

## ***Interactive comment on “Methane in the Danube Delta: The importance of spatial patterns and diel cycles for atmospheric emission estimates” by Anna Canning et al.***

**Anonymous Referee #2**

Received and published: 1 December 2020

This paper reports high-resolution measurements of dissolved CO<sub>2</sub> and CH<sub>4</sub>, as well as O<sub>2</sub>, temperature and conductivity, in the Danube Delta. Three cruises were performed at different months of one year, covering both river, channel and lake systems. River Deltas are highly dynamic systems in terms of both biology and hydrology, and the present study is valuable in its purpose to quantify these dynamics in terms of greenhouse gas emission. This is an impressive dataset, consisting of highly resolved and high-quality measurements in this complex river delta, and I would really like to see it published.

Unfortunately, the paper has several shortcomings when it comes to presentation and

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analysis. Several of these shortcomings are of rather fundamental nature. For example, even though rivers, channels and lakes are extensively discussed as being different from each with respect to greenhouse gases, there is no statistical analysis that supports the existence of any such differences. A “hot spot” of emission is mentioned without providing quantitative evidence for why it is different from the rest of sites. The variability of the gas exchange velocity can be massive at short scales, both in time and space, yet this is not accounted for, neither in calculations nor discussion. Diel cycles are presented and discussed in great length even though it really was only one measured diel cycle (the other diel cycle measurement was not fixed in space, and thus includes spatial variability); based on so little evidence, it seems not justified to draw far-reaching conclusions. There are also many issues with precision in writing, and evidence for many statements is lacking or unclear.

Nevertheless, the dataset of highly-resolved concentration measurements in this highly dynamic ecosystem seems robust, so with more effort, this could be turned into an interesting paper.

In revising this paper, I would like to urge the two senior co-authors to share their vast experience of writing papers with the junior first author.

Detailed comments

Title. Why only Methane? You also measured CO<sub>2</sub>, and that is worthwhile to report and communicate. Also, you only studied surface waters of the Danube Delta, and not the vast reed beds, which should be evident from the title.

L34. Source of what? Please specify.

L34. “Inland waters” are commonly defined as lakes, reservoirs and rivers. Wetlands are typically not part of inland waters.

L37. See the new lake CH<sub>4</sub> emission estimate by Del Sontro et al. 2018, L&O.

L41. This sentence is repetitive.

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L43. To my knowledge, there is no definition of “channel”; aren’t these just running waters that are somehow anthropogenically modified, such as many rivers and streams?

L47. “end of line respiration process” sounds like colloquial language, please revise.

L48-50. No need to go into pathways of methane production, since it is not at all part of this paper. Also Figure 1 is not really needed, since this study is not about establishing a lake methane budget.

L60-64. Unclear in how far this is relevant introduction to this paper. Instead, focus the introduction on “spatial and temporal variability” (L64), because that’s what this paper is about.

L66. Unclear what “monitoring approaches tend to stay within one system” means.

L76. Objective 2 should be rephrased, since you do not address global-scale fluxes in this paper, and you only measured one diel cycle.

Section 2.2. Please describe what distinguishes rivers from channels.

Figure 2. This map shows the travelled track (how long was it in total?), but couldn’t you also make maps that show the concentrations of CO<sub>2</sub> and CH<sub>4</sub> along this track? This would be a very intuitive way to visualize the data. Also: the yellow lake complexes were not studied and do not need to be highlighted. And instead of the various denominations (3, 4, b1, b2, i-v), what about writing the respective names onto the map?

Figure 2 caption: what does “with only slight variations” mean?

L99-100- Is this the annual temperature range, or daily? And what makes it extreme?

L102. “thorough” is subjective, and can be skipped.

L120-125. I have some serious concerns with the way the gas exchange velocity and flux estimates were treated and discussed. Only the concentrations CH<sub>4</sub>water and

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CO<sub>2</sub>water were measured. The concentrations in air were assumed to be at global average, which is doubtful in such a biologically active wetland area. The gas exchange velocity  $k$  was scaled from wind speed (unclear where it was measured) for both lakes and rivers (albeit different exponents were used for lakes and rivers). I assume that the channels were treated as the rivers? My point is that  $k$  is highly variable at short time scales, and largely driven by hydrodynamics, which in turn varies with wind speed, but also with water flow, hydromorphology, and thermal structure. These sources of variability will vary in time and space and between types of systems, and are very unlikely to be captured by scaling from wind speed. The authors need to acknowledge that, and add some discussion on the reliability of their estimate of  $k$ . Given that apparently a study of greenhouse gas emission from the Danube Delta using floating chambers was published recently (Maier et al.), the authors could use the measured  $k$  values from that study for calculation of their own fluxes, or to assess in how far the wind speed-scaled  $k$  values are congruent with measurements of  $k$ . The robust treasure of this study are the highly-resolved and repeated concentration measurements, and it needs to be made clearer that the fluxes reported here are estimates, not measurements. Another important aspect of equation 3: the gas exchange velocity and concentration influence each other. A very high  $k$  can quickly empty the water of gases and thus lead to low concentrations, and low  $k$  prevents emission and can lead to the build-up of high concentrations. It may therefore very well be possible that the sites where the authors have observed high concentrations, the fluxes may not be high if that site was characterized by very stagnant water (possibly in the “hot spot” channel?), instead concentrations might have been high because  $k$  and thus flux was low. A relevant paper on the spatial decoupling of  $k$ , concentration and emission is Rocher-Ros et al. 2019, L&O, their Figs. 2 and 3. This aspect should be added to the discussion.

