Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2020-353-AC1, 2020

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.

Anna Canning et al.

acanning@geomar.de

Received and published: 22 December 2020

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.

Responses to Anonymous Referee 1

Received and published: 12 November 2020

General comments

Overall, the study is an important contribution into methane dynamics in highly heterogenous system of river delta. It also emphasizes important (and often neglected) aspect of diel variability of CH_4 dynamics. I see this study as an ambitious project as it aims to examine spatial and temporal variability of CH_4 in various water bodies including river, side channels and lakes. It is important that authors distinguish between different aquatic systems and focus on more refined delta variability (river, channels, lakes) as these systems may experience distinct and highly variable CH_4 dynamics. Also, this study not only aims to elucidate high spatial variability in the above subsystems of delta, but also adds additional layer of high temporal variability (diel) of CH_4.

Such study design allows to obtain more comprehensive picture of CH_4 fluxes from such delta systems. In general, from reading the abstract and introduction I had an understanding of the study design and the rationale behind the investigations.

Response: Thank you for your positive assessment. Definition of the areas will be made clearer and each comment below has been individually commented to.

However, I see few substantial points which should be addressed before the manuscript can be published. These points are addressed in specific comments. Briefly, my major concerns are:

1. Gas transfer model used to calculate fluxes. As river delta is highly heterogenous system I believe that Cole and Caraco model is not the best choice to derive fluxes from measured concentrations. In the specific comments I propose the alternative gas transfer model, which could be more suitable in this system.

Response: See specific response to Line 144

2. Although diel study is very important aspect here, extrapolation and recommendations based on just two full diel studies is certainly not enough to suggest how to design sampling campaign (time of samplings to reduce bias).

Response: We agree and we will remove explicit recommendations. The extrapolations merely showed the potential bias, and we indicate multiple times that the calculations were highly specific to our observation (e.g. line 337). In the revised version we will communicate this more carefully.

3. CO_2 variability is certainly important and worth to study, however this manuscript focuses mostly on CH_4 There is no information, which would introduce the reader the CO_2 dynamics and in general CO_2 appears in the text only fragmentary. I would suggest that spatial and temporal CO_2 variability has a potential for separate manuscript.

Response: This is a constructive suggestion and we will remove the CO_2 data in the revised manuscript to make the story more concise.

4. There are numerous repetitions, especially regarding results. Values of concentrations and fluxes appear in tables and they are also described in the text, which is redundant.

Response: The text, figures and tables will be revised accordingly to avoid repetitions, thank you.

5. Language is occasionally missing fluency and precision. Some sentences are too composite and reader gets lost, so their structure could be simplified to assure nicer reading of this interesting study.

Response: We will edit language and overall structure for clarity in order to make the m.s. more accessible for the readers.

Specific Comments

Overall abstract is understandable; however it is missing flow in reading occasionally. Below I include several specific comments. However, if authors decide to implement other of my suggested comments (results and discussion) then the abstract would require modifications as well.

Response: Thank you, we will rewrite the abstract to reflect changes made and to improve the overall flow.

Line 7: please add how many days in total? "Over 3 seasons" is misleading and suggests that the concentrations were measured continuously for 3 seasons which is not the case.

Response: The sentence will read "During three expeditions in different seasons…"

Line 14-15: Did authors measured temperature profile to conclude there was a stratification? If not and this is an assumption (may be correct), it is not a result of the study

Response: The statement is backed up by temperature measurements.

Line 15 – 16: Please correct this sentence, it doesn't have correct English structure.

Response: The edited sentence now reads: "Daily spot sampling techniques would miss the effect of diel cycles and underestimate average methane concentrations by 25 $\%$ for channels"

Introduction:

I suggest to shorten introduction slightly. Especially selected parts (please see comments below) should be removed as they provide details which rather distract the reader from the main path of the manuscript instead of leading to the main issue. Instead I would suggest that authors elaborate slightly more on diel variability as this is main topic of the paper.

Response: We will shorten the introduction and emphasize the diel variability.

Line 29: It is not clear:, please specify "Potential driver" of what ?

Response: The modified sentence will read "Biogenic emissions from wetlands (Nisbet et al. 2019) contribute strongly to the overall estimate of 159 (117-212) Tg CH_4 yr^{-1} from inland waters . . ."

Line 37 : substitute "although" with "yet"

Response: This will be implemented.

Line 39-40: repetition "covering" and "covered", please change

Response: This will be changed.

