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Interactive comment on "Spatial variations of CO_2 fluxes in the Saguenay Fjord (Québec, Canada) and results of a water mixing model" *by* Louise Delaigue et al.

Anonymous Referee #2

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Review Manuscript Delaigue et al. 2019

General Comments

Coastal zones play an important hole on the global carbon cycling; however, carbon budges are not yet properly include in global carbon budgets. This paper presents a novel and integrative approach to estimate the relative contribution of known water-sources to the Saguenay Fjord (Quebec, Canada), using geochemical and isotopic tracers coupled with an optimization multiparameter algorithm (OMP). This method, coupled with conservative end-member mixing model, allowed the analysis of dominant factors controlling the CO2 dynamics in the Fjord. The paper is generally well-written

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Discussion paper

and very easy to follow, providing new insights on coastal carbon dynamics. The paper is very succinct, and this is welcome. However, in some passages I would like to see more advances beyond the studied area. In brief, the manuscript lacks to present a better contextualization and to describe the implications of these findings. But of course this does diminish the merits of this manuscript.

The introduction is too short. In recent years, the knowledge of CO2 dynamics was considerable increased in coastal zones worldwide. In this way, I strongly recommend a review of the literature to contextualize your research. In addition, the discussion section is also very short, especially when discussing the governing processes that drive the concentrations and fluxes of CO2 at the air-water interface in the estuary.

The methodology is overall well written, however I have some doubts especially about the OMP analysis. How did you weight "arbitrarily" the parameters included in the OMP calculations? Another question: you argued, "Each source-water type is only appropriate for the fjord and for the period of study". The source-water type definitions were the Saguenay River (SWR), the St. Lawrence Estuary summertime Cold Intermediate Layer (CIL), the Lower St. Lawrence Estuary bottom waters (LSLE) and the St. Lawrence River (SLRW). The sampling campaigns were performed in late spring (May 2016 and May 2018), early summer (June 2017), and early and late fall (September 2014 and November 2017). I mean, the considered water masses encompass all characteristics of the sampled periods? Are there significant differences in the end-members considering these different seasons? Looking at the Appendix, there are some scattering in the end-members of SRW, CIL, SLRW and LSLE. Could this cause influences when calculating the OMP and the mixing model end-members?

The discussion of negative organic alkalinity should be better stressed in the manuscript. This is a very atypical pattern, taking into account that almost all studies that investigate organic alkalinity in coastal zones found positive concentrations. Another point: How did you correct the values of TA (organic alkalinity) to compute the mixing models?

Specific Comments

Line 26 : As you are talking about the concentrations of CO2 in the past, I recommend to include the study of Willeit et al (2019), which suggests that “the current CO2 concentration is unprecedented over the past 3 million years”.

Willeit1, M., Ganopolski, A., Calov, R., Brovkin, V. Mid-Pleistocene transition in glacial cycles explained by declining CO2 and regolith removal. Science Advances, Vol. 5, no. 4, eaav7337. DOI: 10.1126/sciadv.aav7337

Line 28: Here, I think the good reference is Feely et al. (2004).

Feely, R. A. 2004. Impact of Anthropogenic CO2 on the CaCO3 System in the Oceans. Science 305, 362.

Line 31: I could not find this reference. Is it Caldeira and Wickett (2005)?

Line 38-40: This sentence is not clear.

Line 49: What do you refers to trophic status? According to Vollenweider et al. (1998), trophic conditions of marine waters are related to degree of nutrient enrichment. Oligotrophy means nutrient poor (low productivity) and eutrophy means nutrient rich (high productivity) waters. However, the analysis of trophic status “per se” do not give information whether the ecosystems is a source or a sink of CO2 to the atmosphere.

Vollenweider, R. A., Giovanardi, F., Montanari, G., Rinaldi, A. 1998. Characterization of the trophic conditions of marine coastal waters with special reference to the NW Adriatic Sea: proposal for a trophic scale, turbidity and generalized water quality index. Environmetrics, 9, 329-357.

Line 61: I could not find these tributaries in the Fig. 1b.

Lines 80-81: Please, give the range of temperature for the warm brackish surface layer of the St. Lawrence Estuary. What is the tidal amplitude in the Fjord, and the longitudinal variations? Could you include this information?

Lines 132-142: Why did you use different methodologies of pH measurements for Sp >5 (spectrophotometry) and Sp < 5 (potentiometric)? Did you investigate the differences between these methods?

Lines 148-149: It no was clear how you did convert the pHNBS to pHT. Could you explain this procedure in the manuscript? Did you apply correction factors for the pH measurements at NBS scale for the TRIS buffer solutions (for which you have assigned the pHT)?

Line 158: What is the concentration of CO2 that you insert in the vials?

Line 189: "...biogeochemical cycling is imperative if one is to evaluate the movement of nutrients...". Something is missing here.

Lines 214-222: This passage is somewhat confuse. I think you should explain about this "arbitrary choices" in the weighting procedure based on covariance between tracers.

Lines 226-225: "In the context of biogeochemical cycles, a SWT should be defined where the water mass enters the basin, upstream from the mixing region (Karstensen, 2013)." However, if the water masses enter the basins downstream from the mixing region?

Lines 229-233: You argued that "Each definition was captured relative to the fjord, i.e. each source-water type is only appropriate for the fjord and for the period of study". Are you sure that these chosen SWT are representative for the period of study (late spring, May 2016 and May 2018; early summer, June 2017; early and late fall, September 2014 and November 2017)? In addition, did you take into account the seasonal variability of the end-members to calculate the OMP and the mixing models?

Line 265: ðİŘź = −ðİŘů ðİŻ£ðİŚŘ/ðİŻ£ðİŚě. Provide the terms of the equation.

Line 270: The parameterization of Wanninkhof (2014) is recommended for calculations of air-water exchanges in open ocean waters. I think you should include here other

parameterization more appropriate for estuarine environments.

Line 305: It no is clear to me how you separated these segments for the fjord's surface area. Did you separate by salinity? Distance from the mouth?

Lines 383-385: The discussion of the negative organic alkalinity results are poorly presented. I recommend put more efforts in this subject.

Lines 414-420: You attributed the average difference between pCO2(SW-meas) and pCO2(SW-calc) to the uncertain associated with the carbonic acid dissociation constants. One possible alternative is to calculate the pCO2(SW-calc) using other available constants to investigate which one fits better with the pCO2(SW-meas).

Lines 435-446: This paragraph is very interesting, but I missed the comparison with other studies that applied end-member mixing models, contrasting the influences of mixing and biological activities.

Lines 447-457: Where are the results of the fluorometer? I think this section can be strengthened adding with these results. For example you agueed that "Additionally, it is interesting to note that NDIC is chronically negative for all sampling months near the 45 km mark." Maybe the fluorescence call tell something.

Fig. 1b. Please, provide the title of the Y-right axis. In addition, add the riverine positions in the figure and the estuarine sections you used to calculate the air-water CO2 fluxes.

Fig. 10. Normally, the comparison of DIC and AOU are performed by calculating the excess of dissolved organic carbon (E-DIC), which is difference between the in situ DIC and a theoretical DIC at atmospheric equilibrium. Are there differences comparing ΔNDIC x AOU with E-DIC x AOU?

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