Responses to specific comments of Reviewer 1

General comments

• **Statistics.** In order to rely on so many regression analyses I recommend using multivariate analyses: A principal component analysis (PCA) based on the four fluorescence components containing the different lakes, the four seasons and maybe salinity as factor in order to reveal the major controls on fluorescent component distribution, e.g. is the between-lake variability higher than the seasonal variability? In how far might salinity affect the distribution? Though the authors do not aim at extracting differences between freshwater and brackish water DOM fluorescent component composition it might still be interesting to mention in how far salinity could play a role and why it had/ had no effects in this study. Secondly, I suggest performing a model II-ANOVA using season and lake as random effect factors.

Response: Thank you for your suggestion. A principal component analysis (PCA) has been widely used to assess the variation of water quality among water bodies (Bonilla et al., 2009. Phytoplankton and phytobenthos pigment strategies: implications for algal survival in the changing Arctic. Polar Biol, 32, 1293) and the relative distribution of the EEM-PARAFAC extracted fluoresencent components for all sample locations. According to the references (Helena et al., 2000. Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga river, Spain) by principal component analysis. Water Research, 34, 807e816; R. Jaffe´ et al., 2008. spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. Journal of Geophysical Research, 113, G040320; Jami Goldman, 2011. Applications of fluorescence spectroscopy for monitoring water quality in an urban watershed; Zhi et al., 2015. Characterization of the composition of water DOM in a surface flow constructed wetland using fluorescence spectroscopy coupled with derivative and PARAFAC, Environ Earth Sci., 73, 5153–5161), PCA based on the four fluorescence components containing the different lakes, the four seasons have been performed in our study (Figure in the

following). However, the results can not reveal which is the major control on the fluoresencent components between lake-variability and season-variability.

As is shown in Figure 1, a closer analysis of the samples for June 2013 (or April 2014), it shows that the fluorescence distribution for both fresh and saline lakes in the weatern part of Jilin province is controlled by the same of the two PCA components. In particular, the different lake locations in Feburary 2014 (or August 2013 16-28) were broadly distributed along the first two axes (PC1 and PC2). This may be attributed to different CDOM fluorescent components in water for different lakes in winter, or may be the condensed salinity for the lakes when covered by ice may affect the distribution of fluorescence components. We will further focus on extracting differences between freshwater and brackish water CDOM fluorescent component composition with larger saline gradients as presented in Song et al., (2013), and investigating whether or not the elevated gradient of salinity paly a role in affecting the distribution of fluoresencent components.

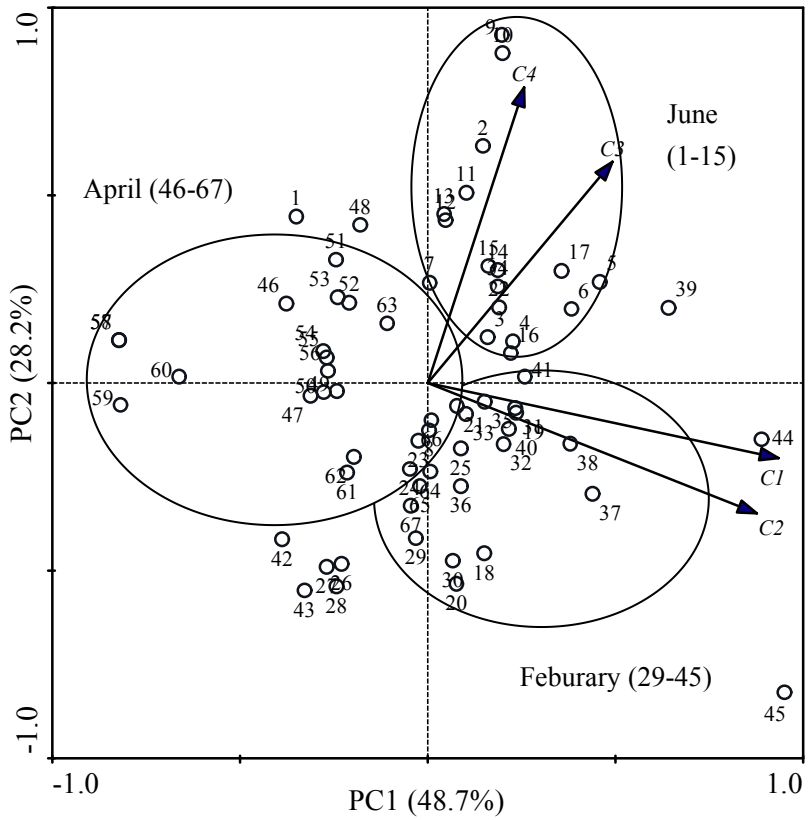

Figure 1 Plots of scores (samples) and loadings (variables) for PC1 and PC2 of CDOM components.

Thank you for your suggestion. We have performed a model II-ANOVA based on the total fluorescence intensity using season and lake as random effect factors in the revised manuscript. The results shows that the seasonal variability (F_1=6.045 > F_{crit1}=4.459, $p < 0.05$) is higher than between-lake variability (F_2=1.742 < F_{crit2}=3.838, $p > 0.05$), and therefore we pooled the seven lakes including both fresh and saline waters in the western part of Jilin province together in order to study the CDOM fluorescence intensity at different season.

The absorption coefficients still lack explanations: why have these specific absorption values been used (a254, a350, a280)? What do they indicate and what conclusions can be drawn from finding correlations with other factors like DOC or salinity?

Response: Thank you for putting out the question. The absorption coefficients have been explained (see responses to specific comments).

Introduction

Line 54: better use "its ability" instead of "this ability"

Response: Thank you for your suggestion. The contents "…this ability…" should be replaced by "…its ability…".

Line 82: unclear what is meant with "…are distributed due to its geomorphology".

Response: We are sorry making the error. The contents "…in which many fresh and brackish waters are distributed due to its geomorphology." should be replaced by "…in which many fresh and brackish waters are distributed according to its geomorphological characteristics."

Line 93: better use "at different seasons"

Response: Thank you for your suggestion. The contents "…which had seasonal variation." should be replaced by "…which varied at different seasons."

Line 97: state why exactly it is interesting to link all of these factors

Response: Thank you for putting forward the question. Linking CDOM fluorescence

intensities, absorption coefficients, DOC concentrations and salinity to each other, is to assess the relationship between CDOM-extracted fluorescent components and water quality parameters. The correlation between DOM quantity (DOC concentration) and DOM quality (absorption or fluorescence) can establish proxies for characterizing bioavailability and photoreactivity in waters (R. Jaffe´ et al., 2008: spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. Journal of Geophysical Research, 113, G04032).

Materials and Methods

Line 105: in how far do these lakes form two groups? Due to geographical position only or are there also other factors? Is there variation within both groups as well (e.g. differences in salinity, temperature…)?

Response: Thank you for putting forward the question. The two groups of lakes were located in the western part of Jilin Province, which belongs to the semi-arid part of the Songnen Plain (Song et al., 2013). The two groups of lakes were divided according to geographical position only because they were distributed over two remote sensing images. The Chagan lake group is in the Songyuan city, and the Yueliang lake group in the Baicheng city. The Songyuan city is adjacent to the Baicheng city. The Chagan lake is approximately 60 km away from Yueliang lake, shown in Figure 2.

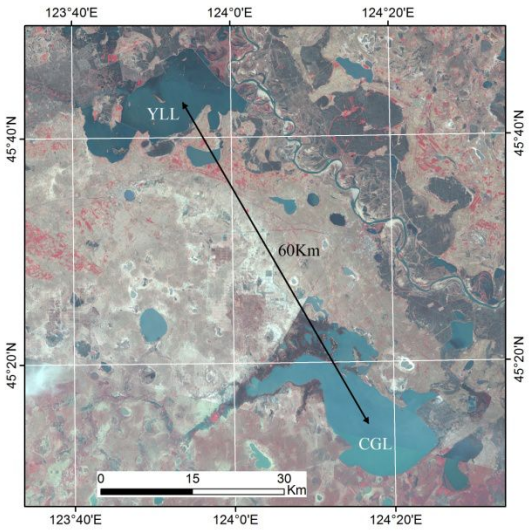

Figure 2 The locations of CGL and YLL

There is also some variations within group as well, e.g., the Chagan lake group

include both fresh lakes (XMP) and salinity lake (XDP). These brackish and fresh water in Jilin province in northeast China are endowed with similar geological, hydrological and climatic settings, thus we presume that similar process may control the CDOM components. When a model II-ANOVA based on the tatal fluorescence intensity 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, and therefore we only pooled seven lakes together in order to study the CDOM fluorescence intensity at different season.

absorption measurement: please state clearly the calculation step for a254 and a280 and a350. Why are these indices used? What are they supposed to indicate? References?

