Review of "Benthic alkalinity and DIC fluxes in the Rhone River prodelta generated by decoupled aerobic and anaerobic processes" by Rassmann, Eitel et al.

This study uses an impressively diverse and high-quality dataset to investigate the source of strong total alkalinity fluxes originating from nearshore sediments in the Rhone River prodelta. The introduction is clear and provides a very good summary of the diagenetic concepts required to follow this study. The methods section is detailed, even though I missed some description of how organic alkalinity was derived, or of what $CaCO_3$ minerals are actually made of. Overall, I found that the authors adequately communicate their conclusions, that the measured high alkalinity fluxes are caused by iron sulfide precipitation and burial, rather than $CaCO_3$ dissolution or denitrification, as well as the novelty of their approach. Nevertheless, I have some small concerns about the veracity of these conclusions that I will detail below. Unfortunately, this manuscript contains a number of inconsistencies that make it not straightforward to follow and understand. This work should be published upon minor revisions, which would include addressing and justifying the potential methodological flaws highlighted here.

The whole $CaCO_3$ treatment is somewhat vague and appears misleading. Statements such as "porewaters are ~~over~~ supersaturated with respect to calcite, suggesting that carbonate mineral dissolution is not significant" (L464-465) or "such saturation state precludes massive carbonate dissolution at the sediment surface" (L473-474) are inducing unnecessary confusion. The fact that porewaters are supersaturated with respect to calcite means that no calcite dissolution occurs, but does not mean anything regarding the other $CaCO_3$ phases, which could very well be dissolving, because more soluble. Although you have detected the presence of Mg-calcite, you never mention the possibility that it could be dissolving, and never mention a saturation state with respect to these Mg-calcite phases. Similarly, the possibility of aragonite dissolving in "microniches" is mentioned only once (L477). With the large pH decrease in the first millimeters below the SWI (L468 and Fig. 2), the presence of Mg-calcite (L297) and possibly aragonite, and given the [Ca] porewater profiles for stations B, K, E and AK, it seems unjustified to rule out $CaCO_3$ dissolution completely. Given that you apparently have data on the solid composition of the sediment, notably in terms of $CaCO_3$ phases and their Mg content, as well all the necessary porewater data necessary to calculate the saturation state profiles with respect to each of the minerals, why not using all this data to determine with certainty whether $CaCO_3$ minerals are dissolving or not?

In situ chambers may have several drawbacks, including landing disturbances, uncertainties regarding chamber mixing and hydrodynamics, leaks, etc. With porewaters being extremely rich in TA (30-40 mM, line 119 and Fig. 5) and bottom waters having a TA of ~2.5 mM, one might be worried that the landing disturbances release some of this alkalinity in the porewaters and cause the measured fluxes to be overestimated. The same applies for DIC. In fact, TA and DIC fluxes (measured with chambers) are 2 to 8 times larger than DOU rates (diffusive flux inferred from microelectrode concentration gradient), which may lead to suspicion. I see two ways this could be addressed. (1) Since you have microelectrode concentration profiles for both TA and DIC, their diffusive fluxes could be computed using Eq. (3) and compared with the chambers measured fluxes. This would be an easy way to validate chamber fluxes. (2) TA and DIC concentrations from the overlying water sampled from the sediment cores were also measured (L144-145). How do they compare with TA and DIC concentrations from the bottom waters sampled in Niskin bottles? That comparison could

help qualitatively estimating TA and DIC releases upon sediment-water interface disturbance by the landing of an instrument.

It is not always clear to me what the production ratios actually stand for, and what they are bringing to the study. Are the production ratios computed for each station as a function of sediment depth or not? I believe that it would be enlightening to plot these ratios, which are currently not shown anywhere, as a function of depth, and compare that to the porewater concentration profiles of Figures 4 and 5.

