

Responses to Anonymous Referee #1 (Responses to the referee's comments are in bold)

This paper uses an extensive dataset of physical and biogeochemical observations to identify water source contributions to a unique Canadian fjord-type system and evaluate the results in relation to the fjord's air-sea CO₂ flux characteristics. Overall, I found this manuscript very well-written, with good explanations of methods used (with one exception I will discuss below), excellent descriptions of data analyses, and clear presentation of results. Also, the paper is concise!

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

While this is very welcome overall, the Introduction and Summary may actually benefit from some additional content. -The Introduction is a little light. Can more detail be added on coastal CO₂ emissions? While there may be little information on CO₂ emissions from fjord-like systems, there have certainly been studies on a variety of other coastal system types which might provide context for this study.

A few sentences will be added to the revised manuscript to summarize the current consensus about CO₂ emissions in estuarine and coastal environments, and the introduction will read:

“Anthropogenic emissions of carbon dioxide (CO₂) have recently propelled atmospheric CO₂ concentrations above the 410 ppm mark, the highest concentration recorded in the past 3 million years (Willeit et al., 2019). The oceans, the largest CO₂ reservoir on Earth, have taken up ca. 30% of the anthropogenic CO₂ emitted to the atmosphere since the beginning of the industrial era (Brewer and Peltzer, 2009; Doney et al., 2009; Orr, 2011, Le Quéré et al., 2012), mitigating the impact of this greenhouse gas on global warming (Sabine et al., 2004). On the other hand, the uptake of CO₂ by the oceans has led to modifications of the seawater carbonate chemistry and a decline in the average surface ocean pH by ~0.1 units since pre-industrial times, a phenomenon dubbed ocean acidification (Caldeira and Wickett, 2005). According to the Intergovernmental Panel on Climate Change (IPCC) “business as usual” emissions scenario IS92a and general circulation models, atmospheric CO₂ levels may reach 800 ppm by 2100, lowering the pH of the surface oceans by an additional 0.3-0.4 units, at a rate that is unprecedented in the geological record (Caldeira and Wickett, 2005; Hönlisch et al., 2012; Rhein et al., 2013). The growing concern about the impacts of anthropogenic CO₂ emissions on climate as well as marine and terrestrial ecosystems calls for a meticulous quantification of organic and inorganic carbon fluxes, especially in coastal environments, including fjords, a major but poorly quantified component of the global carbon cycle and budget (Bauer et al., 2013; Najjar et al., 2018). The very large uncertainty associated with present-day air-sea CO₂ flux estimates in coastal waters, including rivers, estuaries, tidal wetlands, and the continental shelf, impedes meaningful predictions of the effects of climate change on future fluxes (Bauer et al., 2013). The coastal ocean occupies only ~7% of the global ocean surface area, but plays a major role in biogeochemical cycles because it (1) receives massive inputs of terrestrial organic matter and nutrients through continental runoff and groundwater discharge; (2) exchanges matter and energy with the open ocean; and (3) is one of the most geochemically and biologically active areas of the biosphere, accounting for significant fractions of marine primary production (~14 to 30%), organic matter burial (~80%), sedimentary mineralization (~90%), and calcium carbonate deposition (~50%) (Gattuso et al., 1998).

Although the carbon cycle of the coastal ocean is acknowledged to be a major component of the global carbon cycle and budget, accurate quantification of organic and inorganic carbon cycling and fluxes in the coastal ocean — where land, ocean and atmosphere interact — remains challenging (Bauer et al.,

2013; Najjar et al., 2018). Constraining the exchanges and fates of different forms of carbon along the land—ocean continuum is so far incomplete, owing to limited data coverage and large physical and biogeochemical variability within and between coastal subsystems (e.g., hydrological and geomorphological differences, differences in the magnitude and stoichiometry of organic matter inputs). Hence, owing to limited data coverage and suspicious upscaling due to the large physical and biogeochemical variability within and between coastal subsystems, there remains a debate as to whether coastal waters are net sources or sinks of atmospheric CO₂. Recent compilations of worldwide CO₂ partial pressure (pCO₂) measurements indicate that most open shelves in temperate and high-latitudes are sinks of atmospheric CO₂ whereas low-latitude shelves and most estuaries are sources (Chen and Borges, 2009; Cai, 2011; Chen et al., 2013). As noted by Bauer et al. (2013), estuaries are transitional aquatic environments that can be riverine or marine dominated and, thus, they typically display strong gradients in biogeochemical properties and processes as they flow seaward. Chen et al. (2013) reported that the strength of estuarine sources typically decreases with increasing salinity. However, marsh-dominated estuaries, in which active microbial decomposition of organic matter occurs in the intertidal zone, are strong sources of CO₂ (Cai, 2011).

