

Interactive comment on “Carbon degradation in agricultural soils flooded with seawater after managed coastal realignment” by Kamilla S. Sjøgaard et al.

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Dear Editor and co-Authors,

I was happy to have a chance to read this manuscript that provides interesting data about coastal soils that are about to be flooded by seawater under sea level rise. I intended to give constructive comments and suggestions and apologize if some comments seem too harsh, my stylistic skills are quite limited in English.

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Overall comments:

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The study depicted and discussed in the present manuscript represents considerable experimental and analytical work that deserves to be published. In my opinion, the most interesting feature is the almost total replacement of iron oxides by iron sulphides after one year of incubation of a soil with seawater. Such rapid mineralogical transformation suggests rapid anaerobic mineralisation processes that affect the carbonate system and carbon recycling that should be less efficient since the soil tends to become anoxic due to sulfate reduction. Therefore, author main hypothesis is that it should represent a significant negative feedback on atmospheric CO₂ concentrations. There is a major objection to such statement due to the lack of elements of comparison. The authors do not show any mineralisation rate of soils before seawater flooding.

Returning to the mineralogical transformation (i.e. iron oxides turned into iron sulphides), nothing is said about potential release of phosphorus and eutrophication that should also have as important feedback even more important to atmospheric CO₂. Samples exist, I would suggest to analyse P and address its remobilisation.

The considerable amount of data should permit authors to make a temporal mass balance in order to better precise the relative importance of anaerobic respiration processes and secondary reactions that limit reduced iron and free sulphide diffusion within the sediment and toward the soil water interface.

A secondary point but still important is a better discussion about HCl extractions and iron speciation. There is an extensive literature about selectivity of phases extracted by HCl, dithionite and ascorbic acid that should be considered here (e.g. Kotska and Luther, GCA, 1994; Hyacinthe et al., GCA, 2006).

Then, a quick discussion about the limitations of ex situ long term incubations that cut down hydrosedimentary processes should be addressed.

Summarizing, I recommend a major revision of the manuscript by stepping down on conclusions about carbon preservation and atmospheric CO₂ feedback and by examining in more detail the importance of iron cycling.

C2

Abstract:

Should be rewritten in a new version of the manuscript

Introduction:

L64-68 advection processes induced by tidal currents in such porous environment with higher level of connectivity between pores and burrows is not considered here

L83-88 check on in situ experiments by Yucel and Lebris about lignin degradation

Materials and methods:

L152 were cores sliced, centrifuged and conditioned under nitrogen flux?

L162-163 was chloride analysed as well? As a conservative species, chloride is necessary to evaluate sulfate consumption from sulfate profiles in environments of variable salinity. This could refine SR calculations from bulk incubated sediment.

Results

L265-283 Difficult to use TCO₂ data since they are potentially compromised. I always recommend to analyse TCO₂ or alkalinity as soon as the sample was extracted from the core slice to avoid such disagreement. At this point those data seem invalid for publication.

L284-291 The authors mention that incubation time is too short to achieve full saturation over the entire core. I would agree with that and this can be quite well predicted using diffusive models. For instance the Einstein equation ($x = (Dt)^{1/2}$, Boudreau, 1996) suggest that in 12 month a molecule of sulfate would diffuse in free water at 20°C of about 12 cm ($D = 5 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, Krom and Berner, 1980). For one week, diffusion allow sulfate to travel only 2 cm. This would suggest that not only diffusion can explain sulfate data and that during pouring of marine water most of it flowed downward through burrows or gaps in the soil. In order to avoid transport processes and to show sulfate consumption from profiles in variable salinity you could, as mentioned

C3

above, to normalise sulfate by chloride: a decrease of the ratio would indicate sulfate consumption that could be quantified in terms of rate to be compared to SR calculated from anoxic incubations. From IC spectra you should be able to retrieve chloride concentrations at least for low salinity samples. I am afraid samples at the higher salinity have to be diluted and reanalysed. . .

L327-328 add a reference for the SRx2 conversion. Do you achieve a ratio of 2:1 in measured samples? Plotting both measurements should give a nice line with a slope of 2. What about methane oxidation affecting sulfate consumption (1:1 ratio)?

L405-407 You suggest other processes than sulfate reduction to explain carbon mineralisation. You should consider more carefully iron reduction. Data are there to show how important this process is in your soils. This can flaw your main hypothesis that SR is the main mineralisation process going on in your soils after marine water flooding. In a recent study our team showed in intertidal estuarine mudflats that iron reduction remains a major process among sulfate reduction whatever the salinity due to regular replenishment of iron rich particles from the river (Thibault de Chanvalon et al, JSR, 2016). This points out the fact that such long term incubation experiments have somehow to take into account hydrosedimentary processes that can greatly affect organic matter mineralisation.

Discussion

L448-449 Have a look into in situ experiments of wood degradation in marine waters realised by Nadine Lebris team in the Mediterranean (e.g. Yucel et al, Chemosphere, 2013).

L470 The authors claim that SR accounted up to 100% of TCO₂ production. How they explain dissolved iron profiles that still show an effective source of reduced iron that should account for a significant part of anaerobic mineralisation processes.

478-481 there is a bias in the statement since it is made from anaerobic incubations.

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Data show the important sulfate reduction occurs near the surface, station UC and is about to be near zero in the other station. What about sulfate reduction if oxygen still diffuses from the surface? You could assess such question looking at porewater profiles. I would be glad to see TCO₂ time series and how they fit to linear regressions. Maybe there you can find clues about the relative importance of other mineralisation processes than SR.

L494-495 this final statement underlines the importance of having robust CO₂ consumption rates: if the sum of iron and sulfate reduction does not achieve mass balance, it becomes to consider other reducing processes for iron in a way and other mineralisation processes in the other

So far, my concerns seem to suggest that a tentative of achievement of mass balance calculation for C, S and Fe could greatly help interpretations. This could be possible from solid phase speciation and dissolved iron, CO₂ and sulfate profiles

502-504 not a sink, at most a zero source. The whole paragraph lacks of evidence. Especially that there are no unflooded cores as reference.

Section 4.4. could be developed by discussing in more detail the switch from Fe^{III} to Fe^{II} of the solid phase. It would benefit of mass balance calculations as well. Is there any chance of adding some mineral images or analyses? It would be interesting to look at the crystallinity of iron sulphide minerals formed during the experiment. In marine sediment framboidal pyrite is formed. I wonder what would be the impact of refractory organic matter on pyrite formation.

Conclusion

Conclusions should be re-drawn according to discussion's evolution.

Figures

Figures 3 and 4: I would suggest a change in colours for different profiles overtime. The grey scale print is very difficult to read. It would be perfect if colours and grey

C5

scale evolve progressively with time and with more contrast.

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