Biogeosciences Discuss., 11, C8974–C8982, 2015
www.biogeosciences-discuss.net/11/C8974/2015/

# *Interactive comment on* “Seasonal methane accumulation and release from a gas emission site in the central North Sea” *by* S. Mau et al.

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Received and published: 6 March 2015

Interactive comment on “Seasonal methane accumulation and release from a gas emission site in the central North Sea” by S. Mau et al. Anonymous Referee #3 Received and published: 5 February 2015

The manuscript of Mau and co-authors describes the distribution of methane at a methane seep in the North Sea, together with the microbiological methane consuming process, its oxidation. The authors provide data from classical water sampling and additional in situ measurements of the methane concentration. Methane oxidation rates were measured with 3H-tracer, as an appropriate method. Thus, altogether a valuable data set. However, I have difficulties with the modelling part and the kinetics of the Mox rates of the manuscript. I therefore suggest "major revision“.

Modelling 1) Based on the in situ data of methane, the authors have a 3-dimensional data set at hand. Thus it is not clear, why they restrict these data to simple box plots and further restricts the modelling to a 2-dimensional model. At the study site a 3-dimensional model with transport processes in all (or at least 4) directions would be more appropriate.

Author reply 1: We show 2D methane concentration data that are concentration profiles throughout the water column taken along a 6 km transect. We also show in situ UWMS-measurements that were collected near an active seep site in a very small area of 125 m by 150 m (Fig. 2). Therefore, the transect data show a much larger scale than the UWMS-data. The UWMS-data were included to prove that methane concentrations are similarly distributed over the tidal cycle in summer. For comparison of the two data sets (discrete sampling by CTD/rosette and UWMS-records), we found that a contour plot of the discrete samples and a box plot of the UWMS-records are most illustrative. The model was used to correlate summer and winter methane concentrations and methane oxidation rates collected along the transect. The model is restricted to 1 dimension, the vertical dimension or height of the water column, which is (1) defined by the direction of the sea-air flux, which is one of the major sinks of dissolved methane in the water column. Furthermore (2), the main difference between summer and winter data was the seasonal thermocline, which limits the vertical transport also in the dimension of the water column height. As we mentioned in the response to the second reviewer, if horizontal effects would be taken into account (3D), then the source term would need to be increased. The added quantity of methane would be horizontally advected and dispersed, but the vertical exchange processes would remain the same. Moreover, we would have been forced to include additional parameters such as the horizontal eddy diffusivity that all add uncertainty to the outcome of the model.

2) The transport processes used for the modelling are not clear to me. The authors neglect the advective process, as " currents only transport the water from the methane seep away“. However, by doing so, at the study site the methane concentrations will

decrease as methane rich water from the seep will be displaced / mixed with methane poor water. Thus, I think that dilution / mixing of water bodies through currents is an important factor, which should not be neglected.

Author reply 2: The same issue was raised by the second reviewer. We include our response to the other reviewer here again: We agree that currents affect methane distribution, however, currents transport the methane, but do not decrease the concentration as no concentration gradient is included in the equation of the advective flux. Largier (2003) put it that way: “The diffusive flux is then determined by the “eddy diffusivity” K that parameterizes the strength of small-scale motions and acts to smooth out gradients (whereas advection simply displaces them).” and also “advection is the mean movement and diffusion is the spreading out.” We drew a sketch to show the influence of advection/currents (Fig. 1 in the response to reviewer 2) showing that independent of the current velocity, the vertical concentration profile would always look similar: the concentration would exponentially decrease with distance to the seafloor. In addition, the seasonal thermocline will always limit vertical transport, thus, the model is qualitatively correct, but not necessarily quantitatively.

3) The description of the turbulent diffusion seems to me not correct. Fick law of diffusion handles molecular diffusion with only the concentration gradient as driving force. In the case of methane in the North Sea I think that eddy covariance calculations would be more appropriate. The cited literature of Largier 2003, seems to be not appropriate as it is dealing with the distribution of particles and not dissolved molecules by advection!! and diffusion. There are some studies modelling the methane distribution in shallow sea, however they are using numeric modelling. Grunwald, M., Dellwig, O., Beck, M., Dippner, J. W., Freund, J. A., Kohlmeier, C., . . . Brumsack, H.-J. (2009). Methane in the southern North Sea: Sources, spatial distribution and budgets. Estuarine, Coastal and Shelf Science, 81(4), 445-456. Wahlström, I., & Meier, H. E. M. (2014). A model sensitivity study for the sea–air exchange of methane in the Laptev Sea, Arctic Ocean. Tellus B, 66, 24174.

