Response to editor and reviewer comments

We thank all reviewers for commenting on our manuscript and their effort to provide a constructive review. We considered each comment/suggestion and accordingly changed the manuscript. Our replies can be found below each comment.

The main changes comprise:

- Removing the model
- Rewriting the discussion about methane oxidation rate
- Showing the UWMS-data in time versus methane concentration plots instead of the Box-Whisker-plot
- Including more discussion about discrete sampling, isolated plumes, internal wave breaking, and sea-air flux
- Editing the entire manuscript for more clarity

The changes are highlighted in font color blue in the manuscript.

Associate Editor Decision: Reconsider after major revisions (09 May 2015) by Tina Treude
Comments to the Author:
Dear Susan and Coworkers,

thank you very much for submitting your revised manuscript to Biogeosciences.

After your revision, your manuscript was sent out to three referees for a second round of review. The reason for this thorough second review was that during the first review several referees raised concerns about the applied model. One referee considered the shortcomings of the model so severe that he/she rejected the manuscript.

In the second round of review, the revised manuscript was sent to one of the former referees (report #1) as well as to two new referees (report # 2 and #3). As you can read from report # 2 and #3, two referees again raised major concerns against the model approach as being too over simplified and not appropriate even just for the purpose of checking whether your hypotheses are correct. Both referees strongly suggest removing the improper model from the (valuable) dataset.

In the light of these strong criticisms raised against the model in both rounds of reviews, I can only follow the referees' advice and ask you to remove the model before resubmitting a revised version of the manuscript to Biogeosciences. All referees (past and present reviews) are confident that the dataset is strong and valuable without the model. The revised manuscript will then be sent out for a third round of review. Please be aware that after this last review, I will accept only minor revisions.

I further advice you to also carefully follow the referees' comments that are not dealing with the model; specifically the criticism/advice regarding microbial activity raised in report #1.

Some editorial comments on the manuscript:

I have a bit trouble following the argumentation that activity is low (based on a constant k') even at high methane turnover rates. At higher methane concentrations, the tracer is diluted by more unlabeled methane and hence the microbes have to be more active to turn over the same fraction of tracer in the same period of time as if the methane concentrations were lower. The relationship between high methane = high turnover vs. low methane = low turnover is healthy when concentrations lie within the linear part of the enzyme kinetics. Please check your argumentation or extend the discussion by comparing actual k' values with turnover and methane concentration to provide more clarity.

Reply 1: We rewrote the discussion and included the suggested comparison of *k'* values with methane oxidation rates and methane concentrations. We also provided evidence for the linear relationship between methane concentration and methane oxidation rate, i.e., that most of our measurements fall onto the linear part of enzyme kinetics. Page 15 line 495 ff.

Table 2 indicates that in some incubations (24hrs) about half of your tracer/methane was turned over (rate of 840 nM/day vs CH4 of 1628 nM). Such a high tracer/methane turnover in a closed system is critical (but unfortunately sometimes unavoidable in the field), because rates might not have remained stable over the incubation period, which would lead to an underestimation of the potential rate. It would be good to shortly discuss this aspect.

Reply 2: In the example given, *k'* is 0.5, that is higher than *k'* of most of the other samples. As you mentioned this might be due to the closed system, where biomass might have increased and/or activity of methanotrophs increased. However, *k'* should become lower with higher methane concentrations according to enzyme kinetics, when enzymes become more and more saturated. In this case, the rate would be an underestimation. In our case it rather appears that in some bottles there was growths increasing *k'*. We included a brief discussion about our measured elevated *k'* values. Page 15 line 513 ff.

I hope you are not discouraged by the criticism regarding the model. We are very much looking forward to receive your revised manuscript.

With kind regards
Tina Treude
BG Editor

Report #1

Submitted on 13 Apr 2015
Anonymous Referee #3

Anonymous during peer-review: Yes No
Anonymous in acknowledgements of published article: Yes No

Recommendation to the Editor

1) Scientific Significance Does the manuscript represent a substantial contribution to scientific progress within the scope of this journal (substantial new concepts, ideas, methods, or data)?	Excellent **Good** Fair Poor
2) Scientific Quality Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way	Excellent **Good** Fair Poor

(consideration of related work, including appropriate references)?

