

Interactive comment on “Sources, fluxes, and behaviors of fluorescent dissolved organic matter (FDOM) in an estuarine mixing zone: Results from the Nakdong-River Estuary, Korea” by Shin-Ah Lee and Guebuem Kim

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Major comments

In this manuscript, the authors determined variations of dissolved organic carbon (DOC), stable carbon isotope of DOC ($\delta^{13}\text{C}$ -DOC), and fluorescent DOM (FDOM) with tide from monthly observation at a 24 hours monitoring station in the Nakdong-River Estuary, Korea. The authors found significant relationships between salinity and DOC as well as FDOM (both of humic-like and protein-like) throughout a year, implying that

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riverine DOM were conservatively distributed with estuarine mixing but contribution of autochthonous DOM were minor in the estuarine mixing zone. The conservative behavior of terrestrial DOM was also supported by the spatial variation of $\delta^{13}\text{C}$ -DOC at the estuary. The authors also found that the relationships (slopes and intercepts of linear regressions) between salinity and DOC as well as FDOM differed among months, due to different levels of their riverine end-members. From the findings, the authors pointed out that the estimation of annual riverine flux of DOC (and also FDOM) requires careful considerations of seasonal changes. I think the methods in the manuscript are technically sound, and manuscript is logically well written. Even that said, I have two major comments on the manuscript. (1) I thought that data analyses and discussion were insufficient. In the Introduction section, the authors described that the behavior of DOM in the estuarine mixing zone and fluxes of DOM from the river can be determined in the manuscript. However, the authors basically focused differences in fluxes of DOM from the river among months but did not discuss about different behavior of DOM in the estuarine mixing zone. It seemed that correlation coefficients (or coefficients of determination) between salinity and DOM parameters were largely different among months. Such different correlation coefficients imply that the behavior of DOM in the estuarine mixing zone, e.g., photo-degradation, sedimental inputs, autochthonous production, were different among months. I think it's better to add some discussions about different behavior of DOC and FDOM in the estuarine mixing zone among months based on different correlation coefficients.

=> Concentrations of DOC and FDOMH, except FDOMP, in the estuarine mixing zone behave conservatively throughout all seasons. In the revised version, we will add more detailed demonstrations about these mixing trends. The differences in slopes and y-intercepts are discussed in results and discussion (lines 158-160, 201-205, and 212-214). It is very difficult to compare scattering for different seasons since the scattering is generally larger for narrow salinity range. We will mention about this in the revised version.

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(2) The authors evaluated monthly “variable” concentrations (i.e., 174-284 μM) of riverine end-member of DOC from relationships between DOC concentration and salinity. On the other hand, the authors also obtained one “fixed” riverine end-member with 270 μM from the conservative mixing curve of $\delta^{13}\text{C}$ -DOC with the two end-members. These interpretations derived from different analyses seemed to be contradicted. I think the authors should also analyze conservative mixing curve of $\delta^{13}\text{C}$ -DOC for each month.

=> Thank you for your very valuable suggestion. We analyzed the mixing curve of $\delta^{13}\text{C}$ -DOC for each month for the different end-member values and will show in Figure 2B as a dotted line. Except for the winter period, the plot of $\delta^{13}\text{C}$ -DOC for each month fitted well into the overall trend. Larger scattering in winter seems to be due to narrow salinity ranges. We will mention about this in the revised version.

Specific comments

Line 32, line 153 and lines 185-186: I think correlation coefficients of relationships between salinity and DOM parameters should be minus value. For example, in line 32, “ $r=0.55-0.99$ ” should be minus 0.55 to minus 0.99? Otherwise, these values were r^2 ?

=> In the revised version, r^2 values will be shown.

Line 44-45: Please add reference(s) to a description “As FDOM accounts for 20 – 70

=> Will add as suggested.

Line 80: Is 23,380 km^2 area of watershed? Please clarify it.

=> Will add the wording “watershed”.

Lines 89-91: The system of auto-sampler is not clear from the description. Please add some information for the auto-sampler (structure, model number, manufacture etc) or cite previous work(s).

=> Will added the information on the auto-sampler (RoboChemTMAutosampler, Model

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Lines 94-96: How did the authors preserve DOC and $\delta^{13}\text{C}$ -DOC samples? Freezing? Please make it clearer.

=> The DOC and $\delta^{13}\text{C}$ -DOC samples were acidified to pH ~ 2 with 6M HCl to avoid biological process and stored in pre-combusted glass ampoules. Ampoules were fire-sealed for preventing any contaminations. The samples were analyzed within a week for DOC and CDOM samples. This will be mentioned in the revised version.

