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Interactive comment on "Methane emission and consumption at a North Sea gas seep (Tommeliten area)" *by* H. Niemann et al.

H. Niemann et al.

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Comments to anonymous referee remarks.

Referee #1

1) Sulfate concentrations do not decrease to zero at the sulfate-methane interface in the three cold seep cores considered. This observation is interpreted as a sampling artefact. If this is the case, then a considerable error in the ex situ sulfate reduction and AOM rate measurements could have been introduced because rates of organic matter based and methane-based sulfate reduction are very likely dependent on the sulfate concentration. At other seep sites, however, non-zero sulfate concentrations below the SMI are interpreted as due to convective circulation of bottom waters into the sediment. Convection at cold seeps can be driven by salinity and/or temperature contrasts (Henry et al., 1996), entrainment in a gas flow (Haeckel et al., 2004) and emptying of subsurface gas reservoirs (Tryon et al.1999). The origin of the non-zero sulfate con-

centrations below the SMI at the North Sea sites should be discussed further, as well as the consequences of possible sample contamination on rate measurements should be addressed.

Non-zero sulphate concentrations have been measured at some cold seep sites. However, the publications mentioned by referee #1 (Haeckel et al., 2004; Henry et al., 1996; Tryon et al., 1999) are dealing with systems characterised by high fluid flow velocities and/or temperature gradients. I.e, mud volcanoes at the Barbados Trench (Henry et al., 1996; Martin et al., 1996) and Hydrate Ridge at the Cascadia convergent margin of the coast of Oregon, USA (Haeckel et al., 2004; Tryon et al., 1999). These systems are not comparable to the Tommeliten seep area. Henry et al. (1996) proposed that fluids and methane originate from clathrates in subsurface layers, which dissociates as a result of warm water circulation. It is furthermore proposed that seawater convects deep into the sediment (metres below sea floor) through high permeability channels such as cemented carbonate conduits. Although we did not measure heat flux, it seems unlikely that this phenomenon is significant at Tommeliten given the geological setting of the central North Sea. Furthermore, no temperature increase with depth was apparent and no traces for gas hydrates were found (water depth at Tommeliten is $<$100m). At Hydrate Ridge a penetration of sea water due to episodic, strong releases of gas has been proposed by Tryon et al. (1996) to explain distinct phases of negative fluid flow velocities. However, sulphate concentrations at Hydrate Ridge decrease rapidly to zero values (Haeckel et al., 2004; Treude et al., 2005). At Tommeliten, bubbling sites were found previously and during our expeditions, however, only strings of bubbles were emanating from the sea floor. The replacement of subsurface fluids may therefore play a significant role on a very localised scale. This may then foster AOM in near surface sediments leading to reduced conditions and the growth of thiotrophic, microbial mats which have been observed with the ROV. However, it is from our understanding very unlikely that displacement due to bubble rising and/or a buoyancy/heat circulation would be sufficient to draw sea water to a depth in the range of metres below sea floor at Tommeliten. In contrast, we think that the sedimentology of the Tommeliten sedi-

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ments causes a vertical and horizontal distribution of gas along gas bubble pathways, which deviates from typical SMTZ situations. However, a sampling artefact remains possible. This has been clarified in the manuscript. To avoid misunderstandings we have replaced SMTZ with AOM zone throughout the text, which appears more suitable for the situation at Tommeliten.

If sulphate was additionally introduced to the deeper cores by artefact, this will most probably not have a severe effect on turnover rates. Until now there is no marine, sulphate reducing bacterium known with a half saturation constant (K_m) >1mM. However, it is possible that we have overestimated AOM and SRR rates because of a higher sulphate availability as in situ. This is discussed in the manuscript. On the other hand, methane concentrations have a severe effect on methane dependent sulphate reduction as shown by the control incubations without methane (page 1211, section 3.5). Thus, limitations of the electron donor appear to be more important.

We understand that there is the need for some clarification within the manuscript. Thus, some addition with respect to the presence of non-zero sulphate concentrations in highly active systems as well as an estimate on the effect of sulphate contamination have been included in the revised manuscript.

2) In the abstract (line 11) and in page 1215, line 26, the authors conclude that: "From these observations it can be concluded that the seeps of the Tommeliten area contribute to atmospheric methane, especially during deep mixing situations in the North Sea ". This phrase implies that the observations presented in the article show that increased ocean-atmosphere methane fluxes occur in periods of deep mixing. It is better to state that the " contribution of seepage from the Tommeliten area is likely to be enhanced by deep mixing of North Sea waters ".

That is a good suggestion and the manuscript has been changed accordingly.

3) In the first part of the introduction the authors state that: "the contribution of this process [cold seepage] to the global methane budget and the carbon cycle are not

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well constrained ", and that: "The main challenge in constraining methane emission from the ocean is the need for quantitative estimates of the abundance and activity of cold seeps of ocean margins". The authors underline here the outstanding problem of quantifying the role of methane seepage to the global CH4 budget. However, their paper does not add knowledge in this field. As it is correctly explained at the end of the introduction, the authors aim is to " study microbial processes related to methane seepage in shelf sediments ". The beginning of the introduction should be focussed on the knowledge gap concerning the nature of cold seep biogeochemical processes in shallow seas. The question that the authors address in the paper has to be given more relevance in the introduction. Introductive material on the current ignorance on the role of cold seeps in the global methane budget should be cut considerably.

