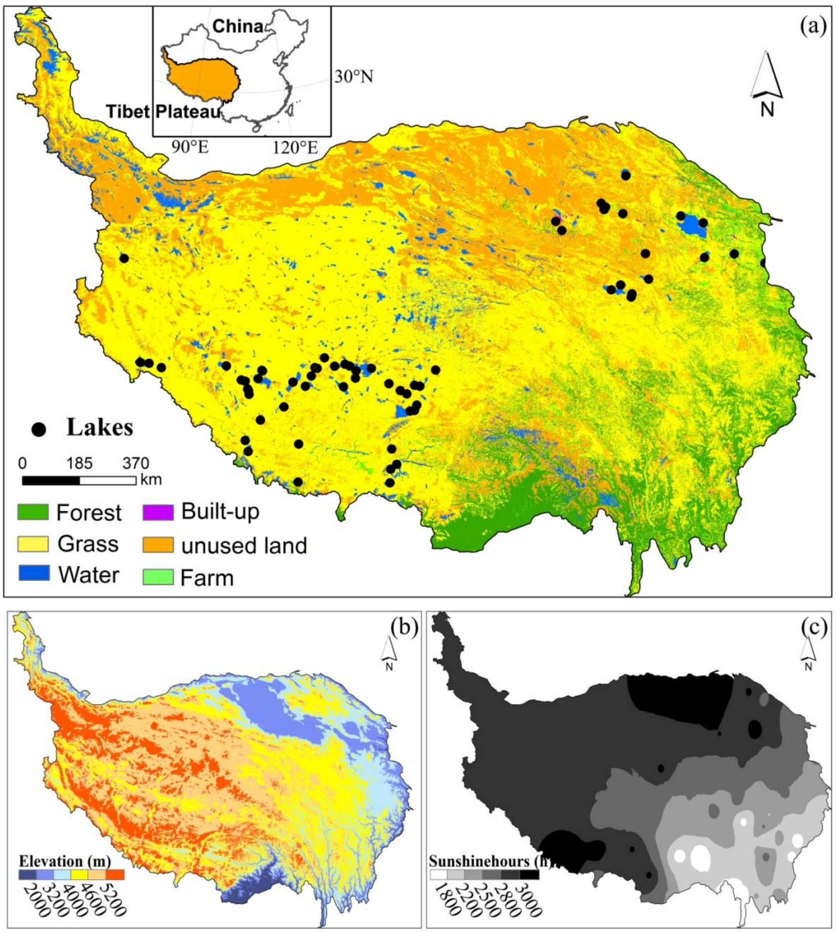

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Figure 2 The DOC, salinity and elevation from 63 lakes collected in Tibet Plateau, (a) The elevation (m) of 63 lakes in Tibet Plateau and corresponding DOC concentrations, and (b) Mean DOC and salinity (EC) of 63 lakes. The full line represents the tendency linear equation of average DOC concentrations. The numbers was the lake name according to Table S1.

