

Interactive comment on “Tracing the sources of dissolved organic carbon occurring in a coastal bay surrounded by heavily industrialized cities using stable carbon isotopes” by Shin-Ah Lee et al.

Anonymous Referee #2

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Review of bg-2019-229 Authors use DOM fluorescence, $\delta^{13}\text{C}$ ratios, and C:N ratios in an attempt to apportion sources of DOM to Masan Bay, near a heavily industrialized region of Korea. Two samplings were conducted in 2011 and again 2016, axial transects along the bay. Results are presented largely as geospatial plots of parameters and against salinity in a binary conservative mixing focused analysis. Over these 2 samplings, 3 groups of DOM were identified by visual inspection of plots against salinity. Discussion delves into mixing and potential inclusion of non-conservative sources and concludes that an urban influence was not definable and that local primary likely explained the general non-conservative behavior of $\delta^{13}\text{C}$ and C:N whereas humic fluorescence was largely conservative. The topic of the manuscript is relevant for BGD but the data presentation and analysis need work. The data are certainly interesting and comprised of measurements that are now being combined to understand better the sources and cycling of DOM in coastal waters beyond any one or two of these measurements alone. So the data are solid and appear to provide some insight into this particular region. I have the following suggestions the authors might consider to improve the manuscript.

=> Thank you for the constructive and valuable comments.

Title – Barring any new insight from further data analysis, it is misleading to have “heavy industrialized cities” in the title. There is no evidence provided and discussed that an urbanization effect was found, only speculation. I think further work is needed on this argument for urban inputs

=> Yes, we will omit the term “heavy industrialized cities” since the title can mislead our major finding. Although we originally expected to have STP sources, these urban/anthropogenic sources were not measurable. We changed the title to “Tracing terrestrial versus marine sources of dissolved organic carbon occurring in a coastal bay using stable carbon isotopes”.

Writing – overall the writing is good but there are many awkward or unclear phrasings which should be revised to improve readability and clarity.

=> We will improve readability and clarity through a native editor.

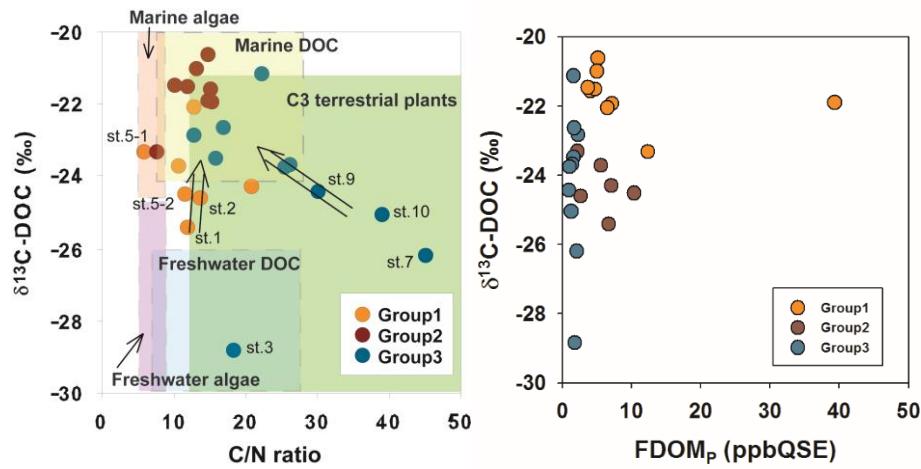
Figure 2 and 3 would benefit from a border around each panel (map) in each figure. **Overall I thought the figures were very good.

=> will change as suggested.

Data analysis would be improved by biplots beyond property vs salinity. For example, the classic $\delta^{13}\text{C}$ vs C:N plot could be done (see Lamb, A. L., Wilson, G. P., & Leng, M. J. (2006). A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}\text{C}$ and C/N

ratios in organic material. *Earth-Science Reviews*, 75(1-4), 29-57.) to clarify a key uncertainty in the manuscript which is determining inputs of urban runoff DOM vs in-situ generation of phytoplankton DOM. One could imagine $\delta^{13}\text{C}$ vs FDOM_P biplot may elucidate the urban source.

