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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.

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This paper reports high-resolution measurements of dissolved CO_2 and CH_4, as well as O_2, 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.

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Response: Thank you for your positive comments! We have replied to each one individually below and the review helps to improve the manuscript significantly.

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

Response: In the revised version we will strive for a more careful balance and avoid too far-reaching conclusions. Details are explained below.

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_2, 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.

Response: We will follow the suggestions by the other reviewer, and remove the CO_2 data to focus on a more concise a story CH_4 concentrations and fluxes. Surface waters will be added to the title, working title of: 'Surface water Methane in the Danube Delta: The importance of spatial patterns and diel cycles for atmospheric emission estimates.' The CO_2 data will be dealt with elsewhere.

L34. Source of what? Please specify.

Response: Source of CH_4. New sentence in next comment below.

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

Response: Rephrased as "Natural wetlands are one of the single largest sources of methane (125–218 Tg CH_4 yr^{-1}), accounting for roughly one third of total (anthropogenic and natural) emissions (Dean et al. 2018; Saunois et al. 2019)"

L37. See the new lake CH_4 emission estimate by Del Sontro et al. 2018, L&O.

Response: We replace Krischke et al. by DelSontro et al. 2018 as follows: "DelSontro et al. (2018) illustrate the large uncertainties in these data. Depending on the upscaling methods these authors arrive at global CH_4 emission rates from lakes in the range of 78 – 248 Tg CH_4 C yr^{-1}."

L41. This sentence is repetitive.

Response: We reorganize this section, starting with lakes and ending with rivers to avoid repetition:

Wetlands are one of the single largest source within the inland waters (125–218 Tg CH_4 yr^{-1}) accounting for roughly one third of total emissions (Dean et al. 2018; Saunois et al. 2019). They are usual intertwined with rivers, channels and lakes making them highly diverse regions. Due to lakes being some of the easier systems to measure and compare, they are the most extensively covered components of inland waters although only covering 0.9% of the Earth's surface. DelSontro et al. (2018) illustrate the large uncertainties in methane emission data. Depending on the upscaling methods these authors arrive at global CH4 emission rates from lakes in the range of 78 – 248 Tg CH_4 C yr^{-1}. Specifically, shallow lakes are known to generally be hot spots in terms of CH_4 emissions (Cole et al. 2007; Davidson et al. 2018).

Rivers emit around 26.8 Tg CH_4 yr^{-1} excluding ebullition (Stanley et al. 2016), however, due to a lack of global data coverage and consistency their role in both carbon transport and storage is not well constrained (Tranvik et al. 2009). In the anthropogenically modified Danube Delta we refer to the internal connections between the main river reaches and the lakes as channels (Kasprak et al. 2016). In general, there is a need for more detailed assessment of the role of methane emissions from rivers and channels as they have been suggested to be more

spatiotemporally variable for CH_4 than CO_2 (Stanley et al. 2016; Natchimuthu et al. 2017).

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?

Response: There are a few reviews on what classes channels and streams (see Rosgen Stream Classification System), and these classifications have been discussed by Kasprak et al., 2016 in the framework of a stream channel classification. The channels accessible by boat in the Danube Delta are modified to keep them open for boat access. Overall, we have gone with channels, as where we measured, they are flowing between regions (e.g. between two lakes, or a river to a lake), and some of which are manmade. We have now added a reference in the modified section under line 41.

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

Response: Will be revised, see below Line 48-50

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.

Response: We will remove Figure 1 and re-focus the paragraph on the transport pathways: "Methane is produced in anaerobic environments, mostly within

sediments (Schubert & Wehrli, 2019). Transport mechanisms to the atmosphere include turbulent diffusion trough the water column followed by diffusive gas-exchange across the water- air interface. Methane oxidizing bacteria in the water column reduces methane concentrations depending on the mixing regime (Mayer et al. 2020). At high supersaturation and low hydrostatic pressure bubbles can form and depending on their size ebullition offers a direct pathway from the sediments to the atmosphere (DelSontro et al., 2015)."

Paragraph to be deleted: Typically, CH_4 is biogenically produced within anaerobic environments ... lateral transport and ground water inputs (Crawford et al. 2014a; Stanley et al. 2016).

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.

Response: We already suggested changes to this section in response to the other reviewer.

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

Response: Often monitoring approaches have prioritized one water type (such as lakes). Will be rephrased as 'Given the complexity of inland water systems, especially wetland complexes, monitoring approaches were often focused on only one water type such as a river reach or a lake.'

L76. Objective 2 should be rephrased, since you do not address global-scale fluxes in

this paper, and you only measured one diel cycle.

Response: This will be rephrased "... data to explore the importance of a diel cycle on local and regional emission rates"

Section 2.2. Please describe what distinguishes rivers from channels.

Response: This will be elaborated on. We classed channels as smaller bodies connecting between regions, with only the two larger branches as rivers, given their size, slightly faster flowing and greater depth.

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_2 and CH_4 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?

