

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, line 333-337, line 348, line 480-483, line 490-492, line

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498-501, line 519-520.

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

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.

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?

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.

Introduction Line 55: Would be good to put the Tg into perspective to the global flux to know the importance. 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? Line 70-1 and 517-9: You also say you do not have data from the ice covered period (line 126) Line

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

Materials and Methods: Line 102: Do you have info about the CH₄, POM and DOM of the effluent of the STP? Line 113: How thick is the rusty brown surface layer? 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. 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 Line Line 134-5: Drying for 2 hours seems short. Did you test if longer drying had an effect? Line 139: "seconds" seems a bit over stated, 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. Line 144: "exactly" delete Line 145: "5M NaCl" that is not a standard treatment, did you test if it halted microbial activity? Why did you not use base? Line 146: If you only leave the sample for 1 hour you will not get all the gas adsorbed to clay minerals. Did you do later measurements to determine if the concentrations were constant? Line 149: What column did you use on your GC? Line 162: "10% HCl" is that 10% concentrated HCl in water or is that a 3.7 dilution of concentrated (37%) 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. Line 185: "(SO₄²⁻)" does not appear in the formula 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. Line 215: Why do you use a different fixing agent for the methane samples? Why do you not use base? Line 225-229: The list of variables and the equation do not fit to each other. Line 233-4: Volumetric units do not match. 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? You assume here that diffusion is the dominant process? Based on what? Later you discuss that bioturbation can affect the transport and shift it from diffusive to advective. Line 248: "Do" why was it recalculated?

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Results Line 263: In the abstract you state that methane concentrations exceeded 6mM. Line 267-270: it is hard to see linearity or concave shapes in log plots. If these are important don't use log plots. Line 271: You state that the methane profiles can not be explained by the T and Corg changes. How about the sulphate profiles? 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. Line 305-7: Why is that happening? 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? 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? 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. 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.

Discussion Line 334-7: Do you have data available to support that? Can you model that it does not fit? Line 342: How about rate studies in temperature gradient blocks e.g. by Sagemann or Arnosti? Line 348: How big could the effect be with this difference in salinity? Line 352: How much Corg comes from the sewage treatment plant? How similar or different is the fjord thus to others? Line 357-9: Where do the high sedimentation rates come from if there is only low river runoff? Line 385: Table 1 has no information about the burial of organic material. Do you have depth profiles supporting that? 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 organ-

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oclastic & methanotrophic sulphate reduction, just by simple numbers. Line 410&2: Figure 4 Line 412-3: Iron and manganese reducers do not always outcompete sulphate reducers, see work by Thamdrup and Vandieken. 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? Line 417-20: How deep is the bioturbation in these sediments? Line 419-21: In advective systems with bioturbation fluxes should increase not decrease. Line 443-5: This is not an explanation, it is just stating that you believe the data in contrast to the scenario below. 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? Line 474-7: In line 445 you state that there is only little link. Line 480-3: Please provide some support for this, maybe with a model. 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. Line 490-2: Do you have any data on changing pressures? What would drive these changes? What would the possible magnitude be? Line 500-1: Do you have any data or reference to support this magnitude? Line 500: "may as much as..." insert "be" Line 497-503: If it is the hydrostatic pressure it is actually not really a seasonal effect?

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! Line 519-20: Why is that if the temperature and Corg input do not play an important role? Line 520-1: Is it no advective or diffusive transport that controls the methane? You keep changing your argument.

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.

Figures Make all the y axis for depth the same scale. Figure 1: The colors do not help reading the map too much, not very clear in black and white at all. Change continent

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to just white or black to make ocean more clear and maybe reduce shades in the water. Figure 2: You use the maximum sulphate penetration from figure 3 here. Maybe change the order of the figure to keep the flow consistent. Figure 3: How do you define your maximum sulphate penetration if there is a sulphate peak in your graphs below it? 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?

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