

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 #1

Received and published: 19 August 2016

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

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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

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

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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).

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).

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.

2.) Specific Comments

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

Line 68: I would delete “summer”

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.

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Lines 127, 129, 133, 148/149 : name equipment manufacture here Lines 180 – 185: total reduced inorganic sulfur should be abbreviated with TRIS, at least it should be consistent with the formula.

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.

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.

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).

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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.

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.

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

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

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)?

Figures: 2-3 It would be helpful to quickly identify the profiles mentioned in the text,

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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.

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.

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.

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 her 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.

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.

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

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Line 314/315 and Fig 5: In the fig 5, highest TOU at H6 is in April ($\sim 33 \text{ mmol m}^{-2} \text{ d}^{-1}$) and at B1 in August ($\sim 22 \text{ nmol cm}^{-2} \text{ d}^{-1}$) or so, contradictory to 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.

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

3.) Technical Corrections

line 144: cut-off

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

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

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

line 162: missing dot after et al.

line 167: missing word after “adjacent”

line 177: 1 cm intervals

line 196: 40 L incubation tank

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

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

line 223: “CH₄ standards at. . .”

line 227/228: 0.003 L / 0.009 L

line 257: 300 μM

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

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