Biogeosciences Discuss., 12, C3021–C3041, 2015
www.biogeosciences-discuss.net/12/C3021/2015/

Biogeosciences Discussions
Open Access

Interactive comment on "Seasonal characterization of CDOM for lakes in semi-arid regions of Northeast China using excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC)" *by* Y. Zhao et al.

Y. Zhao et al.

songks@iga.ac.cn

Received and published: 23 June 2015

Responses to comments: Thank you very much for pointing out some major points which should be reconsidered. - The manuscript contains too many methodological details. To increase the attention of the reader and provide a fluent reading the Introduction as well as the Materials and Methods should be shortened rigorously. Similarly, details about e.g. fluorescent wavelength regions or statistics that can be found in one

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

of the tables do not need to be mentioned in the text again Response: Thank you for your suggestion. The introduction as well as the Materials and Methods should be shortened rigorously (see responses to specific comments from Page 5727 to 5734). and the fluorescent wavelength regions or statistics mentioned again in the text should be skipped (see responses to specific comments).

- As mentioned in the introduction, an initial motivation for this manuscript was to compare fresh water and brackish water CDOM. Therefore two groups of lakes were defined (one group with low, the other with medium salt concentration). Though this might be a quite interesting investigation these two lake groups are not mentioned in the results and discussion part anymore. Were there no significant differences? If so, how could this be explained? Response: The two groups of lakes were defined by the study regions (The Chagan lake group is in the Songyuan, the Yueliang lake group in the Baicheng. The Yuelaing lake group also comprise relatively high salt lake such as Talahong (TLH) as well as low salt lake (YLL). This manuscript is to assess the dynamic of individual CDOM fluorescent component under seasonal variations contained in both fresh and saline lakes in the western part of Jilin province rather than compare fresh and brackish water CDOM.

- The description of the fluorescent components is often not only confusing (e.g. sometimes the PARAFAC component C3 is also referred to as “protein-like peak T” (as defined by other authors) but sometimes also wrong. In general the authors might improve their understanding of PARAFAC fluorescent components, for example the components should be called “fluorescent components” rather than “fluorescence components”. Furthermore, the PARAFAC components should always be referred to as “components” and not as “peaks”. Also, the claim that the two protein-like components “[. . .] consist of two dissolved amino acids, i.e., tryptophan and tyrosine [. . .]” is wrong, they should be rather referred to “tryptophan-like” or “tyrosine-like”. Response: Thank you for your suggestions. In order to understand of PARAFAC fluorescent components, the “fluorescence components” should be replaced by “fluorescent components”. The “trypto-

BGD
12, C3021–C3041, 2015

phan or tyrosine" components should be replaced by "tryptophan-like or tyrosine-like" components. The "PARAFAC peaks" should be replaced by "PARAFAC components" throughout the paper. The reviewer's comments have been incorporated in the revised manuscript.

- For some data statistics need to be clarified. For example, the seasonal changes of fluorescence intensities of the four PARAFAC components is described in the text as "increasing" and "decreasing", partly also "significantly", though Figure 5a hardly reveals any obvious seasonal changes for most of the components. Response: The total fluorescence intensity is defined as the sum of fluorescence intensities of different fluorescent components. For Figure 5a, the total fluorescence intensities varied at different seasons can not be revealed. We are sorry for making the mistakes. When the data were used t-test again, partly there were no significant (t-test, $p>0.05$). On page 5737 in line 16, the contents "The total fluorescence intensity significantly varied from 2.54 $\pm$ 0.68 nm-1 in June to 1.93 $\pm$ 0.70nm-1 in August 2013, and then increased to 2.34 $\pm$ 0.92 nm-1 in February and reduced to the lowest 1.57 $\pm$ 0.55nm-1 in April 2014." should be replaced by "The total fluorescence intensity varied from 2.54 $\pm$ 0.68 nm-1 in June to 1.93 $\pm$ 0.70 nm-1 in August 2013, and then increased to 2.34 $\pm$ 0.92 nm-1 in February and reduced to the lowest 1.57 $\pm$ 0.55 nm-1 in April 2014." Responds to specific comments Page 5727 Line1: DOM consists of several humic acids rather than only one. Further it contains "proteins", not "proteinaceous". Line2: skip "array" in the sentence Response: Thank you for pointing out the mistakes. The contents "Dissolved organic matter (DOM), a heterogeneous mixture of humic acid, proteinaceous and carbohydrates, plays an array of important roles in aquatic ecosystems." should be replaced by "Dissolved organic matter (DOM), a heterogeneous mixture of several humic acids, proteins and carbohydrates, plays an important role in aquatic ecosystems." Line3: CDOM absorbs light of ultraviolet and visible light (not only within the blue region, though the absorption here is in fact typically higher than at the longer wavelengths of visible light). Response: Thank you for pointing out the mistake. The contents "……absorbs light energy in the UV (280–400 nm) and blue region of the

