

Dear editor,

We would like to thank the first referee for his/her clearly positive and encouraging opinions to help us improve our manuscript. We replied to the comments of referee#1 in detail point by point and explained how we have modified the manuscript for publication in Biogeosciences. Referee's comments are shown in black and our responses are shown in blue.

Anonymous Referee #1

«Overall comments» In general, I feel positive about the overall contribution of the paper. The topic is interesting and relevant to the goal of Biogeosciences. The approaches that the authors adopted are interdisciplinary and provide educative information to this topic. The data and interpretation are mostly convincing with several points that I request for further clarification (see comments below). The authors need to improve the presentation a lot as figure 2 is hard to read, some of the references cited are out of date, a few sentences are quite awkward to read, and Table 2 needs more polishing. I've included my detail suggestions for these technical issues in the pdf file. Despite these minor flaws, I strongly encourage to publish this paper after all of my concerns are addressed.

«Detail comments» My major concerns about the paper are as follow: for analytical and model approach-

1) In quite a few of samples, the sulfate concentrations are over seawater value (28mM). The authors explained this as dissolution of anhydrite. The alternative explanation will be re-oxidation of hydrogen sulfide in the porewater samples after they were collected. In the sampling procedure the authors described, I do not see any description such as flushing the porewater samples with N₂ gas or fixing sulfide with Zn(OAc)₂ solution to get rid of sulfide. Some clarification about how this is of concern should be addressed.

Response:

All of the samples were processed inside an anaerobic glove bag with N₂ atmosphere. We added this information to the paper.

2) The authors modeled the system for 1 Myr to reach steady state. I wonder if this is a reasonable assumption to make in this case? From the high sedimentation rate (0.25- 0.35 cm/yr) of these cores, the age of the sediments investigated is not older than several years. Besides, this environment must be very dynamic with episodic input of water from different sources, bioturbation, and even sediment reworking. Why not simulate the system only to their real age, say 1-5 years? I believe this will significantly impact the results.

Response:

Yes, it's true that this is a very dynamic study area. Below in Fig R1 we show the example of modeling with 1 yr and 5 yr simulations for core 1CEL_Oct01. The results are the same as the 1 Myr simulations which means this dataset has reached steady state within 1 yr and using longer time scales does not make a difference. The large simulation time of 1 Myr, was used to ensure

that the results for all cores are under steady state. We now show the data using 5 years as the time needed for steady state and changed the text and figures accordingly.

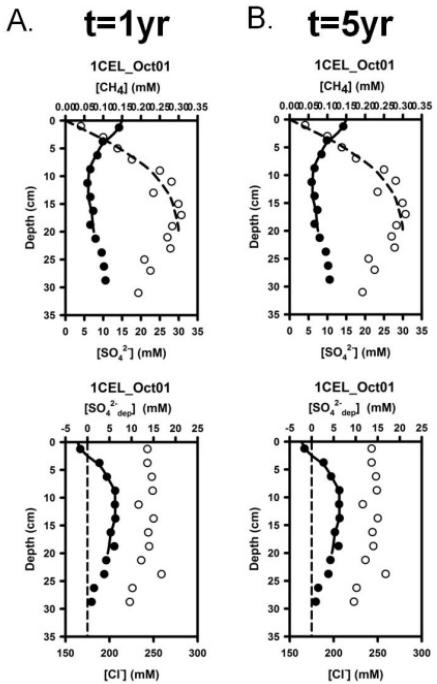


Fig. R1: Depth profiles for modeled (lines) and measured/calculated (symbols) concentration of dissolved methane (dashed line; open circle), sulfate (solid line; solid circle) in the upper panel and sulfate depletion (solid line; solid circle), zero sulfate depletion (dashed line) and chloride (open circle) in the lower panel for core 1CEL_Oct01 for: (A) 1yr and (B) 5yr simulation times.

3) I find it difficult to understand the reactions described in the appendix:
a. Page17931, line20-22: "Since AOM may play a minor role in the methane and sulfate rich sediment and RAOM was included in the net reaction rates of methane and sulfate this is justified." I don't understand at all what does this sentence mean. AOM should play an important role when you have abundant methane and sulfate isn't? What is justified? By what?

Response:

In the reaction stoichiometry, sulfate and methane are both consumed by AOM. In many of our sites, especially cores in group-1 and group-2, we can see methane production along with sulfate loss so this is not consistent with AOM (see Figure R2 below).

