

Author's response

“Annual variability and regulation of methane and sulfate fluxes in Baltic Sea estuarine sediments” by Joanna E. Sawicka and Volker Brüchert

Anonymous Referee #1

1.) General Comments

The paper investigates the effects of changes in temperature, benthic oxygen concentration and eutrophication on the sediment concentrations and fluxes of methane (and sulfate) in two sites in the Baltic Sea, an open-water coastal site and a eutrophic estuarine site over 4 time points (spring, summer, fall and winter) within a 12-month season. In order to address this, the authors measured methane and sulfate concentrations, oxygen uptake and sulfate reduction rates and calculated sulfate and methane fluxes in the sediment in the upper approx. 45 cm of the sediments. The main influence on methane emission from the sediment was found to be by bottom water oxygen enhancing aerobic carbon mineralization and oxidative recycling of sulfate. The authors state that the seasonal changes in sediment methane concentrations are too large to be only the result of changes in methane generation and oxidation. Thus, they suggest advective recharge of methane from deeper, gas-rich sediment layers as possible influencing factor. The methane concentration below the sediment surface is lowered by AOM below the saturation concentration and thus bubble emission does not play a role at the investigated sites. The study presents a well-designed experimental set-up and the experiments are performed thoroughly.

However, the authors fail to formulate a clear scientific objective to conduct this research. It should be clear from the abstract and from the introduction why this study was conducted and what the expected merit would be. The abstract describes the findings and ends with the conclusion but it does not clearly mention the scientific questions addressed. At the beginning, the importance of this study should be made clear to attract the reader attention and interest, e.g. by naming the research question behind. Such questions can then be answered by the findings.

The introduction is well written, describes the state of the art and highlights some gaps in knowledge to justify the study. It also briefly summarizes the methods applied in the study. However, a concise statement what the presented study will contribute would make the paper sound much stronger. As mentioned above, it would be good if the authors state what problem they exactly address and how they do it – in other words, what exactly do they want to find out by the applied methods.

Answer: We reformulated our objectives and scientific aims and emphasized the scope of the study somewhat clearer.

The presentation of the results is confusing. There is major work needed to check the consistency of the figures and the text (see specific comments below). This makes it hard to follow the argumentation as one cannot relate the described results to the profiles. When presenting the results, I would suggest sticking to the same order of the stations throughout the entire manuscript. For example, always describe station B1 first and then station H6 and have the same order also in the tables and figures (i.e., B1 on top and H6 below). The whole section should be rewritten with a focus to guide the reader clearly through the graphs. More attention should be paid to the general consistency in the style of units. For example: mM vs. mmol/L vs. mmol L⁻¹ (or e.g. nmol cc⁻³ d⁻¹ and mmol L⁻¹ OR nmol/cm³/d and mmol/L).

Answer: We have followed these suggestions to improve the clarity. See editions in Results section.

I suggest combining Figure 2 and 3 by plotting CH₄ and sulfate concentration in the same plot with linear concentration scale also for methane. The logarithmic scale for methane makes it hard to follow the changes and it is easily to compare with the sulfate profile if both are on the same scale and together. I also suggest showing all data of the triplicates for the sulfate reduction rates in Figure 4 and making the fit - not only from the medians (see details below).

Answer: We followed the recommendation and combined Figures 2 and 3..

The interpretation and argumentation as well as the conclusions seem reasonable and are well written. The conclusion contains many good arguments and statements of which I think it would be good to mention these in the abstract to raise the interest of the reader.

I suggest publication of this interesting study in Biogeosciences, however, I indicated major revision because the results presentation needs some careful rewriting with better guidance for the reader as well as careful cross-checking of text and figure/table content.

I think it is worth to add than 3 key words, to help finding the paper.

Keywords: Methane cycling, coastal and estuarine sediment, seasonality

2.) Specific Comments

Lines 30-32: rephrase the sentence, and maybe split. At the moment it says that “The effects of temperature [: :] where **(A: where ?)** investigated [: :] for open-water coastal and [: :] sediment.” That is probably not what the authors wanted to say.

Answer: We simplified this sentence, but we are not exactly sure what the reviewer meant by this comment.

Line 68: I would delete “summer”

Done

Figure 1: is of rather bad quality (at least in the document I could print out). It is impossible to read the names of rivers, cities or islands. Maybe the colors could also have more contrast to make the whole picture look sharper. A color code/legend could be helpful to understand the different blue tones (is this water depth?). If this differentiation is not important, a single color for water would be better.

Thanks for the suggestion. We have produced an alternative map in Ocean Data View, however, without the rastered high-resolution bathymetry. We would have liked to retain the bathymetric information, because it is important to understand the sediment deposition pattern, but cannot provide it at an overall satisfying resolution, because the bathymetric data are rastered for a large coastal area and cannot be presented as high-resolution cutouts for Himmerfjärden.

Lines 127, 129, 133, 148/149 : name equipment manufacture here

Okay. Done

Lines 180 – 185: total reduced inorganic sulfur should be abbreviated with TRIS, at least it should be consistent with the formula.

