EGUsphere, author comment AC1
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Reply on RC1

Judith Vogt et al.

Author comment on "Sea-air methane flux estimates derived from continuous atmospheric measurements and marine depth profiles in cold seep regions" by Judith Vogt et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-545-AC1, 2022

Responses to reviewer 1

We would like to thank Dr. Charel Wohl for his thorough feedback and his helpful comments on this manuscript. We would like to note that we identified errors in regards to dissolved methane concentration calculations in the manuscript that led to substantial changes in the results of this study upon revision. Therefore, some of the reviewer's comments may not apply to the latest version of the manuscript anymore. In the following, we try to address the comments as best as possible. Our replies to the reviewer's comments are indicated by italic fonts.

We would like to note that, upon revision, we made changes (partially beyond the comments of the reviewers) to improve the manuscript. Main changes included:

- *Correction of dissolved methane concentrations and metadata*
- *Addition of two depth profiles previously excluded because of a misunderstanding*
- *Re-calculation of sea-air fluxes with updated concentrations and slightly different equations*
- *Correction of timestamps in atmospheric dataset and substitution of logged data with analyzer's raw data to overcome data gaps*
- *Exclusion of atmospheric gas measurements accounting for potential contamination by the ship*

Reviewer's comment on "Methane flux estimates from continuous atmospheric measurements and surface-water observations in the northern Labrador Sea and Baffin Bay" by Judith Vogt

In this manuscript, the authors describe shipborne ambient air, surface seawater and depth profile measurements of methane in the Labrador Sea and Baffin Bay area. The cruise track focusses in particular on sampling near hydrothermal vents. The authors are investigating the importance of the hydrothermal vent sources . Further, the authors present atmospheric measurements of methane and use air back trajectories to explain peak concentrations in their timeseries. They combine air and water measurements to estimate a sea-to-air flux and investigate latitudinal variations of this flux and the basin source.

Overall, the manuscript is well-written. The value of the manuscript lies in the measurements it presents and the processes it investigates. The manuscript is well referenced making good use especially of very recent publications in the field. I recommend publication after minor corrections. Congratulations on this nice piece of work.

General comments

Both these comments are optional and may help improve the readability/intuitive flow of the manuscript.

Maybe the authors could consider reducing the number of display items. The manuscript currently has 7 figures. Maybe figure 2 and figure 7 could be moved to the appendix with a bit more description in the main text instead of these figures.

Thanks for the suggestion. We moved Figures 2 and 7 to Appendix A.

Maye the authors could consider presenting the air measurements before the sea-to-air fluxes. It just feels a bit counterintuitive to present fluxes before air mixing ratios as the air concentrations are used to calculate the fluxes.

We followed the reviewer's suggestion and moved the flux analysis to the end of the Results and Discussion section.

Specific comments

L94: Regarding the linear interpolation of mixing ratios: How long are the data gaps for? What is the longest and shortest data gap here? From the timeseries, I see it is probably very short, but the text in L94 suggests this interpolation was applied to 19 % of the datapoints, which is quite a lot. Maybe consider not doing this linear interpolation for so many points. Instead the authors could set the data to NaN whenever there is a missing value of mixing ratio and report the data in 5 or 10 min (or less) averages. If the authors prefer to proceed with their current data processing, it may be worth highlighting a case study "moment" of how they performed the interpolation as part of the reply to reviewer's comments. Thank you.

Thank you for your comment. The 19% missing data from the gas analyzer were due to logger-analyzer communication issues. The raw data from the analyzer did not show any gaps. So rather than using the logger data, we fitted the raw analyzer data into the dataset in the revised study to avoid the large number of missing values. We commonly use a ~1 s frequency of our datasets to apply the wind correction.

