

Comments on Coupling and decoupling of DIC, TA and O₂ benthic fluxes along the Rhône River-dominated ocean margin. by Ferreira et al.

This manuscript presents the results of a field investigation where benthic fluxes of TA, DIC, and O₂ were measured in ex situ flux incubations during May-June of 2018 and 2022. The benthic fluxes are studied as a function of the distance from the Rhône River mouth represented by three different regions that were characterized by a gradient of organic matter input in previous studies. The data presented in this paper will be a valuable addition to the current literature, as field data on natural TA production is sorely needed given the current push for ocean alkalinity enhancement. The simultaneous measurement of TA, DIC, and O₂ fluxes along a continuous, offshore gradient (proximal domain, prodeltaic domain, and distal shelf) is a novel and complementary addition to the extensive work on the Rhone Delta. This work will have a major contribution to our understanding of TA production in the coastal ocean.

While the data is of high quality, the authors have not demonstrated the same rigor when it comes to the data analysis and interpretation. The manuscript suffers from inconsistent terminology and the authors have been a bit careless with their calculations (unbalanced stoichiometry and unconstrained mass budgets). The discussion is also very superficial, and would benefit from a more quantitative description of the biogeochemical processes discussed. We have indicated where we think there are errors in the assumptions and calculation and also provided suggestions where the discussion can go more in depth below. Inclusion of broader context could also be useful (what can we learn from the observed trends? What does that mean for ocean alkalinity budgets? Potential changes/feedbacks in past or future oceans, human interactions?). There have been some recent high-level publications (Middelburg et al., 2020: global alkalinity budget, Goossens et al., 2026: shelf CaCO₃ budget, van de Velde et al., 2026: fast climate feedbacks to anthropogenic CO₂ emissions, van de Velde et al., 2025: bottom

trawling and alkalinity generation, Bach, 2024: OAE and sediment alkalinity additionality) that could be used for putting your results into context.

These limitations should not prevent the manuscript to be published, and we fully support the publication of this MS after revisions.

Kind regards

Sebastiaan van de Velde

Tom Huysmans

Detailed comments:

General: If you use TOU but then plot negative, you get negative uptake, which is efflux. I would either use TOU and then give a positive value, or say oxygen flux and give the negative value.

The text would also benefit from more consistency in the use of the abbreviations for the fluxes (F_{DIC} (as stated in the M&M) – DIC flux – DIC_{flux} – benthic DIC flux and the same for O_2 and TA) and terminology (e.g. prodeltaic domain vs prodelta)

L9: high input of POC leads to benthic mineralization and burial -> I would rephrase it so it reads more logical

Materials and methods

L90 & 93: In the text station L is referred to as one of the prodeltaic stations but in Fig. 1 AK, K, and B are shown in the prodeltaic domain.

L123-124: Restructure the sentence to make it grammatically correct.

L139: What was the quality control that has been performed?

L143: Add a sentence on the different parameters in the equation and their units.

L151-154: Rephrase this sentence as the stated processes do not all lead to net production of alkalinity but rather have an influence of the net alkalinity flux.

Table 2: Rassmann et al., 2020 is not the best reference for the different reaction that can lead to FeS. We would recommend Pyzik & Sommer (1981) and Rickard & Luther (2007).

Pyzik & Sommer (1981): [10.1016/0016-7037\(81\)90042-9](https://doi.org/10.1016/0016-7037(81)90042-9)

Rickard & Luther (2007): <https://doi.org/10.1021/cr0503658>

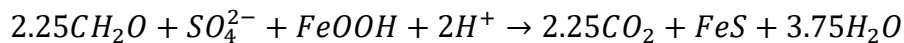
The organic matter is presented in the Redfield ratio ((CH₂O)₁₀₆(NH₃)₁₆; C/N = 106/16) which is most representative of marine phytoplankton. However previous studies in the Rhone delta have shown that the organic matter deposited in this area is of mainly terrestrial origine. Wouldn't it be more correct to use C/N ratio more closely to that of the local sediment?