Okay. Done

Line 189: I think it is better not to use the median here. Out of three measurements (triplicates) the median will always be the measurement in the middle. This means your plot

and the input for the mathematical fit only relies on the one measured result (although there is the information behind that there is one higher and one lower measurement). You might talk about mean values in the text but in general I think you should present all individual measurements and also plot all data in the plots in Figure 5. And then you can calculate a fitted curve and also include this in the plot to visualize trends. It might be that the individual measurements show outliers and individual replicates differ. However, this is not uncommon for rate measurements and the best strategy is to simply show all data. Otherwise it could make the impression that something was tried to hide behind the median.

A: The format was chosen to present the trends in the best possible way. We have revamped the figures and now show all data points.

Line 245/256: be consistent in the order of described results (e.g. B1 as first and H6 as second) within the text for all parameters and also with table 1.

We carefully checked and revised the text to be consistent in the sequence the stations are listed.

Line 262ff: Please indicate the individual figure numbers after each station and result, e.g., "August... at station H6 (Fig. 2f) and : : at station B1 (Fig. 2b) and so on for all mentioned data, this helps to identify the results in the figures. Please also make the order consistent over the entire manuscript. Moreover, here are some inconsistencies between text and figure that could be easily sorted out by referencing to the respective profile. For example, in the text it says highest CH₄ concentrations in August (H6: 5.7 mM, B1 1.9 mM). While for Station H6 (Fig. 2f) this might be true, for station B1 (Fig 2b) the figure I cannot see the 1.9 mM, in fact August 2012 has the lowest methane concentrations. Also in February, only at H6 (Fig. 2h) the CH₄ concentration is lowest, but not at B1 (Fig. 2d). However, the number mentioned in the Text for B1 Feb 2103 (0.1 mM max.) matches the highest values in the B1 Feb 2013 figure (Fig. 2d) but it is not the lowest CH₄ concentration in B1, this is in August 2012 (Fig. 2b).

Thanks for this suggestion. We adapted the changes to the text accordingly.

I am wondering about the use of a logarithmic scale for the methane concentrations, this is unusual for the presentation of sediment methane concentrations. The mentioned linear increase in sediments at H6 is not visible due to the logarithmic concentration scale and also not the described "concave upwards trend" for B1. Also the mentioned differences in maximum concentrations are not visible due to that scale. Here, a linear concentration scale would be better to visualize the concentration changes. It would furthermore allow for a better judgement of the data quality and the efficiency of the sampling protocol (in terms of potential methane loss). A linear scale would also be helpful to compare the data with the sulfate data and the maximum sulfate penetration depth indicated by the green line. When using the linear scale it could be a good idea to combine Methane and Sulfate Profiles (Figures 2 and 3) in one plot for each sampling point.

A: We have reconverted the figures back to a linear scale. We were well aware of the potential criticism the use of a logarithmic scale can draw. However, logarithmic scales have been used frequently, e.g., in the IODP literature. Here the main purpose was to convey the scale of the concentration change and to demonstrate that the sampling technique allows us to capture concentrations above the concentration at atmospheric pressure with consistency, but that the measured concentrations were consistently far below the saturation concentration at in situ pressure. The linear scale does not allow us to do this. However, we welcome the honest opinion of the reviewer, and therefore reverted to the conventional linear scale.

Line 269: "concave upwards trend" what is meant by this? This is very unusual for a profile description. Do you mean increase followed by decrease? Here also a linear

concentration scale would help to understand.

A: Scale was changed back to linear to avoid more confusion.

Line 272ff: I do not see that the sulfate concentration gradient at station H6 in October 2012 (Fig. 3g) . For me it seems that the steepest increase is in August (Fig.3f) (>6 mM over < 10 cm depth)

A: The steepest gradient occurs between 6 and 10 cm depth in October whereas the surface gradient is less steep. This is likely due to the increased O₂ concentrations and the colder temperature in the fall leading to a downward propagation of a less steep sulfate gradient, however, not yet at a depth below 6 cm.

Line 275: better : “At station H6, sulfate was always fully depleted within the cored sediment interval, : :”

A: okay, changed

Line 276: “Depletion already occurred at 5 cm depth in April and October and at 9 cm in August: : :” Depletion occurs all the way down from the surface sediment to the lowest concentration in the profile. Do you mean complete depletion (or depletion until a low constant level)? This is at approx. 9 cm depth at H6 in August 2012 (Fig. 3f) but I cannot see the 5 cm in April (Fig. 3e) and October (Fig. 3g), or do you refer here to Station B1 (Fig. 3a-d)?

A: The reviewer is correct. We changed this.

Figures: 2-3 It would be helpful to quickly identify the profiles mentioned in the text, if station number are indicated, e.g., for each row. The letters (a), (b), etc., should be larger in order to better overview the figure and relate it to the text while reading. The style of the units should be consistent with the format used in the text (mmol/L vs. mM). As mentioned in the comments above, I suggest combining figures 2 and 3 and presenting the methane concentration with a linear scale.