Based on our data it is impossible to know what proportion of sulfate loss is from organoclastic sulfate reduction and what is from AOM. However, since we can see methane production along with sulfate reduction in many of our sites especially cores in group-1 and group-2, we use the

rate derived from $[\text{SO}_4^{2-}_{\text{dep}}] > 0$ profile to represent the rate of organoclastic sulfate reduction (R_{SR}). AOM is still included in the simulations of methane and sulfate profiles (Table A2 in the manuscript) but modeling results in this study also show that AOM plays a minor role in sulfate reduction compared with the organoclastic sulfate reduction (Table 2 in the manuscript).

We include this discussion in the manuscript.

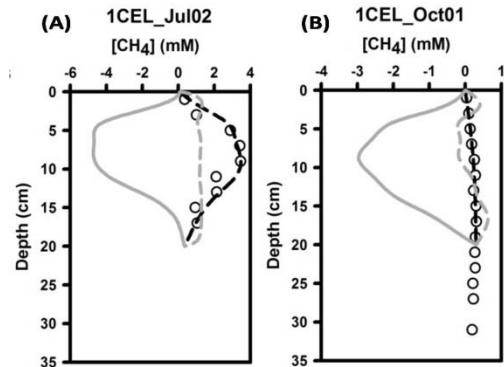


Fig. R2: Sensitivity of methane concentrations for cores 1CEL_Jul02 and 1CEL_Oct01 to the AOM process. (A) $R_{\text{SD}} = R_{\text{AOM}}$ and $R_{\text{CH}_4} = -R_{\text{AOM}}$ (gray solid line) and $R_{\text{CH}_4} = -R_{\text{AOM}} + R_{\text{MB}}$ (gray dashed line; $k_{\text{MB}} = 2000 \text{ yr}^{-1}$), (B) $R_{\text{SD}} = R_{\text{AOM}}$ and $R_{\text{CH}_4} = -R_{\text{AOM}} + R_{\text{MB}}$ (gray solid line; $k_{\text{MB}} = 0.6 \text{ yr}^{-1}$) and $R_{\text{CH}_4} = -R_{\text{AOM}} + R_{\text{MB}}$ (gray dashed line; $k_{\text{MB}} = 25 \text{ yr}^{-1}$). Black dashed curves denote the standard simulation results

b. Eq. A6: so you exclude entirely AOM when $\text{SO}_4\text{-dep}$ is positive? I thought $\text{SO}_4\text{-dep} > 0$ means active removal of sulfate? Not by AOM?

Response:

We use the rate derived from $[\text{SO}_4^{2-}_{\text{dep}}]$ profile to represent the rate of organoclastic sulfate reduction (R_{SR}). AOM is still included in the simulations of methane and sulfate profiles (Table A2 in the manuscript). Please also see the response to comment 3).

d. Eq. A7: I understand you related R_{poc} to R_{sr} assuming all sulfate reduction is organoclastically. Again, is this a good assumption? What's the role of AOM in sulfate reduction? I think you are right that organoclastic SR is important here but you need to explain this better.

Response:

We added a table (Table 3) in the manuscript which shows that maximum AOM rate is four orders of magnitude lower than organoclastic sulfate reduction in sulfate and methane rich sediments. Please also see the response to comment 3).

e. Eq. A12: How does R_{organic} different from R_{POC} ? How does the comparison of these two rates like? From table 2, I see them can be orders of magnitude different (e.g. 1CH_Dec00). Why?

Response:

R_{POC} is organic matter degradation rate calculated from positive sulfate depletion concentration $[\text{SO}_4^{2-}_{\text{dep}}]$ (Eq. A7 in the manuscript). R_{Organic} is the accumulation/consumption rates calculated based on the measured organic matter contents (Eq. A12 in the manuscript). Therefore R_{POC} is not the same as R_{Organic} . Since the measured organic matter contents increase with depth, we obtained accumulation rates (negative values) here. The measured organic matter contents might contain high amount of refractory carbon. R_{POC} represents the degradation rates of labile organic matter carbon pool which has been utilized through organoclastic sulfate reduction and methanogenesis. The labile organic carbon pool may be no longer present in the sediment or exist in the form of dissolved organic matter which was not considered or measured in this study.

This is stated more clearly in the revised manuscript.

4) Refer back to my comment (2), time scale of your model is really important. It determines the scale of your kinetic constants. For example, you use 0.01 1/yr for your k_{org} . It may be a lot different if you only run the model for 5 years and. for scientific interpretation/discussion- I think the experiment and model results support most of the interpretation by the authors. I however feel that the authors should extend the discussion a bit more from the following prospects:
1) Maybe my biggest concern for the paper is the assumption of steady state. The authors should provide good reasons why they think this assumption is adequate as the system is so dynamic.

