

Interactive comment on “Benthic alkalinity and DIC fluxes in the Rhône River prodelta generated by decoupled aerobic and anaerobic processes” by Jens Rassmann et al.

Jens Rassmann et al.

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(Please see formatted response as pdf in supplement AC2-RC2)

Response to Anonymous Referee #2

C: I read carefully the manuscript of Rassmann, Eitel, and collaborators and I recommend it for publication after revision. This paper presents an in-depth analysis of benthic biogeochemical processes and DIC/TA release in different stations in the Rhône River Delta area. I particularly like the multitude of measurements applied to improve understanding of processes driving anaerobic formation of TA and benthic fluxes; par-

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ticularly, combining in situ incubations, potentiometric and voltammetric micro-profiles with more conventional pore water and sediment analyses. This combination of methods is rarely encountered in these types of investigations which often focus primarily on submilli metric processes at the SWI. Furthermore, the amount of data collected is significant, and has to be published, definitively.

C: My main concern is related to the overall perspective of the research. The authors do not convey very clearly the scientific importance of their work. For instance, in the introduction they mention that the objective of the paper was to "investigate if sediments from deltaic regions exposed to large riverine inputs of carbon and minerals represent an alkalinity source to the bottom waters and identify the biogeochemical processes responsible for the net production of alkalinity in these sediments.". There are several studies that have done this in coastal area as well, thus, they should portray how this work is different. And I would say that the combination of methods is unique.

C: After reading the paper several time, I am still not sure to understand the take home message of this study. What is really new?

R: We appreciate the reviewer's comment that the data collected is unique and improves our understanding of the processes driving anaerobic TA formation. In turn, we are disappointed that the reviewer does not understand the novelty of this work and will modify the revised manuscript to emphasize the scientific importance of this work: that the burial of reduced iron and sulfur in the sediment prevents reoxidation of reduced metabolites at the sediment-water interface and therefore contributes to an alkalinity flux to the overlying waters. Although these concepts are not novel, to our knowledge, this manuscript provides for the first time in situ benthic alkalinity flux data and simultaneous biogeochemical evidence from pore water and sediment profiles that substantiate this argument (strong indications that FeS precipitate in the sediment column, calculation of FeS burial compared to Alkalinity generation). The abstract, discussion, and conclusions will be modified to emphasize the fact that this is the first study demonstrating benthic alkalinity flux and simultaneously providing biogeochemical evidence

C2

for the processes responsible for this alkalinity flux.

C: I strongly appreciated the effort to present this very large set of data that includes Fe(III)-Lorg, sulfide species, and methane in addition to major (or classical) diagenetic species. However, I often lost myself in detail that ultimately brings little. For examples, the section on the role of nitrification/ denitrification and the section on IAPs are long but their conclusions are not very relevant for the rest of discussion. Overall the discussion should be shortened.

R: We agree with the reviewer that the IAP section is long and we will move it to the supplemental material to shorten the manuscript as indicated in response to the same comment by Reviewer 1. In turn, we disagree that the role of nitrification/denitrification is not relevant to the discussion. Denitrification is well known to generate TA, though nitrification consumes TA as well such that only exogenous nitrate fed by the River in this case could contribute to TA production. This information has to be provided in the discussion but we will keep it concise in the revised manuscript to satisfy this reviewer's comment.

C: My second concern is on the role of terrigenous organic matter in this type of sediment. The authors characterized the study site as "deltaic sediments exposed to large riverine inputs of inorganic and organic material". In these sediments, coarse particulate organic matter is deposited during flood events and supports the establishment of sulfidic conditions and the precipitation of Fe-S phases (François Charles et al., 2014; Fagervold et al., 2014; Rassmann et al., 2016). As POM, CPOM is probably a source of DOM and organic alkalinity in pore water. What is the role of organic alkalinity on TA in these sediments? Did you calculate the theoretical TA based on DIC and pH?

