

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.

christophe.rabouille@lsce.ipsl.fr

Received and published: 24 May 2019

(Please see pdf attached as a supplement for a formatted version with Figures)

Response to Anonymous Referee #1

C: General comments: In this study, Rassmann, Eitel et al. investigated benthic alkalinity and DIC release from various sites in the Rhône River delta area. These sites differed in their distance from the river mouth, water depth, and sedimentation rates. The authors measured fluxes to quantify the alkalinity and DIC release, and measured a variety of pore water and sedimentary constituents to investigate the responsible

C1

processes. Particular attention was given to the ratio between aerobic and anaerobic organic matter degradation and the role of FeS burial in determining the alkalinity release. After reading the manuscript, I have somewhat mixed feelings. On the one hand, I appreciate the data set and especially the determination of organic-Fe(III) complexes and FeS nanoparticles, something that is new to me in the context of benthic alkalinity release. On the other hand, after reading I asked myself what the novelty and take home message from this work is and I am not sure if I can properly answer that question.

R: We appreciate the reviewer recognizes that the organic-Fe(III) complexes and FeS nanoparticles are useful in the interpretation of this complex data set. In turn, we are disappointed by the comment that the reviewer does not understand the novelty of this work. This work demonstrates 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 the 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. The abstract, discussion, and conclusions will be modified to emphasize the fact that this is the first study demonstrating the link between measured benthic alkalinity flux and biogeochemical processes, namely FeS precipitation and burial, responsible for this alkalinity flux.

C: Despite the length of the manuscript (I'd suggest to at least shorten the description of the results and move Fig. 3 to a supplement) I was still left with quite some questions. What I generally miss in the manuscript is an appreciation of various temporal and spatial scales at which both benthic alkalinity generation and its release can be discussed. For example, if reduced constituents responsible for the alkalinity generation are released to the water column and quickly re-oxidized there, would it still contribute to the CO₂ storage capacity over longer time scales? Under which conditions is or is this not valid? Also, can the authors directly compare the alkalinity efflux due to FeS

C2

burial and the measured effluxes, given the high sedimentation rate, and that effluxes vary on much shorter timescales, and due to many processes other than FeS burial? And finally, how representative are the measured fluxes (and other data) on e.g. an annual timescale given the high variability in inputs over the year? Could the authors indicate that based on their earlier published work?

R: We agree that the manuscript could be shortened, and we will move Fig. 3 (benthic chamber TA and DIC) and Fig. 8 (pIAP) and associated paragraphs presenting the methods and describing or discussing these data to a supplementary material section to shorten the manuscript. The question of temporal and spatial scales is crucial in these dynamic environments and we tried to introduce them in the manuscript, although we probably did not include enough material dealing with this topic in the background (1. Introduction) and field site description (2.1: The Rhône River delta) sections. These two sections will be updated with additional sentences on the temporal and spatial scales as explained below.

Concerning the question on the re-oxidation of reduced components in the water column, re-oxidation of reduced metabolites has the same net effect as re-oxidation in the sediment, i.e. consumption of alkalinity by protons produced during oxidation (see equations 3 and 4 of Table 1). Thus, re-oxidation of reduced metabolites does not contribute to the CO₂ storage capacity over long time scales. This is the reason why the burial of reduced components (FeS and potentially FeS₂) in the deep sediment layers presented in this manuscript is so important: Burial of FeS and FeS₂ prevents re-oxidation in the sediment and in the water column and creates a net flux of alkalinity to the water column. Although we feel that this topic was well covered in the original manuscript (see lines 21-25 of the abstract, lines 51-55 of the introduction, lines 491-493 and 547-550 of the discussion), we will clarify these points in these sections and improve Figure 10 to clearly illustrate the importance of the lack of re-oxidation near the sediment-water interface.

Concerning the spatial scale, we already described in the original manuscript the differ-

C3

ent 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 stations). These points will be highlighted in the revised manuscript. However, even with this local variability (at the station scale) 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). 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, 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). Al-

C4

together, 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.

Concerning the comparison between benthic alkalinity and FeS burial fluxes, 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).

Concerning the “many processes other than FeS burial” which influence the benthic alkalinity flux, we refer to previous studies which demonstrated only two anaerobic processes (iron sulfide burial and N₂ loss by denitrification) contribute to a net release of alkalinity from the sediment through the net loss of reduced species by either of these processes (see for example Hu and Cai, 2011 in GBC). All other internal cycling processes do not represent net sources of alkalinity as highlighted in the discussion already (see lines 419-442 and Table 1). We show in the manuscript that denitrification is a minor source of alkalinity, if any (discussed in section 4.2). The other potential source of alkalinity in sediment is carbonate dissolution which we showed to be absent or minimal due to large oversaturation of the pore waters with respect to calcite (Rassmann et al., 2016 and Figure 9 of this manuscript) supported in this study by the

C5

decreasing Ca²⁺ concentrations in the profiles (Figure 6), certainly indicating CaCO₃ precipitation.

Concerning the “representativity of the measured fluxes”, it is hard to conclude as these measurements represented the first attempt to measure either in situ or ex situ benthic alkalinity fluxes in the Rhône River prodelta. During a more recent cruise in 2018, sediment cores were incubated to estimate DIC and alkalinity fluxes across the sediment-water interface. The (unpublished) results (see Figure AC1 below) display the same pattern as observed in situ in 2015 (this study) with large DIC and TA fluxes in the proximal zone (A, Z, AZ) and decreasing fluxes offshore (AK, K and C, E on the shelf). Insert Figure AC1

To clarify these points in the manuscript, we will add a few sentences in the introduction on the effect of seasonal patterns on the biogeochemistry of river-dominated sediments and a paragraph in section 2.1 containing information on the temporal variation in depositions in the Rhône River prodelta from previous studies. Finally, the discussion will highlight the features described above that argue for the decoupling between aerobic and anaerobic processes and the link between FeS burial fluxes and benthic-pelagic alkalinity fluxes.