This aspect has been changed in the revised version of the manuscript. The role of cold seeps in methane budgets and the role of methane as a greenhouse gas are now just briefly addressed in the introduction in order to highlight the importance of seep studies. In contrast, the major part of the introduction focuses on biogeochemistry and seep related features. We therefore do not agree that more relevance has to be given to this topics.

4) A reference to figure 1 is needed in the introduction when the Tommeliten area is introduced. An inset in figure 1 should be added to show where the Tommeliten area is in the North Sea.

A reference to Figure 1 has been added in the introduction. We also added a North Sea area chart in Figure 1 indicating the Tommeliten seep area within the North Sea.

5) At the beginning of section 2.2 the length of the vibrocorer should be specified. This gives the reader an idea of the type of samples he should expected in the rest of the paper.

The length of the vibrocorer (4m) has been added in the material and method section

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6) The differences in the ratio of in vitro potential AOM and SR rates between the different sites (section 3.4) should be further discussed. What is the origin of the rather large variability (i.e. 1:1 ratio in core 1904 and 0.3:1 ratio in core 1866)?

The overall AOM and SR rates (in vitro as well ex situ) are very small and already close to the detection/quantification limit (0.1 – 0.5 nmol cm^{-3} d^{-1}) and 2 to 3 orders of magnitude lower in comparison to other seep sites. Hence, small differences in incubation conditions may lead to these effects. The sampling horizons for the in vitro rate measurements were rather broad (i.e., 20 – 50 cm), whereas the active AOM horizon is most probably narrower. Hence, it appears very likely that the subsampling procedure introduces this variability. This is now discussed in the manuscript

7) Page 1215, lines 10 to 21, finishing with " ..... Hovland et al., 1993). ": This is in troductory material and should go in the Intorduction section of the paper, where the Tommeliten seepage area is introduced.

This part could indeed be interpreted as introductory material. However, it is important to compare the previous observations with the present day situation. We therefore think that this paragraph improves the readability of the discussion and we would therefore prefer to keep it there.

8) Page 1218, line 13, the MDACs exposed at the surface of the sediment may also have been formed at the surface of the sediment. They are not necessarily formed in the subsurface and subsequently exposed due to erosion.

AOM is a strictly anaerobic process and the North Sea waters are- and have been oxic. The lipid data give evidence that carbonate formation and AOM coincided spatially and temporally. The only place where massive, methane related carbonate build-ups and living AOM Biomass were found above sediment surface are the permanently anoxic parts of the Black Sea. However, the precipitation of MDACs may have occurred just below the oxic interface in the sediment at times of higher gas flux -as we still see some small patches of reduced sediments covered by microbial mats today. An addition to

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"near surface sediments" has therefore been included the revised version.

9) Do the authors have an idea why the archaeal lipids in MDACs are isotopically lighter than those in the sediment (figure 7)?

We speculate that this is because of the putative source organism. Considering literature data of isotopic fractionations of ANME-1 and ANME-2, it appears that ANME-2 is characterised by a higher fractionation than ANME-1. Nevertheless, we do not know the carbon isotopic composition of methane in the system from the past. Thus, the lower δ^{13}C-values in MADCs may also derive from lower δ^{13}C-values of the methane substrate at the the time of carbonate formation. Moreover, biomarkers detected in the sediments may derive from more than one source, resulting in higher biomarker d13C-values in the sediment whereas MADCs biomarkers are formed right at the AOM hot spot. We have added this in the revised manuscript.

Section 2.6, title: The title should read: "Ex situ AOM and SR rate measurements ".

This has been included in the revised manuscript.

Section 2.6, equation 1: The rate of AOM appears on the left side of the equation as

" AOM ". It should be clear that this is a rate. A name analogue to SRR should be introduced for the rate of AOM and should be used in the rest of the paper.

We have used the common abbreviations found in biogeochemical literature on AOM. However, we will add "rate" in the formula.

Section 3.1, title: a better title could be " Water column and sea-floor observations ".

This is an excellent suggestion and has been included in the revised manuscript

Page 1210, line 11: I think the reference to lithology (1) should be changed to (2).

This is correct and will be changed in the revised manuscript.

Figure 1: The camera track on my pdf printout is barely visible. The minute indicator

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“ ’ ” is used in the latitudes and longitudes but degrees are divided in hundredths of a degree.

We will check this with the BG print office.

The position (Latitude and Longitude) is given in degree (°) and minutes (‘), which are then divided in deci-minutes. We think that the legend is formally correct.

Figure 4: The number of the core is missing in the legend.