R: This issue has been discussed as well by reviewer 1. We calculated theoretical TA in the bottom waters based on the DIC and pH values. The departure between theoretical and measured TA provided bottom water organic alkalinity ranging between 8-28 $\mu\text{mol/l}$. In the sediment, we only have pH in the first 2 cm on a vertical resolution of

C3

200 μm whereas DIC and TA have been measured with a vertical resolution of 2 cm. As explained earlier in response to the same comment by reviewer 1, this difference in resolution is an issue that is difficult to overcome, and organic alkalinity increases generally in the anoxic zone deeper in the sediment, where no pH data are available. A first guess using an averaged pH value around 0, 1, and 2 cm depth leads to concentrations of organic alkalinity not exceeding 60 $\mu\text{mol/L}$. These low organic alkalinity concentrations in surface sediments may also prevail in deeper layers as the DIC/TA ratio is close to 1 (Figure 6) which is not the case when large quantities of organic alkalinity accumulate in sediments. The occurrence of large organic alkalinity is definitely an issue that could be resolved in further investigations by measuring pH profiles over longer depths in the sediment. As our dataset is not appropriate for the calculation of organic alkalinity at depth (where it occurs mostly) and the lack of organic alkalinity data does not change the main conclusions of the manuscript, we will not address this comment further in the revised manuscript.

C: The production of organic alkalinity should be discussed and the contribution to TA should be estimated (it's rare to have enough data to do it).

R: Yes, but as already explained, we lack data to estimate the amount of organic alkalinity in the sediments.

C: In addition, the accumulation of refractory organic carbon in sediments appears intimately associated with the sequestering of iron and sulfides in micro-environments (see the works of François). When the authors discuss about the aggregation of FeS, do they talk about microenvironments?

R: No, the main point of mentioning FeS aggregation (size of superior or inferior to 5nm) was to explain the differences between FeS₀ and voltammetrically determined FeS_{aq}, which points to a dynamic system. Microenvironments will be mentioned in the manuscript as they have been shown to play a role in the proximal zone with FeS₂ formation on leaves.

C4

C: I think the role of terrigenous organic matter on these biogeochemical processes should be clarified.

R: Previous investigations used Delta C14 and Delta C13 isotope analyses to highlight the importance of organic material in the Rhône River prodelta (Tesi et al., 2007; Lansard et al., 2009; Cathalot et al., 2013; Pozzato et al., 2018). These studies demonstrated that terrestrial and riverine organic matter (i.e., produced by riverine primary production) constitute the major fraction of organic matter in the sediments close to the river mouth (station A and Z) and that the terrestrial fraction decreases with distance from the river mouth and is lowest at station E. As the characteristics of natural organic matter might be of interest to the reader, we will briefly present the average oxidation state, POM concentrations, and C/N ratios in section 2.1 of the revised manuscript.

C: My third concern is on the time scale of the explored biogeochemical processes. The deltaic sediments cannot be considered at steady state, specifically in the proximal stations. However, the discussion is based on a steady state view of the different reactions. So, what is the impact of floods on the oxygen demand and DIC/TA release? Are these fluxes constant over the year, with no seasonal variations?

R: The question of temporal and spatial scales is crucial in these environments and we tried to introduce them in the paper although we probably did not include enough material dealing with this topic in the background (1. Introduction) and field site description (2.1: The Rhone River delta) sections. These two sections will be updated with additional sentences on the temporal and spatial scales as explained in response to the same point made by Reviewer 1 (see 2nd comment by Reviewer 1). "Concerning the temporal variations, the Rhône prodelta system receives large inputs of particulate material in late fall and early winter during major river floods (as stated line 87-90), including terrestrial organic matter which is mineralized in the spring and summer. Although data are scarce and new programs are underway to address temporal variations, there seems to be a progressive buildup of metabolites in the sediment pore waters and progressive disappearance of fronts during winter and spring (Rassmann,

