

We thank the referee for his constructive feedback, and time spent to review our manuscript. Our responses to the referee's comments follow. The referee's comments are in italics.

1: In the introduction and later in the paper a further processes may be mentioned regulating the pCO₂ in estuarine systems. This is the relation or ratio of dissolved inorganic carbon and alkalinity (DIC:AT) of the riverine waters, which in essence is controlled by the drainage basin characteristics. This has been shown for example for the Baltic Sea by Thomas and Schneider (1999), or Hudson Bay by Burt et al. (2016). I think this process, or possibly its regional variability within or between drainage basins appears particularly relevant for systems, which span a range of climatic regions such as the Gulf of St Lawrence, being at the boundary between subarctic and temperate regions.

The authors implicitly refer to this point in their section 2.1 (geology of catchment area, as well as its vegetation), and I further think that this is relevant when discussing oxygen vs CO₂ saturation levels (lines 522-536, and their Fig. 8), as well as for section 3.3, which in turn more or less is focused on temperature only rather than on what is implied by equation 9.

We thank the reviewer for bringing these studies to our attention as they demonstrate that the DIC/Talk ratio influences pCO₂ changes by determining the buffer capacity of the water. One would expect the buffer capacity to vary among rivers that carry different levels of carbonate alkalinity according to the nature of the rocks being weathered within their drainage basin. Indeed, despite the contribution of the Ottawa River (the largest tributary of the St. Lawrence River) that drains through Paleozoic carbonates (Telmer and Veizer, 1999), we observe a DIC/Talk > 1.0 in the St. Lawrence River (freshwater end-member), but this ratio decreases rapidly with increasing salinity along the Upper St. Lawrence Estuary (USLE) (see the appended Fig. 1). The freshwater runoff from rivers on the north shore of the Lower St. Lawrence Estuary (LSLE) and Gulf, which drain the igneous and metamorphic rocks of the Grenville province, is characterized by DIC/Talk ≈ 1.0. The north shore rivers also carry a significant excess alkalinity, likely in the form of organic alkalinity (a negative alkalinity), due to their high soil-derived humic acid content. The contributions of these rivers to the LSLE and Gulf are typically negligible, except during the spring freshet in April–May, as demonstrated in a follow-up manuscript. This follow-up manuscript will also highlight that DIC inputs from in-situ respiration/remineralization processes (as opposed to riverine DIC inputs or air-sea gas exchange) are mainly

responsible for controlling the spatial variability of mixed-layer $p\text{CO}_2$ in the Upper Estuary.

Telmer, K., and Veizer, J.: Carbon fluxes, $p\text{CO}_2$ and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives, *Chemical Geology*, 159, 61–86, 1999.

