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Biogeosciences
Discussions

Interactive comment on “A large CO_2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil)” *by* L. C. Cotovicz Jr. et al.

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Interactive comment on “A large CO2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil)” by L. C. Cotovicz Jr. et al. W-J. Cai (Referee) wcai@udel.edu

Reviewer Comment 1: The authors presented a well conducted research in Guanabara Bay, Brazil. They suggested their “findings of a net annual CO2 sink indicate that more field data are needed in particular in the highly productive tropical coastal ocean, in order to adequately integrate estuarine CO2 fluxes at the global scale,” and I agree. The paper is also generally well-written and easy to follow. I recommend publication

with a major revision regarding the few points I listed below. If the first author is writing (one of) his/her first research papers, I must congratulate him/her. Well done! Reply 1: We acknowledge Dr W-J Cai for his positive evaluation of our MS and encouraging general comments.

Reviewer Comment 2: While the Results are very nice, I feel the Discussion lacks a rigorous analysis. The authors provided a statistical analysis of data (which environmental and biogeochemistry factors is in control of pCO2 or CO2 flux); that is very good. But can you move a step further by providing a more rigorous biogeochemical analysis. For example, a 1-D (seasonal) analysis on how pCO2 changes with time (from temperature, air-sea flux, mixing, and biological production) at few sites. NEP (or NCP) would come up in this analysis. If the authors feel this is too much to ask, then, they should say why (such as this is good enough, or they need further information to do a more rigorous analysis, or it will be in their next paper, etc.). Reply/Change 2: We have made some significant changes in our revised MS, in order to improve our biogeochemical analysis, as requested by Dr W.-J. Cai. Please note however that the hydrodynamics of the bay is quiet complex and for instance salinity patterns do not allow a simple and classical mass balance analysis based on the mixing between fresh- and saline end-members. Here, we have quantified the influence of water temperature on pCO2 values at seasonal scale with the Takahashi approach (Takahashi et al., 2002) and we observed that the temperature effect (thermodynamic) is very small compared to the biological effect. On the other hand, at the diurnal time scale, we observed that the daytime formation of thermal stratification due to the strong irradiance incidence was an important environmental factor for blooms development. We calculated the Spearman correlation with the average values for each sampling campaign, and the pCO2 was negatively correlated to the DO, Chl a, temperature and wind velocity (see the table R1 at the end of this document). The Spearman correlation was consistent with the PCA analysis. As also pointed by the reviewer 1, we improved the manuscript by calculating NCP (including information in the methods, results, discussion and conclusions), and this strengthened our conclusion one the autotrophic character of the bay in relation with the CO2 sink. Finally, we are now analyzing several other biogeochemical parameters (POC, DOC, 13C-DOC, 13C-DIC…), and we believe these data can contribute to a more quantitative biogeochemical analysis in one future paper, as suggested.

Reviewer Comment 3: This is a low wind regime. You have used two k600 models, one as the upper boundary and the other (RC) as the lower boundary, which is fine. But I thought RC method provided quite high fluxes. Could you at least make a comparison with Wanninkhof 1992 equation or his later revisions? Reply 3: We inserted in the table 2 the values of K600 and related fluxes with the gas exchange coefficient of Wanninkhof 1992. Now, the model of Wanninkhof can be considered the lower boundary of the calculated fluxes as this K600 model was initially developed to open ocean waters, does not account for the specifies of the estuarine environments. Change 3: In the table 2 with the inserted Wanninkhof values (W92). Also, we included in the text some results and comparisons of the three k600 models

