Seasonal characterization of CDOM for lakes in semi-arid regions of Northeast China using excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC)

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Abstract. The seasonal characteristics of fluorescent components in CDOM for lakes in the semi-arid region of Northeast China were examined by excitation-emission matrix (EEM) spectra and parallel factor analysis (PARAFAC). Two humic-like (C1 and C2) and the protein-like (C3 and C4) components were identified using PARAFAC. The average fluorescence intensity of the four components differed under seasonal variation from June and August 2013 to February and April 2014. Components 1 and 2 exhibited a strong linear correlation ($R^2 = 0.628$). Significantly positive linear relationships between CDOM absorption coefficients a(254) ($R^2 = 0.72$, 0.46, $p < 0.01$), a(280) ($R^2 = 0.77$, 0.47, $p < 0.01$), a(350) ($R^2 = 0.76$, 0.78, $p < 0.01$) and F_{max} for two humic-like components (C1 and C2) were exhibited, respectively. A

significant relationship ($R^2 = 0.930$) was found between salinity and DOC. However, almost no obvious correlation was found between salinity and EEM-PARAFAC extracted components except for C3 ($R^2 = 0.469$). Results from this investigation demonstrate that the EEM-PARAFAC technique can be used to evaluate the seasonal dynamics of CDOM fluorescent components for inland waters in the semi-arid regions of Northeast China, and to quantify CDOM components for other waters with similar environmental conditions.

Keywords: CDOM, fluorescent components, EEMs, PARAFAC, DOC, Salinity

1 Introduction

Dissolved organic matter (DOM), a heterogeneous mixture of humic acids, proteins and carbohydrates, plays important roles in aquatic ecosystems (Zhang et al., 2010). Chromophoric dissolved organic matter (CDOM), the colored fraction of DOM, absorbs light energy in the ultraviolet (UV) and visible region of the spectrum and inhibits the propagation of UV radiation. CDOM in waters also affects the transport and bio-availability of materials such as trace metals and other pollutants (Song et al., 2013), so it can be used as a proxy of water quality. In natural water bodies, CDOM originates from the degradation of plant materials and other organisms and terrestrially imported substances, which varies in time and space and is controlled by its structure and composition (Stedmon et al., 2003). CDOM is compositionally complex, making it difficult to isolate hydrophobic from hydrophilic acids using XAD ion-exchange resins (Aiken et al., 1992; Spencer et al., 2010). Nonetheless, some

optically active components of CDOM can emit fluorescence after absorbing light at certain wavelengths (Zhang et al., 2010) so that the fluorescence spectroscopic techniques can be used to provide detailed information about the source and concentration of CDOM. The traditional fluorescence techniques including fluorescence emission spectrometry and synchronous fluorescence scanning applied to examine CDOM components have the drawback that the output was restricted to a linear scan (Hudson et al., 2007).

Recently, excitation-emission matrix fluorescence spectroscopy (EEM) has been applied to identify CDOM components because of its ability to produce synchronous scan spectra in the form of contours (Stedmon et al., 2003; Zhang et al., 2010). The EEM spectroscopy is considered the most effective technique for studying the composition of fluorophores given its high selectivity and sensitivity to CDOM in water columns (Zhang et al., 2010). In recent years, EEM spectroscopy has been widely used to investigate the dynamics of marine, freshwater and ice-water ecosystems as well as snow melting water (Barker et al., 2006, 2009, 2010, 2013; Coble, 2007; Fellmanet al., 2010; Guo et al., 2010; Hudson et al., 2007; Stedmon et al., 2007). Moreover, the EEM spectroscopy can also be used to distinguish allochthonous and autochthonous CDOM sources in aquatic environments (Coble et al., 1998; Mayer et al., 1999; Yamashita et al., 2008, 2010; Zhang et al., 2013). Based on the peak positions in EEMs, two main fluorescent components, i.e., humic-like and protein-like substances, have been identified and investigated (DelCastillo et al., 1999; Jaffe´ et al., 2004). However, overlapped fluorophores of CDOM EEMs could make

68 this traditional ‘peak-picking’ method unreliable to evaluate CDOM dynamics in
69 aquatic ecosystems (Coble, 1996; Stedmon et al., 2003). Recently, the combined
70 EEMs-PARAFAC (parallel factor analysis) technique has been shown to effectively
71 decompose EEM of CDOM into independent fluorescent components and assess the
72 source of CDOM and relationships with other water quality parameters. A number of
73 investigators have used EEMs-PARAFAC to characterize DOM in freshwater and
74 marine aquatic environments (Broisover et al., 2009; Cory et al., 2005; Guo et al.,
75 2010; Stedmon et al., 2003; Stedmon and Markager, 2005; Yamashita, 2008; Zhang et
76 al., 2010, 2011, 2013). Stedmon et al. (2003) introduced PARAFAC and identified
77 five distinct DOM components for a Danish estuary and its catchment. In coastal
78 environments, Yamashita et al. (2008) reported on seven components using the
79 combined EEMs-PARAFAC technique and assessed the dynamic of individual
80 fluorophores and their relationship with salinity in Ise Bay. Zhang et al. (2011) also
81 found three different components by PARAFAC modeling and analyzed the
82 correlations between the fluorescent components and absorption coefficients of
83 CDOM for Lake Tianmu and its catchment.

84 The Songnen Plain is a fluvial plain with semi-arid climate, in which many fresh
85 and brackish waters are distributed according to its geomorphological characteristics
86 (Song et al., 2013). Dissolved organic carbon (DOC) characterisitics of these fresh
87 and brackish waters across the Songnen Plain have been studied by Song et al. (2013);
88 the results indicated that a huge amount of DOC was stored in these waters. In
89 particular, brackish waters would exhibit high average DOC concentrations and

90 significantly contributed the carbon budget to inland waters (Duarte et al., 2008; Song
91 et al., 2013; Tranvik et al., 2009). However, little study has been made on the detailed
92 information of DOC sources for these waters in the Songnen Plain. Therefore, it
93 motivated us to investigate the components in CDOM for both fresh and brackish
94 waters in the semi-arid region. In the present study, the absorption and fluorescence of
95 CDOM were determined for the water samples collected from seven lakes in the
96 western part of Jilin province, which varied at different seasons. The specific
97 objectives of this study are to: 1) characterize CDOM components contained in these
98 lakes using EEMs and their origins through the EEM-PARAFAC method; 2) assess
99 the dynamic of individual fluorescent components of CDOM under seasonal variation;
100 and most importantly 3) link CDOM fluorescence intensities, absorption coefficients,
101 DOC concentrations and salinity to each other, in order to establish proxies for
102 CDOM bioavailability and photoreactivity in waters.
103

104 # 2 Materials and Methods

105 ## 2.1 Lakes and water sampling

106 The water bodies investigated in this study were located in the western part of Jilin
107 Province, which belongs to the semi-arid part of the Songnen Plain (Song et al., 2013).
108 Two groups of lakes were investigated, i.e., the Chagan lake group and the Yuelianghu
109 lake group. The Chagan lake group is made up of Lake Chagan (CGL), Xinmiaopao
110 (XMP), Xindianpao (XDP) and Kulipao (KLP). The Yuelianghu lake group mainly
111 includes Lake Yueliang (YLL), Talahong (TLH) and Xinhuangpao (XHP) (Fig. 1).

