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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We thank Dr. Hong for encouraging and critical remarks. We reply to the comments below and aim to revise the manuscript accordingly.

Referee's comment: Major comments Modeling numerical issue: In conventional models for transportreaction 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.

Author's reply: We thank the referee for sharing his experience with us. The ReacTran package applied in this study (see line 261) accounts for numerical dispersion using total variation diminishing (TVD) slope limiters. A description of the ReacTran package can be found at: https://cran.r-project.org/web/packages/ReacTran/ReacTran.pdf

Referee's comment: 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.

Author's reply: We could not find any indication that the model acceleration impacts the conclusions presented in this study. A higher sedimentation rate in the lake phase, however, largely improves the model efficiency as it significantly reduces the computing time.

Referee's comment: 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.

Author's reply: We used this approach in this study (i.e. we ran the model using various time and space discretizations). The model presented here thus reflects the smallest discretization for which the model results stop changing.

Referee's comment: 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. 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.

Author's reply: We will elaborate on the salinization scenario used in this study and provide potential explanations for the offset with the literature.

Referee's comment: 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.

Author's reply: Sulfate reduction rates derived from pore water profiles represent net sulfate consumption, while rates derived from radiotracer injection and diagenetic modeling reveal total sulfate turnover in the sediment, i.e. gross sulfate reduction rates (e.g. Jørgensen (1978; Geomicrobiol. J.) and Jørgensen et al. (2001; Deep Sea Res. Part I)). Thus, modeled rates are generally higher than rates estimated from pore water profiles. The referee is further kindly referred to lines 365-366 where we provide references to studies that have measured sulfate reduction rates in Black Sea sediments, which compare well with our model results.

Referee's comment: 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 CH4 production rate and SO4-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.

Author's reply: The CH4 production rate depicted in Fig. 6 is not correct, as it should be multiplied with the solid volume fraction of the sediment (increases from ~ 0.05 at the sediment surface to ~ 0.39 at depth) and divided by a factor of two (only 0.5 mole of CH4 are produced per mole of organic matter during methanogenesis; see reaction R5 in Table 3; also see response to referee #2). Actual modeled rates of CH4 production are thus < 30 pmol cm-3 d-1 in the marine deposits, which is an order of magnitude lower than modeled SO4-AOM rates. Our modeled CH4 production rates in the surface sediments are higher compared to previous measurements from the Black Sea (e.g. Knab et al., 2009; Biogeosciences), but still significantly lower than net rates of methanogenesis measured in surface sediments of the Peruvian margin of up to $\sim$ 1 nmol cm-3 d-1 in the sulfate reduction zone (Maltby et al., 2016; Biogeosciences). We will add this information to the revised manuscript.

Referee's comment: 2) Back to fig6, your rates do not seem to balance. The highest CH4 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?

Author's reply: We thank the referee for pointing out these inconsistencies. There

has been an error in the plotting of the rates (see also answer to referee #2). The rate plots of Fig. 6 were not normalized to the same volume, meaning that the SO_4 reduction rate, CH_4 production and S^0 disproportionation should be multiplied by the solid volume fraction of the sediment, while rates of SO_4-AOM and Fe-AOM should be multiplied by the sediment porosity. In addition, only 0.5 mole of CH_4 are produced per mole of organic matter during methanogenesis (see reaction R5 in Table 3). We will carefully check the unit conversion in the plotting, as well as the mass balance and revise Fig. 6 accordingly.

Referee's comment: 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 O_2 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.

Author's reply: Oxic mineralization and nitrate reduction were implemented because of the oxic Black Sea lake phase. Bottom water concentrations of oxygen and nitrate for the Lake phase were taken from Reed et al. (2011; GCA). We agree with the referee that nitrate reduction plays only a minor role (also during the oxic Lake phase), but prefer to keep the reaction in the model, as removing it does not significantly improve the model efficiency.

Referee's comment: 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.

Author's reply: We kindly refer the referee to lines 229-231 and Table 5 where we describe the parameter constraints. We will add a table with the mass balance for each species in the Supplementary Information.

Referee's comment: 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 H_2S 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.

Author's reply: The model does not include pH, because it does not capture the precise underlying reaction mechanisms. Furthermore, we do not have pH data to compare the model results to. Adding pH would be a separate study in itself.

Referee's comment: Minor comments Line 151: Please specify how you measure sulfide, phosphate, and DIC onboard.

Author's reply: We will add this information in the revised manuscript (see reply to referee #1).

Referee's comment: Line 211: why 20 meters? You should mark you explain this in the supplemental material.

Author's reply: The referee is kindly referred to lines 257-258 and Supplementary Fig.

S4.

Line 255: is zero gradient a good assumption for methane? How do you know there is no deeper source of methane?

Author's reply: We have no information about a potential deep source of CH4 at our study site. However, the good fit between the modeled and measured ammonium profile (Fig. 3) indicates that it is likely that most of the CH4 is produced within the model domain. We therefore think that a zero gradient assumption is a reasonable assumption for CH4.

Referee's comment: 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?

Author's reply: If the difference in the CH4 profiles between site 4 and 5 would be due to more CH4 input from greater depth at site 5, it would imply that the measured concentrations at site 4 represent actual in-situ concentrations of pore water CH4. However, we were not able to reproduce the observed ammonium profiles with such low rates of methanogenesis at depth. In contrast, our model suggests that in order to have sufficient pore water ammonium, CH4 concentrations should be significantly higher than the measured concentrations at both sites. The high CH4 concentrations derived from the model are also consistent with our observations of massive CH4 degassing during coring and with a previous observations in the western Black Sea shelf (Jørgensen et al., 2001; Deep Sea Res. Part I). We conclude that the ammonium profiles indicate that most of the CH4 is produced within the model domain, rather than from greater depths, thus supporting our zero gradient assumption.

Referee's comment: Line 304: How do you know the isotopic signature of methane is not affected by degassing?

Author's reply: We base this conclusion on the smooth pore water profiles of d13C-CH4 and dD-CH4 (see Fig. 4). To date, little is known about potential isotopic fractionation during degassing. However, it is thought that fast degassing is unlikely to result in major isotopic fractionation, as all CH4 isotopes are lost simultaneously. We will clarify this sentence in the revised manuscript.

Referee's comment: Line 533: Isn't that this will be capture in your orgP analyses?

Author's reply: Mineral formation in microbial cells is not included in the model. Inclusions of Fe-P minerals initially formed in bacteria could further also still come out in the CDB step of the SEDEX extraction.

Referee's comment: 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?

Author's reply: The C/P ratio observed in the sedimentary record does not necessarily directly relate to the initial C/P ratio of the organic matter deposited on the seafloor due to the preferential regeneration of phosphorus from organic matter during anaerobic degradation (e.g. Ingall et al., 1993; GCA). It is thus of limited use as a constraint in this study.

Referee's comment: 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.

Author's reply: We will follow the referee's suggestion and explain how salinity is converted to chloride concentration in the revised manuscript.

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

Author's reply: We thank the reviewer for pointing this out. We checked the raw data and conclude that the alkalinity data of the multicore at site 4 should not be trusted due to uncertainty over data quality. We will thus remove this data from the Supplementary Information.

Sincerely, on behalf of all authors,

Matthias Egger