Reviewer Comment 4: The carbon budget: p.4697, Is there a strong reason that sediment burial must equal to air-water gas flux of CO2? I was expecting that this section would show how much of CO2 is taken from surrounding mangrove and cities, how much is exported to the sea, how much is buried and how much is recycled, etc. I may have asked too much. So you may ignore me; but at least don't call this section carbon budget. Reply 4: The reason why sediment burial must equal to air-water gas flux of CO2 is that other lateral carbon inputs appear minor. However, we agree that the available data in Guanabara Bay does not allow the construction of a full carbon "budget". However, is interesting the fact that the sink of CO2 at air-water interface is very near of the organic carbon burial in sediments (it seems like one efficient biological pump). We have some considerations: 1) the sediment sampling of Carreira et al (2002) was not conducted in a well spatial design, i.e., the sampling was focused at the upper parts of the bay, and is different of our approach that covered about 80% of the superficial area. 2) Considering the three K600 models, the equaling of CO2

sink and organic carbon burial is visualized in the model of A09, whereas the other two models provided values a bit smaller than the burial of organic carbon. However, again, we need to keep in mind that the spatial sampling was very different between the two studies. If we consider the sectors fluxes, the equality is more consistent. The answers to the other questions, like "how much of CO2 is taken from surrounding mangrove and cities, how much is exported to the sea, how much is buried and how much is recycled" we cannot yet answer due to the scarcity of available data. We have only reports of the Environmental Institute of Rio de Janeiro State (FEEMA) and the published papers of Carreira et al 2002; Rebello et al 1988 and Kalas et al 2009, which results are discussed in the section 4.4, however we have more questions than answers related to the fluxes between the compartments. The river inputs of carbon are still scarce, as well as, the exchanges with the open ocean. Change 4: We included a table in the manuscript that concise the fluxes in the bay (please, see at the end of this review the table R2). Also, modified the title section to the "Air-Water CO2 fluxes in Guanabara Bay"

Reviewer Comment 5: While EDIC to AOU relation is present in the last figure, DIC and TA are hiding somewhere. Why? TA and DIC to salinity plots may illustrate an idea whether all uptake CO2 is buried in sediment or is recycled and exported to offshore. Reply 5: TA and DIC to salinity plots in Guanabara Bay are shown in additional figure R3. It can be seen that in this saline coastal embayment TA and DIC have non-conservative behaviors. Addition of DIC can be observed in the polluted sector 2 and addition of TA in sectors 4 and 5 (probably due to important sulfate reduction in these most eutrophic regions). However the pCO2 versus salinity plot give no consistent information. In addition, the bay presents important lateral inputs that alter the distribution of inorganic C variables in relationship to the salinity. We think in Guanabara Bay, the TA and DIC to salinity plots do not help understanding whether all uptake CO2 is buried in sediment, or recycled and exported. Change 5: No change related to this specific comment. We plan to publish these plots in a future paper that will also include 13C-DIC.

Reviewer Comment 6: pH measurement method is missing in the Method section. Since it is used to calculate DIC, it must be evaluated more rigorous. How much uncertainty is in the calculated DIC? Reply/Change 6: The precision of the pH measurements was about 0.01 (after 7 verifications against NBS standards). We performed a three-point calibration (pH 4.01, pH 7.00 and pH 10.01), and the measurements were made continuously (data logging of 1 minute). As we have overdetermined the carbonate system (pCO2, pH, and TA) and we have chosen to used direct pCO2 measurements and DIC calculated from pCO2 and TA, we use pH measurements only for quality check. We do not use DIC values to perform any budget calculation. We only use pCO2 values for the CO2 budget. Our paper is quiet long enough so we find such detailed DIC quality check secondary in comparison with other topics (eutrophication, stratification, etc. . .). Nevertheless, as requested, we provide to the reviewer the information on the quality of our data that in Figure R4 (comparison between DIC calculated from pH/TA and pCO2/TA) and we added few sentence in the material and methods.

Other points I noted as I read through. Reviewer Comment 7: Title: I do not see the need of the word “large.” Better just say “A CO2 sink enhanced by: : :” Abstract: a bit repeating, can be shortened. Also in the last line, not clear whatyou mean by “behave specifically.” uniquely (being a sink)? Reply/Change 7: We rewrote part of the abstract. We changed “large sink” to a “strong sink”.