Line 39: "give a range", just "range" is enough

Response: This will be changed.

Line 43-44: Do authors aim to assess the role of rivers and channels in methane emissions, not the role of methane?

Response: The edited sentence will read: "Therefore, there is a need for more detailed assessment of the role of rivers and channels for methane emissions, as they have been suggested to be more spatiotemporally variable for CH_4 than CO_2"

Line 46-50: In my opinion this part is redundant as the methanogenesis or methanogenesis related processes are not a topic of this paper. According to me it deviates the reader from the main (interesting) story.

Response: These lines will be removed to make the story more concise.

Figure 1. This scheme is nice and illustrative but rather redundant in the context of this manuscript. This is rather text book knowledge and this scheme does not illustrate neither findings of the paper or concept of the study. In my opinion this scheme is not necessary.

Response: Figure 1 will be removed in the revised version.

Line 63: Please provide reference for this statement

Response: We refer to the reference (Bartosiewicz et al., 2019) in the sentence before. We will make this clear: "These authors suggest that CH_4 production in bottom waters may increase, potentially leading to ..."

Line 64 - 65: Although I see how browning or warming could affect seasonal variability of CH4, I cant see how they would impact diel variability?

Response: Browning is as a complex driver for methane emissions mostly at high latitudes, but as this study has a different focus we decided to omit a reference to it. New line reads: "suggest that global warming will increase surface water temperatures and strengthen lake stratification (Woolway et al., 2019)".

Line 67-68: Real strength of this study: high spatial and temporal variability in different systems

Response: We will emphasize this point as follows: "The acquired high spatial and temporal resolution of methane concentrations and corresponding emissions formed a unique observational data basis. Continuous measurements across the delta allowed us to assess the importance of different systems (lakes, rivers and channels) and the high-frequency data at specific sites yielded insights into diel cycles and the specific day-night dynamics of methane emissions."

Line 73: Please specify what is "extremely high resolution" 10 times a day, every hour, every minute: : :?

Response: Up to one measurement per second. "Here, we take a complementary approach with a measurement frequency up to 1 Hz. This allows not only for high-resolution data both in time and space but also for a detailed look at the diel variability time-scale"

Methods:

Set up: As a reader not specifically familiar with this type of set up, I would appreciate more details. As far as I know this type of setup uses membrane-based equilibrators? I think this information should be in the method description so the reader obtains information about principle of the method. Also, equlibrators may underestimate concentrations (especially CH_4), it would be highly appreciated if authors acknowledge drawbacks of this specific method. I do not try undermine this method and I am aware that every single method has its pros and cons, but for the reader it would be beneficial to know (very briefly) to know its drawback (and benefits too).

Study area is described sufficiently, however I am missing specific information how many km2 were covered regarding each system (lakes, channels, river)?

Response: In order keep the text concise and avoid repetition of what has already been published, we refer to the technical note Canning et al. (2020).

Line 109: Wind speeds may be locally different from what was occurring at the delta therefore its important how far from measurement sites Gorgova weather station was located?

Response: Gorgova is roughly in the middle of the delta: "Barometric pressure as well as wind speed measured at the Gorgova station in the center of the delta were used".

Line 110: I encourage authors to use reference Wannikhof 2014 instead of Wannikhof 1992

Response: We will change the reference as requested. Based on a quick recalculation, however, the switch to Wanninkhof 2014 will not significantly affect the results; the difference will be smaller than the measurement error for concentrations.

Line 113: I think its not correct to disregard stream velocities, especially without information about their values? What are the stream velocities (range) in this system?

Response: Stream velocities within the delta were slow with maxima smaller than 30 cm s^{-1}. With the exception of flood events, the hydrodynamics of smaller canals is much closer to wetland lakes than to estuaries for which Borges et al. (2004) derived their k values. We therefore insist that the Cole and Caraco model is more adequate than other parametrizations for river systems.

Without this information it is difficult to assess if Cole and Caraco is the most suitable gas transfer model used. Please also see my comments below.

Line 114: Since authors didn't measure fluxes directly but derived them from the concentrations, it is very important to assure that authors apply gas transfer model which is the most suitable for measured sites and conditions. Cole and Caraco was developed for lakes mostly and doesn't include impact of variable hydrological settings in delta system, mainly flow velocity, which has an impact on fluxes too. Therefore, I would suggest to calculate fluxes using gas transfer model, including both variables (wind and flow velocity), which have an impact on k in such dynamic system. As there is no "ideal" model, I would still suggest to rather use the way k was derived in "Borges et al 2004" (as I see in reference list authors are already familiar with this publication) than Cole and Caraco gas transfer model.