C: I appreciate that the authors do not try to temporally upscale their fluxes given the variability, but it does mean that samples from different points in time may plot very differently on Fig 11.

R: As no data are available during the fall and winter and evidence suggests that the state of the system is different during these seasons due to flood-related increase in deposition, we prefer not to extrapolate the fluxes over this period. As the aim of the paper was to discuss the link between alkalinity fluxes and sediment diagenetic processes, however, the lack of extrapolation over time does not weaken the message of our paper.

C: The discussion on identification of major biogeochemical processes remains rather

C6

qualitative. I don't think it is possible with the current data to do it differently, but it is a drawback of the manuscript. Figure 10 is a nice summary of concept, but I wonder how valid it is under temporally varying conditions as observed especially at the proximal stations. I think in general more focus could be placed on the factors controlling FeS formation at the various stations and the possible impacts of flooding on these factors.

R: As the reviewer indicates, the identification of the major biogeochemical processes remains qualitative, though corroborative evidence between various data sets helps draw a rather clear biogeochemical picture of the processes taking place in these sediments. We discussed the temporal variability already in the response to the previous point by the reviewer. We think that the concept of Figure 10 is valid when integrating over an entire year but certainly not over each individual season: Indeed, following late fall deposition of flood sediment layers, DIC and alkalinity build up in pore waters during the winter and FeS accumulates in the solid phase as sulfate reduction and iron oxide reduction proceed. In spring and summer, sampling conducted over 5 different years reveals that the diagenetic system is in a similar state on a pluriannual basis (see above): FeS is buried only at the end of the fall when a new flood layer is deposited closing the conceptual diagram of Figure 10. As mentioned above, the temporal variability will be included in the revised manuscript and Figure 10 will be improved to clarify these points.

C: Irrespective of the decision on the manuscript I hope that the following comments will help you further shape it.

R: We appreciate the time spent by the reviewer to carefully evaluate our work and the thoughtful comments that will certainly help us improve our manuscript.

Specific comments:

L. 14-16: What about pore water iron data? Sulfate and nitrate concentrations alone don't tell you something about iron reduction. And what about manganese?

C7

The reviewer is right. Low nitrate concentration does not tell about iron hydroxide reduction. We will add large dissolved iron concentration between "Low nitrate" and "strong pore water sulfate gradient". However, low nitrate concentrations suggest that denitrification is not a major process in these sediments. Furthermore, a model study comparing the proportion of different mineralization pathways concluded that denitrification is only a minor process in this area (Pastor et al., 2011). In turn, sulfate data demonstrates that dissimilatory sulfate reduction is a major respiratory pathway in these sediments (See Rassmann et al., 2016). Pore water manganese data is also presented later in the paper, however, as concentrations of dissolved Mn(II) were low and manganese reduction was not expected to contribute greatly to the biogeochemistry of these sediments we did not feel it was necessary to mention manganese in the abstract.

L. 19-21: This sentence doesn't tell me anything about the underlying mechanisms behind these concurrent observations (which you do explain in the discussion, I noticed later). If these complexes are found, does it mean that sulfide is generally limiting FeS formation?

We agree that this sentence is misleading and needs to be clarified in the abstract. The detection of organic-Fe(III) compounds, which are indicative of dissimilatory iron reduction and are rapidly reduced by sulfide, demonstrates that the system is dynamic as we would not expect to observe these Fe(III) species in zones dominated by sulfate reduction.

C: What do you mean by inorganic? Does it refer to iron oxides?

Yes. This will be clarified in the revised abstract.

L. 54-59: Yes, but this depends on the timescale. The net TA flux due to these processes may not correlate to what you measure as efflux. A diffusive efflux is primarily driven by the gradient at the sediment-water interface and may only reflect processes occurring deeper in the sediment on longer time scales. I would think this is espe-

C8

cially relevant in systems with a (periodically) very high sedimentation rate (see further comments below).

We agree with the reviewer that the efflux is driven by the concentration gradient at the sediment-water interface (SWI), but this gradient is controlled by biogeochemical reactions in the sediment. Yet, the connection between the two can be made if chemical species can migrate over the distance between the biogeochemically active zones and the SWI over a given time. It is possible to calculate the minimal distance (d) that can be traveled by chemical species over time t by calculating the diffusion distance ($d = \sqrt{2 \cdot \text{DiffCoeff} \cdot t}$) where DiffCoeff is the diffusion coefficient of the chemical species). For a period of 6 months (between fall and spring) and with the DiffCoeff of HCO_3^- ($D = 11.8 \cdot 10^{-6} \text{ cm}^2/\text{s}$ at 25°C , around $6 \cdot 10^{-6} \text{ cm}^2/\text{s}$ at 20°C in the sediment), the diffusion distance is around 15 cm. This distance is minimal as bioturbation and bioirrigation will increase transport and thus increase the connection distance. We can thus consider that most probably 20 cm are connected to the SWI and that biogeochemical processes over that depth interval can shape fluxes at the SWI over a 6 months period (the late spring, summer and early fall which certainly corresponds to the “longer time period” that the reviewer quote). This information will be added to section 4.6 to clarify this point.

L. 62-65: Again, this is scale-dependent and only if re-oxidation of reduced constituents does not quickly occur in the water column.

We disagree with this comment. If reduced constituents are buried in sediments, they are not fluxing across the sediment water interface and thus not re-oxidized in the water column (see our initial response above).

L. 65-68: The objectives are formulated in a very qualitative way. I understand this for the second part, but not so much for the first part, which can be formulated more strongly. First, the fluxes were quantified, so you may state that.

Agreed, this will be revised by replacing ‘investigate’ by ‘determine’ in the revised

C9

manuscript.

C: Second, most sediments are alkalinity sources, but not all sediments release more alkalinity relative to DIC. Isn't that what you're mostly interested in, the possible excess over DIC efflux?

