Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2020-272-AC2, 2020

Biogeosciences Discussions
Open Access
EGU

Interactive comment on "Characterizing the origin of excess dissolved organic carbon in coastal seawater using stable carbon isotope and light absorption characteristics" *by* Heejun Han et al.

Heejun Han et al.

gkim@snu.ac.kr

Received and published: 11 September 2020

Reviewer #2

General comments: Han et al provide a short summary of DOM properties in Sihwa Lake, a constructed coastal lake in a heavily industrialized coastal area, over 2 sampling trips taken in spring 2017 and in late summer 2018. Same sites were visited in each sampling. Using a combination of nutrients and optical and stable isotope tracers, they aim to distinguish multiple sources of DOM (though the sources are not clearly identified). The brevity of this manuscript makes it very difficult to follow. Many details are lacking and some deeper analysis is required to support the conclusions made in

Printer-friendly version

Discussion paper

this study. Several conclusive statements are made without a clear logical argument to help the reader reach the same conclusion. These problems occur throughout this version of the manuscript, and, along with some substantial editing for grammar and usage, require more than substantial revision.

-> Thank you for your review and comments. In this study, we focused on determining the sources of excess DOC occurring in this bay. Although we cannot elucidate the exact sources and processes in this study, it is clear that our approach (using DOC–δ13C and optical properties) suggests different sources that cannot be identified with the traditional methods. We showed that the excess DOC dependent on salinity is from marine sources (although it is generally regarded as terrestrial sources), and the excess DOC in the high-salinity water is from terrestrial sources (although it is believed to be from marine sources without our approach). The revised version was thoroughly checked for grammar and usage by a native editor.

Specific comments:

1. L55: Finish the set up for this manuscript. What are the sources expected? It is curious why the authors didn't try to use endmember mixing analysis (EMMA) to disentangle the sources. The primary sources appear to be: terrestrial, marine, phytoplankton, and "anaerobic benthic processes" which I shorten to benthic.

-> The end-member mixing analysis is very useful for tracing different water-mass mixings. However, the excess DOC occurring in this study is either from the sediment or land as the DOC is directly introduced to low-salinity water or seawater. Thus, it is impossible to do EMMA.

2. Methods L68: It appears the sluice gates are mostly closed; what does periodic opening entail? Were the gates opened prior to sampling?

-> The sluice gates are opened twice a day (every low tide and high tide). Samplings were conducted in between the openings. We added more details in the revised ver-

Printer-friendly version

Discussion paper

sion.

3. L70: What vessel was used for sampling? " a ship" is nebulous.

-> It is a small boat ($\sim$1 ton). mentioned in the revised version.

4. L78: How many mL of 6M HCl were used and what was the final pH?

-> We added 20 μL of 6M HCl to each sample. The final pH of the sample was $\sim$2. Details are described in the revised version.

5. L88: Unlikely that the precision of the TOC analyzer for DSR measurement is 2.2 μM, round to 2 μM. How many analyses?

-> corrected as suggested in the revised version. We measured DSR three times per each 10 sample batch.

6. L92: To my knowledge no consensus value of DSR is reported, though similar values have been reported as described here. Reword to indicate this (as was done in earlier work referenced here). If a consensus value is now published, please cite the publication. Also appear report number of analyses (N) for these standards.

-> The δ13C values for the DSR were reported by Panetta et al. (2008) (–21.37$\pm$0.33‰) and Lang et al. (2007) (–21.9$\pm$1.3‰). We added more references in the revised version.

7. Results: Make the colorbar ranges for Figs 2 and 3 the same for each panel for ease of comparison.

-> changed as suggested in the revised version.

8. The PARAFAC results should be tested against the OpenFluor database.

-> Yes, the PARAFAC results are compared with the OpenFluor database. We added the results in the revised version.

9. Here, spectral components are compared to Coble 2007 wherein peaks are visually

identified. Surprisingly, the authors only described 2 of the 4 peaks they find with the model. I recommend they discuss the dynamics of the protein-like component. Given the results presented, it would be informative to see how well this component correlated to other PARAFAC components and in cross section across the lake (ie, as in Figs 2 and 3). Also correlation of this peak with δ13C values.

