We thank the Associate Editor for the opportunity to make revisions to our manuscript in review by *Biogeosciences*. All (three) referee's comments are in italics, our responses are in bold, and our comments to the Associate Editor are in red. Any so-called "appended figure" can be viewed in the Interactive discussion.

In order for the results to be more useful to other users I recommend that the average fluxes also be given according to different salinity ranges. The results are now given for the upper and lower estuaries as well as the gulf. Should the average fluxes be given over different salinity ranges the results would be easier to be integrated into the global carbon flux.

Given the physiography (funnel shape) and the large physical dimensions of the maritime portion of the St. Lawrence Estuary, we pursued an analysis of surface-water pCO_2 and CO_2 flux data in terms of space rather than salinity. With 75% of its total surface area occupied by the Lower Estuary (Tadoussac to Pointe-des-Monts, S > ~21.2), it is more realistic to integrate/weight the fluxes spatially than to provide average fluxes binned by salinity, in order to obtain a representative whole-estuary flux. Furthermore, as you can appreciate from the appended figure (see Fig. 1), active processes along the estuary are not as clearly defined when the data are plotted as a function of surface salinity. Whereas the plot still shows that the Upper Estuary (S < ~24.5; surface salinity fluctuations are found around the Upper-Lower Estuary boundary due to tidally-induced upwelling of salty intermediate/bottom waters) is heterotrophic, it fails to highlight the autotrophic character of the Lower Estuary and the neutral character of the Gulf, the latter being substantially larger in surface area than the combined Upper and Lower Estuaries but contributing little to the net CO_2 flux.

This is addressed by lines 672–675 in the revised manuscript.

Besides, dividing data into only three geographical regions misses an important feature. That is, the undersaturation of CO2 between the 300-600km stretch is neither noted nor discussed. Does the undersaturation correspond to the large river plume where undersaturation is frequently found(see Chen et al., 2012)? Would dividing the data according to salinity better characterize the data?

As noted in lines 643-649, we suggest that biological production is responsible for the observed drawdown of pCO2 in the surface waters of the Lower Estuary as well

as the undersaturation observed near the Estuary-Gulf boundary (i.e., along the 300–600 km stretch).

This is addressed by lines 924–926 in the revised manuscript.

Two minor points: The red line and the dashed black line in Fig. 9 should be identified. Line 41: the fact that the release of CO2 from estuaries is balanced by the absorption of CO2 from shelves was first reported by Chen and Borges(2009) prior to the two references given.

We agree with the reviewer's comment that this needs to be explicitly stated in the revised manuscript. We will identify the red (smoothed temperature data using a moving average filter with a span of 50% of the total number of data points) and dashed (smoothed pCO2(water) data) lines in the Fig. 9 caption, and add the appropriate reference to line 41 in the revised manuscript.

This is addressed by lines 1692–1694 in the revised manuscript.

Page 2 (lines 39-40): The emissions of 0.25 Pg C yr-1 proposed by Regnier et al. (2013) are based on Laruelle et al. (2010) and Cai (2011). Please include this information. See also Chen et al. (2013) and Laruelle et al. (2013), with updated values (0.10 Pg C yr-1).

> *Laruelle et al. (2013). Global multi-scale segmentation of continental and coastal waters from the watersheds to the continental margins. Hydrol. Earth Syst. Sci., 17, 2029–2051.*

We will add the appropriate reference to line 40 in the revised manuscript.

This is addressed by line 48 in the revised manuscript.

Page 2 (lines 42-43): Yes, and I agree. However, studies conducted in marine-dominated estuaries showed that they can present pCO2 values below 400 ppmv and a sink behavior. Please, check Koné et al. (2010); Maher and Eyre (2012), Cotovicz Jr. et al (2015).

> *Koné et al. (2009). Seasonal variability of carbon dioxide in the rivers and lagoons of Ivory Coast (West Africa). Estuar. Coast., 32, 246–260, 2009.*

Maher and Eyre (2012). Carbon budgets for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO2 flux. Global Biogeochem. Cy., 26,GB1032.

Cotovicz Jr. et al. (2015). A strong CO2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil). Biogeosciences, 12, 5125-6146.

Marine-dominated estuaries are briefly discussed in the Introduction in lines 91-99. Although they are underrepresented in data compilations, some behave as net CO_2 sinks. This will be explicitly stated in the revised manuscript and supported by the recommended references.

This is addressed by lines 127–129 in the revised manuscript.

Page 3 (lines 76-78): Please check Borges and Abril (2011) to see details about the drivers of the emissions of CO2 to the atmosphere from estuaries.

Borges, A. V. and Abril, G.: Carbon Dioxide and Methane Dynamics in Estuaries, in: Treatise on Estuarine and Coastal Science, edited by: Eric, W. and Donald, M., Academic Press, Amsterdam, 119–161, 2011.

We thank the reviewer for the referral to Borges and Abril (2011). By analyzing a data set of nine European and two US estuaries, the authors concluded that 10 % of the total emission of CO_2 from inner estuaries could be attributed to the ventilation of riverine CO_2, whereas 90 % of the emission could be attributed to net heterotrophy. These two main drivers of estuarine CO_2 degassing are noted in lines 76-80 of this manuscript. Borges and Abril (2011) also detailed the relationship between freshwater residence time and the relative contribution of riverine CO_2 ventilation. This will be addressed in the revised manuscript.

This is addressed by lines 99–101 in the revised manuscript.

Page 3 (lines 91-95): I think that the most overlooked estuarine typology regarding CO2 emissions are the marine-dominated estuaries.

We agree with the reviewer on this point.

This is addressed by line 115 in the revised manuscript.

Page 4 (lines 119-121): I would like to know about the wintertime period. Did you perform sampling campaigns at this period? Could you give some discussion about this?

With the exception of the 2016 cruise, water samples used in this work were obtained opportunistically on research cruises conducted during the spring and summer seasons. The Estuary and the Gulf are typically covered by ice during the winter months. Coast Guard icebreakers keep shipping lanes open during the winter, but, even though we have been offered berths onboard, the icebreakers will not stop for discrete water sampling. Hence, there is no data for the winter season. We have recently submitted, under a newly-created program, a multimillion-dollar proposal that would provide us with dedicated time on an icebreaker during the wintertime and, possibly, a vessel (CCGS Amundsen) equipped with an underway pCO_2 system.

This is addressed by line 278 in the revised manuscript.

Page 6 (lines 202-203): And also vertically, not?

The Upper Estuary is strongly laterally stratified, but because is it generally shallow and, due to the turbulence generated by tides, winds, and waves interacting with the bottom topography, it is only very slightly vertically stratified. In contrast, the Lower Estuary, because it is much deeper, is strongly vertically stratified. See the appended Fig. 1.

This is addressed by line 257 in the revised manuscript.

Page 7 (lines 225-228): Please, provide more details about the sampling strategy. What is the vertical resolution (water column) of the sampling? How many samples did you take each year? How many samples did you take adding all campaigns?

As the present work focuses on the inorganic carbon chemistry of the surface mixed layer, the total number of surface-water samples (N) taken from the River, Upper Estuary, Lower Estuary, and Gulf are summarized in Table 2. Nevertheless, in all cases the whole water column was sampled, typically at 3 m, 20 m, 50 m, 70 m, 100 m and at 50m intervals to the bottom (or within 10 m of the bottom). These data will be presented in a subsequent manuscript in which the geochemical and isotopic

characteristics of source-water masses and their relative contributions to the Estuary will be examined.

This is addressed by lines 279–283 in the revised manuscript.

Page 8 (lines 240-244): Did you filter the water for the total alkalinity measurements? Previous works showed that for coastal waters the phytoplankton and bacterial cells can affect the measured alkalinity of unfiltered samples (Kim et al. 2006; Chanson and Millero, 2007). Do you have information about the particulate inorganic content (e.g., CaCO3) of the sampled waters? Please, see Kim et al. (2006) and Chanson and Millero (2007) about this problematic.

> *Kim et al. (2006). Contribution of phytoplankton and bacterial cells to the measured alkalinity of seawater. Limnol. Oceanogr. 51 (1), 331-338.*
>
> *Chanson and Millero (2007). Effect of filtration on the total alkalinity of open-ocean seawater. Limnol. Oceanogr.: Methods 5, 293–295.*

The sampling protocol we used is standard for TAlk and DIC measurements in open ocean waters (Dickson and Goyet, 1994). Hence, our samples were not filtered, but when SPM concentrations were high (in the turbidity maximum of the Upper Estuary), the SPM was allowed to settle for several days before the supernatant was sampled for analysis. Previous experiments with filtered and unfiltered samples revealed that results were identical within the analytical uncertainty (±2 µmol/kg) of our measurements.

The phytoplankton community composition in the study area is strongly dominated by diatoms (Devine et al., 2015). There is no significant population of pelagic carbonate-secreting organisms (coccolithophores, foraminifera, pteropods) in the St. Lawrence Estuary and Gulf. Emiliania huxleyi (coccolithophore) can be found at relatively low concentrations (maximum of ~10^7 coccoliths/L) in the upper mixed layer in the Gulf and in the Strait of Belle Isle, while small specimens of Limacina helicina (pteropod) have been found in very low abundance (maximum of 18 individuals/m^2) in the Strait and in the Gulf (Levasseur et al., 1994; Cantin et al., 1996; Levasseur et al., 1997). Detrital carbonates are eroded from the Silurian-Ordovician deposits of Anticosti Island in the Gulf, but our sampling was carried out far from the source.

Dickson, A. G. and Goyet, C. (Eds.): Handbook of Methods for the Analysis of the Various 800 Parameters of the Carbon Dioxide System in Sea Water (Version 2), U.S. Department of Energy, 801 ORNL/CDIAC-74, 1994.

Devine, L., Plourde, S., Starr, M., St-Pierre, J.-F., St-Amand, L., Joly, P., and Galbraith, P. S.: Chemical and biological oceanographic conditions in the Estuary and Gulf of St. Lawrence during 2013, DFO Can. Sci. Advis. Sec. Res. Doc., 2015/013, 45 pp., 2015.

Levasseur, M., Keller, M. D., Bonneau, E., D'Amours, D., and Bellows, W. K.: Oceanographic basis of a DMS-related Atlantic cod (Gadus morhua) fishery problem: blackberry feed, Can. J. Fish. Aquat. Sci., 51, 881–889, 1994.

Cantin, G., Levasseur, M., Gosselin, M., and Michaud, S.: Role of zooplankton in the mesoscale distribution of surface dimethylsulfide concentrations in the Gulf of St. Lawrence, Canada, Mar. Ecol.-Prog. Ser., 141, 103–117, 1996.

Levasseur, M., Sharma, S., Cantin, G., Michaud, S., Gosselin, M., and Barrie, L.: Biogenic sulfur emissions from the Gulf of Saint Lawrence and assessment of its impact on the Canadian east coast, J. Geophys. Res.-Atmos., 102, 28025–28039, 1997.

This is addressed only in the Interactive discussion.

Page 10 (lines-315-327): This paragraph is confused. As you said before "The samples were taken at 3 m…", then why no use this depth for the individual data points of surface-water pCO2 at each sampling location? It is not clear what data were averaged.

For each sampling station, data points in the surface mixed layer (SML), which exchanges heat and gases (e.g., CO_2) with the overlying atmosphere, were averaged. Given limited sampling in surface waters above the cold intermediate layer, the mixed-layer dataset at each station was most often limited to a single sample (from ~2 or ~3m depth), although, in a few cases, it included a sample taken at ~10m depth.

This is addressed by lines 281–283 in the revised manuscript.

Page 10-11 (lines 331-348): This is an important section showing that your results at the low salinity region (0-5) can be overestimated or underestimated. This depends of the formulations of K1 and K2. Could you give more details about this? Did you perform direct pCO2 measurements to compare results? What values of pH and TAlk did you use for the Figure 3? Please include this information in the figure caption.

As noted in lines 301-306, the pCO_2 values used in this work were calculated from the measured pH and TAlk, using the carbonic acid dissociation constants, K_1 and K_2, of Cai and Wang (1998). Whereas we have occasionally carried out DIC measurements on the water samples, direct pCO_2 measurements were not carried out as we do not have access to the proper equipment. We agree with the reviewer that direct pCO_2 measurements would have been desirable to confirm the accuracy of the pCO_2 calculations.

An underway pCO_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 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 pCO_2 measurements near Anticosti Island were in good agreement with the pCO_2 calculated in this study, for neighboring locations sampled in May 2016 aboard the RV Coriolis II (see the appended Fig. 2). Measured and calculated pCO_2 differed by, on average, ~4.2 %.

For the comparison of dissociation constants (results presented in Figure 3), values of pCO_2 were calculated at a constant temperature of 15 °C, at the measured pH and TAlk, using different published formulations of K_1 and K_2: Cai and Wang (1998), Lueker et al. (2000), Roy et al. (1993), Millero (2010), and Millero (1979) for pure water only. This is noted in the Figure 3 caption, lines 1163-1167.