While much attention has recently focused on high latitude waters (e.g., Arctic Ocean), coastal, seasonally ice-covered aquatic environments such as the Saguenay Fjord display comparable inter-annual and climatic sea-ice cover variabilities (Bourgault et al., 2012). Characteristics of Arctic coastal ecosystems are found in the Saguenay Fjord, including the presence of many species of plankton, fish, birds and marine mammals as well as important freshwater inputs and the presence of seasonal ice cover (Bourgault et al., 2012). Fjords stand amongst the most productive ecosystems on the planet, while they have a yet unexplored role in regional and global carbon cycles as part of the estuarine family (Juul-Pedersen et al., 2015). They are crucial hotspots for organic carbon (mostly terrestrial) burial and account for nearly 11% of the annual organic carbon burial flux in marine sediments, while covering only 0.12% of oceans' surface (Rysgaard et al., 2012; Smith et al., 2015). In other words, organic carbon burial rates in fjords are a hundred times faster than the average rate in the global ocean. Rates of organic carbon burial provide insights on the mechanism that controls atmospheric O₂ and CO₂ concentrations over geological timescales (Smith et al., 2015).

This study presents 1) the relative contribution of known source waters to the water column in the fjord, estimated from the solution of an optimization multi-parameter algorithm (OMP) using geochemical and isotopic tracers, and 2) results of a conservative mixing model, based on results of the OMP analysis and from which theoretical surface-water pCO₂ values are derived and then compared to field measurements. The latter comparison serves to identify the dominant factors, other than physical mixing (i.e., biological activity, gas exchange), that impact the CO₂ fluxes at the air-sea interface throughout the fjord and modulate the trophic status of the fjord (i.e. whether it is a source or a sink of CO₂ to the atmosphere)."

Bauer, J. E., Cai, W. J., Raymond, P. A., Bianchi, T. S., Hopkinson, C. S., & Regnier, P. A. (2013) The changing carbon cycle of the coastal ocean. *Nature*, 504(7478), 61.

Bourgault, D., Galbraith, P. S., & Winkler, G. (2012) Exploratory observations of winter oceanographic conditions in the Saguenay Fjord. *Atmosphere-Ocean*, 50(1), 17-30.

Borges, A. V. (2005) Do we have enough pieces of the jigsaw to integrate CO₂ fluxes in the coastal ocean? *Estuaries; Stony Brook*, 28(1), 3–27. <http://dx.doi.org/10.1007/BF02732750>

Brewer, P. G., & Peltzer, E. T. (2009) Limits to marine life. *Science*, 324(5925), 347-348.

Cai, W.-J. (2011) Estuarine and coastal ocean carbon paradox: CO₂ sinks or sites of terrestrial carbon incineration? *Annual Review of Marine Science*, 3(1), 123–145. <https://doi.org/10.1146/annurev-marine-120709-142723>

Caldeira, K., & Wickett, M. E. (2005) Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *Journal of Geophysical Research: Oceans*, 110(C9).

Chen, C. T. A., & Borges, A. V. (2009) Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂. *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(8-10), 578-590.

Chen, C. T., Huang, T. H., Chen, Y. C., Bai, Y., He, X., & Kang, Y. (2013) Air–sea exchanges of CO₂ in the world's coastal seas. *Biogeosciences*, 10(10), 6509-6544.

Doney, S. C., Fabry, V. J., Feely, R. A., & Kleypas, J. A. (2009) Ocean acidification: the other CO₂ problem. *Annual Review of Marine Science*, 1, 169-192.

Gattuso, J.-P., Frankignoulle, M., and Wollast, R. (1998) Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annual Review of Ecology and Systematics*, 29, 405–434.

Hönisch, B., Ridgwell, A., Schmidt, D. N., Thomas, E., Gibbs, S. J., Sluijs, A., ... & Kiessling, W. (2012) The geological record of ocean acidification. *Science*, 335(6072), 1058-1063.