Response: Indeed, there is no ideal model for gas exchange in slowly moving fluvial systems such as the channels of the Danube Delta. For a river with flow velocities that were typically ten times faster than those observed in the Danube Delta DelSontro et al. (2016) calculated the gas transfer coefficient with nine model equations resulting in a range of k values spanning an order of magnitude. For quasi-stagnant waters, which we observed in the delta, however, the lake Cole and Caraco is quite well established. By contrast, Borges et al. (2004) worked on large rivers and a fjord, systems that are hydrodynamically

very different from low-flow regime of the lakes and channels of the delta. In support of our approach, we will follow the approach of Cole et al. (2010) and extend the comparison with the floating chamber measurements by Maier et al. (2020) – see lines 167 169.

Line 122: application of different model will have an impact on n value too

Response: See above.

Results and discussion:

As I already wrote in the General comments above, there are numerous places where results (values) are repeated. This is redundant. If value is already presented in the table, there is no need to repeat it in the text. It allows to keep the manuscript more concise. Also, regarding reporting values, I suggest to use μmol L^{-1} instead of nmol L^{-1} all throughout the text.

Response: This will edit the results section accordingly and use μmol L^{-1} throughout.

Line 147: Please rephrase the sentence, oxygen by itself cant be undersaturated, lake water can be.

Response: "Oxygen concentration in the water was mostly below saturation. . ."

Line 152: "some variability ultimately due to temperature and wind": Currently I cant

see a support for this claim in the presented data. Where do the data show that flux variability was due to the temperature and wind?

Response: This was a general statement and will be removed.

Line 154: What do authors mean by "outgassing flux density"? Do you mean "mean flux"?

Response: Yes, corrected as follows "we got an overall mean outgassing flux of 49 $\pm$ 61 μmol m-2 h-1"

Line 154-156: If such extrapolation exercise is done, then it should rather be described in the method section. Thus, I suggest to move it to method section and in this section present only obtained results. Also, I think it is important that authors measured and presented separate values for different types of water bodies in the delta. Its highly appreciated since such information is less common and shows that even it is one system, CH_4 variability in water bodies located in close proximity to each other can be high. That is why I do not see the reason to pool all the data together and just derive one mean for the whole delta. To include flux variability within such complex system I suggest to (at least) calculate mean flux for each type of water body (channel, river, lake), calculate how much of area is occupied by each type of waters/wetlands and then extrapolate and derive total flux per year.

Response: This is what we did. We took the areas of each water body (lake, rivers and channels) and to these applied the average fluxes observed for the three water types. (lines 152 - 160). The concentrations and fluxes are detailed in Table 1. We will add a sentence outlining the upscaling per system. "We used

the estimated area from Maier et al. (2020) for total area of rivers, channels and lakes (164, 33, 258 km^2 respectively) and the average emission rates in Table 1. Taking the average across all seasons, annual estimates for methane emissions of 16.1, 81.9 and 24.9 μmol m-2 h-1, for rivers, channels and lakes, respectively. The combined overall mean outgassing flux is then 49 $\pm$ 61 μmol m-2 h-1."

Line 162- 168: Good point, it is appreciated that authors acknowledge and discuss importance of ebullition in this system

Response: Thank you!

Line 169 – 170: I am not familiar with specific set up of Maier et al. 2020, but I do not agree that the method used by authors in the manuscript and chamber method cannot be compared at all. Sure, such high variability is missed by chambers, but at least fluxes at the same depths and same systems obtained by both studies could be compared.

Response: Chamber measurements are picking up ebullition, which can be high, whereas our estimates for diffuse fluxes were based on concentration measurements in the surface waters. The two methods are therefore influenced by different processes. However, some general comparison is possible and will be implemented.

Line 173: I agree that its not possible to assess impact of environmental drivers (such as wind) if it wasn't measured in situ. However, if authors suggest that distribution patterns were rather driven by biological or physical factors it should be supported by the data. And I'm not sure if I see such evidence. Plus, which biological and physical

factors do authors mean? It would be important to be more specific.

Response: This paragraph with reference to biological and physical effects comes too early and we will delete it. It will be more evident, when we discuss the patterns shown in Figure 5.