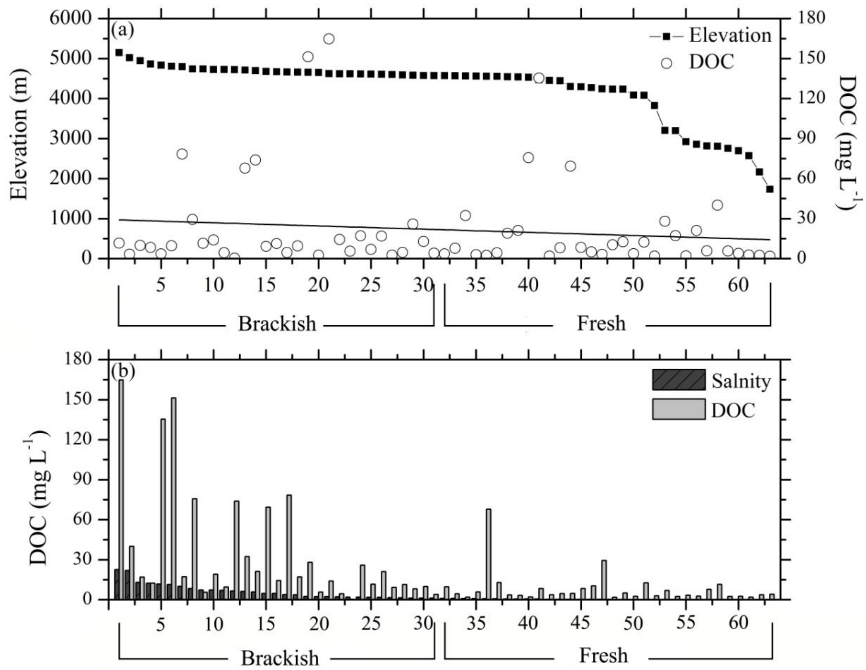

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Figure 3. Box plots of $a(254)$ (a), $a(350)$ (b), M(E_{250}：E_{365}) (c), $S_{275\text{-}295}$ (d) and $SUVA_{254}$ (d) for brackish and fresh waters in the Tibet Plateau. The black line and the hollow squares represent the median and mean values, respectively. The horizontal edges of the boxes denote the 25th and 75th percentiles; the whiskers denote the 10th and 90th percentiles. The black circles represent samples of brackish lakes, and red were fresh lakes. Then the unit of SUVA254 is mg C^{-1} m^{-1}, $S_{275\text{-}295}$ is nm^{-1}, and CDOM absorption at 254 nm and 350 nm is m^{-1}.

