

Dear editor,

We would like to thank the second referee, Dr. Pohlman, for his support of our manuscript and for giving us comments to improve the manuscript. We replied to his comments in detail point by point and explained how we have modified the manuscript for publication in Biogeosciences. Dr. Pohlman's comments are shown in black and our responses are shown in blue.

General Comments:

The authors present sulfate, methane and chloride data from sediment cores collected from two coastal mangrove systems in the Yucatan Peninsula. The authors group the cores into 5 sets that generalize the sulfate and methane profile behavior. Because the analytical data are limited to concentration profiles of 3 constituents, they apply the Wallman et al. 2006 transport-reaction model to explain potential processes affecting the pore water geochemistry. An unusual and interesting observation is that methane and sulfate often coexist in the porewater, suggesting a non-competitive substrate (i.e., one used only by methanogens) allows methanogens to be active in the presence of sulfate reducers. A series of incubations that includes a treatment with the non-competitive substrates TMA and methanol demonstrates the microbial machinery and other factors required to produce methane from these substrates is present in the sediments from the investigated sites. The suggested implication is that mangrove ecosystems may be large methane emitters, provided the observations and model results accurately represent mangrove systems at large.

Although the diversity of data is limited, the authors do a commendable job of testing the hypothesis that non-competitive substrates accounted for the accumulation of methane in the sulfate reduction zone. The study does not provide definitive evidence that the process is active, as the only substrate-level data supporting its activity are from ex situ incubation experiments. The study should be used as motivation for tackling this specific question in greater detail in a mangrove ecosystem. It would appear others have observed the same effect in mangroves, but this appears to be the first to suggest a mechanism for the repeated observation. This is an important and interesting contribution. With moderate revisions, this reviewer recommends publication of this manuscript in Biogeosciences.

Specific Comments:

1. The grouping of the profiles helps to consolidate the data in a way that makes the application of the model more systematic. However, the authors have a tendency to overstate the certainty of their findings. For example, the model does not “illustrate” that methane is produced from DOM...it suggests production from these unmeasured carbon sources is possible. Also, shallow methane production does not necessarily promote high methane fluxes to the water column and atmosphere as the authors state. Although benign in intent, these statements being expressed definitely in the abstract may be misleading because they imply the conclusions are based on data. Be clear that the conclusion are based on modeling results and that no measurements regarding fluxes were obtained.

Response:

We have changed the wording used to be more consistent with our data and less definitive (e.g. change "illustrate" to "suggests" and change "promote" to "increase the likelihood").

We have also made changes throughout the manuscript in order to more clearly differentiate the modeling results from the field and laboratory measurements.

This reviewer recommends the authors provide a figure with generalized sulfate profiles (and methane, if applicable) for each group in Fig 2. Such a model (and a description of each group in the Fig 2 headings) would give the reader a better intuitive sense for the groupings.

Response:

Fig. 2 was moved to supplementary material and replaced with a figure showing one of the typical profiles per group.

2. Why would mangroves have such a high abundance of non-competitive substrates in comparison to other brackish systems?

Response:

This is a question we can only speculate about. Mangrove forests are known to be highly productive ecosystems with the capacity to release high concentrations of DOM to sediment porewaters (Kristensen et al., 2008). Litter from trees (leaves, propagules and twigs) and subsurface root growth provide further significant inputs of organic carbon to mangrove sediments which are unique for this type of system. We have now included these sentences in the manuscript.

Kristensen, E., Bouillon, S., Dittmar, T., Marchand, C., 2008. Organic carbon dynamics in mangrove ecosystems: A review. *Aquatic Botany*, 89(2): 201-219.

3. Using the near surface methane gradients and modeled results, the authors should quantify the differing methane flux potentials for each environment rather than only speculating about the importance of this methane source.