Juul-Pedersen, T., Arendt, K., Mortensen, J., Blicher, M., Søgaard, D., and Rysgaard, S. (2015) Seasonal and interannual phytoplankton production in a sub-Arctic tidewater outlet glacier fjord, SW Greenland. *Marine Ecology Progress Series*, 524, 27–38. <https://doi.org/10.3354/meps11174>

Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., House, J. I., ... & Andrew, R. M. (2012) The global carbon budget 1959–2011. *Earth System Science Data Discussions*, 5(2), 1107-1157.

Najjar R. G., Herrmann M., Alexander R., Boyer E. W., Burdige D. J., Butman D., Cai W. J., Canuel E. A., Chen R. F., Friedrichs M. A. M., Feagin R. A., Griffith P. C., Hinson A. L., Holmquist J. R., Hu X., Kemp W. M., Kroeger K. D., Mannino A., McCallister S. L., McGillis W. R., Mulholland M. R., Pilskaln C. H., Salisbury J., Signorini S. R., St-Laurent P., Tian H., Tzortziou M., Vlahos P., Wang Z. A. and Zimmerman R. C. (2018) Carbon budget of tidal wetlands, estuaries, and shelf waters of eastern North America. *Global Biogeochemical Cycles*, 32, 389–416.

Orr, J. C. (2011) Recent and future changes in ocean carbonate chemistry. *Ocean Acidification*, 1, 41-66.

Rhein, M., S.R. Rintoul, S. Aoki, E. Campos, D. Chambers, R.A. Feely, S. Gulev, G.C. Johnson, S.A. Josey, A. Kostianoy, C. Mauritzen, D. Roemmich, L.D. Talley and F. Wang (2013): Observations: Ocean. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Rysgaard, S., Mortensen, J., Juul-Pedersen, T., Sørensen, L. L., Lennert, K., Søgaard, D. H., ... Bendtsen, J. (2012) High air–sea CO₂ uptake rates in nearshore and shelf areas of Southern Greenland: Temporal and spatial variability. *Marine Chemistry*, 128–129, 26–33.

<https://doi.org/10.1016/j.marchem.2011.11.002>

Sabine, C. L. (2004) The oceanic sink for anthropogenic CO₂. *Science*. 305(5682), 367–371.
doi:10.1126/science.1097403.

Smith, R. W., Bianchi, T. S., Allison, M., Savage, C., and Galy, V. (2015) High rates of organic carbon burial in fjord sediments globally. *Nature Geoscience*, 8(6), 450–453.

<https://doi.org/10.1038/ngeo2421>

Willeit, M., Ganopolski, A., Calov, R., & Brovkin, V. (2019) Mid-Pleistocene transition in glacial cycles explained by declining CO₂ and regolith removal. *Science Advances*, 5(4), eaav7337.

-Similarly, the Summary and Conclusions section is pretty brief. At the very least, what do the authors see as the impacts of this work beyond the studied system? What future work might stem from these findings? –

A few sentences will be added to the revised manuscript to summarize the impacts of this work beyond the studied system, extend the conclusions of the data analysis to an understanding of the factors governing CO₂ fluxes at the air-water interface and how these might apply to other systems (regardless of scale).

“Studying the carbon budget of fjord inlets not only provides information on its trophic status (i.e. source or sink of CO₂ with respect to the atmosphere) and surface-water chemistry, but also explores the magnitude of gas exchange and the amount of biological activity it sustains. In addition to biological production, upwelling, water temperature, and the spreading of freshwater plumes all regulate pCO₂ in costal systems. Wind speed is also critical in estimating gas exchange at the air-sea interface as it heavily impacts sea state (Chen et al., 2013). The importance of wind on controlling the CO₂ flux needs to be further investigated, especially at high latitudes where strong winds are often encountered (Chen et al., 2013) and in narrow inlets where the fetch is limited. Anthropogenic activities are altering the continental water cycle, along with the flows of carbon, nutrients and sediment to the coastal oceans (Borges, 2005), and hence, the sequestration of anthropogenic CO₂ emissions by the oceans. Current research on CO₂ fluxes in coastal zones is still too scarce to make precise climate change predictions (i.e., flux within ± 0.05 Pg·C y⁻¹) on whether they mitigate or accelerate atmospheric CO₂ emissions.”