Lines 101-129: The authors determined DOC concentrations using two different instruments, i.e., TOC-VCPH and TOC-IR-MS with NDIR. Which DOC concentration was used for the manuscript? Please make it clearer. In addition, for some readers who are interested in use of TOC-IR-MS, it would be great if the authors can add some information regarding with comparison of DOC concentrations determined by two different instruments.

=> We use TOC-VCPH for DOC concentration measurements and TOC-IR-MS only for $\delta^{13}\text{C}$ -DOC measurements. DOC concentrations using TOC-VCPH (Shimadzu, Japan) were calibrated with acetanilide and values were verified with deep seawater reference samples (University of Miami). We did not quantitatively measure DOC concentrations for TOC-IR-MS (Elementar, Germany) although they were measured routinely to check any drifting effects. $\delta^{13}\text{C}$ values were verified with the IAEA-CH6 sucrose and deep seawater reference samples (University of Miami).

Lines 131-147: Since DOC concentrations were relatively high, in particular in the low salinity waters, inner filter correction may be necessary to obtain precise EEMs. Did the authors apply an inner filter correction to EEMs? For the inner filter correction, please see Miller et al. (2010) AquatSci 72, 269-275 and references therein.

=> We did not correct EEM data for inner filter effects or dilute the samples before measurements since inner filter effects were found to be negligible for these estuarine

water samples. The correlation between uncorrected and corrected inner filter effect was very significant ($r^2=1$). This will be mentioned in the revised version.

Lines 137-140: Please add validation method(s) of PARAFAC. I think that the authors should show spectra or describe peak positions of two PARAFAC components. In addition, previous EEMs-PARAFAC studies with DOMFluoro toolbox generally identified more than 2 fluorescence components. Did the authors have any idea why only two component model was validated with dataset of this manuscript?

=> More details on PARAFAC analysis will be added as suggested. “The four components were identified in the water samples from the EEMs dataset. Based on the excitation-emission peak location, Component 1 (FDOMH, Ex/Em = 320/418 nm) is associated with terrestrial humic substances which are similar to C peak shown by Coble (2007). Component 2 (FDOMP, Ex/Em = 280/328 nm) is a tryptophan-like component which is produced by microbial processes. Component 3 (Ex/Em = 300,325/364 nm) is associated with marine humic-like component. However, it is highly correlated with that of component 1 ($r^2=0.95$). Thus, we didn’t discuss this component. Component 4 (Ex/Em = 364/482 nm) is not exactly matched with the previous studies. We use two main components component 1 and component 2 for humic-like component and protein-like component in all the samples collected in this study.”

Lines 145-147: How did the authors measure water temperature? Please add the method in the Materials and Methods section.

=> We will add this information in the Materials and Methods section. “The monitoring program at this station produces water temperature data automatically and maintained by Korea Environment Management Corporation (KOEM). The data are available at <https://www.koem.or.kr>.”

Lines 158-160: I could not understand how did the authors exclude high salinity periods. In other words, what was the definition of the high salinity periods? Please explain it in detail.

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=> High salinity periods (December, January, February, and June) are defined by their average salinity values >20 (21.2-25.1). In this range, DOC concentrations are quite similar (103-163 μM). Thus, we expected that the extrapolation of these relationships to fresh water could result in too large uncertainties. In order to avoid misinterpretations, we excluded these periods in the comparison.

Lines 202-205: The authors only discussed the case of October and November here, even though FDOMH slopes were higher for July, August, October, and November compared with other months. How about July and August? Please discuss it.

=> Thank you for the important comment. We will revise the text to include July, August, October, and November to explain higher FDOMH loading in the revised version.

Line 204: The term of “organic weathering” is usually used for the breakdown of rocks by plant or animal action, e.g., extension of roots. Thus, I think “degradation products of soil organic matter” (for example) is much better than “organic weathering products”.

=> Yes, will correct as suggested.

Lines 212-214: Mayer et al. (1999) and Zhang et al. (2009) did not determine the spring and fall phytoplankton blooms in the Nakdong-River. Please cite more proper studies here.

=> The sentence was rephrased to mean that “Zhang et al., (2009) showed that phytoplankton can be one of the important CDOM producers, and Mayer et al., (1999) suggested that protein fluorescence is associated with a plankton bloom”

Line 257: “positive” should be “negative”? Please check it!

=> Thanks, will be corrected.

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