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 pCO_2 measuring systems and data-reduction routines, Deep. Res. Part II, 56(8-10), 512–522, doi:10.1016/j.dsr2.2008.12.005.

This is addressed by lines 382–383, 422–424, and 1617–1621 in the revised manuscript.

Page 11 (lines 362-363) and Page 12 (lines 385): Could you describe the methodology for DIC analyses?

As noted in lines 301-306, most DIC values were calculated from the measured pH and TAlk, using the K_1 and K2 of Cai and Wang (1998). These calculated DIC values, along with the measured TAlk, were used to temperature-normalize the pCO_2, according to the method of Jiang et al. (2008).

Direct DIC measurements were carried out during the 2014 cruise using a Scitech Apollo DIC analyzer. After being thermostated at 25 °C, 1–1.5 mL of the sample was injected into the instrument's reactor where it was acidified with 10 % H_3PO_4 and the evolved CO_2 carried by a stream of pure nitrogen to a LICOR infrared analyzer. A calibration curve was constructed using gravimetrically-prepared Na_2CO_3 solutions, and the accuracy of the measurements was verified using certified reference material solutions provided by Andrew Dickson (Scripps Institute of Oceanography). The reproducibility of the measurements was typically on the order of 0.2 %. Results of the direct DIC and pH measurements were used to assess the contribution of organic alkalinity to the total alkalinity in the Upper Estuary. The latter was found to be negligible (~–20 µmol/kg) relative to TAlk within the freshwater end-member (St. Lawrence River) and decreased seaward with increasing salinity along the Upper Estuary. Hence, measured and calculated DIC values were compatible. The DIC analytical methodology will be added to the revised manuscript.

This is addressed by lines 342–351 in the revised manuscript.

Page 14 (lines 466-474): Do you think that hourly wind speed data averaged over the sampling month is a good approach to obtain a transfer velocity? Did you compare the hourly data average with other approach (minute/10minutes average wind speed) to investigate differences?

As the wind speed data used in this work were obtained from an external source (Environment Canada), we were limited to the data intervals of hourly, daily, or

monthly. Average hourly wind speed data served as our best proxy for the steady (short-term) wind speed required by the equation of Wanninkhof (lines 460-461), which is applicable to estimate the gas transfer velocity from instantaneous wind speed measurements, using, for example, shipboard anemometers. The wind speeds provided by Environment Canada are observed from an anemometer.

It should be noted that shipboard measurements of instantaneous wind speed were available from the ship's log, but only for a limited number of stations from the 2010 and 2013 cruises. We elected to use the historical hourly weather data from Environment Canada for two reasons: (1) the data was more complete across time, and (2) the location of observing stations was consistent across space.

This is addressed only in the Interactive discussion.

Pages 15 and 16 (section 2.6) : The approach of Carrillo et al. (2004) is a good way to compare the distributions and controls of biologically reactive dissolved gases. However, I also suggest compare the Apparent Oxygen Utilization (AOU) (Benson and Krause, 1984) with the Excess of DIC (E-DIC) (Abril et al 2003) that was applied in wide typologies of estuarine systems (e. g., Borges and Abril, 2011). Maybe you can compare the two approaches.

The DO percent saturation (%DO(sat)) values used in this study were calculated as: %DO(sat) = DO/DO* x 100, where DO is the measured DO and DO* is the equilibrium DO computed from the equation of Benson and Krause (1984). Similarly, AOU is defined as: AOU = DO* – DO. Hence, we would expect the two approaches to yield similar results, and, in fact, they do, with the majority of data from the Upper Estuary showing the signature of respiration and the majority of data from the Lower Estuary and Gulf showing photosynthesis. See the appended Fig. 3.

This is addressed by lines 722–726 and by the updated Fig. 8 in the revised manuscript.

Page 17 (lines 559-568): Do you have results of chlorophyll a concentrations? Do you have the results of column water stratification at this region? It's clear that the region of SLE near Pointe-des-Monts (between Tadoussac and Anticosti Island) present the pCO2 values lower than atmospheric pCO2 for all sampling campaigns. I think that some results of chlorophyll a and/or primary production could better support your discussion. I think you should include more discussion.

Whereas direct measurements of chlorophyll-a concentrations were not carried out during the research cruises, a fluorescence sensor was mounted on the CTD probe. Maximum fluorescence values measured in the euphotic zone at each sampling station are shown in the appended Fig. 4. Mean values of transmission (% light transmission) are also shown in Fig. 4. Low transmission values are due to light absorption by suspended particulate matter and colored dissolved organic matter, the latter being negligible in our study area. The maximum fluorescence values, along with high transmission values approaching 100%, were observed in the eastern Lower Estuary and western Gulf, where the system shifts from net heterotrophy to net autotrophy. Hence, these data further support our original interpretations.

The water column is strongly stratified in the Lower Estuary and the Gulf, which enhances biological production as discussed in lines 560-566. See the appended Fig. 1 for vertical profiles of temperature and salinity.

This is addressed by lines 985–990 in the revised manuscript.

Page 17 and 18 (lines 570-580): Could you give comparisons with other studies?

Hunt et al. (2014) indicate that temperature variability is one of the major controlling factors of seasonal changes in pCO_2 in the Kennebec Estuary, a large, river-dominated, macrotidal estuary. Had we been able to assess the temporal variability of pCO_2 in the St. Lawrence Estuary throughout the year (e.g., from summer to winter), we would expect that temperature exerts more control on the pCO_2 changes, due to larger seasonal temperature variability as well as the absence of phytoplankton blooms in winter.

This is addressed only in the Interactive discussion.

Page 18 (lines 606-608): Previous studies identified CO2 sink behavior in estuaries. Please see Koné et al (2010); Maher and Eyre (2012); Cotovicz Jr et al (2015).

We thank the reviewer for bringing these studies to our attention as they demonstrate that some estuarine systems (e.g., those characterized by strong stratification and/or marine dominance) behave as net CO_2 sinks rather than CO_2 sources. We will refer to these studies in the revised manuscript.

This is addressed by lines 128–130 in the revised manuscript.

Page 18 and 19 (Section 3.2): Please, provide comparisons of CO2 fluxes with other studies. Could you identify in the Figure 1 (or other) each segment considered in this study to the calculations of the area-averaged air-sea CO2 fluxes?

We agree with the reviewer's comment that the segmentation of the Estuary for the calculation of the area-averaged CO_2 flux should be shown on a map of the study area. See the appended Fig. 5, which will be used in the revised manuscript.

This is addressed by lines 1570–1571 in the revised manuscript.

Page 19 (lines 628-631): The biological activity can also drawdown the DIC concentrations in water column.

Photosynthesis is mentioned in line 628, but we agree with the reviewer's comment that the biological removal of DIC could be explicitly stated in line 629.

This is addressed by line 910 in the revised manuscript.

Page 20 (lines 645-651): In this section you can find other estuaries that acts as CO2 sink. Also, I think you could search in literature other papers that compared the biological x temperature effects over pCO2 concentrations to better contextualize you work (Bozec et al.,2011; Zhang et al., 2012; Hunt et al., 2014; Cotovicz Jr et al., 2015).

Bozec et al. (2011). Diurnal to inter-annual dynamics of pCO2 recorded by a CARIOCA sensor in a temperate coastal ecosystem (2003–2009). Mar. Chem., 126, 13–26.

Zhang et al. (2012). Distribution and seasonal variation in the partial pressure of CO2 during autumn and winter in Jiaozhou Bay, a region of high urbanization. Mar. Pollut. Bull., 64, 56–65.

Hunt et al. (2014). CO2 Input Dynamics and Air–Sea Exchange in a Large New England Estuary. Estuar. Coast., 37, 1078–1091.

The relative importance of physical and biological controls on spatial variations of surface-water pCO_2 in the St. Lawrence Estuary will be more rigorously examined in

a follow-up manuscript, by applying a quantitative water-mass analysis to remove the effect of physical mixing on the pCO_2 observations.

This is addressed by lines 914–916 in the revised manuscript.

Figure 4: Could you move the legend of Figure 4 to outside the graph? Some points in the graph are over the lines of the axis. I suggest increase the ranges of the axis to put these points totally inside the graph. Also, it's evident that the GSL was sub-sampled compared to the USLE and LSLE regions. I think that it's important write about this in the methodological and discussion sections.

We agree with the reviewer's comment that the legend should be moved outside of the graph for improved readability, and the x-axis extended to encompass all data points.

The Gulf is sub-sampled in comparison to the Estuary because it is so large (~240,000 km^2 to the Estuary's ~12,820 km^2) and exhibits less variability.

This is addressed by the updated Fig. 4 in the revised manuscript.

Figure 9: Some points in the graph are over the lines of the axis. I suggest increase the ranges of the axis to put these points totally inside the graph.

We agree with the reviewer's comment that the x-axis should be extended to encompass all data points.

This is addressed by the updated Fig. 9 in the revised manuscript.

Table 3: I am not sure that the segments that you used to calculate the air-sea CO2 fluxes was the better division. Other graphs showed the results separated in river, upper, lower and gulf regions and maybe you can present the fluxes according.

The Estuary was divided into five equal segments to obtain a representative spatially-integrated whole-estuary CO_2 flux. Given that the Lower Estuary (Tadoussac to Pointe-des-Monts) occupies ~75 % of the total estuarine surface area, and encompasses a fairly wide range of pCO_2 values (standard deviation of 117 µatm), we decided to segment by longitude rather than salinity to, more realistically, area-normalize the sectional fluxes (see Fig. 5).

This is addressed by lines 675–678 in the revised manuscript.

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 that 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 pCO_2 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 pCO_2 in the Upper Estuary.

Telmer, K., and Veizer, J.: Carbon fluxes, pCO_2 and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives, Chemical Geology, 159, 61–86, 1999.

This is addressed by lines 912–914 in the revised manuscript.

2: I appreciate the discussion of the uncertainty associated with the computation of the pCO2 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 pCO2 results themselves, and only then their differences. Also, while I am aware that the authors did not measure pCO2 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 pCO_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 pCO_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 pCO_2 measurements would have been desirable to confirm the accuracy of the pCO_2 calculations, particularly at low salinities. An underway pCO_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 pCO_2 measurements near Anticosti Island were in good agreement with the pCO_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 pCO_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 pCO_2 measuring systems and data-reduction routines, Deep. Res. Part II, 56(8-10), 512– 522, doi:10.1016/j.dsr2.2008.12.005.

This is addressed by lines 1617—1621 in the revised manuscript.

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 CO_2 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 C m^{-2} 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.

This is addressed only in the Interactive discussion.

Spatial variability of surface-water pCO_2 and gas exchange in the world's largest semi-enclosed estuarine system: St. Lawrence Estuary (Canada)

Ashley Dinauer[1] and Alfonso Mucci

GEOTOP and Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, QC H3A 0E8, Canada

[1] Corresponding author (ashley.dinauer@mail.mcgill.ca)

Abstract

The incomplete spatial coverage of partial pressure of CO_2 (pCO_2) measurements across estuary types represents a significant knowledge gap in current regional- and global-scale estimates of estuarine CO_2 emissions. Given the limited research on CO_2 dynamics in large estuaries and bay systems, as well as the sources of error in the calculation of pCO_2 (carbonic acid dissociation constants, organic alkalinity contribution), estimates of estuarine CO_2 degassing may be overestimated. The Estuary and Gulf of St. Lawrence (EGSL) at the lower limit of the subarctic region in eastern Canada is the largest estuarine system in the world, and is characterized by an exceptional richness in environmental diversity. It is among the world's most intensively studied estuaries, yet there are no published data on its surface-water pCO_2 distribution. To fill this data gap, a comprehensive dataset was compiled from direct and indirect measurements of carbonate system parameters in the surface waters of the EGSL during the spring or summer of 2003–2016. The calculated surface-water pCO_2 ranged from 435–765 µatm in the shallow, partially mixed Upper Estuary, 139–578 µatm in the deep, stratified Lower Estuary, and 207–478 µatm along the Laurentian Channel in the Gulf. Overall, at the time of sampling, the St. Lawrence Estuary served as a very weak source of CO_2 to the atmosphere, with an area-averaged CO_2 degassing flux of 0.98 to 2.02 mmol C m^{-2} d^{-1} (0.36 to 0.74 mol C m^{-2} yr^{-1}). A preliminary analysis of factors controlling the spatial variability of surface-water pCO_2 revealed that respiration (Upper Estuary), photosynthesis (Lower Estuary), and temperature (Gulf) were dominant controls.