L103: . "In addition, we determined there was no significant contamination of air samples by considering CO2 mixing ratios when the air inlet was downwind of the ship's (comparatively elevated) exhaust." That is surprising. Is that because the inlet tower is lower than the ship's stack exhaust? Does that mean that the authors did not do any filtering for ship stack contamination? I.e. the authors also use data when the relative winds were from the rear of the ship or in other words; the air inlet was downwind of the ship's exhaust? Can the authors please provide a figure of mixing ratios of methane and if possible CO2 against the ship's relative wind direction to support their claim? Maybe it is worth filtering the air data and only using methane measurements when the relative winds were from the front of the ship as is common in the field.

The air inlet was lower than the ship's exhaust. Methane contamination from the exhaust, *if present, was not available in sufficient quantities to make a difference for methane measurements. However, we decided to exclude CH4 and CO2 mixing ratios for measured wind directions >80° and <280° relative to the ship's bow, and for CO2 levels >420 ppm to follow the reviewer's suggestion, and also to conform procedures used in other studies. A supporting figure was added in the Appendix.*

L148: It is useful that the authors show exactly what equations they are using from the cited references here. Was there partial sea ice cover during the cruise track? Could the authors please account for this by scaling the flux based on the open water fraction as in https://doi.org/10.1002/2016GL069581 and https://doi.org/10.1002/2017GL073593.

We added more explanation and used equations to the Appendix. There was marginal sea ice cover during the cruise (also now shown in Figure 1). However, we can confirm that during the Rosette casts when water was sampled no sea ice cover was present. As we are interested in the instantaneous flux of methane (we clarified this in the Methods), we did not account for sea ice cover for the sea-air flux calculations in this study due to its absence.

Can the authors please provide a few references in which the k for methane has been calculated using the same equation? Maybe it is worth commenting briefly how the parametrisation chosen here compares to other parametrisations of k. This could help explain some of the high fluxes reported in this manuscript.

We decided to use the same parameterization for k as in the Manning et al. (2022) study (by Ho et al., 2006) instead of the parameterization used in the first version of this manuscript and revised the study accordingly. It should also be mentioned that we found errors in the water analysis, so that methane concentrations were much lower than in the first version of this manuscript. We corrected the values throughout the manuscript.

L258 It is worth noting here that the fluxes reported in this paper are extremely high for the stations influenced by seeps and North of 65 N. It may be worth emphasising this. The data collected here is clearly biased, because it was collected near known hotspots of methane seeps.

After correcting errors in the calculations of methane concentrations from the water analysis, fluxes were much lower than in the previous version of this manuscript and match better with previous studies.

L268 Diligently thinking ahead, the authors scale their measurements up to the whole area and exclude "samples with high concentrations". Can the authors please clarify how they have carried out this filtering?

I highly recommend redoing this calculation and accounting for sea ice cover and assuming sea ice acts as a barrier to air-sea exchange. Maybe the author's estimate would nudge closer to the one presented in Manning et al. (2022).

We decided to remove the calculation of a basin-wide flux from this study and focus on instantaneous fluxes.

Furthermore, I note that Manning et al. (2022) and the manuscript under review here use different air sea gas transfer parametrisations for k. This could be another reason why the estimate in this manuscript is much higher than the one from Manning et al. (2022). I am no expert on air sea gas transfer parametrisations for methane and cannot judge which one may be preferable. In the flux methods section, the authors could further defend their choice of air sea gas transfer parametrisation.

Generally, the use and choice of the k parameterization remains debatable and its use in different studies varies. All parameterizations come with uncertainties. We decided to use the same parameterization of k for flux calculations as in Manning et al. (2022) to generally make comparison easier.

Overall, I don't think it is a very good idea to extrapolate on the Baffin Bay and Labrador sea source from the measurements in this manuscript. The measurements in this manuscript are biased to sample in high concentration areas and extrapolation thereof is clearly going to lead to very high contributions/emission fluxes. I suggest the authors delete this section or focus on estimating the contribution of methane seeps to the Arctic methane emission budget. The dataset would be better geared for that. Alternatively, the authors can also keep this section with the modifications suggested above, but I highly recommend adding an explanation that the sampling here was carried out near methane hotspots and is thus biased towards high emission fluxes.