A: We have increased the numbers and assign the station names to each row. We also plot sulfate and methane together in one plot, Figure 2

Line 287 ff: also here, please indicate the related profile in the figure 4 always directly when mentioned in the text, to help the reader understanding the text quickly.

A: Done

Line 288/289: I don't see an SRR increase to 63 nmol cm⁻³ d⁻¹ in any of the profile of B1. The maximum SRR I see is in Fig. 4a at approx. 35 nmol cm⁻³ d⁻¹. Also for station H6, I do not find a maximum of 411 nmol cm⁻³ d⁻¹ in the figure. The maximum measured is around 350 nmol cm⁻³ d⁻¹ in Fig. 4e. Are these the individual measurements (i.e. from one of the triplicates?) As mentioned above, I suggest showing the data of all triplicate samples. If you refer to theoretical values at the very surface calculated from the regression line, please indicate so.

A: We now show all replicates and show the regression lines based on the power law model. The author is correct in that assuming that the reference in the text was made for the individual measurements and not the averages.

Line 305: What is the “peak between 6 and 9 cm depth? Isn’t that a second peak? Sulfate is already mostly depleted at 10 cm and CH₄ seems to be at maximum concentration below 10 cm. Could this increase SRR here not indicate AOM? Again, an overlay of sulfate and methane concentrations profile with linear concentration scale (combined Figs 2 and 3) would help to judge this better.

A: We had of course also debated the second peak. It is a consistent feature, since it is also nicely visible in the 3 replicate SRR. However, there is no change in the sulfate gradient or the methane gradient in this depth intervals that would be expected if the measured rates would be largely attributable to AOM. Therefore, we consider it less likely that the SRR at this depth indicate largely AOM and interpret this peak as due to organiclastic SR.

Figure 4: please indicate what H6 and B1, in the caption and best also in the Figure itself (e.g. for each line of plots). As mentioned earlier, I would like to see all individual data here instead of the median.

A: Done.

Figure 5: A separation line between the four sampling times would be helpful for a better readability.! Maybe also indicate them with Letters and reference to the plots in the text when described. Add the error bars if the errors are mentioned in the text. The figure says February 2013 but the Table January 2013 Line 314/315 and Fig 5: In the fig 5, highest TOU at H6 is in April ($_{33}$ mmol m² d⁻¹) and at B1 in August ($_{22}$ nmol cm⁻² d⁻¹) or so, contradictory to the text.

A: We have changed the figure accordingly and adjusted the text.

Line 315: sulfate flux seems to be lowest at B1 in August not in February and highest in February or April, contradictory to the text.

A: We assume that the reviewer refers to the difference in uptake calculated for the SO₄ gradient and the SRR for August 2012. We have clarified in the new Figure 4 that the sulfate flux data are the ³⁵S data.

Line 398/399 “: : constraints decide on the result of this competition between these two processes.”

A: Done

3.) Technical Corrections

line 144: cut-off

corrected

line 147: replace “to force out” by “to push”

revised

line 149: “CH₄ standards at 100 ppm and : : :”

inserted 'of'

line 156: (cm³) instead of (cubic centimeter)

changed

line 162: missing dot after et al.

added

line 167: missing word after “adjacent”

inserted 'intervals'

line 177: 1 cm intervals

line 196: 40 L incubation tank

line 218: mL (“L” consistent to previous use)

changed

line 221: replace “to force out” by “to push”

changed

line 223: “CH₄ standards at: : :”

'of'

line 227/228: 0.003 L / 0.009 L

inserted the space

line 257: 300 _M

µM

line 467/468: remove one “integrated” in the sentence.

Removed the first 'integrated'

Interactive comment on “Annual variability and regulation of methane and sulfate fluxes in Baltic Sea estuarine sediments” by Joanna E. Sawicka and Volker Brüchert

Anonymous Referee #2

Received and published: 23 August 2016

Review “Annual Variability and regulation of methane in sulphate fluxes in Baltic Sea estuarine sediments.” by Joanna E. Sawicka and Volker Bruechert

Sawicka and Bruechert study the seasonality of methane flux and sulphate reduction in two coastal sites in Sweden. With estuaries being important players in the global methane cycle, it is important to gain more insight into the controlling factors of methane oxidation in these systems.

Major comments:

There are several assumptions in the manuscript that are not backed up by either data or references.

E.g.

Line 47-48: Importance of advective processes.

See comments below

Line 333-337: Temperature regulation inference.

A: Sole temperature regulation would imply that methane oxidation is less temperature-sensitive than methanogenesis preventing methane oxidizers from keeping up with the enhanced methane flux during summer. This requires significantly different values of Q_{10} of methanogens and methane oxidizers. Publications from lake environments and terrestrial environments, e.g., King (1992), Wik et al. (2014), Nguyen et al (2011) suggest that aerobic methane-oxidizing bacteria may have higher Q_{10} than methanogens, but this argument remains unproven for marine habitats. In case of anaerobic methane oxidation, it is difficult to argue for a temperature adaptation disadvantage of AOM compared to methanogenesis, because of the tight coupling between sulfate reduction and methane oxidation and the phylogenetic proximity w/ respect to 16S of ANME to known methanogens, but also with regard to Archaeal membrane lipid composition, which should be considered strong physiological regulator for cross-membrane transport.