This is incorrect, sediments are generally weak sources of alkalinity because only denitrification based on external NO_3^- input and FeS (or FeS_2) burial represent net sources of alkalinity (which is not common). Even sediments with high rates of aerobic and anaerobic respiration followed by re-oxidation of all reduced species produced during anaerobic respiration would not act as a net alkalinity sources although the large DIC quantities produced by these processes diffuse out of the sediment. Thus, measurement of multiple species was conducted to determine the extent and mechanism of alkalinity production in these sediments and its relation to diffusion across the sediment-water interface, as described in the text. This point will be emphasized in the revised manuscript.

L. 91: What about temporal variability in sedimentation rate in the prodelta?

The temporal variability in sediment rate in the Rhône River prodelta is largely unknown, except for the paper by Cathalot et al (2010, BG) which shows deposition of an abnormal flood in June 2008. It is known that the majority of the sediments in the vicinity of the river mouth is deposited during flood events which occur mostly in fall and early winter. Thus, the sedimentation rates vary due to episodic events. This information will be provided in the revised manuscript.

L. 106: Can you include a range of how far above the sea floor samples were approximately taken?

We used the depth estimation from the winch for sampling and checked the real depth with a mounted underwater depth gauge. Bottom water samples were taken within 1-2 m above the seafloor. This information will be provided in the revised manuscript.

C10

C: And did you also sample overlying water from the sediment cores used for the pore water and solid phase analysis? In my experience, the composition of that water can be quite different from a Niskin bottom water sample.

Yes, overlying water from the sediment cores was measured and in good agreement with the bottom water DIC and TA concentrations. This information will be mentioned in the revised manuscript.

L. 108-110: At what temperature are the pH data presented, in situ or 25 degrees? Please add.

The pH samples were measured at 25°C and the pH values recalculated to in situ temperature, salinity, and pressure using CO2sys. The pH data is presented at in situ temperature and pressure. This information will be provided in the revised Method section.

L. 114: What are the 'main redox species'? Specify. In the results only DIC and TA lander data are presented.

This part of the sentence will be removed from the paper as the results from the in situ voltammetric sensors in the lander chamber (iron, manganese, sulfide) are not used in this manuscript.

L.119: Which redox chemical species? Specify, this is too vague.

This part of the sentence will be removed from the paper as the results from the in situ profiles are not used in this manuscript.

L. 124-125: Which method is used for measuring DIC and TA? Same as in section 2.6? If so, refer to it.

Yes, DIC and TA measurements were conducted using the same method as described later in the paper. As this section just describes the benthic chamber deployments we prefer to keep the analysis methods in section 2.6, and we will refer to it in the benthic

C11

chamber section.

L.128 (Eq. 1): Did H remain constant over time or did it decrease over time as a result of the sampling? If so, have you corrected for that?

The volume (and thus the height) of the chamber remained constant during the deployment and the syringe volume was compensated by an equal amount of bottom water. This was accounted for in the calculations.

L. 144: How many cores were taken per station? I counted 3: 1 for porosity, 1 for voltammetry, 1 for pore water and sediment sampling. Correct?

Six cores were taken at each station: 1 short core (~30 cm length) for pore water extraction under N₂, one long core (~50 cm length) for pore water extraction in lab, one core for porosity measurement, one core for methane concentrations, one core for voltammetric profiles, and one core for archives.

L. 158: Why is S₀ mentioned as part of total dissolved sulfide?

S₀, including S₀ from polysulfides, may contribute to the total sulfide voltammetric peak (Taillefert et al., 2000) as the electrochemical reaction involves simultaneous oxidation of Hg(0) and reduction of S₀ at the electrode surface to form HgS at the same potential as that of the oxidation of Hg(0) in the presence of H₂S. As a result, S₀, polysulfides, H₂S, and HS⁻ cannot easily be distinguished and are typically reported as total dissolved sulfide (2S) when measured electrochemically. This information will be provided in the revised manuscript.

L. 159-160: Does this imply that you can only make a relative comparison between stations of the same cruise? Or can you compare your results with current intensities from other cruises?

Normalized intensities can be compared to any data sets collected at any time because they are only normalized to the sensitivity of a particular electrode at the time it was used.

C12

L. 173-174: What was the sample volume used for alkalinity titrations?

The sample volume used for alkalinity titrations was 3-6 ml of pore water, according to available quantity. This information will be provided in the revised manuscript.

L. 177-178: Did you make any replicate measurements?

Yes, triplicate measurements were made for DIC and either duplicate or triplicate measurements were made for TA, depending on the total pore water volume available. Replication adopted for the chemical analyses will be provided in section 2.6 of the revised manuscript.

L. 199-200: How was the sediment extracted? Slicing and centrifuging? More details would be appreciated.

The sediment was collected using Rhizons as mentioned in the original manuscript (lines 167-169).

L. 210-212: I have to say I'm not familiar with this method, but I don't think I understand this.

FeS0 consists of two pools, one measured by voltammetry (FeSaq), one not (larger nanoparticles). Spectrophotometry measures both pools. So how can the difference between both measurements be used to quantify both pools? I probably misunderstand, so could you explain it differently? FeS0 represents the difference between two measurements of Fe(II) by spectrophotometry and by electrochemistry. The Fe(II) measured spectrophotometrically in extracted pore waters includes both Fe(II), FeS(aq), and larger FeS nanoparticles which may pass through the rhizon filters used to extract pore waters but are not measured by electrochemistry due to their limited diffusion to the electrode. In turn, the Fe(II) measured electrochemically includes only Fe(II) and small FeS(aq) molecular clusters that are smaller than 5 nm and thus voltammetrically measurable. As a result, the difference between these two measurements represents the FeS nanoparticles (named FeS0) that are small enough to pass through the rhizon

C13

filters but too large to diffuse to the electrode. We feel this information is well presented in lines 204-209 and Equation 2. Unfortunately, we cannot directly compare FeS(aq) and FeS0 concentrations as FeS(aq) determined by voltammetry is not quantifiable but is reported in normalized current intensities (as described in lines 161-162). This last point will be highlighted in the revised manuscript.