We decided to remove this section from the manuscript.

L291 In this section, the authors use back trajectories to explain three peak concentrations observed during the cruise track. Back trajectories are often used in atmospheric measurement papers, but they have also limits and uncertainty associated with them. The authors clearly also show that they get slightly different results based on what model or archive they use. In this paragraph, there are only three back trajectory runs shown and the conclusions are not very convincing. The authors could consider removing this section. To further strengthen their argument, the authors may want to analyse where their lowest methane concentrations come from or do some more complex back trajectory analysis including multiple runs.

From an atmospheric science point of view, we think the back-trajectory analysis gives a valuable insight into the possible movement of air parcels in this study. The reviewer is right though, that this analysis comes with uncertainties. We were mainly interested to see if air rather moved from land or the open ocean towards the point of measurement. The air may come from along the lines of the trajectories, but we acknowledge that discrepancies to the model are possible. We generally amended the statements in this section, and the respective figure was moved to the Appendix.

L298 "Instead, we inferred from a back-trajectory analysis that the elevated CH4 mixing ratios likely [use "maybe" here] originated from sources onshore such as waterbodies or wetlands." This sentence would benefit from a reference or an additional explanation that waterbodies and wetlands can be sources to the atmosphere. Following on from the previous comment as well, this statement is not very well supported by showing air back trajectories alone. Just because the air travelled over areas of potential sources cannot explain that the high mixing ratios. Was the source strong enough to change air mole fractions? Did the air mass spend enough time near the source? The latter two questions are just to stimulate thought on this topic.

We added a reference to support our statement and softened it as suggested.

Detailed comments

Title: Maybe Change the title to emphasise the depth profiles. A large part of the results and discussion is dedicated to this though it is not mentioned in the title. There is also no mention of the cold seeps in the title. Including this may increase readership.

We changed the title.

L 11: I suggest to remove permafrost from the abstract and maybe replace it by hydrothermal vents? The manuscript focusses on hydrothermal vents, not on permafrost.

We removed "permafrost" from the abstract.

L 15: Here and throughout; Remove "real-time". I don't think this is the right word. The authors may be thinking of "high-resolution"? Maybe also remove "along with ambient air temperature and wind parameters" as these are routine measurements.

We followed the reviewer's suggestions.

L 17: "up to 71°N", give full lat rage of cruise

We revised this and state the full latitudinal range.

L 18: Here and throughout: Why highlight "selected stations"?

We revised this and use "various stations" instead.

L 18: Note that ppb is not an SI unit and can be misleading. Maybe consider replacing it by "ppbv" or adding a sentence to clarify that the authors mean "nmol mol-1" with ppb(v) in this manuscript.

We replaced "ppb" by "ppbv" and "ppm" by "ppmv" throughout the manuscript.

L19: Maybe worth adding a line somewhere to clarify the authors mean "nmol dm-3", when talking about "nM" as the latter is also not strictly speaking an SI unit.

We replaced "nM" with "nmol/L" in the abstract and made a note in the Methods section.

L21: Where the calculated fluxes always from sea to air? If so, maybe worth highlighting this in the abstract with "consistently supersaturated"

We added "at all stations" to emphasize that all sea-air fluxes were positive, i.e. from sea to atmosphere.

L23: "Highest atmospheric CH4 mixing ratios were detected in the Cumberland Sound in Nunavut, suggesting onshore sources from nearby waterbodies and wetlands, whereas ocean-based contributions at this location could not be ruled out." This is a bit of a weak conclusion as the authors highlight in the same sentence as well. Maybe this is not essential to highlight in the abstract? It would be fine to leave it if the authors prefer so. Replace "whereas" by "however".

We removed the sentence.

L30: "radiative activity" – Do the authors mean "radiative-forcing"?

Yes. We revised that. Thank you.