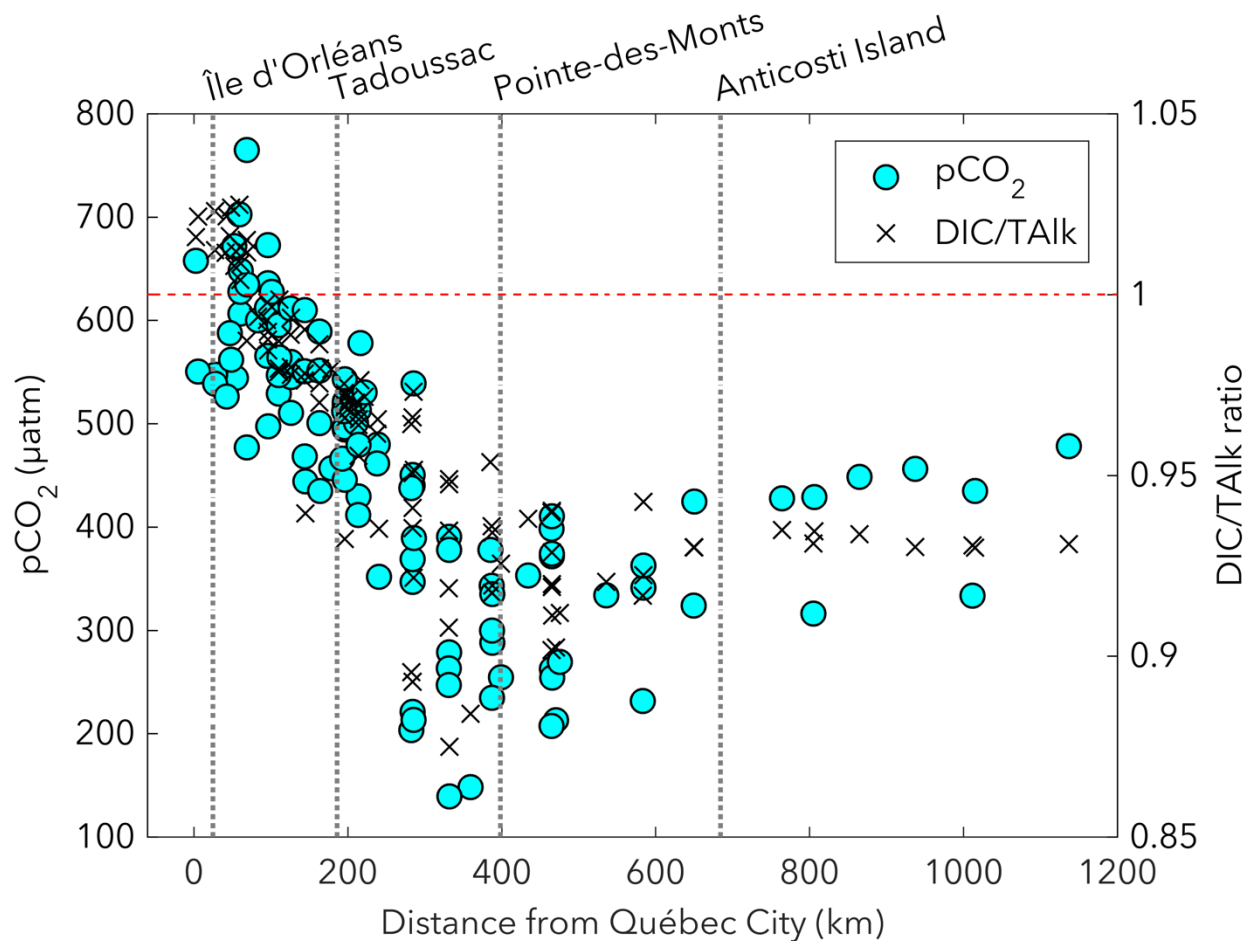


Fig. 1. Spatial distributions of surface-water $p\text{CO}_2$ (circles) and the DIC/TALK ratio (x symbols) in the St. Lawrence River, Estuary and Gulf during spring/summer cruises. Horizontal dashed line delineates DIC/TALK = 1.

2: I appreciate the discussion of the uncertainty associated with the computation of the $p\text{CO}_2$ from alkalinity and pH. I find this - crucial part of the paper - somewhat difficult to follow. I would suggest to add a panel to Figure 3 showing different $p\text{CO}_2$ results themselves, and only then their differences. Also, while I am aware that the authors did not measure $p\text{CO}_2$ directly, possibly a short discussion could be added how the computed values compare to direct measurements, which is actually what the reader would be interested in.

The reviewer is referring to section 2.3.2. in the manuscript which offers a brief discussion of the uncertainty in the calculation of $p\text{CO}_2$ from the different published formulations of the carbonic acid dissociation constants (K_1 and K_2). For our comparison of dissociation constants, values of $p\text{CO}_2$ were calculated at a common temperature of 15 °C, at the measured pH and TAlk, using different sets of K_1 and K_2 . The results presented in Fig. 3 were shown as a function of salinity in order to demonstrate that the best-practices formulations of K_1 and K_2 are not suitable for the low-salinity conditions found in estuaries ($S_P < 19$). Per the reviewer's suggestion, a second plot was added to Fig. 3 to show the actual calculations alongside the discrepancies in the calculated values. It should be clear from both plots in the appended Fig. 2 that agreement between the calculations is poorest at low salinities.

We agree with the reviewer that direct $p\text{CO}_2$ measurements would have been desirable to confirm the accuracy of the $p\text{CO}_2$ calculations, particularly at low salinities. An underway $p\text{CO}_2$ system (General Oceanics model 8050) was operated by a colleague at the University of Manitoba, Prof. Tim Papakyriakou, and his students on the Canadian Coast Guard Ship (CCGS) and icebreaker Amundsen as it made its way through the Gulf of St. Lawrence to the Arctic Ocean for a scientific survey in early June 2016. Unfortunately, although the vessel left from its port-of-call in Québec City, the system was not turned on until well into the Gulf of St. Lawrence (near Anticosti Island) and through the Strait of Belle Isle. When in operation, the system was continuously sampling water from a high-volume inlet located at a depth of 5 m. Water was cycled through the underway system at a rate of 2.4 – 2.8 L min⁻¹ and calibrations of the system's infrared gas analyzer (LI-COR model LI-7000) were monitored twice daily against three certified gas standards traceable to WMO standards. The underway system has an expected accuracy of 2 μatm (Pierrot et al., 2009). The underway $p\text{CO}_2$ measurements near Anticosti Island were in good agreement with the $p\text{CO}_2$ values calculated in this study, for neighboring locations sampled in May 2016 aboard the RV Coriolis II (see the appended Fig. 3). Measured and calculated $p\text{CO}_2$ differed by, on average, ~4.2 %.

Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Lüger, T. Johannessen, A. Olsen, R. A. Feely, and C. E. Cosca (2009), Recommendations for autonomous underway $p\text{CO}_2$ measuring systems and data-reduction routines, *Deep. Res. Part II*, 56(8-10), 512- 522, doi:10.1016/j.dsr2.2008.12.005.

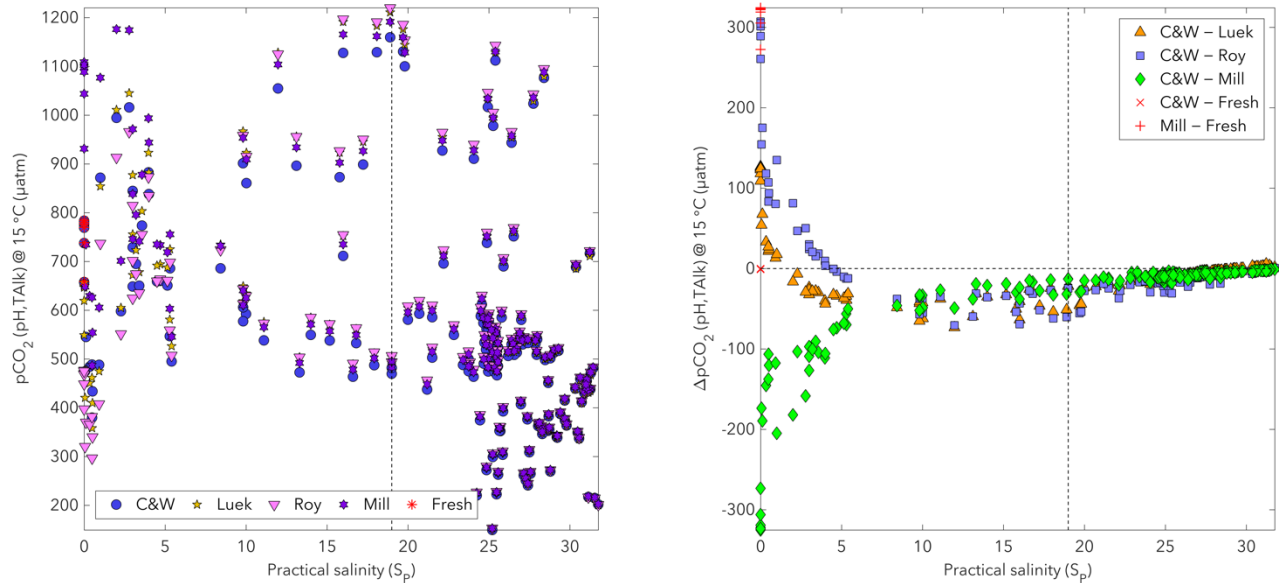


Fig. 2. Calculated values of pCO₂ using different published formulations of K₁ and K₂ including Cai and Wang (1998) [C&W], Lueker et al. (2000) [Luek], Roy et al. (1993) [Roy], Millero (2010) [Mill], and Millero (1979) for pure water only (S_P = 0) [Fresh]. All calculations were carried out at 15 °C (pCO₂ @ 15 °C) with measured pH and TALK.

