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Biogeosciences Discussions

Interactive comment on "Distributions of surface water CO_2 and air-sea flux of CO_2 in coastal regions of the Canadian Beaufort Sea in late summer" *by* A. Murata et al.

Anonymous Referee #1

Received and published: 9 February 2009

GENERAL COMMENTS :

Murata and colleagues report an interesting and valuable data-set of CO2 measurements during late summer in coastal Arctic waters (Canadian Beaufort Sea). This data set confirms the role of high latitude waters as strong sinks for atmospheric CO2, and highlights complex dynamics of CO2 in the Mackenzie River plume. Besides several minor corrections detailed hereafter, I have some concerns at a methodological level (choice of the dissociation constants) and with data manipulation and related interpretation (use of TCO2/TAlk plots), and some serious concerns with the method to normalize TCO2 to a constant salinity that in my opinion lead to a biased data interpretation.

SPECIFIC COMMENTS :

Page 5094 / Line 5 : please round atmospheric pCO2 values to the unit (considering precision and accuracy of shipboard measurements)

Page 5094 / Line 13 : Please specify months of sampling with years (here and elsewhere in the ms).

Page 5094 / Lines 18-20 : This statement should be toned down since it is based on a single measurement obtained with dubious sampling methods for gas analysis (with a bucket).

Page 5095 / Lines 1-6 : In this sentence several methods that provide different types of estimates are mixed together : uptake of anthropogenic CO2 (e.g. Sabine et al. 2004) and contemporary fluxes of CO2 (combining anthropogenic and natural CO2 fluxes) (e.g. Takahashi et al. 2002).

Page 5095 / Lines 8-9 : paper of Canadell et al. (2007) could be useful here.

Page 5095 / Lines 17-22 : A caution is needed here. Climate changes could also lead to the mobilisation of terrestrial organic carbon that if transferred to the coastal zone will be degraded and vented to the atmosphere, hence inducing a source (or a reduction of the sink) of atmospheric CO2 from coastal arctic areas.

Page 5096 / Lines 16 : provide make and model of the infrared analyzer

Page 5096 / Lines 17-19 : provide the xCO2 of the operational standards used on board

Page 5096 / Lines 17-19 : provide the xCO2 of the SIO standards

Page 5096 : SOCAT is an initiative and not a project

Page 5096 : I strongly encourage the authors to submit the TAlk and TCO2 data from

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vertical profiles to CDIAC

Page 5097 / Line 3 : please remove ' by the system '

Page 5097 / Line 5 : please replace ' recalibrated ' by ' calibrated '

Page 5097 / Line 17 : ' within +/- 30min of hours ' is unclear, please reformulate

Page 5097 / Line 19-22 : the equation of TAlk is unnecessary, I suggest to remove it

Page 5097 / Line 23-24 : There is a general agreement that the constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) give the most consistent computations as discussed at length by Wanninkhof et al. (1999) and Lee et al. (2000). I'm surprised that the authors chose to use the constants given by Goyet & Poisson (1989). The constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) are valid down to a temperature of 0°C, while the constants of Goyet & Poisson (1989) are valid down to a temperature of minus 1°C. This difference of 1°C does not in my opinion justify the use of the Goyet & Poisson (1989) constants.

Page 5098 / Line 2 : please specify the affiliation of D. Pierrot

Page 5098 / Line 2 : is the software available freely ? If from internet, please specify URL

Page 5098 / Line 11 : please replace ' transfer velocity ' by ' gas transfer velocity '

Page 5098 / Line 12 : please just specify that deltapCO2 is the air-sea gradient of pCO2

Page 5098 / Line 17-18 : there is now sufficient evidence that the Liss and Merlivat (1986) formulation clearly under-estimates k at high wind speeds (e.g., Ho et al. 2006)

Page 5098 / Line 23 : It is not necessary to give the equation for the W92 formulation, especially if the authors do not give the equations for the other formulations used for the flux computations.

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Page 5098 / Line 24 : wind speed is usually noted as u10 and not w10 by the gas exchange community.

Page 5099 / Lines 7-8 : here and elsewhere in the ms, please systematically refer to ' September 2000 ' instead of ' 2000 ' and ' September 2002 ' instead of ' 2002 '

Page 5099 / Line 9 : please specify the data providers and URL of data source for the Point Barrow atmospheric pCO2.

Page 5099 / Line 10 : please round atmospheric pCO2 values to the unit (considering precision of shipboard measurements)

Page 5099 / Line 12 : ' differed little ' is not rigorous. Please provide a statistical test for the differences.

Page 5099 / Line 14 : please round atmospheric pCO2 values to the unit (considering precision of shipboard measurements)

Page 5099 / Line 16 : please replace ' sequential day ' by ' year day ' (here and elsewhere in the ms, including the figures).