Line 181: Flooding is an important aspect in a frame of seasonality. As I imagine such system experiences reoccurring flooding, which may have big impact on CH_4 fluxes (see for example Gatland et al 2014, JGR). To obtain more comprehensive picture on CH_4 seasonality in delta system, it would be important to acknowledge flooding phenomena in a bit more detail.

Response: Good point we will include a reference to flooding and flood recession. Flooding will push oxygenated water into the reed stands and decrease emissions, while flood recession will move anoxic water from the reed into the channels and trigger ebullition.

Line 185-187: Please rewrite this sentence, I'm not sure what authors meant here.

Response: Rephrased to, 'Aug had the lowest water levels of each season, and although it showed the largest CH_4 range among the seasons, it had the lowest measured median values, coinciding with the hypothesis that there is an overall decreased CH_4 concentration values during lower water levels (Melack et al. 2004; Marín-Muñiz et al. 2015; McGinnis et al. 2016).

Line 189-190: The sentence is structured like authors actually measured decomposition of OM and subsequent CH_4 liberation. If authors didn't do such measurements, I would suggest to change it to:": : :.of biodegradation of OM could have triggered: : :which could be responsible for: : :."

Response: This will be changed thank you!

Line 192: Please change to "may explain" or "could explain"

Response: Will be changed!

Line 193-194: Not only lakes are sources of labile organic matter, also rivers and channels too. Please provide reference

Response: Good point "River reaches, channels and lakes are sources of labile organic carbon that fuels methanogenesis (Schubert & Wehrli , 2019).

Line 195 - 196: "Channels..: : :..in O_2": If authors make such statement, reference would be appreciated or these are results of this study? It is not clear.

Response: Will insert reference to Maier et al. 2020, where O_2 date for all three systems have been evaluated.

Line 201: Why such conductivity points into groundwater influence?

Response: High conductivity is a reliable tracer for groundwater exfiltration.

(see Harvey et al., 1997). We found this region had a peak in conductivity compared to regions surrounding this location.

Line 199 - 203 : Authors raise here the potential impact of groundwater on 'hot spot' conductivity. Also, the impact of groundwater on surface water CH_4 concentrations may be very important too (especially in wetlands). So, if authors raise here importance of groundwater, then its potential impact on CH_4 in this system should be acknowledged as well. Of course, one cant measure everything and I wouldn't expect the actual results but one or two sentences about potential impact of 'hot spot' groundwater on surface water CH_4 in this system.

Response: Groundwater can have an impact on overall gas supersaturation within the water column (Crawford et al., 2014), potentially leading to increased CH_4 concentrations within specific locations throughout the delta.

Line 202: Please clarify. What do authors mean by "water dropping further into the 'hot spot' ?

Response: Water temperature decreased the further away we got from the channels joining to the hot spot. Rephrased to, 'Given the dramatic change within the concentrations and properties of the water, such as the water temperature decreasing the further away from the channel we travelled into the 'hot spot', even within summer, this would further provide evidence from cooler groundwaters or potential waters from the reed beds also suggested by Maier et al. (2020).'

Line 206: In general the word "significant" is usually used in a statistical context, which is not the case here. I would suggest using other word

Response: We replace “significant” by “strong” influence

Line 211-222: I agree that this may be the case that more production happens in the delta, not in the river, and that such hot spots may impact the system's concentrations. Thus, this paragraph is important, however I have difficulty to follow the way it is currently presented, I guess because many values are included in the text. I would suggest maybe to draw simple conceptual figure, which could illustrate possible impact of channels and hot spot on a system. With colors representing concentrations? It would be easier to grab this interesting concept. If authors do not wish to illustrate this idea and stick to written text, I would suggest to rewrite it so its easier to follow.

Response: The edited section now reads: “The fluvial delta (rivers and channels) works as the supply of incoming water into the main part of the delta, accounting for the base level of CH_4 concentrations being laterally transported. We found very little evidence that intrusions from the Black Sea may have reached into the delta and have an impact such as suggested before (Durisch-Kaiser et al. 2008; Pavel et al. 2009). This would be important to explain reduced methane production as sulfate reduction becomes the dominating anaerobic mineralization pathway. Rivers had the lowest range of concentrations for CH_4 with the smallest variability out of all systems and the delta (Fig. 3). When excluding the ‘hot spot’, median values for channels were larger than those for rivers and fairly consistent throughout May and Aug while increasing during Oct. While in comparison, the hot spot measured the largest concentrations during May and Aug respectively, and thereby changed the overall channel dynamics during Aug by increasing the overall channel median. The influence of the hot spot showed the significant influence one spot can have on a system, providing evidence that most of the CH_4 production happens within the delta,

not the river itself.’ An illustration may be added.