Introduction Reviewer Comment 8: P. 4673, line 23, “suite a lot of: : :” don’t know what you mean. Reply/Change 8: we removed the part “and a suite a lot of anthropogenic perturbations” in our revised MS.

Reviewer Comment 9: P. 4674, “which”? “with”? Reply/Change 9: we modified to “. . .which are net heterotrophic. . .”

Reviewer Comment 10: p. 4674, line 23, may replace “incipient” with a more commonly used word or term. Reply/Change 10: we replaced “incipient” by “scarce”.

Reviewer Comment 11: p.4674, line 27, I don’t think “Amazon River plume” is an appro-

priate example here. It is very different from what you are talking here. Reply/Change 11: we excluded in our revised MS the part of the Amazon plume.

Reviewer Comment 12: p.4674, line 12, in this context, you may want to reference works from the Mississippi River plume 1. Guo, X., Cai, W.-J., Huang, W-J., Wang, Y., Chen, F., Murrell, M.C., Lohrenz, S. Dai, M., Jiang, L-Q. and Culp, R., 2012. CO2 dynamics and community metabolism in the Mississippi River plume. Limnology and Oceanography 57(1):1-17. And/or 2. Huang, W-J., Cai, W-J., Wang, Y., Lohrenz, S.E., and Murrell, M.C. 2015. The carbon dioxide (CO2) system on the Mississippi River–dominated continental shelf in the northern Gulf of Mexico – I: Distribution and air-sea CO2 flux, Journal of Geophysical Research-Ocean (in press, paper #2014JC010498). Reply/Change 12: we cited the two papers in our revised MS.

Reviewer Comment 13: p.4675, line 25, extremely low (not extreme low)? 2.1 Reading figure 1, I can’t tell where is the sea? Does seawater come from S1 or S4? Mark it. Reading further to the 2nd paragraph and to line 26 of p. 4677, I guess then see S1 is near bay mouth. Better make it clear. Reply/Change 13: We performed the correction to “extremely low”. We also included in the figure the location of the sea to better clarify the study area.

Reviewer Comment 14: 2.3.1 How was pH measured? Since it is a critical parameter that is used to calculate DIC (from pH and TA). You must document it in details. Reply/Change 14: Please, see the reply/change 6. Note that as we have overdetermined the carbonate system (pCO2, pH, and TA) and we have chosen to used direct pCO2 measurements and DIC calculated from pCO2 and TA, we use pH measurements only for quality check.

Reviewer Comment 15: 2.3.3, I think it is better just use Merbach refitted by Dickson and Millero (1987), rather than the composite one with Hansson data. Since DIC is calculated, possible issues related to the calculation should be mentioned. Reply/Change 15: We used Merbach et al., (1973) refited by Dickson and Millero (1987) instead of the Hansson and Merbach in the revised MS.

Reviewer Comment 16: Fig. 2, make the label larger and shorter (just precipitation and temperature; leave other words such as atmosphere in figure caption). I can barely read them. Reply/Change 16: We agree with the considerations. We modified the fig. 2. In addition, we inserted the standard deviation in the bars.

Reviewer Comment 17: 3.3 Spatial screening??? Reply/Change 17: we changed to "Spatial distributions. . ."

Reviewer Comment 18: Fig. 4, caption. What is "superficial waters"? Does it tell a different meaning from the more commonly used term "surface or surficial waters"? also, p.4688, line 14. Reply/Change 18: We performed the correction to "surface waters".

Reviewer Comment 19: p.4685, line 4 relatively stable Reply/Change 19: Modified as suggested.

Reviewer Comment 20: p.4685, line 8, I don't know what is the meaning of the word "activation" here. Reply/Change 20: We deleted the word "activation".

Reviewer Comment 21: p.4689, line 1, here you may reference to low pCO2 in the Mississippi plume (Huang et al. 2015, above). Reply/Change 21: In this context, we inserted in the MS the part ". . .and on the Mississippi River-dominated continental shelf (Huang et al., 2015). . ."