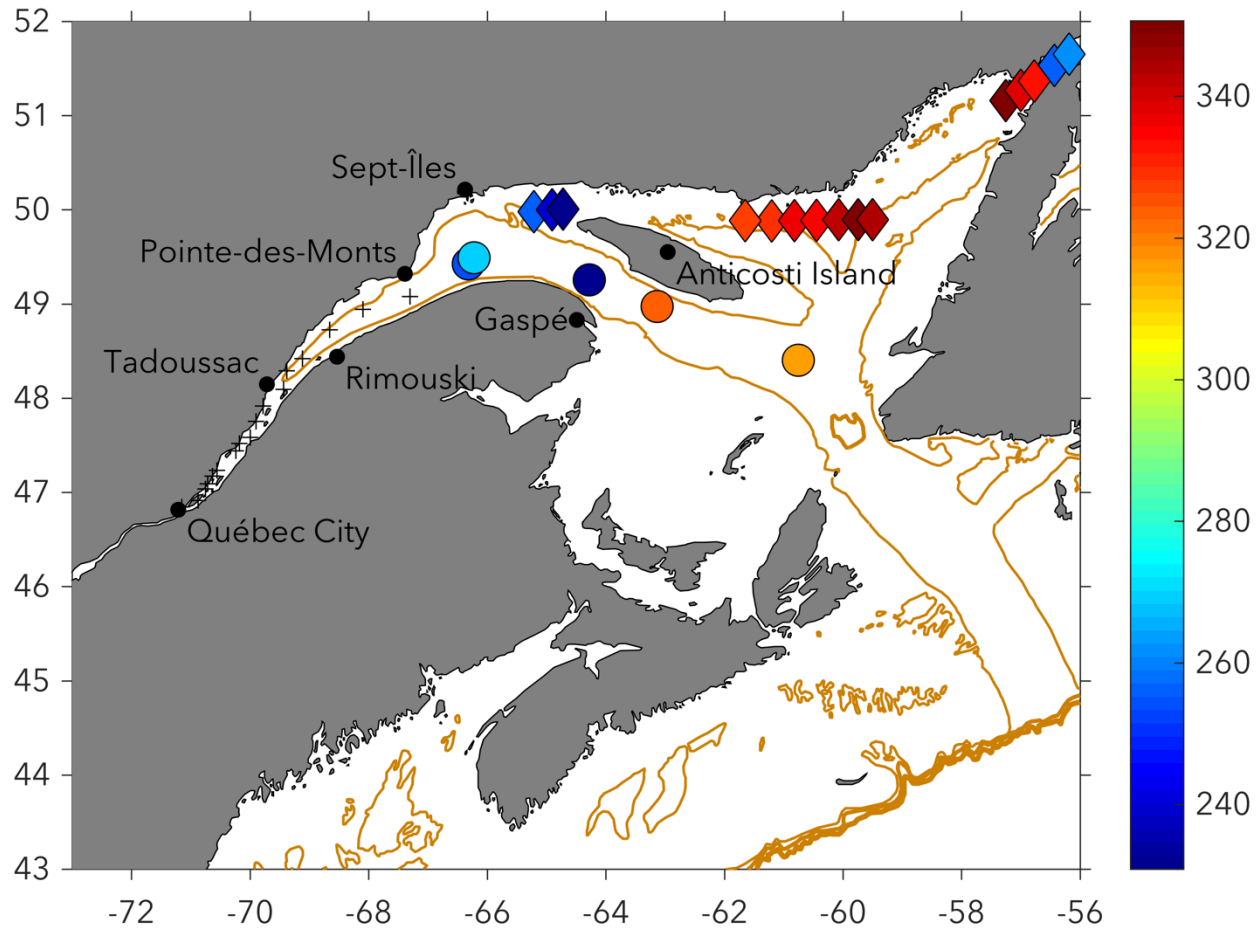


Fig. 3. Spatial distribution of surface-water pCO₂ (µatm) in the Gulf of St. Lawrence during Spring 2016. The circles show pCO₂ calculated from the data collected aboard the RV Coriolis II (May 2016), whereas the diamonds show pCO₂ measured from the underway system aboard the CCGS Amundsen (June 2016). The + symbols show all sampling locations during the May 2016 RV Coriolis II cruise.

3: Gulf of St Lawrence and another systems. While the river runoff into the Gulf of St Lawrence in North America is only second to the Mississippi system, its runoff is of similar magnitude than the one into the North Sea (300km³ per year, e.g Thomas et al., 2005), and about two thirds of the runoff into the Baltic Sea (500km³ per year). I furthermore think, a comparison with the well-studied Baltic Sea would be enlightening here as the Baltic is similarly located at the boundary between subarctic and temperate regions and is a (comparably) similar estuarine system.

We thank the reviewer for bringing to our attention the study describing the carbon budget of the North Sea. The authors indicate that the North Sea acts as a net CO₂ sink, absorbing 1.38 mol C m⁻² yr⁻¹ from the atmosphere (Thomas et al., 2005). The North Sea contrasts with the St. Lawrence Estuary, which outgasses 0.37 to 0.75 mol

$\text{C m}^{-2} \text{ yr}^{-1}$ during the late spring and early summer (i.e., at the height of biological productivity). As noted by the reviewer, this is an interesting comparison to make as both systems are marine-dominated and seasonally stratified.