Line 348 salinity variation.

A: Data shown in Table 1 indicate that the salinity for the different sampling periods varied little.

Line 480-483 Variability in methane concentrations not due to variability in methane oxidation rates alone

A: The emphasis here is on the word alone. The whole first paragraph of the discussion emphasizes the different regulatory processes that affect methane concentrations and two important ones are of course temperature and bottom water oxygen.

Line 490-492: Changes in the upward transport rate of methane

A: Methanogenesis rates can only increase due a temperature increase, since the availability of organic carbon for methane production in buried sediment does not change. These effects were modelled by Dale et al. (2006) and are discussed here.

Line 498-501. Migration of the methane saturation zone due hydrostatic pressure changes

A: There is acoustic echosounder evidence for free gas presence in these sediments and the authors have personal communication (Tom Floden) evidence that the depth of the free gas zone as seen on the acoustic echosounder changes substantially from year to year. The mechanisms that affect gas migration in these sediment are manifold. They can have to do with atmospheric pressure changes, wind direction or affecting water levels and these in turn affect the solubility of methane at a given temperature. An additional parameter is groundwater movement. There is also geophysical evidence from other areas in the outer Himmerfjärden area that suggest groundwater seepage. This implies a complex aquifer hydrology that was not accessible with the coring methods used here, but that has indirect effects on methane solubility, advective transport, and effective methane flux. A mechanistic or model-based evaluation of all these processes is far beyond the scope of this paper and cannot be adequately addressed in addition to the data presented here. We have explained this in lines 547-553 in the text.

Line 519-520. The period of ice cover has low flux rates. Extrapolation of rates during open-water conditions for a whole year would therefore be overestimates.

A: Yes, we agree. To our knowledge, this is one of the very few studies that reports sulfate reduction rates in a fully ice-covered estuary. These rates were very low compared to the open-water season. Extrapolation of these rates for the ice-covered period will necessarily give lower annually integrated rates compared to rates based on open-water measurements in spring/summer/fall. During certain years, the ice-covered season lasts from late December to early April. Ignoring winter data for extrapolations would give very erroneous numbers.

The authors go back and forth about stating if the methane transport is controlled by diffusion or advection. Sediment permeability would help to understand what role advection can play.

A: We do not have measurements of permeability available. While this could help, we would like to point out that even low-permeability sediment emit bubbles.

They state that changes in the hydrostatic pressure drives the changes in methane profiles, but do not explain what drives the changes in hydrostatic pressure, nor if that is related to season or not.

A: Changes in hydrostatic pressure in the Baltic Sea are influenced by air pressure, prevailing wind direction, and general sealevel stand due to the balancing effects of saltwater entry through the Danish straits and freshwater discharge in the northern Baltic, and from the rivers flowing in from the south. Additional effects are caused by the local coastal topography. These multiple parameters result in complex subsurface hydrology and complexity in estuarine water level conditions that make it difficult to use general meteorological observations to predict local sealevel variability. Hydrographic data are only reported for the general area in open water at the Landsort island, but these are not the same as in the archipelago.

A lot of equations are listed that are just taken from other publications. Those do not need to be listed again.

A: We have chosen to retain the formulas. There are enough readers that are unfamiliar with some of the methods. Without going into too much detail, these equations provide the basic framework.

It helps reading the manuscript if you keep the order of things the same, best throughout the manuscript (e.g. first mention station B1 then H6) but definitely in the same or consecutive sentences (e.g. Line 185-186, line 287 to 291). The order changes frequently in the manuscript making it harder to follow the arguments.

A: We have revised the manuscript to make sure the sequence is adhered to consistently.

Minor comments

Title “Annual variability : : :” if it is mostly the pressure it seems that the year plays not an important role here, so I think annual is not very good. If it is the seasons, I think seasonal is better. “: : : Baltic Sea estuarine: : :” but you say later that you investigated an estuarine and an open water station. Better say coastal?

A: Thanks for pointing this out. We changed this.

Abstract Line 41: You list 5.7mM as max in line 263 Line 43-4: “: : :lowering: : : far below the saturation concentrations.” Your methane concentrations are also below the saturation concentrations below the sulphate penetration and seem to be mostly constant. Thus, the anaerobic methane oxidation does not seem to be lowering it far below the saturation concentration.

A: This is only observed for the winter observation and actually the major reason why we invoke an advective addition of methane. The other methane data are above saturation below the SMT.

Introduction Line 55: Would be good to put the Tg into perspective to the global flux to know the importance.

A: We have added data on the proportion of coastal emissions and compare them to the total estimated marine methane emission. However, the choice of a good number is difficult, partly because of the ongoing debate on the contribution of coastal methane emissions from thawing permafrost in the Siberian Arctic and uncertainties in correctly assessing macro/micro-seep-related emissions.

Line 66 and later in the methods: If the methane flux shows high spatial heterogeneity, why do you only measure the flux in one core?