Response: We will be adding figures of the concentrations along the tracks – especially for spatial variability visualisation. This figure will be made clearer with the removal of boxes not needed.

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

Response: We will omit this statement in the caption, because it is confusing. Instead we mention the deviation in the cruise track in a new sentence following

line 104 as follows "Using the small houseboat, the set-up was fixed, and a thorough transect throughout the delta was carried out with extensive lake transects completed in all three seasons for comparability (Fig 2). Due to blockages in the channel between Lake Puiu and Lake Rosu, the transect had to be changed slightly between seasonal campaigns."

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

Response: This is the annual temperature range. It was meant to illustrate that the delta experiences extreme temperatures (30 + to below freezing): The delta is within the temperate climate system, but experiences a broad annual ranges of air temperature from below freezing to more than 30° C (ICDP 2004).

L102. "thorough" is subjective, and can be skipped.

Response: Corrected

L120-125. I have some serious concerns with the way the gas exchange velocity and flux estimates were treated and discussed. Only the concentrations CH4water and CO2water 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 speedscaled 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.

Response: The first point was expressed by the editor as well, therefore experiments were conducted using differing measurements of air concentrations for CH_4, such as the nearest Global Greenhouse Gas Reference Network station Hegyhatsal (HUN), Hungary. This made negligible difference in the overall fluxes due to the extreme water-side supersaturation, and therefore is not considered an issue, but this will be stated clearer. For the second point, the wind was taken from the Gorgova station (roughly middle of the delta, will be included in review). We will definitely be acknowledging this point more so in the review as we are very aware k can vary significantly. Maier et al. (2020) measured in different years to this excursion so direct use of their k value would probably

not be accurate. However, comparison between the k values produced from the models will be done and added to the supplementary. It will be made clearer that these are estimates. All of this will be discussed in the discussion and it will be made clearer.

L126. This statement needs a reference.

Response: This will be added: Schilder et al. (2013).

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

Response: Following the advice of the other reviewer we will edit the results and discussion section to improve clarity and remove redundancies. We feel that separating discussion from results might contradict this effort.

L132. Consistent, not constant.

Response: Will be changed.

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.

Response: Correct, also in response to the other reviewer will replace the word "significant", if it is not backed up by statistical analysis. We will use a Kruskal-Wallis test to compare rivers, channels and lakes.

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

Response: As the data usually are not normally distributed, we will use medians and ranges.

L137. What is meant by "water type boundaries"?

Response: Water type boundaries means areas such as channels leading into lakes, the mixing areas, as stated within the manuscript. This description will be added in the description describing the sectioning processes.

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

Response: Yes. Will be corrected.

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

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Response: This will be implemented visually with the figures stated above. It is visible closer to the edges of the lakes where the wetland is situated.

L140. What is a “boundary crossover”?

Response: Between two boundaries, such as where channels enter lakes. Rephrased to ‘These boundary crossovers, where higher concentrations were visible to proceeding regions, were due to. . .’.

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

Response: All areas and locations will be made clearer on the figure, larger maps will also be included into the supplementary .

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 CH4 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.

Response: A statistical analysis will be added to this section.

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

Response: Rephrased: ‘The highest median was observed during Oct for

rivers, lakes and channels (median: 559, 693 and 1500 nmol L-1 respectively), potentially due to macrophyte senesces and decomposition.

L147. "measurements were not distributed proportionally" – this not only applies to O_2 measurements, but to all measurements, so this would affect all your data and conclusions?

Response: This should not affect the diel cycles, and this would have no effect. This could potentially skew the overall median values; however, this is why we split the data into different categories (lakes, rivers and channels) and attempted to get mapping coverage of each of these regions. Therefore, when analyzing the data while in each separate region, it shouldn't affect the outcomes.

L150. This sentence is speculative and should be removed.

Response: We disagree. It is well known that water that spent time in close contact to wetland vegetation looses oxygen and builds up CO_2 concentrations (see for instance Zurbrügg et al. 2012). We will rephrase this as: "These values included the 'hot spot'. Wetland waters entering the fluvial systems are often de-oxygenated (Zuidgeest et al. 2016). As this station represents sites receiving water from the wetland it is likely not the only such site in the delta."

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_2 concentrations here. And please include statistical testing to infer any differences between categories. Also, please label the panels of this figure. Two observations: O_2 saturation was frequently

very low, indicating strong respiration in the water or the reed belt. And the distribution of CH_4 was very skewed, with generally rather low values, but quite a bunch of very high values.

Response: Thank you for the constructive comments to improve Figure 3. Concentrations and fluxes will be separated. Panels will be labelled, and statistics between the regions will be inserted. CO_2 will be removed from the manuscript as previously stated.

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.

Response: This is a very valid comment but not completely true. Fluxes would have been much more accurate if they were based on in situ measured wind measurements. However, we did use wind data from Gorgova (roughly in the middle of the delta) to calculate k and therefore fluxes include the effect of wind speed. This can be observed in Fig. 3 in lakes and channels especially and the k values did vary. But this will be commented on in the manuscript and made clearer.