Regarding mass transfer through the sediment-water interface (SWI), and the presence of a diffusive boundary layer (DBL), there may be either a lack of documentation or assumptions that are not clearly stated. The authors never mention the presence of a DBL sitting above the seabed throughout this manuscript, which is known to control the diffusive fluxes of certain solutes through the SWI. If the authors are assuming that the DBL has a negligible influence in this system, they should bring evidence supporting this statement, or at least state this assumption explicitly. Benthic chambers alter the fluid flow above the SWI and modify the DBL shape and thickness. By stirring the water within the chamber, they may cause the DBL to be thinner than without a chamber, and enhance the diffusive fluxes. What was the stirring rate in these chambers? How can the authors quantify the effect of stirring on benthic fluxes? More discussion is required on this side. Besides, as the SWI is a plane, there can be no gradient at the interface (line 262). Given, the use of the diffusion coefficient in sediments in Eq. (3), I assume that the concentration gradient used in Eq. (3) is within porewaters only and does not extent on the water-side of the interface. If so, please state it. If, instead, the authors are referring to a concentration gradient between just above and just below the interface, then there is a diffusive boundary layer that they are not acknowledging. See the approach of Hicks et al. (2017, Biogeochemistry, 135, 35-47) who computed DOU rates using O_2 concentration gradients within the DBL.

Specific comments

Abstract

L11-12: Where is the "solid composition data shown in this manuscript"? If not shown, remove that from the abstract.

L13-15: Specify in which direction these fluxes are going.

L20: Make it clear that 12.5 mmol/m2/d is the burial flux of iron sulfides, with [m2] standing for the sediment surface area.

Introduction

L33: "account for more than 40% of POC burial in the oceans": it deserves a reference

L48: "carbonate saturation state": "carbonate" is vague. It should be "carbonate minerals", "calcite" or "aragonite"

L49: "supersaturation" instead of "oversaturation". Please correct here and elsewhere.

Methods

L95-98: The mentioned accumulation rates do not correspond to what is being presented in Table 2, which does not correspond to what is being presented in Table 3. Please be consistent, or explain better where the accumulation rates from Tables 2 and 3 are coming from.

L100: "total organic carbon content is higher than 2%"at which depth(s) / range of depths ?

L102: "mostly composed of calcite": A more detailed description of these composition is given in section 2.9, but I feel that it should also appear here.

L140: The CO2SYS software can provide very different in-situ pH values depending on which equilibrium constants are used, which carbonate system pair is used as an input (TA, DIC, pH), if silicate and phosphate concentrations are used or not, etc. More description on this is required. Besides, if the authors used the new version of that software described in Orr et al. (2018, Marine Chemistry 207, 84-107), which they should definitely do, as it properly propagates the uncertainties, they should reference it.

L142-143: The sentence "Dissolved oxygen concentrations … 0.5 microM" already appeared in the text a couple of lines above.

L156-157: Please provides more background on the REML approach that is used, mention any software used, and explain how were uncertainties of individual measurements taken into account.

L160: Fig. S2, which presents the concentration as a function of time in the chambers, is only referenced in the results section. It should be mentioned, and more importantly described, in this section as well, as it shows how long chambers were deployed, and the linear dependency between concentration and time.

L167: "their response to variations in oxygen concentrations is linear": it deserves a reference.

L181: This is not the same sediment density than in Table 4. Please be consistent.

L202: Is it proven that the air within the glove bag was indeed anaerobic or is it an assumption? Are there any oxygen concentration data supporting this statement?

L224: "NH_4^+" instead of "NH^+_4"

Eq. (3): This should be referred to as an "oxygen flux" or a "DOU rate". Please reword this elsewhere in the manuscript too.

Eq. (5): Are the diffusion coefficients for free-water conditions, or for sediments, corrected for tortuosity?

L298-301: I do not understand the logic behind the $CaCO_3$ reactions correction in the TA and DIC changes. If ΔCa is positive upon $CaCO_3$ dissolution and negative upon precipitation, in order to correct for $CaCO_3$ reactions, we should subtract [2 D_{Ca} ΔCa] to [D_{TA} ΔTA] instead of adding it, and subtract [D_{Ca} ΔCa] to [D_{DIC} ΔDIC]. This would be much easier to understand and would correct for both $CaCO_3$ dissolution and precipitation.

L306: Instead of saying "see below", please indicate the section you are referring to.

Results

L400: Porewaters may be supersaturated with respect to calcite but what about Mg calcite and aragonite? A little bit of aragonite and Mg-calcite dissolution near the interface would make a big difference in terms of TA release.

Discussion

L491: How was organic alkalinity estimated? No detail is given on the method. The authors say in L305 that they do not have enough data to estimate it.

Eq.(6): "D" should be "D_s"

L630: A reference is needed to support the statement of slow pyrite precipitation.

Figures

Fig. 9: This figure seems to never be referenced in the text. Describe it in the text, or remove it. Besides, wouldn't it make more sense to plot the fluxes ratios as a function of the horizontal distance from the coast or river mouth, rather than water-column depth?