Reviewer Comment 22: p.4689 lines 7-21, and figure caption. What exactly is this 1:1? Need to say this in the figure caption and probably a bit more in the text. Reply/Change 22: We included in the last paragraph of the section 4.1 the sentence: "The 1:1 line represents the quotient between CO2 and O2 during planktonic primary production and aerobic respiration (Borges and Abril 2011). The values near this ratio for Guanabara Bay suggests that gross primary production and total (autotrophic and heterotrophic) respiration are coupled and largely dominated the signal, with a strong biological control on the production/consumption of these gases." In addition, we included in the

figure caption the sentence: "The 1:1 line represents the theoretical quotient between CO2 and O2 during the processes of photosynthesis and aerobic respiration".

Reviewer Comment 23: p. 4694, line 17, (also line 1 the next page) while many carbonate chemists also make this mistake, you cannot say "the pCO2 concentrations." Here p, the partial pressure, already means concentration (in gas phase). I suggest "pCO2 values." Reply/Change 23: We agreed and performed the correction.

Reviewer Comment 24: p.4697, Is there a strong reason that sediment burial must equal to air-water gas flux of CO2? I was expecting that this section would show how much of CO2 is taken from surrounding mangrove and cities, how much is exported to the sea, how much is buried and how much is recycled, etc. I may have asked too much. So you may ignore me; but at least don't call this section carbon budget. Reply/Change 24: Please, see the reply/change 4.

Additional figure captions

R1: Spearman correlation matrix for PAR (μmol m-2 s-1), accumulated precipitation of 7 days (Accum Prec 7; mm), wind velocity (Wind; cm s-1), dissolved oxygen (DO; %), chlorophyll a (Chl a; μg L-1), pCO2 (ppmv), salinity, temperature (Temp; $^{\circ}$C) and CH4 (nmol L-1) in the Guanabara Bay. The values were calculated with averages for each sampling campaign.

R2: Summary of the documented carbon fluxes in the Guanabara Bay.

R3: Variations of pCO2, DIC and TA against salinity. R3A: Measured surface water pCO2 against the salinity gradient in the Guanabara Bay, N=9002; R3B: Calculated DIC against salinity gradient in the Guanabara Bay, N=195: R3B: Measured TA against salinity gradient in the Guanabara Bay, N=195. Note that the data set was classified by sectors and the results represents all the sampling campaigns.

R4: Linear Regression between DIC calculated from pH/TA and pCO2/TA. (R2=0.994; Slope: 1.008 $\pm$ 0.006; slope significantly different from 0; p<0.0001). The slopes are not statistically different from 1 ($p = 0.20$) and the intercepts are not significantly different from 0 ($p = 0.86$). The method used is one equivalent to an Analysis of Covariance (ANCOVA), according to the GraphPad Guide User Manual 6.0.

Interactive comment on Biogeosciences Discuss., 12, 4671, 2015.

	PAR	Accum Prec 7	Wind	DO	Chl a	pCO_2	Salinity	Temp
PAR		0.11	0.83**	0.87**	0.87**	-0.83**	0.02	0.68*
Accum Prec 7	0.11		0.29	0.47	0.43	-0.46	-0.55	0.27
Wind	0.83**	0.29		0.88**	0.83**	-0.91**	-0.08	0.66
DO	0.87**	0.47	0.88**		0.76*	-0.93**	-0.36	0.76
Chl a	0.87**	0.43	0.83**	0.76*		-0.85**	-0.06	0.60
pCO_2	-0.83**	-0.46	-0.91**	-0.93**	-0.85**		0.38	-0.86**
Salinity	0.02	-0.55	-0.08	-0.36	-0.06	0.38		-0.43
Temp	0.68*	0.27	0.66	0.76*	0.60	-0.86**	-0.43	

*Correlations significant at $p < 0.05$; **Correlations significant at $p < 0.01$