Keywords:
Coastal ocean, Estuaries, CO_2, Carbon cycle, Air-sea CO_2 exchange, St. Lawrence Estuary, Gulf of St. Lawrence, Laurentian Channel

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1. Introduction

Although estuaries occupy a very small fraction (0.2 %) of the global ocean surface area, their CO_2 emissions are disproportionately large compared with CO_2 exchanges between the open ocean and the atmosphere (Bauer et al., 2013). With an estimated global efflux of 0.10–0.15 Pg C yr^{-1} (Chen et al., 2013; Laruelle et al., 2013), estuarine CO_2 degassing is thought to counterbalance CO_2 uptake on the continental shelves (Chen and Borges, 2009; Laruelle et al., 2010; Cai, 2011). Almost every estuary on Earth, for which data are available, is generally supersaturated with CO_2 with respect to the atmosphere (Cai and Wang, 1998; Frankignoulle et al., 1998; Borges, 2005; Borges et al., 2005; Borges et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010; Cai, 2011; Chen et al., 2012; Bauer et al., 2013; Chen et al., 2013; Regnier et al., 2013), with CO_2 partial pressures (pCO_2) ranging from 400 to 10,000 µatm (in contrast, the atmospheric pCO_2 in coastal zones was approximately 360–385 µatm in year 2000) (Cai, 2011). Although estuaries are generally net sources of CO_2, there is considerable variability and uncertainty in estimates of their CO_2 emissions, reflecting the limited spatial and temporal coverage of pCO_2 measurements in estuaries as well as their heterogeneous nature (hydrological and geomorphological differences, differences in magnitude and stoichiometry of carbon and nutrient inputs) (Bauer et al., 2013; Regnier et al., 2013).

Estuaries are geochemical reaction vessels through which continentally weathered organic matter and inorganic nutrients must pass to enter the coastal ocean (Kaul and Froelich, 1984). Horizontal transport is controlled by a set of physical attributes (tides, wind, bathymetry, basin geography, river flow) that determine the estuarine filter function (Cloern, 2001). The longer the freshwater flushing (or turnover) time of the estuary, the more opportunity there is for water-column biological activity, benthic exchanges and particle-dissolved phase interactions to influence its biogeochemistry (Statham, 2012). DIC enrichments and pCO_2 supersaturations observed in estuaries can be mainly attributed to the *in situ* microbial degradation of internally and externally supplied organic carbon and the lateral transport of inorganic carbon from rivers, coastal wetlands and ground waters (Bauer et al., 2013).

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In strongly tidal (macrotidal) systems, long water and particle residence times (on the order of weeks to months; Middelburg and Herman, 2007) allow for the extensive modification and degradation of particulate organic carbon during estuarine transport (Borges et al., 2006; Chen and Borges, 2009). In the absence of seasonal or permanent water stratification, the decoupling between production and degradation of organic matter at and below the surface, respectively, does not occur, resulting in less efficient export of dissolved inorganic carbon (Borges, 2005). Strongly tidal estuaries also tend to exhibit lower levels of photosynthetic activity (Monbet, 1992) and carry greater suspended particulate matter loads within their high-turbidity regions (Uncles et al., 2002; Middelburg and Herman, 2007) wherein suspended particles and organic-rich aggregates serve as "hot spots" of microbial recycling (Statham, 2012). Field measurements suggest that 10 % of the total CO_2 emissions from the inner estuary of macrotidal systems is sustained by the ventilation of riverine CO_2, whereas 90 % is due to local net heterotrophy (Borges et al., 2006) fueled by inputs of terrestrial and riverine-algae derived (planktonic) detritus and, in populated areas, sewage (Chen and Borges, 2009). In estuaries with long freshwater residence times, the riverine CO_2 will be fully ventilated to the atmosphere within the estuary, and the total CO_2 emissions can be attributed to net heterotrophy (Borges and Abril, 2011).

North American estuaries rank first in terms of global estuarine surface area (41 %) but account for the lowest numerically averaged CO_2 flux per unit area (12 %) among all continents (Chen et al., 2013). These estimates are subject to large uncertainties due to data paucity. A recent synthesis by Regnier et al. (2013) highlighted the meagre spatial coverage of estuarine pCO_2 measurements, particularly along the Canadian eastern seaboard. Ironically, the Estuary and Gulf of St. Lawrence (EGSL) in eastern Canada is the largest semi-enclosed estuarine system in the world, and is among the world's most intensively studied estuaries (El-Sabh and Silverberg, 1990), but was left unmentioned in recent global (Cai, 2011; Chen et al., 2012; Chen et al., 2013) and regional (Laruelle et al., 2015) data compilations. Furthermore, previous estuarine CO_2 studies have focused on small river-dominated estuaries, whereas there has been limited research on CO_2 dynamics in large estuaries and bays (Joesoef et al., 2015), i.e., marine-dominated systems, including the areas of mixing at sea (outer estuaries or river plumes) (Borges et al., 2005). A comparative study by Jiang et al. (2008) revealed large differences in CO_2 degassing between non-

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riverine and river-dominated estuaries and, more recently, Koné et al. (2009), Maher and Eyre (2012) and Cotovicz Jr. et al. (2015) reported small CO_2 uptake by strongly stratified and/or marine-dominated systems. On the U.S. east coast, the ratio of non-riverine (flushed by tidal action and receiving minimum freshwater inputs) to river-dominated estuaries is nearly 1:1, demonstrating the geographic importance of coastal estuaries/bays on the eastern seaboard of North America (Cai, 2011).

The large-scale (width often considerably greater than the internal Rossby radius; Cyr et al., 2015), macrotidal (mean tidal range greater than 2–4 m; Monbet, 1992) St. Lawrence Estuary is an excellent analogue of marine-dominated systems. Throughout its length, the full spectrum of oceanic variability can be found (Mertz and Gratton, 1990). Moreover, the basin characteristics and water transport time scales of the St. Lawrence Estuary provide an almost ideal natural laboratory for geochemical studies. Its surface waters have a renewal time of several months while its bottom waters take several years to replenish, allowing for a comparison of spatial-temporal variations in physical and chemical properties (El-Sabh and Silverberg, 1990). Given its bimodal bathymetry, the St. Lawrence Estuary also permits the investigation of biogeochemical processes in two types of estuary: (1) the shallow, partially mixed Upper Estuary where physical mixing and abiotic processes dominate, and (2) the deep, stratified Lower Estuary where biological cycling and oceanic processes prevail (Yeats, 1990). As yet, no systematic study of the CO_2 dynamics in the St. Lawrence has been published and, hence, the present study provides the first comprehensive description of its mixed-layer carbonate chemistry, including (1) a multi-year compilation of springtime and summertime pCO_2 calculated from direct measurements of pH and alkalinity; (2) an area-averaged estimate of the air-sea CO_2 gas flux; and (3) an analysis of the relative importance of thermodynamic (temperature) and biological (photosynthesis, respiration) processes in controlling the spatial variability of surface-water pCO_2.

2. Materials and methods

2.1. Study area—St. Lawrence Estuary and Gulf

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The greater St. Lawrence system (Fig. 1) connects the chain of Great Lakes, the second largest terrestrial freshwater reservoir in the world, to the Atlantic Ocean (Yang et al., 1996). With a drainage basin of approximately 1.32 million km^2, the St. Lawrence River channels the second largest freshwater discharge (11,900 m^3 s^{-1}) on the North American continent, second only to that of the Mississippi (El-Sabh and Silverberg, 1990). The catchment area geology is dominated by silicate rocks of the Precambrian Shield and carbonates of the Paleozoic lowlands, whose components influence the downstream evolution of river chemistry (Yang et al., 1996). The erosion of the carbonate rocks of the drainage basin is practically constant, as the quantity of bicarbonate ions carried by the river varies little from season to season (Pelletier and Lebel, 1979). On a yearly basis, between 15–20 % of the outflow of dissolved inorganic carbon from the St. Lawrence River into its estuary originates from the system's tributaries (e.g., Ottawa River, Mascouche River) while 80–85 % is from the Great Lakes (Hélie et al., 2002). The St. Lawrence Estuary (SLE) begins at the landward limit of the salt water intrusion near Île d'Orléans (~5 km downstream of Québec City) and stretches 400 km seaward to Pointe-des-Monts where it widens into the Gulf of St. Lawrence (GSL) (El-Sabh and Silverberg, 1990), a semi-enclosed sea with an area of approximately 240,000 km^2 (Dufour and Ouellet, 2007) connected to the Atlantic Ocean through Cabot Strait and the Strait of Belle Isle (Coote and Yeats, 1979).

Traditionally, the SLE is divided into two segments based on its bathymetry and hydrographical features (Ingram and El-Sabh, 1990). The Upper St. Lawrence Estuary (USLE), from Île d'Orléans, where the estuarine circulation begins, to Tadoussac, near the mouth of the Saguenay Fjord, covers an area of 3,470 km^2. It is relatively narrow (2 to 24 km wide) and mostly shallow (depths less than 30 m; d'Anglejan, 1990), and features an uneven, fairly complex bottom topography characterized by several disconnected channels and troughs separated by ridges and islands (El-Sabh and Murty, 1990). Topographically modified flows give rise to very large tidal ranges and currents (up to 10 m and 3 m s^{-1}, respectively; Mertz and Gratton, 1990). In this tidally energetic region, wind mixing is one to two orders of magnitude smaller than tidal mixing (Painchaud et al., 1995). Owing to the resuspension of bottom sediments (tide, wind or wave generated) and the net non-tidal estuarine circulation (d'Anglejan and Smith, 1973), a well-developed turbidity maximum stretches between Île d'Orléans and Île-aux-Coudres (Painchaud and Therriault, 1989) where suspended particulate

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matter concentrations vary from 10 to more than 200 mg l^{-1} (Silverberg and Sundby, 1979). The sources of particulate organic matter (POM) in the estuary are still debated (Gearing and Pocklington, 1990). Carbon isotope studies indicate that less than half of the POM is derived from terrestrial sources (Pocklington and Leonard, 1979) and is quite refractory to biodegradation (Lucotte et al., 1991), whereas the major contributor to POM is believed to be "fresh" organic matter, i.e., living or recently living material, of river-borne origin (Tan and Strain, 1983; Hélie and Hillaire-Marcel, 2006). During the spring freshet in April–May, when freshwater discharge delivers 40 % of the annual solid inputs to the estuary, the input of terrigenous POM is equivalent to the average POM kept in suspension in the turbidity maximum (Lucotte, 1989).

The Lower St. Lawrence Estuary (LSLE) is fairly unique in that its character is more oceanic than most estuaries due to its grand size in all three dimensions and unimpeded connection with Labrador and Slope waters from the Atlantic Ocean (El-Sabh and Silverberg, 1990). Relative to the USLE, the LSLE is much larger (9,350 km^2; d'Anglejan, 1990), wider (30 to 50 km) and deeper (~300 m), and displays a smoother, less variable bottom topography. Tidal currents are weaker (on the order of 30 cm s^{-1} or less; Mertz and Gratton, 1990) and, under these less turbulent conditions, the Lower Estuary is the major sink of continental inputs to the St. Lawrence system. Most (~75 %) of the terrigenous POM carried by the St. Lawrence River is deposited on the LSLE floor (Lucotte et al., 1991). The dominant bathymetric feature of the LSLE is the Laurentian Channel (or Trough), a deep, central, U-shaped glaciated valley that extends 1,240 km from the eastern Canadian continental shelf break through the GSL and into the LSLE (d'Anglejan, 1990). The termination (head) of the Laurentian Channel at an abrupt and shallow sill near Tadoussac marks the region of transition between the Upper and Lower Estuary and is an area of complex tidal phenomena (Gratton et al., 1988). Due to rapid shoaling, tidal movements (e.g., internal tides and strong flows over the steep sill) locally generate significant mixing of surface freshwater with cold, nutrient-rich waters from the intermediate and deep layers of the Gulf, resulting in a fertile surface layer that flows continuously seaward (Coote and Yeats, 1979; Saucier and Chassé, 2000) and sustains important feeding habitats for several large marine mammals (Dufour and Ouellet, 2007). The Lower Estuary's seaward outflow, together with the Gaspé Current, a rapidly moving coastal jet, are a major input of nutrients and zooplankton to the near-surface waters of the GSL (Coote and Yeats, 1979; Plourde

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and Runge, 1993). Mesoscale features such as coastal jets, internal Kelvin waves, baroclinic eddies and unstable waves are all possible due to strong Coriolis effects (Ingram and El-Sabh, 1990).

The Lower St. Lawrence Estuary is one of the most laterally stratified estuaries in the world (Larouche et al., 1987), and is also strongly vertically stratified. During summertime, the SLE can be described as a three-layer system on the basis of its thermal stratification (Gratton et al., 1988). Each spring, a new surface layer flow is initiated by the freshwater runoff from the St. Lawrence River, Saguenay Fjord and rivers on the north shore of the estuary (Dufour and Ouellet, 2007; see Fig. 1). Discharge from the St. Lawrence River (mean annual discharge of 10,000 m^3 s^{-1}, peaking at 15,000 m^3 s^{-1} during the spring freshet; Painchaud and Therriault, 1989) provides about 80 % of the total freshwater input to the estuary (Ingram and El-Sabh, 1990), whereas the combined runoff from the Saguenay and Manicouagan Rivers accounts for most of the remainder (Tee, 1990). The warm and relatively fresh surface layer (0 to 30 m) overlies the cold intermediate layer or CIL (30–150 m deep; S_P = 32.0 to 32.6) that is formed by advection of the Gulf's wintertime surface mixed layer (Galbraith, 2006). Below the CIL, a warmer (2 to 6 °C) and saltier (S_P = 33 to 35) bottom layer (>150 m deep), originating from the mixing of western-central Atlantic and Labrador shelf waters that intrude at depth primarily through Cabot Strait, flows sluggishly landward (~0.5 cm s^{-1}; Bugden, 1988) toward the head region of the Laurentian Channel (Saucier et al., 2003; Gilbert et al., 2005).