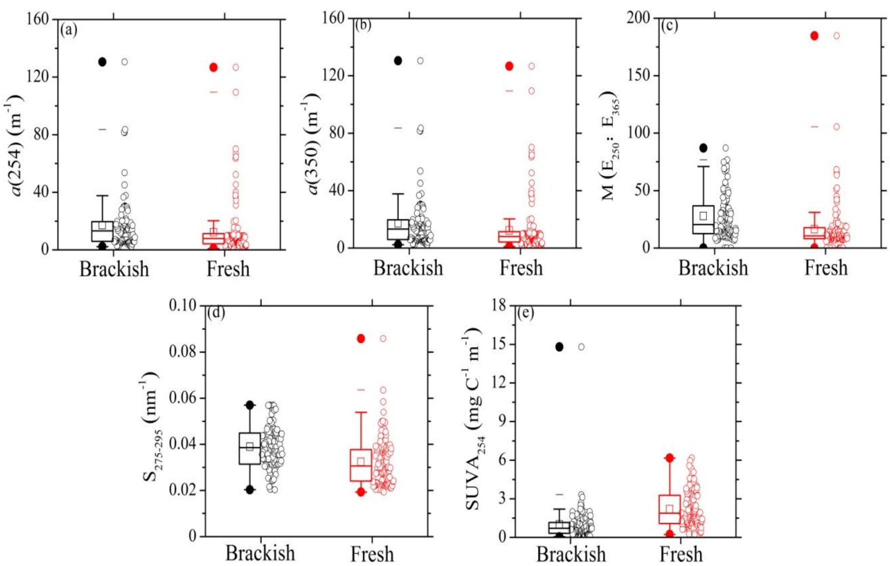

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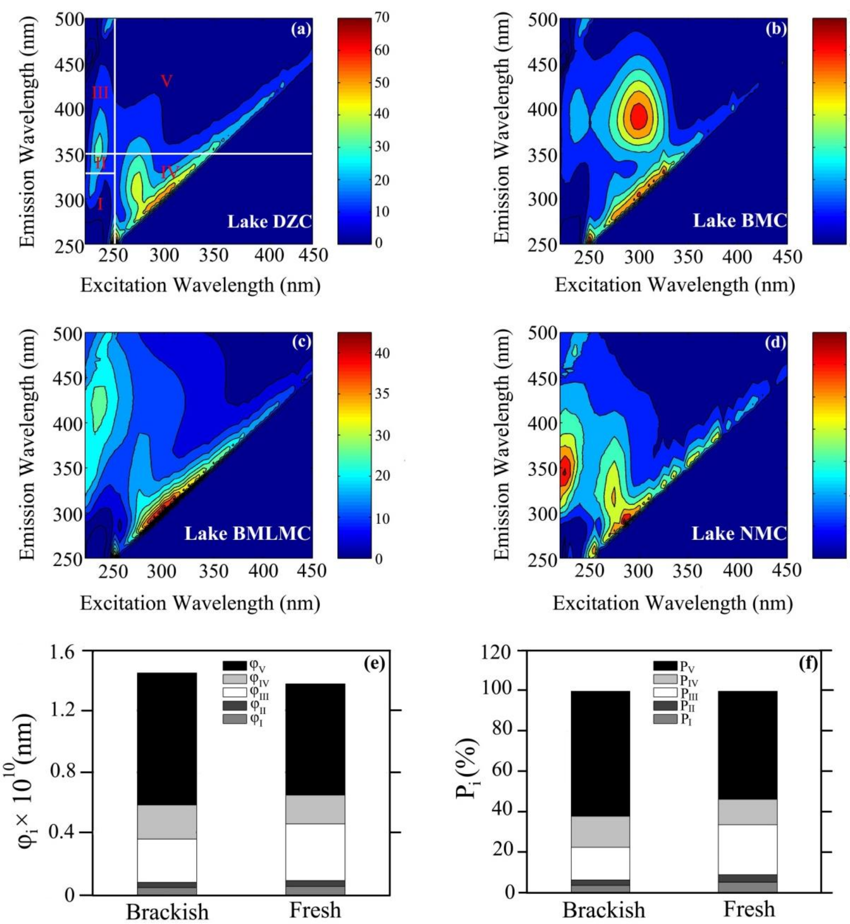
Figure 4. Four typical EEM fluorescence spectra (a-d) and FRI results, (a) Lake DZC, (b) Lake BMC, (c) Lake BMLMC, (d) Lake NMC, (e) The proportion and cumulative volume proportion of EEMFRI-extracted average FDOM components from five regions in brackish lakes and fresh lakes in Tibet Plateau and (f) distributions of percentages of EEM-FRI extracted FDOM.



883 **Figure 5**. Normalized EEM-FRI fluorescence component and spatial characteristics from 63 lakes in Tibet Plateau, (a) normalized cumulative volume φ_i of EEM-FRI extracted average FDOM components from five regions in brackish lakes and fresh lakes, (b) percentages P_i of EEM-FRI extracted FDOM in brackish lakes and fresh lakes, (c) spatial distributions of normalized cumulative volume φ_i in brackish lakes and fresh lakes and (d) spatial distributions of percentages P_i of EEM-FRI extracted FDOM in brackish lakes and fresh lakes.