112 The two groups are about 60 km away from each other, of which each includes both
113 fresh and brackish waters. The primary economic value for these lakes is fisheries,
114 agricultural irrigation and recreation. The average annual precipitation is about 391
115 mm, but the average evaporation is up to 1790 mm, resulting in water scarcity. Due to
116 the area dominated by saline-alkali soil, the rainfall flush and agricultural catchment
117 land use can result in an increase of lake salinities. These seven lakes are endowed
118 with similar geological, hydrological and climatic settings, thus we presume that
119 similar processes may control the CDOM components. In order to characterize the
120 CDOM fluorescent components under seasonal variation using EEMs-PARAFAC, 67
121 water samples were collected from the surface of the seven lakes in 1-liter
122 acid-cleaned plastic bottles during four field campaigns in June and August 2013 as
123 well as in February and April 2014, respectively. These samples were collected during
124 the ice covering period using an ice drilling auger. The under-ice surface water was
125 coming up when a hole was drilled in the ice layer by the auger. The ice shavings
126 were collected in plastic bags and the under-ice surface water was collected in plastic
127 bottles. The collected samples were held on ice and immediately transported to the
128 laboratory in the Changchun City of Jilin province within 3-5 hours. In the laboratory,
129 these samples were filtered within 24 h and then kept at 4 ℃ until analysis within two
130 days. Latitude and longitude of each sample location were recorded *in situ* using a
131 Trimble Global Positioning System (GPS).

132

133 **Figure 1. Locations of the water sampling sites for 7 lakes in the western part of Jilin**
134 **province, Northeast China. a) Yueliang lake group: YLL, Yueliang Lake; XHP;**

Xinhuangpao; TLH; Talahong; b) Chagan lake group: CGL, Chagan Lake; XDP, Xindianpao; XMP, Xinmiaopao; KLP, Kulipao.

2.2 Analytical procedures

To characterize the basic parameters of water quality, salinity was measured through a DDS-307 electrical conductivity (EC) meter in the laboratory. Salinity was expressed in the basis of the UNESCO practical salinity unit. The pH was measured using a PHS-3C pH meter at room temperature (20 ± 2 ℃) in the laboratory. Water turbidity was determined using the Shimadzu UV-2600PC UV-Vis dual beam spectrophotometer with matching 3 cm quartz cells at room temperature (20 ± 2 ℃) with Milli-Q water as the reference (UV talk letter vol. 10, https://shimadzu.com.au/uv-talk-letter-volume-10). To determine DOC concentrations, water samples were filtered through 0.45 μm filters and then measured using a Shimadzu TOC-5000 Analyzer and a 1.2 % Pt on silica catalyst at 680 °C. Potassium hydrogen phthalate was used as a standard. The reproducibility of the analytical procedure was within 2-3 % for the current study (APHA, 1998; Song et al., 2011).

2.3 Absorption measurement

In the laboratory, all the samples were filtered at low pressure, first through a pre-combusted Whatman GF/F filter (0.7 μm), and then through a pre-rinsed 25 mm Millipore membrane cellulose filter (0.22 μm) into glass bottles. Absorption spectra of the samples were measured between 200 and 800 nm at 1 nm increments using the Shimadzu UV-2600PC UV-Vis dual beam spectrophotometer with a 1 cm quartz

158 cuvette and Milli-Q water as reference. The absorption coefficient a_{CDOM} was
159 calculated from the measured optical density (OD) of the sample using Eq. (1):

160 $$a_{CDOM}(\lambda) = 2.303\left[OD_{(\lambda)} - OD_{(null)}\right]/\gamma \quad (1)$$

161 where γ is the cuvette path length (0.01 m) and the factor 2.303 converts from base 10
162 to base natural logarithm transformation. Some fine particles possibly remained in the
163 filtered solution (Babin et al., 2003; Bricaud et al., 1995), therefore it was necessary
164 to correct for scattering by fine particles and in this case, $OD_{(null)}$ is the average optical
165 density over 740-750 nm where the absorbance of CDOM can be assumed to be zero.

166 A CDOM absorption spectrum ($a_{CDOM}(\lambda)$) can be expressed as an exponential
167 function (Babin et al., 2003; Bricaud et al., 1995):

168 $$a_{CDOM}(\lambda_i) = a_{CDOM}(\lambda_r)\exp[-S(\lambda_i - \lambda_r)] \quad (2)$$

169 where $a_{CDOM}(\lambda_i)$ is the CDOM absorption at a given wavelength λ_i, $a_{CDOM}(\lambda_r)$ is the
170 absorption estimate at the reference wavelength λ_r(440 nm), and S is the spectral
171 slope of the CDOM absorption. According to Helms et al. (2008), S is calculated by
172 fitting a linear model to the data over a wavelength range of 275 to 295 nm (*S1*) or
173 350 to 400 nm (*S2*). To eliminate the inter-laboratory variability, the slope ratio S_R=
174 *S1*/*S2* is defined to indicate the molecular weight and photo-bleaching of CDOM
175 (Helms et al., 2008; Zhang et al., 2010).

176

177 **2.4 Three-dimensional fluorescence measurement**

178 The EEMs analysis of CDOM were conducted using a Hitachi F-7000 fluorescence
179 spectrometer (Hitachi High-Technologies, Tokyo, Japan) with a 700-voltage xenon

lamp. The scanning ranges were 200–450 nm for excitation, and 250–500 nm for emission. Readings were collected in the ratio mode at 5 nm intervals for excitation, and at 1 nm intervals for emission, using a scanning speed of 2400 nm min^{-1}. The band-passes were 5 nm for both excitation and emission. A Milli-Q water blank of the EEMs was subtracted to eliminate the water Raman scatter peaks (McKnight et al., 2001; Stemdon et al., 2003; Zhang et al., 2010, 2011).

The inner-filter effect, which results from reabsorption and excitation of the fluorescence itself, can reduce the fluorescence intensity by 5% (Larsson et al., 2007; McKnight et al., 2001). In order to eliminate the inner-filter effect, the EEMs were corrected for absorbance by multiplying each value in the EEMs with a correction factor based on the assumption that the average path length of absorption of the excitation and emission light is one-half length of the cuvette (McKnight et al., 2001; Zhang et al., 2010). The correction function is expressed as follows:

$$F_{corr} = F_{obs} \times 10^{(A_{ex}+A_{em})/2} \quad (3)$$

where F_{Corr} and F_{obs} are the corrected and uncorrected fluorescence intensities and A_{ex} and A_{em} are the absorbance values at the respective excitation and emission wavelengths.