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2.2. Water-column sampling and analytical procedures

Water samples were collected aboard the RV *Coriolis II* during ten research cruises within the St. Lawrence Estuary and Gulf in the ice-free spring or summer season between 2003 and 2016. Water sampling was conducted mainly along the central axis of the St. Lawrence Estuary and the Laurentian Channel. The sampling locations are shown in Fig. 2. Samples were taken from discrete depths throughout the water column, typically at 3 m, 20 m, 50 m, 70 m, 100 m and at 50m intervals to the bottom (or within 10 m of the bottom). A comprehensive dataset was compiled from field or laboratory measurements of the following physical–chemical properties: temperature (T), practical salinity (S_P), pH_{NBS} and/or pH_T, total alkalinity (TAlk), dissolved inorganic

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carbon (DIC), soluble reactive phosphate (SRP), and dissolved silicate (DSi), nitrate (NO_3) and oxygen (DO).

T and S_P were determined *in situ* using the conductivity-temperature-depth (CTD) probe (SeaBird SBE 911) mounted on the sampling rosette. The temperature probe was calibrated by the manufacturer, whereas the conductivity sensor was calibrated by the manufacturer and recalibrated using discrete salinity samples collected throughout the water column and analyzed on a Guildline Autosal 8400 salinometer calibrated with IAPSO standard seawater. Water samples destined for pH and TAlk measurements were transferred directly from the 12L Niskin bottles mounted on the CTD-rosette system to, respectively, 125mL plastic bottles without headspace and 250mL glass bottles as soon as the rosette was secured onboard. In the latter case, a few crystals of $HgCl_2$ were added before the bottle was sealed with a ground-glass stopper and Apiezon® Type-M high-vacuum grease.

pH was determined onboard at 25 °C, potentiometrically on the NBS/NIST scale (infinite dilution convention, pH_{NBS}) for low salinity waters (S_P < 5) and potentiometrically and/or colorimetrically on the total hydrogen ion concentration scale (constant ionic medium convention, pH_T) for higher salinity waters. Potentiometric pH measurements were carried out using a Radiometer Analytical® GK2401C combination glass electrode connected to a Radiometer Analytical® PHM84 pH/millivolt-meter. Prior to each measurement, the electrode was calibrated against three NIST-traceable buffer solutions: pH-4.00, pH-7.00 and pH-10.00 at 25°C. The electrode response to these buffers was then least-squares fitted to obtain the Nernstian slope. For S_P > 5, pH measurements were converted to the pH_T scale using TRIS buffer solutions prepared at S_P = 5, 15, 25, or 35 for which the pH_T was assigned at 25°C (Millero, 1986). Colorimetric pH measurements were carried out using a Hewlett-Packard UV-Visible diode array spectrophotometer (HP-8453A) and a 5cm quartz cell after thermal equilibration of the plastic sampling bottles in a constant temperature bath at 25.0 ± 0.1°C. Phenol red (Robert-Baldo et al., 1985) and *m*-cresol purple (Clayton and Byrne, 1993) were used as color indicators. The pH_T of the water samples and buffer solutions were calculated according to the equation of Byrne (1987). The reproducibility of the pH measurements was typically better than ± 0.003.

TAlk was measured at McGill University using an automated Radiometer (TitraLab865®) potentiometric titrator and a Red Rod® combination pH electrode (pHC2001). The dilute HCl titrant was calibrated prior, during, and after each titration session using certified reference materials provided by Andrew Dickson (Scripps Institute of Oceanography). Raw titration data were processed with a proprietary algorithm specifically designed for shallow end-point detection. The reproducibility of the method was better than 0.5 %.

Direct DIC measurements were carried out during an additional cruise in 2014 using a Scitech Apollo DIC analyzer. After being thermostated at 25 °C, 1–1.5 mL of the sample was injected into the instrument's reactor where it was acidified with 10 % H_3PO_4 and the evolved CO_2 carried by a stream of pure nitrogen to a LICOR infrared analyzer. A calibration curve was constructed using gravimetrically-prepared Na_2CO_3 solutions, and the accuracy of the measurements was verified using certified reference material solutions provided by Andrew Dickson (Scripps Institute of Oceanography). The reproducibility of the measurements was typically on the order of 0.2 %. Results of the direct DIC measurements were used to assess the contribution of organic alkalinity to the total alkalinity in the Upper Estuary, as discussed in Section 2.3.2.

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DO concentrations were determined by Winkler titration (Grasshoff et al., 1999) on distinct water samples recovered directly from the Niskin bottles. The relative standard deviation, based on replicate analyses of samples recovered from the same Niskin bottle, was better than 1 %. These measurements further served to calibrate the SBE-43 oxygen probe mounted on the rosette. For the determination of nutrient concentrations, aliquots of the water samples taken from the Niskin bottles were syringe filtered through a 0.45µm Millipore polycarbonate (MA) filter. DSi was measured onboard on the same day of sampling using the method described in Grasshoff et al. (1999). Water samples destined for NO_3 and SRP measurements were transferred, respectively, into acid-washed 15ml polyethylene and borosilicate tubes, quickly frozen and stored at –20 °C. Their concentrations were determined using standard colorimetric methods adapted from Grasshoff et al. (1999) with a SEAL Autoanalyzer III at the Institut des Sciences de la Mer de Rimouski. The analytical detection limit was 0.04 µM for NO_3, 0.05 µM for SRP and 0.1 µM for DSi. Based on

replicate analyses of the standards, the reproducibility of these measurements was typically 1 %.

The *in situ* pressure and density of the samples were calculated from the Thermodynamic Equation of Seawater – 2010 (TEOS-10) using the Gibbs Seawater (GSW) Oceanographic Toolbox (MATLAB-version 3.05; McDougall and Barker, 2011). All field measurements reported in µmol L^{-1} were converted to µmol kg^{-1} using the *in situ* density data.

2.3. Calculation of aqueous pCO_2

2.3.1. pCO_2 in mixed-layer waters

Aqueous pCO_2 (pCO_2(water)) is defined as the partial pressure of carbon dioxide in wet (100 % water-saturated) air that is in equilibrium with the water sample. Because direct pCO_2 measurements were not available from the RV *Coriolis II* cruises, pCO_2(water) (µatm) and DIC (µmol kg^{-1}) were calculated from the measured pH (total or NBS scale) and TAlk (µmol kg^{-1}), at *in situ* temperature (°C), salinity (S_P) and pressure (dbar), using the program CO2SYS (MATLAB-version 1.1; van Heuven et al., 2011) and the carbonic acid dissociation constants (K_1, K_2) of Cai and Wang (1998) for estuarine waters. Wherever data were available, the contributions to TAlk from phosphate and silicate were included in the calculations. Although the K_1 and K_2 formulations from Lueker et al. (2000) are recommended for best practices by Dickson et al. (2007), they are not suitable for the low-salinity conditions found in estuaries (S_P < 19) (Orr et al., 2015). The revised equations for K_1 and K_2 from Cai and Wang (1998) are applicable over a larger range of salinities (0 to 40) and, thus, were used to examine the carbonate system in the estuarine waters of our study area.

This study focuses on the CO_2 dynamics in near-surface waters. To obtain individual data points of surface-water pCO_2 at each sampling location, the pCO_2 data in the surface mixed layer (SML) were averaged. The SML is the site of active air-sea interaction where heat and gases are exchanged directly with the atmosphere and within which physical (temperature, salinity, density) and chemical (dissolved gases) properties are vertically homogeneous due to turbulent mixing (Sprintall and Tomczak,

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1992). The lower limit to air-sea interaction, i.e., the mixed layer depth (MLD), is demarcated by a pycnocline, a sharp density gradient that generally coincides with both a temperature (thermocline) and salinity (halocline) gradient. Here, we determine the thickness of the SML using a density-based criterion which defines the MLD as the depth at which a threshold difference of 0.03 kg m^{-3} from the sea surface occurs (de Boyer Montégut et al., 2004). In the following sections, surface-water pCO_2 will be taken to mean the SML-averaged pCO_2.

2.3.2. Sources of error in pCO_2 calculation

In this study, pH/TAlk was used as the input combination to study the consistency between calculations of pCO_2 using different sets of carbonic acid dissociation constants. The importance of using appropriate formulations of K_1 and K_2 in estuarine waters is shown by the discrepancies in the calculated pCO_2 values (pCO_2 @ 15 °C) at low salinities (Fig. 3). The percent difference between values calculated using the dissociation constants of Cai and Wang (1998) and those calculated using the best-practices constants of Lueker et al. (2000) was on average 3.07 %. At S_P < 19, differences between the calculated pCO_2 values were as large as 18.0 % (average difference of 6.88 %), whereas, at S_P > 19, the calculated values were in better agreement (only ~1.48 % difference). The K_1 and K_2 formulations of Millero (2010), the most recent set of constants proposed for estuarine waters (S_P = 1 to 50), yielded pCO_2 values that differed substantially from those derived using the constants of Cai and Wang (1998) at S_P < 19, with the largest divergence reaching 34.4 % (average difference of 13.6 %). At S_P = 0, the pCO_2 values calculated using the constants of Cai and Wang (1998) compared very well with those given by the Millero (1979) constants for freshwater (difference of only ~0.08 %), whereas the pCO_2 values calculated using the constants of Millero (2010) showed very poor agreement with the freshwater results (differing by ~34.3 %). These discrepancies highlight the need for new or revised measurements of the carbonic acid dissociation constants under estuarine conditions (in brackish waters) especially at S_P < 5. Studies which use the best-practices formulations of K_1 and K_2 to calculate estuarine pCO_2 may underestimate CO_2 emissions at low salinities, whereas those that implement the Millero (2010) formulations may produce overestimates.

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Another potential source of error in the calculation of pCO_2 (pH/TAlk) in low-salinity estuarine waters is the contribution of dissolved organic compounds to the total alkalinity. The contributions of borate, phosphate and silicate species are taken into consideration in CO2SYS, whereas the magnitude of organic alkalinity (Org-Alk, or excess alkalinity) is usually assumed to be small or negligible, and is simply ignored when using TAlk to calculate pCO_2 in open ocean waters. In riverine and coastal waters, however, the contribution of organic species to the TAlk can be significant (Yang et al., 2015). Rivers draining organic-rich soils and non-carbonate rocks have low DIC concentrations (a few hundred µmol L^{-1}) that are often exceeded by dissolved organic carbon (DOC) concentrations (Abril et al., 2015). As discussed by Hunt et al. (2011), a significant contribution of Org-Alk (the organic acid anions in DOC) leads to an overestimation of calculated pCO_2 using any algorithm that accounts only for the contributions of inorganic species to TAlk. A comparison of the calculated TAlk (DIC/pH) and the measured TAlk from the 2014 cruise reveals that Org-Alk is on the order of –20 µmol kg^{-1} for the St. Lawrence River end-member, whereas it is as high as –120 µmol kg^{-1} for the Saguenay River end-member (A. Mucci, pers. comm.). Given that TAlk exceeds ~1000 µmol kg^{-1} throughout our study area and the Saguenay River contribution to the surface waters of the SLE is limited (at most ~6 % at the head of the Lower Estuary; Mucci et al., in revision), consideration of the Org-Alk in the calculation of pCO_2 (pH/TAlk) yielded values that were at most 1.9 % different from those uncorrected for Org-Alk. Bearing in mind the uncertainties in the K_1 and K_2 formulations as well as the analytical uncertainties, the influence of Org-Alk on the calculated pCO_2 (pH/TAlk) did not represent a significant source of error.

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2.4. Temperature normalization of pCO_2

The effect of temperature on aqueous pCO_2 is primarily the manifestation of changes in the solubility of CO_2 gas in water (Takahashi et al., 1993). The temperature dependence of pCO_2 in seawater, i.e., $\partial \ln(pCO_2) / \partial T = 0.0423\ °C^{-1}$, was determined experimentally by Takahashi et al. (1993) on a single North Atlantic surface water sample with $S_P = 35.380$ under isochemical conditions. As this oft-used approximation for thermally induced changes in pCO_2 was derived from direct measurements in open ocean waters, we use a different approach to remove the temperature effect on the estuarine pCO_2 in our study area. The *in situ* pCO_2 were normalized to the average

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surface-water temperature ($pCO_2(\overline{SST})$, $\overline{SST}$ = 7.82 °C), using the temperature normalization method of Jiang et al. (2008) in which pCO_2 values are re-calculated from the TAlk and DIC data at a common temperature. The results yielded a temperature coefficient of ∂ ln(pCO_2) / ∂T = 0.0402 °C^{-1} (R^2= 0.99), in excellent agreement with that of Takahashi et al. (1993). The pCO_2 changes due to temperature deviations from $\overline{SST}$ ($\Delta pCO_2(temp)$) were calculated as:

$$\Delta pCO_2(temp) = pCO_2(obs) - pCO_2(\overline{SST}) \quad (1)$$

where $pCO_2(obs)$ is the *in situ* pCO_2 and $pCO_2(\overline{SST})$ is the temperature-normalized pCO_2. Since changes in pCO_2 at a common temperature primarily reflect changes in DIC, the spatial variations in $pCO_2(\overline{SST})$ can be attributed to the combined influences of non-thermal processes that affect DIC (water mass mixing, biological activity). Theoretically, $pCO_2(\overline{SST})$ can be further partitioned into the pCO_2 change due to biology and that due to mixing through an analysis of the water mass structure, e.g., an optimum multiparameter (OMP) water mass analysis. Results from its application will be presented in a subsequent study.