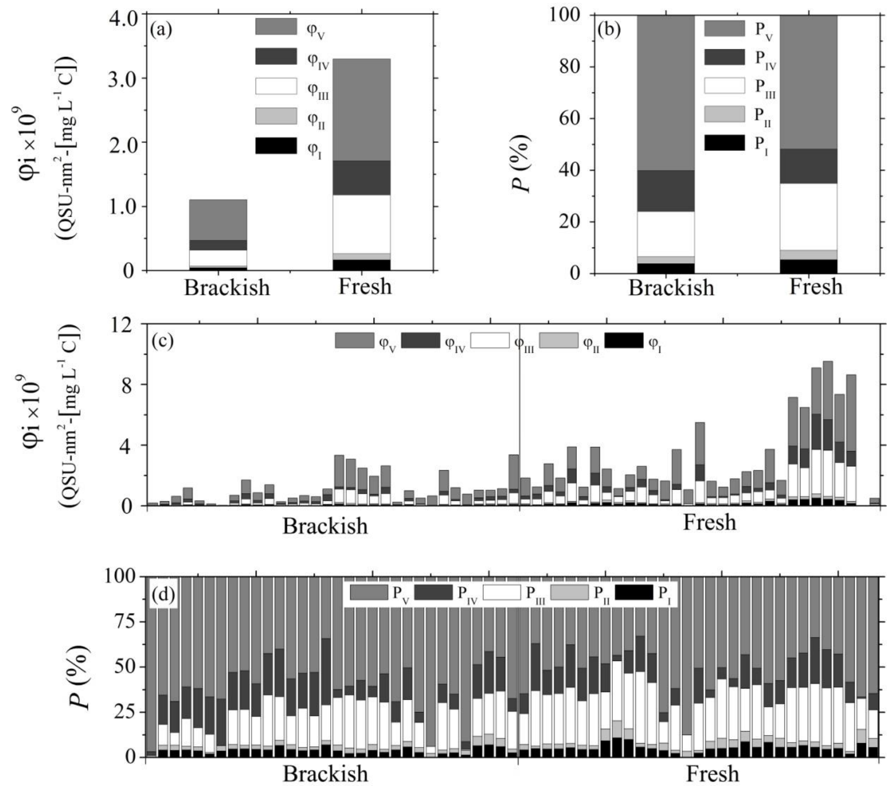


Figure 6. Box plots of *HIX* (a), FI_{370} (b) and FI_{310} (c) for brackish and fresh waters in the Tibet Plateau. The black line and the hollow squares represent the median and mean values, respectively. The horizontal edges of the boxes denote the 25th and 75th percentiles; the whiskers denote the 10th and 90th percentiles. The black circles represent samples of brackish lakes, and red were fresh lakes.

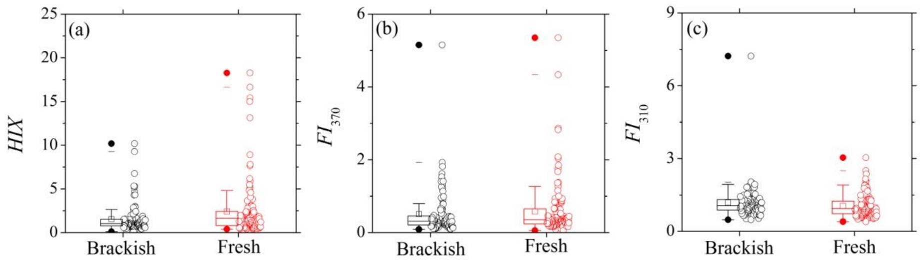


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Figure 7. Principal component analysis (PCA) results of normalized cumulative volume φ_i by EEM-FRI. (a) Loadings of PCA factors and (b) property-property plots of PCA factor scores of 63 lakes. The unit of normalized cumulative volume φ_i (i=I, II, III, IV, V) is QSU-nm^2-[mg L^{-1} C].

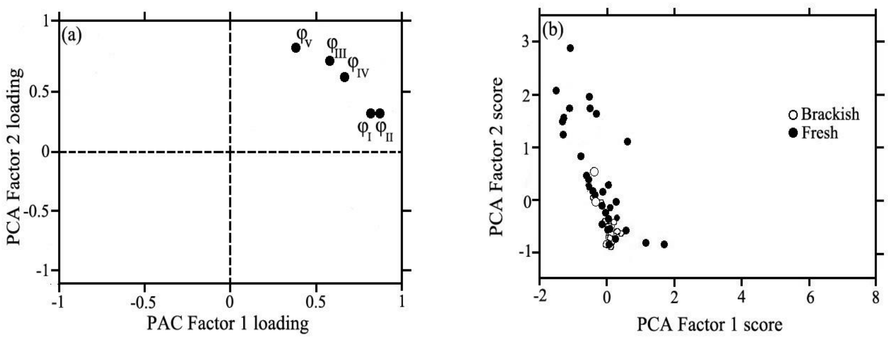

Figure 8. The correlations between normalized cumulative volume φ_{I} and φ_{II} by EEM-FRI for water samples in brackish lakes and fresh lakes (a); the correlations between normalized φ_{I} and φ_{IV} (b); the correlations between normalized φ_{II} and φ_{IV} (c); the correlations between normalized $\varphi_{III\&IV\&V}$ and $\varphi_{I\&II}$ by EEM-FRI (d); the correlations between *a*(350) and FI_{370} (e), and the correlations between *a*(350) and *HIX* (f). The unit of normalized cumulative volume φ_i (*i*=I, II, III, IV, V) is QSU-nm^2-[mg L^{-1} C], and *a*(350) was nm^{-1}.