3) Presentation Quality Are the scientific results and conclusions presented in a clear, concise, and well structured way (number and quality of figures/tables, appropriate use of English language)?	Excellent **Good** Fair Poor

For final publication, the manuscript should be

accepted as is

accepted subject to **technical corrections**

accepted subject to minor revisions

reconsidered after **major revisions**

I would like to review the revised paper

I would NOT be willing to review the revised paper

rejected

Please note that this rating only refers to this version of the manuscript!

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

I still recommend omitting the 14C tracer experiments. Yes, by adding 14C-CH4 the methane concentrations were increased, but if the MOX rate is limited by methane, why are the 14Crates very much lower than the rates measured with 3H-CH4 ?? And the 500 nM concentration (resulting from the added 14C tracer) are still within the range of the linear Michaelis Menten kinetics, as shown in figure 8.

Reply 3: True that elevated methane concentrations should result in elevated rates, the discrepancy cannot be readily explained by MM-kinetics, one could assume that one was still in a lag-phase and, thus, bacteria did not respond to elevated methane concentrations, however as we have no proof for the lag-phase assumption, we omit these results as suggested.

I also still not see the advantage of calculation k via the slope of a regression line versus an average of the single measurements. The number of data points should be the same for each way. Especially as there seems to be a mistake in the kinetic approach. In environments with low methane concentrations, methanotrophs are thought to have a high substrate affinity, resulting in low Km values AND low vmax. While in methane rich environments we find a low affinity, with high Km AND high vmax. Thus I suggest omitting this paragraph and calculate k as average of 120 data points.

Reply 4: It is correct that *k'* derived by linear regression and the average *k'* provide the same result. We omitted the paragraph.

Report #2

Submitted on 13 Apr 2015
Anonymous Referee #5

Anonymous during peer-review: Yes No
Anonymous in acknowledgements of published article: Yes No

Recommendation to the Editor

1) Scientific Significance Does the manuscript represent a substantial contribution to scientific progress within the scope of this journal (substantial new concepts, ideas, methods, or data)?	Excellent **Good** Fair Poor
2) Scientific Quality Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way (consideration of related work, including appropriate references)?	Excellent Good **Fair** Poor
3) Presentation Quality Are the scientific results and conclusions presented in a clear, concise, and well structured way (number and quality of figures/tables, appropriate use of English language)?	Excellent **Good** Fair Poor

For final publication, the manuscript should be
accepted as is
accepted subject to **technical corrections**
accepted subject to **minor revisions**
reconsidered after major revisions
I would like to review the revised paper
I would NOT be willing to review the revised paper
rejected

Please note that this rating only refers to this version of the manuscript!

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)
Comments to revised version of Mau et al. and related reviews:

After reading the revised version of Mau et al., the supplement, and all related reviews I am convinced that the measured data set and observations should be published. Especially the summer/winter comparison of dissolved methane distributions and Mox activities are rare data sets and should be brought to public. However, my feeling is that the authors should focus on the microbial and dissolved methane studies at the gas seepage site as their oceanographic data recording was limited during their sampling campaign. In the following summary I highlight some specific issues which were also raised during the review process by the reviewers involved before.
I have no further suggestions related to reviewer#1 comments as they are fully acknowledged and the mainly microbiological and kinetic arguments are considered in the revised manuscript.
Whereas reviewer#1 is generally positive, the comments of reviewer#2 are more critical and his arguments mainly focus on the weaker part of the manuscript (the oceanographic

constraints and modelling attempts).
Unfortunately, the authors failed to monitor the local oceanographic conditions during their measuring campaigns (e.g. by using ADCP, Microstructure CTD). Instead they have to rely on published (general) or estimated (modelled) current data. The missed chance to measure the current regime during sampling campaigns is a big lack of the paper, and limits a sound “methane release” story for the study site.
It is hard to compare UWMS data with Niskin bottle data. A table with Niskin CH4 data would help (Appendix).

Reply 5: such a table was added as appendix

Furthermore a time vs. concentration plot for the different water depth tracks would help to understand the local (3D) concentration pattern at W2/W8 area.