Response: Thank you for putting forward the question. The absorption coefficient is calculated by the Eq. 1 : $a_{CDOM}(\lambda^{'}) = 2.303\left[OD_{(\lambda)} - OD_{(null)}\right]/\gamma$

$OD_{(null)}$: the average optical density over 740-750 nm, where the absorbance of CDOM was assumed to be zero.

a(254)=2.303$OD_{(254)}$ /0.01

a(280)=2.303$OD_{(280)}$/0.01

a(350)=2.303$OD_{(350)}$/0.01

$OD_{(254)}$, $OD_{(280)}$, $OD_{(350)}$ and $OD_{(null)}$ can be measured by the Shimadzu UV-2600PC UV-Vis dual beam spectrophotometer with a 1 cm quartz cuvette and Milli-Q water as reference.

Finally, the absorption coefficients were corrected for backscattering of small particles and colloids, which pass through filters, using Eq. 2 (Bricaud et al., 1981. Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domain. Limnology and Oceanography, 26, 43–53, 1981): $a_{CDOM}(\lambda) = a_{CDOM}(\lambda^{'}) - a_{CDOM}(750) * \lambda / 750$

a(254) can be used to measure the contribution of CDOM which is rich in humic-like

substance, i.e., the optical properties of DOC aromaticity (Weishaar et al., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol., 37, 4702-4708; R. Jaffe´ et al., 2004).

a(280) is correlated with DOC biodegradation (McDowell et al., 2006: A comparison of methods to determine the biodegradable dissolved organic carbon from different terrestrial source. Soil Biol. Biochem., 38, 1933-1942).

a(350) is usually used as a proxy for characterizing CDOM concentration (Guo et al., 2010; Zhang et al., 2011).

In wavelength region from 250 to 400 nm, the correlation between absorption coefficient a(λ) and DOC (or salinity) can indicate the bioavailability and photoreactivity in waters (R. Jaffe´ et al., 2008).

Results and discussion

Line 246 ff: I do not understand this sentence.

Response: Thank you for putting forward the question. The contents in line 246-248 should be replaced by "With respect to the protein-like components, they, i.e., tyrosine-like and tryptophan-like substance, mainly consist of dissolved amino acids."

Line 255ff: going into detail on this specific lake seems pretty unnecessary. Figure 2 might better belong to the supplementary. Furthermore, any discussions about seasonal variations should be done at the respective chapter later in the manuscript.

Response: Thank you for your suggestion. Figure 2 has been placed to the supplementary.

Line 264ff: Skip the details about the split-half analysis. Further Figure 3 should be left out, it does not contain relevant information.

Response: Thank you for your suggestion. Figure 3 has been left out in the revised-manuscript.

Line 293: what is (B) referring to? (citation!)

Response: B refers to the tyrosine-like peaks also found by Henderson et al. (2009) and Hudson et al. (2007).

Line 299: which lakes or seasons did not contain some of the fluorescent components? Are there any interesting patterns?

Response: The contents in line 299 indicates the tyrosine-like (C4) components was almost included in ice when the lakes freeze, as is shown in Figure S2a. The tyrosine-like (C4) components could be obscured by other fluorescent components (C1 or C3) (Figure S1c) in the underlying water. The fluorescent components in ice-melt water need to be further studied.

Line 322ff: Do these values represent the sum of the four components for each season? Maybe this Fmax-values for each of the seasons can be added to plot 5? How about the ice samples?

Response: Thank you for putting forward the question. The total fluorescence intensity (in line 322 to 324) represent the sum of the four components for each season. We are sorry for making the error. The F_{max}-values for each of the seasons has been added to plot Figure 3c in the revised manuscript. The F_{max}-values of the ice sample is very weak and need to be further studied.

Line 353: biological activities might be highly reduced, but not prohibited completely. Maybe there might still be a bit of production of C3 and C1 which could explain the difference in behavior of the terrestrially imported C2 that did not display significant differences between august and february?

Response: Thank you for your suggestion. The contents in line 352-354 should be replaced by "…vigorous biological activities in the lakes would be highly reduced at low temperature and low light level (Thomas K., 1983; Uusikiv et al., 2010; Wharton, et al., 1993). Although the biological activities was very weak, there still be a bit of production of C1 and C3 in lake water.… Therefore, the C1 and C3 in the water of the lakes beneath the ice layers would be produced and cumulated simultaneously."

Line 371: I do not understand this sentence. how can lake-CDOM be dominated by all four components?

Response: Thank you for putting forward the question. The contents in line 371-372

should be replaced by "However, the underlying lake CDOM included both humic-like (C1 or C2) and protein-like (C3 or C4) components."

CDOM VS EEM-PARAFAC extracted components

Line 390: obviously sunshine-induced evapo-condensed DOC concentration had no significant effects here, otherwise DOC concentration would be highest in summer and not in winter?! Please state, shortly, the observed patterns here (which hydrological, climate and landscape patterns like stated in line394?)

Response: Thank you for putting forward the question. The authors are sorry for making the error. The DOC concentrations varies from April to August 2013, demonstrating a seasonal dynamics that can be attributed to hydrological, climatic and landscape variations (Song et al. 2013). The highest averaged DOC concentration (55.04 ± 20.00 mg L^{-1}) was present in February 2014. This can be attributed to the accumulated DOC when the lakes freeze in winter, which leaves DOC in the liquid phase, resulting in a higher DOC concentration in the underlying water.

The contents from line 388 to 397 should be replaced by "…The DOC concentrations ranged from 10.03 to 56.60 mg L^{-1} with an average value of 31.66 mg L^{-1} during the study period from April to August 2013, demonstrating a seasonal dynamics that can be attributed to hydrological, climatic and landscape variations (Song et al., 2013). It is because the prolonged sunshine duration can result in an evapo-condensed DOC concentration in the Songnen Plain. The highest averaged DOC concentration (55.04 ± 20.00 mg L^{-1}) was present in February 2014; whereas, relatively constant values of approximate 30 mg L^{-1} were observed in the other three seasons. This can be attributed to the accumulated DOC when the lakes freeze in winter, which leaves DOC in the liquid phase, resulting in a higher DOC concentration in the underlying water (unpublished material)…".

Line 404: The SR as calculated here merely represents DOM molecular weight (Helms, 2008)?

Response: Thank you for putting forward the question. The authors are sorry for making the error. The S_R represents DOM molecular weight (Helms et al., 2008). The contents in line 404 should be replaced by "…represent DOM molecular weight…"

Line 413 ff: As mentioned in the general comments, please adapt the statistics. Anyway, the correlations presented here lack interpretation (e.g. C1 and C2, why do they correlate though they derive from different sources?)

Response: Thank you for your suggestion. We have adapted the statistics (see response to general comments). The strong correlation between C1 and C2 shows that the two fluorescent components may derived from a common FDOM source, i.e., the humic-like substance (Baker et al., 2004. Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy, Sci. Total Environ., 333, 217-232; Zhang et al., 2011).

Line 425: I do not understand this argument.

Response: Thank you for putting forward the question. As there is no obvious correlation between DOC and fluorescent components, the linkage of the fluorescence signal to DOC was very complicated. The seasonal impacts, such as increased rainfall, algal blooms and ice-cover, can affect the DOC concentration. Moreover, DOC contains both steady and labile CDOM fluorescent components. The fluorescent signal would changes with the ratio of fluorescence and non-fluorescence CDOM components.

The contents in line 425-428 should be replaced by "…The linkage of a fluorescence signal to DOC was very complicated because of the seasonal impacts, i.e., increased rainfall, algal blooms and ice-cover, which affect the DOC concentration. Since DOC contains both steady and labile CDOM fluorescent components, the fluorescent signal would changes with the ratio of fluorescent and non-fluorescent CDOM components (Henderson et al., 2009; R. Jaffe´ et al., 2008: spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. Journal of Geophysical Research, 113, G04032)."