The flux is the average of four core incubations and one diffusive flux measurement.

Naturally, this variability is a sampling problem if porewaters are used.

Line 70-1 and 517-9: You also say you do not have data from the ice covered period (line 126)

A: This must be a misunderstanding, because we collected samples in late January/February with a ship capable of breaking the coastal ice.

Line 91: If you measure over four seasons, I feel seasonal is better than annual.

A: We changed this.

Materials and Methods: Line 102: Do you have info about the CH₄, POM and DOM of the effluent of the STP?

A: We have provided reported numbers on the treatment plant emissions for 2012. We would like to point out, however, that because of continuous improvement in the sewage treatment operation since the 80's, but at the same time the rapid growth of the Stockholm metropolitan area, the emissions and C/N/P composition have changed historically. Today's numbers may be misleading to understand the effects for buried sediment carbon from 20 to 30 years ago and only N and P data are available for the long period. For example, in 1994 the treatment plant treated the sewage of 250000 people for the southern Stockholm area. Today, the plant operates at its capacity and treats the sewage of 314000 people + 35000 additional people equivalents from industry (<http://www.syvab.se/himmerfiardsverket/energi-och-materialflode>), but N and P emissions are at pre-1970's levels.

Line 113: How thick is the rusty brown surface layer?

A: It changes significantly from 1 cm to complete absence.

Line 113-116: Do you have information about the grain size or permeability? That would really be needed to argue for or against advective transport.

A: These sediments are fine-grain muds with a small sand fraction. No exact grain size has been performed.

Line 125-6: What did it mean that there was ice coverage? Line 127:"until for the experiment" change Line 133: "1N HCl" please change to 1M

A: Changed.

Line 134-5: Drying for 2 hours seems short.
Did you test if longer drying had an effect?

A: As a matter of fact, the actual period was longer than that since the samples were retained in the oven. The calculated porosities are consistent with measurement from nearby stations.

Line 139: "seconds" seems a bit overstated, especially knowing that it takes already probably more than seconds before the core was on the ship.
"less than a minute" still sounds very impressive and is more realistic.

A: Less than a minute passes before we start removing samples. To avoid doubt, we have changed this to minutes since the whole procedure takes about 5 minutes for a Multicore.

Line 144: "exactly" delete

A: Changed

Line 145: "5M NaCl" that is not a standard treatment, did you test if it halted microbial activity? Why did you not use base?

A: If one calculates the solubility of CH₄ in 5M NaCl, CH₄ solubility is negligible, and due to the osmotic effect microbial activity likely ends very quickly as well. We do not agree that this is a non-standard method. There are plenty of publications, which use strong NaCl brine. NaOH is useful, if one is interested in the DIC concentration, but in our case we did not process for DIC. Also, the resultant solution is harmless and

cheap (kitchen salt) as opposed to strong base. In addition, the exchange of clay-bound CH_4 is enhanced in strong salts, which cannot be achieved with 2.5% NaOH.

Line 146: If you only leave the sample for 1 hour you will not get all the gas adsorbed to clay minerals.

A: This is very likely the case in these muddy samples.

Did you do later measurements to determine if the concentrations were constant?

A: Yes, the concentrations remain constant. We have conducted long-term tests, but for the sake of space in the methods description, we chose not to include every aspect.

Line 149: What column did you use on your GC?

A: The GC is equipped with a Porapak Q pre-column (3 feet) followed by a Hayesep D (9 feet) analytical column. We use two sequential 1ml+1ml loops for injection with luerlocked glass syringe. Injection occurs through a dried Na_2SO_4 filter bed with quartz wool endings. Flow rate of the GC is 60 ml flow rate (N_2 5.0). The FID operation occurs with zero air produced clean over a carbon filter and H_2 is produced with a Schmidlin H_2 generator. Gas cleanup occurs via activated carbon-cleaned cartridges. More details have been added to the method description.

Line 162: "10% HCl" is that 10% concentrated HCl in water or is that a 3.7 dilution of concentrated (37%)

A: We changed this to 1 M HCl.

Better give M concentrations.

Line 174: Why did you add cold sulphate to the tracer solution? That introduces sulphate into the sulphate free zone and does not do much in the not sulphate free zone.

A: We disagree. Non-amended tracer yields unrealistically high rates in the SMT because of limited sulfate and very high tracer turnover up to 50% of the added tracer, i.e., this would not be a tracer experiment any longer. In order for all incubations to be considered equivalent, a tracer turnover of less than 1% during the incubation is desirable to avoid kinetic limitation due to Michaelis Menten effects, irreversibility effects, etc. An additional beneficial effect is that potential SRR below the SMT can be detected and a cryptic sulfur cycle can be recognized.

Line 185: "(SO₄²⁻)" does not appear in the formula

A: Thanks. We corrected this.

Line 188-189: If you only show the median, what is the error? Plot it in the graph, or if it pretty much constant, state it here.

A: The standard error is now reported in the revised Figure 4. Replicate measurements are shown in Figure 3.

Line 215: Why do you use a different fixing agent for the methane samples? Why do you not use base?