BGD
12, C3021–C3041, 2015

spectrum" should be replaced by ". . . . .absorbs light energy in the UV (280–400 nm) and visible region of the spectrum". Line9: autochthonous CDOM does not only originate from plant materials but also from a range of other organisms (e.g. algae, microorganisms) Line10: use "terrestrially imported substances" Responses: Thank you for pointing out the mistakes. The contents ". . .CDOM originates from the degradation of plant materials and terrestrial imported substance" should be replaced by ". . .CDOM originates from the degradation of plant materials and other organisms and terrestrially imported substance". Line12: use "making it difficult to isolate. . ." Response: Thank you for pointing out the mistakes. The contents " . . ...which makes it difficult to isolate. . ." should be replaced by ". . ., making it difficult to isolate. . .". Line14: the terms "OACs" and "SFS" are never again used in the paper. I suggest to skip these abbreviations Response: Thank you very much for pointing out the mistakes. These abbreviations "OACs" and "SFS" should be skipped. Line23: skip "and then" ResponseïijŽThank you for pointing out the mistake. The contents ". . .and then. . ." should be skipped. Line26: use "resulting in an emission of lower energy" Response: Thank you for pointing out the mistake. The contents ". . .resulting in the emission energy lower than . . ." should be replaced by ". . .resulting in an emission of lower energy. . ." page 5728 Line 6: abbreviation of EEM has already been mentioned before Response: Thank you for your suggestion. The contents "the fluorescence excitation-emission matrix s (EEMs)" should be replaced by "EEM spectroscopy". Line 8: better write "EEM spectroscopy" than "EEMs" Response: Thank you for your suggestion. The contents "EEMs" should be replaced by "EEM spectroscopy". Line 11ff: though sometimes equalized in literature, "allochthonous" is not necessarily "humic-like", neither is "autochthonous" necessarily "protein-like". Line 12: not only CDOM from coastal environments have been investigated, also from freshwater and other systems Line 15: re-formulate the sentence, e.g. ". . .of marine, freshwater and ice-water ecosystems as well as snow" Responses: Thank you for pointing out the mistakes. The contents ". . .distinguish allochthonous (humic-like fluorophores) and autochthonous (protein-like fluorophores) CDOM source in coastal environment. . . and to investigate the dynamics

BGD
12, C3021–C3041, 2015

of various aquatic ecosystem including marine, freshwaters and snow, ice-water systems" should be replaced by ". . .distinguish allochthonous and autochthonous CDOM source and to investigate the dynamics of coastal environment, marine, freshwater and ice-water ecosystems as well as snow". Line17: skip repetitive content (see line 19ff, page5727) Response: Thank you for your suggestion. The contents ". . .two main fluorescence components, i.e., humic-like and protein-like (Peaks B and T) substance . . ." should be replaced by ". . .the humic-like and protein-like substances. . .". Line 26ff: skip parts that are repetitive to line 21ff Response: Thank you for your suggestion. The contents ". . . Stedmon et al., 2003. . ." in line 21should be skipped. Page 5729 Line 3: use "PARAFAC modelling" and "correlations of the fluorescent components. . ." Response: Thank you for suggestion. The contents ". . .by PARAFAC model and analyzed the correlations the fluorescence components. . ." should be replaced " . . . by PARAFAC modeling and analyzed the correlations between the fluorescent components. . .". Line 8: use "low average SUVA254" Response: Thank you for pointing out the mistake. The contents "small average SUVA254" should be replaced "low average SUVA254". Line 9: use "indicate" Line 9: SR indicates "low average DOM molecular weight" Response: Thank you for your suggestion. The contents ". . .indicating large portion of lower molecules . . ." should be replaced by ". . ., which indicate large portion of low average DOM molecular weight. . .". Line 11: ". . .may be stored. . ." Response: Thank you for pointing out the mistake. The contents ". . .may store. . ." should be replaced by " . . .may be stored. . .". Line 12: skip "furthermore" Line 12: maybe better use "Therefore" instead of "to achieve this goal" Response: Thank you for your suggestion. The word "furthermore" should be skipped. The contents "to achieve this goal" should be replaced by "Therefore". Line 14: "at different seasons" Response: Thank you for your suggestion. The contents ". . . in different seasons. . ." should be replaced by ". . .at different seasons. . .". Line 17: "assess the dynamics of individual fluorescent components under seasonal variations" Response: Thank you for your suggestion. The contents ". . .assess the dynamic of individual fluorescence component of CDOM with seasonal variations. . ." should be replaced by ". . .assess the dynamics of individual flu-

BGD
12, C3021–C3041, 2015

orescent components under seasonal variations. . .". Line 19: unclear which factors are related to each other. I suggest "[. . .] link CDOM fluorescence intensities, absorption coefficients, DOC concentrations and salinity to each other." Response: Thank you for your suggestion. The contents ". . .link CDOM fluorescence intensity and the absorption coefficients, DOC concentration and salinity as well." should be replaced by". . . link CDOM fluorescence intensities, absorption coefficients, DOC concentrations and salinity to each other." Materials and methods Response to general: - When were the lakes covered with ice? How were samples taken during ice coverage? Response: The lakes were covered with ices in late November every year. During ice coverage, the samples were collected by using an ice drilling. After the ice layer was drilled a hole, the underlying water was coming up. The ice shavings was collected in the plastic bags and the lake water was collected in the plastic bottles.

- were any other parameters measured that could have affected CDOM measurements? (e.g. iron content) Response: The existing data in this study can not explain the question. The other parameters e.g. iron content that could have affected CDOM measurements will be measured in the later study.