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.

Response: As also pointed out in the reply to reviewer 1, we now cite the average values for the three systems in Table 1 on which the upscaling is based.

L159 “this estimate “ – which estimate?

Response: Meaning the calculated fluxes: " However, these calculated fluxes include only diffusive emissions.”

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.

Response: We will delete the reference to the 277% present and focus on the local comparison. The paragraph will start with “In their study over two years, however, Maier et al. (2020) found evidence that bubble emission of methane in the Danube Delta lakes and channels, potentially accounted for 70%.”

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.

Response: We will focus on the comparison of the two emission data, the direct flux chamber measurements by Maier et al. (2020) and our calculations.

Table 1. These are descriptive statistics. Also, please include CO_2 here and save CH_4 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?

Response: Terminology will be changed and clarified. When taking the median, the hot spot is not exceptional, except for Aug, however the entire concentration range is far higher. The ** footnote means there was influence on the edges from the channels into the lakes, across the border but meaning they had a few meters of extreme concentrations.

L173. Please show these correlations, or give regression statistics in the text. This sentence could also be interpreted as an indication that scaling k from wind speed at some met station was not really relevant.

Response: In response to similar comments by reviewer 1 we will delete this paragraph and discuss patterns and their possible drivers later.

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

Response: We will remove this paragraph see response to 173.

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

Response: The statement was not meant in a statistical sense and the paragraph will start with "Different processes influence the seasonal carbon turnover and methane production in the delta".

L183. Concentrations and stuartion of what?

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Response: CH_4, this will be implemented!

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

Response: Yes, this will be implemented. "... the process of macrophyte degradation within the delta in both, lakes and channels, was linked ..."

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.

Response: This is a helpful suggestion. We will add more plots illustrating the spatial patterns of CH_4 concentration, part of them will be presented as Supplementary information.

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

Response: Channels have quite high sedimentation rates and the larger ones are dredged to maintain navigation.

Section 3.1.3. Again, this needs to statistically supported.

Response: This will be implemented. We will provide a statistical comparison of the hot-spot to the other sites. As also mentioned in the remarks to review 1, we will replace the term "significant influence" by "strong influence"

L209. Movement of water?

Response: Yes, will be clarified.

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

Response: This is stated on line 212 – rivers and channels.

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

Response: This will be clarified as follows: "Based on continuous conductivity measurements, we found no evidence for saltwater intrusions from the Black Sea that could suppress methane production by high sulfate concentrations as suggested before (Durisch-Kaiser et al. 2008. . .)"

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

Response: For sure, and the rivers are far deeper and faster flowing. This was a statement to make it clear.

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

Response: This is over the 3 campaigns, it will be made clearer: "Overall our calculated mean flux for all months of the three campaigns. . ."

L242. This is evidence that the emission might not have changed much, but for assessing eutrophication, you would need data on phosphorus, nitrogen or chlorophyll.

Response: Yes, will remove "eutrophication" from the statement.

L246-249. Here's several statements that require to be supported by showing evidence: enhanced CH_4 production, increasing concentrations coming to the lakes, oxidation, visible on the edges of lakes.

Response: Evidence will be implemented, this will be combined with the spatial plots which was stated before.

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

Response: The statement is rephrased below and will be illustrated with additional concentration maps. Macrophyte distributions with the lakes were visible from the O_2 concentrations, and were shown to change over the lake over the seasons. "The spatial differences and seasonal changes in the surface methane concentrations were far clearer in the lakes than the channels. Distribution

of macrophytes in lakes could be linked to the map of O_2 and decaying plant biomass explained the high CH_4 levels in October."

L256. Ebullition is also a flux from the sediment.

Response: This is true, however, diffusive transport and ebullition are usually discussed separately and we will write: "Diffusive release from sediments is usually the primary source of methane in surface waters (Peeters et al. 2019). Ebullition, however, adds a second pathway of CH_4 emissions to the atmosphere which is much more variable between systems and locations (see Bastviken . . .'

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

Response: As mentioned, we will expand the discussion of local dynamics and spatial variability and support this with additional maps and improved Figures.

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)

Response: Reviewer 1 remarked that data on the diel cycle are interesting but mentioned that generalizations would take the discussion too far. However, the parallel measurements of temperature and dissolved gases do allow some careful mechanistic interpretation. The movement during the diel cycle was taken into account (line 270), however the spatial variability follows clearly the overall diel pattern, especially as we measured stationary until after sunrise where we saw a decrease in CH_4 concentrations.

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

Response: An example for CH_4 is shown in Fig. 5. We will add similar plots for the other parameters.

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.

Response: Good suggestion, as mentioned already, we will add more maps and improve the figures.

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

Response: No measurements were taken in the reed beds because these sites were not accessible by houseboat. We see the influence from the edges of the lakes however, and in Maier et al. 2020 they state evidence for this flowing in from the edges too.

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