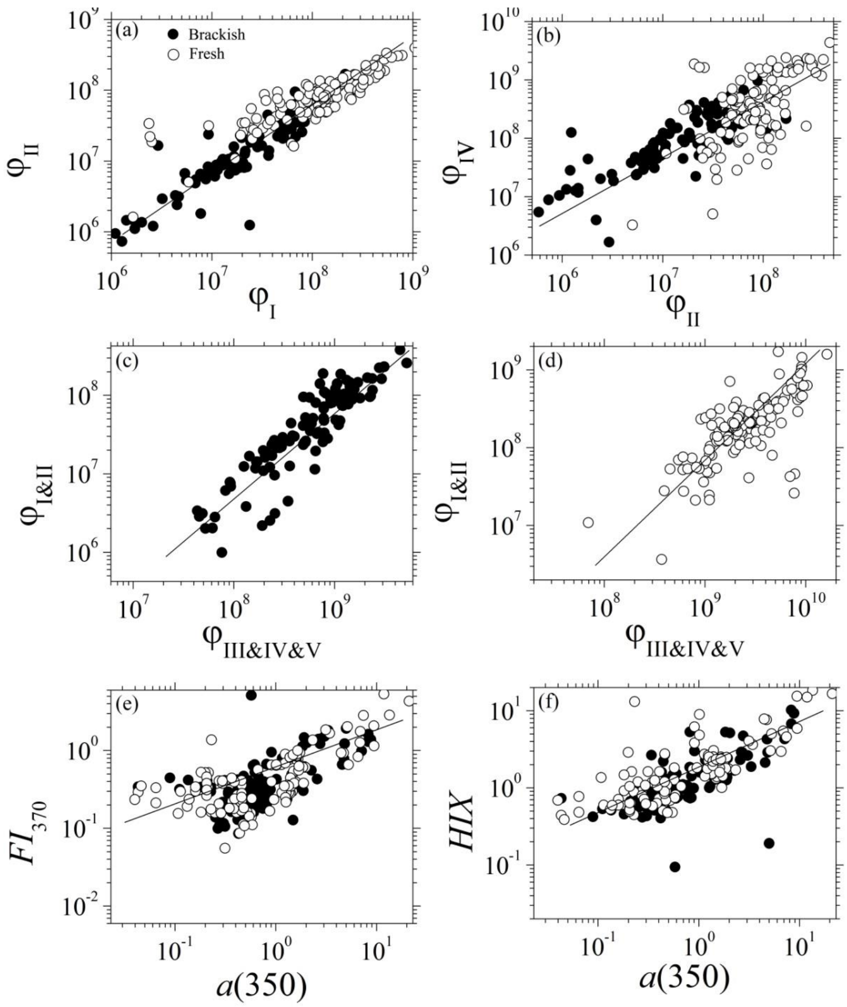

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Figure 9. Redundancy analysis (RDA) of CDOM spectroscopic parameters and the water quality parameters ib (a) brackish lakes and (b) fresh lakes Tibetan Plateau. φ_I was deleted due to large inflation factor (>20). The solid arrows and black font represent the environmental explanatory variables, and hollow allows and blue fonts were species variables, respectively. (c) and (d) are the correlation between *a*(254), DOC and FI_{370} in brackish and fresh lakes. The unit of TN, TP and DOC was mg L^{-1}; Chl-a was μg L^{-1}; salinity is ‰; turbidity is NTU (nephelometric turbidity unit). Then the unit of *a*(254) and *a*(350) is m^{-1}; $SUVA_{254}$ is L mg C^{-1} m^{-1};φ_i (i=I, II, III, IV, V) is QSU-nm^2-[mg L^{-1} C].