Line 428 ff: C3 might be useful to detect water pollution but a correlation with DOC solemnly does not necessarily indicate water pollution. Some other factors correlating with C3 (i.e. nutrients) might help to underscore the usefulness of C3 as a pollution indicator.

Response: Thank you for your suggestion. The correlation between protein-like

components (C3) and nutrients can indicate C3 can be used as a pollution indicator (Baker et al., 2004: Protein-like fluorescence intensity as a possible tool for determining river water quality. Hydrol. Processes 18 (15), 2927–2945). As the linkage of the fluorescence signal to DOC was very complicated (Response to Line 425), only a correlation between C3 and DOC can not indicate water pollution. The contents in 428-431 "Component 3 of the CDOM fluorescence can be used to detect water pollution (Baker et al., 2004)" should be delete.

Line 432ff: The co-linearity of DOC and salinity could be explained by evapotranspiration but, as mentioned before, obviously some other factors play crucial roles in this study since both display highest concentrations in winter rather than in summer where higher evapotranspiration rates are expected. How can this pattern be explained?

Response: Thank you for putting forward the question. The DOC significantly correlated with salinity ($R^2 = 0.931$) during the study period. This is because DOC is evapo-condensed from spring to autumn and freeze-accumulated in winter in the semi-arid region. A prolonged sunshine duration can result in an evapo-condensed DOC concentration from April to August 2013. On the other hand, the DOC is accumulated when the lakes freeze in winter, which leaves DOC in the liquid phase resulting in a higher DOC concentration in the underlying water.

Line 438: I do not understand this argument.

Response: The DOC significantly correlated with salinity ($R^2 = 0.931$) but there is no obvious correlations between salinity and EEM-PARAFAC extracted components during the study period in our paper, i.e., there is no relationship between DOC and fluorescent components. The linkage of a fluorescence signal to DOC was very complicated because of the seasonal effects of increased rainfall, algal blooms and ice-cover, which affect the DOC concentration by changing the ratio of both steady and labile fluorescence : non-fluorescence CDOM components. For example, with the sunshine duration hours increasing in warm season, the photo-degradation and microbial activities become stronger, leading to a more efficient transformation of labile fluorescence CDOM into non-fluorescence CDOM component (Song et al.,

2013).

Conclusions: might be adapted to potential new findings using multivariate statistics. Overall it should contain the important main findings and underscore the importance of this study and maybe provide an outlook for the future (e.g. how is the microbial degradability of these fluorescent components? what would be the effects on this ecosystem?)

Response: Thank you for your suggestion. We have adopt the multivariate statistics (see response to general comments). When a model II-ANOVA based on the total fluorescence intensity 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. The fluorescent components between-lake variability (e.g. with larger saline gradients) should be studied further in the semi-arid regions. In order to understand the biogeochemical effects on the aquatic ecosystem, it is important 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.

Figure 6 should better be part of the supplementary

Response: Thank you for your suggestion. Figure 6 has been placed in the supplentary in the revised manuscript.

Responses to specific comments to Reviewer 2

Introduction

Line 44: "for us" is not necessary

Response: Thank you for your suggestion. The contents "…for us…" should be skipped.

Line 58-64: too long sentence

Response: Thank you for your suggestion. The contents "In recent years, …as well as snow melting water" should be replaced by "In recent years, EEM spectroscopy has been widely used to investigate the dynamics of marine, freshwaters 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 source in aquatic environment (Coble et al., 1998; Mayer et al., 1999; Yamashita et al., 2008, 2010; Zhang et al., 2013)."

Line 74: not necessary to put citation twice

Response: Thank you for your suggestion. The content "…(Stedmon et al., 2003)…" should be skipped.

Line 82: "fresh and arid waters are distributed due to its morphology": reformulate this sentence

Response: Thank you for your suggestion. The contents "…in which many fresh and brackish waters are distributed due to its geomorphology." should be replaced by "…in which many fresh and brackish waters are distributed according to its geomorphological characteristics."

Line 88: "little studied has" should be either "little study has" or "little studies have"

Response: We are sorry for making the error. The content "little studied has…" should be replaced by "little study has…"

Materials and methods

Line 117: reformulate the sentence "After the ice..."

Response: Thank you for your suggestion. The content "After the ice layer was

drilled a hole, the under-ice surface water was coming up." should be replaced by "The under-ice surface water was coming up when the ice layer was drilled a hole by the auger."

Line 121-122: reformulate the sentence "In the laboratory..."

Response: Thank you for your suggestion. The contents "In the laboratory, these samples were kept at 4 ℃ until analysis after filtered within two days." should be replaced by "In the laboratory, these samples were filtered within 24h and then kept at 4 ℃ until analysis within two days."

Line 133-135: missing reference for turbidity?

Response: Thank you for your suggestion. The turbidity measurement is referred to the reference titled "UV talk letter vol. 10".

https://shimadzu.com.au/uv-talk-letter-volume-10

Line 152: "it is necessary" change to "it was necessary"

Response: Thank you for your suggestion. The contents "…it is necessary…" should be replaced by "…it was necessary…".

Line 196-198 this sentence belongs rather to introduction

Response: Thank you for your suggestion. The contents in line 196-198 should be placed in line 73 "…2011, 2013). A number of investigators have used EEMs-PARAFAC to characterize DOM in freshwater and marine aquatic environments (Cory et al., 2005; Stedmon et al., 2003; Stedmon and Markager, 2005; Yamashita, 2008; Zhang et al., 2010, 2011). Stedmon et al. (2003) introduced…".

Results and discussion

Line 228-237: It is not necessary to describe what is already in Table1. For example, line 231-pH 8.55-this information is already in Table1.

Response: Thank you for your suggestion. The contents "…(mean, 8.55)…(mean, 0.48 PSU)…(0.70 PSU)…with the mean of 62.18 ± 79.07 NTU…" should be skipped.

Line 246-248: reformulate the sentence

Response: Thank you for your suggestion. The contents "With respect to the protein-like components, i.e., tyrosine-like and tryptophan-like substance, mainly

consist of dissolved amino acids." should be replaced by "With respect to the protein-like components, they, i.e., tyrosine-like and tryptophan-like substances, mainly consist of dissolved amino acids."

Line 253-254: not necessary sentence here, this belongs to methods

Response: Thank you for your suggestion. The contents in line 253-254 should be placed in line 187 "The measured fluorescence intensity is dependent on the concentration of the dissolved fluorophores in water bodies. Finally, the fluorescence intensities…"

Line 280-300: this paragraph should be reduced significantly, it is not necessary to describe the components and their maxima if this information is already in the Table 2.

Response: Thank you for your suggestion. The authors have reduced the paragraph in line 280-300. The revised manuscript is written as "In our study, four separate fluorescent components (Fig. 4a-d) and the excitation and emission loadings (e-h) of the four components identified by EEM-PARAFAC are summarized in Fig. 4 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 288 (A and C) defined by Coble (1996). Component 3 resembles the tryptophan-like (T) component as found by Baker et al. (2004) and 291 Hudson et al. (2007). For component 4, it is likely related to tyrosine-like component (B). 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 298 (Fig. 4c-d). In this study, not all of the four components were present in all of the samples."

Line 318: not clear, What do authors mean by "other organisms"?

Response: Thank you for putting forward the question. The "other organisms" means algae and microorganisms, etc. The contents "…originated from phytoplankton

degradation and other organisms." should be replaced by "…originated from the degradation of phytoplankton and microorganisms."

Line 355: I think "matters" is not appropriate here. Do you mean "material"?

Response: Thank you for your suggestion. The word "matters" should be replaced by "materials".

Line 386-408: it is not necessary to repeat results which are already presented in Table 3.

Response: Thank you for your suggestion. The authors have revised the paragraph in line 386-408. The revised manuscript is written as "The concentration of DOC, CDOM absorption coefficients and the slope ratio S_R are shown in Table 3. The DOC concentrations ranged from 10.03 to 56.60 mg L^{-1} with an average value of 31.66 mg L^{-1} during the study period from April to August 2013, demonstrating a seasonal dynamics that can be attributed to hydrological, climatic and landscape variations (Song et al., 2013). It is because the prolonged sunshine duration can result in an evapo-condensed DOC concentration in the Songnen Plain. The highest averaged DOC concentration (55.04 ± 20.00 mg L^{-1}) was present in February 2014; whereas, relatively constant values of approximate 30 mg L^{-1} were observed in the other three seasons. This can be attributed to the accumulated DOC when the lakes freeze in winter, which leaves DOC in the liquid phase, resulting in a 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). a(254) can be used to character 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 represent DOM molecular weight (Helms et al., 2008). The lowest mean of S_R was present in August 2013…."