Response:

Model derived methane fluxes to the water column are listed in Table 2 ($F_{\text{methane (top)}}$) and reveal fluxes (0.011-21 mmol CH₄ m⁻²d⁻¹) that are similar or up to two orders of magnitude larger than fluxes reported for other mangrove systems in Florida (0.02 mmol CH₄ m⁻²d⁻¹, Barber et al., 1988; Harriss et al., 1988), Australia (0.03-0.52 mmol CH₄ m⁻²d⁻¹, Kreuzwieser et al., 2003), and India (5.4-20.3 mmol CH₄ m⁻²d⁻¹, Purvaja and Ramesh, 2001). Since all of the different types of methane depth profiles (Group-1, Group-2, etc) were found during each sampling trip and no differences 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 suggest a very dynamic system with high methane production and efflux rates. We have included this in the discussion section of the manuscript.

4. The site description should include a description of where and why anhydrite might contribute excess sulfate. An alternate possibility not discussed is oxidation of sulfides. Total sulfides were not measured, so their potential contribution cannot be discussed. Perry and others have written much about why anhydrites and gypsum are found on the Yucatan platform. More details would make this argument more convincing. The evidence for contributions from anhydrite are not especially compelling. Basically, the authors state that there is anhydrite in the area, so that explains the excess sulfate. From looking at one of the Perry references, it is not clear that one would expect a groundwater contribution in the Chelem lagoon (inside the Chicxulub impact zone). More details would be helpful. Sr data would be even better, but that is not likely to be available and is not required.

Response:

Perry et al. (2002) identified dissolution of evaporites within the freshwater lens as the probable source of the excess 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 contribute to Celestún lagoon.

Though there are no published SO_4 and Sr data for groundwater and surface water in Chelem lagoon, Perry et al., (2009) measured strontium concentrations greater than seawater in the saline groundwater of the Northern Yucatan Peninsula east of the Ring of Cenotes, and Chelem lagoon is located within this region. We included this in the discussion section of the manuscript.

5. Were the sediments dried and prepared for TOC analysis as part of this study, or Gonnee et al., 2004? The methods do not include the analysis. The results do not specify the origin of the data. Please clarify.

Response:

The original data are from Gonnee et al., (2004) and Eagle, (2002, master thesis). The TOC study utilized splits of the sediment cores collected for methane concentration analysis.

We have included both references in the manuscript.

6. Increasing OM content with depth? How is this? Suggestion of a changed depositional pattern not discussed.

Yes, organic matter profiles show a changed depositional pattern (Gonnea et al., 2004). Since this pattern can't be used for organic matter degradation calculations, we simulate $[\text{SO}_4^{2-}]_{\text{dep}}$ profiles to derive organic matter degradation rates. To avoid the confusion between TOC analysis, TOC data expressions and reaction rates for R_{organic} (Eq. A11) and R_{POC} (Eq. A7) in this version, we have removed the sampling and analytical methods, results, discussions and the model equation related to the measured particulate organic contents from our manuscript and refer the measured organic matter contents to Gonnea et al (2004) and Eagle (2002, thesis).

7. Why would negative sulfate depletion be observed at the surface and not at depth if the source of the excess sulfate is from depth? See Core 7CH-Oct01.

Response:

It may be possible that some H_2S is oxidized in the shallow subsurface of the cores due to oxygen penetration due to bioturbation.

Therefore, excess sulfate could potentially be from H_2S 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. We now include this option in the revised manuscript, whilst further noting that, since R_{SD} is the net sulfate depletion, model results may underestimate the true R_{POC} and R_{M} 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.

Technical Corrections:

17921, line 21: 'porewater'

17923, line 7: delete 'that'

17923, line 12: 'sites'

17927, line 5: 'inhibited'

17930, line 3: 'atmosphere'

17920, line 20: 'chloride'

Response:

These technical corrections have been revised in the manuscript.

Figures:

1. Put letters on the figure panels

Response:

The figure has been revised.

2. Some units on figures indecipherable (e.g., CH₄ conc)

Response:

The figure has been revised.