Line 25: use "two groups of lakes. . ." Response: Thank you for pointing out the mistake. The contents "Two group of lakes. . ." should be replaced by "Two groups of lakes. . .". Line 27: use "with a relatively high mean salinity of. . ." Response: Thank you for pointing out the mistake. The contents "with the mean high salinity" should be replaced by "with a relatively high mean salinity of. . .". Page 5730 Line 4: skip "related to" Line 4: skip "for the study region" Response: Thank you for your suggestion. The contents ". . .related to. . ." and "For the study region" should be skipped. Line 5: "the average annual precipitation is about 1790mm" Response: Thank you for your suggestion. The contents ". . .the average annual precipitation is 391mm" should be replaced by ". . .the average annual precipitation is about 391mm". Line 7: better use "agricultural catchment land use" Response: Thank you for your suggestion. The contents ". . .agricultural practice. . ." should be replaced by ". . .agricultural catchment land use. . .". Line 10:

BGD
12, C3021–C3041, 2015

"...field campaigns in June and August 2013 as well as in February and April 2014" might be easier to read Response: Thank you for your suggestion. The contents "...four field campaigns in July, August 2013 and February, April 2014, respectively" should be replaced by "...four field campaigns in June and August 2013 as well as in February and April 2014, respectively.". Line13: have the samples been stored unfiltered? Response: The water samples were filtered and then stored before analysis. Page 5731 Line 2: skip "were" Line 2: Whatman GF/F filters have a 0.7 μm nominal pore size Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The contents "...water samples were filtered through pre-combusted 0.45 μm Whatman GF/F filters and then were measured..." should be replaced by "...water samples were filtered through 0.45 μm filters and then measured...". Line 20: "...where the absorbance of CDOM..." Response: Thank you for pointing out the mistakes. The contents "...that the absorbance of CDOM..." should be replaced by "...where the absorbance of CDOM...". Line 24: equation: Why has 440nm been used as reference wavelength? Response: The wavelength 440 nm has been chosen as reference wavelength in other literatures (Babin et al., 2003; Bricaud et al., 1995; Song et al., 2013; Zhang et al., 2010). That is because CDOM absorption coefficients become exponentially increase in the shorter wavelength regions (280-400nm) than 440nm. Page 5732 Line 4: The slope ratio SR by Helms et al., 2008 further indicates the molecular weight and photo-bleaching of DOM Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The contents "...indicate the contribution of different sources in terms of their molecular weights" should be replaced by "...indicate the molecular weight and photo-bleaching of CDOM". Line15: I would not refer the inner-filter effect as "the major problem with EEMs measurement of CDOM". It highly depends on DOC concentration and the contribution of humic and fulvic acids. Response: Thank you for your suggestions. The major problem with EEMs measurement of CDOM depends on DOC concentration and the contribution of humic and fulvic acids. The contents "The inner-filter effect is the major problem with EEMs measurement of CDOM because of ..." should be replaced by "The inner-filter

BGD
12, C3021–C3041, 2015

effect is because of. . .” Line 17: “[. . .] can reduce the fluorescence intensity by 5%” Response: Thank you very much for your suggestion. The contents “. . .can reduce the intensity of fluorescent component by 5%” should be replaced by “. . .can reduce the fluorescence intensity by 5%”. Line 23: If written in this form, the formula needs more brackets surrounding (Aex + Aem)! Response: Thank you for your suggestion. The formula “(Aex+Aem/2)” should be replaced by “(Aex+Aem)/2 ”. Line 25: rather use “respective” than “current”?! Response: Thank you for your suggestion. The word “current” should be replaced by “respective”. Line 27: I guess the Milli-Q water Raman peak was “measured” daily rather than “collected”? Response: Thank you for your suggestion. The contents “. . .collected daily” should be replaced by “. . .measured daily”. Page 5733 Line 4: PARAFAC modeling decomposes the CDOM fluorescence signal into separate fluorescent signals Response: Thank you for pointing out the mistake. The contents “. . .decompose EEMs of the complicate mixture CDOM into individual fluorescence groups” should be replaced by “. . .decompose the CDOM fluorescence signal into separate fluorescent signals”. Line 18: matrices Line 18: Excel (Microsoft office)? Response: Thank you for pointing out the mistake. The word “matrixes” should be replaced by “matrices”. The “Excel file” refers to “Microsoft office Excel file”. Line 19: step (2) and (3) described here are repetitive to line 3ff of page 5734 and should be deleted here! Response: Thank you for your suggestion. The paragraph “In our study. . .carried out in the “N-way DOMFluor toolbox for MATLAB” should be skipped. Page 5734 Line 2: Andersson et al. Response: Thank you for pointing out the mistake. The contents “. . .Andersso et al., 2000” should be replaced by “. . .Andersson et al., 2000”. Line 6: “the Rayleigh bands do not represent DOM fluorescence” Response: Thank you for your suggestions. The contents “. . .do not describe DOM fluorophore in the area” should be replaced by “. . .do not represent DOM fluorescence in the area”. Page 5735 Line 5: “[. . .] the set of samples was pooled together [. . .]” Response: Thank you for your suggestions. The contents “When the whole set of samples were pooled together. . .” should be replaced by “When the set of samples was pooled together. . .”. Line 7ff: better write e.g. “. . .whereas the other three seasons exhibit relatively constant