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 strong linear correlation (R^2 = 0.633). 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 = 0.931) 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 ~~for us~~ 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 this ability of producing 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 distinguish allochthonous and autochthonous CDOM source in aquatic environment (Coble et al., 1998; Mayer et al., 1999; Yamashita et al., 2008, 2010; Zhang et al., 2013), and to investigate the dynamics of marine, freshwaters 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~~). 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 this traditional 'peak-picking' method

unreliable to evaluate CDOM dynamics in aquatic ecosystems (Coble, 1996; Stedmon et al., 2003). Recently, the combined EEMs-PARAFAC (parallel factor analysis) technique has been shown to effectively decompose EEM of CDOM into independent fluorescent components and assess the source of CDOM and relationships with other water quality parameters ~~(Broisover et al., 2009; Guo et al., 2010; Zhang et al., 2010, 2011, 2013).~~ Stedmon et al. (2003) introduced PARAFAC and identified five distinct DOM components for a Danish estuary and its catchment ~~(Stedmon et al., 2003)~~. In coastal environments, Yamashita et al. (2008) reported on seven components using the combined EEMs-PARAFAC technique and assess the dynamic of individual fluorophores and relationship with salinity in Ise Bay. Zhang et al. (2011) also found three different components by PARAFAC modeling and analyzed the correlations between the fluorescent components and absorption coefficients of CDOM for Lake Tianmu and its catchment.

The Songnen Plain is a fluvial plain with semi-arid climate, in which many fresh and brackish waters are distributed ~~due to its geomorphology~~ (Song et al., 2013). Dissolved organic carbon (DOC) characterisitics of these fresh and brackish waters across the Songnen Plain have been studied by Song et al. (2013); the results indicated that a huge amout of DOC were stored in these waters. In particular, brackish waters would exhibit high average DOC concentration and significantly contributed the carbon budget to inland waters (Duarte et al., 2008; Song et al., 2013; Tranvik et al., 2009). However, little ~~studied~~ has been made on the detailed information of DOC sources for these waters in the Songnen Plain. Therefore, it

motivated us to investigate the components in CDOM for both fresh and brackish waters in the semi-arid region. In the present study, the absorption and fluorescence of CDOM were determined for the water samples collected from seven lakes in the western part of Jilin province, ~~which had seasonal variation~~. The specific objectives of this study are to: 1) characterize CDOM components contained in these lakes using EEMs and their origins through the EEM-PARAFAC method; 2) assess the dynamic of individual fluorescent component of CDOM under seasonal variation; and most importantly 3) link CDOM fluorescence intensities, absorption coefficients, DOC concentrations and salinity to each other.

2 Materials and Methods

2.1 Lakes and water sampling

The water bodies investigated in this study were located in the western part of Jilin Province, which belongs to the semi-arid part of the Songnen Plain (Song et al., 2013). Two groups of lakes were investigated, i.e., the Chagan lake group and the Yuelianghu lake group. The Chagan lake group is made up of Lake Chagan (CGL), Xinmiaopao (XMP), Xindianpao (XDP) and Kulipao (KLP). The Yuelianghu lake group mainly includes Lake Yueliang (YLL), Talahong (TLH) and Xinhuangpao (XHP) (Fig. 1). The primary economic value for these lakes is fishery, agricultural irrigation and recreation. The average annual precipitation is about 391 mm, but the average evaporation is up to 1790 mm, resulting in water scarcity. Due to the area dominated by saline-alkali soil, the rainfall flush and agricultural catchment land use can result in

an increase of lake salinities. In order to characterize the CDOM fluorescent components under seasonal variation using EEMs-PARAFAC, 67 water samples were collected from the surface of the seven lakes in 1-liter acid-cleaned plastic bottles during four field campaigns in June and August 2013 as well as in February and April 2014, respectively. These samples were collected during the ice covering period using an ice drilling auger. ~~After the ice layer was drilled a hole, the under-ice surface water was coming up.~~ The ice shavings were collected in plastic bags and the under-ice surface water was collected in plastic bottles. The collected samples were held on ice and immediately transported to the laboratory in the Changchun City of Jilin province within 3-5 hours. ~~In the laboratory, these samples were kept at 4 ℃ until analysis after filtered within two days.~~ Latitude and longitude of each sample location were recorded *in situ* using a Trimble Global Positioning System (GPS).

Figure 1. Locations of the water sampling sites for 7 lakes in the western part of Jilin province, Northeast China.

2.2 Analytical procedures

To characterize the basic parameters of water quality, salinity was measured through a DDS-307 electrical conductivity (EC) meter in laboratory. Salinity was expressed in the basis of the UNESCO practical salinity unit (PSU 1978). The pH was measured using a PHS-3C pH meter at room temperature (20 ± 2 ℃) in 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. 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 ℃. Potassium hydrogen phthalate was used as 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 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 cuvette and Milli-Q water as reference. The absorption coefficient a_{CDOM} was calculated from the measured optical density (OD) of the sample using Eq. (1):

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

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

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

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

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

2.4 Three-dimensional fluorescence measurement

The EEMs analysis of CDOM were conducted using a Hitachi F-7000 fluorescence 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.

Finally, the fluorescence intensities of all sample's 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 contour figures of the EEMs were plotted using the Matlab 10.0 software package (Math Works, Natick Massachusetts, America).

2.5 The PARAFAC modeling

PARAFAC, a three-way method, is applied to decompose the CDOM fluorescence into separate fluorescent signals (Andersen and Bro, 2003; Stedmon and Bro, 2008). ~~A number of investigators have used EEMs-PARAFAC to characterize DOM in freshwater and marine aquatic environments (Cory et al., 2005; Stedmon and Markager, 2005; Yamashita, 2008; Zhang et al., 2010, 2011).~~ According to Stedmon and Bro (2008), a similar PARAFAC analysis is carried out in the present study using the DOMFluor toolbox in MATLAB with the "N-way toolbox for MATLAB"

(Andersson et al., 2000). Before PARAFAC modeling, the excitation wavelengths from 200 to 220 nm and the emission wavelengths from 250 to 300 nm were deleted because of their poor quality. In order to remove the effect of Rayleigh scatter on PARAFAC modeling, the missing values (NaN-Not a number) were inserted in the regions ($Ex\text{-}20 \leqq Em \leqq Ex+20$ and $2Ex\text{-}20 \leqq Em \leqq 2Ex+20$; unit: nm) which are significantly influenced by the first and second order scattering from the measured spectroscopic data (Hua et al., 2007; Stedmon and Bro, 2008).

To determine the appropriate number of PARAFAC components, the split-half validation procedure was executed to verify whether the model was valid by comparing the emission and excitation loadings from each half (Stedmon and Bro, 2008). Split-half analysis is the most effective method for implementing the PARAFAC models, in which the EEMs are randomly divided into four groups of equal size, and then analyzed for two half splits (1-2 and 3-4 half) respectively. If the 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}. The difference is considered to be statistically significant when *p*-values are less 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 ~~(mean, 8.55)~~ and high salt contents ~~(mean, 0.48 PSU)~~. The highest salinity ~~(0.70 PSU)~~ was present when the lakes were frozen in February 2014, whereas relatively constant values (around 0.40 PSU) were exhibited in other three seasons. Also the water bodies were highly turbid ~~with the mean of 62.18 ± 79.07 NTU~~. 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, mainly consist of dissolved amino acids. As an example, Fig. 2 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). The measured fluorescence intensity is dependent on the concentration of the dissolved fluorophores in water bodies. The fluorescence properties of CDOM had seasonal variation. For Xindianpao, the protein-like fluorescence peaks were higher than the humic-like fluorescence peaks in June 2013, whereas the humic-like fluorescence peaks were higher than the protein-like peaks in August 2013.

Figure 2. 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}).