It would probably make more sense to write each reaction in 'alkalinity-neutral' terms, except for OH⁻ or H⁺, as this would make it much easier to immediately spot the TA and DIC for the reader (and yourself). For example, write NH₄⁺ as NH₃ and HCO₃⁻ as CO₂.

It seems that the stoichiometry for some of those reaction does not add up. In the CaCO₃ reaction you should have 1 H₂O instead of 16. For the first reaction in the FeS precipitation and burial section you have 401.3 H on the left side and 399.7 H on the right, and the O's are also not correct.

I also do not follow the statement: 'FeS precipitation can arise following different pathways and lead to variable ratio of TA production to FeS burial.' That only makes sense if you are creating a TA loss or gain somewhere else, but from a mass balance perspective it cannot be. The way you are writing your reactions you are also creating elemental sulfur (S₀), but that is not a stable phase and will react further (either into FeS₂ or disproportionate into SO₄ and

H₂S) and affect that TA balance. You can make your life much easier by assuming that you are only generating FeS, and write the reaction as (ignoring ammonium for the moment)

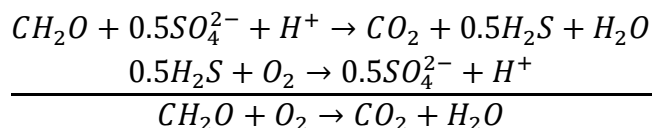


And here you directly see that you create 2 mole TA (by consuming H⁺) per mole of FeS.

It would also be informative to give some explanation why you stop at FeS and not complete the reaction to FeS₂ (which gives the same results but is the end member of the reaction and is more stable). Gagnon et al. (1995) could be a good reference to build your case for using FeS instead of FeS₂ under conditions in the Rhone delta.

Gagnon et al. (1995): [10.1016/0016-7037\(95\)00163-T](https://doi.org/10.1016/0016-7037(95)00163-T)

L164: if you have CaCO₃ precipitation it will lead to DIC removal, so that calculation does not work. Also, it is not only aerobic mineralization that matters, but the mass balance – anaerobic mineralization will create reduced species and TA, but when they reoxidize they will consume the TA again and the net effect will be the effect of aerobic mineralization (you say this in L310) – for example with H₂S;

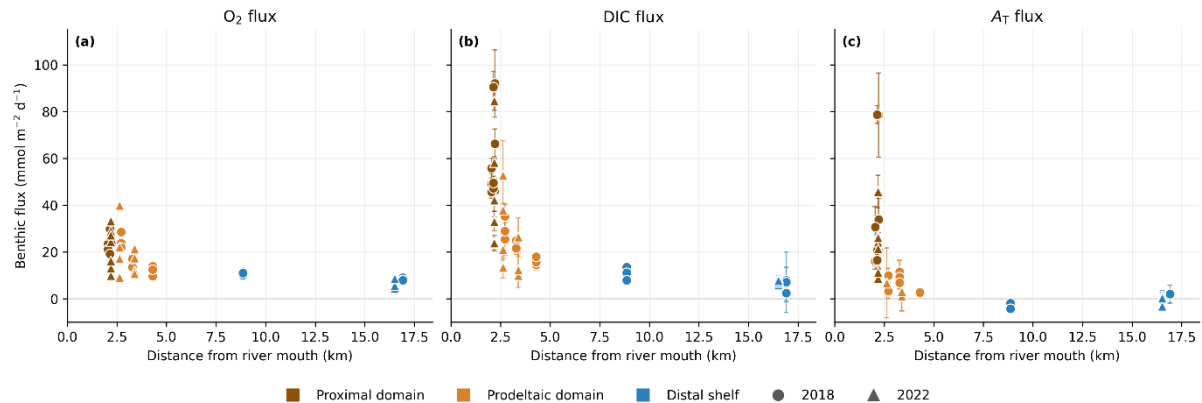


So it is the total oxygen consumption that you should use to calculate the contribution to TA, not the modelled aerobic mineralization rate.