2.5. Air-sea CO_2 flux estimation

Air-sea CO_2 gas exchange (F, mmol C m^{-2} d^{-1}) at each sampling location was estimated as follows:

$$F = k \cdot K_0 \cdot (pCO_2(water) - pCO_2(air)) \quad (2)$$

where k (cm h^{-1}) is the gas transfer velocity of CO_2, K_0 (mol kg^{-1} atm^{-1}) is the solubility coefficient of CO_2 at *in situ* surface-water temperature and salinity (Weiss, 1974), and pCO_2(water) and pCO_2(air) (µatm) are the partial pressures of CO_2 in the water and the air, respectively. The difference between pCO_2(water) and pCO_2(air) (ΔpCO_2) determines the direction of gas exchange across the air-sea interface. Positive values of F indicate CO_2 release by the surface water, whereas negative values indicate CO_2 uptake. Conversion factors were applied to express the final F with the aforementioned units.

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Atmospheric pCO_2 (pCO_2(air)) was calculated using the monthly averages of the measured mole fraction of CO_2 in dry air (xCO_2, at the greenhouse gas observational station in Fraserdale, Ontario) obtained from the Climate Research Division at Environment and Climate Change Canada. The mean pCO_2(air) in the sampling month was computed using the relationship (Takahashi et al., 2002):

$$pCO_2(air) = xCO_2 \cdot (P_b - P_w) \quad (3)$$

where xCO_2 is in ppm, P_b (atm) is the atmospheric (or barometric) pressure at the sea surface, and P_w (atm) is the equilibrium (or saturation) water vapor pressure at *in situ* surface-water temperature and salinity (Weiss and Price, 1980). One-month averaged barometric pressures were calculated using the hourly station pressure data from Environment Canada at the following weather observing stations: Québec/Jean Lesage International Airport (Upper Estuary), Mont-Joli Airport (Lower Estuary), and Gaspé Airport (Gulf of St. Lawrence). The P_b at station elevation was converted to mean sea level pressure using the formula of Tim Brice and Todd Hall (NOAA's National Weather Service, http://www.weather.gov/epz/wxcalc_stationpressure).

The formulation of the gas transfer velocity, k, is the largest source of error in the computation of air-sea CO_2 fluxes (Borges et al., 2004a,b). Properly constraining values of k in estuaries is problematic (Raymond and Cole, 2001) due to their hydrodynamic and geomorphologic complexity (Abril et al., 2000). Gas transfer is thought to be regulated by turbulence at the air-water interface (Wanninkhof, 1992). Wind stress plays a key role in the generation of turbulence at the ocean surface through the transfer of momentum to waves and currents (Ho et al., 2011), whereas, in estuarine environments and especially macrotidal estuaries, surface turbulence can be created by interactions of wind forcing, tidal currents and boundary friction (Zappa et al., 2003, Borges et al., 2004a,b; Zappa et al., 2007) and, in turbid estuaries, attenuated by suspended material (Abril et al., 2009). The turbulence generated from bottom stress varies with water depth and tidal velocity (Raymond et al., 2000), and is important only in shallower estuaries with high current velocities (Cerco, 1989). Raymond and Cole (2001) have shown that wind stress controls turbulence at the air-water interface for all systems with depths greater than 10 meters (at depths < 10 m, either wind or bottom stress may dominate).

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Several different predictive relationships between wind speed and gas transfer velocity have been proposed based on laboratory and field studies. Here, we estimate the latter from short-term (or steady) wind speed measurements using the equations of Wanninkhof (1992) revised by Wanninkhof (2014) and Raymond and Cole (2001):

k from Wanninkhof (2014), denoted as k_{W-14}:

$$k_{W-14} = 0.251\, u^2 (Sc\ /\ 660)^{-0.5} \quad (4)$$

k from Raymond and Cole (2001), denoted as $k_{R\&C-01}$:

$$k_{R\&C-01} = 1.91\, e^{0.35u} (Sc\ /\ 660)^{-0.5} \quad (5)$$

where u is the wind speed (m s^{-1}) and Sc is the Schmidt number (Sc = μ/D, where μ is the kinematic viscosity of the water and D is the diffusion coefficient) for CO_2 gas in solution. The Schmidt number for CO_2 in seawater at 20 °C is 660 and was adjusted to Sc=600 for freshwater. Hourly wind speed data were obtained from Environment Canada at the aforementioned weather observing stations, and averaged over the sampling month to obtain short-term wind speeds. The correction to a common Schmidt number was performed using the equations of Wanninkhof (1992) for the temperature dependence of Sc for CO_2 gas in seawater (S_P=35) and freshwater, respectively, and assuming that k is proportional to $Sc^{-0.5}$.

Because of increased turbulence, one would expect k values calculated from estuarine parameterizations to be higher than those predicted from oceanic parameterizations at equivalent wind speeds (Abril et al., 2000). Within the confines of the SLE, estimates of k using the Wanninkhof (2014) relationship ranged from 1.6 to 4.5 cm h^{-1} whereas those calculated from Raymond and Cole (2001) were between 3.8 and 8.1 cm h^{-1}. Hence, we take the air-sea CO_2 flux values calculated with k_{W-14} to be the theoretical lower limit of gas exchange (F_{W-14}), whereas those computed from $k_{R\&C-01}$ represent the upper limit of gas exchange ($F_{R\&C-01}$).

In order to estimate the area-averaged CO_2 flux in the SLE, the estuary proper was divided into five segments, with each section containing at least one sampling location. Given that the Lower Estuary occupies ~75 % of the total estuarine surface

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area, and encompasses a fairly wide range of pCO_2 values (standard deviation of 119 µatm), the SLE was divided into longitudinal sections (Fig. 2) rather than segmented by salinity. The fluxes in each segment were normalized to the sectional surface area and then summed to obtain a spatially integrated air-sea CO_2 flux ($F_{area\text{-}avg}$) for the whole estuary, as follows (Jiang et al., 2008):

$$F_{area-avg} = \frac{\sum F_i \cdot S_i}{\sum S_i} \quad (6)$$

where F_i is the average of all the fluxes within segment i, and S_i is the surface area of segment i. Sectional surface areas were tabulated in MATLAB using the land mask of eastern Canada obtained from Fisheries and Oceans Canada. An area-averaged CO_2 flux was obtained for both the upper and lower limits of gas exchange in the SLE. These two final estimates are assumed to bracket the real areal CO_2 flux.

2.6. Conceptual framework for the analysis of variations in biogenic gas concentrations

A comparison of the distribution of biologically reactive dissolved gases, i.e., CO_2 and O_2, can provide useful information about the physical (thermal) and biological processes controlling their concentrations (Richey et al., 1988). Temperature-related gas solubility effects occur in the same direction for CO_2 and O_2, whereas biological production and respiration affect CO_2 and O_2 in opposite directions. Following the approach of Carrillo et al. (2004), the saturation states (or % saturation) of pCO_2 and DO, with respect to the atmosphere, were compared in order to determine the relative importance of temperature effects (heating or cooling) and biological activity (photosynthesis or respiration) in the surface waters at each sampling location. The pCO_2 percent saturation (pCO_2(% sat)) was calculated as follows:

$$pCO_2(\%\ sat) = (pCO_2(water) / pCO_2(air)) \cdot 100 \quad (7)$$

The DO percent saturation (DO(% sat)) was calculated as:

$$DO(\%\ sat) = (DO/DO^*) \cdot 100 \quad (8)$$

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where DO^* is the equilibrium DO concentration (μmol kg^{-1}) at *in situ* surface-water temperature and salinity (Benson and Krause, 1984). The relationship between DO(% sat) and pCO_2(% sat) is roughly analogous to that of the apparent oxygen utilization (AOU) and excess DIC (eDIC) (Abril et al., 2000). The former is defined as the difference between DO^* and DO, whereas the latter is defined as the difference between the observed DIC and a theoretical DIC at atmospheric equilibrium.

According to the method of Carrillo et al. (2004), data points fall into one of four quadrants on a graph of DO(% sat) versus pCO_2(% sat), with the origin at 100 % saturation for both gases. Quadrant I (upper left; supersaturated DO, undersaturated pCO_2) suggests net photosynthesis, Quadrant II (upper right; supersaturated DO and pCO_2) indicates the effects of heating, Quadrant III (lower right; undersaturated DO, supersaturated pCO_2) implies net respiration, and Quadrant IV (lower left; undersaturated DO and pCO_2) represents the effects of cooling. Although general patterns become apparent, we urge caution in the interpretation of these results as significant limitations apply. Surface-water CO_2 and O_2 may be acted upon by other forcings such as air-sea gas exchange. The net transfer of CO_2 and O_2 gases occurs across the air-sea interface whenever their partial pressures in the SML differ from those in the atmosphere. Because of their differential gas exchange rates (i.e., O_2 exchanges ~19 times faster than CO_2; Peng et al., 1987), CO_2 and O_2 dynamics may be decoupled in surface waters, causing an asymmetry in the observed CO_2:O_2 relationship (Carrillo et al., 2004).

3. Results and discussion

3.1. Spatial variability of surface-water pCO_2

Data were compiled from all ten cruises to describe the inorganic carbon chemistry in the mixed-layer waters of the St. Lawrence River, Upper Estuary, Lower Estuary and Gulf (Table 1). Large spatial variations in surface-water pCO_2 were observed within the EGSL system, with values ranging from 139 to 765 μatm (452 ± 134 μatm) during the spring/summer sampling periods. Overall, the pCO_2 were higher in the USLE (571 ± 72 μatm) than in the LSLE (394 ± 119 μatm) and GSL (352 ± 80 μatm), whereas the atmospheric pCO_2 showed less variability, ranging from 372 to 405 μatm,

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during the sampling years. As shown in Fig. 4, the USLE was always a CO_2 source (i.e., surface-water pCO_2 were above atmospheric level) while the LSLE and GSL were generally either a CO_2 sink or nearly neutral (i.e., surface-water pCO_2 were below or close to atmospheric level).

Within the confines of the SLE, the surface-water pCO_2 generally decreased with increasing distance from the head of the estuary (Île d'Orléans) and along the salinity gradient (Fig. 4 and 5). The highest values of pCO_2 were observed near the landward limit of the salt water intrusion in the SLE's upper reaches, in the vicinity of the Cap Tourmente intertidal flats and marshes. This area (3×10^6 m^2) is located along the core of the estuary's maximum turbidity zone (MTZ) (Lucotte and d'Anglejan, 1986). The lowest surface-water pCO_2 were found downstream of the MTZ in the lower reaches of the SLE near Pointe-des-Monts, where the channel widens into the gulf. Due to favorable environmental conditions (nutrients, light, stratification), phytoplankton blooms typically occur in late spring or early summer in the LSLE (Zakardjian et al., 2000), with maximal biological production occurring in its downstream portion due to the mixing of cold, nutrient-rich waters, upwelled at the head of the Laurentian Channel, with warmer freshwaters flowing in from the north shore rivers (Savenkoff et al., 1994). Seaward from the estuary-gulf boundary, the pCO_2 gradually increased from 207 to 478 µatm, coinciding with rising surface-water temperatures (T = 3.9 to 13.7 °C).

The spatial variability of surface-water pCO_2 due to temperature variations was removed by normalizing the pCO_2 data to a common temperature (T = 7.82 °C). From a comparison of the *in situ* and corresponding temperature-normalized pCO_2, spatial variations in surface-water temperature lowered or raised the pCO_2 by –122 to 181 µatm within the EGSL system. The maximum (minimum) values of ΔpCO_2(temp), expressed as a percent change, were 38 % (–14 %) in the USLE, 24 % (–20 %) in the LSLE, and 29 % (–17 %) in the GSL. Temperature normalization, however, removed only a small part of the overall spatial variability of surface-water pCO_2 (Fig. 6). Given that the spread of the $pCO_2(\overline{SST})$ data remained large (153–668 µatm; 447 ± 133 µatm), most of the spatial variability in surface-water pCO_2 can be explained by non-thermal physical and biological processes that affect DIC concentrations in the mixed layer.

