Dear Prof. Dr. Jack Middelburg,

Please find attached the second revision of our paper submitted to Biogeosciences accompanied by the response. Most required modifications were made according to the reviewer's comments.

Our answers to the individual comments are given in blue and when the manuscript has been modified, the modifications are given in italic for small changes. When entire paragraphs have been rewritten, only the line numbers are indicated to avoid unnecessary length of this response letter.

All minor comments have been taken into account. When only typos etc. where spotted, no specific comment is given in the response letter.

We hope that our responses are satisfying and that our manuscript has evolved towards a publishable form for Biogeosciences.

Kind regards,
Dr. Christophe Rabouille

Reviewer #1
Review of "Benthic alkalinity and DIC fluxes in the Rhone River prodelta generated by decoupled aerobic and anaerobic processes" by Rassmann, Eitel et al.
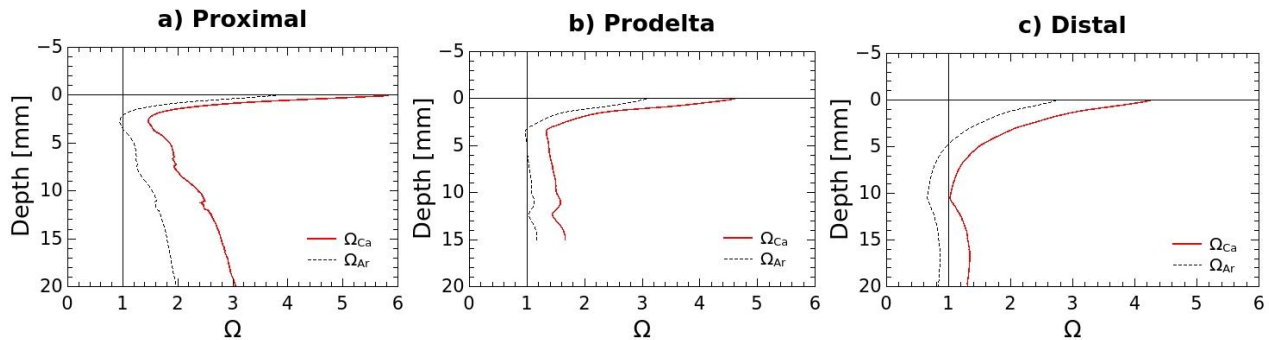
Reviewer comment (RC): This study uses an impressively diverse and high-quality dataset to investigate the source of strong total alkalinity fluxes originating from nearshore sediments in the Rhone River prodelta. The introduction is clear and provides a very good summary of the diagenetic concepts required 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 CaCO3 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.

Author response (AR): We thank the referee for his thoughtful comments that we address within this response letter and the joined revised manuscript. We especially reworked the sections about organic alkalinity and carbonate dissolution and sincerely hope that this revision will help to get rid of these inconsistencies.
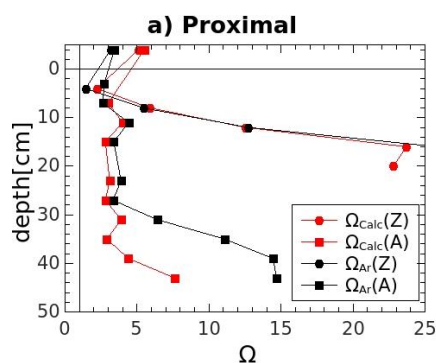
RC: The whole CaCO3 treatment is somewhat vague and appears misleading. Statements such as "porewaters are over supersaturated with respect to calcite, suggesting that carbonate mineral dissolution is not significant" (L464-465) or "such saturation state precludes massive carbonate dissolution at the 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 CaCO3 phases, which could very well be dissolving, because more soluble.

AR: The reviewer is right about this remark, a supersaturation regarding calcite does not exclude the dissolution of aragonite or magnesian calcite. In the paper we remind the readers that solid phase analyses have demonstrated, that calcite accounts for more than 95 % of the $CaCO_3$ phases (Rassmann et al., 2016). We recalculated the saturation state with respect to aragonite (shown below). It shows that there is indeed a depth +/- 1 mm around the pH minimum, where aragonite is at saturation or very slightly below. This new figure replaces the ancient figure 6 in the new version of the paper in order to give a representation of other more soluble classes of carbonate minerals.

For magnesian calcite, estimations are more difficult to make, as until today, we do not know the Ca:Mg molar ratio of this mineral in these sediments.

Calculations made from pore water TA and DIC concentrations indicate supersaturation with respect to aragonite in proximal zone stations (A and Z) (see Figure below).

