

Dear editor,

We would like to thank the first referee for his/her clearly positive comments that help us improve our manuscript. We replied to the comments of referee#1 in detail 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 red. **Although we uploaded our reply to Referee#1 on 29 Dec. 2015, we want to update this to explain how we have modified the manuscript according to both referees' and other coauthors' comments. The replies to Referee#1 are marked in red in this updated file.**

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 The authors need to improve the presentation a lot as figure 2 is hard to read, some of the references cited are out of date, a few sentences are quite awkward to read, and Table 2 needs more polishing.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 N<sub>2</sub> gas or fixing sulfide with Zn(OAc)<sub>2</sub> 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 N<sub>2</sub> atmosphere. We added this information to the paper. However the reviewer is correct that it may be possible that some H<sub>2</sub>S is oxidized in the shallow subsurface of the cores due to oxygen penetration due to bioturbation.**

**Therefore, excess sulfate could potentially be from H<sub>2</sub>S oxidation and/or from sulfate input from groundwater. We note that in this specific site groundwater has been previously identified as a source of excess sulfate and excess Sr. Regardless we now include the option of H<sub>2</sub>S oxidation in the revised manuscript, whilst further noting that, since R<sub>SD</sub> is the net sulfate depletion, model results may underestimate the true R<sub>POC</sub> and R<sub>M</sub> due to sulfide oxidation. However, this is only relevant for very few cores in Group-1 and Group-2 where a shallow subsurface excess sulfate is observed. Although we mention this option for completion we believe that groundwater input is**

a more likely source due to correlation between excess sulfate and excess Sr which has been previously described and is consistent with groundwater input.

Perry et al. (2002) identified dissolution of evaporites within the freshwater lens as the probable source of the excess  $\text{SO}_4^{2-}$  found in some Yucatán groundwater by using the ratio between sulfate and chloride ( $100 \times (\text{SO}_4/\text{Cl})$ ). Ratios higher than seawater (average seawater is 10.3) are expected where gypsum/anhydrite dissolution is involved (Perry et al. 2002). The other indicator is Sr/Cl ratio which in groundwater is invariably higher than the seawater value and indicates dissolution of celestite (from evaporite) and/or aragonite (Perry et al. 2002). The region east and south of Lake Chichancanab, Mexico, referred to as the Evaporite Region by Perry et al. (2002) is characterized by distinctive topography and the high-sulfate content of groundwater (Perry et al. 2002). The groundwater from the presumed source region, Lake Chichancanab, flows northward into the Celestún Estuary which can be recognized by the progressive decrease in the ratio  $[\text{SO}_4/\text{Cl}]_{\text{groundwater}}/[\text{SO}_4/\text{Cl}]_{\text{seawater}}$  in water from southeast to northwest (Perry et al., 2009). These parameters in Celestún lagoon published in Young et al., (2008) are consistent with our interpretation that gypsum/anhydrite dissolution involved in the groundwater contributes to Celestún lagoon.

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 or less and using longer time scales does not make a difference.

Specifically we note that the long simulation time of 1 Myr is a default setting in this version of the model to ensure that the results for all cores are under steady state. However, we see the possible confusion. The 5 year simulation time now reported can be justified using the following equation (Boudreau, 1997):

$$t = \frac{L^2}{2 \times D_M}$$

where t is time, L is the distance involved in a typical diffusive movement (length of the model column) and  $D_M$  is the molecular diffusion coefficient. The time for methane and sulfate diffusion over the length of modeled sediments (20 cm) is less than 0.6 yr ( $D_{\text{M}(\text{CH}_4)}=659 \text{ (cm}^2 \text{ yr}^{-1})$  and  $D_{\text{M}(\text{SO}_4^{2-})}=382 \text{ (cm}^2 \text{ yr}^{-1})$  for e.g. core 1CEL\_Oct01). Now we show the data using 5 years as the time needed for steady state and changed the text and figures accordingly. This makes no difference to the results.

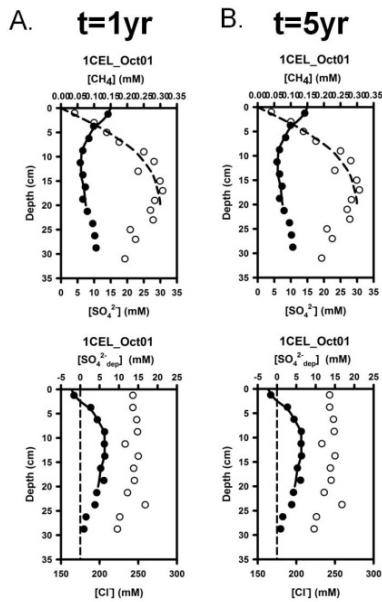


Fig. R1: Depth profiles for modeled (lines) and measured/calculated (symbols) concentration of dissolved methane (dashed line; open circle), sulfate (solid line; solid circle) in the upper panel and sulfate depletion (solid line; solid circle), zero sulfate depletion (dashed line) and chloride (open 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:

We have now simplified the model set-up because, based on our data, we cannot accurately quantify the relative proportion of sulfate loss due to organoclastic sulfate reduction and AOM. The sentence pointed out by the reviewer was unclear and has been removed.

b. Eq. A6: so you exclude entirely AOM when SO<sub>4</sub>-dep is positive? I thought SO<sub>4</sub>-dep>0 means active removal of sulfate? Not by AOM?