3.2. Air-sea CO_2 flux and spatial integration

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Large spatial variations in the air-sea CO_2 flux were observed within the EGSL system during the spring/summer sampling months, with fluxes ranging from –21.9 to 28.4 mmol m^{-2} d^{-1} (Fig. 7). Values of F were always positive in the USLE (2.0 to 28.4 mmol m^{-2} d^{-1}) and either negative or positive in the LSLE (–21.9 to 15.1 mmol m^{-2} d^{-1}) and GSL (–8.4 to 3.6 mmol m^{-2} d^{-1}). As expected, $F_{R\&C\text{-}01}$ (estuarine parameterization of k) were larger than $F_{W\text{-}14}$ (oceanic parameterization of k) due to the inherently greater surface turbulence in estuarine systems. The average difference between CO_2 fluxes calculated using the two formulations of the gas transfer velocity (equations 4 and 5) was 71.7 %. Details of the k and F values given by each parameterization of k are shown in Table 2. Irrespective of the parameterization, the calculated CO_2 fluxes were more positive in the USLE (9.2 ± 5.3 mmol m^{-2} d^{-1}) than in the LSLE (0.8 ± 7.2 mmol m^{-2} d^{-1}) and GSL (–1.2 ± 3.0 mmol m^{-2} d^{-1}).

The SLE was divided into five segments to obtain an area-averaged CO_2 flux for the whole estuary. The data used to calculate the $F_{area\text{-}avg}$ are listed in Table 3. Overall, the SLE served as a weak source of CO_2 to the atmosphere at the time of sampling, with an area-averaged degassing flux of 0.98 to 2.02 mmol C m^{-2} d^{-1} (0.36 to 0.74 mol C m^{-2} yr^{-1}) during the late spring and early summer. This efflux compares favorably with that of the Delaware Estuary (2.4 ± 4.8 mol C m^{-2} yr^{-1}; Joesoef et al., 2015), another large estuarine system with a long water residence time, but is significantly lower than estimates in the marine-dominated Sapelo and Doboy Sound estuaries (10.5 to 10.7 mol C m^{-2} yr^{-1}; Jiang et al., 2008). From a compilation of 165 estuaries worldwide, almost all systems, with the exception of those in the Arctic (–1.1 mol C m^{-2} yr^{-1}), serve as sources of CO_2 to the atmosphere (Chen et al., 2013). Chen et al. (2013) concluded that the world's upper estuaries (S_P < 2) are strong sources (39.0 ± 55.7 mol C m^{-2} yr^{-1}), mid estuaries (2 < S_P < 25) are moderate sources (17.5 ± 34.2 mol C m^{-2} yr^{-1}), and lower estuaries (S_P > 25) are weak sources (8.4 ± 14.3 mol C m^{-2} yr^{-1}). Predictably, with its maritime region occupying almost three-fourths of the total surface area, the SLE behaves like an outer estuary with only small CO_2 evasion. The lack of temporal coverage of surface-water pCO_2 data, however, prevents us from reliably synthesizing an annual air-sea CO_2 flux.

3.3. Major drivers of estuarine pCO_2 variability

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The pCO_2 in the surface mixed layer is a function of its temperature (T), salinity (S_P), dissolved inorganic carbon (DIC) and total alkalinity (TAlk), as described by the following relationship (Takahashi et al., 1993):

$$dpCO_2 = (\partial pCO_2/\partial T)dT + (\partial pCO_2/\partial S_P)dS_P + (\partial pCO_2/\partial DIC)dDIC + (\partial pCO_2/\partial TAlk)dTAlk \quad (9)$$

Through changes in T, S_P, DIC and TAlk, variations of surface-water pCO_2 are mainly controlled by dynamic processes (water mass mixing), thermodynamic processes (temperature and salinity changes), air-sea gas exchange, and biological processes (photosynthesis, respiration) (Poisson et al., 1993). Among these, the effects of temperature and DIC, i.e., the addition or removal of DIC through biological activity and mixing processes, are generally the most important drivers of estuarine pCO_2 variability. In the absence of a significant source or sink of TAlk (e.g., calcium carbonate formation/dissolution, anaerobic organic matter decomposition), changes of DIC determine the buffer capacity (DIC/TAlk ratio) of the water. Whereas the physically and biologically induced changes of DIC/pCO_2 will be quantified in a future study, using a modified OMP water mass analysis, here, we evaluate the relative importance of thermal and biological processes in controlling the spatial distribution of pCO_2 in the St. Lawrence Estuary and Gulf.

To disentangle the biological and temperature effects on the spatial variability of pCO_2, the DO(% sat) were plotted against the pCO_2(% sat), with the origin at 100 % saturation for both gases. This simple approach uses the four possible combinations of pCO_2(% sat)/DO(% sat) as integrated measures of thermally and biologically induced changes. As shown in Fig. 8 (top), microbial respiration was the major driver of pCO_2 variability in the USLE, whereas photosynthesis and temperature were the dominant controls in the LSLE and GSL. We found similar results from a comparison of eDIC and AOU (Fig. 8, bottom). In the strongly stratified Lower Estuary, as well as near the estuary-gulf boundary, the biological drawdown of CO_2 counteracted the decrease in CO_2 gas solubility due to increasing temperature (Fig. 9). Its waters were mostly undersaturated with CO_2 with respect to the atmosphere (values of pCO_2 were below atmospheric level) despite a general trend of surface-water warming (T = 2.7 to 12.6

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°C). This pattern is consistent with the finding that, in spring/summer, the increasing effect of warming on pCO_2 is counteracted by the photosynthetic utilization of CO_2, particularly in a strongly stratified shallow mixed layer (Takahashi et al., 1993). Whereas direct measurements of chlorophyll-a concentrations were not carried out during the research cruises, a fluorescence sensor was mounted on the CTD probe. As shown in Fig. 10, maximum fluorescence values, as well as high values of transmission (% light transmission approaching 100%), were observed in the eastern Lower Estuary and the western Gulf of St. Lawrence, where the system appears to shift from net heterotrophy to net autotrophy. Farther into the Gulf (near Anticosti Island), the temperature dependence of pCO_2 exerted a stronger influence, causing values of surface-water pCO_2 to increase concomitantly with temperature (Fig. 9).

4. Conclusions

Because of its large physical dimensions and unimpeded connection to the Atlantic Ocean, the St. Lawrence Estuary encompasses both a river-dominated inner estuary, where physical mixing and abiotic processes dominate, and a marine-dominated outer estuary, where biological cycling and oceanic processes prevail. The physical and biogeochemical processes of these contrasting environments are reflected in the spatial distribution of surface-water pCO_2 (139–765 µatm). The shallow, partially mixed Upper Estuary, with a turbidity maximum controlled by tide- and wind-induced turbulence, was, during our sampling period, a net source of CO_2 to the atmosphere due to microbial respiration (low biological productivity), whereas the deep, stratified Lower Estuary, with its stable, summertime three-layer vertical structure, was generally a net sink of atmospheric CO_2 due to the enhanced biological drawdown of pCO_2 (light availability, nutrient supply, strong stratification).

Overall, the large subarctic St. Lawrence Estuary was a weak source of CO_2 to the atmosphere, with an area-averaged CO_2 degassing flux of 0.98 to 2.02 mmol C m^{-2} d^{-1} (0.36 to 0.74 mol C m^{-2} yr^{-1}). This efflux is somewhat smaller than the numerically averaged CO_2 flux per unit area (2.19 mol C m^{-2} yr^{-1}) reported from North American estuaries by Chen et al. (2013), highlighting their relatively small contribution (~12 %) to global estuarine CO_2 emissions. The pronounced shift in source/sink dynamics in the St. Lawrence Estuary, between its river-dominated (9.2 ± 5.3 mmol m^{-2} d^{-1}) and

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marine-dominated (0.8 ± 7.2 mmol m^{-2} d^{-1}) regions, is consistent with the conclusions of the comparative study carried out by Jiang et al. (2008) that revealed large differences in CO_2 degassing between riverine (inner) and maritime (outer) estuaries. Given the limited research on CO_2 dynamics in large estuaries and bay systems, which cover approximately one-half of the estuarine surface area on the U.S. east coast, as well as the large uncertainties in the indirect measurement of pCO_2 (carbonic acid dissociation constants, organic alkalinity contribution), current global-scale estimates of estuarine CO_2 degassing may be overestimated. To better constrain the role of large estuaries/bays in the coastal ocean carbon cycle, more extensive spatial and temporal coverage of direct pCO_2 measurements across estuary types is needed.

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Data availability

Data presented in this paper (Figures 4 and 8) are available upon request from one of the authors (alfonso.mucci@mcgill.ca).

Author contribution

A.D. and A.M. conceived the project. A.M. acquired and processed the data prior to 2016. A.D. conducted the data analysis and wrote the first draft of the paper whereas A.M. provided editorial and scientific recommendations.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1. Mean, standard deviation and range of the surface-water temperature (T), practical salinity (S_P), dissolved inorganic carbon (DIC), total alkalinity (TAlk) and *in situ* partial pressure of CO_2 (pCO_2) in the St. Lawrence River (near Québec City), Upper Estuary (Île d'Orléans to Tadoussac), Lower Estuary (Tadoussac to Pointe-des-Monts) and Gulf (Pointe-des-Monts to Cabot Strait) during all sampling months.

	T (°C)	S_P	DIC (µmol kg^{-1})	TAlk (µmol kg^{-1})	pCO_2 (µatm)
River (N=3)	14.2 ± 3.9 (9.8–17.2)	0.03 ± 0.05 (0–0.09)	1242 ± 132 (1148–1335)	1204 ± 99 (1124–1314)	604 ± 76 (550–658)
Upper (N=46)	9.6 ± 3.6 (4.2–17.4)	10.9 ± 8.0 (0–24.5)	1514 ± 242 (1081–2005)	1492 ± 272 (969–2030)	571 ± 72 (435–765)
Lower (N=60)	6.2 ± 2.2 (2.7–12.6)	26.2 ± 2.1 (21.2–30.4)	1837 ± 82 (1634–2005)	1957 ± 82 (1752–2088)	394 ± 119 (139–578)
Gulf (N=30)	8.8 ± 3.1 (3.9–13.7)	30.1 ± 1.5 (25.5–31.5)	1936 ± 64 (1761–2032)	2096 ± 61 (1921–2175)	352 ± 80 (207–478)

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Table 2. Mean, standard deviation and range of ΔpCO_2, k_{W-14}, $k_{R\&C-01}$, F_{W-14} and $F_{R\&C-01}$ in the surface waters of the St. Lawrence River, Upper Estuary, Lower Estuary and Gulf during all sampling months. k_{W-14} are the gas transfer velocities given by the Wanninkhof (2014) relationship, whereas $k_{R\&C-01}$ are those given by Raymond and Cole (2001). Values of F_{W-14} are taken to be the theoretical lower limit of air-sea gas exchange, whereas values of $F_{R\&C-01}$ are the upper limit; the extreme F data points are shown in bold.

	ΔpCO_2 (µatm)	k_{W-14} (cm h^{-1})	$k_{R\&C-01}$ (cm h^{-1})	F_{W-14} (mmol m^{-2} d^{-1})	$F_{R\&C-01}$ (mmol m^{-2} d^{-1})
River (N=3)	217 ± 99 (147–287)	3.0 ± 1.4 (1.9–4.5)	6.1 ± 2.0 (4.3–8.2)	5.8 ± 3.2 (**3.5**–8.0)	12.7 ± 6.4 (8.2–**17.3**)
Upper (N=46)	184 ± 72 (43–386)	2.8 ± 0.8 (1.6–4.5)	5.6 ± 1.1 (3.8–8.1)	6.1 ± 3.0 (**2.0**–14.7)	12.3 ± 5.4 (3.6–**28.4**)
Lower (N=60)	9.2 ± 116 (–266–188)	3.2 ± 0.4 (2.0–3.8)	5.9 ± 0.6 (4.3–6.9)	0.6 ± 4.9 (–12.1–8.3)	1.0 ± 9.0 (**–21.9**–**15.1**)
Gulf (N=30)	–31.0 ± 90 (–178–107)	1.2 ± 0.3 (0.8–1.7)	3.4 ± 0.3 (2.8–4.1)	–0.8 ± 1.5 (–3.6–1.1)	–1.7 ± 3.9 (**–8.4**–**3.6**)

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Table 3. Sectional and area-averaged air-sea CO_2 fluxes (mmol C m^{-2} d^{-1}) in the St. Lawrence Estuary during all sampling months. To obtain the area-averaged CO_2 flux, the SLE was divided into five segments at equal intervals. The first row of the table shows the surface area (km^2) of each segment. The flux data in each segment were numerically averaged to obtain sectional fluxes, which were then area weighted and summed to obtain the spatially integrated whole-estuary flux (in bold). The $F_{W\text{-}14}$ and $F_{R\&C\text{-}01}$ data provide the lower and upper estimates, respectively.