The measured fluorescence intensity is dependent on the concentration of the dissolved fluorophores in water bodies. Finally, the fluorescence intensities of all samples' EEMs were normalized to the area under the Milli-Q water Raman peak (λex=350 nm, λem=371-428 nm) measured daily (Lawaetz and Stedmon, 2009). The

202 contour figures of the EEMs were plotted using the Matlab 10.0 software package
203 (Math Works, Natick Massachusetts, America).
204
205 **2.5 The PARAFAC modeling**
206 PARAFAC, a three-way method, is applied to decompose the CDOM fluorescence
207 into separate fluorescent signals (Andersen and Bro, 2003; Stedmon and Bro, 2008).
208 According to Stedmon and Bro (2008), a similar PARAFAC analysis is carried out in
209 the present study using the DOMFluor toolbox in MATLAB with the "N-way toolbox
210 for MATLAB" (Andersson et al., 2000). Before PARAFAC modeling, the excitation
211 wavelengths from 200 to 220 nm and the emission wavelengths from 250 to 300 nm
212 were deleted because of their poor quality. In order to remove the effect of Rayleigh
213 scatter on PARAFAC modeling, the missing values (NaN-Not a number) were
214 inserted in the regions (Ex-20 ≦ Em ≦ Ex+20 and 2Ex-20 ≦ Em ≦ 2Ex+20; unit: nm)
215 which are significantly influenced by the first and second order scattering from the
216 measured spectroscopic data (Hua et al., 2007; Stedmon and Bro, 2008).
217 To determine the appropriate number of PARAFAC components, the split-half
218 validation procedure was executed to verify whether the model was valid by
219 comparing the emission and excitation loadings from each half (Stedmon and Bro,
220 2008). Split-half analysis is the most effective method for implementing the
221 PARAFAC models, in which the EEMs are randomly divided into four groups of
222 equal size, and then analyzed for two half splits (1-2 and 3-4 half) respectively. If the
223 correct number of components is chosen, the excitation and emission loadings from

the two groups should show the same shape and size (Bro, 1997, 1999). The fluorescence intensity of every component was represented by F_{max} (Raman unit: nm^{-1}) (Stedmon and Markager, 2005).

2.6 Statistical analysis

Statistical analysis was conducted using the SPSS 16.0 software package (Statistical Program for Social Sciences). Regression and correlation analysis was used to describe the relationship between CDOM absorption coefficient, DOC concentration, salinity and F_{max}. A model II-ANOVA was performed to determine seasonal variability is higher than between-lake variability. The difference is considered to be statistically significant when *p*-values are less than or equal to 0.05.

3 Results and discussion

3.1 Water quality conditions

The water quality parameters, i.e., pH, salinity, turbidity for the 67 water samples collected from June 2013 to April 2014 in the western part of Jilin province are displayed in Table 1. When the set of samples from various field trips was pooled together, the waters had high pH values and high salt contents. The highest salinity was present when the lakes were frozen in February 2014, whereas relatively constant values (around 0.40) were exhibited in the other three seasons. Also the water bodies were highly turbid. The highest turbidity was present in June 2013, and then reduced in August 2013, and the lowest value was recorded in February 2014. Compared with

February 2014, the turbidity had almost no change in April 2014 (Table 1).

Table 1. Mean value of water quality parameters from June 2013 to April 2014.

3.2 EEMs characterization of CDOM

Based on the EEMs 'peak picking' technique, the key fluorescence peaks can be observed in 67 water samples: two humic-like and two protein-like substances (Coble, 1996; Stedmon et al., 2003). The humic-like components are the mixture of aromatic and aliphatic compounds-humic-like acids from terrestrial substances, and aquatic humic-like substances of phytoplankton origin. With respect to the protein-like components (i.e., tyrosine-like and tryptophan-like substance), they mainly consist of dissolved amino acids. As an example, Fig. S1 displays the EEMs of samples from lake Xindianpao at different seasons. The peaks comprise two humic-like fluorescence peaks: one in the ultraviolet range (Ex/Em = 220-240/410-430 nm) and the other in the visible range (Ex/Em = 300-340/410-450 nm) and the protein-like fluorescence peaks: tyrosine-like (Ex/Em = 210-230, 270-280/310-330 nm) and tryptophan-like (Ex/Em = 220-230, 280-300/350-370 nm).

In our study, four separate fluorescent components (Fig. 2a-d) and the excitation and emission loadings (e-h) of the four components identified by EEM-PARAFAC are summarized in Fig. 2 and Table 2. The first fluorescent component (C1) was a biological degradation humic-like component comparable to

humic-like peaks (M and N) in marine and in phytoplankton degradation experiments for inland waters (Coble, 1996; Zhang et al., 2009). Component 2 was consistent with the humic-like peaks (A and C) defined by Coble (1996). Component 3 resembles the tryptophan-like (T) component as found by Baker et al. (2004) and Hudson et al. (2007). For component 4, it is likely related to tyrosine-like component (B) (Hudson et al., 2007). Components 3 and 4 represent autochthonous semi-labile CDOM associated with bacteria activity and phytoplankton degradation (Borisover et al., 2009; Stedmon et al., 2003). Particularly, there was a shoulder at the excitation wavelength 310-330 nm in component 3 and 330-340 nm in component 4, which may be due to the residual Raman peaks in some water samples (Fig. 2c-d). In this study, not all of the four components were present in all of the samples.

Figure 2. The PARAFAC modeling output shows the contour plots of the four PARAFAC fluorescent components (a-d) and excitation (black) and emission (red) loadings (e-h) of each component. Fluorescence is in Raman units: nm^{-1}.

Table 2. Positions of the fluorescence maximum peaks of the four components identified by PARAFAC modeling in the present study compared with those previously identified. Secondary excitation maxim is given in brackets.

