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Biogeosciences Discussions

Interactive comment on "Spatial variability of surface-water pCO_2 gas exchange in the world's largest semi-enclosed estuarine system: St. Lawrence Estuary (Canada)" *by* Ashley Dinauer and Alfonso Mucci

Anonymous Referee #2

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General Comments

The paper under review for Biogeosciences presents a multi-year compilation of springtime and summertime air-water CO2 fluxes in the world's largest semi-enclosed estuarine system (St. Lawrence Estuary, Canada). The paper is generally well-written and easy to follow. However, I just have some questions/comments that I think are important to resolve:

The sampling campaigns were conducted in springtime and summertime, but I missed some information about the wintertime. In addition, despite the large surface area of

the St. Lawrence Gulf, this region was poorly sampled (spatially and temporally). For example, in the Figure 4 we can see only 4 points (sampled at Jul.2010) covering the whole area from Anticoasti Island until the connection to the Atlantic Ocean. I think that these gaps in data collection need to be better described in methodology and discussion sections.

The drawdown of pCO2 values between Tadoussac and Anticosti Island must be better discussed. Do you have results of Chlorophyll a concentrations and/or primary production?

I think that you should improve the discussion section through comparisons with other studies in estuaries worldwide (pCO2 values, fluxes and governing factors) to better contextualize your research.

Specific Comments

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 marginsHydrol. Earth Syst. Sci., 17, 2029–2051.

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.

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

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?

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

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?

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.

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.

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.

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

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?

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.

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 Aticosti 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.

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

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).

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?

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

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.

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.

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.

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.

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