L. 212-217: Has any particular software been used for the saturation calculations?

IAP can be calculated based on Eq. 3 with the parameters described in lines 217-220. This calculation was done in Microsoft excel as ionic strength and activity coefficients from conventional seawater were used in these calculations. The equilibrium constant was recalculated at the ionic strength of seawater, 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). These details will be provided in the supplemental material of the revised manuscript.

L. 243-246: Indeed this is common practice and I'm perfectly fine with it. So more out of curiosity: do your seacarb or other calculations indeed show that HCO₃⁻ constitutes >90% of TA? Using your pH and DIC data, can you say anything about the possible presence of organic alkalinity?

Yes, the calculations using Seacarb show that HCO₃⁻ concentrations in the pore water are always > 90%, except for one point at 30 cm depth at station K where HCO₃⁻ represents "only" 89 % (see new figure below-AC2).

Insert Fig. AC2

To estimate the amount of organic alkalinity, we could theoretically calculate carbonate alkalinity using DIC concentrations and pH and subtract the result from the measured value of total alkalinity. The difference should equal the organic part of alkalinity. In the bottom water samples, we measured pH, TA and DIC. The calculations give a con-

C14

centration of organic alkalinity between 8 and 28 $\mu\text{mol/L}$ ($< 1\%$ of TA) in the bottom water samples (sampled with the Niskin bottle) without any particular spatial trend. In sediments, the issue is more complicated. pH microprofiles were measured in situ down to 20 mm only, with a vertical resolution of 200 μm . DIC and TA were measured in extracted pore water samples, with a vertical resolution of 2 cm. Furthermore, these extracted pore waters represent an average value of several mm around the rhizons. This means, that we only have an overdetermined carbonate system down to two cm sediment depth with one single value for DIC and TA and a full pH profile with around 100 values ranging from 8.1 to 7.2. We could still use an averaged pH value together with the DIC value in order to calculate the fraction of carbonate alkalinity and non-carbonate alkalinity in the pore waters, but as these calculations are sensitive to pH, the approach is questionable. A first guess using an averaged pH value around 0, 1, and 2 cm depth lead to concentrations of organic alkalinity not exceeding 60 $\mu\text{mol/L}$. These low organic alkalinity concentrations in surface sediments may also prevail in deep sediments as the DIC/TA ratios are close to 1 (Figure 6), which is not the case when large quantities of organic alkalinity accumulate in sediments (Lukawaska-Matuszewska et al. 2018 Marine Chemistry, doi: 10.1016/j.marchem.2018.01.012). This is definitely an issue that could be resolved in further investigations by measuring pH profiles over longer depths in the sediment. As this question by the reviewer was merely out of curiosity and as the lack of data on organic alkalinity deep in the sediment does not change the main conclusions of the manuscript, we will not address this comment further in the revised manuscript.

L. 247-254: This method applies if there are no other fates of Ca^{2+} aside from precipitation or dissolution of CaCO_3 . Can you add a sentence acknowledging this?

In sediments, calcium is essentially related to calcite (pure or magnesian). Calcium could as well be consumed by the formation of $\text{Ca}(\text{Mg})\text{CO}_3$. The Mg fraction can get as high as 50 % (dolomite) but is generally around 20% in magnesian calcites. If this is the case, the Ca/DIC and Ca/TA ratios would be lower than for CaCO_3 . For

C15

simplicity and having no information about the Mg content of the reprecipitating mineral phase, only CaCO_3 is considered. We have also to keep in mind that the correction itself affects the ratios by less than 10 %. A sentence will be added in the manuscript acknowledging that most Ca^{2+} is trapped in Ca-rich carbonate.

L. 279-281: Fluxes are highest at station Z, but also most variable (highest s.d.). More interestingly, the two sampling dates show opposing trends in the TA/DIC flux ratio (below 1 for Z, above 1 for Z', although I haven't checked the statistical significance of this), something you don't specifically discuss. Can you place this observation in the larger context of spatial and temporal variability?

It is difficult to account for statistical significance from just two flux calculations. Given the error bars for the two flux measurements, one cannot tell if the TA/DIC ratio is different for the two flux measurements at station Z and Z'. Spatial heterogeneity (at the scale of several meters) between the deployment Z and Z' is certainly present as shown by the significant variation of fluxes. This is due to the deposition conditions during floods which may vary locally (both in quantity and quality, see response to an earlier comment by the reviewer). Yet the large difference and the significant alkalinity fluxes observed at this station compared to the shelf site are indicative of specific processes in the proximal zone. Sediment core incubations conducted in 2018 (Figure AC1 shown above) seem to point in the direction of TA/DIC flux below 1. TA/DIC flux superior to 1 could mean, that a high fraction of TA is organic or that calcium carbonates dissolve at the surface. But as reported in this article and in Rassmann et al. (2016), bottom waters and pore waters are oversaturated with respect to calcium carbonates and calcium concentration decreases with depth. We can therefore only stress that the fluxes have been measured in situ with a benthic chamber enclosing 30x30 cm of sediment surface and should therefore be considered a robust measure of the benthic fluxes during the sampling period. These points will be highlighted in the revised discussion.

L. 325-326: What happened at station E that it is not mentioned here?

C16

Due to small variations in sulfate concentrations with depth at station E the variations with depth are of the same order of magnitude as the measuring uncertainties. As a result, sulfate to DIC or alkalinity ratios were not included in Table 3. The text will be modified to clarify this point in the revised manuscript.

L. 330-333: What's going on at station Z? There is clearly something different between the duplicate cores at 20-25 cm depth, as reflected in the DIC, TA and SO₄ data. Can you explain this deviating pattern in the duplicate core, and do you consider them reliable? (also given the extremely high value of Ω_{ca}) From which of both cores are the CH₄ data, can I rely on same symbols coming from the same core?

