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Biogeosciences Discussions

Interactive comment on "Methane oxidation in permeable sediments at hydrocarbon seeps in the Santa Barbara Channel, California" *by* T. Treude and W. Ziebis

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Reviewer 2, Hans Røy

Authors: We would like to thank Hans Røy for his very useful comments on our work in permeable sediments, which we think improved specifically the method and the discussion part of our manuscript. Below are listed our answers to individual comments of the reviewer.

Reviewer 2: General comments:

The manuscript by Treude and Ziebis address methane seeping and oxidation in a

challenging and dynamic environment. Thus, any useful information extracted will be a valuable addition to our understanding of shallow marine gas seeps. Unfortunately the main conclusion from the data is that the target process was missed because the sediment was cored too shallow. The manuscript does have an interesting discussion on why the methane oxidation did not occur at the expected rates in the investigated surface layers. But the focus is placed on assumed high rates below the investigated layers. This gives the manuscript an unfortunate character of listing stray data with little direct link to the conclusions.

Authors: We changed the focus of the manuscript and concentrated on the data measured. The hypothesis of a deep AOM activity has been much shortened and we pointed out that it remains speculative.

Reviewer 2: The manuscript span the ecology of anaerobic and aerobic methane oxidizers, the prevailing transport properties of coastal sands and the geochemical imprint that methane oxidation leave under those conditions. It would have strengthened the study if the dynamic solute transport had been considered during the measurements of ephemeral compounds such as methane and oxygen.

Authors: We agree, but unfortunately such measurements were not possible.

Reviewer 2: The impact of the transition from advective transport in situ to stagnating condition during measurements is not discussed and the details about the condition during incubation (MOX) and measurement (oxygen) is not given so that the reader can asses it independently. The large drop in oxygen concentration in the overlying water during profiling indicates that there is a problem concerning depletion. Thus, it is also hard to infer the transport properties from the shape of the oxygen profile.

Authors: We added a full paragraph on the sampling/stagnation problematic prior to our data discussion. Furthermore, we clarified where (at which depth) we expect either aerobic or anaerobic methane oxidation given the stagnant conditions and decrease of oxygen penetration during incubation.

Reviewer 2: A substantial part of the data is presented as 2D plots while the authors discuss that data as individual vertical profiles. Thus, it would be better to present the data as such. That would also resolve a number of technical issues concerning gridding and extrapolation.

Authors: We deleted the 2D plots and replaced it by the original profiles.

Reviewer 2: The significance of aerobic methane oxidation and absence of ANME clusters in the surface layer is similar to the methane seeps in the Wadden Sea. The sediment properties at the two sites is also comparable. Thus, the conclusions of the present study can be supported by comparison to the studies of the methane cycle in the sand flats of the German Wadden Sea (http://www.watt.icbm.de/).

Authors: Unfortunately, this study has not been published yet.

Reviewer 2: Specific comments:

P. 1907 L. 26-29: The data do not indicate the deep AOM, that's the authors' assumption.

Authors: The sentence has been deleted.

Reviewer 2: P. 1909. Information on agitation of the water in the cores during recording of the micro profiles is missing. So is the time span from coring by the diver until measurement. This is critical because the driving force behind advective mixing is later discussed based on the profiles. It is well known that a core form an advection dominated environment will change dramatically within minutes when removed from the seabed (e.g. MEPS 145 63-75). Especially in a seep enviroment (e.g. Limnol. Oceanogr., 50(1), 2005, 113–127). The oxygen concentration apparently changed rapidly in the overlying water prior to profiling. It must have changed even faster in the pore water.

Authors: Micro profiles were measured 2-4 hours after sampling at the seafloor. Between sampling and measuring the cores were transported to the shore by boat and

from the boat to the laboratory by car. Disturbances were kept to a minimum and cores were transported in cooling boxes to prevent heating. This information has been added. During microsensor profiling, cores were not moved.

Reviewer 2: P. 1910 L. 25: Give time span from sampling the core until the sediment sample was fixed and sealed.

Authors: Not clear what is meant here. Probably the reviewer refers to page 1909 L. 25 (?). For each method, the time span from core sampling at the seafloor to fixation of a final sub-sample was different depending on the method protocol (e.g. methane, FISH, porosity). Equal to all sediment sampling methods was, that it took 2-4 hours from sampling at the seafloor to first sub-sampling of the core. Only porewater was extracted from the microsensor core after profiling.

Reviewer 2: P. 1910 L. 18-22: What was the content of organic carbon and fine fraction? Those are critical for the permeability. The permeability of the sand bed is a key issue and I am surprised to find its determination based on a correlation to size fractions without further discussion (still I will not be to surprised if the correlation will work better than direct measurements due to the challenging sampling of sandy cores).

