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Interactive comment on “The role of alkalinity generation in controlling the fluxes of CO₂ during exposure and inundation on tidal flats” *by* **P. A. Faber et al.**

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This paper reports an experiment of using “artificial” sediments (mixed and DOM enriched) to simulate DIC and Alk fluxes (during inundation) and CO₂ flux (during exposure) from subtidal mudflats. The authors also used an early diagenetic model to interpret and simulate the experiment output. (the latter is the focus of this paper) They found that CO₂ flux (to atm during exposures) is generally less than DIC flux to the overlying water (during inundations), and this is particularly true when Alk production is high under high Fe(III) scenario. I think the subject is important and is broadly interesting to the readers of BG. It also has implications in whether benthic fluxes are

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important in controlling the CO₂ level and acidification condition of coastal waters. This is probably the first comparison of DIC/CO₂ flux during inundation and exposure and by both experiment and model. Therefore, I support the eventual publication of this manuscript. However, I feel the manuscript is very weak in many aspects and major revision or rewrite is needed in order to make it an important contribution to the current scientific knowledge.

My major concerns are given below. Experiment part. The experiment was either not well designed or not clearly described. First, why a 5-cm core thickness was chosen? Did this influence the experiment result (leading to the depletion of Fe(III) and near zero Alk production)? How well does this simulate natural processes? The result shows that DIC flux was nearly constant (except when OM was added on day 70), indicating a similar overall lability of the OM or a constant OM decomposition rate over the experiment period. Thus, it appears what was depleted was Fe(III).

Second, the analytical method for Fe analysis was mentioned in the method section (p.5449), but the Fe (III or total?) content of the sediments was never reported (or that was buried somewhere) nor the [Fe(III)] change over the experiment period. Later, in p.5453, line 22-24, the authors speculated without any data support “The most likely explanation for this observation is that there was an initial formation of a large pool of iron sulfides. Initially, a large pool of Fe(III) is formed during sediment pretreatment, which is subsequently gradually depleted and turned into metal sulfides.”

Third, I initially didn't know it was a 6- and 6-hour cycle but figure it out later in the model part (in p.5452, line 10). Maybe an illustration graph of how the experiment was setup and run will help. It appears to me that the authors have little interest to presenting the experiment.

Model part. I understand that this paper applies an existing diagenetic model that comes from a leading modeling group. However, as it deals with the CO₂-carbonate system, I am still shocked to see there is no description on how the authors dealt

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with the production/consumption and diffusion of various inorganic carbon species and other acid-base species aspects of the sediment diagenetic processes. This weakness was reflected not only in the description of the model but also in how the model was set up and what parameters are need to be measured in the experiment. For example, what are exactly included in their Alk definition? Were HPO_4^{2-} and DOM considered as acid-base species in the Alk equation (see p. 442 in Cai et al. 2010)?

The second thing I am not happy with the paper is there is no information on species profiles and production/consumption rates that the model generated internally. When we read such an experiment-model comparison paper, the readers not only are interested in knowing the result (CO_2 flux during exposure < DIC flux during inundation), we also want to know how the CO_2 -DIC-Alk fluxes are facilitated. What are the reduced species that are oxidized (at what depths) that also produces proton and become an Alk sink? For an example, in most sediment pore waters, TA and DIC values/concentrations are similarly elevated (as both are dominated by HCO_3^-) in a few examples that both were measured (see for example Cai et al. 2006), why DIC flux appears so much higher than the Alk flux? In an early paper (Cai et al. 2000), I have shown that within the sediment, inorganic carbon diffusion is still facilitated by HCO_3^- as it is the dominated species even at a fairly low pH. However, once HCO_3^- diffuses to the pH minimum zone a few mm below the sediment-water interface, it is converted to CO_2 (due to the oxidation and acidification processes occurring there) and diffused out to the water (or the air) as CO_2 . The amount of CO_2 -(vs. HCO_3^-) facilitated diffusion, of course, depends on the pH level. I think your model results have such information that are of interest to many.

Your paper mentioned that CO_2 production (should be flux) was decreased when Alk production was high in the high Fe(III) case. But the real reason is not the rate of CO_2 production rate (the OM decomposition rate to CO_2 and OH or to DIC was actually higher at high [Fe(III)]), but rather it is the pH level that created the CO_2 gradient near the interface and controlled the CO_2 flux. I think such mechanistic discussion will be

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very interesting and will raise the profile of this paper (whether it supports or negates my argument is less important and it depends on systems). In your paper, you often talked about the net is this and that; I think the power of having a model is that you can show the processes and the gross rates of individual process and how they lead to the final net result.

You have argued that denitrification is not important and thus can be ignored in your system. I can agree with you on the net result (and there is no NO_3 flux from the overlying water). But you also have the coupled nitrification (oxidation of NH_4 from OM decomposition, which produces acid) and denitrification (which produces base). This will impact the pH at various depths. How can you say this is not important? As the model from this group already has N cycle built-in, why you need to ignore it?

I also am wondering why there is no comparison of the current ms with another experiment and modeling effort in a relevant system by Cook et al. (2009), an coauthor of the current ms. (Cook PLM, Van Oevelen D, Soetaert K, Middelburg JJ (2009) Carbon and nitrogen cycling on intertidal mudflats of a temperate Australian estuary. IV. Inverse model analysis and synthesis. Mar Ecol Prog Ser 394:35-48)

The authors think that there was initial a large pool of Fe(III) , which was consumed and resulted in negligible Alk production by days 60 days (p.5453, line 23). Then, why Alk production increases after OM addition at day 70 without adding reactive Fe(III) ? Need to explain this.