3.3 Temporal distribution of PARAFAC components

These fresh and brackish water in Jilin province in northeast China are endowed with similar geological, hydrological and climatic settings, thus it is presumed that similar processes may control the CDOM components. When a model II-ANOVA using

season and lake as random effect factors was performed, it shows that the seasonal variability ($F > F_{crit}$, $p < 0.05$) is higher than between-lake variability. Therefore, the water samples from different lakes for every season were pooled together in order to study the seasonal variation of the fluorescent components. As shown in Fig. 3a, the average fluorescence intensity of the four components had seasonal variation. When all the water samples at different seasons were pooled together, the average value of total fluorescence intensity was 2.05 ± 0.93 nm^{-1}, corresponding to the intensities of 0.71 ± 0.32 (C1), 0.33 ± 0.11 (C2), 0.50 ± 0.24 (C3), and 0.51 ± 0.26 (C4) nm^{-1} for different components. These results can demonstrate that the fluorescence intensity was dominated by C1, implying most of the CDOM for the seven inland lakes originated from the degradation of phytoplankton and microorganisms. The protein-like components (C3 and C4), related to bioavailability and microbial activity of CDOM, had almost the same magnitude. At all four seasons, the fluorescent component C2, which was terrestrially imported to water bodies, contributed less to total fluorescence than the other three. The total fluorescence intensity differed under seasonal variation, varying from 2.54 ± 0.68 nm^{-1} in June to 1.93 ± 0.70 nm^{-1} in August 2013, and then increased to 2.34 ± 0.92 nm^{-1} in February and reduced to the lowest 1.57 ± 0.55 nm^{-1} in April 2014 (Fig. 3c). The intensities of four fluorescent components (i.e., 0.75 ± 0.17 (C1), 0.32 ± 0.06 (C2), 0.69 ± 0.24 (C3), and 0.77 ± 0.20 (C4) nm^{-1}) (Fig. 3d) from the samples collected in June 2013 exhibited similar trends to that for the pooled data set. These values were higher than the seasonal average except C2 (0.32 ± 0.06 nm^{-1}). This can be explained by enhanced activities

314 from plant degradation and microbial activities, but less terrestrial substances were
315 imported to the water bodies in June and therefore the fluorescence intensity of C2
316 was lower than the seasonal average. Compared to the fluorescence intensity in June,
317 the three fluorescence intensities (0.65 ± 0.14 (C1), 0.33 ± 0.16 (C3), 0.52 ± 0.36 (C4)
318 nm^{-1}) from the samples collected in August 2013 were reduced, but an increased value
319 was recorded for C2 (0.42 ± 0.05 nm^{-1}) (Fig. 3d). Especially, the fluorescence
320 intensities of two protein-like components showed an obvious difference. This can be
321 attributed to substantially increased precipitation up to 180 mm in July from June to
322 August 2013 (Fig. 3b) so that floods occurred when rainfall continued to increase in
323 August. Gradually, DOM contained in terrestrial CDOM was flushed by rainfall to the
324 lakes so that the C2 (0.42 ± 0.05 nm^{-1}) fluorescence intensity became higher. In
325 accordance with Cheng et al. 2010, the rainwater CDOM for this study was largely
326 characterized by protein-like components (Cheng et al., 2010). The fluorescence
327 intensity of the rainwater CDOM was very weak, and also the rainwater CDOM
328 contained much lower humic-like concentration (Fig. S2b). The intensities of the
329 other three components decreased because of dilution resulting from heavy rain and
330 relatively weak microbial decomposition of plants.

331 The highest C1 (1.02 ± 0.38 nm^{-1}) presented in February 2014, and the C2 (0.39
332 ± 0.12 nm^{-1}) intensity remained almost the same as that in August 2013. However, the
333 protein-like components indicated that the C3 (0.57 ± 0.25 nm^{-1}) intensity was higher
334 than the C4 (0.35 ± 0.17 nm^{-1}) intensity, which was opposite to the results from other
335 months (Fig. 3d). In cold winter, the surface waters formed a thick layer of ice

336 covering the lake waters. Because the ice cover reduced light penetration and
337 restricted gas exchange between the underlying water and atmosphere, vigorous
338 biological activity in the lakes would be reduced at low temperature and low light
339 level (Thomas K., 1983; Uusikiv et al., 2010; Wharton, et al., 1993). Although the
340 biological activity was very weak, there could still be a bit of production of C1 and
341 C3 in lake water. Also, dissolved materials were left in the underlying surface waters
342 and little terrestrial matter was imported to the lakes once covered by ice (Stedmon et
343 al., 2007). Therefore, the C1 and C3 in the water of the lakes beneath the ice layers
344 would be produced and accumulated simultaneously, whereas, the C2 remained the
345 same. Obviously, the fluorescence intensity of component 1 reached the highest value
346 for the winter samples. As shown in Fig. S2a, another striking feature for the winter
347 samples was that the fluorescence of CDOM in the ice was dominated by the
348 tyrosine-like C4 component, which is consistent with the findings of Barker et al.
349 (2009, 2013) and Stedmon et al. (2007). It showed that the C4 component was left in
350 the ice-cover when the lakes were frozen. Therefore, it is not surprising that the
351 intensity of component C4 for water beneath ice layers was reduced and the
352 concentrated C3 showed a much higher fluorescence intensity. In April 2014, the
353 intensities of four fluorescent components (0.47 ± 0.17 (C1), 0.25 ± 0.08 (C2), 0.40 ±
354 0.16 (C3), and 0.45 ± 0.13 (C4) nm^{-1}) (Fig. 3d) exhibited similar seasonal trends
355 though these values were much lower than the average. Our interpretation is that the
356 ice CDOM was characterized by tyrosine-like component (C4) (Fig. S2a), and the
357 fluorescence intensity of C4 contributed by the ice-melt water was very weak.

However, the underlying lake CDOM included both humic-like (C1 and C2) and protein-like (C3 or C4) components. When the ice in the lakes melted into water with warming weather and biological degradation and human activity was weak, the lake CDOM was diluted by the ice-melted water and the fluorescence intensity would reach to the lowest value in early spring.

Figure 3. a) Seasonal average of F_{max} for EEM-PARAFAC components (C1, C2, C3 and C4) for lakes in the western part of Jilin province; b) Monthly variation of rainfall for the lakes in western part of Jilin province from April 2013 to February 2014; c) Seasonal variation of the total fluorescence intensity at different seasons; d) Seasonal variation of the four EEM-PARAFAC components at different seasons. The error bars represent one standard deviation.

3.4 CDOM versus EEM-PARAFAC extracted components

The concentration of DOC, CDOM absorption coefficients and the slope ratio S_R are shown in Table 3. The DOC concentrations ranged from 835.83 to 7345.83 μmol L^{-1} with an average value of 3133.05 ± 1504.14 μmol L^{-1} during the period from June 2013 to April 2014, demonstrating a seasonal dynamics that can be attributed to hydrological, climatic and landscape variations (Song et al., 2013). The highest average DOC concentration (4587.03 ± 1666.83 μmol L^{-1}) was present in February 2014 (ice-covered period); whereas, relatively constant values of approximate 2500 μmol L^{-1} were observed in the ice-free season. The relative high DOC concentration in ice-free season was caused by evapo-condensed effect due to the prolonged sunshine duration for the lakes in the Songnen Plain. With respect to the higher DOC

concentration in winter, it can be attributed to the accumulated DOC left in the liquid phase when ice formation took place, resulting in the higher DOC concentration in the underlying water (unpublished material). Generally, the absorption coefficient a(350) is used as a proxy for characterizing CDOM concentration (Guo et al., 2010; Zhang et al., 2011), a(280) is related to DOC biodegradation (McDowell et al., 2006), and a(254) can be used to characterize the optical properties of DOC aromaticity (Jaffe´ et al., 2004; Weishaar et al., 2003). The highest averaged CDOM absorption coefficients a(350), a(280), a(254) were also present in February 2014, corresponding to the highest DOC concentration. The S_R values of the two wavelength ranges (275-295 nm over 350-400 nm) were used to represent DOM molecular weight (Helms et al., 2008). The lowest mean of S_R was present in August 2013 suggesting the relatively weak microbial decomposition of plants and lots of terrestrially imported substances through rainwash resulted in the higher average molecular weight of DOC.