Similarly to the previous figure, this graph shows that the dissolution of calcium carbonates, whether calcite or aragonite, remains unlikely in the proximal zone where the strong TA fluxes were measured.

Section 4.2 has been modified to emphasize these aspects (lines 469-488) and a sentence has been added at the results section (line 406)

RC: 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 CaCO3 dissolution completely.

AR: Indeed, as shown above with the new Fig. 6, dissolution of aragonite and magnesian calcite could appear around the depth of the pH minimum, if microniches show lower saturation states that the average. Aragonite has been included into the discussion (see comment above). In turn, to estimate saturation states of magnesian calcite, the Mg:Ca molar ratio has to be determined,

something that has yet to be done. This is for sure an interesting topic for a future investigation in the prodelta stations (B, K, and AK). It is noteworthy that stations A and Z where high alkalinity fluxes are measured do not indicate undersaturation with respect to aragonite and show porewater Ca2+ decrease with depth.

RC: Given that you apparently have data on the solid composition of the sediment, notably in terms of CaCO3 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?

AR: The only information that we have about the $CaCO_3$ phase relies on a previous cruise (Rassmann et al., 2016) and indicates that it is composed of more than 95 % of calcite and to a minor fraction of aragonite and magnesian calcite of unknown Mg:Ca ratio. As a result, the TA and DIC concentrations of the pore waters have been used to calculate the saturation states of calcite and aragonite. However, we judged useful not to overcharge Fig. 5 with Ω_{ar} profiles as aragonite is completely minor and is generally supersaturated.

RC: 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.

AR: We thank the reviewer for this comment. It has been long debated if benthic chamber accurately estimate benthic fluxes and several complementary approaches have been developed (see Eddy correlation techniques) that have their own drawbacks. Clearly, no technique is perfect but in situ benthic chamber (and core incubations) fluxes have been used for more than 30 years with a fairly good success. In our deployments, we rule out massive disturbance of the sediment and porewater mixing with bottom water as the starting concentration in the chamber was 2.3 ± 5% mM for DIC and 2.6 ± 8% mM for TA. The graph below is in the Appendix (Fig. S1) of the present paper, and will be in the revised version as well. We added a sentence in the method section to acknowledge the limited impact of landing disturbance based on this argument. Line 334 *"Minimal disturbance of the sediment-water interface during deployments was evidenced by the initial DIC and TA concentrations which were within 5% and 8% respectively of the bottom water concentration (Fig. S1).* »
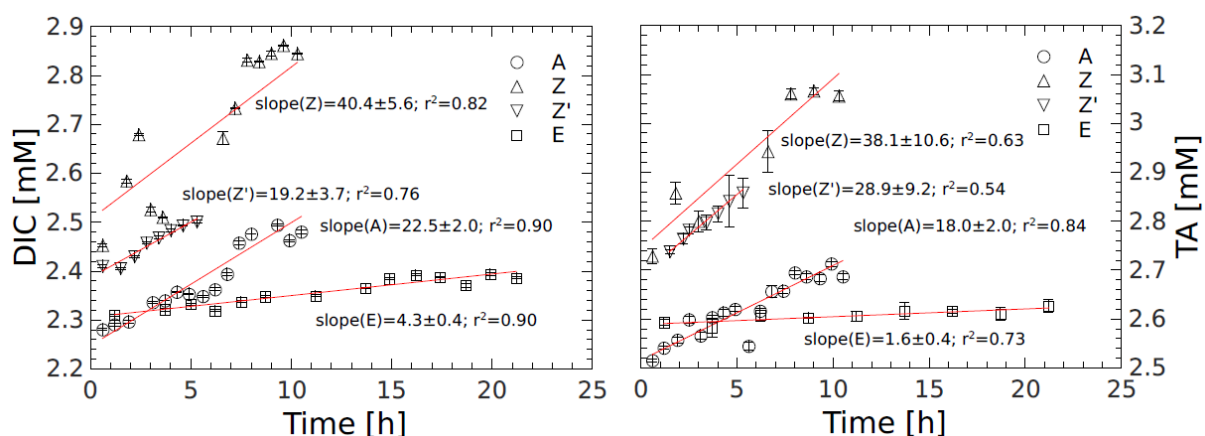

Figure S2: Temporal evolution of DIC and total alkalinity concentrations in the benthic chamber at stations A, Z (measured during two deployments), and E. Error bars represent analytical

uncertainties determined from triplicate measurements. The benthic fluxes and their standard deviations are provided in the text, in Figure 4 and in Table 2.

