**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.

**Matthias Egger et al.**

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We thank Dr. Sivan for her positive review and the compliment. We reply to the comments below and aim to revise the manuscript accordingly.

Referee's comment: The model is not detailed and explained enough. You should cite less Rooze et al 2016 and provide more details here. Also, you should perform sensitivity tests for the various uncertainties. I did not have access to Rooze et al paper, but from its title I am assuming it is not on the same system so there is no overlapping. You should however upload this paper.

Author's reply: We will expand the model description in the revised version of the

manuscript. In addition, we will perform appropriate sensitivity tests to demonstrate the various uncertainties (see also reply to referees #2 and #3). The study by Rooze et al. can be at http://onlinelibrary.wiley.com/doi/10.1002/lno.10275/abstract

Referee's comment: The Fe2+ increase in the deep sediments could be from deep Fe-AOM as we see in lakes and coastal sediments (Sivan et al., 2011; Egger et al., 2015), however it can also be organoclastic. There may be reactivation of less soluble Fe(III) minerals in this system by other means other than methane oxidation (e.g as described by Sivan et al., 2016). You indeed mention it, however, you should refer to it as a possible option.

Author's reply: We will clarify that the reactivation of more crystalline Fe oxides by methanogens as described by Sivan et al. (2016) represents a possible mechanism for the Fe reduction at depth in the sediment.

Referee's comment: The assumption that the total dissolved Fe and Mn (as measured by AE-ICP) are Fe(II) and Mn(II) is probably fine, however you should test it and show it in at least in one of the profiles in the Black sea sediments (or cite other works that did it there). You should compare the Fe(II) to Fe(total) by another method (as the Ferrozine), or compare your assumed Fe(II) to Fe(II) from the Ferrozine or another method.

Author's reply: Unfortunately, we cannot test this as we acidified our pore water samples prior to analysis for Fe and Mn with ICP-OES. Although the solubility of $Fe(OH)_3$ is very low at natural pH and the occurrence of dissolved $Fe^{3+}$ is highly unlikely in reducing sediments, $Fe(OH)_3$ or $Fe(OH)_2+$ complexes could pass through the 0.45 $\mu$m filters used in this study (Raiswell and Canfield, 2012; Geochem. Perspect.). In addition, a small fraction of the dissolved Mn could indeed be present as $Mn3+$, as shown for suboxic surface sediments (Madison et al., 2013; Science). We will clarify that the dissolved Fe and Mn in our study refers to Fe and Mn passing through a 0.45 $\mu$m filter and thus likely consists of a mixture of truly dissolved (aqueous), as well as organically

complexed, colloidal and nanoparticulate Fe and Mn species in the method section of the revised manuscript.

Referee's comment: You should discuss in more detail the sulfate profile and – its apparent "diffusion" profile (linear curve) with organoclastic sulfate reduction, and the cryptic S cycle in the upper part of this profile. You should also compare the downward flux of sulfate to the SMTZ and the upward flux that you calculated for methane and discuss it.

Author's reply: As suggested by the referee, we will discuss the sulfate profile in more detail and also elaborate on the relative fluxes of sulfate and methane to the SMTZ.

Referee's comment: The $\delta$13C of methane similarity to Yoshinaga's data is convincing and satisfactory. Interpretation/speculations regarding the profile of $\delta$D of methane should be given.

Author's reply: The profile of $\delta$D-CH4 will be discussed in more detail in the revised manuscript.

Referee's comment: L 84-85: Vivanite was found also in Lake Kinneret (Sivan et al., 2011), it can support your finding and related processes.

Author's reply: We will add this additional reference in the text.

Referee's comment: L 92-93: Also propose the other option for Fe reduction.

Author's reply: Reactivation of more crystalline Fe oxides by methanogens will be added as an additional option (see comment above).

Referee's comment: L 141-142: See comment regarding this method above.

Author's reply: We will revise these lines according to the comment above.

Referee's comment: L. 151: I assume the auto analyzer was based on IR. How did you remove of the sulfide?

Author's reply: Samples for HPO42-, DIC and HS- were analyzed colorimentrically on two separate QuAAtro (SEAL Analytical, Germany) auto-analyzers in thermo-stated containers. HPO42- was measured at 880 nm after the formation of molybdophosphate-complexes (Murphy and Riley, 1962; Anal. Chim. Acta). Samples for DIC were acidified online after being oxidized by H2O2 to prevent H2S loss and analyzed as described by Stoll et al. (2001; Anal. Chem.). The sulfide was trapped with NaOH and analyzed using the methylene blue method as described by Grasshof (1969; Woods Hole Oceanographic Institute). We will add these details in the manuscript.

Referee's comment: L. 236-242: Clarify and explain this part in more details.

Author's reply: We will expand this paragraph in the revised manuscript.

Referee's comment: L. 288: Show how you calculated to this saturation value and under which salinity conditions. Mark this value on the figures of methane too.

Author's reply: We will provide information about how this saturation concentration was derived and, as suggested by the referee, we will indicate the saturation concentration of CH4 under atmospheric conditions in the Figures.

Referee's comment: Add the bottom water values on the porewater profiles

Author's reply: The bottom water values are already given in the pore water profiles (depth of 0 cm).

Referee's comment: L 297: Change the sentence to a more precise one.

Author's reply: This sentence will be improved in the revised version.

Referee's comment: L. 381: Explain the other 91% based on the profile (see main comment).

Author's reply: We assume the referee means 81 %. We will add the explanation in the revised manuscript.

Referee's comment: L 445-451: See the main comment regarding organoclastic Fe reduction.

Author's reply: We will expand this section and discuss why we assumed Fe-AOM as the only Fe reduction pathway in the model (also see comments to referee # 2).

Referee's comment: L. 566-568: You don't need this trivial sentence, your work is good and nice enough without it.

Author's reply: We thank the referee for the compliment, but prefer to keep this sentence. In our opinion, it is important to include this statement because such diagenetic redistributions are often not considered in paleoceanographic studies.

Referee's comment: Fig. 3: No sulfate measurements in the sapropel depths ? Add saturation of methane. What could be the reaction precipitating phosphate in the upper 300 cm (hydroxyl-apatite)?

Author's reply: Unfortunately, the pore water samples for sulfate measurements in the sapropel depths were lost prior to analysis. We will provide information about the CH4 saturation concentration in the revised version. We suggest that the removal of dissolved phosphate in the upper 300 cm of sediment is due to authigenic apatite formation as observed previously in sediments of the Black Sea (Dijkstra et al. 2014; PlosONE). We will add this information to the revised manuscript.

Referee's comment: Fig. 4: Again with the saturation of methane.

Author's reply: See comment above.

Referee's comment: L 339: Start a new subchapter.

Author's reply: We will add a subchapter for the rates and temporal evolution.

Sincerely, on behalf of all authors,

Matthias Egger

**BGD**

Interactive comment