

## Responses to Anonymous Referee #2 (Responses to the referee's comments are in bold)

Coastal zones play an important role on the global carbon cycling; however, carbon budgets are not yet properly included 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 CO<sub>2</sub> dynamics in the Fjord. The paper is generally well-written 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 CO<sub>2</sub> dynamics was considerably increased in coastal zones worldwide. In this way, I strongly recommend a review of the literature to contextualize your research.

**We thank the referee for his(her) detailed and very positive comments.**

**A few sentences will be added to the revised manuscript to summarize the current consensus about CO<sub>2</sub> emissions in estuarine and coastal environments.**

**Please see response to Referee #1.**

In addition, the discussion section is also very short, especially when discussing the governing processes that drive the concentrations and fluxes of CO<sub>2</sub> at the air-water interface in the estuary.

**A few sentences will be added to the revised manuscript:**

**“These results highlight the importance of the freshwater plume from the Saguenay River in regulating the pCO<sub>2</sub> dynamics in the fjord. Winds, in addition to regulate the gas exchange coefficient, are also known to have a direct influence on air-sea CO<sub>2</sub> fluxes by driving upwelling of CO<sub>2</sub>-rich waters along with the entrainment of nutrients in surface waters, thus increasing biological activity (Wanninkhof and Triñanes, 2017). However, wind speeds are relatively low in the studied system ( $1.89 \text{ m s}^{-1} < u < 4.2 \text{ m s}^{-1}$ , Table 2), implying a calm sea state (Frankignoulle, 1998), and hence reinforcing that changes in pCO<sub>2(SW-SST)</sub> can mainly be attributed to microbial respiration and photosynthesis modulated by water renewals rather than winds.”**

**Frankignoulle, M. (1988) Field measurements of air-sea CO<sub>2</sub> exchange 1. *Limnology and Oceanography*, 33(3), 313-322.**

**Wanninkhof, R., and Triñanes, J. (2017) The impact of changing wind speeds on gas transfer and its effect on global air-sea CO<sub>2</sub> fluxes. *Global Biogeochemical Cycles*, 31(6), 961-974.**

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? *Coupled with specific comment:* 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.

Parameters were weighted arbitrarily according to their mixing behaviors (i.e., whether they behave conservatively or not, are affected by biological activity or gas exchange across the air-water interface) following [Lansard, B., Mucci, A., Miller, L. A., Macdonald, R. W., and Gratton, Y.: Seasonal variability of water mass distribution in the southeastern Beaufort Sea determined by total alkalinity and  $\delta^{18}\text{O}$ , *J. Geophys. Res-Oceans*, 117, 2012.]. Furthermore, several OMP analyses were carried out using different weights for each parameter while always considering their conservative behavior (i.e., low, medium or high) and results were not affected significantly. To clarify, the following text will be added to the revised manuscript:

**“Several OMP analyses were carried out using different weights for each parameter, while weighing their conservative behaviour appropriately (i.e., highly conservative vs. lightly conservative). Results were not affected significantly.”**

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?

**A seasonality analysis was carried out in order to make sure the SWT definitions are appropriate for the period of study. Insignificant variations were observed in tracers such as  $^{18}\text{O}$ , DIC, TA, DO and  $S_p$ . The only significantly variable tracer was T, which was given the lowest possible weight in the OMP analysis as to not skew the water mass analysis results.**

**We are currently writing a manuscript in which we tackle this issue in depth, including seasonal variations of bottom-water renewals in the fjord. It will include a thorough analysis of the seasonality of the SWT definitions.**

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.

**As noted in our response to Reviewer#1’s inquiry, negative organic alkalinities (acidity) in rivers are relatively common in temperate regions where soil profiles are well developed and the bedrock is made up of crystalline rocks (igneous or metamorphic silicates) devoid of carbonates. In fact, all the rivers along the north shore of the St. Lawrence Estuary are characterized by circum-neutral pHs and negative Org-Alk (acidity) as they drain the metamorphic/igneous rocks of the Canadian Shield. The negative Org-Alk (acidity) most likely originates from soil humic acids and all these rivers, including the Saguenay River, are highly colored.**

Another point: How did you correct the values of TA (organic alkalinity) to compute the mixing models?

**Line 320: “The organic alkalinity of the fjord waters was estimated from the difference between the measured and calculated TA”. To avoid organic alkalinity skewing the results, TA was calculated ( $\text{TA}_{\text{calc}}$ ) using DIC and pH. The corrected TA were then used in the mixing model.**

Line 26 : As you are talking about the concentrations of CO<sub>2</sub> in the past, I recommend to include the study of Willeit et al (2019), which suggests that “the current CO<sub>2</sub> concentration is unprecedented over the past 3 million years”.

