

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.

Anonymous Referee #1

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General Comments

In this study the authors investigated the sources and seasonal variability of chromophoric dissolved organic matter (CDOM) in several lakes in Northeast China. The lakes were separated into two groups: one set of lakes exhibits a relatively high salt concentration, the other a medium salt concentration. Samples were taken 4 times a year and analyzed using absorption and fluorescence spectroscopy resulting in

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excitation-emission matrices (EEMs) followed by parallel factor (PARAFAC) analysis. Overall fluorescence intensities, intensity of the four modeled PARAFAC components and absorption coefficients were related to each other as well as to DOC concentration and salinity.

Though the submitted manuscript does not present many striking new findings it sustains a better understanding of CDOM composition and its dynamics in freshwater/brackish water environments. There are some major points that 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 of the tables do not need to be mentioned in the text again
- 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?
- 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,

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they should be rather referred to “tryptophan-like” or “tyrosine-like”.

- 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.

- Some of the results lack appropriate discussion and/or argumentation (see specific comments).

Specific comments

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line1: DOM consists of several humic acids rather than only one. Further it contains “proteins”, not “proteinaceous”.

line2: skip “array” in the sentence

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)

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”

line12: use “making it difficult to isolate. . .”

line14: the terms “OACs” and “SFS” are never again used in the paper. I suggest to skip these abbreviations

line23: skip “and then”

line26: use “resulting in an emission of lower energy”

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line6: abbreviation of EEM has already been mentioned before

line 8: better write “EEM spectroscopy” than “EEMs”

line 11ff: though sometimes equalized in literature, “allochthonous” is not necessarily “humic-like”, neither is “autochthonous” necessarily “protein-like”.

line12: not only CDOM from coastal environments have been investigated, also from freshwater and other systems

line15: re-formulate the sentence, e.g. “. . .of marine, freshwater and ice-water ecosystems as well as snow”

line17: skip repetitive content (see line 19ff, page5727)

line 26ff: skip parts that are repetitive to line 21ff

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line3: use “PARAFAC modelling” and “correlations of the fluorescent components. . .”

line8: use “low average SUVA₂₅₄”

line9: use “indicate”

line9: SR indicates “low average DOM molecular weight”

line11: “. . .may be stored. . .”

line12: skip “furthermore”

line12: maybe better use “Therefore” instead of “to achieve this goal”

line14: “at different seasons”

line17: “assess the dynamics of individual fluorescent components under seasonal variations”

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line19: unclear which factors are related to each other. I suggest “[. . .] link CDOM fluorescence intensities, absorption coefficients, DOC concentrations and salinity to each other.”

Materials and Methods

general:

- When were the lakes covered with ice? How were samples taken during ice coverage?

- were any other parameters measured that could have affected CDOM measurements? (e.g. iron content)

line25: use “two groups of lakes. . .”

line27: use “with a relatively high mean salinity of. . .”

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line4: skip “related to”

line4: skip “for the study region”

line 5: “the average annual precipitation is about 1790mm”

line7 : better use “agricultural catchment land use “

line10: “. . .field campaigns in June and August 2013 as well as in February and April 2014” might be easier to read

line13: have the samples been stored unfiltered?

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line2: skip “were”

line2: Whatman GF/F filters have a 0.7- μm nominal pore size

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line20: “. . .where the absorbance of CDOM. . .”

line24: equation: Why has 440nm been used as reference wavelength?

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line4 The slope ratio SR by Helms et al., 2008 further indicates the molecular weight and photo-bleaching of DOM

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

line17: “[. . .] can reduce the fluorescence intensity by 5%”

line23: If written in this form, the formula needs more brackets surrounding (A_{ex} + A_{em})!

line25: rather use “respective” than “current”?!

line27: I guess the Milli-Q water Raman peak was “measured” daily rather than “collected”?

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line4: PARAFAC modeling decomposes the CDOM fluorescence signal into separate fluorescent signals

line18: matrices

line18: Excel (Microsoft office)?

line19: step (2) and (3) described here are repetitive to line 3ff of page 5734 and should be deleted here!

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line2: Andersson et al.

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line6: "the Rayleigh bands do not represent DOM fluorescence"

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line5: "[. . .] the set of samples was pooled together [. . .]"

line7 ff: better write e.g. ". . .whereas the other three seasons exhibit relatively constant values of approximately 0.40PSU."

line11: Why does turbidity decrease with increasing rainfall?

line10 ff: For easier reading I suggest to skip the values here and refer to the corresponding table.

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")

line15ff: 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").

line18ff: see General Comments

line23: 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."

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line3ff: this paragraph is partly redundant to the second last paragraph of page 5734 and should only be described in the method-section.

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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

line 22ff: I would not compare C2 to C1 like in "Compared with C1 [. . .] component 2 shifted to the red spectral region".

line25: maybe use "C3 resembles the tryptophan-like component as found by (author name).

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line4: maybe better write "In this study not all of the four components were present in all of the samples."

line13ff: 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"?

line19ff: Message unclear, please reconstruct the sentence

line23: what is meant with "others"?

line27: is there a significant difference? According to Figure 5a there is none.

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line2: this refers to Figure 6b. Further, to me it is unclear if Figure 6 is from Cheng et al., 2010 or from this study.

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?

line12: maybe you could add a quotation for the statement "strong biological activities would be prohibited". Ice cover solemnly does not prevent biological activities.

line12f: why would C1 and C3 accumulate simultaneously? If "strong biological pro-

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cesses” 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?

line16: 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?

line18ff: In how far is it not surprising that C4 fluorescence intensity beneath the ice was reduced?

line21ff: message unclear. what is meant with “similar trends with the whole”?

line23ff: 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?

line26ff: skip last paragraph since it will be mentioned in the conclusions again anyway
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line 4: there are no salinity values in Table 3

line6ff: DOC-concentration: I suggest giving a short explanation for seasonal DOC dynamics.

line9: ...was used as a proxy...

line12ff: partly repetitive

line15: 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?

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line18: “SR” might better be called slope ratio (Helms et al. 2008)?

line21: low values of SR indicate high molecular weight! Therefore the interpretation here is wrong.

line21: what is meant with “high activity of biology and others”?

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line1: 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?

line3: what is meant with “other human waste”?

line5: again, a non-existing correlation between the fluorescent components among the four seasons does not necessarily indicate different sources

line7: What is meant with steady and labile fluorescence?

line10ff: 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 nm wavelength (Baker 2004, Coble 1996).

Are there any other measurements performed on the sampling sites to measure pollution (e.g. phosphate concentrations)?

line 24ff: parallel factor analysis itself leads to fluorescent components, it is not used to “characterize the seasonal variation of fluorescent components”!

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

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dynamics should be outlined.

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?

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”.

Table 3: DOC concentration should be in “mg L⁻¹”. Instead of “item” I would write e.g. “sampling season”.

Table 4: state clearly that the values in the table represent R and the asterisks represent the p-value

Figure 2: It should be mentioned that fluorescence is in Raman units [m⁻¹].

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?

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].

Figure 5a: The bars showing F_{max} 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”

Figure 6a): what is meant with the “ice-melted water sample”?

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Figure 7: What kind of test has been used?

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