Fig. 1. see caption in response text

Inputs of carbon to Guanabara Bay	*mmol C m^{-2} d^{-1}*	*Comment*
CO_2 air-water flux	26 – 49*	All bay average; This study
CO_2 air-water flux	33 – 102*	Sectors 3, 4 and 5; This study, strong and permanent annual CO_2 sink area
Organic carbon load from sewage	43	All bay average; FEEMA (1998), majority of organic carbon seems to be mineralized in sewage network
River DIC, DOC and TOC inputs	Undocumented	
Internal Processes	*mmol C m^{-2} d^{-1}*	*Comment*
NCP	51 – 225 (143)**	Sectors 4 and 5; This study
NPP	60 – 300 (170)**	Sectors 2, 3 and 5; Rebello et al., (1988)
Total Respiration	Undocumented	
Degassing / Burial / Export	*mmol C m^{-2} d^{-1}*	*Comment*
CO_2 air-water flux	54 – 177*	Sector 2; This study, permanent CO_2 degassing in a restricted area
Total organic carbon burial	27 – 114	Sectors 3, 4 and 5; Carreira et al., (2002) ; Monteiro et al., (2011)
DIC and TOC export to the coastal area	Undocumented	

*Annual average according to the k600 model parameterizations of Wanninkhof (1992) and Abril et al., (2009). The lower value refers to the model of Wanninkhof (1992), whereas the higher value refers to the model of Abril et al. (2009);

** Range and annual average (in parenthesis).

Fig. 2. see caption in response text

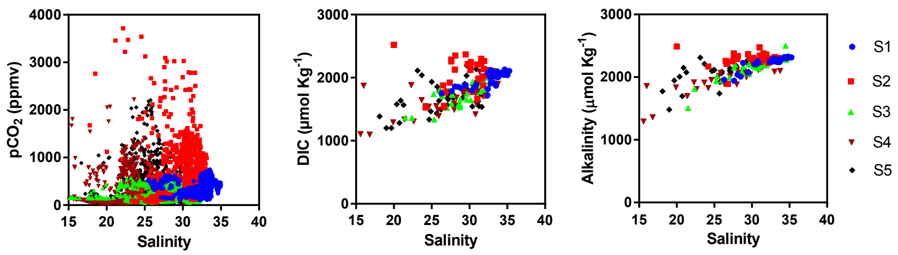

Fig. 3. see caption in response text

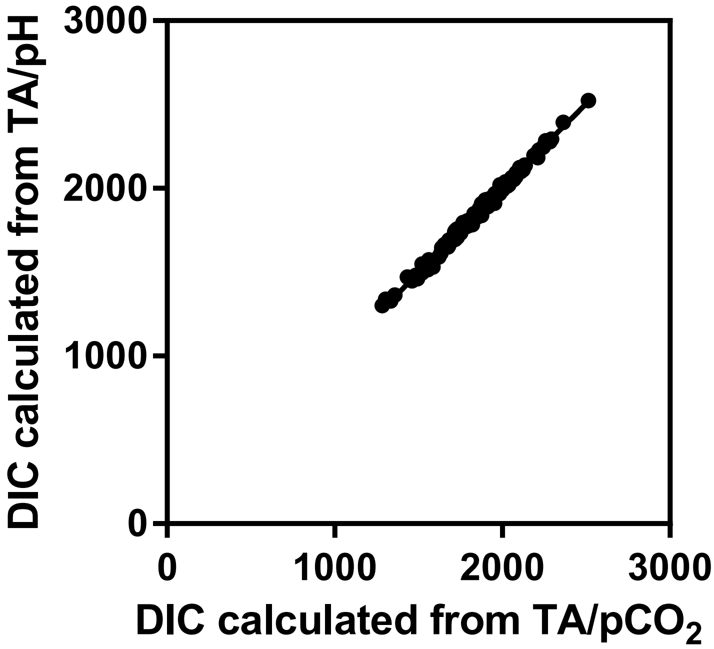

Fig. 4. see caption in response text