C5

unpublished data). One good example is found in Pastor et al. (2018, CSR) which describes an atypical flood in the spring and the evolution of the pore water profiles over 6 months from May to December (see DIC profiles of the prodelta station A in Fig. 4 of Pastor et al., 2018). In the general case of the fall floods, the most intense organic matter mineralization rates are reached in spring and summer in the proximal zone, where organic matter accumulation is highest, as presented in Rassmann et al (2016) for June 2014 where sulfate reduction drives the sulfate concentrations to almost 0, producing 30-40 mM of DIC and alkalinity with 500-800 μ M of dissolved iron and no sulfide in the pore waters (see also Pastor et al., 2011 for a similar situation in April 2007). In addition, this pattern was found over several sampling campaigns in April 2013 (Dumoulin et al., 2018), 2014 (Rassmann et al., 2016), 2015 (this paper), and 2018 (unpublished results). Altogether, the pore water data collected over the years in the Rhône prodelta system are consistent and indicate that biogeochemical processes in the critical proximal zone reaches a reproducible state on a yearly basis due to the regularity of flood deposition in late fall and maturation of the system in spring and summer. This reproducibility of the spring-summer conditions applies probably to the observed fluxes as well."

C: "[. . .] their presence in zones of sulfate reduction suggest these sediments are highly dynamic with periods of intense sulfate reduction alternating with periods during which sulfate reduction is repressed and replaced by microbial iron reduction (line 458-460). Does this sentence mean that there are two different conditions depending of the flood conditions or seasons? What are the consequences on FeS precipitation and on TA release? This sentence is too vague and raises questions on the temporal representativeness of the data (episodic event? Seasonal variations?).

R: Both reviewers were puzzled by this sentence (see specific comment by Reviewer 1 about lines 458-460), and we think the sentence is misleading. It will be modified to "suggest these sediments are highly dynamic with concomitant intense sulfate reduction, microbial iron reduction and rapid FeS precipitation" as already discussed in

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response to Reviewer 1. The abstract will also be modified to reflect this comment.

C: I have the same questions on the spatial representativeness of the data. How do the authors explain the difference between the two replicates Z and Z'? Then, I encourage the authors to discuss about the spatio-temporal representativeness of observations.

R: The difference between both samplings can be due to spatial heterogeneity at the local scale due to differential deposition at these sites. As explained in response to the same comment by Reviewer 1 (see spatial variations in response to the 2nd comment by Reviewer 1), we have already described the different zones of the Rhône delta from the proximal zone to the continental shelf (lines 82-86) and their characteristics (sedimentation rates, depth, organic carbon content; see also Table 2) in the original manuscript. Something surely missing in this paragraph is an appreciation of the spatial heterogeneity at the local scale. As the main deposition of sediment occurs during floods, sediment layers are heterogeneous at the meter scale, and differences in pore water profiles can be detected at that scale (e.g. DIC and TA profiles on Fig. 6 for station A and Z taken from two different cores at the same station). These points will be highlighted in the revised manuscript. However, even with this local variability taken into consideration, the difference between the proximal zone stations and stations in the prodelta or the continental shelf are still obvious as highlighted in the discussion of the original manuscript (see sections 4.5, 4.6, 4.7, and 4.8) (see also Rassmann et al., 2016).

C: My last issue is on the role of bioturbation. I think about bioturbation when I looked at the figure 10. According to the frequency of flood events and to the accumulation rates at the proximal stations, the diffusive transport of the anaerobically-produced alkalinity in the flood deposit to the SWI, takes time no? (see the work of Anschutz and collaborators in natural turbidites (Anschutz et al., 2002; Chaillou et al., 2006) and in experimental turbidites (Chaillou et al., 2007)).