Author reply 3: Fick’s law is not only used for molecular diffusion, but also for eddy or turbulent diffusion in the ocean or large lakes. Wahlström, I., & Meier, H. E. M. (2014) used also turbulent diffusion and a reservoir to calculate the change of concentration over time and depth, similar to our approach; they wrote:

$\partial C/\partial t+W*\partial C/\partial z=\partial/\partial z*(\Gamma C*\partial C/\partial z)+SC$ (1)

where x is the dependent variable (methane concentration in our case), t time, z vertical coordinate, W (m s-1) vertical water velocity, $\Gamma C$ (m2 s-1) the exchange coefficient (also named diffusion coefficient) and SC is the source and sink term for the dependent variable. The first term to the right represents turbulent diffusion and is according to Fick’s first law. In this paper and also by Soetaert and Herman (A practical guide to ecological modelling, 2009, Springer) is stated that turbulent eddy diffusion applies not only for particles, but also for molecules. The turbulent diffusion coefficient is much larger than the molecular diffusion coefficient (diffusion in water (molecular) ∼ 10ˆ-11 – 10ˆ-7 m2/s, vertical diffusion in the ocean, kz ∼10ˆ-5- 10ˆ-3 m2/s, horizontal diffusion in the ocean, kx ∼ 1 - 1000 m2/s). Largier (2003) was cited as we used the horizontal diffusion coefficients reported in this paper. Largier wrote: “Further, a comparison of different studies indicates an exponential increase in Ky with distance from the shore (Fig. 3A): in wave-driven nearshore waters (y∼0.1 km) values on the order of 1–10 m2/s are found (Smith and Largier 1995), whereas values on the order of 100 m2/s are found over the wind-driven shelf (y∼10 km; Davis 1985, Largier et al. 1993), and much larger values on the order of 1000 m2/s or greater are found in the offshore waters of the California Current (y∼100–1000 km; Swenson and Niiler 1996).’ Eddy covariance is, as far as we know, applied in the atmosphere to calculate vertical turbulent fluxes within atmospheric boundary layers. This technique is also used to derive benthic oxygen fluxes between seafloor and overlying water. Covariance means that two variables vary, wind and concentration vary in the atmosphere, oxygen concentrations and vertical velocity vary near the seafloor in the case of oxygen fluxes. Both variables are measured. What we have are vertical methane concentration profiles, but no measurements of vertical displacement. Therefore, we cannot use this technique. Furthermore, Sundermeyer and Price (1998) wrote: “Put another way, mixing processes are those which can (or must) be modeled by diffusion, i.e., molecular or very small-scale advective processes in which individual exchange events are not resolved, while stirring processes are resolved events, e.g., the streaking and folding of a tracer within a resolved eddy field.”

Kinetics of MOx I cannot follow the conclusion that MOx rates are low. The MOs rates from this study lay well within the range of other marine areas, as the authors state. And even a comparison of the turnover times, which is independent from the M.conc. show that data from this study (100 d) are comparable with 80 - 1000 d from Gentz et al 2013, or 127 - 455 d from the Baltic Sea ( Jacobs et al 2013). There are two ways of calculation k’ the first order constant. It can be obtained via arithmetic, i.e. calculation the average or median of the single measurements or – as suggested by the authors – graphically i.e. the slope of the linear regression. However, if using the latter one has to prove / test the linearity of the relation and give as well the confidence interval of the regression line. But no matter how k’ was calculated, it still will be only k’ in the end.

Author reply 4: The reviewer is completely right that k’ is still k’ in the end, no matter how one derives the value. We could have also just taken the average of all k’ and state the turnover time of 100 d to point out that the activity of methane oxidizing bacteria is low. Our main point is that high MOx-rates do not indicate a highly active methane oxidizing bacterial community. If one has a k’ of 0.01 d-1, but different methane concentrations, e.g. 1000 nM and 1 nM, then one would get MOx-rates of 10 nM/d and 0.01 nM/d, respectively. The former suggests a fast consumption of methane whereas the latter a slow consumption, but actually the uptake rate of methane (or the activity of the bacteria) is the same.

The authors also use data from literature of the Km and a range of marine Mox rates to interpolate a Michaelis Menten kinetics. However, the methane concentrations of this study are in very low range and not even near the half-saturation concentration (1–

12M = 1.000 -12.000 nM). For a kinetic study to obtain vmax or Km much more data with a broader range of Mconc are needed. See also Lofton et al 2014. Thus I do not follow the interpolated values of vmax and Km given in the text and in figure 7.