Reply 6: We exchanged the Box Whisker plot with the suggested time vs. concentration plots. See Fig. 5

The methane concentration determination by using HS-technique was performed with 55 ml seawater aliquots. It depends on the exact GC configuration, but my first guess is that detection limit is in the range of normal background levels of atmospheric methane equilibrated with seawater (2-3 nM). Could you verify that the high surface methane concentrations (around 20 nM) are not created by upscaling the ppm values from the head space to a nM concentration?

Reply 7: We derived the nM concentration as described in Magen et al. (2014) using the partial pressure of methane measured, the volume of headspace and water and the Bunsen coefficient. Page 5 line 146

Reviewer 2 asked for CH4 concentration profile data (CTD sampling). This data should be plotted/shown (e.g. figure with concentration log-scale vs depth in an appendix).

Reply 8: has been added as Supplementary Material 4

Reviewer#3 mainly focusses on determination of rate constant and Mox activity and sees also severe problems in the box modelling and transport approaches. Many of his comments are discussed in length in the authors’ answers. Maybe these answers should also be included in the revised version to some extent?

Reply 9: We rewrote part of the methane oxidation interpretation (see section 4.2) as well as included statements of the replies to reviewer #3 in the method section (Page 7 line 239 ff.).

Mox rate constant calculations based on a narrow range of methane concentration data are highly questionable (reviewer#3). This problem is still the case in the revised version.

Reply 10: see reply 4 above

Reviewer#3-Authors’ reply10: the reply does not help. Bubbling intensity (frequency, bubble size, CH4 init., other gases?) may vary but water column imaging with echosounding could still suggest “intense” seepage. The bubble stream must be visually observed or detailed frequency-dependent multibeam investigations are necessary to give a sound argument here. Winter and summer echosounding data should have been compared in the study!

Reply 11: We collected echosounding data only in the winter time. Page 4 line 110

I also agree with reviewer#4's (Kessler) concerns about the sampling: the water sampling by discrete vertical hydrocast sampling along a straight 6 km line crossing the release sites. The chance to miss isolated CH4 plumes is extremely high, especially when sampling strategy is not adapted to tidal current direction changes, which could be perpendicular to the profile direction. Furthermore, hitting subsea targets by using a non-DP vessel in the North Sea (rough weather?) is challenging. The authors' answer to the sampling issue is not helpful. In principle they agree, but the issue is addressed by adding a few general words in line 564 only. The sampling problem needs some more discussion by e.g. estimation of dissolved CH4 plume diameter (concentration gradients) and lateral plume shift relative from the release site during sampling.

Reply 12: We extended the discussion and included the suggested estimation, see page 14 line 466 ff.
'We considered whether the low observed concentrations during winter may be due to the fact that during this survey we only partially sampled isolated plumes. Although the east-west-transect directly crust the cluster 1 flares (Fig. 2) and was oriented in direction of the tidal movement in that area, the stronger northward component of the current in winter (Supplementary Material 2 and 3) displaced methane plumes more rapidly than in summer. The elevated methane concentrations at the central seep site and along the western transect (although with much lower methane concentrations) suggest that we indeed sampled methane plumes (Fig. 4B). We note that the horizontal concentration gradient in surface water were 0.01 to 0.02 nM m^{-1} during summer and winter, respectively. As a first order approximation we take the highest concentration measured (39 in summer and 73 nM in winter) and a general current speed of 0.2 m s^{-1} to estimate a plume size of ~4 km in diameter that would take ~5 h to cross our sampling transect. Since we always sampled 5 stations in ~3 h for the eastern or western segments of the transect, it seems rather unlikely that we completely missed a methane plumes.'

The water column images of B13 gas flares observed during summer cruise should be presented.

Reply 13: see reply 11 above

I wonder if echosounder signals reflecting bubble streams are also visible up to 6 m water depth in summer indicating bubbles in the upper water layer. Schroot et al., 2005 e.g. presented echosounder images of gas flares emanating from the seafloor in the same area (B13) reaching at least up to 10 meter below sea level. This is well within the upper layer and was imaged during the summer stratification period (August, 2002).
The 250 nM CH4 measured above the thermocline in July 2013 (revised version) also indicates efficient vertical methane transport into the upper water mass probably by bubbles (e.g. McGinnis et al., 2005 and 2011). It demonstrates that gas bubble transport of methane cannot be neglected in the model. Therefore initial bubble sizes and gas content should have been measured (see also referee 2).
Moreover, bubble dissolution is affected by stratification by separating micro-bubbles from main bubble streams. Microbubbles can be laterally transported within the thermocline (tides, main current regime).