=> Thank you for your valuable comments. The plot between $\delta^{13}\text{C}$ -DOC values and C/N ratios will be added as shown below. The plot further supports that the source of Group1 is mainly influenced by freshwater DOC and the source of Group2 is from marine phytoplankton. The source of Group3 seems to be associated with C3 terrestrial plants, although the specific source is unknown. As shown below, we could not determine the urban source from the $\delta^{13}\text{C}$ vs FDOM_P biplot, which was not included in the revised version.



Specific comments (line number indicated):

L60 – Phytoplankton $\delta^{13}\text{C}$ values are based on the value of the C they fix; the range specified is for marine phytoplankton. This point should be clarified and considered in lieu of the production in the estuary.

=> will clarify this as “marine phytoplankton” instead of phytoplankton. “those derived from marine phytoplankton range from -18 to -22‰ (Kelley et al., 1998; Coffin and Cifuentes, 1999).”

L75 – Sentence should be the concluding sentence of the preceding paragraph or otherwise this point should be expanded upon. For example, has there been no prior work on DOM in the region? What are the probable sources of urban DOM that could confound a simple binary mixing analysis?

=> We will describe specific goals and scientific questions more clearly in the revised version: “Masan bay is surrounded by cities with thousands of industrial plants and a population of 1.1 million. In association with large anthropogenic nutrient loading, this area has been recognized as a highly eutrophic embayment (Lee and Min, 1990; Yoo, 1991; Hong et al., 2010). The development of red tides and hypoxic water mass in the bottom layer has occurred annually in the spring and summer seasons (Cho et al., 1998; Lee et al., 2009). In addition, there is a sewage treatment plant (STP) as a point source that manages domestic and industrial wastewater of

Masan and Changwon cities. Therefore, in this study, we attempted to use $\delta^{13}\text{C}$ -DOC, FDOM, and DOC/DON ratios to differentiate different sources and characteristics of DOM in Masan bay waters which have complicated DOM sources.”

L84 – From satellite imagery, it appears this bay is in a mountainous region, but are there any salt marsh inputs to the bay? This is important because of the effect that C4 plants such as Spartina might have on DOM inputs.

=> The shore is mostly composed of rocks and concrete walls (no salt marshes or large beaches).

L103 – I am confused by DIN as “inorganic nutrients”. First, no nutrient data are shown. Second, DIN typically refers to dissolved inorganic nitrogen (sum of NH_4^+ , NO_2^- / NO_3^-). Please clarify.

=> will be corrected to “nitrogen” instead of nutrient. We did not display DIN data since DIN (sum of NH_4^+ , NO_2^- / NO_3^-) data were just used for calculating dissolved organic nitrogen (DON = TDN (total dissolved nitrogen) - DIN).

L112 – “qualitatively” instead of “entirely”

=> will be corrected as suggested.

L136 – equivalents NOTE: More information is needed about the PARAFAC analysis; split-half validated spectra; Plots of the components and distribution of components across stations. Please test the components against the OpenFluor database for matches with other coastal waters. Otherwise does it matter to do PARAFAC? What do BIX and HIX and other derived parameters from fluorescence provide that might obviate the need for PARAFAC?

=> More information will be added for the component contours and excitation/emission loadings in the revised version (supplementary section). We will compare the components through OpenFluor. Although we attempted to compare HIX and BIX with salinities, they do not show a good trend as Figure 4 (PARAFAC data). So, we use PARAFAC data in this study.

L149: give values when specifying these maxima and minima

=> will add as suggested.

L156: EEM “PARAFAC” analyses

=> will correct as suggested.

L174: By how much does the freshwater end member vary in its DOC concentration? A freshwater input at 300 μM DOC could produce conservative mixing patterns (just freshwater and seawater mixing) with a changing freshwater end member value.