L31: "determine" – Do the authors mean "immediately detect"?

We followed the reviewer's suggestion.

L33: "The Arctic Ocean contains large amounts of CH4 in sediments along the continental margins." Reference required.

We added references.

L40: “dissolution” hints somewhat at solubility. Suggest changing to “distribution in surface waters and in the water column”.

We followed the reviewer’s suggestion.

L 42: Typo? Two times CH4 in same sentence.

We revised the sentence accordingly.

L50: “mobile” – unusual choice of words. Suggest remove.

We removed “mobile”.

Figure 1: In the methods sections, the authors are showing their methane air mole fractions, which are results. Consider maybe colouring the cruise track by sampling date as the cruise track is not straight forward. Beyond that, overall a great figure. Can the authors maybe indicate sea ice in this map as faint shading or would this interfere with the bathymetry colouring?

We moved the figure into the Results section. We want to avoid repetition of the figure (showing cruise track in the methods and methane mixing ratios in the results). We retrieved satellite-based sea ice data (EUMETSAT), and added the small area of sea ice cover >10% in the map.

L 61: Before mentioning the seafloor gas seepage points, maybe worth highlighting that they are indicated in the map.

We added a reference to Figure 1.

L65: Maybe consider shortening the description of currents and reduce it to what is necessary for the understanding of the manuscript? Or move this description to later on in the manuscript where the authors are talking about the latitudinal flux gradient.

We shortened the description.

L 93: “over a distance of 5100 km between July 20, 2021, and August 10, 2021,” -unnecessary repetition, maybe delete.

We removed “over a distance of 5100 km” but kept the dates since they slightly differ from the dates of the cruise allowing time at the beginning and the end to set up and take down instruments.

L99: Please review the references of “(Amundsen Science Data Collection, 2021c)”. It seems C is before A and B in the main text.

The references were reviewed.

L101: “benchmarking” is that the same as blanking the instrument or determining instrument background? If so, “benchmarking” is an odd choice of words.

For atmospheric greenhouse gas measurements, benchmarking is performed to verify drift of the analyzer and it is a commonly used term. During the process of benchmarking, we exposed the analyzer to the same dry air on a daily basis to determine a potential drift of the analyzer.

L121: Just as a suggestion; Maybe the authors could consider naming the CTD stations numerically or alphabetically as well as the “station name” given already. Maybe this would make it more accessible for a reader less familiar with the station names.

We acknowledge the suggestion, but want to avoid confusion of missing numbers/stations for example for the depth profiles that were not taken at all stations listed here.

Figure 3: This figure needs a legend for the blue and black dashed line. “A legend should clarify all symbols used and should appear in the figure itself, rather than verbal explanations in the captions (e.g. "dashed line" or "open green circles").” See https://www.biogeosciences.net/submission.html#figurestables. This comment applies to all figures in this manuscript (also the map etc.). Maybe the marker size could also be increased to make it clearer at what depths measurements were taken.

We added a legend, increased the markersize and revised the figure.

Is there oxygen data available from the mixed layer which could be used to explain interannual variability in surface water concentrations? Some of the interannual variability in surface water concentrations could be due to methane oxidation rates. The authors present the importance of methane oxidation in controlling concentrations later in the text.

After the correction of the concentrations, we did not observe strong interannual variability anymore. However, we retrieved oxygen data from CTD measurements for 2021, but that data did not support our hypotheses that higher oxygen levels could be found where methane concentrations were low. Instead, we found a positive relationship between mean oxygen and methane levels within the mixed layer for most stations and included this finding in the Results.

Maybe some indication of the mixed layer depth would be useful in these figures to illustrate the role of mixed layer bacterial activity in reducing concentrations near the surface.

We added the (generally very shallow) mixed layer depth determined from CTD data in the figure and compared the relationship of mean methane and oxygen levels among stations, which showed a positive relationship as mentioned above.