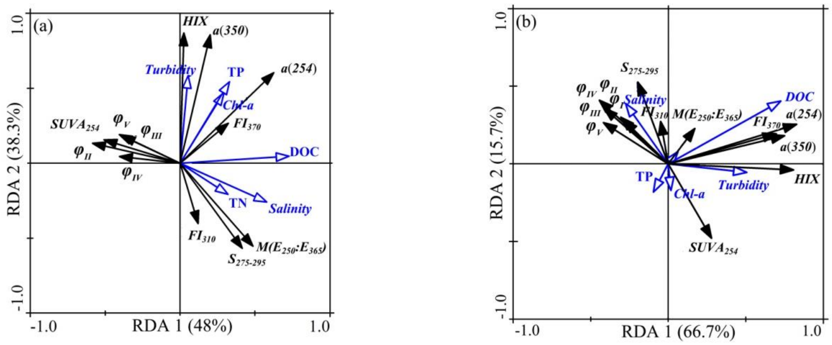

Figure 10. The correlation between average DOC concentrations and *a*(254) in annual total sunshine hours > 2900h (a), annual total sunshine hours > 2800h (b) and annual total sunshine hours > 2600h (c). Then the correlation between average DOC concentrations and FI_{370} in annual total sunshine hours > 2900h (d), annual total sunshine hours > 2800h (e) and annual total sunshine hours > 2600h (f). The annual total sunshine hours in Tibet are from the China metrological data sharing service system.

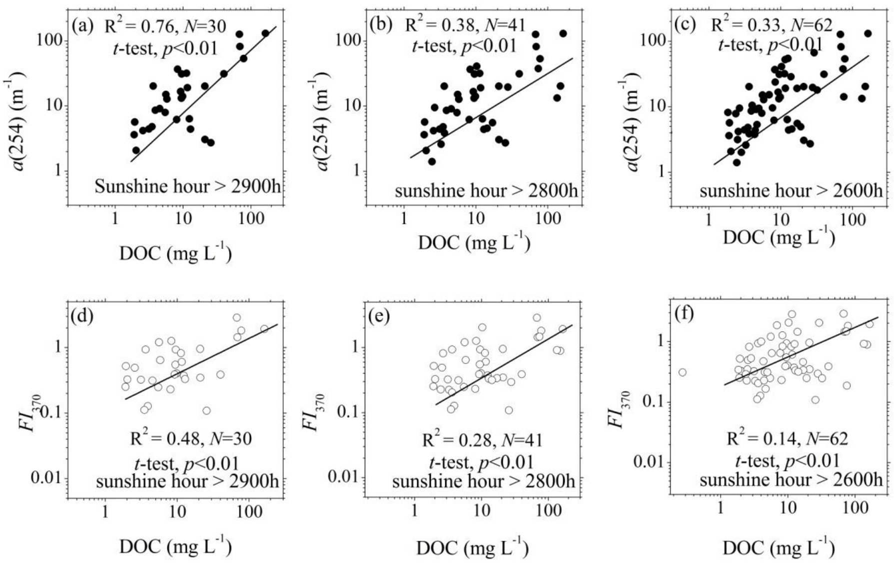

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Figure 11. (a) Box plots of normalized φ_{III}, φ_{IV} and φ_V in basins with large grass area (averaged area 14876 km^2; *N*=10 basins, B1, B10, B19, B2, B11, B17, B12, B5, B20, B14), and basins with small grass area (averaged area 1976 km^2; *N*=10 basins, B4, B6, B8, B9, B3, B15, B18, B16, B13, B17). (b) Box plots of normalized φ_{III}, φ_{IV} and φ_V in basins with large forest area (averaged area 633.9 km^2; *N*=5 basins, B2, B1 B4, B11, B10), and in non-forest land. (c) Box plots of normalized φ_{III}, φ_{IV} and φ_V in basins with large unused land area (averaged area 9049 km^2; *N*=10 basins, B1, B4, B2, B17, B3, B10, B11, B20, B19, B12), and basins with small grass area (averaged area 170 km^2; *N*=10 basins, B6, B14, B8, B9, B15, B16, B7, B13, B5, B18). The black line and the hollow squares represent the median and mean values, respectively. The horizontal edges of the boxes denote the 25th and 75th percentiles; the whiskers denote the 10th and 90th percentiles. (d) The correlation between DOC and normalized humic like φ_V of 20 basins in Tibet Plateau.