R: As pointed out in response to similar comments by Reviewer 1 (see 2nd main com-

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ment and specific comment of L501-504), the spring-summer diagenetic processes described in this paper are the result of the late fall deposition of flood layers and their maturation. The fluxes of alkalinity and DIC certainly vary over time with the progressive buildup of alkalinity and DIC in pore waters, as sulfate reduction, iron oxide reduction, and FeS precipitation proceed during the spring and summer seasons. The alkalinity flux, however, is linked to the net precipitation of FeS, which is the difference between precipitation and re-oxidation due to transport in the oxic zone. Burial occurs when a new flood layer is deposited (in late fall) which traps the FeS produced during the year below a new sediment layer of 10-30 cm ensuring its preservation. This yearly preservation of FeS ensures the concomitant benthic alkalinity flux to represent a net flux to the bottom waters which is not affected by FeS oxidation, contrarily to sediments exposed to low sedimentation rates where FeS can be entrained by bioturbation to the oxygenated layer and be re-oxidized (therefore consuming alkalinity). As a result, the net alkalinity flux can arise by diffusion over a depth of 15 cm as the diffusion time over this distance is 6 months (with $D(\text{HCO}_3^-) = 6 \times 10^{-6} \text{ cm}^2/\text{s}$). In the first 5 centimeters, transport may be increased by bio-irrigation as can be observed in the A and Z concave DIC/TA profiles. Except for the flood period, advection is limited as sedimentation remains low. Hence, the processes that produce alkalinity (i.e., FeS precipitation) and occur in the first 20 cm of sediment can most probably be linked to the bottom water fluxes by diffusion during the late spring, summer, and early fall. These concepts will be added to the revised manuscript to clarify this point. Anschutz et al. (2002) on a 4 month-old natural turbidite and Chaillou et al. (2007) on artificial turbidite showed that after a few month steady-state was not reached (10 months, Chaillou et al., 2007) but that a relative buildup of nutrients (i.e., NH_4^+ as an integrative diagenetic indicator) occurred. In Anschutz et al (2002), concentration of $\text{NH}_4^+ > 400 \mu\text{M}$ were recorded at the bottom of the turbidite layer implying rapid diagenesis after turbidite deposition. Unfortunately, DIC was not measured in these studies, although it is likely that DIC profiles would have been similar to NH_4^+ profiles. In Pastor et al. (2011) in the Rhone prodelta, a peculiar flood (occurring in spring) was followed over 6 months: DIC con-

C8

centrations reached 35mM at the bottom of the flood layer (30 cm) after 6 months, with a shape similar to normal-year spring and summer profiles. We will acknowledge the non steady-state issues in the new manuscript by referencing these papers.

C: Bioturbation and biodiffusion could be an efficient mechanism to transport anaerobically-produced metabolites, as TA from the anaerobic zone to the surface. Did the authors measure the bioturbation coefficients in the incubations? Did they consider the macrofauna in the studied sediment? What about the difference between total fluxes and diffusive fluxes of DO, TA and DIC? Are they similar (same magnitude)?

R: Bioturbation or bioirrigation was not measured during this cruise, although macrofauna has been measured in previous cruises (see Charles et al., 2014 or Bonifacio et al., 2014). In addition, bioirrigation is poorly quantified in the study area except the paper by Lansard et al. (2009) in which total oxygen Uptake (TOU) was compared to Diffusive oxygen uptake (DOU) in sediment incubations to estimate the effect of bioirrigation. TOU/DOU ratios of 1.2 ± 0.4 were found over the offshore transect indicating that bio-irrigation is probably not particularly efficient in this zone. The role of bioturbation on the transport of TA and other pore water constituents can unfortunately not be determined by comparing diffusive fluxes of TA and DIC to benthic TA and DIC fluxes, as the vertical resolution of the rhizons is too low (~ 2 cm) to be able to estimate accurate gradients near the sediment-water interface. TOU fluxes were unfortunately not measured.