Response:

SO<sub>4</sub>-dep>0 means that active removal of sulfate is dominated by organoclastic sulfate reduction, although R<sub>SD</sub> includes R<sub>SR</sub> and R<sub>AOM</sub>. Since we can see evidence for 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 [SO<sub>4</sub><sup>2-</sup>]<sub>dep</sub> profile (R<sub>SD</sub>) to represent the rate of organoclastic sulfate reduction (R<sub>SR</sub>).

In the sulfate reduction zone, we assume the co-occurrence of the following reactions:





In the reaction stoichiometry,  $R_{\text{SR}}$  in reaction (1) is  $0.5R_{\text{POC}}$ . In terms of net sulfate reaction,  $R_{\text{SD}}=R_{\text{SR}}+R_{\text{AOM}}$ . Since the 3 reactions are coupled in the sulfate reduction zone and reaction (2) + reaction (3) is equal to reaction (1), this means that  $R_{\text{SD}}=0.5R_{\text{POC}}$ . Hence,  $R_{\text{AOM}}$  is negligible compared with  $R_{\text{SR}}$  for  $R_{\text{SD}}$ . We have revised the equations for  $R_{\text{SD}}=R_{\text{SR}}+R_{\text{AOM}}=R_{\text{SR}}=0.5R_{\text{POC}}$ . To estimate the fraction of organic matter degradation via methanogenesis ( $R_{\text{M}}$ ) and organoclastic sulfate reduction ( $R_{\text{SR}}$ ), Michaelis-Menten kinetic limitation term used for methanogenesis ( $R_{\text{M}}$ ) and organoclastic sulfate reduction ( $R_{\text{SR}}$ ) are expressed as:

$$R_{\text{SR}} = 0.5 \cdot R_{\text{POC}} \cdot f_{\text{SO}_4^{2-}}$$

$$R_{\text{M}} = 0.5 \cdot R_{\text{POC}} \cdot (1 - f_{\text{SO}_4^{2-}})$$

AOM may occur in these systems, but the data and model sensitivity results indicate that it is insufficient to prevent  $\text{CH}_4$  escape to the bottom water, probably because of the abundant organic matter available for sulfate reducers to use instead of  $\text{CH}_4$ . We have revised this in the manuscript.

d. Eq. A7: I understand you related  $R_{\text{poc}}$  to  $R_{\text{sr}}$  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:

AOM plays a minor role in sulfate reduction. Please see the response to comments (3).

e. Eq. A12: How does  $R_{\text{corganic}}$  different from  $R_{\text{poc}}$ ? 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:

The reason we simulate  $[\text{SO}_4^{2-}]_{\text{dep}}$  profiles to derive rates of organic matter degradation, organoclastic sulfate reduction and methanogenesis is because measured organic matter contents in this area show evidence for a change in depositional regime over time (Gonnea et al., 2004, and Fig. 4 in this version). Organic matter cannot therefore be used for accurate organic matter degradation calculations. To avoid the confusion between  $R_{\text{corganic}}$  and  $R_{\text{POC}}$ , we have removed the sampling and analytical methods, results, discussions and the model equation related to the measured organic contents from our manuscript and refer to measured organic matter contents from Gonnea et al (2004) and Eagle (2002, thesis).

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  $k_{\text{corg}}$ . 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 running the model for 5 years to reach steady state (see comment above). We use a steady state model because we do not have enough data to constrain a dynamic model such as regular monitoring of porewater sulfate, methane and chloride concentrations. The steady state model is still useful because we apply it to a wide range of profile types which represent the different conditions in the system and capture the system dynamics.

2) The authors presented tremendous amount of temporal/spatial porewater data in this paper but did not spend much effort in discussing these. The grouping 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:

We have included additional discussion to show there is no relation between profile time and location or season and that the variability is a result of the system being heterogeneous and probably highly dynamic. We do not have sufficient data to differentiate between temporal and spatial trends, however as we show cores collected at the same time close to each other may differ and cores collected at the same sites during different times also differ from each other hence we believe that if we monitored any one site continuously it is likely that all profile types will be captured at one site.

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 H<sub>2</sub> 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 (Max-R<sub>SR</sub>). Maximum methane production rates estimated from TMA, methanol and H<sub>2</sub> 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. Model derived 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). Although our model results show that organoclastic sulfate reduction dominates organic matter degradation, model derived 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:

Model derived methane fluxes to the water column are listed in Table 2 ( $F_{\text{methane (top)}}$ ) and reveal that fluxes (0.011-21 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>) are similar or up to two orders of magnitude larger than fluxes reported for other mangrove systems in, e.g., Florida (0.02 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Barber et al., 1988; Harriss et al., 1988), Australia (0.03-0.52 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Kreuzwieser et al., 2003), and India (5.4-20.3 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Purvaja and Ramesh, 2001). Our values as well as the depth-integrated rates (Fig. 2) show no relation between sampling time and location or season. Since all of the different types of methane depth profiles (group-1, group-2, etc) were found during each sampling trip, and no obvious trends in spatial and temporal distribution (seasons and sampling locations) were observed, model derived methane effluxes to the water column and the variability in the porewater methane concentrations and depth-integrated turnover rates suggest a very dynamic system with high methane production and efflux rates.

We have included this in the discussion section of 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 have improved the English structure.**

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:**

**Fig. 2 was moved to supplementary material and replaced with a figure showing one typical profile per group. All figure qualities were improved.**

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 intuitively 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.**