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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.

Anonymous Referee #1

Received and published: 28 March 2019

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 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 ap-

preciate 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. 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 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? 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.

The discussion on identification of major biogeochemical processes remains rather 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. Irrespective of the decision on the manuscript I hope that the following comments will help you further shape it.

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? 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? What do you mean by inorganic? Does it refer to iron oxides? 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 especially relevant in systems with a (periodically) very high sedimentation rate (see further comments below). L. 62-65: Again, this is scale-dependent and only if re-oxidation of reduced constituents does not quickly occur in the water column. 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. 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? L. 91: What about temporal variability in sedimentation rate in the prodelta? L. 106: Can you include a range of how far above the sea floor samples were approximately taken? 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. L. 108-110: At what temperature are the pH data presented, in situ or 25 degrees? Please add. L. 114: What are the 'main redox species'? Specify. In the results only DIC and TA lander data are presented. L. 119: Which redox chemical species? Specify, this is too vague. L. 124-125: Which method is used for measuring DIC and TA? Same as in section 2.6? If so, refer to it. 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? L. 144: How many cores were taken per station? I counted 3: 1 for porosity, 1 for voltammetry, 1 for pore water and

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sediment sampling. Correct? L. 158: Why is S0 mentioned as part of total dissolved sulfide? 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? L. 173-174: What was the sample volume used for alkalinity titrations? L. 177-178: Did you make any replicate measurements? L. 199-200: How was the sediment extracted? Slicing and centrifuging? More details would be appreciated. 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? L. 212-217: Has any particular software been used for the saturation calculations? 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? L. 247-254: This method applies if there are no other fates of Ca2+ aside from precipitation or dissolution of CaCO3. Can you add a sentence acknowledging this? 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? L. 325-326: What happened at station E that it is not mentioned here? 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 Ωca) From which of both cores are the CH4 data, can I rely on same symbols coming from the same core? Maybe identifying the SMTZ would be easier if only data from a single core are used. L. 375-377: How are these systems different or comparable from the study area? Would

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that explain their lower fluxes relative to this work? 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? Also, do you have any information on nitrification rates in the sediment from earlier studies? 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. 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. 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. L. 414-417: Any reason why AOM would be less important at stations A&Z compared to B? At first sight, the SO4 and other profiles do not look too different from each other. 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) 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. 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? L. 448-452: It'd be nice to read about the possible pathways of organic-Fe(III) complex formation earlier in the 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? 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? 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. 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? Second, a point that I am just realizing: with this very high burial rate, it'll take 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? L. 526-529: I agree that microniches can be important, but do your Ca2+ porewater profiles give any indication of CaCO3

dissolution at the top of the sediment? L. 534-539: Is FeS the dominant form of solid-phase S in the sediment, or is pyrite also present in substantial amounts? 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? L. 545-547: but is Fe or S generally limiting FeS formation at the proximal sites? L. 556-559: so at station E Fe is limiting FeS formation, what about the prodelta sites? 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. 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.

Technical corrections: 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. 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. F_i, H, C_i, 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. 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 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.