Reply 14: The model has been removed as such data were not collected.

Conclusion
The field data comprises a valuable data set and a proper description and discussion of all measured data (including UWMS concentration patterns, which was also asked for by rev#2 and #3) would be fine in such a paper about methane release from shallow gas pockets, dissolved methane concentration distribution in the North Sea, and CH4 degradation by Mox. However, I do not suggest publishing it with having a weak and maybe misleading box model as a bag-pack. The authors answer to the harsh criticism of reviewer#2 about their modelling approach is “Our simple model is rather thought to check if our hypothesis to explain our data is correct.” However, what does it mean when the model is incorrect or inappropriate to describe the real situation?

Reply 15: The model has been removed.

Report #3

Submitted on 24 Apr 2015
Anonymous Referee #6

Anonymous during peer-review: Yes No
Anonymous in acknowledgements of published article: Yes No

Recommendation to the Editor

1) Scientific Significance Does the manuscript represent a substantial contribution to scientific progress within the scope of this journal (substantial new concepts, ideas, methods, or data)?	Excellent Good **Fair** Poor
2) Scientific Quality Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way (consideration of related work, including appropriate references)?	Excellent Good **Fair** Poor
3) Presentation Quality Are the scientific results and conclusions presented in a clear, concise, and well structured way (number and quality of figures/tables, appropriate use of English language)?	Excellent Good **Fair** Poor

For final publication, the manuscript should be
accepted as is
accepted subject to **technical corrections**
accepted subject to **minor revisions**
reconsidered after major revisions
I would like to review the revised paper
I would NOT be willing to review the revised paper

rejected

Please note that this rating only refers to this version of the manuscript!

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

This paper has two components, a well written component on microbial oxidation, and a poorly written component on the fate and transport of methane in which the authors try and use an overly simplistic model to interpret a sparse data set. Underlying the concern, the text is filled with numerous incorrect statements regarding bubble mediated transport that suggest the authors are far from expert in the field.

For example, on line 75, the authors state McGinnis et al (2006) showed only bubbles shallower than 100 m can reach the sea surface; however, Solomon et al. (2009) in a field study showed that bubbles from 550 m do reach the upper wave mixed layer. The author than quotes Mau et al for the SB channel that half the methane reaches the atmosphere; however, neglects that Clark et al (2000) – showed about half directly reaches the atmosphere in the near field from bubbles and near plume turbulence. And Clark et al (2000) is cited in Mau et al! However, as this paper is for seeps in 45 m, its unclear why she is incorrectly trying to argue about the fate of bubbles deeper than 45 m water based on incorrect and unstated assumptions.

Reply 16: Indeed Solomon and co-authors showed indications that bubbles from 550 m depth could reach the surface, but a more recent survey by Hu et al. (2012) showed that except of a few isolated patches, which are in addition temporarily constrained, the general contribution of methane to the atmospheric methane budget is low from these deep sources. Mau et al. (2012) reports the fate of the dissolved methane, while Clark et al. (2000) reports on the gaseous phase. Taking these two studies together, one can roughly say, that half of the gaseous phase reaches the atmosphere directly and the other half is dissolved, of the dissolved part again half reaches the atmosphere indirectly via sea-air flux and the other half remains in the ocean and is oxidized.
However, we omitted the paragraph as it is not relevant as suggested by the reviewer.

There are many aspects that in general I find extremely troubling. For example, even after reviewers pointed out that turbulence transport in the ocean is not molecular (Fickian), the authors kept the formula using the well known symbol for molecular diffusion, D. I recommend no more erudite a source than wikipedia, "Fickian Diffusion" is for molecular. If you mean eddy diffusion (and you do), then DO NOT call it Fickian! This is really basic stuff (Fluid dynamics 101), and it is very alarming that after reviewers pointed it out, the authors did not understand this point.

