Biogeosciences

Discussions

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Interactive comment on "Anaerobic oxidation of methane alters sediment records of sulfur, iron and phosphorus in the Black Sea" *by* Matthias Egger et al.

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Overall comments In the paper, Egger et al. present very comprehensive porewater and sediment geochemical data to discuss the cycles of C, S, Fe, and P in sediments that are unique in the sense of their depositional sequence and history. The authors collectively discuss the data with a rather complicated model, which is understandable due to the complexity of the system they work with. The paper is well-written and structured. The authors' attempt to elucidate the mass balance of several elements in this environment provide valuable insights to the coupling of these elements and the complexity of it. In general, the conclusions are convincing and well support by their data and modeling. As also a user of such transport-reaction models (Hong et al.,

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2014a&b; Torres et al., 2015; Hong et al., 2016), my major concern of the paper will be on the assumptions and setup of the model as well as several interpretations the authors made based on the model results. In conclusion, I think this is a very nice piece of work considering all the data and modeling work.

Major comments Modeling numerical issue: In conventional models for transport-reaction models, advection (i.e. sediment burial) often inevitably results in numerical dispersion, concentration will decrease as time progresses with burial even without any reaction. This effect will be especially obvious when using high advection rate (burial rate), large time discretization, and a long modeling time. I've done some tests before (Hong et al., 2016 accepted by limnology and oceanography) by simulating time progression of a profile with sharp concentration change. After 140 years of simulation, the concentration is 20% reduced compared to the value it should have (see the attached file for this comparison). As for the sharp increase of OM content in your environment, you will inevitably encounter this numerical issue. I urge the authors to run some simulations with only burial (no diffusion and other reactions), and see how your sediment and porewater profiles will progress.

I also wonder what is the consequence to accelerate your model. The price of numerical issues will be greater when you accelerate it by using larger time steps and/or faster rates. It is almost no way to have a model that is both efficient and accurate. There is always a sacrifice.

The other potential numerical issue I want to point out for the authors is the convergence of the model results. You have to make sure you use temporal and spatial steps small enough so that the results are stable. This can be done by running the model several times (the same reactions and setup) with smaller time/space discretization for each run. Chose the smallest discretization that your model results stop changing.

Conflict between observations and model results: In a few places in the paper, the authors didn't explain clearly the conflict between observations and model results.

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One example is the choice of chloride changes with time. The authors used a very different evolution pattern from what literature suggested because it provides a better fit of their chloride concentration. However, the time scale adopted by the authors (100yrs) is an order smaller than what is suggested in the literature (2000yrs). The authors provide no explanation about such difference. I envision that if the author use constant chloride from 2000yrs BP until now and increase fluid advection rate (larger u), they might be able to fit the profile. I think the authors should explain better why choosing such condition.

The other example is from line 369 to 371. The authors claimed the SR rates they estimated from the model in zone I & II are more correct the estimation from porewater profiles. This statement raises the question that, then how do you know the SR rate you estimated from these two zones are accurate since you have no data to support you.

Very high methanogenesis rate in sulfate reduction zone: In fig 6, there are two peaks of methane production (one in bottom water or first cm of sediment? While the other in zone II). My questions are two: 1) It is apparent that this methanogenesis is from OM decomposition. However, methanegenesis should be suppressed when the sulfate content is high, as in the case of zone II. I understand that although methanogenesis is inhibited by sulfate content (E5 & E6 in Table 4), model can still produce very high ME rate when there is ultrahigh OM content. However, a model is a model, do you have any prove such high methanegenesis from your zone I and II. Considering the CH_4 production rate and SO_4-AOM rate from Fig.6. you should see either high methane or light d13C of methane in zone I and II if the rate is this high. I however don't quite see those from your profiles.

2) Back to fig6, your rates do not seem to balance. The highest CH_4 production rate approaches 300 pmol/cm3/d which only stimulates an AOM rate less than maybe 20 pmol/cm3/d. If there is more production than consumption, isn't that you will methane accumulates in the porewater (i.e., high methane from that depth in the sediments).

SR rate is over 2000 pmol/cm3/d in this section but sulfide production is only 300 pmol/cm3/d. where is the rest of sulfide production?

The very complicated model: The authors use a rather complicated model in this study by choosing many reactions that are not totally necessary. For example, the authors choose to include aerobic processes (R1, R7-R12) and nitrate reduction (R2) even though there is no constraints on O2 and nitrate content in the porewater. I would also doubt the importance of these reactions due to the anoxic bottom water in Black Sea. The authors chose not to include Mn reduction due to its low content, which is fine with me, but decide to include all other processes that cannot be constrained? That is an odd decision to me. By excluding these unnecessary reactions, the authors can also improve the efficiency of the model.

I also wonder, with all the reactions assigned in the model, do the authors have enough constraints? I believe the answer should be close to yes as the authors have many data to support the model (which is very nice). I would urge the authors to spare a section in the text discussing the constraints for the model. To me, this is an extremely important but often ignored aspect in papers like this. I have done some initial analyses based on the reaction network in Table 3. For example, for Fe2+, the authors have R3, R9, R10, R13, R14, and R20 for sources, and R8, R15, R23, and R24 for sinks. Some source and sink terms may be constrained by the data of iron mineral speciation. When the same analyses being applied on HS in porewater, it seems like the abundance of different Fe-S minerals also depend on the source and sink terms of HS. A table such as tab6 but with more species included may be useful for such discussion.

One last comment on the complicated model, how does the model describe pH, which should be very important determining the type of dissolved sulfide and DIC. I don't see reactions such as H2S becomes HS-+H+ in Tab3 which describe the buffer capability of HS species (need same reactions for carbonate systems) . Although there is usually no good constraint on pH, it's good to make sure pH falls in the right range especially when including pH-sensitive reactions.

Minor comments Line 151: Please specify how you measure sulfide, phosphate, and DIC onboard. General model: What is the initial condition? Line 211: why 20 meters? You should mark you explain this in the supplemental material Line 255: is zero gradient a good assumption for methane? How do you know there is no deeper source of methane Line 289 to 293: You have same ammonium but higher methane in site4 and 5. Of course more severe degassing during core recovery in site 4 can be one explanation, but maybe there is more methane input from site 5 from greater depth. This echoes back my previous comment: is zero gradient really a good assumption for methane? Line 304: How do you know the isotopic signature of methane is not affected by degassing? Line 533: Isn't that this will be capture in your orgP analyses?

Line 827: Do you have any constrain on C/P ratio? Maybe this explains why the fitting on porewater phosphate profile is not as good?

Salinity/chloride: In many places of the paper, the authors mixed the term salinity and chloride concentration (e.g., line268-282). Of course these two properties are usually linear dependent on each other but they are fundamentally different and may correlate with each other very differently when Black Sea was more of a "lake" or a "Sea". I suggest the authors to use chloride concentration throughout the paper or explain how they convert salinity to chloride concentration.

FigS3: What is going on with the very high alkalinity at very top? where dic concentration looks normal...

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2016-64/bg-2016-64-RC3-supplement.pdf

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