In split-half analysis, the 67 EEMs were randomly divided into four halves and then analyzed for two different splits (1-2 and 3-4 half split). When the number of components was chosen to be four, the excitation and emission loadings from the output results of the 1-2 and 3-4 split-half analysis largely overlapped, respectively

(Fig. 3). It should be noted that for the 3-4 split-half analysis, the excitation and emission loadings of component 3 and component 4 were reversed. In fact, the output results of the split-half analysis were valid as long as the excitation and emission loadings of the fluorescent component were overlapped at the same wavelength and these components in different colors in the two groups only represent the order of appearance of the components according to their contributions (Stedmon and Bro, 2008).

Figure 3. Results from split-half analysis (1-2 top a); 3-4 down b)) in PARAFAC models. The plots represent spectral shapes of the excitation and emission loadings from the two halves (1-2; 3-4 split -half analysis) modeling.

In our study, four separate fluorescent components (Fig. 4a-d) and the excitation and emission loadings (e-h) of the four components identified by EEM-PARAFAC are summarized in Fig. 4 and Table 2. The first fluorescent component (C1) was a biological degradation humic-like component that displays two excitation maxima (at 230 and 300 nm) with a single emission wavelength (at 425 nm) 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 had the maximum excitations (at 255 and 350 nm) and an emission wavelength (at 460 nm) (Fig. 4a-b), which was consistent with the humic-like peaks (A and C) defined by Coble (1996). Component 3 demonstrated two excitation maxima (at 225 and 275 nm) and one emission maximum (at 360 nm), which

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), ~~which was characterized by the maximum excitations at 225 and 275 nm and the emission wavelength was found at 310 nm~~. 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. 4c-d). In this study, not all of the four components were present in all of the samples.

Figure 4. 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 maxima is given in brackets.

3.3 Temporal distribution of PARAFAC components

As shown in Fig. 5a and b, 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 part of the CDOM for the seven inland lakes was originated from ~~phytoplankton degradation and other organisms~~. 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. ~~5b~~). 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}) 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 from plant degradation and microbial activities, but less terrestrial substances were imported to the water bodies in June and therefore the fluorescence intensity of C2 was lower than the seasonal average. Compared to the fluorescence intensity in June, the three fluorescence intensities (0.65 ± 0.14 (C1), 0.33 ± 0.16 (C3), 0.52 ± 0.36 (C4) nm^{-1}) from the samples collected in August 2013 reduced, but an increased value was recorded for C2 (0.42 ± 0.05 nm^{-1}). Especially, the fluorescence intensities of two protein-like components showed an obvious difference. This can be attributed to substantially increased precipitation up to 180 mm in July from June to

August 2013 (Fig. ~~5c~~) so that flood occurred when rainfall continued to increase in August. Gradually, DOM contained in terrestrial CDOM was flushed by rainfall to the lakes so that the C2 (0.42 ± 0.05 nm^{-1}) fluorescence intensity became higher. In accordance with Cheng et al. 2010, the rainwater CDOM for this study was largely characterized by protein-like components (Cheng et al., 2010). The fluorescence intensity of the rainwater CDOM was very weak, and also the rainwater CDOM contained much lower humic-like concentration (Fig. ~~6b~~). The intensities of the other three components decreased because of dilution resulting from heavy rain and relatively weak microbial decomposition of plants.

The highest C1 (1.02 ± 0.38 nm^{-1}) presented in February 2014 and the C2 (0.39 ± 0.12 nm^{-1}) intensity remained almost the same as that in August 2013. However, the protein-like components indicated that the C3 (0.57 ± 0.25 nm^{-1}) intensity was higher than the C4 (0.35 ± 0.17 nm^{-1}) intensity, which was opposite to the results from other months (Fig. ~~5~~b). In cold winter, the surface waters formed a thick layer of ice covering the lake waters. ~~Because the ice cover reduced light penetration and restricted gas exchange between the underlying water and atmosphere, vigorous biological activities in the lakes would be prohibited at low temperature and low light level (Thomas K., 1983; Uusikiv et al., 2010; Wharton, et al., 1993).~~ Also, dissolved ~~matters~~ were left in the underlying surface waters and little terrestrial matters were imported to the lakes once covered by ice (Stedmon et al., 2007). Therefore, the C1 and C3 in the water of the lakes beneath the ice layers would ~~cumulate~~ simultaneously, whereas, the C2 remained the same. Obviously, the fluorescence intensity of

component 1 reached the highest value for the winter samples. As shown in Fig. 6a, another striking feature for the winter samples was that the fluorescence of CDOM in the ice was dominated by the tyrosine-like C4 component, which is consistent with the findings of Barker et al. (2009, 2013) and Stedmon et al. (2007). It showed that the C4 component was left in the ice-cover when the lakes were frozen. Therefore, it is not surprising that the intensity of component C4 for water beneath ice layers was reduced and the concentrated C3 showed a much higher fluorescence intensity. In April 2014, the intensities of four fluorescent components (0.47 ± 0.17 (C1), 0.25 ± 0.08 (C2), 0.40 ± 0.16 (C3), and 0.45 ± 0.13 (C4) nm^{-1}) exhibited similar seasonal trends though these values were much lower than the average. Our interpretation is that the ice CDOM was characterized by tyrosine-like component (C4) (Fig. 6a), and the fluorescence intensity of C4 contributed by the ice-melt water was very weak. However, the underlying lake CDOM was dominated by both humic-like (C1 and C2) and protein-like (C3 and C4) components. When the ice in the lakes melt 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 5. 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) Seasonal variation of the four EEM-PARAFAC components at different seasons; c) Monthly variation of rainfall for the lakes in western part of Jilin province from April 2013 to February 2014. The error bar represents standard deviations.

Figure 6. Representative examples of EEMs for a) lake ice-melt water sample, and b) rainwater CDOM in the western part of Jilin province (Raman: nm^{-1}).

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 10.03 to 88.15 mg L^{-1} during the study period, with an average value of 37.60 ± 18.05 mg L^{-1}. It is because the prolonged sunshine duration can result in an evapo-condensed DOC concentration in the Songnen Plain. The highest averaged DOC concentration (55.04 ± 20.00 mg L^{-1}) was present in February 2014; whereas, relatively constant values of approximate 30 mg L^{-1} were observed in the other three seasons, demonstrating a seasonal dynamics that can be attributed to hydrological, climatic and landscape variations (Song et al., 2013). This can be attributed to the accumulated DOC when the lakes freeze in winter, which leaves DOC in the liquid phase, resulting in a higher DOC concentration in the underlying water (unpublished material). Generally, the absorption coefficient a(350) was used as a proxy for characterizing CDOM concentration, which was 5.73 ± 1.68 m^{-1} in June 2013, 5.82 ± 0.81 m^{-1} in August 2013, 6.36 ± 2.17 m^{-1} in February 2014, 4.17 ± 1.49 m^{-1} in April 2014, respectively, with an seasonal average of 5.40 ± 1.84 m^{-1}. 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 the ratio of molecular weight of humic acid and fulvic acid. The mean of S_R for all water samples was up to 1.21 ± 0.20, with the lowest 0.96 ± 0.22 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. 7, 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 = 0.633), indicating that the concentrations of the two humic-like components were controlled by common sources. There was a weak relationship (R^2 = 0.051) between the protein-like components (C3 and C4) because of a complex origin of CDOM such as rainfall in summer, ice in winter and organic pollutants derived from domestic, agricultural and industrial sewerage, which represent the complex origins of CDOM. However, there was almost no correlation between the humic-like and protein-like components. The linkage of a fluorescence signal to DOC was very complicated because of the seasonal effects of both steady and labile fluorescence and non-fluorescence CDOM components as a result of increased rainfall and algal blooms which affect the DOC concentration (Henderson et al., 2009). Component 3 of the CDOM fluorescence can

be used to detect water pollution (Baker et al., 2004). A weak relationship (R^2 = 0.42) (Fig. 7d) was found between DOC and component 3 from the decay of plants through microbial activity or the pollution from human and animal wastes.

The most important finding for the water samples collected at different seasons from the Songnen Plain is a significant relationship (R^2 = 0.931) between salinity and DOC (Fig. 7e), which implies that a prolonged sunshine duration can result in an evapo-condensed DOC concentration. Different from the findings by Yamashita et al. (2008) for ocean water, this study did not find obvious correlation between salinity and EEM-PARAFAC extracted components with the exception of C3 (R^2 = 0.469) (Table 4 and Fig. 7d). It was because that with the sunshine duration hours increasing, the photo-degradation and microbial activities become stronger, leading to a more efficient transformation of labile fluorescence CDOM into non-fluorescence CDOM component (Song et al., 2013).