The values measured are reliable. The system is heterogenous and intra-station differences can be quite important. Yet the two profiles (short and long cores) for station A and Z match at some point at depth. Furthermore, the profiles measured at station A and Z are comparable with DIC, TA, and SO₄²⁻ profiles measured in other campaigns (e.g.: Rassmann et al., 2016; Pozzato et al., 2017). Despite the different shapes of the individual profiles, the DIC/TA and DIC/SO₄²⁻ ratios (and if we would look at them also the DIC/Ca ratios) are always the same. The CH₄ core was a different core and the symbols do not indicate that CH₄ was measured on the same core. This information will be provided in the revised manuscript.

C: Maybe identifying the SMTZ would be easier if only data from a single core are used.

The concentrations of dissolved methane were measured in another core than the concentrations of DIC, TA, and SO₄²⁻ for practical reasons, as it more efficient to use horizontal mini-cores at each depth in the sediment core to sample this insoluble gas (see methods). This information will be provided in the revised manuscript.

L. 375-377: How are these systems different or comparable from the study area? Would that explain their lower fluxes relative to this work?

C17

A first point to stress here, is that measurements of in situ TA fluxes across the sediment water interface in river dominated margins are still rare in the literature. In terms of freshwater discharge, the Rhône river (1700 m³/s) transports much more water than the Guadalquivir (160 m³/s), but is comparable with the Po (1500 m³/s). The Danube (8200 m³/s), the Fly river (6000-7000 m³/s) and the Mississippi (15,000-18,000 m³/s) transport even more water and particles. (Friedl et al., 1998; Hammond et al., 1999; Aller et al., 2008; Ferron et al., 2009; Lehrter et al., 2012). The Guadalquivir, the Po and the Rhône dominated margins are microtidal, mediterranean systems and bottom waters display comparable oxygen concentrations, temperatures and salinities. In contrast, the Fly river bottom waters are warmer and less saline and the Mississippi bottom waters experience seasonal hypoxia. The fluxes we compare have all been measured in water depth between 10-150 m. The sediments are either of cohesive nature or contain sandy layers. All systems are characterized by organic rich sediments and high respiration rates and are within the same range of Alkalinity fluxes. The only exception is the Po River delta for which the stations were located in the shelf zone (rather than the prodelta) and are closer in nature and Alkalinity flux to station E from this study (1-5 mmol m⁻² d⁻¹). A sentence will be added in the text to explain this point. The position of the stations in different studies cited here are partly further on the shelf and reflect the low TA fluxes as measured on the continental shelf near the Rhone River delta. This is mostly the case in A sentence will be added in the text to explain that.

L. 390-391: This statement can be sharpened. Coupled nitrification-denitrification does not produce TA in a net sense, so any net TA production from denitrification must come from riverine nitrate inputs. Can you use e.g. monitoring data to make an estimate about the importance of this?

In microtidal systems such that Rhône River delta, haline stratification is strong, such that riverine nitrate is confined in the surface river plume (e.g., 0.5 to 1 m, Many et al., 2018 PiO) where it is either diluted or consumed by phytoplankton growth. The marine origin of the bottom water is assessed by their salinity (37.5-38.0; Table 2) and their

C18

low nitrate concentrations (Bonin et al., 2002, *Wat. Res.* 36, 722-732). Furthermore, nitrate profiles presented in Pastor et al. (2011) all show an increase of concentration in the porewater indicating that the nitrate flux is directed from the sediment to the water column. Therefore, riverine nitrate does probably not influence denitrification observed in the proximal zone sediment as of the bottom waters. This explanation will be provided in the revised manuscript.

C: Also, do you have any information on nitrification rates in the sediment from earlier studies?

Unfortunately, no nitrification rates are available in the sediments for this area. Few data in the surface and bottom waters of the Rhône River mouth are available (see Bonin et al., 2002, *Wat. Res.* 36, 722-732). This paper will be cited in the revised manuscript.

L. 400-402: True, but as you already discuss later on, if dissimilatory iron reduction is coupled to FeS burial (or re-oxidation of Fe²⁺), its net efflux on alkalinity is zero. So the process definitely contributes to bulk alkalinity production, but that doesn't necessarily mean it is linked to either alkalinity effluxes or long-term net alkalinity release.

We agree with the reviewer that dissimilatory iron reduction contributes to alkalinity production (buildup in pore waters), but not necessarily to its efflux out of the sediment. Therefore, we called it "bulk TA production" in the original manuscript, to differentiate with the "net TA production" (the difference between bulk production and consumption). This information will be clarified in the revised manuscript. In turn, we disagree on the first part of the comment: FeS burial and Fe²⁺ reoxidation have opposite effects on TA efflux. Indeed, FeS burial generates an alkalinity efflux (this is the main point of this paper as displayed on Fig. 10, red arrows). In contrast, re-oxidation of Fe²⁺ consumes alkalinity at the oxic-anoxic boundary and may cancel the diffusion of alkalinity generated during iron oxide reduction out of the sediment. We feel that these differences are well presented in the manuscript and do not require further clarification.

C19

C: If I understand the Burdige and Komada method (L. 406-409) correctly, you already assume this by linking DIC and TA production solely to sulfate consumption. It'd be good to be explicit about this and state which processes are included in this method.

Burdige and Komada discuss how the rcs (DIC/SO₄²⁻ ratio) can be modified by other processes (methanogenesis, carbonate precipitation/dissolution) or by the fact, that organic matter is already partly oxidized when undergoing sulfate reduction. In this manuscript, we add another possibility for the modulation of rcs: the interaction with the iron cycle. Indeed, as shown in Table 1, this ratio (DIC/SO₄) may vary with the iron reaction pathways (from -2.25 to -1.8). This point will be clarified in the revised manuscript.