L166: see above, that ratio is likely incorrect

Results

L181-182 & Figure 3: Figure 3 would be more informative if it would be plotted as stated here, showing the different fluxes in function of the distance to the river mouth instead of as bar plots per station (see example graph).



L183: Previously in the material and methods and equation 1 F_i was used for the fluxes of the different solutes. Here (and further in the text), DIC_{flux} is used instead F_{DIC} . Be consistent in the use of abbreviation in the text and figures.

L185-195: Make it clear that you compare **average** fluxes per domain especially as there is a significant heterogeneity within each domain.

L189: I would not use ‘intense’ for a flux – it is a high flux, you could say intense biogeochemical cycling - same throughout the MS

L204 – 206: Would the large bottom water temperature not also have influenced the rates at the two different sampling times?

L212 – 215: Which statistical test were performed? Only Mann Whitney tests? Why only look at the difference between the zones and not look at the direct relationship between the fluxes and the distance to the river mouth?

L224-226: Is the difference in DIC flux:TOU in the prodeltaic domain related to the distance from the river mouth or is this only due to strong heterogeneity between cores?

Figure 4: The slope is not supposed to be 1 if you take into account nitrification but 0.77 if you assume Redfield ratio or higher if the C/N ratio increases. The figure could also benefit from a legend.

Figure 5: Plotting it like this might give a false image – because you plot the relations anchored to 0, it looks like the carbonate dissolution relation is way off. However, to have carbonate dissolution to happen in sediment, you first need DIC production from aerobic respiration. You would thus expect the fluxes to fall on the 0.15 line when they are low, and then gradually to shift towards carbonate dissolution (but never completely, as the fluxes are driven by a combination of processes). So, what you really should look for is which TA-DIC pairs move along the 2:1 or 0.15 vectors, not those relations anchored to zero. It makes more sense to plot a free-standing set of vectors indicating the carbonate dissolution relation in the corner somewhere.

We would also include a relation if OM mineralization coupled to FeS precipitation is the cause of TA production.

Discussion

L258-259: We would suggest adding the uncertainty to these numbers as well (e.g. 36 ± 24 to $53 \pm 10 \text{ mmol m}^2 \text{ d}^{-1}$).

L260: Show also the range in TA fluxes in the proximal domain, not only the highest value as you compare it to the ranges from previous studies.

L264: This is not clearly visible in how you present figure 3 at the moment. It would be beneficial to really show the fluxes in function of the distance to the river mouth.

L308-310: During aerobic mineralization, O_2 is not exactly consumed at equivalent molar rates than DIC is produced. This ratio depends on the respiratory quotient (RQ; see Jorgensen et al. 2022). For purely aerobic mineralization (direct aerobic mineralization and oxidation of reduced compounds) this depends mainly on the C/N ratio of the organic matter. For example,

assuming Redfield ratio this would be 0.77 DIC per O₂ assuming full nitrification of ammonia. If the C/N ratio increase the RQ increases as well. In Jorgensen et al. (2022), they assume a RQ of 0.9 for the inner shelf.

Jorgensen et al. (2022): [10.1016/j.earscirev.2022.103987](https://doi.org/10.1016/j.earscirev.2022.103987)

Figure 7: We recommend to add uncertainties on your estimated fluxes per process.

L395-396: Be more specific than “very limited number of fluxes”. State clearly that they measured in situ benthic fluxes of two station (A and Z) in the proximal domain and one (E) on the distal shelf. Comparing this to your dataset which covers the three domains and measures TOU, DIC, and TA together is the real strength and novelty of this paper.

L404-406: Wouldn't it be more informative to link this the transition to the sediment input from the Rhone river than state threshold of DIC flux?

L411: I find it puzzling that CaCO₃ does not dissolve in your shelf sediments. We recently reviewed CaCO₃ dissolution in shelf sediments (<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2025GB008936>), and most sediments would support dissolution. What is limiting it? That would be an interesting question to address here, as CaCO₃ is an important TA source from sediments, and seems completely absent here.