Authors: We did not measure the organic carbon content. The equation applied after Krumbein produces permeability values that significantly correlate with measured one, but which can on average reach values 4 times higher (Rusch et al. 2001). We added this information to the method part and pointed out that this needs to be considered for the interpretation of the gained data (Rusch et al., 2001). However, even if the real values are 4 times lower than calculated ones, permeability would still range between 1.8 10^{-12} – and 1.8 10^{-11} m^2, i.e. the conclusion that Brian Seep is characterized by permeable sediments would not change. We changed values in the discussion by providing only magnitudes.

Reviewer 2: P. 1911 L. 15-17: How much pore water was extracted, in mL and in % of the total pore water volume?

Authors: 2-3 ml porewater (depending on clogging of needles) were withdrawn simultaneously from all depth intervals by the underpressure in the vacutainers, which accounts for approx. 20-30% of the total porewater volume in a 1 cm thick sediment layer (core diameter 5.4 cm, porosity $\sim$0.4). This information has been added.

Reviewer 2: P. 1913 L. 14: An alternative explanation is that the core was messed up during recovery. Did the core have time to recover? Note the catch 22. If you measured immediately (within a few minutes) you must prove that you did not disturb the cores. If you measured later you must have provided a realistic advective regime including the source of electron donors from below.

Authors: We can exclude that the deeper oxygen penetration results from disturbance during sampling, because the core was measured 2-4 hours after sampling on the seafloor and the cores had some time to recover after transport. We rather argue that maybe some small irrigating biota pumped oxygen down to explain the straight profile.

Reviewer 2: P. 1913 L. 16: This can only be true if profiling was started on the first core within minutes after the diver capped the core. Was that the case? The oxygen depletion in the water column should be used to calculate a minimum flux to see if the explanation is plausible.

Authors: See above, the first core was usually measured 2-4 hours after sampling on the seafloor. In-situ oxygen concentrations should reach up to 276 μM (saturation at 11˚C and salinity 35 for April). The concentration in the first core measured was already reduced to 200 μM (difference 76) and the second core had 140 μM in the overlying water (difference 136). We see no other possibility than sediment oxygen consumption that could decrease oxygen in the overlying water. The overlying water column had an approximate volume of 400 ml, i.e. we roughly assume that 0.4 L x 76 μmol/L = 30 μmol and 0.4 L x 136 μmol/L= 54 μmol oxygen were consumed over a surface area of 23 cm2 (i.d. of core 5.4 cm) over a maximum of 4 and 5 hours after sampling, respectively. Therefore the sedimentary oxygen consumption must have

ranged between 78 and 113 mmol m^{-2} d^{-1}, which seems reasonable in comparison with other coastal sandy sediments (e.g. Rusch et al., 2006).

Reviewer 2: P. 1914 L. 3: Or the cores have now been standing long enough for the pore water to be depleted for oxygen.

Authors: We deleted the comment about diffusion, since it seemed to be too much interpretation at this point.

Reviewer 2: P. 1915 L. 9: The data is not gridded by nearest neighbor. Looks more like a "Triangulation with linear interpolation", which is, by the way, the correct method. The data should be blanked outside the measured points. This can be done with blanking files (described in Surfer help) or with photoshop. Use the same distance between isolines and the same color map for all plots of the same parameter. Otherwise it is impassible to compare patterns by eyeballing.

Authors: The 2D plot has been deleted and replaced by the original profiles.

Reviewer 2: P. 1915 L. 15: This appears to be an artifact from the gridding. The peak is a gost of the 0-cm-N produced by extrapolation.

Authors: The 2D plot has been deleted and replaced by the original profiles.

Reviewer 2: P. 1916 L. 8-11: The pattern will look much different when extrapolated data (the lower left corner) is removed.

Authors: The 2D plot has been deleted and replaced by the original profiles.

Reviewer 2: P. 1916 L. 25: The permeability was not measured. Is the method used able to pick up those changes?

Authors: Should be. As mentioned above, calculated permeabilities are very likely higher than the measured ones but would still significantly correlates with them, i.e. relative changes in vertical profiles should be real.

Reviewer 2: P. 1919 L. 1-10: The counting statistics is not provided (number of counted samples, number of counted aggregates). The S.D is not a useful description of the goodness of the estimate in a counted number, especially if the number is small. It is also misleading to place S.D. as a symmetrical error bar on a counted number. It would be elegant and easy to give confidence intervals on the numbers assuming Poisson distribution.

Authors: The counting statistics were provided in the method part of the discussion paper (P 1912, L 23-25). We deleted the S.D. since it seems not common to show variations. Furthermore, we deleted the depth graph (aggregate abundances) in Fig. 4, but provided this information exclusively in the text. Our goal was to offer preliminary estimates of abundances at the surface compared to larger depths rather than showing a real depth profile.

Reviewer 2: Figure 1: The order of the sub-plots does not help the reader grasp the figure and it is hard to read. I suggest to have the 3 columns of graphs corresponding to the 3 sites and leave blank areas for the missing graphs so that he reader can run a finger along a line and se the progressive change in one parameter. That appears to be the original idea but it did not work for me in the present form. The scaling of panels is different and this hides the differences between the plots (e.g A versus J).