C: The authors are kindly asked to see the attached annotated PDF with my suggestions

R: The comments of the attached annotated pdf document will be taken into account. Most of them are minor comments. Here we will only respond to the comments on the content of the manuscript. Finally, we agree with the majority of the specific comments provided below, and these comments will be incorporated in the revised manuscript unless addressed specifically below.

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L19: "Not sure to understand the link between organic-Fe(III) and the variability of the organic and inorganic particulate input. . ."

This point was already brought up by Reviewer 1 that some statements need context in the abstract (see response to specific comments of lines 19-21 by Reviewer 1).

L45: "produce?" implied to be better than 'create TA'

The change will be done

L55: reference needed

Several references were already provided in the sentences immediately above this one, such that we feel they do not need to be repeated here.

L66: "what is the role of the organic alkalinity produced by the terrestrial OM? Please discuss about the role of OM source on the production of TA."

See the response to the 2nd concern of Reviewer 2 above.

L77: "? Fe-rich particles?"

We mean mostly iron oxyhydroxides ($\text{Fe}(\text{OH})_3$) . This comment will be ignored.

L95: "It 's very high. Detrital IC input from where? geology in the watershed?"

The carbonate content quoted here comes from numerous studies of C in sediments. There are many calcareous formations in the drainage basin of the Rhône River especially in the Southern Alps.

L99: "does it mean that you will performed diffusif and total flux calculations? what about the role of bioturbation to the exfluxes of TA and DIC?"

As mentioned above in response to the last main concern of the reviewer, we cannot compute the diffusive DIC and TA fluxes as the vertical resolution of the rhizons is too low (~ 2 cm) to determine accurate gradients near the sediment-water interface. Concerning the role of bio-irrigation on the fluxes, see remarks above and the low

C10

TOU/DOU ratio measured in the area (1.2±0.4).

L105: "ok, see my comment on the table 2"

L114: "Which ones? please detailed"

This information will be provided in the revised manuscript.

L122: "Do you measure the bioturbation / bioirrigation coefficient? "

No, we did not measure bioturbation, as indicated earlier.

L125: "with the syringe system?"

Yes, with the syringe system described by Jahnke and Christiansen, 1989.

L130: "and oxygen? "

Unfortunately not, due to technical issues.

L141: "no TRIS?"

We did not use TRIS buffers, but corrected the salinity shift by using pH values of the bottom water measured via spectrophotometry (line 139). This information will be provided in the revised manuscript.

L145: "what is the porewater volume you collected? ~20mL? enough to measure all the parameters?"

Pore water volumes were between 12 and 15 ml. 3 to 5 ml were used for DIC, 3 ml for TA, 1 ml for NH₄⁺ and 1 ml for SO₄²⁻, 1-2 ml for Ca²⁺, 1 ml for phosphate and dissolved iron. CH₄ was measured on a separate core.

L169: "I know this technique but I am surprised by the volume you collected with the pore size of 0.1µm. "

According to the manufacturers, this is the pore size of the rhizomes.

C11

L171: "Viollier et al. for Fe²⁺? The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters."

We used Stookey (1970) as a basis for the method. The method of Viollier et al. is based on Stookey's method and only uses a 10 minute reaction period with hydroxylamine which we extended to 24 hours, as initially reported in Stookey. We feel this information is not needed in the revised manuscript, as the methods section only needs to report what was conducted.

L181: "these methods seem complicated. Why not use the Rodier method? I am just curious. Why two different methods? what is the difference"

These two methods are HPLC methods which are more precise than the nephelometric method (quoted as Rodier). HPLC ensures a precision of around 1% for sulfate determination and requires 100 µl whereas the nephelometric method requires larger samples and has an uncertainty of 3-5%. As some of our stations had limited SO₄²⁻ decrease and the amount of sample was small, we preferred using HPLC methods. We used two methods to establish a comparison between the methods for our own purposes. Motivation for the two HPLC methods will be provided in the revised manuscript.

L188: "I suppose it is only for the porewater Ca concentrations. not for the determination of total Ca fluxes in the chamber."