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

Figure 7. 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

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 PARAFAC model. 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 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 component in rain and ice-melt water. Component 1 and 2 exhibited strong linear correlation (R^2 = 0.633). 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 = 0.42) was found between DOC and component 3 from the decay of plants through microbial activity or the pollution from human and animal wastes. ~~Most importantly, a significant relationship (R^2 = 0.931) was found between salinity and DOC. 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.~~

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Zhang, Y. L., VanDijk, M. A., Liu, M. L., Zhu, G. W., and Qin, B. Q.: The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: Field and experimental evidence. Water Res., 43, 4685–4697, 2009.

649 Table 1. Mean value of water quality parameters from June 2013 to April 2014. Turb
650 denotes water turbidity; N denotes sampling numbers.
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Sampling season	pH	Salinity (PSU)	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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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 maxima is given in brackets.

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	Terrstrialhumic-like	A and C	1 and 4
C3	225 (290)	360	Autochthonous tryptophan-like	T	
C4	220 (275)	320	Autochthonous tyrosine-like	B	8

Fluoresence peaks were named as Components (Coble) and (Zhang) by Coble et al. (1996, 1998) and Zhang et al. (2010, 2011), while as Componets (Stedmon and Markager) by Stedmon and Markager (2005).

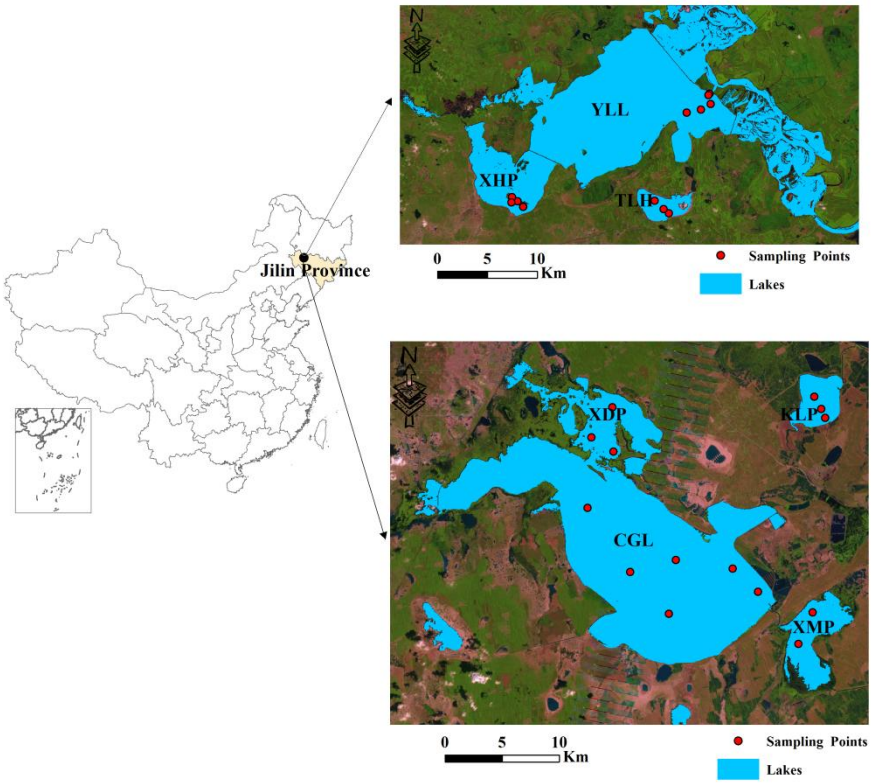
Table 3. Mean values of DOC concentration and CDOM absorption coefficients groups at different seasons. S_R: the slope ratio of $S_{275\text{-}295nm}$: $S_{350\text{-}400nm}$.

Sampling season	a(254) m^{-1}	a(280) m^{-1}	a(350) m^{-1}	S_R	DOC mg L^{-1}	N
Jun.2013	38.39±9.23	25.98±6.38	5.73±1.68	1.29±0.16	31.84±14.67	15
Aug.2013	29.71±4.73	19.36±2.91	5.82±0.81	0.96±0.22	32.83±14.78	13
Feb.2014	52.88±18.13	34.62±11.54	6.36±2.17	1.18±0.11	55.04±20.00	17
Apr.2014	34.43±11.38	22.45±7.36	4.17±1.49	1.32±0.13	30.86±10.91	22
All	39.08±14.73	25.73±9.58	5.40±1.84	1.21±0.20	37.60±18.05	67

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

	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**

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



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735 Figure 1. Locations of the water sampling sites for 7 lakes in the western part of Jilin

736 province, Northeast China.

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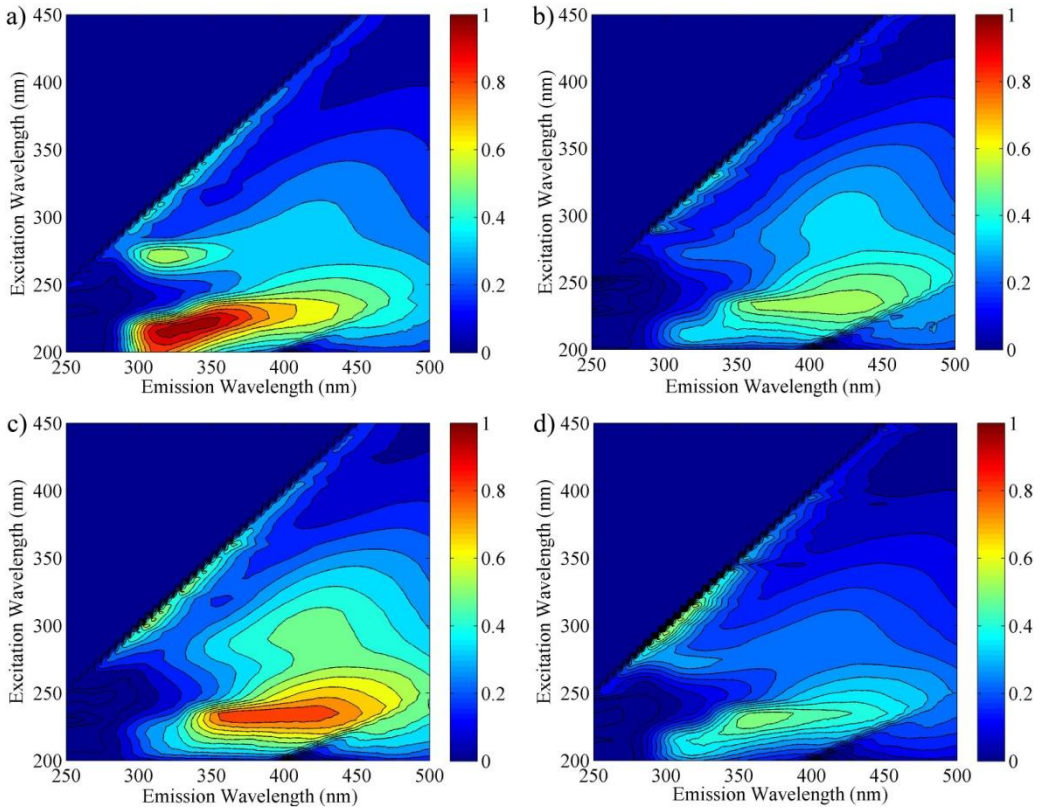

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743 Figure 2. Examples of EEMs for one water sample from Xindianpao Lake in the

744 western part of Jilin province at different seasons a) June 2013; b) August 2013; c)