Page 5099 / Line 16 : please replace ' mostly lower than ' by ' most of the time below '

Page 5099 / Line 21 : add ' where salinity was lowest ' after Mackenzie river

Page 5099 / Line 21-23 : Sentence could be replaced by something like ' pCO2 was positively correlated to TCO2 and SST, whereas it was negatively correlated to SSS '.

Page 5099 / Line 24-26 : I'm surprised by this explanation, since there is a sufficient number of TAlk values to provide robust comparisons with pCO2. Another explanation is that TAlk values in freshwaters of the Mackenzie river are high, hence there is a less marked TAlk signal than SSS. Reeder et al. (1972) reported TAlk values in freshwater of the Mackenzie river ranging from 44 to 4194 μM with a discharge-weighted value of 1760 μM. Telang et al. (1991) reported TAlk values in freshwater of the Mackenzie river ranging from 1920 to 2240 μM with a discharge-weighted value of 2051 μM. Hence,

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the river-end member TAlk value is close to the marine-end member value (1900 μM) which explains that TAlk varies little with SSS, and that pCO2 correlates poorly with TAlk, but better with SSS. More TAlk data in the Mackenzie river have been reported by Millot et al. (2002) and Gordeev et al. (1996).

Page 5100 / Line 6 : please replace ' although supersaturation of surface water pCO2 ' by ' although CO2 supersaturation of surface waters '

Page 5100 / Line 18 : One conclusion from this study that deserves to be noted (here and elsewhere) is that the plume of the Mackenzie River was either a source of CO2 or a sink of CO2 depending on the cruises, for a similar SSS decrease.

Page 5100 / Line 20 : Remove ' calculated as the (. . .) '. deltapCO2 has already been defined in the ms.

Page 5102 / Line 15 : NCP, autotrophy and heterotrophy are concepts that were not introduced by Hanssell & Carlson (1998) and have been around since the early work of Odum in the late '50s. Hence, reference is inadequate.

Page 5102 / Lines 20-24 : I find it unlikely that there is no drawdown of TCO2 by biological activity. One source of error that could give a bias in this approach and conclusions, could be procedure to normalize the TCO2 data. The simple procedure (TCO2normalized=TCO2_at_observed_salinity/Observed_salinity*salinity_of_normalization), assumes intrinsically that for a zero salinity TCO2 is zero. Based on the above TAlk values reported for the Mackenzie River freshwaters, this hypothesis can hold true. Hence, the normalization must be made with care, refer to Friis et al. (2003) for a discussion on this matter and alternate procedures. This is particularly important since the normalization to a constant salinity is made over a large interval of salinity, about 6.0 psu based on Figure 11.

Page 5102 / Lines 20-24 : The finding that there is no biological drawdown of TCO2 must be confirmed by nutrient, oxygen and chlorophyll-a data, that should also be available from these cruises. An analysis of remote sensed chlorophyll-a should also be useful.

Page 5102 / Lines 20-24 : The finding of higher TCO2 values in surface waters than in bottom waters is counter-intuitive, and authors must provide some sort of hypothesis to explain this puzzling observations. Again, I think that these findings are biased due to an inadequate normalization of the TCO2 data to a constant salinity.

Page 5103 / Lines 1-4 : these sentences are obscure; please specify what is meant by ' nTCO2 were associated with river discharge '. Please specify what is meant by ' biological processes in the river discharge '.

Page 5103 / Lines 5-11 : It is essential that the authors also show the plots of TAlk versus salinity and the plots of TCO2 versus salinity, and that they interpret and discuss these plots.

Page 5103 / Lines 5-11 : I'm not sure that the TCO2/TAlk approach is effective in areas of large salinity change, where TCO2 and TAlk change mainly because of mixing of different water masses that will impose the main signal. The TCO2/TAlk ratio in principle should give approximately the relative change of [CO2]. In this respect, I would feel more confident at looking at pCO2 versus salinity variations rather than TCO2/TAlk versus salinity.

Page 5103 / Line 11 : It is unclear what is the 'expected trend'.

Page 5103 / Line 11 : Please note that ' trend ' usually refers to a change of a variable as a function of time. The term ' pattern ' would be more adequate.

Page 5103 / Line 25 : I suggest to replace ' water mixing and cooling of a water mass ' by ' cooling and mixing of water masses '.

Page 5103 / Line 27 : I suggest to replace ' to confirm this ' by ' to investigate this '.

Page 5104 / Line 3-4 : Is this mixing or could this also be advection and temperature

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change of the same water mass ?

Page 5104 / Lines 20-21 : I suggest to replace ' The calculated pCO_2 values well reproduced the observed pCO_2 distributions .' by ' The observed pCO_2 values followed a distribution close to the one expected from conservative mixing. '

Page 5104 / Lines 27 : please replace ' on some legs ' by ' during some legs '.