Table 3. Mean values of DOC concentration and CDOM absorption coefficients groups at different seasons. S_R: the slope ratio of $S_{275\text{-}295nm}$: $S_{350\text{-}400nm}$.

When the whole data set (N = 67) was pooled together, there were significantly positive linear relationships between a(254), a(280), a(350) and F_{max} for two humic-like components (C1 and C2), respectively, but mostly such correlations were not observed for the protein-like components (Fig. 4a and b, Table 3). These results were in accordance with previous investigations (Zhang et al., 2010, 2011). Components 1 and 2 were strongly linearly correlated with each other (R^2 = 0.628)

405 (Fig. 4c), indicating that the concentrations of the two humic-like components were
406 controlled by common sources (Baker and Spencer, 2004). There was a weak
407 relationship (R^2 = 0.051) between the protein-like components (C3 and C4) possibly
408 because of a complex origin of CDOM such as rainfall in summer, ice in winter and
409 organic pollutants derived from domestic, agricultural and industrial sewerage, which
410 represent the complex origins of CDOM. However, there was almost no correlation
411 between the humic-like and protein-like components. The linkage of a fluorescence
412 signal to DOC was very complicated because of the seasonal impacts, i.e., increased
413 rainfall, algal blooms and ice-cover, which affect the DOC concentration. Due to both
414 steady and labile CDOM fluorescent components in DOC, the fluorescent signal
415 would change with the ratio of fluorescent and non-fluorescent CDOM components
416 (Henderson et al., 2009). A weak relationship (R^2 = 0.411) (Fig. 4d) was found
417 between DOC and component 3 likely from the decay of plants through microbial
418 activity or the pollution from human and animal wastes.

419 Different from the findings by Yamashita et al. (2008) for ocean water, this study
420 did not find obvious correlation between salinity and EEM-PARAFAC extracted
421 components with the exception of C3 (R^2 = 0.469) (Table 4 and Fig. 4f). The most
422 important finding for the water samples collected at different seasons from the
423 Songnen Plain is a significant relationship (R^2 = 0.930) between salinity and DOC
424 (Fig. 4e). This is because DOC is evapo-condensed from spring to autumn and
425 freeze-accumulated in winter in the semi-arid region. A prolonged sunshine duration
426 can result in an evapo-condensed DOC concentration in ice-free season. On the other

hand, the DOC is accumulated when the lakes freeze in winter leaving DOC in the liquid phase.

Table 4. Correlation coefficients (R) and significance levels (*p*) of the linear relationships between CDOM absorption, DOC, salinity and fluorescent components.

Figure 4. Relationships between CDOM absorption coefficient a(350) with a) F_{max}(C1), b) with F_{max}(C2), c) peak F_{max}(C1) versus F_{max}(C2), d) peak F_{max}(C3) versus DOC, e) Salinity versus DOC, f) Salinity versus F_{max}(C3).

4 Conclusions

A model II-ANOVA using season and lake as random effect factors shows that the seasonal variability ($F > F_{crit}$, $p < 0.05$) is higher than between-lake variability. In this study, the application of EEM-PARAFAC to characterize four fluorescent components under seasonal variation in CDOM was presented with 67 water samples collected from June 2013 to April 2014 in the semi-arid region of the Songnen Plain. Two humic-like and the protein-like components were identified using the PARAFAC modeling. The average fluorescence intensity of the four components differed under seasonal variation from June 2013 to April 2014. The highest C1 1.02 nm^{-1} was presented in February 2014 probably due to the condensed CDOM caused by ice formation in winter. Especially in summer when quantities of rainfall take place and in winter when water is frozen, the fluorescence intensity is dominated by tyrosine-like components in rain and ice-melt water. Component 1 and 2 exhibited a strong linear correlation (R^2 = 0.628). There were significantly positive linear

relationships between F_{max} and CDOM absorption coefficient a(254) (R^2 = 0.72, 0.46, $p < 0.01$), a(280) (R^2 = 0.77, 0.47, $p < 0.01$), a(350) (R^2 = 0.76, 0.78, $p < 0.01$) for two humic-like components (C1 and C2), respectively. A weak relationship (R^2 = 0.411) was found between DOC and component 3 from the decay of plants through microbial activity or the pollution from human and animal wastes. However, almost no obvious correlation was found between salinity and EEM-PARAFAC extracted components except C3 (R^2 = 0.469), though the correlation was not as strong as with DOC concentration. Most importantly, a significant relationship (R^2 = 0.930) was found between salinity and DOC. In order to understand the biogeochemical effects on the aquatic ecosystem, further study should be required to identify CDOM source and assess physical/chemical, bioavailable and photoreactive transformation in various lakes with larger saline gradients in the semi-arid region, Northeast China.

Acknowledgements

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642 Table 1. Mean value of water quality parameters from June 2013 to April 2014. Turb
643 denotes water turbidity; N denotes sampling numbers.
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Sampling season	pH	Salinity	Turb (NTU)	N
Jun.2013	8.54	0.40	166.20±108.73	15
Aug.2013	8.63	0.37	63.13±31.21	13
Feb.2014	8.35	0.70	21.33±15.87	17
Apr.2014	8.67	0.43	22.24±16.42	22
All	8.55	0.48	62.18±79.07	67

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667 Table 2. Positions of the fluorescence maximum peaks of the four components
668 identified by PARAFAC modeling in the present study compared with those
669 previously identified. Secondary excitation maxima is given in brackets.
670

Component No	Ex_{max}(nm)	Em_{max}(nm)	Description and source	Components (Coble) and (Zhang)	Components (Stedmon and Markager)
C1	230 (300)	425	Marine humic-like (phytoplankton degradation)	M	6
C2	255 (350)	460	Terrstrial humic-like	A and C	1 and 4
C3	225 (290)	360	Autochthonous tryptophan-like	T	
C4	220 (275)	320	Autochthonous tyrosine-like	B	8

671 Fluoresence peaks were named as Components (Coble) and (Zhang) by Coble et al. (1996, 1998) and Zhang et al.
672 (2010, 2011), while as Componets (Stedmon and Markager) by Stedmon and Markager (2005).
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Table 3. Mean values of DOC concentration and CDOM absorption coefficients groups at different seasons. S_R: the slope ratio of $S_{275\text{-}295nm}$: $S_{350\text{-}400nm}$.