A: See above.

Line 225-229: The list of variables and the equation do not fit to each other.

A: We adjusted the units.

Line 233-4: Volumetric units do not match.

A: Thanks: We changed ppm to nmol.

Line 237-42: Did you see any signs of burrows in your cores? Why do you only do one replicate if you know that it is spatially heterogeneous?

A: Marenzelleria is the dominant bioturbator in these sediments, but does not play a large role for CH₄ emissions (Bonaglia et al., 2013 MEPS). Microelectrode profiling (Bonaglia et al., 2014) has not shown distinct subsurface increase due to pumped O₂ from burrowing or bioirrigating animals. Bioturbation is seen at Station B1 in the topmost 2 cm as described in the text. These, however, do not pertain to the diffusive flux calculations done for the SMT processes. As far as accounting for the degree of bioturbation is concerned, the resolution of the sampling at the sediment surface is the same as the bioturbation depth. Therefore, there is no possibility to account for bioturbation at the resolution of the sediment sampling.

A: The whole-core incubations are based on core replicates, the methane porewaters are singular cores. Our choice of data is a balance between replication, station time, sample numbers. Almost all core studies on porewater methane in the literature are on singular cores. We have conducted selected replicate experiments, but not for the whole dataset.

Line 248: "Do" why was it recalculated?

A: D^o is sensitive to temperature and salinity. See Boudreau (1996).

Results

Line 263: In the abstract you state that methane concentrations exceeded 6mM.

A: We corrected to 5.7 mM.

Line 267-270: it is hard to see linearity or concave shapes in log plots. If these are important don't use log plots.

A: We have followed the recommendations by the reviewers, and have changed to a linear scale in addition to showing sulfate and methane data in the same graph (Figure 2a-h). The decision in favor of logarithmic plots was primarily because we wanted show the variability of the pore water concentration relative to the saturation concentrations during the different observation periods. In addition, the range of the concentration changes in a core is very substantial so that a logarithmic scale does better justice to the variability within a core (see ODP/IODP results). The in-situ saturation limit lines disappear if the natural range of concentrations were shown.

Line 271: You state that the methane profiles cannot be explained by the T and Corg changes. How about the sulphate profiles?

A: Our analysis indicates that the gradient of sulfate is as much influenced by heterotrophic sulfate reduction as by methane oxidation. The two cannot be

separated, and it is therefore not possible to judge on T and org C changes for sulfate reduction alone.

Line 303: You would also get a rate in the sulphate free zone if you would have injected tracer only. If you use the sulphate concentrations from your profile to determine the sulphate reduction rate? It does not matter that the tracer is reduced. If there is no sulphate the rate is still 0.

A: We disagree. There are now a number of publications that demonstrate the existence of the cryptic sulfur cycle (Holmkvist et al., 2014 GCA), and also indications by e.g., Leloup et al (2009) Environmental Microbiology) that demonstrate the existence of active sulfate reducers below the SMT zone.

Line 305-7: Why is that happening?

A: An interpretation is provided in the text? See above.

Line 313-7: All those rates should not be negative. A negative oxygen uptake of the sediment means diffusion of oxygen out of the sediment. Did you test if you could detect changes in sulphate concentrations in the whole core incubations?

A: No, we did not check for changes in sulfate, since the sulfate concentration is large compared to the uptake and the precision of a sulfate analysis is no better than 100 μM . By convention, fluxes into the sediment are negative (i.e., oxygen and sulfate, whereas fluxes out are positive, i.e., CH_4 . This is what is indicated in the table and text.

Line 319: how about reoxidation by oxygen not only iron? Why do you suddenly have reactive iron here, when you state in line 484 that there is no other electron acceptor available?

A: Bonaglia et al (2014) give oxygen penetration depths for these sites. These are between 100 μm and 0.5 cm. If there is a lack of a sulfate gradient, it is more likely that iron is the intermediate oxidizing agent.

Line 319: You have to keep in mind that the methane profile does not really give you a rate of methane diffusion out of the sediment. If there is oxygen in the surface sediment there is likely aerobic methane oxidation as you discuss yourself. Thus, this is an over estimation of the methane flux, and you do not know by how much. You need to have methane concentration data at the scale of the oxygen consumption to determine that.

A: We agree. Therefore we have in addition conducted whole-core incubations, with the caveats that this method has due to depressurization effects. Published data often use porewater gradients and it is therefore useful to present both types of analyses.

Line 328-9: As your diffusion based fluxes are overestimated (see comment above) there is no agreement, and thus bioturbation and irrigation, as well as advection as a result of your stirring probably affects the flux.

A: The diffusion-based fluxes are not overestimated at depth, where the resolution is sufficient and oxygen plays no role.

Discussion

Line 334-7: Do you have data available to support that? Can you model that it does not fit?

A: We have added two sentences in lines 547-553 to explain what a satisfying model would need to deliver. Such a model would have to be rather advanced and is not available to us, and would probably not be sufficiently constrained by the necessary physical background data.

Line 342: How about rate studies in temperature gradient blocks, e.g. by Sagemann or Arnosti?