	Seg 1 (N=17)	Seg 2 (N=23)	Seg 3 (N=21)	Seg 4 (N=17)	Seg 5 (N=8)	Whole estuary
Surface area (km^2)	1,098	2,250	2,726	3,404	3,303	12,781
$F_{W\text{-}14}$ (mmol m^{-2} d^{-1})	7.2	5.4	4.3	-1.8	-4.0	**0.98**
$F_{R\&C\text{-}01}$ (mmol m^{-2} d^{-1})	14.5	11.0	7.9	-3.5	-7.4	**2.02**

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Figure 1. Map of the greater St. Lawrence system, including the chain of Great Lakes, the St. Lawrence River, the Upper St. Lawrence Estuary (USLE), the Lower St. Lawrence Estuary (LSLE), and the Gulf of St. Lawrence (GSL). From: Overview of the State of the St. Lawrence 2014 (with permission).

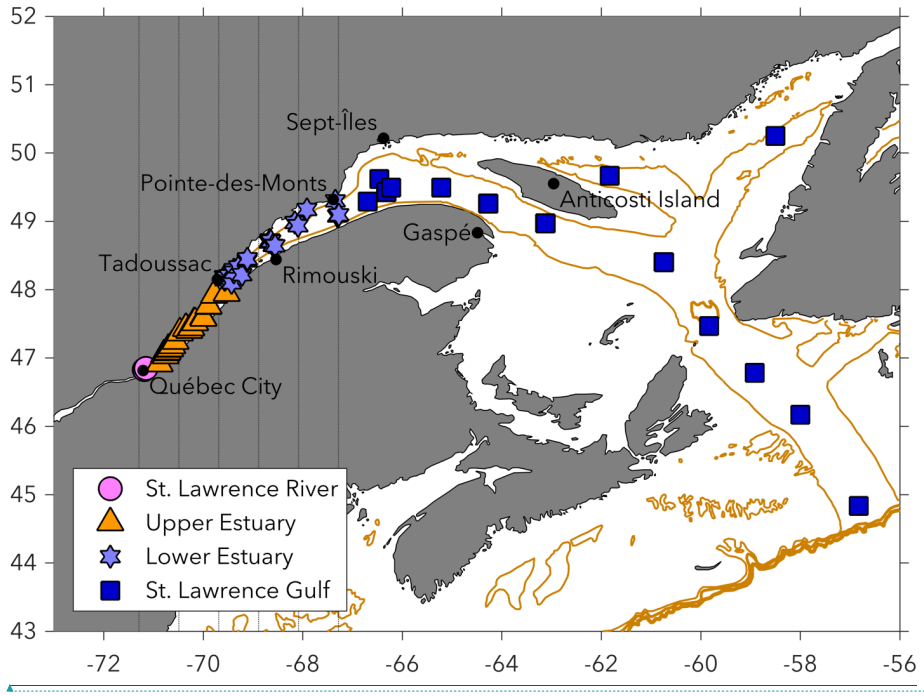

Figure 2. Map showing the four principal subdivisions of the study area and the sampling locations (markers). Water samples were collected during ten spring/summer research cruises: July 2003, June 2006, May 2007, July 2007, June 2009, July 2009, July 2010, May 2011, June 2013 and May 2016. The estuary, from the landward limit of the salt water intrusion near Île d'Orléans (~5 km downstream of Québec City) to Pointe-des-Monts, where the coastline diverges, extends ~400 km and covers a total surface area of ~12,820 km^2. The solid gold line follows the 200m isobath of the Laurentian Channel. The vertical dotted lines delineate the five segments of the estuary used for the calculation of the area-averaged CO_2 flux.

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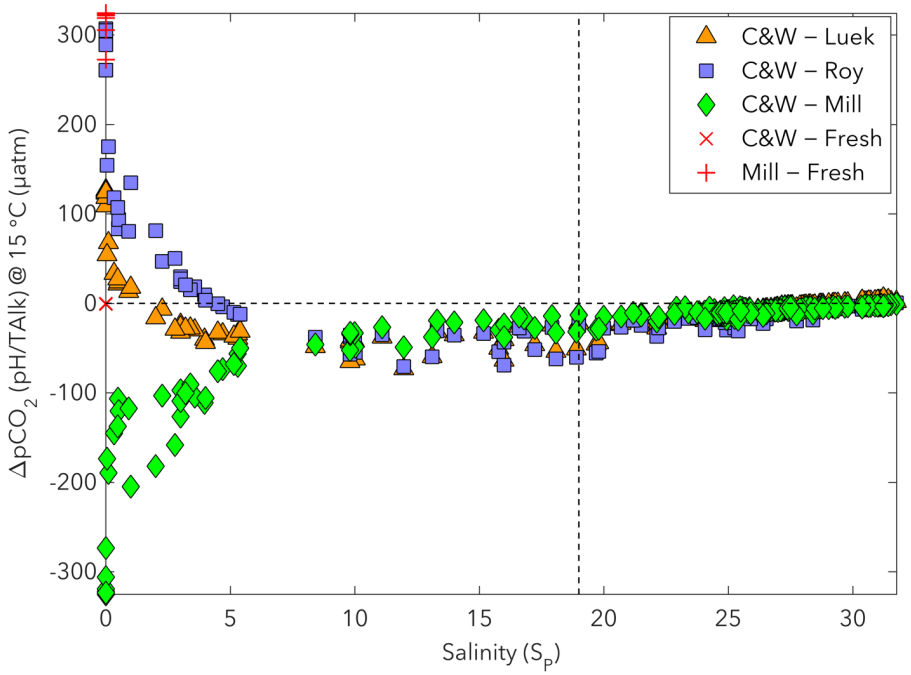

Figure 3. Differences in pCO_2 (ΔpCO_2) calculated using different published formulations of K_1 and K_2, including Cai and Wang (1998) [C&W], Lueker et al. (2000) [Luek], Roy et al. (1993) [Roy], Millero (2010) [Mill], and Millero (1979) for pure water only (S_P = 0) [Fresh]. All calculations were carried out at 15 °C (pCO_2 @ 15 °C) with measured pH and TAlk. The constants of Lueker et al. (2000) are recommended for best practices by Dickson et al. (2007), whereas those of Roy et al. (1993) (S_P = 5 to 45) are recommended by Dickson and Goyet (1994). Both the constants of Cai and Wang (1998) and Millero (2010) have been proposed as more appropriate for the study of the carbonate system in estuarine waters.

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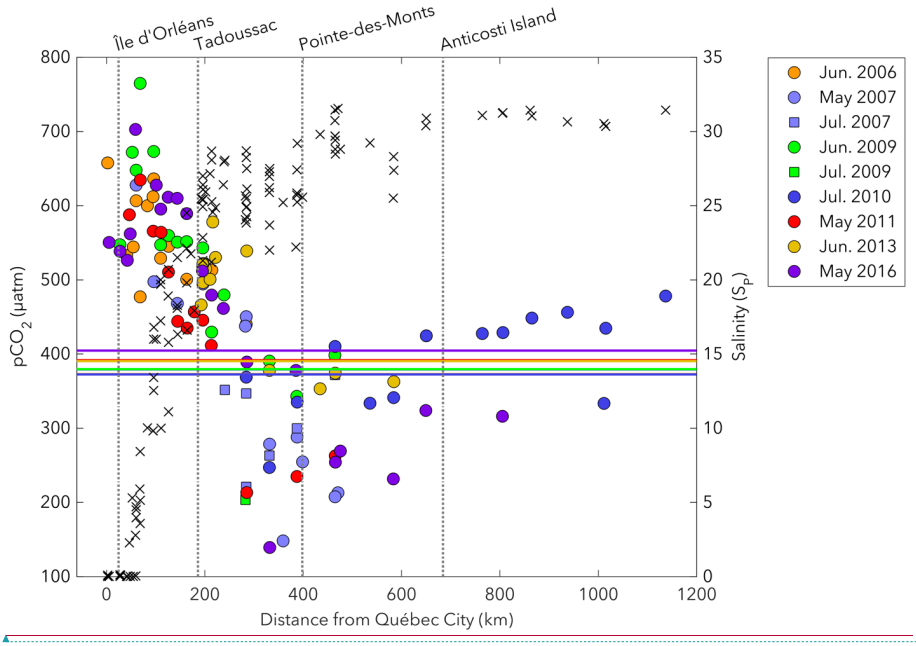

Figure 4. Spatial distributions of surface-water pCO_2 (circles, squares) and practical salinity (x symbols) in the St. Lawrence River, Estuary and Gulf during spring/summer cruises. Horizontal lines show the mean pCO_2(air) in the sampling months. The pCO_2 data points above atmospheric level are sources of CO_2 to the atmosphere whereas those below atmospheric level are sinks of atmospheric CO_2.

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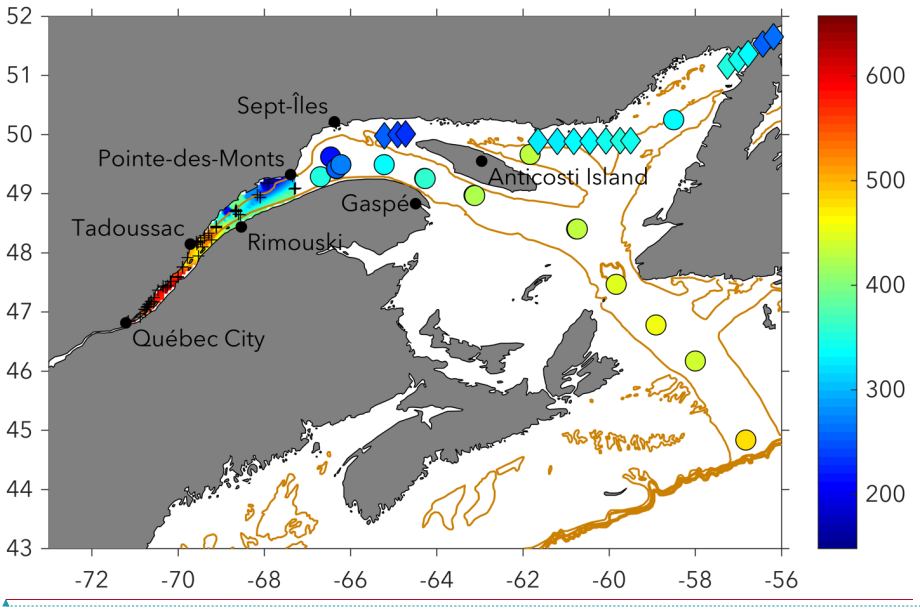

Figure 5. Spatial distribution of surface-water pCO_2 (µatm) in the St. Lawrence Estuary and Gulf during all spring/summer cruises. Linear interpolation was used between the sampling locations in the estuary (+ symbols). Circles show calculated pCO_2 (pH/TAlk), whereas diamonds show pCO_2 measured by the underway system (General Oceanics model 8050) aboard the CCGS *Amundsen* in June 2016 (Dr. Tim Papakyriakou/University of Manitoba, pers. comm.). For neighboring locations sampled in May 2016 aboard the RV *Coriolis II*, measured and calculated pCO_2 differed by, on average, ~4.2 %. The mean atmospheric pCO_2 during the sampling months ranged from 372 to 405 µatm.

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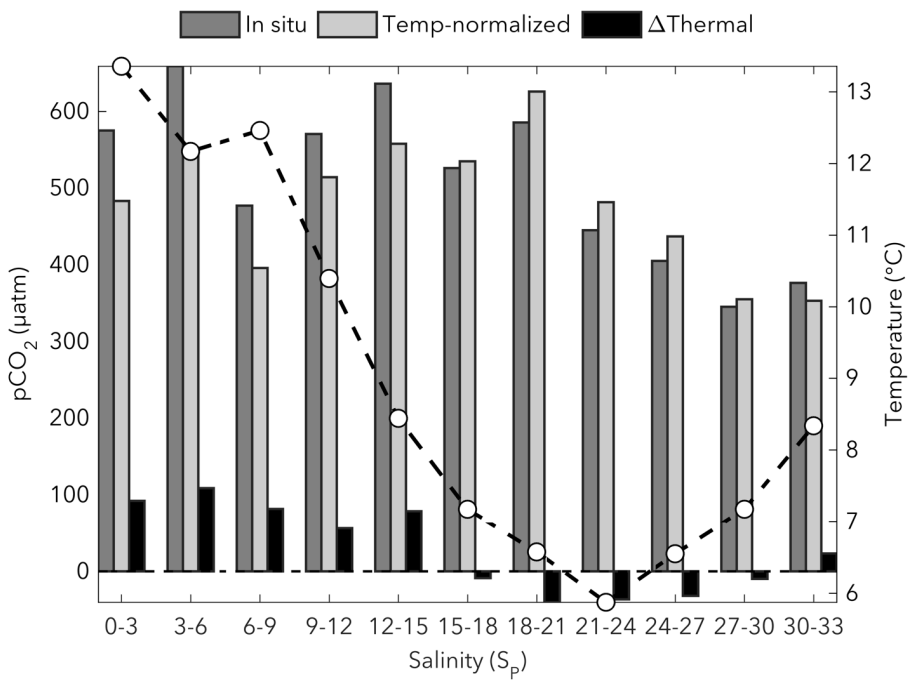

Figure 6. Surface-water *in situ* pCO_2, temperature-normalized pCO_2, and ΔpCO_2(temp) averaged over salinity bins of 3. The open circles show the average temperature for each salinity bin. To correct for the increasing/decreasing effect of temperature on surface-water pCO_2, the *in situ* pCO_2 were normalized to the average surface-water temperature of the study area (T = 7.82 °C). The ΔpCO_2(temp) are the thermally-induced pCO_2 changes due to temperature deviations from T = 7.82 °C, whereas variations in temperature-normalized pCO_2 are due to water mass mixing and/or biological activity.