BGD
12, C3021–C3041, 2015

values of approximately 0.40 PSU." Response: Thank you for your suggestions. The contents "The salinity for lakes with other three seasons was almost the same, which was about 0.40 PSU" should be replaced by "...Whereas the other three seasons exhibit relatively constant values of approximately 0.40 PSU". Line 11: Why does turbidity decrease with increasing rainfall? Response: When the particulate substances in the lakes are resuspended with the wind-induced mixxing, the turbidity of waters can correspond to change. To the shallow lakes in the Songnen Plain, the wind is relatively small from July to August every year. Though terrestrial matters are imported to water bodies through rainwash with rainfall increasing, the particulate substances deposited immediately. Also, the turbidity of pure rainwater is about 0. Therefore, the turbidity reduced to 63.13 $\pm$ 31.21 NTU in August 2013 with rainfall increasing. Line 10ff: For easier reading I suggest to skip the values here and refer to the corresponding table. Response: Thank you for your suggestions. The contents "The highest turbidity was present in June 2013 with 166.20 $\pm$ 108.73 NTU, then reduced to 63.13 $\pm$ 31.21 NTU in August 2013 with rainfall increasing, and then reduced to the lowest 21.33 $\pm$ 15.87 NTU in February 2014. Compared with the turbidity in February 2014, the turbidity had almost no change in April 2014 with 22.24 $\pm$ 16.42NTU." should be replaced by "The highest turbidity was present in June 2013, then reduced in August 2013, and then reduced to the lowest value in February 2014. Compared with the turbidity in February 2014, the turbidity had almost no change in April 2014 (Table 1)."

Which of these changes are statistically significant? What about the average salinities of the two groups of lakes? Are there any significant seasonal changes on pH? This might be important since pH can affect fluorescence (e.g. see Reynolds 2003: "Rapid and direct determination of tryptophan in water using synchronous fluorescence spectroscopy") Response: Thank you for recommending the reference "Reynolds 2003: "Rapid and direct determination of tryptophan in water using synchronous fluorescence spectroscopy". Table 1 showed that the values about water quality parameters pH, salinity, turbidity at different seasons in both fresh and saline lakes. Since there are no significant seasonal changes on pH which can affect fluorescence. The

BGD
12, C3021–C3041, 2015

manuscript is to assess the dynamics of individual fluorescent components under seasonal variations in both fresh and saline lakes in the western part of Jilin province in Northeast China rather than compare the difference in fluorescence between fresh water and saline water. Line 15ff: I would rather say “fluorescent components” instead of “fluorescence peaks”. Further, to avoid confusion, I would rather compare the fluorescent components of this study with those of other studies only once in the beginning but then stick with the terminology given in this study (e.g. use “C1”, “C2” etc. throughout the manuscript instead of switching to “A” or “C”). Response: Thank you for your suggestions. The contents “fluorescence peaks” should be replaced by “fluorescent components” throughout the manuscript. We would use “C1, C2, C3 and C4” throughout the manuscript rather than “A”, or “C” or “B” or “T”. The reviewer’s comments have been incorporated in the revised manuscript. However, in here, based on the EEMs “peak picking” technique, the fluorescence peaks e.g. humic-like A and C and protein-like B and T was firstly defined by Coble et al. 1996, which is only cited here in the manuscript. Line 18: see General Comments Response: Thank you for your suggestion. The contents “The humic-like component is a complex mixture of aromatic and aliphatic compounds-fulvic acids and humic acids, . . .i.e., tryptophan and tyrosine. . ..” should be replaced by “The humic-like component is a complex mixture of aromatic and aliphatic compounds- humic-like acids. . .i.e., tryptophan-like and tyrosine-like substances. . .”. Line 23: I suggest reconstructing the structure of the sentence, e.g. “As an example, Figure 2 displays examples of EEMs of lake Xindianpao at the four different seasons.” Response: Thank you for your suggestions. The contents “Taking Xindianpao as an example with different seasons (Fig. 2)” should be replaced by “As an example, Figure 2 displays examples of EEMs of lake Xindianpao at the four different seasons”. Page 5736 Line 3ff: this paragraph is partly redundant to the second last paragraph of page 5734 and should only be described in the method-section. Response: Thank you for your suggestions. The contents “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 excita-

BGD
12, C3021–C3041, 2015

tion loadings from each half (Stedmon and Bro, 2008)" should be placed in the Method section on Page 5734 in Line 11. Line 18ff: I did not find evidence in literature that dedicates component C1 to phytoplankton degradation, rather relations to marine humic-like substances, waste water treatment or agricultural catchment land use Response: In marine environment, C1 displayed similar fluorescence peaks to marine humic-like substances (Coble et al. 1996). For inland waters, the component C1 is related to phytoplankton degradation which is found by Zhang et al. 2009 (The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: Field and experimental evidence. Water Res. 43: 4685–4697). Line 22ff: I would not compare C2 to C1 like in "Compared with C1 [. . .] component shifted to the red spectral region". Response: Thank you for your suggestions. In order to differentiate component C1 from C2 which are both related to the humic-like components, we use "Compared with C1 [. . .] component 2 shifted to the red spectral region". The contents "Compared with C1 [. . .] component 2 shifted to the red spectral region" should be replaced by "Component 2 showed a maximum excitation (at 255 and 350 nm) and emission (at 460 nm) characteristics. . .". Line 25: maybe use "C3 resembles the tryptophan-like component as found by (author name). Response: Thank you for your suggestions. The contents "Component 3 demonstrated two excitation maxima (at 225 and 290 nm) and one emission maximum (at 360 nm), which is considered to be similar to tryptophan." should be replaced by "Component 3 demonstrated two excitation maxima (at 225 and 290 nm) and one emission maximum (at 360 nm) , which resembles the tryptophan-like component as found by Baker et al. 2004 (Baker et al., 2004; Hudson et al., 2007)." Page 5737 Line 4: maybe better write "In this study not all of the four components were present in all of the samples." Response: Thank you for your suggestions. The contents "However, these results from our study do not mean all the four components were shown in every water sample." should be replaced by "In this study, not all of the four components were present in all of the samples." Line 13ff: The message here is unclear. Maybe better write e.g. "At all four seasons the fluorescent component C2 contributed less to total fluorescence than C1"? Response:

BGD
12, C3021–C3041, 2015

Thank you for your suggestions. This means the average fluorescence intensity of C2 is the lowest than the other three components (C1, C3 and C4). The contents “The lowest C2 intensity represented only a small portion of CDOM. . .” should be replaced by “At all four seasons, the fluorescent component C2 contributed less to total fluorescence than the three others. . .” Line 19ff: Message unclear, please reconstruct the sentence Response: Thank you for your suggestions. The contents “ In June 2013, the intensities of four fluorescence components (0.75 $\pm$ 0.17 (C1), 0.32 $\pm$ 0.06 (C2), 0.69 $\pm$ 0.24 (C3), 0.77 $\pm$ 0.20 nm (C4)) exhibited the similar trends to the whole set of samples, but higher than the average except the C2 0.32 $\pm$ 0.06nm-1” should be replaced by “ In June 2013, the intensities of four fluorescent components (0.75 $\pm$ 0.17 (C1), 0.32 $\pm$ 0.06 (C2), 0.69 $\pm$ 0.24 (C3), 0.77 $\pm$ 0.20 nm (C4)) exhibited similar trends to the pooled data set.”. Line 23: what is meant with “others”? Response: The “others” means “microorganisms”. The contents “This can be explained by enhanced activities from plant degradation and others.” should be replaced by “This can be explained by enhanced activities from plant degradation and microorganisms.” Line 27: Is there a significant difference? According to Figure 5a there is none. Response: Compared with the fluorescence intensity in June, the two protein-like components (C3 and C4) showed almost no same values in August 2013. Page 5738 Line 2: this refers to Figure 6b. Further, to me it is unclear if Figure 6 is from Cheng et al., 2010 or from this study. Response: Thank you for putting forward the questions. The results in Figure 6b are from our study, which are consistent with Cheng et al. 2010. The contents “The fluorescence intensity of rainwater was mostly characterized by protein-like components and lower humic-like concentration (Fig. 7b) (Cheng et al., 2010).” should be replaced by “ In accordance with Cheng et al. 2010, the fluorescence intensity of rainwater for this study was mostly characterized by protein-like components. Also the rainwater CDOM contains much lower humic-like concentration (Fig. 7b)(Cheng et al., 2010).” 1st paragraph: If rainwater contains a lot of protein-like substances why does the protein signature of the lake EEMs decrease during rainfall? Is the fluorescence weak and weighted out by the dilution effect? Response: Thank you for putting forward

BGD
12, C3021–C3041, 2015

the questions. Though the rainwater was dominated by protein-like components, the fluorescence intensity was very weak. The CDOM fluorescent components for lake water was importantly affected by both the degradation of plant materials and terrestrially imported substance in August 2013, of which the fluorescence intensities only became weaker with the rainfall increasing compare to the fluorescence intensity of fluorescent components in June 2013. The intensities of the other three components but C2 decreased because of dilution with a lot of rain. Line 12: maybe you could add a quotation for the statement “strong biological activities would be prohibited”. Ice cover solemnly does not prevent biological activities. Response: The ice cover reduces light penetration and restricts gas exchange between the underlying water and atmosphere. Therefore, when ice was covered, the biological activities in lake waters became weak at the low tempreture and low light level (Thomas K., 1983. Under Landfast ice. Arctic, 36, 328-340; Wharton, R. A., Jr., McKay, C. P., Clow, G. D., and Andersen, D. T., 1993. Perennial ice covers and their influence on Antarctic lake ecosystems. Antarct. Res. Ser. 59, 53–70). Line 12f: why would C1 and C3 accumulate simultaneously? If “strong biological processes” are really prohibited how can C3 accumulate? What about C4? Where can an increase in fluorescence come from in winter during ice coverage? (autochthonous production? groundwater inflow?) Are some components preferentially “taken up” into the ice during ice formation? Response: Thank you for putting forward the questions. Compared with the intensities of the fluorescent components in August 2013, the C1 and C3 accumulated simultaneously in winter (Figure 5a). During ice formation, C4 was preferentially taken up into the ice. Because the ice water was dominated by C4, the fluoresecent components (C1 and C3) of lake water were cumulated and C4 in lake water decreased. With the ice layer covering, the water temperature decreased severely. Therefore, the strong biological activities in waters would be prohibited. Line 16: here it is unclear what is meant by “ice DOM fluorescence”. Were samples from ice taken as well? If so, what are the properties of the ice DOM compared to lake DOM? Response: Thank you for putting forward the question. The samples from ice were taken as well when the water samples were collected in