Response:

Please see the response to comment (2). We are now modeling the profiles using 5 years for steady state. We use a steady state model because we do not have enough data to formulate such a model. Unless we have continuous monitoring of porewater sulfate, methane and chloride concentrations to know the temporal changes in sulfate depletion profile $[\text{SO}_4^{2-}_{\text{dep}}]$ and its built up at each time steps, we cannot discuss the biogeochemical reactions between sulfate and methane under non-steady state. Here we apply steady state approaches to understand the maximum amount of methane that can be produced through methanogenesis at each core. We have another manuscript submitted to L&O which focuses on the fluxes from pore waters to the atmosphere in which we discuss the possibility of a non-steady state situation. We do not refer to this paper because it is still under revision but we will include that if/when it is accepted.

2) The authors presented tremendous amount of temporal/spatial porewater data in this paper but did not spend much effort in discussing these. The groping of data is based on the shape of profiles and thus their dominate reactions. Do these groups correspond to any particular location or season that might explain the such dominance in terms of biogeochemistry?

Response:

There is no relation between profile time and location or season and the variability is a result of the system being dynamic and us capturing snap shots of temporally diverse conditions. As noted above we discuss this in another manuscript which we will refer to once we know the status of the submission. If it is OK with the journal we can refer to the publication as Chuang et al., 2016 as we expect that it will be published in 2016.

3) Results from incubation experiments are one of the highlights in this paper but the authors only mentioned it briefly in 5.1 section. I wonder are the authors able to derive some rates from the experiments that can be compared with the rates estimated by modeling. Also, how do all these rates compared to other similar environments? I feel like the authors should put their results in a larger global context to reveal the significance of their data.

Response:

Yes, we are able to derive some rates from the experiments which have been added to Table 1 in the manuscript. An additional table (Table 3) includes rates estimated by modeling which can be used to compare with the rates from the experiments.

The maximum methane production rates listed in Table 1 from TMA, methanol and H₂ treatments are higher than the methane production rates from coastal freshwater and brackish wetland sediments which were measured using radiolabeled acetate and bicarbonate in slurries and reported in Segarra et al. (2013).

In addition to depth-integrated rates, Table 3 listed model derived maximum methanogenesis (Max-RM), sulfate reduction and AOM rates. Maximum methane production rates estimated from TMA, methanol and H₂ treatments of sediment slurry incubations (Table 1) are similar to values reported by model derived Max-RM at station 16CEL (Table 3) the site from which sediments were collected for sediment slurry incubations. Max-RM in some cores can reach to 1-2 orders of magnitude higher than rates derived from the sediment slurry incubations (e.g., cores 1CEL_Jul02, 1_1CH_Oct01, 2CEL_Oct01 and 14CEL_Dec00). Though organoclastic sulfate reduction dominates organic matter degradation, Max-RM are even higher than the maximum sulfate reduction rates in cores 1_1CH_Oct01 and 1_2CH_Oct01. Methanogenesis rates in this study area are more important than in other mangrove systems where methanogenesis is negligible (e.g., Thailand, Kristensen et al., 2000; Malaysia, Alongi et al., 2004; Australia, Kristensen and Alongi, 2006).

We include this in the discussion section of the manuscript.

4) The authors introduced the different seasons of this area and the potential impact to the sediment and porewater systems. However, I do not see further discussion about how their results reflect such seasonality. I feel a great pity that the authors did not translate the “numbers” they got from their modeling and experiments into something helpful to understand the spatial and temporal heterogeneity of the environment.

Response:

This has been discussed in another manuscript submitted to Limnology and Oceanography. The different seasons did not have a major control on the rates we calculate since profiles of all types were captured in all seasons. We added this information to the manuscript.

«Minor/technical comments»

1) My biggest comments on the technical part of the paper is its presentation. The lead author tend to use long sentences with many clauses.

I would suggest split the long sentences into shorter ones which will be more understandable for readers who know nothing about modeling especially.

Response:

We tried to shorten sentences and make it easier to read.

2) The authors also need to consider more recent literatures. When the hypothesis was built solely based on some 80' and 90' papers, it's hard not to think there may be different views in the current research.

Response:

More recent literature has been included.

3) The Figure 2 is small and difficult to read. You need to figure out a different way to present these.

Response:

The figure has been revised.

4) I have a few comments for Table 2. You need to be more careful about the significant digits. I don't think the model can give that many meaningful digits. The use of "F" at header row is confusing. I know you explain below but it is intuitionnally awkward especially when you mixed the real fluxes with depth-integrated rates. The negative sulfate depletion rates and sulfate reduction rates are also awkward. It makes no physical sense unless you meant the reactions are reversible, which I think are not.

Response:

The table has been revised.