745 February 2014; d) April 2014 (Fluorescence is in Raman unit: nm^{-1}).

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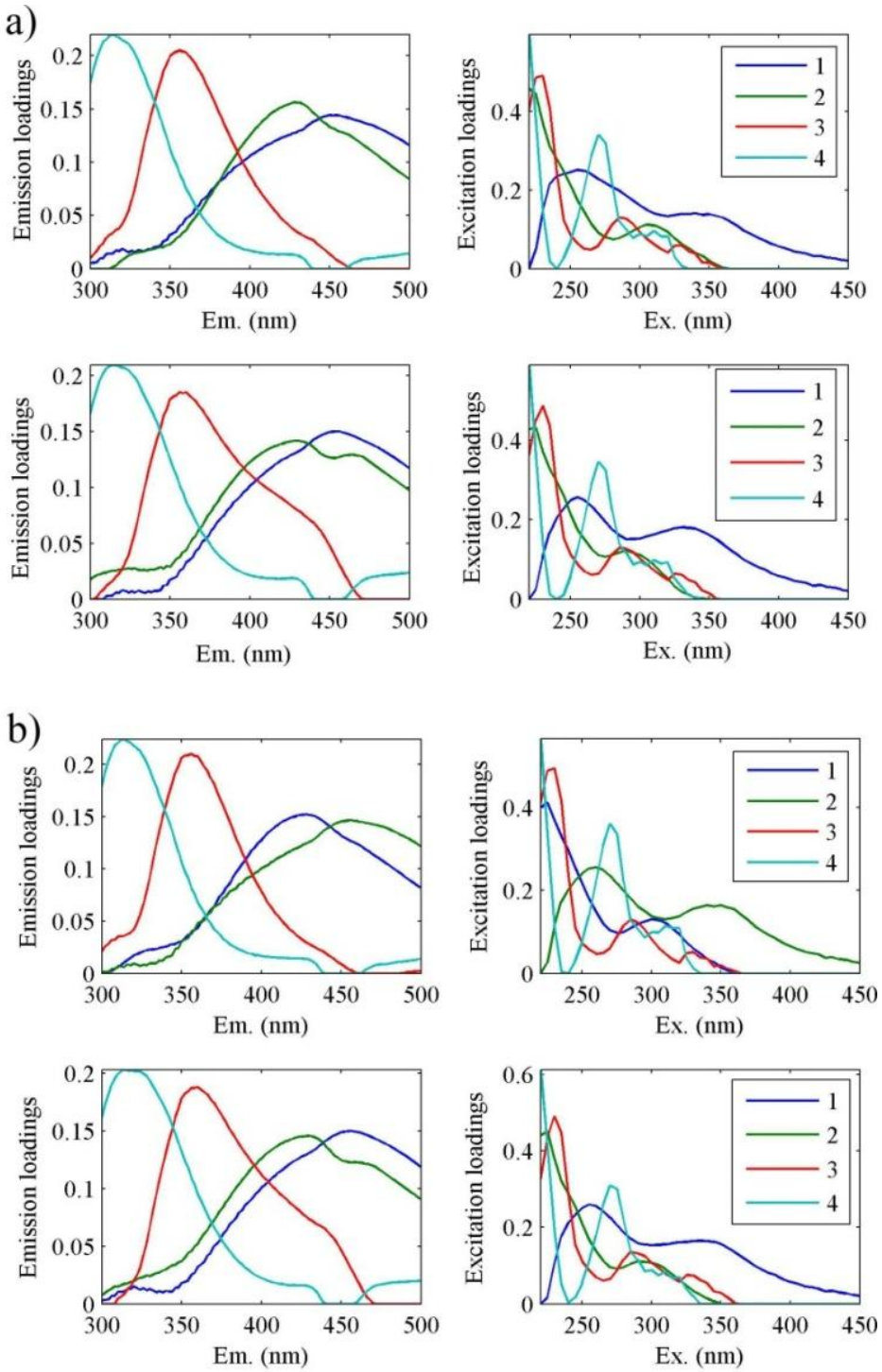


~~Figure 3. Results from split-half analysis (1-2 top a); 3-4 down b)) in PARAFAC models. The plots represent spectral shapes of the excitation and emission loadings from the two halves (1-2; 3-4 split -half analysis) modeling.~~

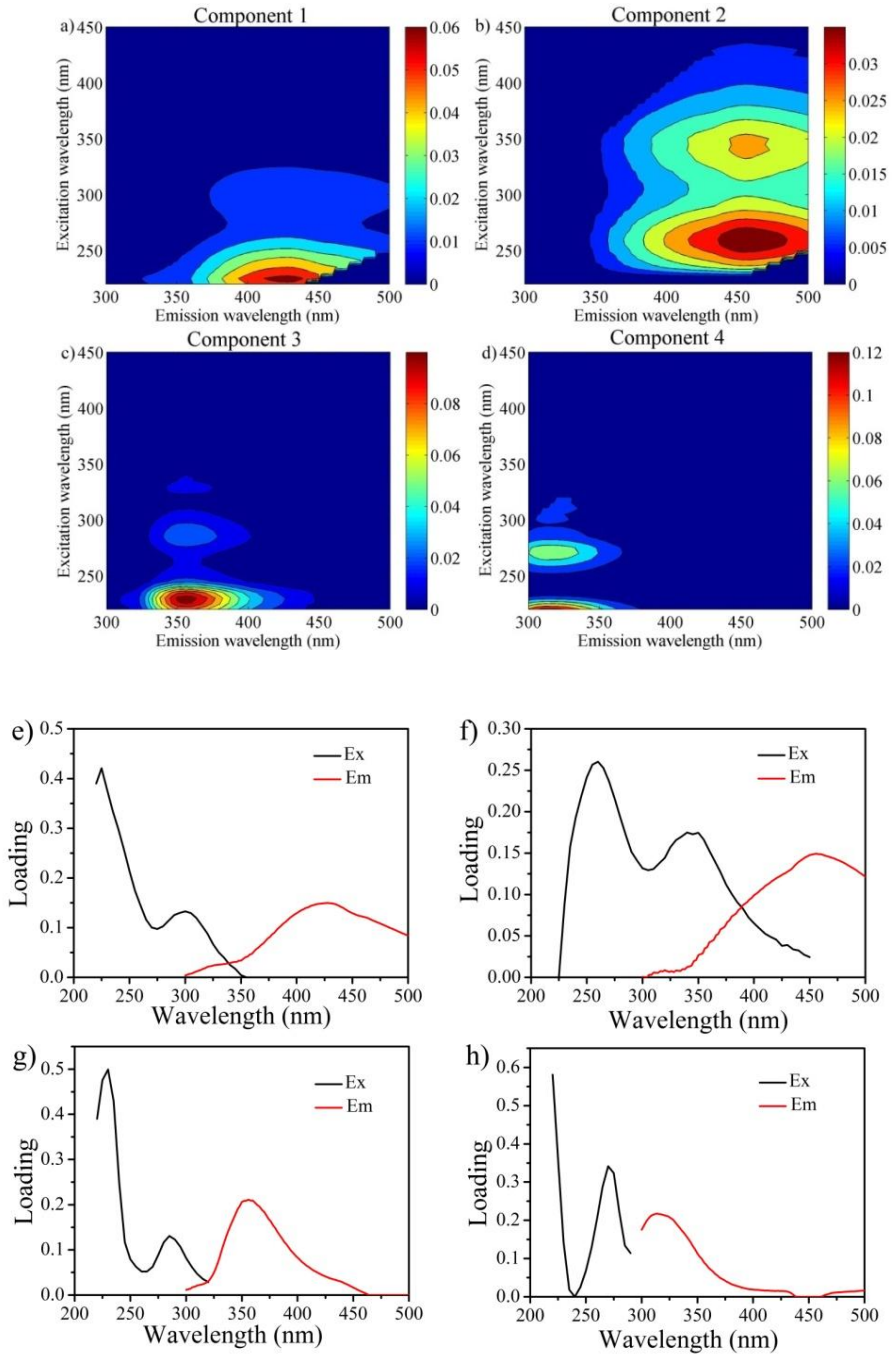
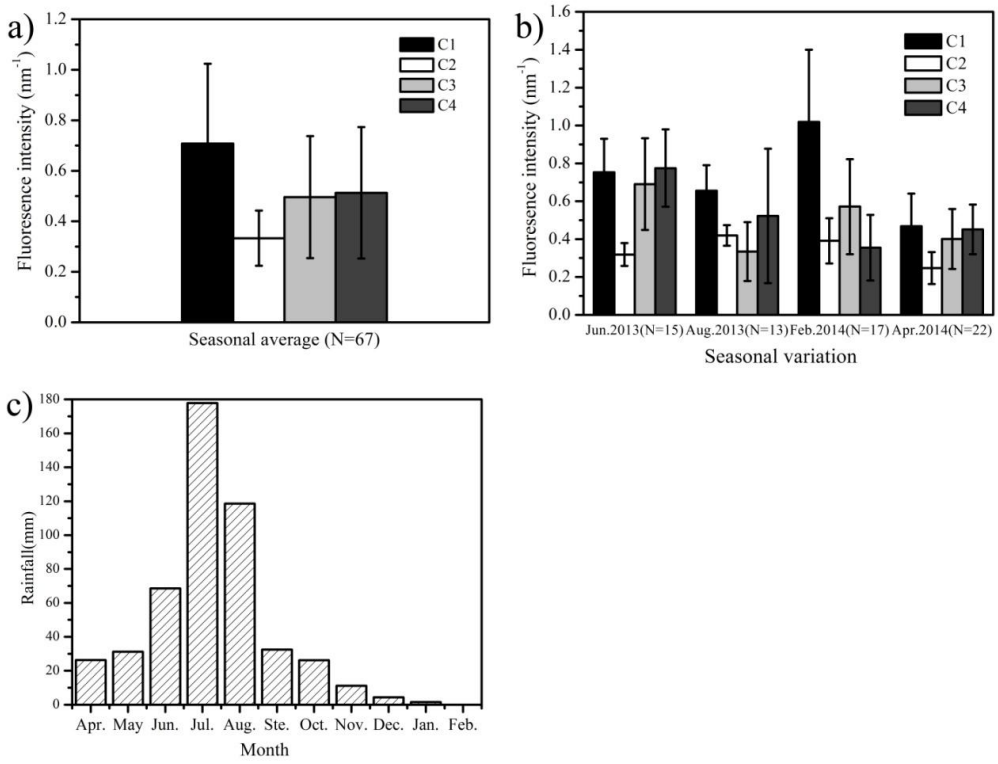