RC: 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.

AR: Contrarily to reviewer 1, we do not believe that the gap between DIC and DOU fluxes should lead to suspicion, because most of the reduced chemical species (Fe, H2S) produced during anaerobic mineralization and production of DIC and TA are combined together in FeS and buried. This creates a large decoupling between mineralization i.e. production of DIC and TA and the oxygen fluxes for which re-oxidation of Fe2+ and H2S plays a major role. This is indicated in our article title "Benthic alkalinity and DIC fluxes in the Rhône River prodelta generated by decoupled aerobic and anaerobic processes"). The effect of large FeS burial on the decoupling between DIC and O2 fluxes had already been postulated in Pastor et al. (2011) for the same stations.

RC: 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.

AR: We thank the reviewer for this comment but unfortunately we do not have "micro-electrode" DIC and TA profiles at high resolution, but only at low resolution (see Fig. 5; first data point at 1-2 cm and spacing of 2 cm below). This is not enough for calculating a diffusive flux and for comparing it to the benthic chamber DIC and TA fluxes.

RC: (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.

AR: As mentioned above, we have directly compared TA and DIC in the chamber to TA and DIC in bottom waters (see answer above). We can rule out massive disturbance of the sediment and porewater mixing with bottom water as the starting concentration in the chamber was 2.3 ± 5% mM for DIC and 2.6 ± 8% mM for TA (see also Fig. S1)

RC: 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.

AR: We thank the reviewer for his comment on the production ratio which points towards a lack of clarity in the method section concerning the calculation of production ratios (line 282-285). Indeed, the production ratios are a classical way to investigate dominant reaction pathways by comparing the observed ratios (DIC/SO4 or DIC/TA) to theoretical ratios. The best recent example stands in Burdige and Komada (2011) for $r_{C:S}$, the DIC production to sulfate consumption ratio. In the present paper, these ratios show that the proposed set of reaction (sulfate reduction, Fe(OH)3 reduction and FeS or FeS2 precipitation) is compatible with the observed C/S, TA/S and C/TA ratios (see Table 1-theoretical and 3-observed).

The lack of clarity of our paper lies in the description of the method which led the reviewer to think that we calculated one ratio at each depth of the cores and that we can thus plot the ratio's variation with depth in each core. On the contrary, for robustness of the calculation, we calculated only one ratio per station using the entire profile of DIC, TA or SO4 represented in a concentration-concentration plot. It is thus not possible to plot the variations with depth of these ratios.
In the method section, we modified the description of the ratio calculation (line 286-291):

"For each station, experimental stoichiometric ratios were obtained from the slope and standard deviation of the linear regression of ΔTA, ΔDIC, and ΔSO_4^{2-} property-property plots. The Δs represent concentration changes with respect to bottom water concentrations and were corrected by multiplying their values by their diffusion coefficient ($\Delta i * D_i$; Berner, 1980). The corresponding diffusion coefficients corrected for temperature and salinity (cm^2 s^{-1}) were adopted from Li and Gregory (1974)."

RC: 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.

AR: Indeed, the DBL has to be taken into account when dealing with processes that take place on the same scale than the DBL (Boudreau and Guinasso, 1982). From micro electrode measurements, we estimated a DBL of about 400 µm. We know that the DBL has a strong impact on mass transfer of oxygen across the sediment water interface, but we did not measure oxygen fluxes in the benthic chamber as done by Hicks et al. 2017.

Concerning the DIC and TA fluxes, the pore water profiles and mineralization extend deep in the sediment down to 10-20 cm. Therefore as stated in Boudreau and Guinasso (1982), the impact of the "resistance" caused by the DBL should be minimal on these species, as mineralization kinetics and diffusion in the sediment column dominates. Therefore, in this case, fluxes should not be influenced to a large degree by the change of DBL due to stirring rate. The stirring rate in the chamber was regulated following Jahnke & Christiansen (1989) as written in the methods section (line 153) in order to reproduce a DBL thickness comparable to the in situ situation. We extended the description of the stirring mechanism and provided the stirring rate as well as a reference that calibrated the DBL thickness as a function of the stirring rate for that particular benthic chamber (~260 µm for 10 rpm). Line 155:
"A mechanical stirrer integrated in the chamber lid was run at 10 rpm to homogenize the overlying waters in the chamber without interfering with sediment-water exchange processes (Buchholtz-Ten Brink et al., 1989)."
Concerning DBL, we did not introduce this point of discussion as we think that it is out of the scope of this paper to discuss this point and the paper is already too long.