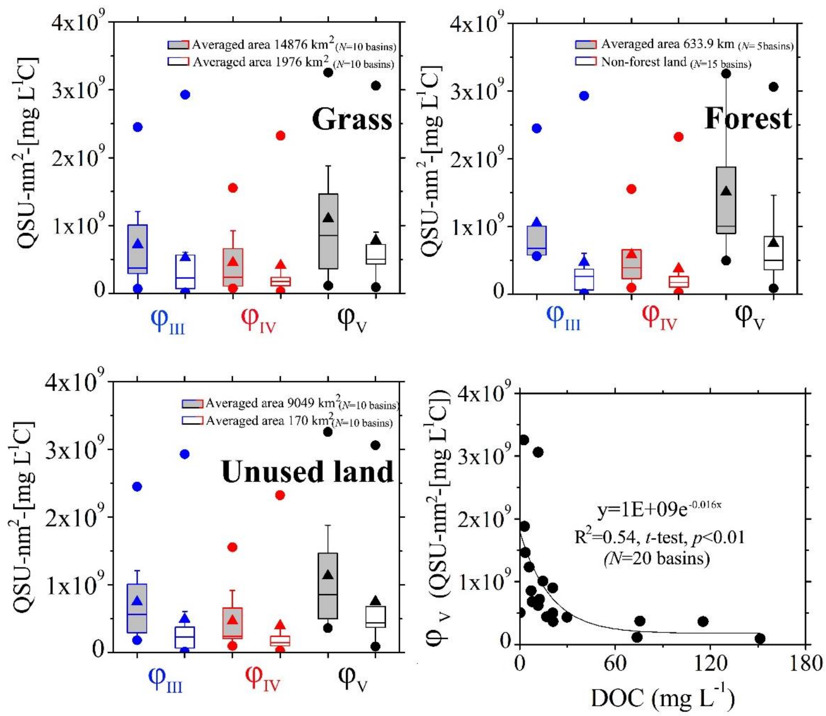

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Table 1 Water quality parameters of samples from 63 lakes (*N*=244) in Tibet Plateau

Parameters	Brackish Lakes (*N*=109)		Fresh Lakes (*N*=135)	
	Mean	Max-Min	Mean	Max-Min
Turbidity	14.63±24.40	0-87.78	16.7±43.61	0-212.51
EC	8880.23±8235.912	1673-33141.2	536.55±332.29	120.1-1369.2
Salinity	6.01±5.60	1.14-22.54	0.36±0.22	0.08-0.93
TN	4.54±4.32	0.31-15.56	2.31±2.64	0.16-10.15
TP	0.45±1.35	0.006-6.79	0.04±0.03	0.001-0.08
Chl-a	2.57±5.73	0-31.37	1.4±2.68	0.09-14.68
DOC	35.69±43.52	0.27-164.8	7.94±12.17	1.84-67.79

TN, TP, DOC, DTC, and DIC represent total nitrogen, total phosphorus, dissolved organic carbon, dissolved total carbon and dissolved inorganic carbon concentrations, respectively (mg L^{-1}). EC represents the electrical conductivity of water samples (μs cm^{-1}). Chl-a, chlorophyll-a concentration (μg L^{-1}). The unit of turbidity is NTU, nephelometric turbidity unit, and salinity is ‰.