BGD
12, C3021–C3041, 2015

Feburary 2014. Compared with lake water DOM, The “ice DOM fluorescence” was dominated by tyrosine-like component (B), of which fluorescence intensity was very weak. Line 18ff: In how far is it not surprising that C4 fluorescence intensity beneath the ice was reduced? Response: When the ice was drilled through, the lake water was coming up and then collected in the plastic bottles. The intensity of C4 for the collected lake water beneath ice layer was reduced. Line 21ff: message unclear. what is meant with “similar trends with the whole”? Response: Thank you for putting forward the question. In April 2014, the intensities of four fluorescent components showed the similar trends with the whole. This means the four fluorescent components (C1, C2, C3, C4) exhibted the same variations with the seasonal average values, respectively. Line 23ff: Unclear interpretation. What exactly is tried to be explained? Is the ice DOM expected to exhibit the same DOM composition as the lake DOM and therefore just dilutes lake DOM without changing fluorescent component proportions when the ice melts in spring? Response: Thank you for your suggestion. In April 2014, the intensities of four fluorescent components was lower than the seasonal average when the set samples as a whole. This was because when the ice in the lakes melt into water with the weather warming, and the biological degradation and human activity was weak. Therefore, CDOM in lake waters was diluted and the fluorescence intensity of the four fluorescent components reached to the lowest, respectively. The ice DOM was characterized by tyrosine-like component (C4)(Figure 6a), while the lake DOM was dominated by both humic-like (C1 and C2) and protein-like (C3 and C4) components. It can be demonstrated that when the ice melts in spring, the fluorescent component proportions changes from Feburary to April 2014 (Figure 5a). Line 26ff: skip last paragraph since it will be mentioned in the conclusions again anyway. Response: Thank you for your suggestion. The contents “Compared with previous works. . .and ice-melt water.” should be placed in Line 23 on page 5741. Page 5739 Line 4: there are no salinity values in Table 3. Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The content “ . . .salinity. . .” should be skipped. Line6ff: DOC-concentration: I suggest giving a short explanation for seasonal DOC dynamics. Response: Thank

BGD
12, C3021–C3041, 2015

you for your suggestions. The highest DOC concentration 55.04 ± 20.00 mg L-1 was present in Feburary 2014, wheras the other three seasons exhibit relatively constant values of approximately 30 mg L-1, demonstrating a seasonal dynamic that can be attributed to hydrological, climatic and landscape variation (Song et al., 2013). This is because the DOC was accumulated when lakes freeze in winter, which left DOC in the lake waters, resulting in a high DOC concentration in the underlying water (unpublished material). Line 9: ... was used as a proxy... Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The contents "...was used as an proxy..." should be replaced by "...was used as a proxy...". Line12ff: partly repetitive Response: Thank you for your suggestions. The contents "The highest CDOM absorption coefficients a(350) 6.36 ± 2.17m-1, a(280) 34.62 ± 11.54m-1, a(254) 52.88± 18.13m-1 were present in February 2014, corresponding to the highest DOC concentration of 55.04 ± 20.00mg L-1." should be replaced by "The highest CDOM absorption coefficients a(350), a(280), a(254) were present in February 2014, corresponding to the highest DOC concentration." Line 15: explanation for DOC concentration increase in winter questionable. Might there be an increase in DOC concentration because of the water freezing (leaving DOM in the liquid phase) rather than DOC-expel from the ice? Response: Thank you for your suggestions. The contents "This can be attributed to the accumulated dissolved organic carbon when lakes freeze in winter, which expels DOC from ice..." should be replaced by "This can be attributed to the accumulated dissolved organic carbon when lakes freeze in winter, which leaves DOC in the liquid phase...". Line 18: "SR" might better be called slope ratio (Helms et al. 2008)? Response: Thank you for your suggestions. The content "...the spectral ratio (SR)..." should be replaced by "...the slope ratio (SR)...". Line 21: low values of SR indicate high molecular weight! Therefore the interpretation here is wrong. Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The contents "...which indicated the higher activities of biology and others resulting in decomposition of higher molecule carbon into lower molecule." should be replaced by "...which indicated the higher activities of biology and terrestrially imported substance through

BGD
12, C3021–C3041, 2015

rainwash resulting in higher average molecular weight in DOC". Line 21: what is meant with "high activity of biology and others"? Response: The "high activity of biology and others" means the CDOM in lakes was originated from phytoplankton degradation and terrestrially imported substance and microorganisms in August 2013. Page 5740 Line 1: I would not claim that C1 and C2 are "controlled by common sources". They both might derive from terrestrial sources and maybe e.g. underlie common processing mechanisms leading to similar dynamics? Response: Thank you for your suggestions. The component C1 originated from phytoplankton degradation and C2 derived from terrestrially imported substance. The "two humic-like components were controlled by common sources" maybe indicate a common processing mechanisms leading to similar dynamics (Zhang et al., 2010, 2011). Line 3: what is meant with "other human waste"? Response: The "other human waste" means organic pollutants derived from domestic, agricultural and industrial sewerage contribute to increase the DOC concentration in lake waters which were characterized by the tryptophan-like (T) component (Baker et al., 2004). Line 5ïijŽagain, a non-existing correlation between the fluorescent components among the four seasons does not necessarily indicate different sources. Response: Thank you for pointing out the mistakes. The contents "However, almost no correlation between humic-like peaks and protein-like peaks shows that the two components were derived from different sources." should be replaced by "However, there is almost no correlation between humic-like components and protein-like components." Line 7: What is meant with steady and labile fluorescence? Response: The "steady and labile fluorescence" refers to the changes in the ratio of humic-like : protein-like substances and fluorescent : nonfluorescent DOC (Henderson et al., 2009). Line 10ff: Conclusion unclear. High DOC concentrations do not necessarily indicate pollution. Therefore a correlation between DOC concentration and C3 does not designate C3 is an indicator for pollution. Anyway, in my opinion C3 of this study has a quite high emission fluorescence peak and is marginally comparable to tryptophan (which lies according to literature between 340-350 Em wavelength (Baker 2004, Coble 1996). Response: Thank you for your suggestions. The contents "A weak relationship (R2 =

