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Biogeosciences
Discussions

Interactive comment on “Regulation of anaerobic methane oxidation in sediments of the Black Sea” *by* N. J. Knab et al.

N. J. Knab et al.

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Reply to Reviews:

We highly apprechiate the effort of the reviewers and the contribution to our study. The suggestions they provided were constructive suggestions and significantly improve the manuscript. The specific comments will all be considered when submitting a corrected version of the manuscript. Structural and language mistakes will be corrected as suggested by the reviewers.

The main issue that all three reviewers mention is that it should be more carefully explained how the transition between the marine and limnic sediments was defined and they suggest to include additional sedimentary and geochemical data (TOC, TC, CN, CaCO3) for that purpose. The marine-limnic transition has been defined mostly based

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Interactive Discussion

Discussion Paper

on sedimentary characteristics (eg. the location of the organic rich sapropel layer) in comparison with geochemical data refering to the description of these parameters in Black Sea sediments by Jørgensen et al., 2004. Since in that publication the geochemical gradients and how they relate to the transition between limnic and marine conditions has been described in detail the we did not intent to repeat the same definition again. Moreover, we did not consider the precise determination of the transition essential, as the argument is based on the observation that the location of the SMTZ in relation to the sapropel layer is significantly different. But as it is requested in unison by the three reviewers we can provide the TC,TOC and CaCO3 data together with a rough sedimentary overview in a revised manuscript and explain how the marine-limnic transition was defined.

All three reviewers also ask for a better definition of measurement accuracy, errors and detection limits. Where not stated yet in the text detection limits will be included in a revised manuscript; it was 0.006 mM for methane and 0.001 mM for H2S. For DIC and VFAs it was not determined since the values are far above the limit of the measurement. In contrary to concentrations the detection limit of rates cannot be provided as an actual rate value because it is determined from zero-time incubations. The detection limit of rates is typically determined by the amount of produced 14C-CO2 (for AOM), 14C-CH4 (for MTG) or 35S-TRIS (for SRR) of 5 replicate zero time incubations plus twice their standard deviation as it is described in the method description with reference to the original definition). The rate values are only presented as datapoint if the produced labelled product is higher than this detection-limit theshold. The detection limit is only valid for each respective core with the batch of tracer used for these samples and cannot be compared between different sites. In order to avoid giving errorbars of rate measurements all three parallel replicates were plotted instead of a mean value for each sample depth. The reason for this was that a mean value for these measurements will always contain a high prejudice. Presenting the individual replicates is therefore a common practice for rate measurements to avoid this problem and still provide information about the variability of the measurements.

Reply to Referee #1:

It has been demonstrated by earlier publications cited here and by Weber et al. (Deep-Sea Research I, 48, 2001) that sulfate reduction of organic matter is the dominant sulfate sink in the Black Sea and that the upper units of the sediment are very rich in organic matter (Hay, Paleoceanography, 3, 1988). Unfortunately it is not fully understood yet, why the sulfate gradients are so often linear in marine sediments. Borowski et al. (as mentioned by the reviewer) provided an explanation for linear sulfate gradients in sediments above gas hydrates, but the linear gradients can also be observed in sediments where organic matter is the dominant substrate for sulfate reduction (e.g. Knab et al, Geochimica et Cosmochimica Acta, 72(12), 2008).

The expression “methane tailing” has been introduced by Jørgensen et al. (2001) specifically to describe the special feature of the methane profile in the Black Sea. It emphasizes the difference between the nearly linear upwards diffusion of methane in the Black Sea versus the concave upwards profiles commonly observed in other locations and we therefore believe it should be maintained as an expression here. The units on p.2316/l.17+18 have been checked and will be corrected. The CH4 flux is correct but the H2S flux should be 12 (13) μmol m-2 d-1, since the diffusion coefficient used was in m2s-1 instead of cm2s-1.

In comparison to AOM rates measured at other sites the rates presented here seem indeed reasonable. Yet, some uncertainty always remains when measuring very low AOM rates in sediments, because the increasing methane concentration multiplied by the produced CO2 can lead to artificially high rates, even though CO2 production and therefore actual AOM rates are low.

Indicating a line of sulfate depletion would be helpful. However, we do not know if the background sulfate could be considered as an existing sulfate pool, a background concentration that cannot be used by enzymatic reations, or a measurement artifact. Therefore, we might instead of a sulfate depletion line indicate the SMTZ in the plots in

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Interactive Discussion

Discussion Paper

a revised version of the manuscript, the bottom end of which represents the end of the zone where sulfate is metabolized.

Reply to Referee #2:

The scales on the methanogenesis rate measurements ought to be comparable, of course. In Fig.2 the bic-MTG data is actually plottet on a x10-4 scale, like the ac-MTG next to it, but the labelling is not correct. This will be corrected and we apologize for the confusion it caused. For the other plots the scaling was chosen in respect to the highest measured values and reflect the distribution of bic-MTG in the cores as good as possible. Since the magnitude of methanogenesis is different between the cores we feel that a uniform scale for all the rates would not be very helpful for presenting the data.