Sampling season	a(254) m^{-1}	a(280) m^{-1}	a(350) m^{-1}	S_R	DOC μmol L^{-1}	N
Jun.2013	38.39±9.23	25.98±6.38	5.73±1.68	1.29±0.16	2653.08±1222.14	15
Aug.2013	29.71±4.73	19.36±2.91	5.82±0.81	0.96±0.22	2735.99±1231.61	13
Feb.2014	52.88±18.13	34.62±11.54	6.36±2.17	1.18±0.11	4587.03±1666.83	17
Apr.2014	34.43±11.38	22.45±7.36	4.17±1.49	1.32±0.13	2571.38±909.47	22
All	39.08±14.73	25.73±9.58	5.40±1.84	1.21±0.20	3133.05±1504.14	67

712 Table 4. Correlation coefficients (R) and significance levels (*p*) of the linear
713 relationships between CDOM absorption, DOC, salinity and fluorescent components.
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	a(254)	a(280)	a(350)	DOC	Salinity	C1	C2	C3	C4
DOC	0.711**	0.646**	0.294*	1.000**					
Salinity	0.650**	0.579**	0.159	0.965**	1.000**				
C1	0.850**	0.875**	0.873**	0.496**	0.383**	1.000**			
C2	0.677**	0.686**	0.885**	0.414**	0.270*	0.796**	1.000**		
C3	0.452**	0.417**	0.134	0.648**	0.685**	0.267*	0.103	1.000**	
C4	-0.040	-0.016	0.078	-0.101	0.135	0.084	0.069	0.225	1.000**

715 **p< 0.01 level ; *p<0.05 level.
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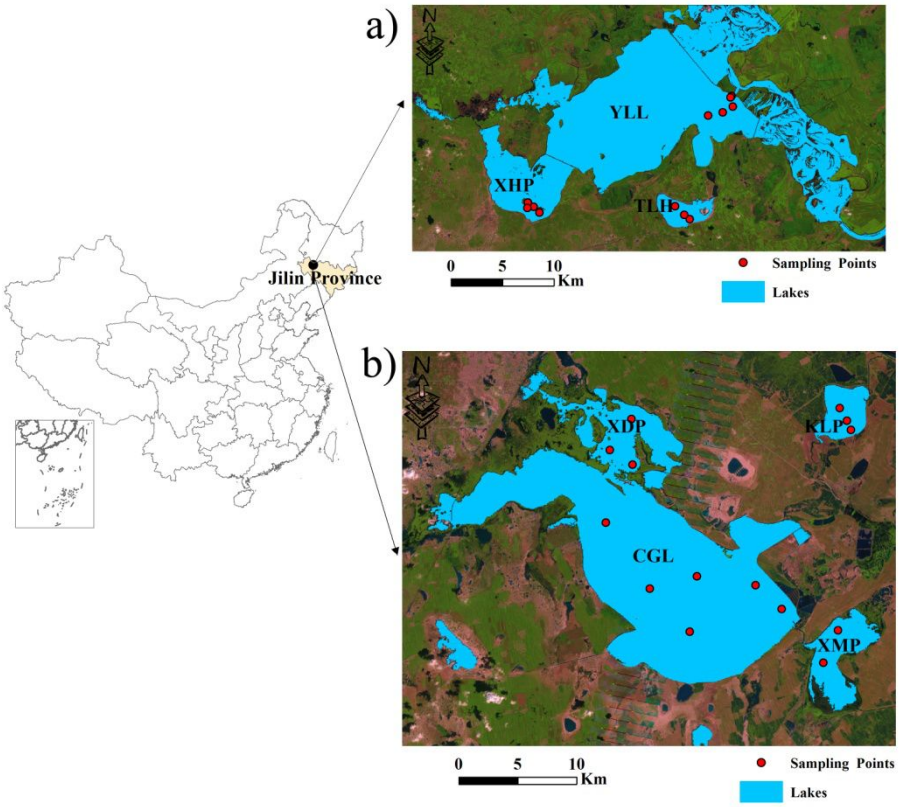


Figure 1. Locations of the water sampling sites for 7 lakes in the western part of Jilin province, Northeast China. a) Yueliang lake group: YLL, Yueliang Lake; XHP; Xinhuangpao; TLH; Talahong; b) Chagan lake group: CGL, Chagan Lake; XDP, Xindianpao; XMP, Xinmiaopao; KLP, Kulipao.