Specific comments (notes I did as I read through the text; some repeats the major concerns; some may be trivial, and you may ignore them).

p.5446, Line 24-25, the argument that DIC is hard to measure than CO_2 is odd as one can argue the other way. For example, though both DIC and CO_2 are measured in an incubation simulation system (core covered by water or air), it is a lot easier to simulate water flow (with reasonable stir) and measure the right DIC flux than to simulate air flow and measure the correct CO_2 flux.

It's good to know that most people study tidal mudflats measures the CO₂ gaseous flux not DIC, but I can also give you one opposite example from Sapelo Island marshes (see Table 2 in Cai et al. 1999, L&O).

p.5447, line 15-16, not sure why bio-irrigation cease upon emersion (submerge the sediment core under water).

p.5447, line 20-28, what about acidification via oxidation of reduced species? This can decrease Alk and increase CO₂ at the sediment surface.

p.5448, line 11, change sediment to sediments; line 12 delete sediment and change was to were.

p.5448, line 17, what is the justification of using a 5-cm core? What is the impact of this short core on the flux change at the end of incubation period?

p.5448, section 2.1, line 20-23. Not clear how the experiment was done. I assume there is a 6hr cycle of inundation/exposure. (yes, you explained it later; these are averages over the cycle). Maybe you should add a graph to illustrate how the experiment (the cycle) was performed.

p.5448, line 23, are you sure you mean leaving no pond during “emersion” not during “exposure”? (in my 2nd and 3rd read, I understand it is emersion as this is the time you pump-in water and the initial drops would create a pond.) Again, an illustration graph would help.

I also suggest not use the word “emersion” as you already have “inundation”. Why confuse readers, in particular those English are not their first language? (feel free to ignore me)

p. 5449, line 14, where (in a room temp or a refrigerator) were samples stored (what kind of vials) and how long were they stored? Was pH measured at 25C? Line 17, how are you going to deal with contributions of other acid-base species such as HPO₄²⁻ in the Alk (in your modeling)? (See p.442 in Cai et al. 2010 for the reason why I ask this)

p.5450, Line 13, the sediment core was completely mixed, not sure what does it means for bioturbation. Some discussion is needed.

p.5451, line 13 (also Table 3), how was the piston velocity determined? (in Table 1 it was only 1 cm/h) You had stir in the overlying water, but nothing in the overlying air. What will be the impact on CO₂ flux? (ok, I see you have a long discussion on this later. The bottom line is this, once $k > 1$ cm/hr, the lowest value that one may see in nature outdoor environments, the CO₂ flux rate is controlled by the CO₂ supply in sediment not the diffusion to the air. If not because of this reason, I would say your conclusion has no practical meaning as you have a stagnant air.)

p.5451, line 20, English problem?

p.5453, line 23, the authors think that there was initial a large pool of Fe(III), which was consumed and resulted in negligible Alk production by days 60 days. Then, why ALK production increases after OM addition at day 70 while no reactive Fe(III) was added? Need to explain this.

p.5456, line 6-7, OM degradation produces NH₄. When this NH₄ diffuses upward and meets O₂, oxidation of NH₄ produces acid. This is not important?

p.5457, section 4.3. what it boils down is when piston velocity > 1 cm/h, then the flux is limited by the rate of CO₂ production in sediments not CO₂ diffusion across the interact. You should point out the obvious. Also, a premise is that water level is below the sediment surface, otherwise, CO₂ can be supplied from HCO₃⁻ buffer (a much greater pool).

p.5458, line 5, a large amount of Fe leads to a higher rate of alkalinity production through FeS₂ 5 burial, and a corresponding lower rate of CO₂ production. This conclusion is not properly stated. The total amount of CO₂ production is not reduced, but increased. But because of proton consumption, the net result is an increased Alk production and decreased CO₂ flux (and an accumulation of HCO₃⁻ in the porewater).

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How will this accumulation of HCO₃⁻ and CO₃²⁻ during exposure influence the DIC flux in the following inundation?

p.5459, line 8-14, the following statement is probably not true—that total inorganic carbon fluxes for intertidal sediments have generally been estimated using only gaseous CO₂ fluxes on the exposed sediments (Mign'e et al., 2005; Middelburg et al., 1996) as there are many opposite examples (for example, Cai et al. 1999).

Wei-Jun Cai

Reference I mentioned in my comments (I certainly have no intention to ask you to reference my work. I simply want to bring in examples, that are handy to me, to support a point).

1. Cai, W.-J., George W. Luther, III, Jeffrey C. Cornwell, Anne E. Giblin. 2010. Carbon cycling and the coupling between proton and electron transfer reactions in aquatic sediments in Lake Champlain. *Aquatic Geochemistry*. 16:421-446, DOI 10.1007/s10498-010-9097-9.
2. Cai, W.-J. , F. Chen, E. Powell, S. Walker, K., M. Parsons-Hubbard, G. Staff, Y. Wang, K, Ashton-Alcox, W. R. Callender, C. Brett. 2006. Preferential dissolution of carbonate shells driven by petroleum seep activity in the Gulf of Mexico. *Earth and Planetary Science Letters*, 248:227-243.
3. Cai, W.-J. Zhao, P. and Wang, Y. 2000. pH and pCO₂ microelectrodes measurement and diffusive behavior of carbon dioxide species in coastal marine sediments. *Marine Chemistry*, 70:133-148.
4. Cai, W.-J., L. R. Pomeroy, M. A. Moran and Y. Wang. 1999. Oxygen and carbon dioxide mass balance in the estuarine/intertidal marsh complex of five rivers in the Southeastern U.S. *Limnology and Oceanography*, 44:639-649.

Please also note the supplement to this comment:

C2335

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<http://www.biogeosciences-discuss.net/9/C2329/2012/bgd-9-C2329-2012-supplement.pdf>

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