One very interesting finding of the paper is the negative Org-Alk of the Saguenay River and the fjord waters (Figure 2, manuscript lines 383-388). I am familiar with work detailing positive Org-Alk findings (i.e. calculated TA lower than that measured directly), but I can't think of another example of negative Org-Alk. Negative total alkalinity is common in very acidic waters, but the total alkalinity in this river is positive (although low). This implies to me that in the total alkalinity titration, there is some excess of acid that is not reflected in the pH and DIC measurements. What could this be? This leads me to wish there were more description of the TA measurement method. At which pH range was the titration carried out? What is a shallow end-point detection algorithm? Where might the excess acidity be

coming from? A short discussion of the factors that could explain the negative Org-Alk would be a welcome addition.

The negative Org-Alk (acidity) component of this manuscript could make up a manuscript of its own and a detailed discussion is, therefore, beyond the scope of this study. For a discussion of the acid-base properties of dissolved organic matter in estuaries and the impact of OrgAlk on pH, acid-base dissociation and carbonic acid speciation, the reviewer should consult Cai et al. (1998) and Muller and Bleie (2008). Although positive values are most often reported, negative organic alkalinities (acidity) have been reported in coastal waters (e.g., Yang et al., 2015) and discussed (Ulfsbo et al., 2015). They are relatively common in rivers and stream waters of 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 (Wilkinson et al., 1992). The negative Org-Alk (acidity) most likely originates from soil humic acids and all these rivers, including the Saguenay River, are highly colored. We added the following text to the revised manuscript:

“The negative Org-Alk (acidity) of the Saguenay River water most likely originates from soil humic acids that are flushed by percolation with groundwaters that drain the metamorphic and igneous rocks of the Canadian Shield.”

Total alkalinity was measured by metered weak acid solution additions between pH 7 and 4, sometimes requiring flushing of the sample solution with N₂ to lower the pCO₂ and increase the initial pH. The shallow end-point detection algorithm is a proprietary software of the manufacturer, Radiometer, for weak acid/base potentiometric titration.

Cai W. J., Wang Y. and Hodson R. E. (1998) Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA. *Geochim. Cosmochim. Acta* 62, 761 473–483

Muller F. L. L. and Bleie B. (2008) Estimating the organic acid contribution to coastal seawater alkalinity by potentiometric titrations in a closed cell. *Anal. Chim. Acta* 619, 183–191.

Ulfsbo A., Kuliński K., Anderson L. G. and Turner D. R. (2015) Modelling organic alkalinity in the Baltic Sea using a Humic-Pitzer approach. *Mar. Chem.* 168, 18–26.

Wilkinson K.J., Jones H.G., Campbell P.G.C. and Lachance M. (1992) Estimating organic acid contributions to surface water acidity in Quebec (Canada). *Water, Air and Soil Pollution* 61, 57-74.

Yang B., Byrne R.H. and Lindemuth M. (2015) Contributions of organic alkalinity to total alkalinity in coastal waters: A spectrophotometric approach. *Mar. Chem.* 176, 199-207.

-The air-sea CO₂ flux calculations were based on discrete measurements of DIC and pH at individual stations. However, to produce the overall fluxes for the system, the estuary must have been divided up spatially into segments, as implied by equation 5. However, these segments are not discussed or shown on the map (Figure 1), and should probably be included and delineated in the map.

The fjord was divided in segments based on the overall trend of the surface water pCO₂ (pCO_{2(sw)}) along the main axis of the fjord (Fig. 4): the first segment includes the larger inner basin (over which

$p\text{CO}_{2(\text{SW})}$ is much higher than $p\text{CO}_{2(\text{air})}$ and decreases rapidly downstream) whereas the second segment encompasses the two outer basins (over which $p\text{CO}_{2(\text{SW})}$ is close to $p\text{CO}_{2(\text{air})}$ and varies little downstream). Segments will be identified on Figure 1.a.