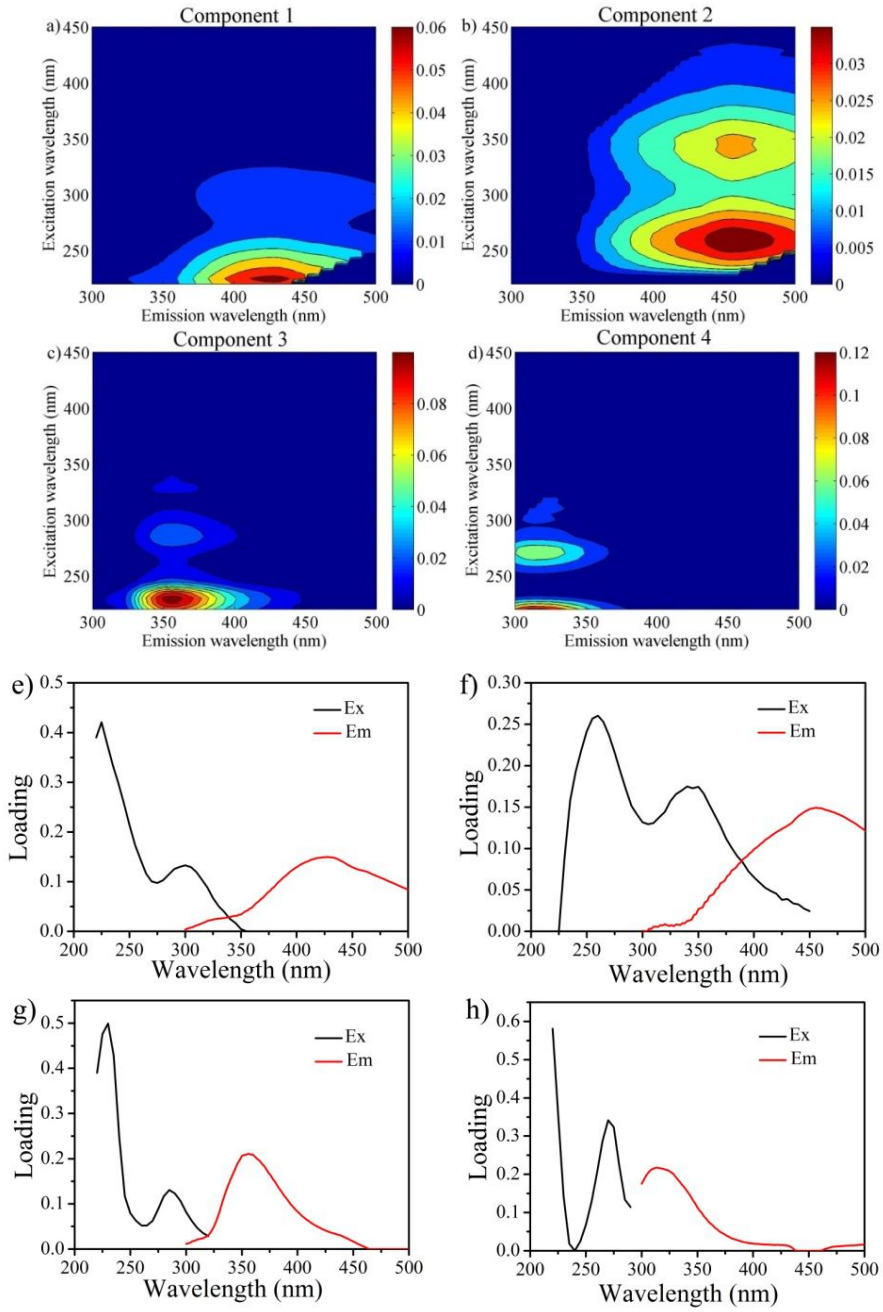
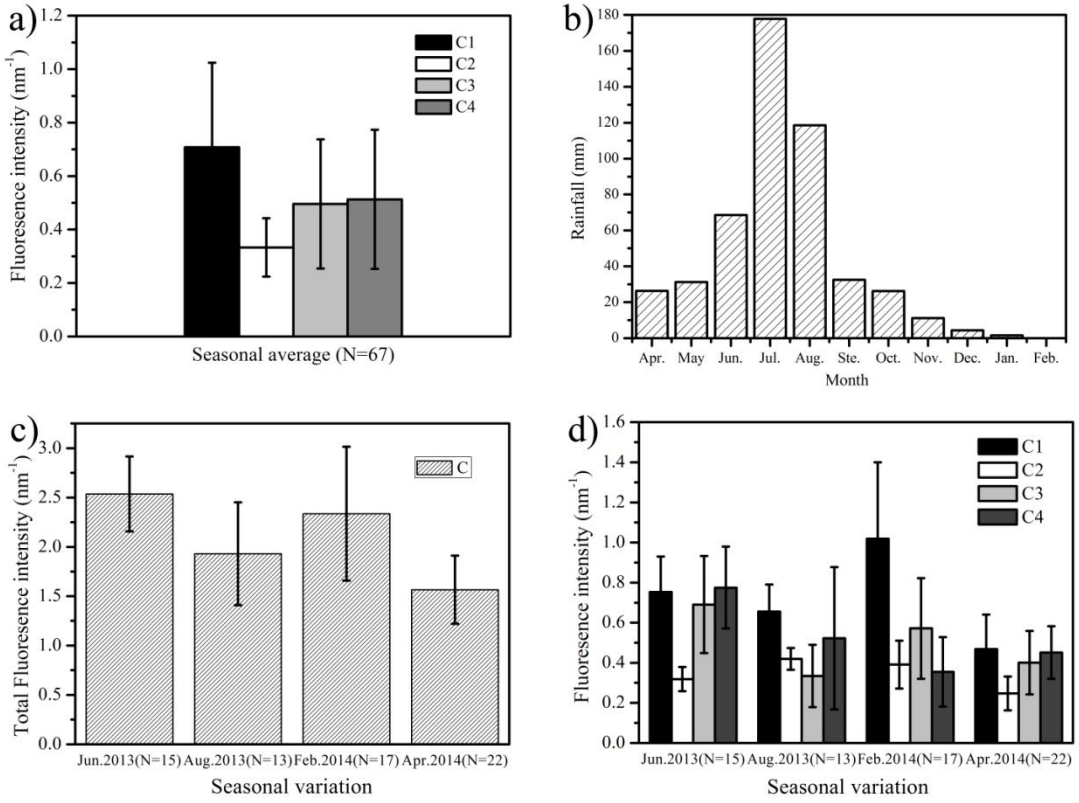


Figure 2. The PARAFAC model output shows the contour plots of the four PARAFAC fluorescent components (a-d) and excitation (black) and emission (red) loadings (e-h) of each component. Fluorescence is in Raman units: nm^{-1}.



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759 Figure 3. a) Seasonal average of F_{max} for EEM-PARAFAC components (C1, C2, C3
760 and C4) for lakes in the western part of Jilin province; b) Monthly variation of rainfall
761 for the lakes in western part of Jilin province from April 2013 to February 2014; c)
762 Seasonal variation of the total fluorescence intensity at different seasons; d) Seasonal
763 variation of the four EEM-PARAFAC components at different seasons. The error bars
764 represent one standard deviation.

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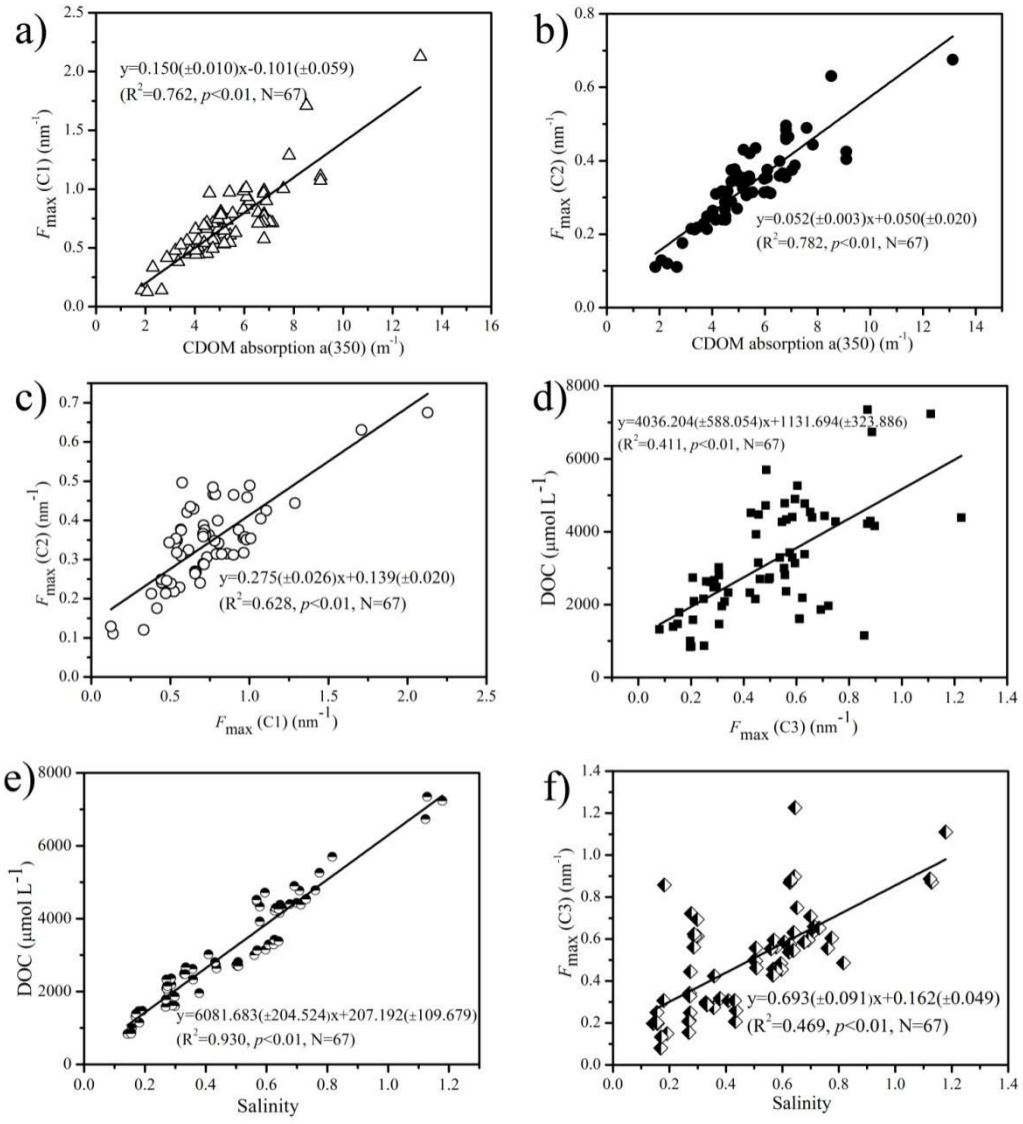