A: We have unpublished temperature gradient block data on SRR for Himmerfjärden sediment. These support the existence of a broadly psychrotolerant/mesophilic SRB community and support the statement in the text. Apart from that, we would like to point out that temperature gradient block experiments of the kind the reviewer refers to are not adequate to address the temperature hypothesis for seasonal changes.

Line 348: How big could the effect be with this difference in salinity?

A: It is not relevant, mostly because sulfur cycling in the topmost cm makes sulfate multiple times available far in excess of concentrations variations due to salinity changes.

Line 352: How much Corg comes from the sewage treatment plant?

A: Although considerable (1676 tons for 2012, now mentioned in the text), the sewage treatment emits relatively small amounts of POM and DOM compared to the inorganic nutrients nitrate and phosphate, which stimulate plankton production in the estuary (Bonaglia et al., 2014). It is the nutrient effect that is most relevant for the carbon cycle in the estuary, not the heterotrophic carbon. Carbon estimates of the contribution by the sewage treatment plant were done by Savage et al. 2010 and indicate a local effect surrounding the sewage treatment plant due rapid deposition in the near area surrounding the outflow.

How similar or different is the fjord thus to others?

A: The inner parts of the fjord share similarities with other eutrophied fjord systems, e.g., Oslo fjord, whereas the outer parts are quite pristine and may be comparable to other northern latitude fjord-type systems. However, many fjord systems bordering the Atlantic have significantly higher salinities so that sulfate reduction prevails over a thicker sediment layer than in these sediments. Another difference is the glacial and postglacial history of the Baltic Sea. During glacial times organic-poor lake sediments were deposited followed Fe-rich post-glacial clay that is also low in organic carbon. In other fjord sediments, this discontinuity from a freshwater to a brackish/marine phase may not exist. This will affect the methane generation potential and thereby the methane flux.

Line 357-9: Where do the high sedimentation rates come from if there is only low river runoff?

A: These sediments are accumulation bottom sediments, which have a significant proportion of resuspended fine-grained material that is transported laterally and deposited in the bathymetric depressions of the fjörd.

Line 385: Table 1 has no information about the burial of organic material. Do you have depth profiles supporting that?

A: Published organic carbon concentration profiles can be found in Thang et al. (2013). Mass accumulation rates of organic carbon are reported in Thang et al. to be 9

– 9.5 mol m⁻² y⁻¹ (24 - 26 mmol m⁻² d⁻¹) for a station close to H6. At Station B1, we do not have information of mass accumulation. However, data for similar sediments suggest C_{org} MAR of 3.3 mol m⁻² y⁻¹. We have added these data to the site description section.

Line 391: Salinity of B1 is 7‰

Line 392-4: A little too often “compar*”

We have modified the text to address unnecessary repetitions.

Line 392-8:

Lower sulphate concentrations mean that there is less sulphate available for organoclastic & methanotrophic sulphate reduction, just by simple numbers.

We do not dispute this. This is stated in lines 428-432.

Line 410&2: Figure 4

Line 412-3: Iron and manganese reducers do not always outcompete sulphate reducers, see work by Thamdrup and Vandieken.

Yes, but in these sediments this is the case. We have conducted bag incubation and iron and Mn speciation analysis in bag incubations in core profiles to 10 cm depth. These data indicate that BSR account for 75% of anaerobic organic matter oxidation, Fe reduction about 6.5 % and Mn reduction about 2.5%. The rest is accounted for by heterotrophic denitrification (Goldschmidt presentation Downs and Bruchert (2013); Bonaglia et al. (2014) Biogeochemistry).

Line 414-5: You state that the main driver for the differences is the advective flow based on the hydrostatic pressure, but here you speculate about more sulphate reduction leads to less methanogenesis. Which process is now the important one?

A: We would like to emphasize that it is not one OR the other, but an interplay of multiple processes with varying influences on the system. This is also why these sediments would be extremely hard to model accurately in one-dimensional reaction-transport models.

Line 417-20: How deep is the bioturbation in these sediments?

A: An exact bioturbation depth would be arbitrary. Macrofauna analysis at H6 and B1 has shown that Marenzelleria does generally not go deeper than about 4 cm, but can occur occasionally down to 10 cm.

Line 419-21: In advective systems with bioturbation fluxes should increase not decrease.

A: We disagree. Since more oxygen can be imported, it is possible that methane oxidation increases.

Line 443-5: This is not an explanation, it is just stating that you believe the data in contrast to the scenario below.

A: Possible explanations are provided in the following lines. 479-487

Line 454: "law" replace with "function"

A: Done

Line 461-3: Sentence not clear

A: We rephrased the sentence: now lines 498-500

Line 465: What is the percentage if you compare the methane flux into the SMTZ with the accumulated SRR or the total methane flux with the SRR? Do the numbers fit what model says?

A: Lines 503 state what the reviewer asks for, i.e., the depth-integrated SRR relative to methane flux rates fit well with the model.

Line 474-7: In line 445 you state that there is only little link.

I am sorry but we do not see the apparent contradiction the reviewer states.