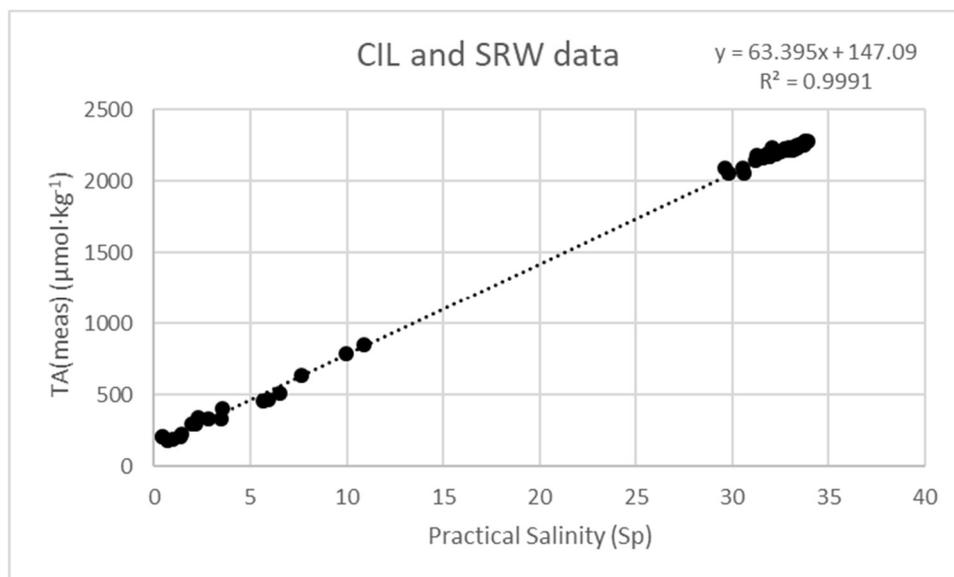
-Also, pH data were important to this study, but are never shown. At the least it seems that the pH data should be shown in the Appendix figure, but really there should be a discussion of the pH findings before they are used to calculate $p\text{CO}_2$.

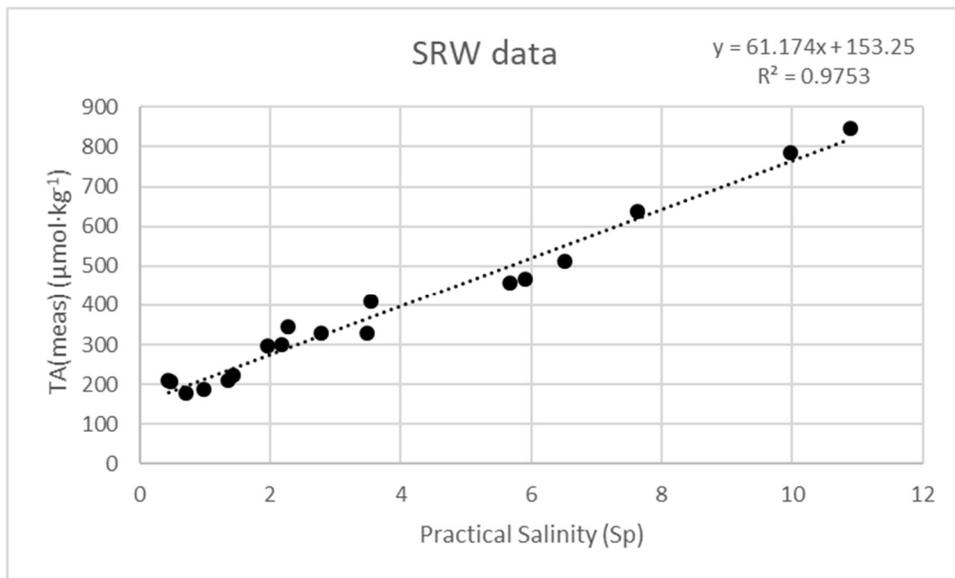
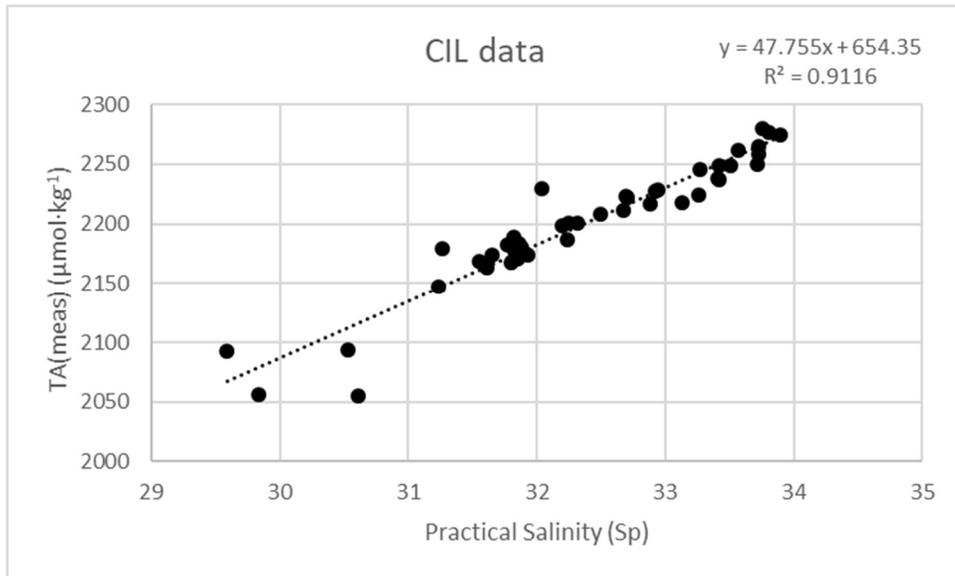
A table will be added to the Appendix with the raw pH data.

