

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

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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: 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 in the Q_{10} of methanogens and methane oxidizers. Publications from lake environments and terrestrial environments, e.g., King et al. (1988), Wik et al. (2016) 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 compared to methanogenesis, because of the tight coupling between sulfate reduction and methane oxidation and the phylogenetic proximity of ANME and ANME to known methanogens, in particular with regard to membrane lipid composition, which should be considered the strongest physiological regulator.

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: Again, 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

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 accessible with the coring methods used here, but that has indirect effects on methane solubility, advective transport, and effective methane flux. A mechanistic 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.

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: 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 lower the annually integrated rates.

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: 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.

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 sealevel variability. Hydrographic data are therefore reported for the general area only.

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

Fine – this can be changed, but there are still many 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.

We will carefully check 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?

Thanks for pointing this out. We will change 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.

This is only observed for the winter month 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.

Good point. Will present this a percentage of the total marine methane emission.

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)

Unfortunately, there was a problem with the analysis of the winter data, which we deemed problematic chose not to use.

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

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

These can be provided, but historically, because of continuous improvement in the sewage treatment, but at the same time 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. 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/himmerfjardsverket/energi-och-materialflode>).

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

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.

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

Will do.

Line 134-5: Drying for 2 hours seems short.

Did you test if longer drying had an effect?

Yes, this works if the oven is at the temperature and no more than 1 g of sediment is used. In operation, the samples are left in the oven until it has cooled to room temperature. Therefore sediments tends to be in the longer for longer than the two hours.

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.

We are not talking about 10 seconds or less, but less than a minute, i.e., tens of seconds. We are really fast with this, because the boat's freeboard is low and the core is very quickly brought on deck, but we can change this.

Line 144: "exactly" delete

Okay

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

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 CH₄ 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.

This is very likely the case in these muddy samples.

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

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?

Porapak Q pre-column (3 feet) with Hayesep D (9 feet), 1ml+1ml sequential loop injection with luerlocked syringe through dried Na₂SO₄ filter with quartz wool endings, 60 ml flow rate (N₂ 5.0). FID operation with zero air produced, H₂ produced with H₂ generator. Carrier activated carbon-cleaned cartridges and H₂O removal, simultaneous detectors for FID and ECD on hard-cut program.

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

We will change this. 10% of concentrated, i.e., 3.7% 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.

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

Thanks. Will correct 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.

The standard error is now reported in the revised figure 5. Replicate measurements are shown in Figure 2.

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

See above

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

We will adjust the units.

Line 233-4: Volumetric units do not match.

Thanks: We will change 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: 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.

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.

Line 248: "Do" why was it recalculated?

Do is sensitive to temperature and salinity. See Boudreau (1996).

Results

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

We will correct 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.

The decision in favour of logarithmic plots was primarily because we wanted show the variability of the porewater concentration relative to the saturation concentrations during the different observation periods. In addition, the range of the concentration changes in a core are also very substantial so that the logarithmic scale does better justice to the variability within a core. The saturation limit lines would disappear if the natural range of concentrations were shown. We are following the recommendations by the reviewers, and have changed to a linear scale in addition to showing sulfate and methane data in the same graph, but want to emphasize the advantages of the logarithmic presentation.

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

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 you 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.

We disagree. There are now a number of publications that demonstrate the existence of the cryptic sulfur cycle (Holmkvist et al., 2014 GCA), but also indications by 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?

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?

No, we did not check for changes in sulfate, since the sulfate is vary 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., CH₄). This is what is indicated in the tabel 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?

Bonaglia et al (2014) give oxygen penetration depths for these sites. These are between 100µm 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.

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

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 effects the flux.

The diffusion-based fluxes are not overestimated at depth, where the resolution is sufficient and oxygen plays no role. We will, however, address this aspect in the discussion.

Discussion

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

This was a statistical test that showed the lack of correlation. We do not think that a model would provide a satisfying or sufficently reliable answer to this question.

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

We have unpublished temperature gradient block data on SRR for Himmerfjärden sediment. These support the statement in text.

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

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?

The sewage treatment emits minor amount of POM and DOM compared to the 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 carbon. Carbon estimates of the contribution by the sewage treatment plant were done by Savage et al.

How similar or different is the fjord thus to others?

The inner parts of the fjord share similarities with, e.g., Oslo fjord, whereas the outer prarts are quite pristine and may be comparable to other northern latitude fjord-type systems. However, many fjord systems have significantly higher salinities so that sulfate reduction pervails over a thicker sediment layer than in these sediments.

Another difference is the glacial history of the Baltic Sea sediment. During this time organic-poor lake sediments were deposited. In other fjord sediments, this discontinuity to a freshwater phase may not exist in the geological record. 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?

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

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

Published organic carbon concentration profiles can be found in Thang et al. (2013). At Station B1

Line 391: Salinity of B1 is 7‰

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

Line 392-8:

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

We do not dispute this.

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 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?

As said above, 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?

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.

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.

Possible explanations are provided in the following lines. 444f

Line 454: "law" replace with "function" Line 461-3: Sentence not clear 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?

We can replace 'law' with function, but the term has been used in the literature since Jorgensen (1979) and also in Jorgensen and Parkes (2010). Lines 467f 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.

It is the data that showed an abrupt decrease in porewater concentrations 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 the 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.

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.

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.

Will revise this sentence to make it clearer

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 at 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. 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"

Will correct this

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 50 μ M to 400 μ M 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.