Figure 4. The PARAFAC model output shows the contour plots of the four PARAFAC fluorescent components (a-d) and excitation (black) and emission (red) loadings (e-h) of each component. Fluorescence is in Raman units: nm^{-1}.



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799 ~~Figure 5. a) Seasonal average of F_{max} for EEM-PARAFAC components (C1, C2, C3~~

800 and C4) for lakes in the western part of Jilin province; b) Seasonal variation of the

801 four EEM-PARAFAC components at different seasons; c) Monthly variation of

802 rainfall for the lakes in western part of Jilin province from April 2013 to February

803 2014. The error bar represents standard deviations.

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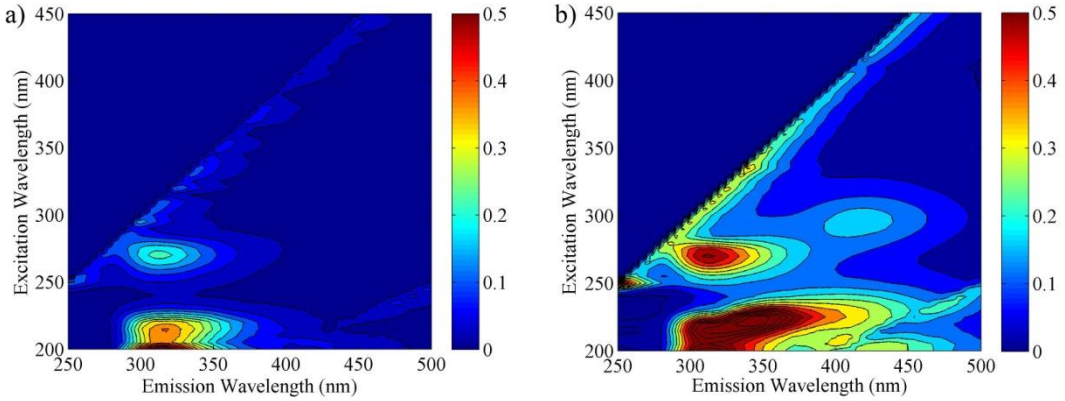

Figure ~~6~~ 1. Representative examples of EEMs for a) lake ice-melt water sample, and b) rainwater CDOM in the western part of Jilin province (Raman: nm^{-1}).

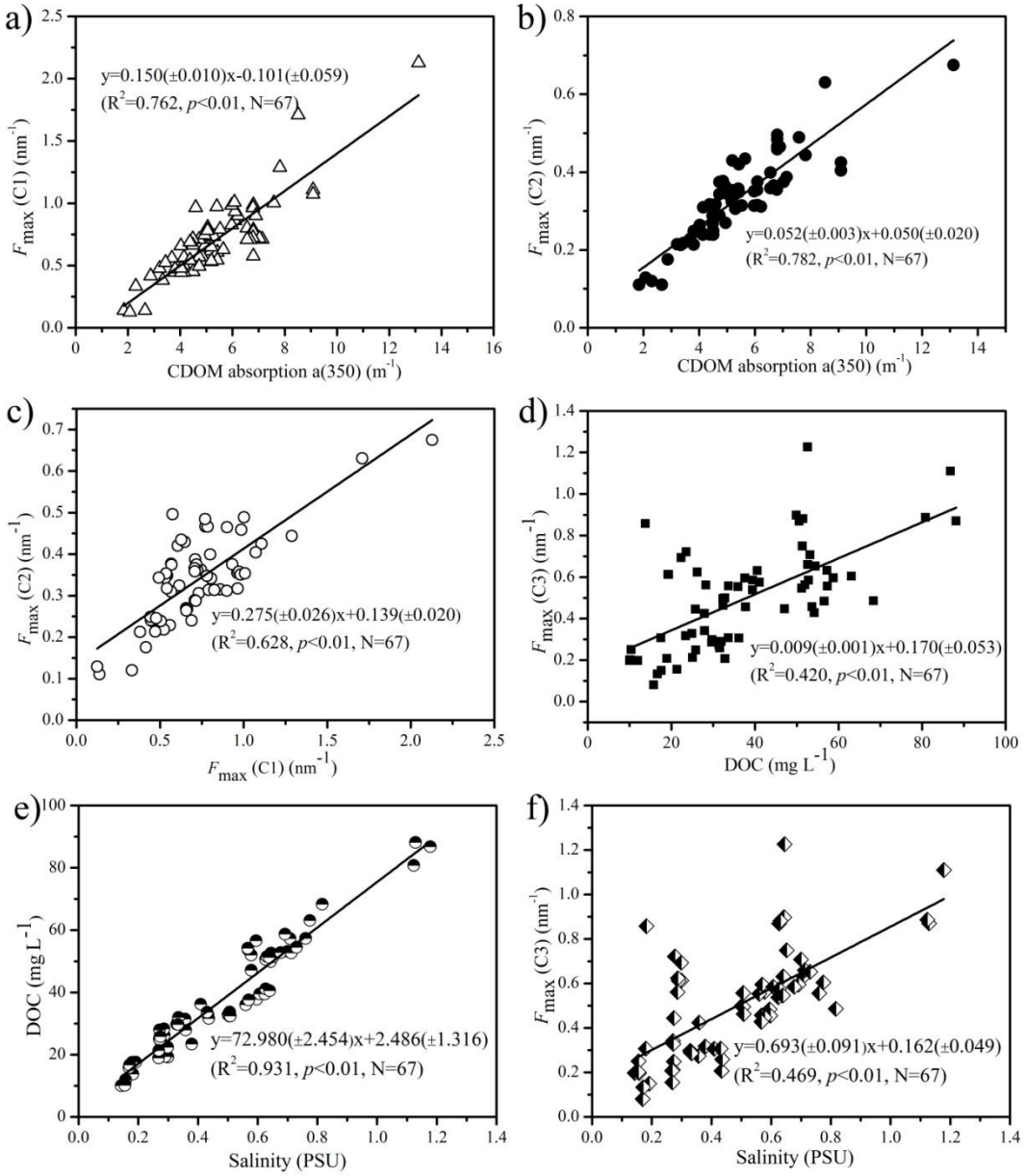

Figure 7. Relationships between CDOM absorption coefficient a(350) with a) F_{max}(C1), b) with F_{max}(C2), c) peak F_{max}(C1) versus F_{max}(C2), d) peak F_{max}(C3) versus DOC, e) Salinity versus DOC, f) Salinity versus F_{max}(C3).