Author reply 5: In Fig. 7A we show the range of kinetically possible uptake of methane by methanotrophs using Km and maximum MOx-rates published in literature. This figure shows that methane oxidation ranges from a rapidly increasing uptake of methane as soon as methane is available (MM1) to a slowly increasing methane-uptake although methane concentrations reach high values (MM2). In Fig. 7B we fit a MM-curve to our data, that is, we adjusted Km and vmax starting with the MM2-values until a good fit was reached. As noted in the response to the first reviewer having a related comment; the fitted curve has a R2 of 0.81 in the range of our data. However, the reviewer is right that there is no proof beyond Km. Therefore, we will rewrite the section and include a linear fit to the data assuming that we are in the linear range of the MM-kinetics based on the literature values. The linear fit gives a k’ value of 0.01 d-1 with an R2 of 0.82. However, this k’ is based on 120 measurements instead of only replicates (n=2-3) or a time series (n=6-9). Therefore, k’ is still k’ but statistically more precise.

Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/11/C8517/2015/bgd-11-C8517-2015-supplement.pdf

How much water was filtered? This would be important to know to explain the failure of the PCR to detect any methanotrophs.

Author reply 6: A similar comment was raised by reviewer 1. Here is our response: We think that our DGGE-results are reliable, because we filtered 8 L of water, had good DNA-extracts, and used sufficient DNA for PCR. The quality of the winter samples was not as good as the quality of the summer samples, but from our experience with pelagic samples, the results are plausible, too.

I do not think that Ficks first law is valid here. It deals with molecular diffusion, assuming no turbulence or water movement. I think turbulent, eddy correlation would be more appropriate here. Furthermore, I do not see why this diffusion (if any) would only occur in two directions (west and east) but not north and south. So, the two dimensional assumption is difficult to support in a three dimensional water column.

Author: see reply 3 above

As I am not really convinced of the validity of the basic model (see above) I do not comment on the further application of this model.

Author: We described the validity of the equations in reply 3 above, which are the fundamentals of the model.

But in section 3.1 you state that there was no influence of the tides on the seepage intensity ????

Author reply 7: That is correct and the UWMS-data confirm this statement.

It would be nice to have a contour plot of the MOX-rates as well, for better comparison with the methane concentrations.

Author reply 8: Figure 7 shows the direct comparison of methane concentration and methane oxidation rates, thus, we think that a contour plot of MOx-rate data is not necessary. Moreover, we don't have a sufficient comprehensive data set of MOx-rates that would result in a reliable contour plot. Measurements were performed in five distinct water depth at each station and were partly excluded as some measurements were below the limit of detection.

But this is very strange if more methane is added to the sample, one would expect higher oxidation rate, but they seem to be lower than the 3H-rates??? I suggest omitting the 14C-data.

Author reply 9: We found similar results in Storfjorden, Svalbard (Mau et al., 2013). There, we suggested that the methane-oxidizing-community is not capable to consume more methane and, thus, cannot utilize the additional high methane load provided if

using 14C-CH4 adding ∼500 nM in contrast to adding about 2-3 nM in the case of 3H-CH4. In this paper, we further proposed that the use of 14C-CH4 as tracer allows to identify if methane oxidizing microorganisms in a water mass are capable to consume elevated methane concentrations or not.

This is an unexpected finding. Did the authors run positive controls to be sure that the PCR was working at all? How much water was filtered on the filter?

Author: see reply 6 above

But a lower seepage rate in winter would also lead to lower methane concentrations. . .

Author reply 10: Certainly, the seepage rate can be variable in time. However, the gas flare observations shown in the paper are observations of seepage in the winter that indicate an intense seepage although dissolved methane concentrations are low.

Figure 2: numbers for the clusters are much too small!, correct July 2013 (S12-20) and January 2014 (W2-12)

Author reply 11: We will change the number size and figure caption accordingly.

Figure 4: Are there 2 stations with 0 km? In the figure there are different sampling depth for the eastern and western transect. But three scales for 4 figures are too much. You could try with a log-scale or two scales with some data above or below the scale.

Author reply 12: Yes, there are two stations at 0 km as described in the method section. We corrected the different depth scales, but think that less scales for methane concentrations would decrease the information provided by the measurements.

Figure 5: It would be nice to show the MOx-rates in the same way as the Mconc in figure 3. Thus it would be more evident where the MOx-rates are elevated. As pointed out in the discussion, the turnover time or k' are also important parameters, thus it would be nice to also depict them. The figure on the linearity of the incubation time is a basic assumption and could go to the supplementary info.

Author reply 13: Please refer to the reply 8 above for illustration of MOx-rates. We will include a supplementary figure that shows the measured k'. We included the figure of the time series to show that only a small amount of the tracer was oxidized by microroganisms over four days suggesting a slow uptake of methane and confirming our hypothesis that microbial methane oxidation is a small sink of methane in the research area.

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Interactive comment on Biogeosciences Discuss., 11, 18003, 2014.