=> DOC in freshwater endmembers (various creeks) in 2011 were in the range of 120-800 μM . In the case of Group 1, the extrapolated endmember concentration of 200 μM in freshwater seems to be conservatively mixed with open ocean water in the bay.

L177: Explain what is meant here in more detail

=> Although we can extrapolate the concentration and isotope value of the freshwater that influences Group 1, we do not know whether this is natural or anthropogenic sources. So, we

state that Group 1 is influenced by natural and/or anthropogenic land sources in the revised version. The detail of this is included in the next section.

L180: Seems to argue for multicomponent mixing models

=> Yes, we point out the excess source over the two-endmember mixing trend. This excess source is discussed in the next section.

L182: Please clarify the evidence for this

=> In this sentence, we just list up any possible sources for high salinity waters. The evidence is clarified in the next section.

L188: period missing or otherwise this needs revising to clarify

=> will be changed as suggested: “Group 1, Group 2 in 2011, and Group 3 in 2016 (Fig. 4a)”

L196: what does “relatively well” mean? Please be specific. Only 2 points fall on the mixing line.

=> Although $\delta^{13}\text{C}$ values of Group 1 are slightly heavier than the mixing line, the trend falls into the mixing line within 1.5 ‰. This will be mentioned in the revised version.

L197: -34‰ – is this meant to be terrestrial? It is too depleted a value without some reference to the riverine input or other terrestrial runoff. However, it is possible to be riverine or estuarine phytoplankton with DIC values <-5‰

=> will be corrected to -32‰ for C3 land plant.

L215: This is not convincing and the implications of urbanization need to be thought through some more. I would perhaps argue that phytoplankton DOM, enabled by nutrient runoff from land, is the major effect on DOM rather than specifying some non-quantifiable (i.e., according to the manuscript, the data do not exist) urbanized DOM input.

=> We conclude that the source of Group 2 is from biological production based on both isotope values and $\delta^{13}\text{C}$ versus DOC/DON ratio plots that you suggested. We rephrase this sentence to be read as “this source could originate from in-situ production”.

L218: Are these tidal creeks with marsh/wetland habitat? How much DOM do they export?

=> There is no marsh/wetland habitat in Masan Bay. This will be mentioned in the revised version.

L233: What does “natural level” mean?

=> We meant “no excess DOC is observed” at the station near STP according to the mixing line. This will be clarified in the revised version: “This STP appeared to reduce TOC concentrations which are not discernible from the two endmember mixing, as shown in several other estuaries (Abril et al., 2002).”

L245-247: Why?? Support this final point; I don’t understand how the authors arrive at this conclusion.

=> We will clarify this in the revised version: ”These results suggest that DOC in Group 3 is

influenced by terrestrial DOC sources which include lower FDOM. The plot between $\delta^{13}\text{C}$ -DOC versus C/N ratio further indicates that the main source of Group 3 is C3 terrestrial plants. Because salinities of Group 3 are high (26-32), high DOC, depleted $\delta^{13}\text{C}$ -DOC, and high C/N ratio indicate that this water is directly influenced by terrestrial organic matter.

L251: high and lower than what?

=> will be specified as “than the Group 3”.

L253: This is not correct; refractory nature of DOM cannot be determined by C:N ratios

=> Yes, C:N ratios and refractory nature are not correlated directly, although DOM which has higher C:N ratios is generally more refractory in the ocean (Andrews et al., 1998). We removed the term “refractory” in the sentence.

L266: This statement is very clear and summarizes what should be made clearer in the discussion. Tie together these points in the Discussion and the manuscript will be far more convincing based on the results. I think this is where the biplots I mention above could be very useful.

=> Thank you.

L267: Unclear; please explain in the discussion how the island can influence DOM.

=> Yes, we will explain about this in the revised version.

L272: I don't understand this last statement in context of this study. Please revise.

=> will clarify in the revised version: “Our results show that the combination of multiple DOM tracers, including $\delta^{13}\text{C}$ -DOC, FDOM, and DOC/DON ratios, is powerful for discriminating the complicated sources of DOM in coastal waters.”

[END]