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769 Figure 4. Relationships between CDOM absorption coefficient a(350) with a)

770 F_{max}(C1), b) with F_{max}(C2), c) F_{max}(C1) versus F_{max}(C2), d) F_{max}(C3) versus DOC, e)

771 Salinity versus DOC, f) Salinity versus F_{max}(C3).

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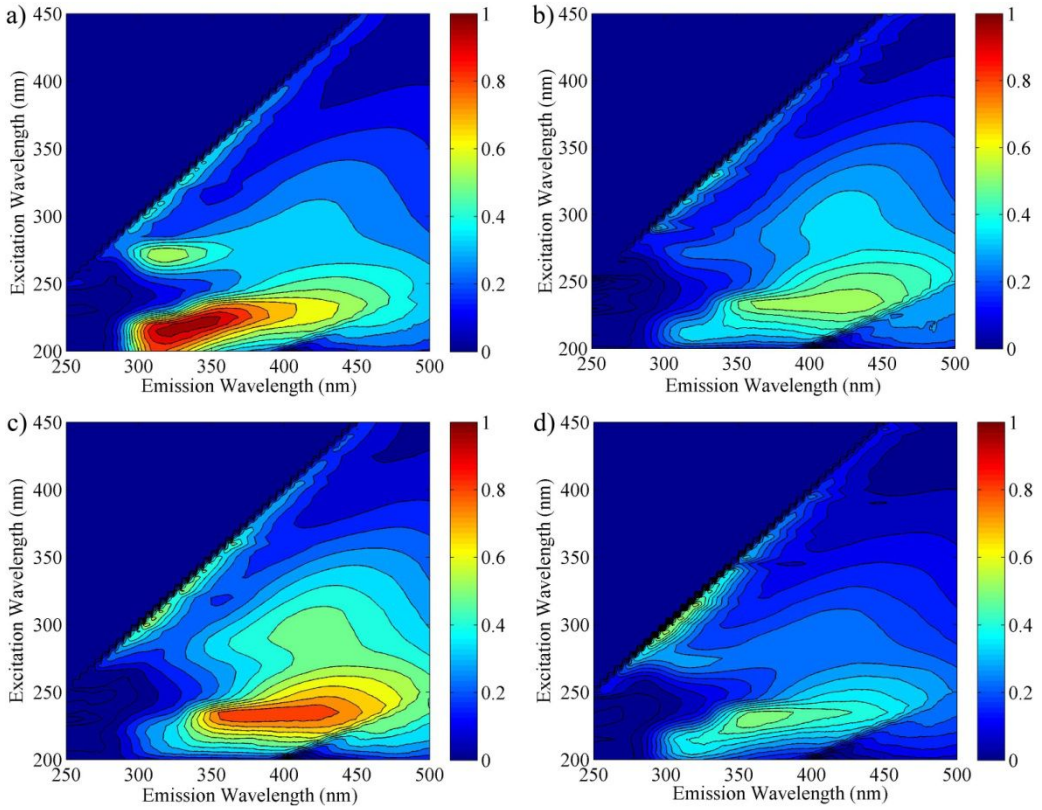
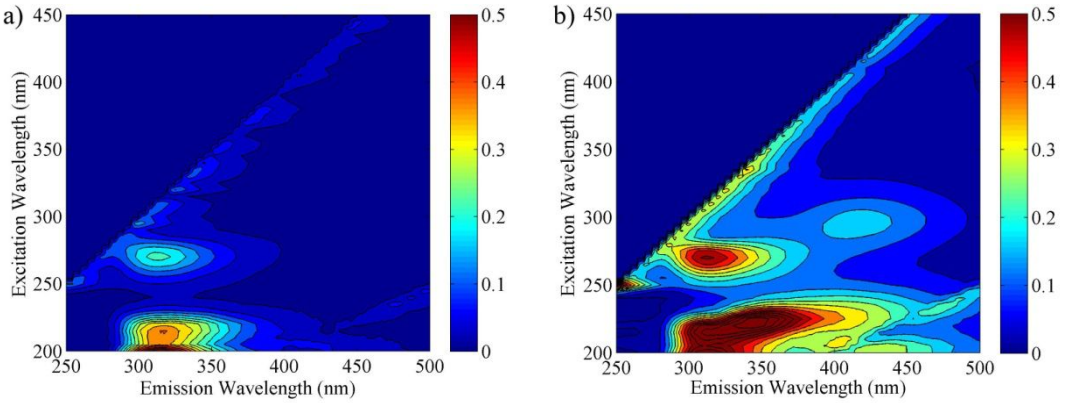


Figure S1. Examples of EEMs for one water sample from Xindianpao Lake in the western part of Jilin province at different seasons a) June 2013; b) August 2013; c) February 2014; d) April 2014 (Fluorescence is in Raman unit: nm^{-1}).



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790 Figure S2. Representative examples of EEMs for a) lake ice-melt water sample, and b)

791 rainwater CDOM in the western part of Jilin province (Raman: nm^{-1}).