C: Also, I recently came across a paper (<https://doi.org/10.1016/j.marchem.2019.03.004>) that uses DIC and TA pore water profiles to quantify sulfate reduction rates. I don't know how their methods are applicable to your work but it might be interesting to include it.

In the cited paper, the shape of TA pore water profiles is used as a proxy for sulfate reduction rates in order to disentangle OSR (Organoclastic Sulfate Reduction) and AOM (Anaerobic Oxidation of Methane) which both consume sulfate. The authors use a reactive transport model and include the precipitation/dissolution of CaMgCO₃ to estimate sulfate reduction rates and contributions of the different pathways. Their approach is applied to long sediment cores where such processes develop over several meters (as opposed to our short sediment cores). In contrast to our paper, they do not have iron data, and they discuss the coupling with iron reduction and the precipitation of iron sulfide minerals on a purely theoretical level, which is different than our study. We agree it would be interesting to expand our research with a model study, but we think this should be the object of a different manuscript. This comment will not be addressed further in the revised manuscript.

L. 414-417: Any reason why AOM would be less important at stations A&Z compared

C20

to B? At first sight, the SO₄ and other profiles do not look too different from each other.

The reason for proposing that AOM is more significant at station B than at stations A and Z is based on the the low DIC/SO₄²⁻ ratio observed at station B (the lowest in the whole data set). Unfortunately, we do not have any pore water CH₄ data at this station. Station B is still located in the main deposition area of the river plume and receives more organic matter than station AK and K. Compared to station A and Z, station B is characterized by a deeper water depth and lower accumulation rates which may favor long-term stability and therefore development of AOM. As these statements were already speculative, we will likely not expand this discussion in the revised manuscript.

L. 424-425: Can you place this pH of 7.2 into context? Why is a minimum of 7.2 not a 'significant lowering'? (L.423)

pH minima between 7.2 and 7.4 were found just below the oxygen penetration depth in the sediments of all stations. The pH minimum at station A, Z and B was the same as the minimum at stations AK, K and E, where less sulfate was consumed in the sediments. We will modify the revised manuscript to put this information in the context of all the pH profiles collected.

L. 426-442: I spent quite some time looking at equations 12-17 and this method. First, I'd like to see how these equations are derived (e.g. eq. 12 combines eq. 6 and 9, 10). This helps checking them and also the derivation of the ratios. Second, if you look carefully at the equations, you'd see that they are all normalized to SO₄. Per mole SO₄ the changes in TA and (obviously) SO₄ are the same for all six reactions. So the differences in the presented ratios are solely due to the differences in DIC production. Of course this would be different if the equations were presented per mole HCO₃ (ratios would be the same, but the changes in TA, DIC and SO₄ would be different), but it shows that if you want to link S burial to alkalinity generation (as you do in L. 501-503), the exact pathway of iron sulfide mineral formation doesn't matter.

It is incorrect to state that "the exact pathway of iron sulfide mineral formation does

C21

not matter' as, in this manuscript, we relate alkalinity generation to FeS burial and not SO₄²⁻ consumption in the sediment. As can be established from equations 12 and 15, the TA/FeS production ratio can be $2/(2/3)=3$ in equation 12 and $2/1=2$ in equation 15. Hence, the exact pathway matters and we favor (see paper) the dissimilatory pathway for iron hydroxides with sulfate reduction and precipitation of FeS, hence a ratio of 2. Either way, when comparing measured to theoretical ratios, the method assumes that there is no other removal pathway of DIC (e.g. siderite formation, to name an option). Can this indeed be excluded?

The precipitation of iron and sulfide is extremely fast, likely much faster than precipitation of siderite (FeCO₃). Thus, we did not consider this or other pathways in our calculations. This information and the appropriate references supporting that statement will be added in the revised manuscript.

L. 448-452: It'd be nice to read about the possible pathways of organic-Fe(III) complex formation earlier in the manuscript

We recognize that this information could have been provided in the introduction. However, to focus the introduction on the role of carbon mineralization processes on alkalinity generation and avoid increasing the length of the manuscript we chose to not present any detailed biogeochemical pathways in the introduction. This comment will not be considered further in the revised manuscript.

L. 458-460: This statement is less vague than in the abstract, but it still raises questions. At what time scale do these alterations take place? Should I regard 'dominated by sulfate reduction' as the default state of the sediment, only periodically (episodically? seasonally?) replaced by 'dominated by iron oxide reduction' in periods of intense flooding and sediment deposition? Is FeS mineral formation limited by sulfide and if so, does that mean that the flooding periods overprint the default state?

The number of questions raised by the reviewer indicates that this sentence is misleading. Furthermore, the limited amount of information on temporal dynamics on this

C22

system regarding the redox state of the pore waters prevents a sound answer to these questions. We thus decided to change the sentence, keeping the dynamic nature of the system “these sediments are highly dynamic” but to remove the potential temporal succession “periods of intense sulfate reduction alternating with . . .” by “suggest these sediments are highly dynamic with concomitant intense sulfate reduction, microbial iron reduction and rapid FeS precipitation” which is a plausible explanation. Further work will be needed to elucidate these processes and their temporal succession. The abstract will also be modified in that direction.

L.478-481: So if I understand this correctly, it means that pIAPs are poor indicators of mineral formation, as they are highest at the site with least burial (station E). Does this mean that microenvironments play an important role in the formation of FeS? I'm also not sure if I understand what you mean to say by the argument of stronger aggregation of FeS (L. 483). If FeS is currently more aggregated, does that mean that FeS formation is not active now (given undersaturation and no FeSaq) but that it had been active in the recent past in a time when the sediments were sulfate-dominated instead of iron-dominated? (this links back to my previous comment). Or does it simply mean that FeS formation just take place in microniches where local conditions are different?