-In Figure 2, the SRW and CIL TA data are plotted against salinity. It's unclear to me where exactly these data were collected, or how they were selected. The SRW data fall into the salinity range of 0 to ~18 while the CIL data are saltier, from salinity ~22-35. A regression line is included (although I am skeptical of the R^2 of 1.0 shown, given that there is at least some scatter in the data). However, to my eye it seems that the regression line of just the CIL data would produce a different (shallower) slope and (higher) y-intercept than that of the combined SRW and CIL data. If the CIL endmember TA:salinity regression were different, how would that affect the water mass mixing results?

$R^2 = 0.999$, which was rounded to 1 for ease of reference. It will be modified back to 0.999.

The reviewer is right (see below) in saying that the slope of the regression line to the CIL data is slightly shallower ($\text{TA}/S_p = 47.8$ vs 63.4) but the extrapolations to $S_p = 0$ (the SRW endmember) from the low salinity data ($S_p < 11$) alone are nearly identical ($\text{TA} = 153$ vs $147 \mu\text{mol}/\text{kg}$). Hence, the water mass mixing results would not be affected significantly if the data were binned. The CIL definition was taken directly at the source of the endmember. As few data ($0 < S_p < 5$) were available to define the SRW, we used the full set of data from the fjord water column to correlate TA and S_p and extrapolate the definition of the SRW endmember to $S_p = 0$.





-L13-L15: this sentence is pretty awkward, can it be simplified?

The sentence will be simplified to ease understanding. In the revised manuscript, it will read:

“Nonetheless, the CO₂ dynamics in the fjord are modulated with the rising tide by the intrusion, at the surface, of brackish water from the upper estuary, as well as an overflow of mixed seawater over the shallow sill from the lower estuary.”

-L26: is there a newer citation for atmospheric CO₂ levels than this 2008 work?

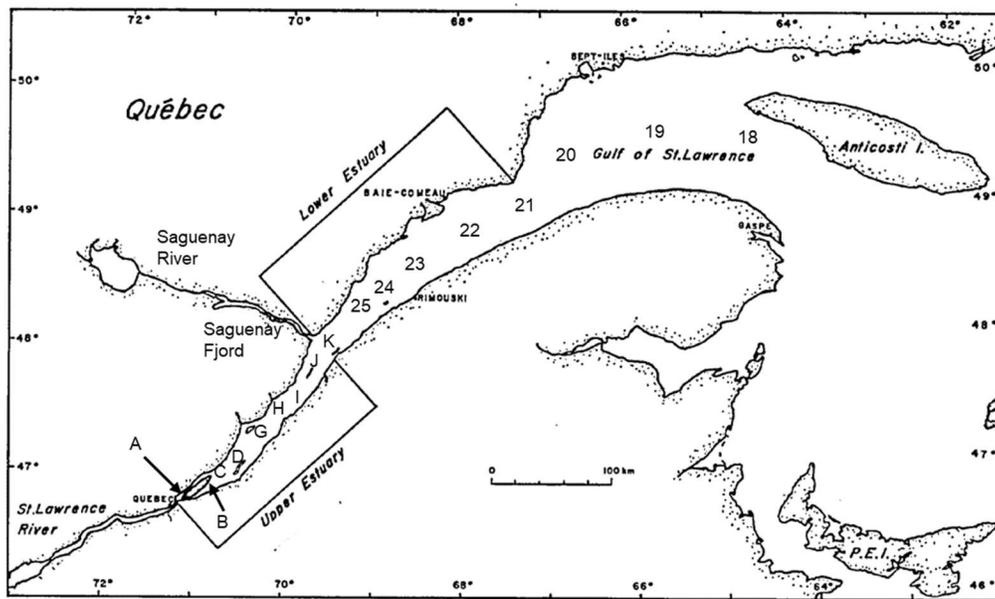
The other referee suggested Willeit et al (2019), which will be incorporated in the revised manuscript

- L77: the terms “Tmax” and “Sp” have not been defined

The terms will be defined in the revised manuscript. “Tmax” will be changed to “T”, which stands for Temperature (in °C) whereas “Sp” refers to the practical salinity of the waters.