**We thank the referee for his(her) suggestion, as the other referee also recommended the use of a more recent reference.**

Line 28: Here, I think the good reference is Feely et al. (2004).  
Feely, R. A. 2004. Impact of Anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> System in the Oceans. Science 305, 362.

**The reference will be added to the revised manuscript.**

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

**Yes, it is. The in-text citation will be modified accordingly.**

Line 38-40: This sentence is not clear.

**The sentence will be simplified to ease understanding. It will read:**

**“High latitude waters such as the Arctic Ocean have recently been given most of the attention, while coastal, seasonally ice-covered aquatic environments, such as the Saguenay Fjord, display comparable inter-annual and climatic sea-ice cover variabilities all the while being much more accessible (Bourgault et al., 2012).”**

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 CO<sub>2</sub> 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.

**Trophic status is indeed directly linked to primary productivity and microbial respiration. In our definition of the trophic status, we differentiate between surface waters that are net sources and net sinks of CO<sub>2</sub> to the atmosphere. An autotrophic system will generally be a sink of CO<sub>2</sub> to the atmosphere whereas a heterotrophic system will generally be a source, but there might be exceptions in transition zones between CO<sub>2</sub>-charged waters and productive estuarine waters.**

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

**Tributaries will be added to Fig. 1a of the revised manuscript. We thank the referee for catching this mistake.**

Lines 80-81: Please, give the range of temperature for the warm brackish surface layer of the St. Lawrence Estuary.

**The range of temperatures for the warm brackish surface layer of the St. Lawrence Estuary will be added to the revised manuscript.**

What is the tidal amplitude in the Fjord, and the longitudinal variations? Could you include this information?

**The requested information will be added to the revised manuscript.**

**According to Seibert et al. (1979), the tidal amplitude at the mouth of the fjord near Tadoussac averages 4.0 m and increases slightly toward the head of the fjord (4.3 m near Port Alfred). Spring tides may reach an amplitude of 6 m.**

**Seibert, G. H., Trites, R. W., and Reid, S. J. (1979) Deepwater exchange processes in the Saguenay Fjord, J. Fish. Board Can., 36(1), 42–53.**

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

**The differences between these methods have been investigated by Mucci's research group over many cruises in the St. Lawrence Estuary and the Saguenay Fjord over the past 15 years. Low salinity waters ( $S_p < 5$ ) are often colored, turbid and poorly buffered and, thus, are often not amenable to spectrophotometric measurements with colored dyes.**

Lines 148-149: It no was clear how you did convert the pH<sub>NBS</sub> to pH<sub>T</sub>. 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 pH<sub>T</sub>)?

**We calculated the difference between the assigned pH<sub>T</sub> of a TRIS buffer of salinity close to the sample ( $\pm 2.5$ ) and the measured pH(NBS) of the TRIS buffer. The sample pH(NBS) was then converted to pH<sub>T</sub> by subtracting this value from the measured pH(NBS) of the sample.**

Line 158: What is the concentration of CO<sub>2</sub> that you insert in the vials?

**99.998% pure CO<sub>2</sub> (Research Grade) was injected in dual inlet mode.**

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

**The sentence starts on line 188 and reads as follows: “Resolving the effects of mixing and biogeochemical cycling is imperative if one is to evaluate the transport of nutrients and tracers in a water body.”**

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?

By “upstream from the mixing region”, we mean before the SWT enters the mixing region, and therefore at the source of the SWT itself. The sentence will be reworded for clarity and will read:

**“In the context of biogeochemical cycles, a SWT should be defined where the water mass enters the basin, before it enters the mixing region (Karstensen, 2013).”**

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)?

**A seasonality analysis was carried out in order to make sure the SWT definitions are appropriate for the period of study. Insignificant variations were observed in tracers such as  $\delta^{18}\text{O}$ , DIC, TA, DO and  $S_p$ . The only highly variable tracer was T, which was given the lowest possible weight in the OMP analysis.**

In addition, did you take into account the seasonal variability of the end-members to calculate the OMP and the mixing models?

**As noted above, there is insignificant seasonal variability when it comes to the SWT definitions.**

Line 265: “ $F = -D \delta c / \delta x$ ”. Provide the terms of the equation.

**Terms of the equation will be defined in the revised manuscript:**

**F is the diffusion flux in mole  $\text{sec}^{-1} \text{m}^{-2}$**

**D is the diffusion coefficient in  $\text{m}^2 \text{sec}^{-1}$**

**C is the concentration of  $\text{CO}_2$  in mole  $\text{m}^{-3}$**

**x is the distance in m**

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.

**Dinauer and Mucci (2017) analyzed which parameterization was best in the context of the St. Lawrence Estuary system and the parametrization of Wanninkhof (2014) was deemed the most appropriate.**

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?