The scales for methanogenesis and the presentation of data in this manuscript is not connected to the publication mentioned by the reviewer. These are two independent studies with completely different focus, approach and purpose. Hence, they are published separately. Indeed, some of the data from site P806GC is also used in that publication, which we find a legitimate way to analyze available data under a new aspect and making comparisons between different settings where AOM takes place, of which the Black Sea is only one. There is hardly any topical overlap in both publications and we would consider it rather inapropriate and confusing to include the thermodynamic control of AOM in several European margin sediments together with the geochemical description of AOM in the Black Sea, presented here.

Reply to Sabine Kasten:

The limnic marine transition (which in accordance to the suggestion will be used as a consistant term). As mentioned above, we are aware that this definition is not very precise (as indicated by approximations in table 1), especially since the profiles for P806GC and P824GC are not as distinct as for P771GC and previously described sites. Yet, we had not intented to provide sedimentological detail and an accurate determination of the transition, as we think it is not relevant for the aim of this manuscript. For the purpose of this study the sediment above the sapropel was defined as depositions under marine conditions and the organic-poor clay below the sapropel as limnic. The sapropel layer marks the transition between both conditions, including several different transitional stages in the vicinity of the sapropel. The SMTZ in both P771GC and P806GC were located deep below the sapropel in uniform grey clay and therefore considered to be in the limnic zone of the sediment. In P824GC it is located just below the sapropel and therefore much closer to the marine deposits. We will provide the TC, TOC, CaCO3 data and a rough description of the major sedimentary units to alow a more acurate determination of the limnic-marine transition and indicating this transition in the graphs will be a helpful addition. However, a detailed distinction and discussion of individual sediment layers or inflow events was not the scope of this manuscript and we have no new insights than those described already by earlier publications (eg. Jørgensen et al., 2004).

To consider the influence of the different depositional factors that determine the depth of the SMTZ at the three sites is a very interesting yet difficult point. At both P771GC and P806GC the STMZ seems to be in a similar depth relative to the sapropel layer and only the marine deposits above the sapropel vary, presumably because of erosion on the slope of the ridge, where P806GC was located. In core P824GC the SMTZ is located higher up in the core than it would be expected from the pattern at the other sites. As described in the text the major difference of this site is the thicker layer of marine deposits. The influence this extra marine deposits really have on the depth of the SMTZ or the AOM rates is not clear and the discussion would be only speculation. It could be assumed that the electron acceptors are consumed more rapidly and that all processes are shifted upwards. The sulfate concentration would be depleted earlier and the methane would diffuse up higher untill a new equilibrium is established. Such a situation could lead to the elevated SMTZ close to the limnic-marine transition in core PP824GC. The question as raised under the second point, to discuss the factors in the limnic sediment that are responsible for the sluggish AOM rates is closely related to

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Interactive Discussion

Discussion Paper

the difference the marine deposits could make on AOM rates, and would, of course, be very beneficial. Yet, we do not have a good conclusive explanation so far or detailed information about the differences between these two sediment horizons. The major difference between the limnic and the marine deposits seems to be the content of organic material, but it is not clear how this would influence AOM rates. At the moment the hypothesis stated here, that the depositional history might have an influence on AOM rates, is only derived from our observations with the hope that future studies reveal more insights on the details of this difference that we are not able to explain at this point.

The concentrations of Fe2+ above ˜ 400 cm are most probably not real, but represent a background value of the measurement. The description in the text will be changed accordingly. Core P771GC was sampled on the shelfbreak in the Danube Canyon. The expression will be changed to avoid confusion. The term “reactive iron” is used here as reduced iron reactive to sulfide. Pore water was obtained with nitrocellulose filters, which will be included in the method description. The black FeS bands occur where the sulfide produced above meets Fe2+ in the limnic sediments. It is therefore expected that they are located above increased Fe2+ concentrations. In core P824GC the maimum AOM rates at 290 cm depth are likely not representing actual rates as indicated by tracer turnover (Fig. 7). The expression is indeed misleading and will be changed. The absolute highest rate is 18.6 nmol cm-3 d-1, but the value mentioned here refered to the average of the three repliate samples. Since the other values mentioned in the text were the absolute values as well, this will be changed to absolute values as well. The lack of sulfide below 300 cm depth in core P771GC is the reason why we believe that the sulfate background does not just reflect an artifact of pore water sampling, but an actual remaining sulfate pool. A supplement statement will be included in the reviesed manuscript. At the sulfidization front the Fe2+ will presumably precipitate as FeS and finally be turned over to pyrite. It will be stated more accurately in the text.

Interactive comment on Biogeosciences Discuss., 5, 2305, 2008.