RC: 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 O2 concentration gradients within the DBL.

AR: In this study, the oxygen gradient used for the calculation was taken "below" the interface, down to 400 µm depth. This information was added to the manuscript (line 268-269)

Specific comments

All specific comments of the reviewer have been taken into account.

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

We removed "solid composition" from the abstract, even if nanoparticular solid FeS was measured.

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

We added "into the water column"

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.

We added " with an estimated burial flux of"

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

The reference was (Hedges and Keil, 1995; Muller-Karger et al., 2005) and has been moved to line 34-35.

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

We reworded to: "drives the calcite and aragonite saturation state of the pore waters towards supersaturation, and potentially triggers carbonate mineral precipitation"

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

We replaced oversaturation by supersaturation in the whole manuscript

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.

We corrected the mistake in the manuscript for the sedimentation rates and are now consistent between the text and table 2. These rates are ranges for the corresponding domains (proximal,

prodelta and distal). In table 4, we used sedimentation rates corresponding to the selected stations estimated according to the equation and figure 8 from Lansard et al., 2009. Our calculation is a first estimation of AVS burial in the aim of seeing if the order of magnitude of FeS burial and TA fluxes match.

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

The 2 % refer to surficial sediments (0-0.4 cm). The information has been added to the manuscript (line 102)

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.

The precisions have been incorporated into lines 103-106 and shortened the corresponding phrase in line 303.

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.

We used the equilibrium constants from Luecker et al., 2000 and added the missing information to the manuscript (lines 143-147).
Changing the equilibrium constants and varying slightly the silicate and phosphate concentrations influences the computed carbonate saturation state by a few hundredth of unit. In this paper, we do not try to obtain such accuracy and thus the precision obtained by our calculations is enough for the purpose of this paper.

L142-143: The sentence "Dissolved oxygen concentrations ... 0.5 microM" already appeared in the text a couple of lines above.
We removed this sentence from the manuscript

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.

We used the "lm" function in R that can make a linear approximation taking into account +/- values of individual data points. The information has been added to the manuscript.

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.

The figure was removed from the manuscript as requested by previous reviewers. The linearity of the concentrations changes with time was already mentioned (line 332) and the duration of the deployments (10-22 hrs) was added at the same line of the revised manuscript.

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

A reference was added.

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

The density value has been corrected to 2.5 g cm-3

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?

We monitored the oxygen concentration in the glove box with an oxygen sensor and made a test with a 2 % $((NH_4)_2 Fe(SO_4)_2 \cdot 6H_2O)$ solution that changes its colour in the presence of oxygen even in trace concentration. This information has been added to the manuscript (line 207).

L224: "NH 4+ " instead of "NH +4 "
This was changed (line 229)

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

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

Equation 5 was removed from the paper as we think it was misleading (see above response to major comment). In our calculations, the diffusion coefficients are for sediment and are corrected for tortuosity of the sediments. As production ratio are corrected at the numerator and the denominator by tortuosity, an alternative is to use free-water diffusion coefficient.

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.

If one unit of CaCO3 precipitates, 2 units of TA are consumed. As we want to know how much TA has been produced by reactions other than precipitation, we have to add this (absolute) precipitation value to the measured concentration as the measured concentration equals the TA produced by OM mineralization reduced by the TA consumed to precipitate CaCO3. The same goes for DIC.

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

We referenced section 4.2 where organic alkalinity is discussed.

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.

We calculated the pore water saturation state with respect to aragonite as explained in response to the main comment of the reviewer above. The problem with magnesian calcite is that we do not know its Ca:Mg ratio.

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.

Organic alkalinity is classically computed as the difference between observed alkalinity and the alkalinity computed using DIC and pH. We adopted this method. For the bottom waters, organic alkalinity could be estimated using DIC and pH to calculate carbonate alkalinity and compare it to the measured total alkalinity. In the pore waters, only TA and DIC concentrations are known, but not pH except at the very surface which is not enough. As a consequence, we cannot estimate organic alkalinity in the pore waters. We rephrased: "In the bottom waters, organic alkalinity was estimated from bottom water TA, pH and DIC concentrations to represent less than 1% of TA"

Eq.(6): "D" should be "D S "
This was modified in the text

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

Two references were added, one for pyrite precipitation rates and one for FeS precipitation rates. The differences in overall second order rate constants is 12 orders of magnitude at 25°C. Line 636

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

Figure 9 was referenced in the text at line 667 (now line 673). We chose to show the F_{TA}/F_{DIC} with respect to the water depth because it is expressed that way in Hu and Cai (2011).