-> We added more details and figures about the fluorescent components identified with the model in the revised version. Since δ13C values fall into a narrow range (marine source), no correlation was found for the FDOM components.

10. L140: Range of values does not capture the most negative value reported (–27.8‰).

-> The DOC–δ13C values ranged from –22.6‰ to –27.8‰ċhanged as suggested in the revised version.

11. Discussion L155: How is “significant excess” being defined? It is unclear what the authors mean by this phrase and how they quantified it.

-> specified in the revised version ($\sim$75% higher than the mixing line).

12. L158: What does land-seawater interaction mean? Mixing? Proportional mixing would not add an excess of DOC; an excess implies production in spite of mixing... unless a 3rd source is implied. In this case, binary mixing analysis won't work. Perhaps the authors should suggest here the benthos as a potential source; but that source also should be parameterized (eg, what is its δ13C-DOC values, FDOMH, FDOMM values, SR etc.).

-> We suggest that “land-seawater interaction” is due to the tidal inundation of seawater on the reclaimed land. This process can cause increases in DOC with depleted DOC–δ13C values, high SR values, and non-fluorescent, without salinity decreases. This is more clearly explained in the revised version.

13. L180: The groupings appear arbitrary; what criteria were used to separate them? I

don't understand how the terrestrial source of DOM can be not fluorescent, give that the authors identify humic fluorescence as a specific marker. This section of the discussion is extremely hard to follow.

-> As mentioned above, the DOC in the reclaimed land could be non-fluorescent as it is exposed to sunlight for a long period of time. Otherwise, please suggest alternative explanation for our observed trend. Since this paper is for the observed results, we only can suggest the most plausible mechanism. The groups (1 and 2) were separated based on its DOC concentrations, DOC–δ13C values, and salinity. We added the details in the revised version.

14. L197: No evidence is provided for photochemical or bacterial degradation in this study.

-> Based on DOC–δ13C values, high SR values, low FDOM and NH4+ concentrations, we suggest the most plausible sources.

15. L201: As suggested earlier, the possibility to use EMMA or other multivariate means with these data are encouraging. I recommend the authors try to analyze their results with an aim of using exploratory methods (eg. Ordination such as PCA or non-parametric techniques) and perhaps 2-way analyses wherein the difference or season (or stream flow if available; not presented) is considered. A clearer way of quantifying the Groups (1 and 2) must be presented at the very least, so that readers can follow the study.

-> PCA or other statistical techniques are useful in differentiating various sources. However, in this study, the excess DOC occurred different locations (low salinity water, high salinity water, and near benthic water). So, we simply try to determine the source of the excess in each sample group.

16. L210: No analysis was presented to demonstrate the linkage of δ13C values and NH4+ values.

-> A previous study (Kim and Kim, 2018) suggested the anaerobic benthic production of FDOMH in low salinity water in this region based on NH4+ concentrations. In this study, we support this finding based on our NH4+ relationships (NH4+ versus DOC and FDOMH correlations) and DOC-δ13C values (marine source). We showed that the source is not due to terrestrial inputs! This is clarified in the revised version.

References

Kim, J. and Kim, T.-H.: Distribution of humic fluorescent dissolved organic matter in lake Shihwa: the role of the redox condition, Estuar. Coast., https://doi.org/10.1007/s12237-018-00491-0, 2018.

Lang, S. Q., Lilley, M. D., and Hedge, J. I.: A method to measure the isotopic (13C) composition of dissolved organic carbon using a high temperature combustion instrument, Mar. Chem., 103, 318–326, 2007.

Panetta, R. J., Ibrahim, M., and Gélinas, Y.: Coupling a high-temperature catalytic oxidation total organic carbon analyzer to an isotope ratio mass spectrometer to measure natural-abundance δ13C-dissolved organic carbon in marine and freshwater samples, Anal. Chem., 80, 5232–5239, https://doi.org/10.1021/ac702641z, 2008.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2020-272, 2020.

Printer-friendly version

Discussion paper