Reply 17: We found lecture notes and book chapters that state that turbulent flux behaves as a Fickian diffusion, see for example:
http://www.mit.edu/course/1/1.061/www/dream/SEVEN/SEVENTHEORY.PDF
http://users.itia.ntua.gr/panospap/DPMS_PERIBALLONTIKH%20YDRAULIKH/Other_Material/Roberts_Turb_Diffusion.pdf.
In order to limit confusion, we changed the D to κ and wrote: 'If advective transport were to be uniform, then it would simply displace methane, but differences in current velocity and direction with depth lead to turbulent mixing, i.e., eddy diffusion. The strength of small-scale motions that act to smooth out concentration gradients can be parameterized by the eddy diffusivity κ , such that mass transport is proportional to the mean concentration gradient (Largier,

2003; Roberts and Webster, 2002)'. Page 7 line 239 ff.

Meanwhile, the authors have (unmeasured) ranges of kE that can realistically span an order of magnitude yet they claim that the uncertainty in their results are 25% from non-linearity in the wind gas exchange rate. This is not a reasonable uncertainty analysis, this is an effort to sweep an uncertainty that makes the overly linearized approach with no fluid dynamics data under the rug of meaningless interpretation.

Presentation is poor to highly deceptive.

For example, why represent concentrations as a whisker plot? And how can the ¼--3/4 box sit at 0 on several of the data groups, with negative concentration for the lowest quartile? Such errors make me wonder if the authors really critically reviewed the manuscript before submission.

Reply 18: The UWMS has a detection limit of 16 nM, all measurements below this limit were recorded as 0. Therefore, the 1st quartile and in the case of the 10 m water depth records even the mean is 0. However, we exchanged this figure see reply 6.

To highlight another significant troubling concern, the in situ mass spec data were collected over a significant fraction of the tidal cycle, yet no effort was made to correct for where downstream and where upstream were at the different depths which correspond to shifts in the tidal flows. This means the contour plots (Fig. 4) likely is somewhere between meaningless and deceptive for use in an underlying a flux model, and the authors have no atmospheric data to estimate direct and indirect transfer to the atmosphere.

Reply 19: The UWMS-data was included in the manuscript to show that the stratification persists over the tidal cycle. The contour plots show methane concentrations analyzed from discrete samples/CTD-rosette samples and not from UWMS data. As there are other concerns about the model, this section was deleted.
As for the estimation of the sea-air flux, we used an atmospheric methane concentration measured at a station close to the study area similar to numerous other papers. One can also find often the use of more or less recent global tropospheric methane concentration. In our case the Ocean Station M, Norway, as in Schneider von Deimling et al. (2011), was the closest to get data from. Indeed this concentration can vary as shown e.g. by Hu et al. (2012) from 1.71-3.83 ppm methane in the northern Gulf of Mexico. However, in the manuscript we state an error of one order of magnitude, the error as a result of variable methane concentration in the atmosphere falls within this overall error. Page 9 line 281 f. and page 17 line 580 ff.

In fact, this is my main issue – several reviewers have pointed out that this is a complex three dimensional system with no velocity measurements, and should be modeled as 3D. The authors response was IMO unsatisfactory, and model validation is impossible as they have no atmospheric measurements. Yes, physicists model cows as spheres, but that gives absolutely no insight as to how they will bounce when dropped. The data clearly hint at complexity in the source (the intrusion at -10 m demonstrates significant bubble transport to near the surface, they have no idea of direct transport, but wave it away by claiming an exponential decrease with height, which is only true for small bubbles – but of course they have no size data. The CTD data suggests internal wave breaking, never mentioned, as a mechanism for vertical transport.

Reply 20: We assume that the CTD data rather indicate successive warming of the surface (Pomar et al., 2012) instead of internal wave breaking. But internal waves cannot be rules out in the study area, close to the Dogger Bank. Unfortunately, we did not take a time series of CTDs at the same location due to time constriction, thus we don't have data to verify any internal waves. However, we discuss this topic in relation to the vertical diffusion coefficient. Thank you for pointing out this mechanism. Page 17 line 575 ff.

The truth is that anyone who has worked in the North Sea knows there is significant complexity in water motions both above and below stratification. Thus, a 1-D model based on many untestable assumptions with no direct water column velocity measurements to ground it is as likely to lead to incorrect interpretation rather than a qualitatively informative interpretation.

Reply 21: The model was removed from the manuscript.