L126. This statement needs a reference.

Results and Discussion: I wonder if it would not be helpful to separate the Results from the Discussion, and to present the results step by step (concentrations, maps of

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concentration, then estimates of emission flux, then an upscaled emission for the entire Delta), to then Discuss the ensemble of the findings.

L132. Consistent, not constant.

L133. Another point of serious concern: This study completely lacks statistical testing of the reported differences, and the term “significant” should only be used if a statistical test can support that the difference between e.g. systems or sampling campaigns was statistically significant. The authors must include statistical testing in their revision.

L134. Using maximum values is not very helpful, better to report means, medians or ranges.

L137. What is meant by “water type boundaries”?

L138. If I remember right, Crawford et al. studied streams, not channels.

L139. “were found to have higher concentrations” – where is this visible?

L140. What is a “boundary crossover”?

L142. On the map, there is channel north of Lake Puiu?

L143. Using the term “hot spot anomaly” requires some quantitative and statistical underpinning. It seems from Table 1 that this site was only showing elevated CH<sub>4</sub> in Aug, but not in May and Oct. So is this site really significantly different from other sites, i.e. other river reaches, or other lakes, or other channels? Statistical testing is warranted.

L146. Briefly explain that in October, macrophytes senesce and can be expected to start decomposing in the water.

L147. “measurements were not distributed proportionally” – this not only applies to O<sub>2</sub> measurements, but to all measurements, so this would affect all your data and conclusions?

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L150. This sentence is speculative and should be removed.

Figure 3. I suggest to present only concentrations, and give some aggregated numbers for fluxes later. Fluxes are only calculated estimates, which are derived from your actual measurements. Instead, also include CO<sub>2</sub> concentrations here. And please include statistical testing to infer any differences between categories. Also, please label the panels of this figure. Two observations: O<sub>2</sub> saturation was frequently very low, indicating strong respiration in the water or the reed belt. And the distribution of CH<sub>4</sub> was very skewed, with generally rather low values, but quite a bunch of very high values.

L152. Fluxes correspond to concentrations because your k estimate is essentially a constant, which k certainly is not in nature. On the contrary, it can be very variable at short scale of space and time. This observation is an artefact.

L154. For upscaling, it is very important to detail how the calculations were performed, and which assumptions were made, step by step. This was not really the case here.

L159 “this estimate “ – which estimate?

L161-164. Confusing that both a 277% and 70% underestimation of total flux are cited. Using the 70% estimate seems more realistic, because that stems from the same system.

L169-170. Use those floating chamber measurements to calculate k values, which you then can use for your upscaling. It would also be informative to compare the floating chamber measurements of emission to your calculations of emission.

Table 1. These are descriptive statistics. Also, please include CO<sub>2</sub> here and save CH<sub>4</sub> flux for later. “stinky channel hot spot” does not seem appropriate terminology, and it does also not seem to have extremely high concentrations compared to the other channels. And what does the footnote \*\* mean?

L173. Please show these correlations, or give regression statistics in the text. This

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sentence could also be interpreted as an indication that scaling k from wind speed at some met station was not really relevant.

L175-176. Which external factors? Aren't the most important factors biological and physical?

L179. Change with respect to what? And again, "significantly" requires some form of statistical testing.

L183. Concentrations and stuartion of what?

L188. I would expect that macrophyte degradation should also be high in the channels, not only the lakes?

L189. This could be explored further. With your data, you could make maps and actually at which locations concentration were elevated. For the lakes, you might want to make a correlation between distance from shore and concentration.

L194. Methanogenesis takes places in anoxic sediments, and I assume the channels don't have very much sediment accumulation at their bottoms?

Section 3.1.3. Again, this needs to statistically supported.

L209. Movement of water?

Section 3.1.4. Unclear what "fluvial" is. Everything minus lakes? Are channels included? And aren't the lakes part of the fluvial delta?

L213. "Little evidence" – please show the evidence that you have.

L222. This is expected, since there is very little sediment accumulation expected at the bottom of rivers.

L230. Unclear what time period this estimate covers. The three months of measurement? Or the entire year, based on the 3 sampling occasions.

L242. This is evidence that the emission might not have changed much, but for as-

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sessing eutrophication, you would need data on phosphorus, nitrogen or chlorophyll.

L246-249. Here's several statements that require to be supported by showing evidence: enhanced CH<sub>4</sub> production, increasing concentrations coming to the lakes, oxidation, visible on the edges of lakes.

L250-251. Which changes in morphology? What evidence is there for higher productivity in the channels. And what is meant by "macrophyte distributions"?

L256. Ebullition is also a flux from the sediment.

L260. With your data, you are in a very good position to explore local dynamics, by making maps and showing them.

Section 3.2. This section is far too long, mainly because there was only one true diel cycle measured; during the other diel-cycle measurements, the boat was moving, and thus spatial variability is included in the measurement. Also, the authors lack data that help to explain the diel cycle, e.g. water column profiles of temperature (to address convection) or of gases, measurements of k, or similar. Therefore, the discussion is quite vague. Based on so little data and machnistic understanding, it does not seem warranted to draw the conclusion that diel cycles are important in the Danube Delta, and need to be accounted for (e.g. in the abstract, or L339-341)

Figure 4. I would prefer simpler plots, with time of the x axis and the analytes on the y axis.

Figure 5. I would like to see more of this! More maps with concentrations, and further analyses of spatial patterns of elevated (and low) concentrations.

L370. Is there any data or other evidence for high concentrations in the reed bed?

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-353>, 2020.