Mineral formation can be determined from the pIAP assuming the system is at equilibrium. At all stations besides station E, the pore waters were either undersaturated or near saturation with respect to FeS, even though the presence of significant FeS0 concentrations and removal of sulfide from pore waters indicated mineral formation. This disagreement with the calculated pIAP here indicates that the system was not at equilibrium and provides another piece of evidence for a highly dynamic system. As indicated earlier, to shorten the manuscript and not diluting the take-home message of the manuscript, the pIAP calculations will be moved to the supplementary material. Per line 483: the lack of FeS(aq) signals, but presence of high FeS0 concentrations (which pass through the rizon filters) suggests that that iron sulfide particles were already aggregated at the time of sampling. Again this points to a dynamic zone with iron

C23

sulfide precipitation dependent on organic and inorganic (i.e., Fe(III) oxides) inputs. As suspected by the reviewer, microniches, such as leave fragments in the proximal zone, have been shown to play a role in FeS/FeS2 formation (see Charles et al., 2014 and response to Reviewer 2 below). These may have changed local conditions or exacerbated FeS formation kinetics such that the system may appear undersaturated. This part of the comment will be addressed together with pIAP calculation in the supplementary material.

L. 493-495: This depends on the fate of the other products, i.e. what happens to the produced S0. But if you assume that the S0 will also be buried (or converted to FeS, which are both more likely options than reoxidation), the alkalinity release will always be 2 moles per mole S burial.

It is correct to state that 2 moles of TA will be released per mole S buried, but our interest is on the FeS form which was measured as AVS. In that respect, the ratio of net alkalinity flux to buried FeS will not be 2 (but 3 see above) if S0 is buried which would be the most probable option given the high sedimentation rate and the short residence time of the sediment layer near the sediment-water interface. In our case, we favor Eq. 15 (see explanation in text) and adopted a conservative ratio of 2.

L. 501-504: First, why don't you compare the AVS burial flux with the measured alkalinity flux of station A only, instead of combining A and Z?

The idea of this paper was to check if the conceptual link between FeS burial and alkalinity flux was substantiated by the flux values. Therefore, we tried to come up with order of magnitudes rather than attribute numbers to a single station. Furthermore, recent sedimentation rates were only available for the overall area but not for individual stations. We therefore chose to compare average alkalinity fluxes in the proximal zone and average FeS burial in the same zone. This information will be provided in the revised manuscript.

C: Second, a point that I am just realizing: with this very high burial rate, it'll take

C24

a long time before alkalinity produced in the sediment is diffused out. You'd expect that its transport is dominated by advection, not diffusion. So that would mean an even stronger decoupling between net TA generation in the sediment and measured effluxes. Or is there bioturbation that impacts the benthic release?

As pointed out above in response to a previous comment by the reviewer, the spring-summer diagenetic processes described in this paper are the result of the late fall deposition of flood layers and their maturation. The progressive buildup of alkalinity and DIC in pore waters begins during winter and is certainly accompanied by FeS precipitation as sulfate reduction and iron oxide reduction proceed. The net alkalinity flux produced is linked to the net precipitation of FeS, which represents the difference between precipitation and re-oxidation due to bioturbation 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 before below a new sediment layer of 10-30 cm, ensuring its preservation. 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 $D(\text{HCO}_3^-) = 6 \times 10^{-6} \text{ cm}^2/\text{s}$ see calculations provided earlier). In the first 5-10 centimeters, transport may be increased by bio-irrigation as can be observed in A and Z DIC/TA profiles which are concave. 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.

L. 526-529: I agree that microniches can be important, but do your Ca^{2+} porewater profiles give any indication of CaCO_3 dissolution at the top of the sediment?

In the sediment surface layer at station A and Z, Ca^{2+} concentrations either decrease (St.A) or remain constant with a further decrease deeper (St.Z), thus providing no sign of carbonate dissolution in the upper layers. Furthermore, with the uncertainty of 2-3 % as reported in the method section (line 191), it is difficult to detect minor changes of

C25

Ca^{2+} linked to small dissolution of carbonate. This evidence for low CaCO_3 dissolution from the data collected will be highlighted in the revised manuscript.

L. 534-539: Is FeS the dominant form of solid-phase S in the sediment, or is pyrite also present in substantial amounts?

Only FeS was measured in these sediments in a limited number of cores as these analyses take considerable time. Pyrite precipitation may probably explain the unaccounted TA flux from the FeS burial calculations, but given the residence time of the sediment layers in the Rhône River prodelta, pyrite precipitation most probably occurs after a few years, when the sediment is buried deep in the sediment. This discussion will be provided in the revised manuscript. L. 540-541: On what timescale do these processes take place? Under steady-state conditions I understand this figure, but given the highly variable sedimentation rate at especially the proximal sites, does it still apply under these dynamic conditions?

See comments above about the temporal variations. A couple of sentences explaining the time frame in which biogeochemical processes occur in these proximal sediments will be provided in the revised manuscript.

L. 545-547: but is Fe or S generally limiting FeS formation at the proximal sites?

As no or little sulfide was found in pore waters, it seems reasonable to assume that sulfide is the limiting element. This information will be provided in the revised manuscript.

L. 556-559: so at station E Fe is limiting FeS formation, what about the prodelta sites?

At Station E, the largest fraction of OM oxidation occurs via oxic and suboxic respiratory processes, and FeS concentrations are much lower than at the prodelta sites. Based on the high deposition rates observed in the prodelta, these sites receive increased iron inputs from the Rhône and are thus less likely to be iron limited. In turn, sulfide seems to be the limiting element at these sites. These facts will be emphasized in the revised manuscript.

C26

L. 574-576: but if the FeS burial sink is permanent, it definitely impacts water-column TA and carbonate system dynamics on the long term, as you also indicate on L.576-578 and L.601-604. I think this statement unnecessarily weakens the relevance of your manuscript.