Line 480-3: Please provide some support for this, maybe with a model.

A: The data showed an abrupt decrease in porewater concentrations from Oct 2012 to January/February 2013 for which an explanation is required. The above discussion intended to lay out that neither temperature, salinity, nor changes in organic matter influx alone can explain this change. The sentence does not intend to say more than that. It is beyond the scope of the paper to develop a unifying model that can address these processes satisfactorily. Even some of the currently most complete models, such as by Mogollon et al. (2011) JGR are idealizations that may not yield satisfactory fits with our data, but that does not necessarily dispute either model or data.

Line 484: Did you determine the concentrations of other electron acceptors like Fe? In line 319 you state that it is available for sulphide reoxidation.

A: Fe data are available from the nearby Station H5 and published in Thang et al. (2013). In addition, there are unpublished data for nearby Stations H3 and H2 that indicate the limitation of reactive iron in the postglacial mud. In the glacial lake clays, however, reactive iron is more abundant again, but these latter sediments do not control the methane production, because their C_{org} contents are too low.

Line 490-2: Do you have any data on changing pressures? What would drive these changes? What would the possible magnitude be?

We have tried to obtain water level data and air pressure data for the periods of observation at the sampling stations, but these were not archived or could be found for the precise localities, only for the open Baltic nearby. However, local data is what was needed to have an accurate idea of the hydrostatic pressure.

Line 500-1: Do you have any data or reference to support this magnitude?

The best reference to address this question is the study by Mogollon et al (2011 JGR Biogeosciences), who modelled the free gas depth and AOM rates for two stations in southwestern Baltic Sea sediment. In that study temperature, and not tidally influenced pressure change, were found to be the dominant regulators of the free gas depth variation. Our differing interpretation is based on the observation that the seasonal variability in temperature at the two sites studied there are much greater than the ones studied here.

Line 500: "may as much as : : " insert "be"

Done

Line 497-503: If it is the hydrostatic pressure it is actually not really a seasonal effect?

Yes

Conclusion

Line 508-9: Sentence not clear.

Line 515-6: How is it seasonal/annual if it is the hydrostatic pressure? Not clear.

Line 517-9: You also state that you do not have data from the ice covered times!

This must be a misunderstanding, since we have the February data. This is one of the few study that present data for conditions during ice cover.

Line 519-20: Why is that if the temperature and Corg input do not play an important role?

We emphasize that there are two aspects to be considered. Our winter and early spring data give low rates. Generally, in the literature, there are very few data available for sites with measurements during ice cover. If late spring/summer/fall rates are therefore extrapolated over a whole year, overestimates can result. Models, however, may account for this effect, if they are able to parameterize temperature and reactive organic carbon correctly (and the hydrological complexities of an archipelago setting riddled with fault lineaments). Secondly, while our observations indicate that hydrostatic changes or changes in porewater advection may have a considerable influence, this still does not take away from the fact that there is also seasonal variability. To model the annual variability based on organic carbon and temperature alone may therefore unfortunately also give the wrong results, because these factors have not been accounted to a degree that may reflect the specific regional situation. These two aspects need to be considered separately.

Line 520-1: Is it no advective or diffusive transport that controls the methane? You keep changing your argument.

Please see the comment above.

Tables

Table 2: "no AOM zone3" for H6 January 2013, change to "no AOM zone4"

Table 3: "Exponential coefficient (a)" this one is not exponential.

Will correct this

Figures Make all the y axis for depth the same scale.

Will correct this.

Figure 1. The colors do not help reading the map too much, not very clear in black and white at all. Change continent to just white or black to make ocean more clear and maybe reduce shades in the water.

We will consider a black and white map, or a map with sufficient contrast, clear legends and geographic locations.

Figure 2: You use the maximum sulphate penetration from figure 3 here. Maybe change the order of the figure to keep the flow consistent.

We will do that and then consequently also change the sequence in the results description.

Figure 3: How do you define your maximum sulphate penetration if there is a sulphate peak in your graphs below it?

Sulfate penetration depth was defined as the first lowest concentration measured. It is a common observation that traces of sulfate in the range of concentrations 50µM to 400 µM remain detectable in porewaters to substantial depths of several meters far into the methanogenic zone. This observation has been addressed in detail by Roey et al., Holmkvist et al and is part of the argument in favour of a cryptic sulfur cycle, which the authors of this manuscript also agree to. We also observe non-zero sulfate concentrations in the methane-rich zones of our sediment cores. We have therefore

chosen to define the sulfate penetration depth as that at which the sulfate changes sharply and the sulfate concentration is below 0.5 mM. We think that this combined criterion best reflects the condition of a transition from a dominating sulfate reduction environment to an environment in which methane-cycling processes start to prevail (while acknowledging low rates of cryptic bacterial sulfate reduction).

Figure 5: Keep order consistent between listing in the graph and in the caption. If you keep all the values positive it is much easier to compare the values. Which method are the methane fluxes based on?

We use the convention from the perspective of the water column, i.e., loss fluxes are fluxes into the sediment and negative and gain fluxes into the water column are positive.