Yes, it is only for pore waters. Actually, we tried both, but the changes in Ca²⁺ concentrations over time were too small compared to the uncertainty of the used method. This comment will not be addressed in the revised manuscript.

L191: "please add the limits of detection"

L212: "Did you use the PHREEQC software to do the IAP calculation? please add information Same question for the omega calcite calculations "

As mentioned in response to a similar comment by Reviewer 1, IAP were estimated in a spreadsheet. The equilibrium constant was recalculated at the ionic strength of sea-

C12

water, the measured Fe²⁺ concentrations were used as 'free' available Fe²⁺, as Fe²⁺ does not form strong complexes, and 2S concentrations were used to calculate the speciation of sulfide species (assuming no elemental sulfur or polysulfide were present in the pore waters). Finally, the activity coefficients provided in the methods section were used for these calculations. These details will be provided in the supplemental material of the revised manuscript. For the OMEGA calcite calculations, the Seacarb package for R was used.

L227: "Whatever the depth? DO you calculate de AVS burial for each depth/layer?"

As mentioned in these lines, we estimated an average concentration for the core and multiplied by the sedimentation rate and porosity. We feel the description was clear enough to not warrant any modifications in the revised manuscript.

L235: "this is the data reported in the table 3 (corrected from Diffusion and Ca). Ok I understand now! It is difficult to understand what do you want to do. I think you need to better introduce the goal of these calculations. What is the advantage to do these calculations compared to use a DIC - TA diagram where you add the theoretical slopes of the different reactions and the corrected data? Please see the last paper of Pain et al. 2018 and the figure 9 therein"

These calculations will be better introduced in the revised manuscript though similar calculations were already reported in Rassmann et al. (2016). We are not sure if adding a new figure would be useful, but we will reference the paper of Pain et al. 2018 to clarify the methodology used.

L242: "Do Di and Dj corrected from temperature?"

Yes, the diffusion coefficients were calculated as a function of temperature, pressure, and salinity. This information will be provided in the revised manuscript.

L242: "Did you use a softawar (Seacarb or PHREEQC?"

No, these calculations were conducted in Excel using the functions reported in the

C13

literature (Li and Gregory, 1974). This information will be provided in the revised manuscript.

L246: "ok but TA is not only carbonate alkalinity $TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + 2[H_2SiO_4^{2-}] + [HS^-] + 2[S^-] + [NH_3^+] + [Org^-] - [H^+] - [H_3PO_4]$ See my previous comment on the role of OM and organic alkalinity on TA"

Yes, but carbonate alkalinity is the major fraction of TA. As already explained above in response to a similar comment by this reviewer, we are lacking data to estimate the non-carbonate alkalinity fraction accurately.

L247: "You measure TA but you talk about carbonate alkalinity in the text. Please clarify " This comment is not clear, as we did not discuss carbonate alkalinity in the lines identified by the reviewer. We only describe the effect of the precipitation of calcium carbonate on TA and DIC variations in this sections.

L270: "please change the number it is figure 3."

The figure number is correct. Oxygen was measured with Clark type electrodes (Figure 2) and by voltammetry (Figure 5). Both methods concur. Figure 3 shows the evolution of DIC and TA concentrations in the benthic chamber over time and will be moved into the supplementary material.

L287: ""relative importance" : not clear, what does "importance" mean ?"

L289: "what about Mn²⁺? not used? please delete the data from the figure" A statement will be added to explain that Mn²⁺ was undetected in most sediments from the Rhône River prodelta

L292: "mean value over the lenght of the core?"

Here we are actually describing maximum concentrations. These details will be added to the revised manuscript.

C14

L343: "below the limit of detection or not measured?"

As mentioned in this sentence, dissolved phosphate was not measured at station B. As this sentence is clear enough, this comment will not be considered further in the revised manuscript.