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Table 2 Regression analysis equations of DOC concentration and normalized cumulative volume φ_i (i=I, II, III, IV, V) for all the water samples from 63 lakes (N=244) in Tibet Plateau

Salinity	Averaged EC	Regression equation	R^2
		DOC & φ_I **(Tyrosine like)**	
>19	23764	$y=3E+07e^{-0.013x}$, (N=29)	0.73
>7	10945	$y=3E+07e^{-0.014x}$, (N=64)	0.42
>2	5708	$y=3E+07e^{-0.014x}$, (N=84)	0.34
>1	2119	$y=4E+07e^{-0.015x}$, (N=109)	0.34
<1	586	$y = 1E+08e^{-0.034x}$, (N=135)	0.03
		DOC & φ_{II} **(Tryptophan like)**	
>19	23764	$y=1E+07e^{-0.009x}$, (N=29)	0.64
>7	10945	$y=2E+07e^{-0.012x}$, (N=64)	0.41
>2	5708	$y=2E+07e^{-0.012x}$, (N=84)	0.34
>1	2119	$y=2E+07e^{-0.014x}$, (N=109)	0.34
<1	586	$y = 8E+07e^{-0.023x}$, (N=135)	0.03
		DOC & φ_{III} **(Fulvic like)**	
>19	23764	$y = 9E+07e^{-0.009x}$, (N=29)	0.30
>7	10945	$y = 1E+08e^{-0.01x}$, (N=64)	0.15
>2	5708	$y = 2E+08e^{-0.01x}$, (N=84)	0.08
>1	2119	$y = 2E+08e^{-0.01x}$, (N=109)	0.08
<1	586	$y = 7E+08e^{-0.023x}$, (N=135)	0.02
		DOC & φ_{Iv} **(Microbial protein like)**	
>19	23764	$y=1E+08\ e^{-0.010x}$, (N=29)	0.52
>7	10945	$y=1E+08\ e^{-0.012x}$, (N=64)	0.37
>2	5708	$y=1E+08\ e^{-0.012x}$, (N=84)	0.27
>1	2119	$y=1E+08\ e^{-0.012x}$, (N=109)	0.28
<1	586	$y = 4E+08e^{-0.034x}$, (N=135)	0.02
		DOC & φ_v **(Humic like)**	
>19	23764	$y=4E+08\ e^{-0.008x}$, (N=29)	0.59
>7	10945	$y=4E+08\ e^{-0.009x}$, (N=64)	0.28
>2	5708	$y=4E+08\ e^{-0.009x}$, (N=84)	0.23
>1	2119	$y=5E+08\ e^{-0.010x}$, (N=109)	0.25
<1	586	$y = 2E+09e^{-0.02x}$, (N=135)	0.03
		DOC & $\varphi_{III\&VI\&V}$ **(Humic like& Microbial protein like & Fulvic like)**	
>19	23764	$y = 5E+08e^{-0.009x}$, (N=29)	0.58
>7	10945	$y = 6E+08e^{-0.01x}$, (N=64)	0.30

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>2	5708	$y = 7E{+}08e^{-0.01x}$, (N=84)	0.24
>1	2119	$y = 8E{+}08e^{-0.011x}$, (N=109)	0.26
<1	586	$y = 3E{+}09e^{-0.025x}$, (N=135)	0.03
		DOC & $\varphi_{I\&II}$ **(Tyrosine like & Tryptophan like)**	
>19	23764	$y = 4E{+}07e^{-0.013x}$, (N=29)	0.74
>7	10945	$y = 5E{+}07e^{-0.014x}$, (N=64)	0.45
>2	5708	$y = 5E{+}07e^{-0.014x}$, (N=84)	0.32
>1	2119	$y = 6E{+}07e^{-0.015x}$, (N=109)	0.34
<1	586	$y = 2E{+}08e^{-0.03x}$, (N=135)	0.03

950 The unit of EC is μs cm $^{-1}$; salinity is ‰; DOC concentration is mg L^{-1}; φ_i (i=I, II, III, IV, V) is QSU-
951 nm^2-[mg L^{-1} C].