Line 216- 229 Many values described in this paragraph are already in the table 1, so there is no need to write and describe all the values here again. It is unnecessary repetition and can be removed.

Situation of CH_4 in lakes

I suggest changing the paragraph header to “CH_4 concentrations and fluxes in lakes” or “CH_4 dynamics in lakes” Many values described in this paragraph are already in the table 1, so there is no need to write and describe all the values here again. The discussion of obtained results is enough.

Response: We will edit the results section and delete redundant values.

Line 254: What do authors mean by “averaging” the lakes? Is it average of fluxes, of total fluxes, from all lakes? Its unclear from the text.

Response: Average fluxes over all of the measured lakes. Will be made clearer.

Line 260: What authors mean by “intermediate” sampling ?

Response: Intermediate is meant as sampling at specific times, or in specific places such as just at channels joining the lakes. This will be made clearer.

Diel CH4 cycling

Line 269 – 270: This sentence is not clear, requires clarification what authors intended to say here?

Response: Rephrased to, ' As the mapping transect in Lake Rosu started around 9:00, some spatial variability from varying concentrations due to proximity to the shore line (Fig. 5) is superimposed onto the dominant diel cycle, causing CH_4 concentrations to vary over the range 200–500 nmol L-1.

Line 266: Please indicate the letters in Fig. 4 instead of "left"

Response: This will be implemented

Line 273-275: Do authors mean here convective mixing? If yes, its good to mention this term here

Response: Corrected: "A possible explanation for this hysteresis: the water column stratifies during the day, and undergoes convective mixing as the surface water is cooling during the night"

Line 284- 310 As I wrote in the general comments, CO_2 deserves its own story. Including it suddenly into the manuscript distracts the reader from the main story, which as my understanding is, covers almost solely CH_4. Also, so far the whole text above included only CH_4 patterns. Additionally, this section has a title which points to CH_4 daily patterns only. I suggest to remove CO_2 dynamics from the manuscript.

Response: CO_2 will be removed from this manuscript.

Figure. 4: Nice and informative figures.

Response: Thank you!

Line 326 – 327: I think authors mean here "day light data", not "day night data" ? Please clarify.

Response: Yes, will be corrected.

Line 334-354: It is a valid and very good point that authors' aim is to emphasize importance of diel variability and bias which occurs due to spot sampling. This may be one of the reasons for bias in current CH_4 estimates or upscales. However, I would avoid giving recommendations how to minimize bias during lake CH_4 sampling based on 2 full diel cycles. I see this manuscript as important work to bring attention into neglected issue of CH_4 diel cycle in delta system, but to draw firm conclusions and give sampling recommendations, more full diel surveys would be necessary. Also, it is important to acknowledge that these two diel cycles captured by this study could be a snapshot as well. Thus, if being measured another day (or season), the opposite situation could have occurred with higher late daytime fluxes compared to the nigh time (for example, see Sieczko et al. 2020 and references therein).

Response: We will remove the recommendations and focus more on the spatial variability as previously noted. Acknowledgement of few diel cycles and poten-

tially only capturing a 'snap shot' will be implemented, 'Although capturing the diel variability, it must be noted that few diel cycles were captured and these may well be different at other times and locations and therefore not be representative of the overall situation in the delta.'

Table 2. I propose to visualize the table in a form of figure. It will be easier for the reader to see more clear the impact of day light (DL) vs. full diel cycle (FD) sampling on CH_4 flux and concentration.

Response: We will add such a figure as suggested.

Line 349-350: The cited studies actually acknowledge and emphasize existence of CH_4 diel cycle. They do not undermine it as this sentence suggests. The sentence or the references requires modification.

Response: This sentence was meant to reference said references as acknowledging the existence of diel cycles. Therefore, to make this clearer, this will be modified to: 'There have been multiple studies looking into diel cycles (see Nimick et al. 2011; Zhang et al. 2018; van Bergen et al. 2019; 350 Sieczko et al. 2020 for examples), yet these are usually undetected or not fully resolved and therefore ignored, particularly in studies with...'

Line 379: Did authors measure organic carbon and showed that it was derived from macrophytes?

Response: Unfortunately, this was not measured by us.

Technical Comments

Line 170: please change "location" to "locations"

Response: Done

Line 177: Please change "decease" to "decrease"

Response: Done

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