Authors: We re-worked all figures (increased font size, symbols etc., added color coding, re-organized) and split each figure into two to three sub-figures to increase the size of the single graphs and to enable better comparisons.

Reviewer 2: Technical corrections:

P. 1907 L. 2 and 5: Use compatible units so that the numbers can be compared.

Authors: Everything converted to m^3.

Reviewer 2: P. 1908 L. 23-24: Naming; avoid using “A” for both a transect and a vent.

Authors: We renamed transects into –Apr and –Nov.

Reviewer 2: P. 1909 L. 18: At what pH, how was pH controlled (buffered) and measured and what pKa was assumed?

Authors: A stock solution of S_2^- (0.01M total sulphide) was prepared anaerobically by dissolving 0.22g Na2S * 9 H2O in 100mL of N_2-flushed water in a closed container. The final concentration of the stock solution was determined by standard analysis (e.g. Cline, 1969). 0.1 M Phosphate buffer (pH 7) was prepared (flushing with N_2 gas for 10 minutes and adding a reductant (Ti(iii)Cl) at a final concentration of 1 mM) and aliquots of the stock solution was added to known volumes. The sulfide profiles were measured in parallel with Ph profiles and the PKa was determined accordingly to calculate the total sulfide concentration.

Reviewer 2: P. 1909 L. 22: Move the instrument description up to the sensor description in line 10.

Authors: Paragraph has been re-written.

Reviewer 2: The PA 2000 is not especially high sensitivity.

Authors: Paragraph has been re-written.

Reviewer 2: P. 1911 L. 1-5: Hard to follow.

Authors: Sentences have been smoothened.

Reviewer 2: P. 1912 5: ... aliquots of 1.5 kBq...

Authors: Changed accordingly.

P. 1912 L. 10: or 20%

Authors: Changed accordingly.

Reviewer 2: P. 1913 L. 14: Reword, the fluids are not transported by diffusion.

Authors: Changed into "suggesting transport mechanisms other than diffusion"

Reviewer 2: P. 1914 L. 4: The sulfate minimum is a single measurement. Most likely an outlier.

Authors: The applied analysis is pretty robust and precise producing smooth profiles in other types of sediments. Many different parameters measured in the present study revealed sometimes zig-zag profiles. Vertical heterogeneity seems to be a natural phenomenon in these sediments. It seems therefore not correct to depict all fluctuations as outliers.

Reviewer 2: P. 1914 L. 16: In conclusion; this site is more stratified.

Authors: We added a comment on this.

Reviewer 2: P. 1914 L. 19: Take the in situ pressure into account when discussing the methane concentration relative to saturation.

Authors: We added information accordingly: methane saturation at in-situ and at atmospheric pressure.

Reviewer 2: P. 1419 L. 21: I don't see this that clear. It is supported by MOX, but isn't that driven by the high CH4?

Authors: The differences are actually pretty clear. We often observe shifts in the methane oxidation distribution within the top 10 to 20 cm of seep sediments that are correlated with methane fluxes (respectively methane availabilities at the time of the incubation). It may remain of course a subject of speculation if the observed differences follow a trend or are just random heterogeneity.

Reviewer 2: P. 1915 L. 20: ??43‰ and ??54‰ appears to be within the same error bar.

Authors: The trend is clear. See the added new profiles (2D plots have been deleted).

Reviewer 2: P. 1915 L. 24: The peak at 20 cm is a single point that sticks out on one profile.

Authors: As mentioned above, seep sediments are generally very heterogeneous, i.e. single outstanding peaks are nothing surprising and usually no artifacts.

Reviewer 2: P. 1916 L. 3: Again a single data point that sticks out.

Authors: See above.

Reviewer 2: P. 1920 L. 11-13: Rephrase.

Authors: Sentence was deleted and porosity/permeability information was added at the beginning of the chapter.

Reviewer 2: P. 1920 L. 22-25: Redundant.

Authors: Deleted.

Reviewer 2: P.1921 L. 16-20: Sentence applies to vents, not to deep sea in general it is written.

Authors: No, we explicitly wrote "seep" sediments.

References

Cline, J. D.: Spectrophometric determination of hydrogen sulfide in natural waters, Limnol. Oceanogr., 14, 454-458, 1969.

Rusch, A., Forster, S., and Huettel, M.: Bacteria, diatoms and detritus in an intertidal sandflat subject to advective transort across the water-sediment interface, Biogeochemistry, 55, 1-27, 2001.

Rusch, A., Huettel, M., Wild, C., and Reimers, C. E.: Benthic oxygen consumption and organic matter turnover in organic-poor, permeable shelf sands, Aquat. Geochem., 12, 1-19, 2006.

Interactive comment on Biogeosciences Discuss., 7, 1905, 2010.