Page 5105 / Lines 4-9 : It is unclear how these computations were made, some details on the computations could be useful.

Page 5105 / Lines 4-9 : Please note that in this system changes of SSS and TAlk are not independent, hence, it should be clearly explained how the authors managed to evaluate these variations independently.

Page 5105 / Line 11 : As far as I understand it's mixing of fresh-water and sea-water end-members that would control pCO_2 and not 'river discharge'.

Page 5106 / Line 17 : I suggest to replace ' moderated ' by ' smoothed '.

Page 5107 / Lines 3-4 : I suggest to replace ' indicate that upwelling of lower temperature and saltier water brought up water rich in CO_2 ' by ' indicate upwelling of cooler, saltier and CO_2 rich waters '.

Page 5107 / Lines 5-6 : I'm very surprised that system stratified in 2 hours, with an increase of temperature of 1°C and a decrease of salinity of 4.5 psu over such a short time interval. I think that the most probable explanation is that a different water mass was advected into the area during the time interval between the two stations. A careful analysis of the underway data of SSS, SST and pCO_2 data during the time interval could provide additional insights (if the ship stayed on station).

Page 5107 / Line 21 : Please specify where the Bates (2006) data were obtained.

Page 5108 / Lines 10-13 / Lines 18-20 : Please use uniform units for the flux values and not a mixture of mmol/m2/d and mol/m2/year.

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Interactive Discussion

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Page 5110 / Line 8 : What other ' physical and chemical properties ' ?

Page 5110 / Lines 13-25 : I find it odd that this section based on bucket sampling appears in the Conclusions. I also find odd that only one data point is presented. I have the impression that this section was added at the last minute to the ms. This section would be more appropriate in the discussion section, and more convincing if more data points are added and compared. A more detailed description of the procedures to sample from the bucket needs to added to the material and methods section. Also the accuracy and precision of pCO_2 computed from TCO_2 and Talk needs to be evaluated and specified in the Material and methods section.

Page 5110 / Lines 13-25 : The salinity from the bucket sample is 17.80 and the salinity at 4m is 17.21. Hence, there are strong salinity gradients in the top 4 m meters making the comparison of pCO_2 in the bucket with pCO_2 at 4 m even more difficult.

Page 5110 / Lines 13-25 : Was care taken to avoid exchange of gas with the atmosphere while sampling with a bucket (a rather unorthodox method to sample for CO_2 measurements) ?

Page 5110 / Lines 17-18 : round pCO_2 values to the unit.

Page 5110 / 23-25 : I find it odd that suddenly biological activity plays an important role in CO_2 dynamics in the study area, while during most of the ms, the authors argue that biological drawdown of TCO_2 is negligible.

Page 5110 / 23-25 : The role of the difference in salinity between the bucket sample and the sample at 4 m should be also evaluated on the pCO_2 difference.

Page 5112 / Line 32 : Buat-Ménard

Page 5116 / Table 1 : atmospheric pCO_2 data can be rounded to the unit. Specify month and year of the 2 cruises. However, this table does not seem very useful since the data are already mentioned in the text.

Page 5117 / Table 2 : surface pCO2 data can be rounded to the unit. Specify month and year of the 2 cruises.

Page 5118 / Table 3 : Specify month and year of the 2 cruises.

Page 5119 / Table 4 : Specify month and year of the 2 cruises.

Page 5120 / Table 5 : deltapCO2 data can be rounded to the unit. Specify month and year of the 2 cruises.

Page 5121 / Legend of Fig. 1 : Specify month and year of the 2 cruises. Please spell out ODV.

Page 5122 / Legend of Fig. 2 : Specify month and year of the cruise.

Page 5122 / Fig. 2 : units of pCO2 are missing from top panel.

Page 5123 / Legend of Fig. 2 : Specify month and year of the cruise.

Page 5124 / Legend of Fig. 4 : Specify month and year of the 2 cruises.

Page 5125 / Legend of Fig. 5 : Specify month and year of the 2 cruises.

Page 5126 / Legend of Fig. 6 : Specify month and year of the 2 cruises.

Page 5127 / Legend of Fig. 7 : Specify month and year of the 2 cruises.

Page 5128 / Legend of Fig. 8 : Specify month and year of the 2 cruises.

Page 5129 / Legend of Fig. 9 : Specify month and year of the 2 cruises.

Page 5130 / Legend of Fig. 10 : Specify month and year of the 2 cruises.

Page 5131 / Legend of Fig. 11 : Add date of sampling, time (hh) of the 2 profiles, position of station (lat/long).

Page 5132 / Legend of Fig. 12 : Specify month and year of the 2 cruises.

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