L357: "so it's mainly based on a qualitative approach. Despite the length of discussion, there is still some questions on: - the "steady state" approach of the redox processes under sedimentary transient conditions, (especially at the proximal stations A Z and to a lesser extent AK

L357 does not address the 'steady-state' approach, and this comment by the reviewer is not clear. However, the problem of comparing profiles obtained at one time period to TA fluxes integrated over several months has already been addressed in response to the 3rd main concern of the reviewer (see above). This comment will not be addressed further at this location in the revised manuscript.

- the role of terrestrial organic matter on benthic TA, mainly in the proximal zone

Similarly, we already addressed the role of terrestrial organic matter on the benthic TA flux in response to the 2nd main concern of Reviewer 2. We refer to our above response to address this comment.

- the role of bioturbation to explain the exfluxes of TA and DIC

As mentioned above in response to the last main concern of Reviewer 2, bioturbation is poorly constrained in this area, though high resolution electrochemical profiles show no apparent effect on the gradients near the sediment-water interface. In addition, the measured benthic TA and DIC fluxes are in situ fluxes over 30 x 30 cm of enclosed sediment such that bioturbation should be accounted for in these measurements. Besides the changes highlighted in response to the last main concern of the reviewer, this comment will not be addressed further here.

The sections on the formation of iron sulfide species and FeS precipitations are too

C15

long and could be shortened. I don't understand what is really new here

The section will be shortened and the novelties better highlighted to shorten the discussion.

L426: "just the distance between the two fronts (>5cm)"

This comment is not clear and cannot be addressed easily. Sulfide concentrations are low in each sediment core below the oxygen penetration depth, suggesting not oxidation but FeS precipitation. This comment will not be considered further in the revised manuscript.

L456: "I am not sure this figure is necessary" for Fig. 7

We disagree as the correlation between Fe²⁺ and organic-Fe(III) provides strong evidence for the microbial reduction of Fe(III) oxides as discussed in the manuscript. This information appears important to highlight the possible concomitant nature of the microbial processes in these sediments. This comment will not be considered in the revised manuscript.

L488: "so is it necessary to present the PIAP (in supplementary material?). The discussion should be shortened "

We agree, as acknowledged in response to comments of both reviewers. This will shorten the manuscript significantly.

L491: "yes, but the accumulation is not constant over the year... not at steady state after the deposition"

We recognize that these sedimentation events are extreme and the temporal variations of sedimentation rates will be emphasized in the revised manuscript as explained above in response to the comments of both reviewers.

L511: "For me, it is the first step of the discussion (it is also the first reaction presented in the table 1). I suggest to the authors to move this section to start the discussion."

C16

This is an interesting idea by the reviewer, as we could move this section earlier in the discussion (after section 4.1), though the conclusion of this section requires to present the effect of FeS burial on the alkalinity flux for comparison. Although minor, we will definitely consider this option in the revised manuscript.

L546: "Yes but I suppose this rate is not constant : massive input of "new" and terrigenous-rich OM material"

We addressed the seasonal variations associated with flood events in the fall and slow build up of alkalinity during the spring and summer seasons in response to comments made by both reviewers. The discussion will be strengthened by such discussion.

L868: "Why do you show the results in red? I would remove these incubations (Z and Z' in red)"

As mentioned in response to a similar comment by Reviewer 1, this was the result of an error during data plotting. The correct figure will be provided in the revised manuscript.

L891: "below the dl?"

No, not measured. We feel this statement is unambiguous here.

Fig 1: "compared to the others figures, this one is "ugly" !"

The figure will be modified to improve its clarity.

Fig 2: "change the color between O2 and pH. At this scale, dotted lines are not visible"

The figure will be modified for better visibility.

Fig 3: red triangles??

The figure will be reformatted and moved into the supplement section.

Table 2: "Concentrations in the bottom water? please add the information"

This information will be provided in the revised version.

C17

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-32/bg-2019-32-AC2-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-32>, 2019.

C18