We agree with the reviewer that “ [The TA source] definitely impacts water-column TA and carbonate system dynamics on the long term”, but the sentence line 574 still holds as the sediments release more DIC than TA and thus contribute to increasing pCO₂ of bottom waters rather than decreasing. In turn, this increase of pCO₂ is weaker due to the concomitant TA release compared to what it would be if only DIC is released. Hence, it is crucial to determine the TA sources from anaerobic sediments. This sentence will be modified slightly to emphasize these points.

Fig. 9: What if TA data were used for this calculation? I agree though that using DIC is wiser given the possible presence of organic alkalinity.

For these calculations, it is not possible to use the alkalinity profile as its shape near the SWI (at the centimeter scale) is unknown and probably very different from the DIC profile, as it is likely affected by the eventual reoxidation of reduced species (Fe²⁺, Mn²⁺, NH₄⁺, HS⁻) which consume TA. In this paper, we conclude that a major fraction of these reduced species is buried within the anaerobic sediment layers, but some may still be oxidized and thus consume TA in the first mm of the sediment. Although uncertain, the assumption of a linear DIC profile is reasonable but already questionable and represents the best option given the potential variations in the TA profiles. Given this argument, this comment will not be considered further in the revised manuscript.

Technical corrections: Unless addressed specifically below, we agree with all the technical corrections provided below, and these comments will be incorporated in the revised manuscript.

L. 3-6: This sentence is too complex. OC respiration in sediment or water column? I'd suggest to rewrite and / or split it in two sentences. L. 31-33: Ambiguous sentence.

C27

Does “of which about half is buried” refer to total oceanic POC or the 40% that is buried in shelf regions? L. 56: typo in ‘anaerobic’ L. 77: replace ‘sediments’ with ‘suspended matter’ or ‘particles’ L. 98: “These”. All sediments or those in the proximal region only? L. 127-130 and various other sections in the manuscript (basically everywhere where equations are presented): add units to the variables you discuss here (i.e. Fi, H, Ci, etc). L. 235-239: This sentence is too complex. Please split into two or rephrase. L. 242: Add scale and temperature to pH. L. 244: For which salinity are these numbers valid? Result section: may be shortened L. 288: change to “the absolute value of the DOU fluxes” or equivalent as they have opposing signs. L. 306: ‘station’ instead of ‘stations’ L. 522: seacarb is written without capitals. Figures: Add units to the captions. Fig. 1: Add the depth to the last (lowest) line of the bathymetry. Fig. 2: Use different lines (e.g. solid and dotted) for O₂ and pH. Printed in black & white the figure is currently very difficult to read. Fig. 3: Could be moved to an online supplement. Add what the difference between the red and black symbols means. The error bars complicate reading of the symbols a bit, but I appreciate that they're in.

The red symbols were used involuntarily in this figure and will be converted to black symbols in the revised version. The figure will be moved into the supplemental material section to decrease the length of the manuscript.

Fig. 4: I'd only plot the error bars outwards, this makes the bar plot better readable and the error bar is not visible in the black bars anyway. Fig. 5: Make it clear which measurements are from the duplicate core by using the same symbols for DIC, TA and SO₄, and make them clearly different from the main core data. Fig. 6: Add a (dashed) line at $\Omega_{ca}=1$. Also, the DIC data are poorly visible as they are mostly hidden behind the TA data. I'd leave it like this only if the point you're trying to make is that they are so similar. Fig. 7: I'd suggest not splitting the axes into two domains, given the small jump on both axes it complicates more than that it helps reading. Fig. 11: “as a function of water depth”. Add the source of the North Sea data (Brenner et al.?). Hu & Cai (2013) is not in the list of references. Table 1: Be

C28

consistent with sulfate and SO₄ in the caption. I think that in equation (5) it should read -1/5 H⁺ (instead of -2/5). Show how you derived equations (12) to (17), see earlier comment. Table 2: Add the depth interval over which mean porosity was calculated.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-32/bg-2019-32-AC1-supplement.pdf>

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

C29

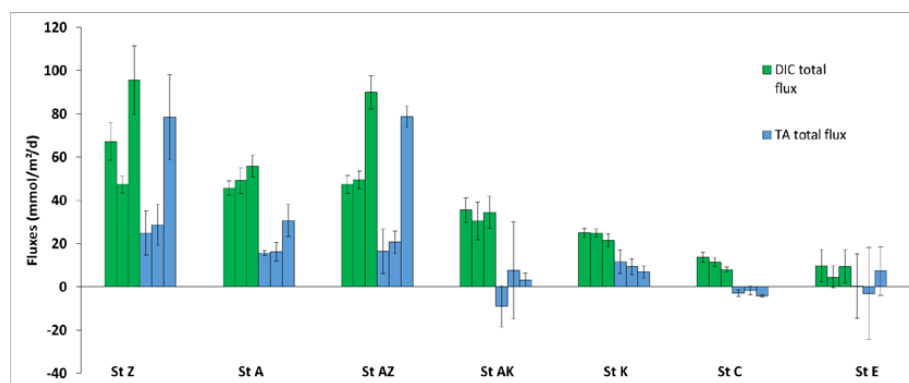


Figure AC1 : DIC and TA fluxes measured on cores in the Rhone Prodelta and shelf in May 2011

C30

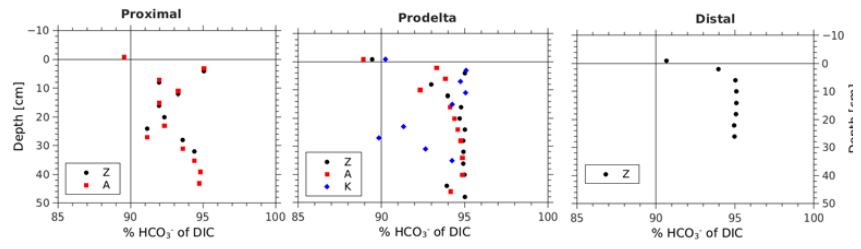


Fig. AC2 : proportion of HCO_3^- in DIC during the Amor-BFlux cruise in 2015