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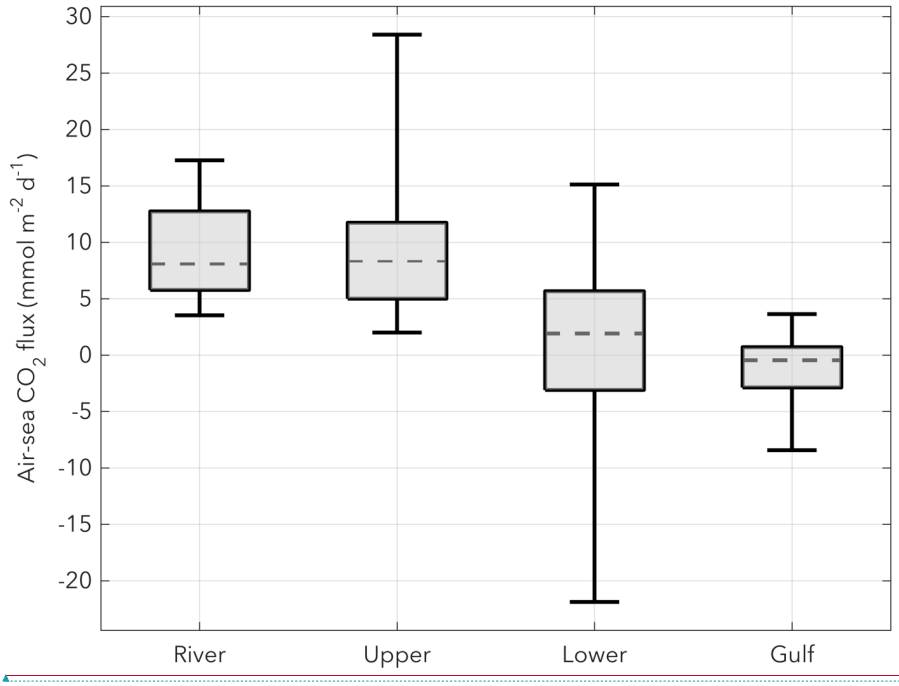

Figure 7. Box plot showing the variability of air-sea CO_2 fluxes in the four principal subdivisions of the study area (St. Lawrence River, Upper Estuary, Lower Estuary and Gulf). The box spans the interquartile range (25–75 percentiles), the dashed line is the median, and the whiskers extend to the extreme data points. The $F_{W\text{-}14}$ data were combined with the $F_{R\&C\text{-}01}$ data from all spring/summer sampling months to depict the upper and lower limits of gas exchange.

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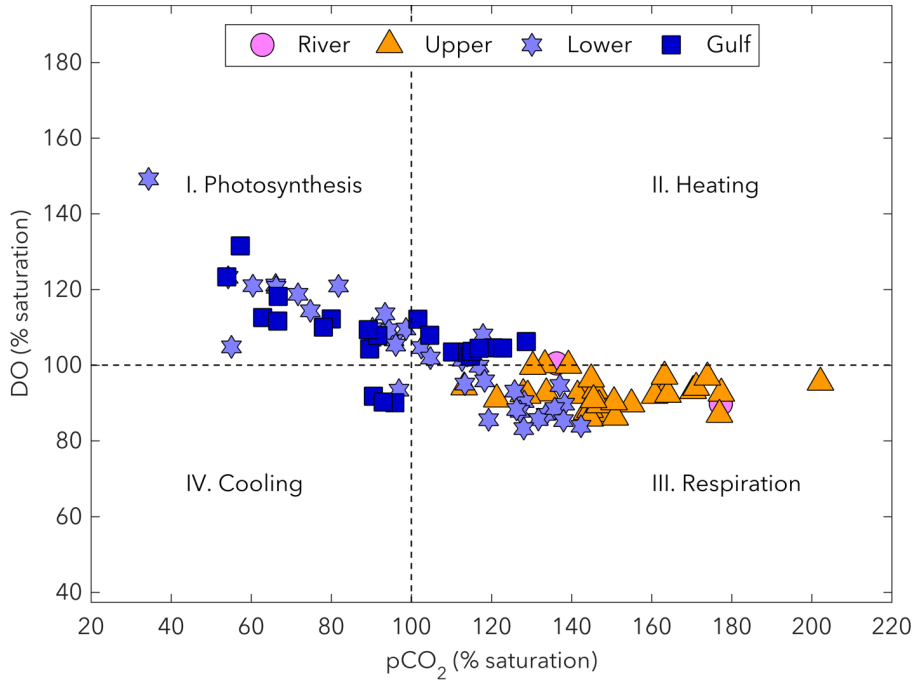

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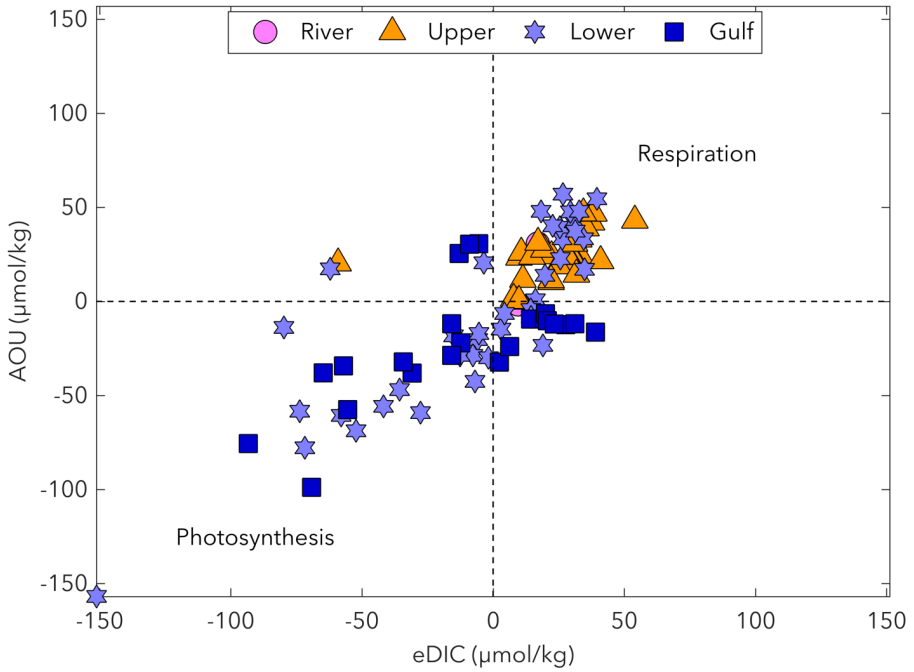

Figure 8. Top: comparison of the saturation states (or % saturation) of pCO_2 and DO in the mixed-layer waters of the St. Lawrence River, Estuary and Gulf. Dashed lines delineate the 100 % saturation levels for both gases. Surface-water samples (markers) fall into one of four quadrants representing the dominant controls on CO_2/O_2 dynamics. Quadrants I and III indicate the effects of photosynthesis/respiration, whereas Quadrants II and IV indicate heating/cooling. Bottom: comparison of the apparent oxygen utilization (AOU) and excess DIC (eDIC). Respiration/remineralization processes are reflected in positive values of AOU and eDIC, whereas the effects of photosynthesis are reflected in negative values.

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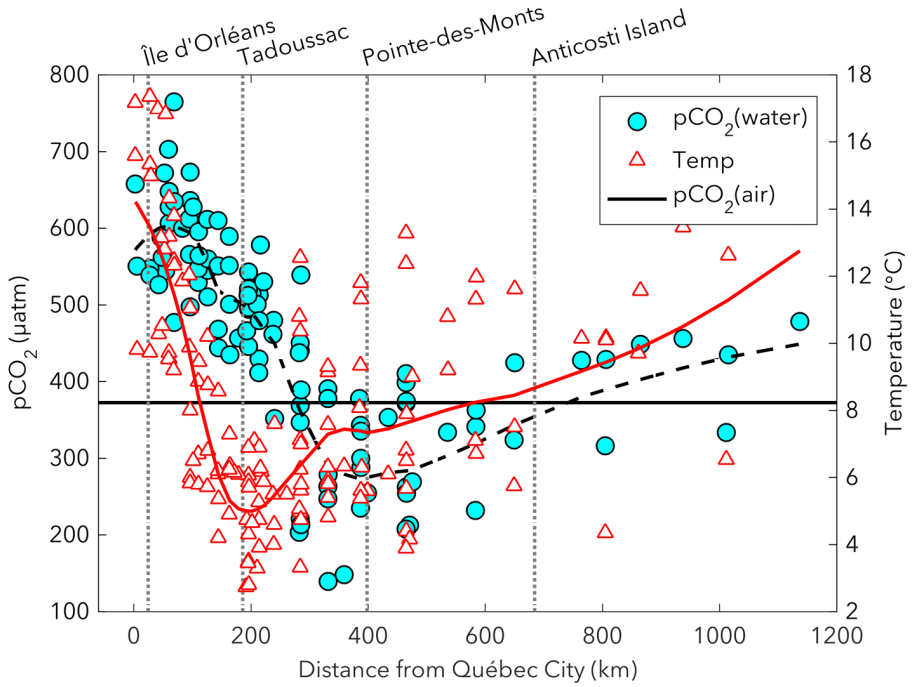

Figure 9. Spatial distributions of surface-water pCO_2 (circles) and temperature (triangles) in the St. Lawrence River, Estuary and Gulf during spring/summer cruises. Temperatures ranged from 4.2 to 17.4 °C (generally decreasing) in the USLE, 2.7 to 12.6 °C (generally increasing) in the LSLE, and 3.9 to 13.7 °C (generally increasing) in the GSL. The horizontal line shows the mean atmospheric pCO_2, pCO_2(air), during all sampling months. The dashed line is the smoothed pCO_2(water) data using a moving average filter with a span of 50% of the total number of data points, whereas the red line is the smoothed temperature data.

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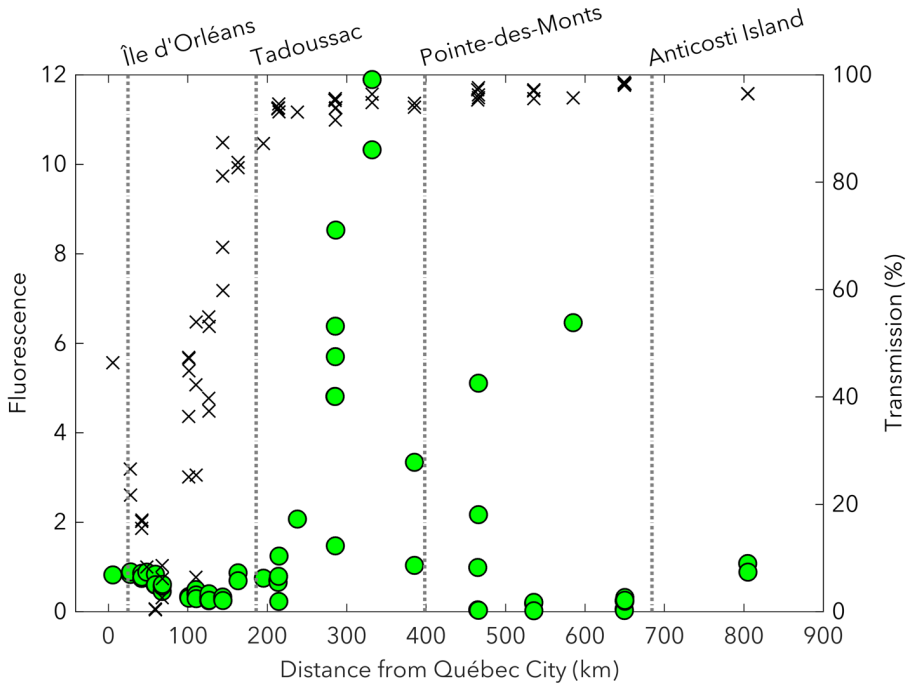

Figure 10. Spatial distributions of maximum fluorescence values (circles) and mean transmission values (x symbols) in the euphotic zone of the St. Lawrence River, Estuary and Gulf during the May 2016 cruise. Fluorescence is a primary production proxy, whereas transmission is an excellent proxy for turbidity (low transmission values are due to light absorption by suspended particulate matter and/or colored dissolved organic matter).

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variations in pCO_2 due to water mass mixing and those due to *in situ* biological activity

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