BGD
12, C3021–C3041, 2015

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, indicating that the component 3 of the CDOM fluorescence (protein-like peak T) can be used to detect water pollution (Baker et al., 2004)." should be replaced by "The component C3 of the CDOM fluorescence (tryptophan-like peak) can be used to detect water pollution (Baker et al., 2004; Hudson et al., 2007). A weak relationship (R2 = 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." C3 (Ex/Em=225(290)/360 nm) has a longer emission wavelength compare to the study from Baker et al. 2004 and Coble 1996, but is almost consistence with the study from Hudson et al. 2007.

Are there any other measurements performed on the sampling sites to measure pollution (e.g. phosphate concentrations)? Response: Thank you for your suggestion. The other measurements e.g. phosphate concentrations to indicate pollution should be investigated in future study. It has been demonstrated that the tryptophan-like fluorescence intensity strongly correlated with phosphate concentration (Baker et al., 2004). Therefore, the tryptophan-like fluorescence intensity can be applied to monitor water quality timely instead of the traditional approaches. Line 24ff: parallel factor analysis itself leads to fluorescent components, it is not used to "characterize the seasonal variation of fluorescent components"! Response: Thank you for your suggestions. The contents "In this study, the application of excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC) to characterize the seasonal variation of four fluorescence components in CDOM was presented for 67 water samples collected from July 2013 to April 2014 in the semi-arid region of Northeast China." should be replaced by "In this study, by the excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC), four fluorescent components under seasonal variations in CDOM was presented for 67 water samples collected from June 2013 to April 2014 in the semi-arid region of Northeast China." Page 5741: Conclusion general: should be adapted to the revision of the paper. Furthermore, the importance of this study for a better understanding of freshwater/brackish water CDOM dynamics should be outlined.

BGD

12, C3021–C3041, 2015

Response: Thank you for your suggestions. The conclusions should be adapted to the revision of the paper. The contents “In this study, the application of excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC) to characterize the seasonal variation of four fluorescence components in CDOM was presented for 67 water samples collected from July 2013 to April 2014 in the semi-arid region of Northeast China. Two humic- like peaks (C1 Ex/Em= 230 (300)/425nm and C2 Ex/Em= 255 (350)/460 nm) and two protein-like (B Ex/Em= 220 (275)/320nm and T Ex/Em= 225 (290)/360 nm) peaks were identified using PARAFAC model. The average fluorescence intensity of the four components differed with seasonal variation from July 2013 to April 2014. In general, the fluorescence intensity was dominated by peak C1 indicating that most part of CDOM for inland waters was originated from phytoplankton degradation. The lowest C2 represents only a small portion of CDOM from terrestrial import to water bodies through rainwash and soil leaching. The two protein-like intensities (B and T) have almost the same magnitude. Especially, in August 2013 and in February 2014, the two protein-like peaks showed obviously different and the highest C1 1.02nm-1 presented in February 2014. Component 1 and 2 exhibited strong linear correlation (R2 = 0.633) indicating that the concentrations of the two humic-like components were controlled by common sources. There were significantly positive linear relationships between Fmax and CDOM absorption coefficient a(254) (R2 = 0.72, 0.46, $p < 0.01$), a(280) (R2 = 0.77, 0.47, $p < 0.01$), a(350) (R2 = 0.76, 0.78, $p < 0.01$) for two humic-like components (C1 and C2), respectively. A weak relationship (R2 = 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 which indicated that the components 3 (protein-like peak T) can detect lake pollution derived from fluorescence CDOM. 20 Most importantly, a close relationship (R2 = 0.931) was found between salinity and DOC. However, almost no obvious correlation was found between salinity and EEM-PARAFAC extracted components except C3 (R2 = 0.469), though the correlation was not as strong as with DOC concentration. Also, the study was to assess the dynamics of individual fluorescent components of CDOM with seasonal variations in both