-L90: the St. Lawrence River and Estuary frequently appear in this manuscript, but it’s unclear where these features begin and end in relation to the Saguenay system.

The original inset in Figure 1 will be replaced by the following map that also includes the location of sampling stations in the estuary and the gulf from which the SLR, CIL and LSLE endmember definitions were derived.



-L99: were samples from the St. Lawrence estuary included in the Appendix plot? There seem to be data in this plot that are quite different than those in Figure 2. If so, the locations of the St. Lawrence stations should be shown in Figure 1, and the difference between data from inside and outside the fjord should be clearer.

Samples from the St. Lawrence Estuary were included in the Appendix plot, specifically stations used to define endmembers other than the SRW. The location of sampling sites outside the fjord for which data are used in this plot will be identified in the new inset map (see above) and are identified by letters (A to K) in the Upper Estuary and numbers (18 to 25) in the Lower Estuary and the Gulf. The data taken inside and outside the fjord are distinguished by distinct symbols for each water mass.

-L110: what is the distinction between “TA” and “TA/DIC” samples?

“TA” refers to samples collected in 250 mL glass bottles throughout the water column and analyzed at McGill University. “TA/DIC” refers to surface water samples taken in 500 mL glass bottles and sent to Dalhousie University to be analysed by Dr. Helmut Thomas for both TA and DIC. Methods, Lines 170-184 describe the analytical methods in detail.

-L124: what is “Rio Tinto Alcan”?

Rio Tinto Alcan is a large multinational aluminum smelter/producer. The company constructed and manages its own hydroelectric dam on the Saguenay River. We collaborated with a Water Management Consultant who provided us with freshwater discharge data as part of their bank stabilization programme.

-L275: can the location of the weather station be included on the map? What was the measurement height for the wind speed?

The weather station location will be included on the map. The weather station’s elevation is 152 m above sea level.

-L276-277: this is a really nice, concise description of the Schmidt number

We thank the referee for his(her) positive comment

-L284: specify water temperature here

L284 will be rephrased in the revised manuscript and will read: “[...] where T is the temperature (°C) and A, B, C, D and E are fitting coefficients for seawater ($S_p = 35$) and freshwater ($S_p = 0$), for water temperatures ranging from -2°C to 40°C (Wanninkhof, 2014).”

-L298: is there a way to cite or list the conversion formula from NOAA-NWS?

Unfortunately, we have not found a way of citing Tim Brice’s (very useful!) work. However, a portable version of the Weather Calculator is now available ([here](#))

-L336: How was the correction for organic alkalinity performed?

Line 320: “*The organic alkalinity of the fjord waters was estimated from the difference between the measured and calculated TA*”. The organic alkalinity was then subtracted from TA_{meas} to give TA_{calc} .

-L414-424: this correlation analysis assumes that the sensor pCO_2 measurements are totally correct; however, there is a fair amount of uncertainty associated with these sensors. Error bars in both the x- and y-directions would be helpful in Figure 5.

As noted in the manuscript, “the manufacturer claims a 1% accuracy, but the performance of the instrument may be even better (Hunt et al., 2017)”, an insignificant instrumental error. However, surface water pCO_2 s recorded by the probe can vary by as much as 5% as the ship drifts from its position, water flows past the ship and probe, or waters are mixed by turbulence. Error bars will be added to Figure 5 in the revised manuscript.

-Figure 1: the color scale needs a label (‘Salinity’ etc)

The proper label will be added to Figure 1 in the revised manuscript.

-Figure 6(a): the line is dashed-black in my copy, not red as described in the caption

We thank the referee for catching this mistake! The figure caption will be modified accordingly in the revised manuscript.

-Figure 8: can the mean temperature used to normalize the data be listed somewhere in this figure, for ease of reference?

Temperatures used to normalize the data were listed on lines 430-432 of the original manuscript but will be listed in the figure caption for ease of reference.