**As noted in our response to Reviewer#1’s comment, the fjord was divided in segments based on the overall trend of the surface water  $\text{pCO}_2$  ( $\text{pCO}_{2(\text{SW})}$ ) along the fjord (Fig. 4): the first segment includes the larger inner basin (over which  $\text{pCO}_{2(\text{SW})}$  is much higher than  $\text{pCO}_{2(\text{air})}$  and decreases rapidly downstream) whereas the second segment encompasses the two outer basins (over which  $\text{pCO}_{2(\text{SW})}$  is close to  $\text{pCO}_{2(\text{air})}$  and varies little downstream). Segments will be identified on Figure 1.a.**

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

See above for response to Reviewer#1's comment.

Lines 414-420: You attributed the average difference between  $p\text{CO}_2(\text{SW-meas})$  and  $p\text{CO}_2(\text{SW-calc})$  to the uncertain associated with the carbonic acid dissociation constants. One possible alternative is to calculate the  $p\text{CO}_2(\text{SW-calc})$  using other available constants to investigate which one fits better with the  $p\text{CO}_2(\text{SW-meas})$ .

Dinauer and Mucci (2017) investigated which set of carbonic acid dissociation constants returned the most realistic values of  $p\text{CO}_2$  in the St. Lawrence Estuary system, which is why the constants from Cai and Wang (1998) were used in this study. As reported in Dinauer and Mucci (2017) other sets of constants return  $p\text{CO}_2(\text{SW-calc})$  values that differ by as much as  $\pm 300$  ppm at salinities below 5.

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.

We kindly suggest the referee have a look at the following studies:

Dinauer, A., and Mucci, A. (2017). Spatial variability in surface-water  $p\text{CO}_2$  and gas exchange in the world's largest semi-enclosed estuarine system: St. Lawrence Estuary (Canada). *Biogeosciences*, 14(13), 3221-3237.

Dinauer, A., and Mucci, A. (2018). Distinguishing between physical and biological controls on the spatial variability of  $p\text{CO}_2$ : A novel approach using OMP water mass analysis (St. Lawrence, Canada). *Marine Chemistry*, 204, 107-120.

Lines 447-457: Where are the results of the fluorometer? I think this section can be strengthened adding with these results. For example you argued 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.

We thank the referee for his/her suggestion. We used the CTD profiles from 2014 and 2016 (since the mixing responses are different between these two years) but the fluorescence data do not reveal any significant chronic change that could explain the negative  $\Delta\text{NDIC}$  at the 45 km mark (red line).

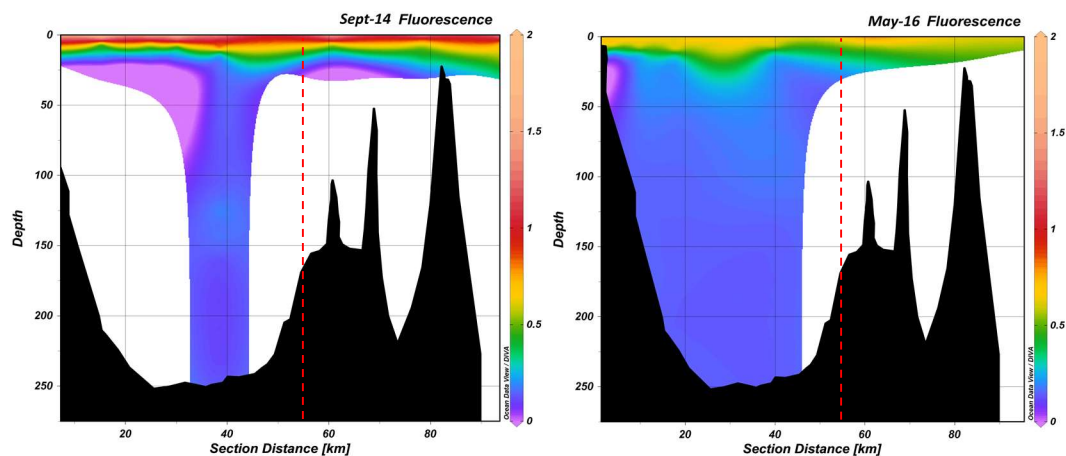


Fig. 1b. Please, provide the title of the Y-right axis. In addition, add the riverine positions in the figure and the estuarine sections you used to calculate the air-water CO<sub>2</sub> fluxes.

**The requested information will be added in the revised manuscript.**

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

**It is true that calculating E-DIC is a more conventional way of plotting these data. Nevertheless, there appears to be no notable difference between  $\Delta$ NDIC x AOU and E-DIC x AOU except for May 2016. This, however, does not change the conclusion of the manuscript given that our focus is on how  $\Delta$ NDIC changes spatially.**