BGD
12, C3021–C3041, 2015

fresh and brackish waters rather than compare fresh water and brackish water CDOM." should be replaced by "In this study, by the excitation-emission matrices fluorescence and parallel factor analysis (EEM-PARAFAC), four fluorescent components under seasonal variations in CDOM was presented for 67 water samples collected from June 2013 to April 2014 in the semi-arid region of Northeast China. Two humic-like components and two protein-like components were identified using PARAFAC model. The average fluorescence intensity of the four components differed under seasonal variations from June 2013 to April 2014. In general, the fluorescence intensity was dominated by peak C1 indicating that most part of CDOM for inland waters was originated from phytoplankton degradation. The C2, from terrestrially imported to water bodies through rainwash and soil leaching, contributed less to the total fluorescence than the three others. The two protein-like intensities (C3 and C4) have almost the same magnitude. Especially, in August 2013 and in February 2014, the two protein-like peaks showed different and the highest C1 1.02 nm-1 presented in February 2014. Component 1 and 2 exhibited strong linear correlation (R2 = 0.633) indicating that the concentrations of the two humic-like components were controlled by common sources. There were significantly positive linear relationships between Fmax and CDOM absorption coefficients a(254) (R2 = 0.72, 0.46, $p < 0.01$), a(280) (R2 = 0.77, 0.47, $p < 0.01$), a(350) (R2 = 0.76, 0.78, $p < 0.01$) for two humic-like components (C1 and C2), respectively. A weak relationship (R2 = 0.42) was found between DOC and C3. Most importantly, a close relationship (R2 = 0.931) was found between salinity and DOC. However, almost no obvious correlation was found between salinity and EEM-PARAFAC extracted components except C3 (R2 = 0.469), though the correlation was not as strong as with DOC concentration." Also, the study was to assess the dynamics of individual fluorescent components of CDOM under seasonal variations in both fresh and brackish waters rather than compare fresh water and brackish water CDOM. Tables and Figures Table 1: are there significant changes in salt concentration between the seasons? If so, might there be any possible effects on CDOM absorbance/fluorescence measurements? Response: There are significant changes in salt concentration be-

BGD
12, C3021–C3041, 2015

tween the seasons. When the lakes were frozen, the highest salinity 0.70 PSU was present in February 2014. Whereas the other three seasons exhibit relatively constant values of approximately 0.40 PSU. The salinity may has some effects on CDOM absorbance/fluorescence measurements which will be studied further later. Table 2: "max" and "min" of the "Exmax" and "Emmax" labels should be written in subscript. Instead of "Label 1" and "Label 2" I suggest writing e.g. "Components (Coble)" and add details in the table description. Further, I would rather use "secondary maxima" instead of "secondary band". Response: Thank you for your suggestion. The labels "Exmax" and "Emmax" should be replaced by "Exmax" and "Emmax". The "Label 1 and Label 2" should be replaced by "Components (Coble or Zhang) and Components (Stedmon and Markager)." The "Secondary excitation band" should be replaced by "Secondary excitation maxima". Table 3: DOC concentration should be in "mg L-1". Instead of "item" I would write e.g. "sampling season". Response: Thank you for pointing out the mistakes. The contents "DOC mg-1 L-1" should be replaced by "DOC mg L-1". The word "item" should be replaced by "sampling season". Table 4: state clearly that the values in the table represent R and the asterisks represent the p-value Response: Thank you for your suggestion. The description "Correlation coefficients (R) and significance levels (p) of the linear relationships between CDOM absorption, DOC, salinity and fluorescence components." should be replaced by "Correlation coefficients (R) and significance levels (p) of the linear relationships between CDOM absorption, DOC, salinity and fluorescent components (the values represent R and the asterisks reprensent p value)." Figure 2: It should be mentioned that fluorescence is in Raman units [m-1]. Response: Thank you for your suggestion. It has been mentioned that the fluorescence in Raman units [nm-1] (Larsson et al., 2007; Stedmon et al., 2003). Figure 3: What is "(1-2 left; 3-4 right") related to? Do "a)" and "b)" each display the results of one split half analysis? Response: Thank you for pointing out the mistakes. We are sorry for making the mistakes. The content "Results from split-half analysis (1–2 left; 3–4 right) in PARAFAC models" should be replaced by "Results from split-half analysis (1–2 up; 3–4 down) in PARAFAC models". "a)" and "b)" each display the results of

BGD
12, C3021–C3041, 2015

one split half analysis. Figure 4: The figure description here is not correct. This figure 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 [m-1]. Response: Thank you for pointing out the mistakes. The contents "The PARAFAC model output showing fluorescence signatures of the four fluorescence components (a–d), the contour plots represent spectral shapes of excitation and emission. The line plots represent split-half validation results (e–h): excitation (left) and emission (right) spectra." should be replaced "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 (Larsson et al., 2007; Stedmon et al., 2003)." Figure 5a: The bars showing Fmax of the seasonal average might be visually separated from the four single seasons and may be better referred to as e.g. "seasonal average" than "all samples". The n should be given in the description. The components might be better referred to as "EEM PARAFAC components". Further I suggest writing "The error bars represent standard deviations" Response: Thank you for your suggestion. The contents "All samples; Jun. 2013; Aug. 2013; Feb. 2014; Apr. 2014 " should be replaced by "Seasonal average (N=67); Jun. 2013 (N=15); Aug. 2013 (N=13); Feb.2014(N=17); Apr.2014(N=22)". The contents "Seasonal variation of Fmax values of the four components. . ." should be replaced by "Seasonal variation of Fmax values of EEM- PARAFAC components. . .". The content "The error bar represents SD." should be replaced by "The error bars represent standard deviations." Figure 6a): what is meant with the "ice-melted water sample"? Response: The "ice-melted water sample" showed that the fluorescence intensity of lake ice-melted water is characterized by tyrosine-like components which was very weak though. (Figure 6a). Figure 7: What kind of test has been used? Response: The linear regression has been been used.

Interactive comment on Biogeosciences Discuss., 12, 5725, 2015.