This will be added in the revised version

Referee #2

The methane-sulfate transition zones detected share a common feature namely that sulfate penetrates into the methane zone. This is unusual as acknowledged by the authors and is explained by a artefact of the coring technique used, which apparently caused a smearing of the sulfate profile. What is however not clear is why this didn’t effect the methane and especially the sulfide profiles?

The Tommeliten seep area certainly differs from the typical SMTZ known from margin sediments. We think that this is mostly due to the sedimentology of the site, but we admit that a subsampling artefact is possible. This is now better explained in the manuscript. Also we have replaced the term “SMTZ” with AOM zone for a better understanding throughout the text.

If a sampling artefact took place, sulphate was most affected due to the subsampling procedure. The sulphide concentrations were measured with a macroelectrode, which was stuck immediately after sampling in the middle of the sediment core. Smearing therefore had a minor effect on these measurements. Subsamples for methane concentrations were taken just after opening the core, whereas subsampling for sulphate concentrations were second. We have improved clarity of this part of the manuscript in the revised version.

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Is there no other possible explanation for the deep sulfate profiles? For instance, the more-or-less solid marl may not support the growth of bacteria involved in anaerobic methane oxidation or subsurface porewater flows.

Yes, we have clarified this now in the text that the marl does not transport gas and hence profiles must deviate from a typical SMTZ profile.

There is quite a variation in ratios between sulfate reduction and methane oxidations rates, and they tend to deviate from the expected 1:1 ratio. There is however very little discussion on this.

We have added a comment on the error of the method at these low rates and the problem of subsampling a very thin AOM horizon

Discussion on fatty acid data suggests that the concentrations and compounds detected agreed with previous studies on ANME-I and -II dominated methane seeps. However, the relative contribution of the various compounds detected is very different from other observations. It was surprising to see major amounts of 18:2w6, which is a uncommon fatty acid in bacteria but is generally found in eukaryotes like certain algae, fungi and animals. This therefore indicates a major contribution of eukaryotic biomass, which is however not discussed and would be very surprising given the biogeochemistry of the system.

We are aware that $C_{18:2\omega6,9}$ is an unusual fatty acid for subsurface, benthic environments as this compound is rather typical for eukaryotes. DMDS adduct of poly unsaturated fatty acids are characterised by ring inclusions denoting the position of the double bonds (Mejanelle et al., 2002). However these DMDS adducts are found in the background of the chromatogram, which makes it difficult to extract clear mass spectra. After reviewing the DMDS mass spectrum we stepped back from the annotation of double bond positions of the $C_{18:2}$ fatty acid. Never the less, polyunsaturated fatty acids are commonly found in eukaryotes. However this seems unlikely at Tommeliten. At the surface, the $C_{18:2}$ fatty acid is comparably low in concentration (also indicating

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that this compound is produced *in situ* in subsurface sediments). Cholesterol, a typical component in eukaryotes shows, in contrast, a comparably high concentration at the surface but 5-fold lower concentrations at depth of the SMTZ. However, an origin from certain bacteria remains speculative. Isotope measurements of the $C_{18:2}$ fatty acid have been attempted but were not successful due to the partial co-elution of this compound with a UCM peak. However, the fatty acid appears to have a δ^{13}C-value of –25 to –30L' directly indicating that the source organism is not involved- or feeding on AOM biomass. We have now mentioned that high abundances of a $C_{C18:2}$ fatty acid in subsurface sediments are atypical but that this component is not AOM related. However, we think that further discussions on the origin of this and other non-AOM related lipids remain hypothetical and exceed the frame of the manuscript.

Another unusual feature is the ratio between monounsaturated 16-carbon fatty acids. In subsurface samples, more 16:1w9c was detected than 16:1w7c, whereas this is highly uncommon in organisms. Although major efforts were made, the authors may want to have another look at the identification of these unsaturated fatty acids.

We are aware that higher amounts of $C_{16:1\omega9}$ than $C_{16:1\omega7}$ (4 : 1) are unusual, whereas abundances as found in surface sediments with major amounts of $C_{16:1\omega7}$ and minor amounts of $C_{16:1\omega9}$ (0.2 : 1) reflects expected ratios. The identity of $C_{16:1\omega9}$ and $C_{16:1\omega7}$ has been verified by the analysis of their DMDS adducts and by graphical overlays of sample chromatograms and those containing known compounds. However, the δ^{13}C-signature of $C_{16:1\omega9}$ does not give indications that the source organism of this compound is involved- or heterotrophically feeding on AOM biomass. As with the $C_{C18:2}$ fatty acid, the source of $C_{16:1\omega9}$ remains speculative and is not, from our understanding, of important for the manuscript.

We agree that there is a need to mention this point in the revised version of the manuscript.

The reference to Blumenberg et al lacks page numbers.

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This has been added in the revised version of the manuscript.

Included the core number in Fig. 4.

This has been added in the revised version of the manuscript.

Editors suggestions:

[. . .] I suggest to shorten the abstract (to improve readability) and to replace S2- with total H2S since S2- does not exists given the pK value of 18.

The abstract has been shortened to some extend and $H_2S/HS^-/S^{2-}$ are replaced by total sulphide.

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