L159: Please add a space before “%” throughout. See “Spaces must be included between number and unit (e.g. 1 %, 1 m).” https://www.biogeosciences.net/submission.html

We revised the manuscript accordingly.

L209: Overall this discussion is well written and suggests large methane concentrations near seeps and large inter-annual variability of these high concentrations.

These results changed during the revision.

Figure 4: The presence of the seeps in the dataset makes it very difficult to extract much useful information from this figure on what is “generally” happening in the study area. In the figure, no obvious trends are visible. Maybe the authors could “hide” or “highlight” points potentially affected by the seeps. This allows them to comment on what is generally happening in the area or what water masses are most affected by the seeps. Apart from that, the discussion of the figure is very clear.

After revising the error in the water sample analysis, the fluxes match those from previous studies better. In addition, we highlighted the points in proximity (within 50 km) of the Scott Inlet seep, which comprise the highest methane concentrations over the years.

L242: The figure reference to Fig. 5 disrupts the flow a bit here. Consider removing it and moving the first mention to later in the text. Maybe even just the next sentence where the difference 65 N and S is discussed.

We revised accordingly and moved the reference to the next sentence.

L245 Maybe it would be worth indicating the Labrador current in Figure 1.

We added an arrow for the Labrador Current in the figure.

L246 It is hinted here a little bit, but I was wondering if the authors had considered to look at sea ice cover as a controlling factor of methane concentrations. Sea ice cover controls factors such as bacterial activity (10.1525/elementa.2020.00113), mixed layer depth (10.1525/elementa.372) and air-sea flux (https://doi.org/10.1002/2016GL069581 and https://doi.org/10.1002/2017GL073593). These should also influence dissolved methane concentrations. See 10.1038/srep16179

We did not directly collect water samples in areas with sea ice cover. There was some sea ice cover at other locations during the cruise, but water sampling was not performed there and we made clear that we determined instantaneous sea-air fluxes in this study.

Figure 5: Similar to figure 3, a figure legend is missing.

We added a legend.

L260 "featuring large uncertainties" Can the authors please elaborate on this? What is the source of these uncertainties?

Sorry for the confusion. We referred to the large uncertainties of the mean, ie. the high standard deviations of the sea-air fluxes stated in the text. However, these results changed after the revision of methane concentrations and fluxes.

L269 "in which case the ocean may act as a small CH_4 source or sink to the atmosphere" I thought the fluxes measured during this cruise were always out of the ocean? Do the authors suggest this because the standard deviation here is larger than the mean? A larger standard deviation than the mean could also be because the data is skewed and the mean is influenced by outliers of high concentration.

Correct, we suggested that since the standard deviation was higher than the mean. As already mentioned, the values changed after the revision of methane concentrations and fluxes lie within a closer range.

L271 Delete "therefore" and replace by: Using our estimate of the contribution of Baffin Bay and Davis Strait to the Arctic Ocean methane source, …

We removed this section from the manuscript.

L277 "After filtering measured data," See an earlier comment. It is not very clear how this filtering was done.

Here we applied a Savitzky-Golay filter after Savitzky and Golay (1964) of second polynomial order as mentioned in the Methods. We clarified that we used this filter here.

L278 "of 2021" – of the sampling year 2021 and L279 "but were within range of recent (year 2020) values from surface flask-air measurements" change to "but were within range of values from surface flask-air measurements from the year 2020"

We followed the reviewer's suggestion.

L280 The authors are comparing their methane measurements from Baffin Bay area to many other stations in the Arctic. I suggest comparing the author's measurements only to the closest station (Alert?). Doing so, illustrates that the concentrations measured in this deployment are higher than that station's mean. This is likely because the cruise track focussed on sampling air near methane seeps and thus emission hotspots.

We removed the Iceland and Norway flask samples but consider the Nunavut and Greenland stations reasonable to mention, also given that they are about the same distance to the cruise track. We implemented the reviewer's interpretation to clarify the use of mentioning the flask samples.

L283 "growth" replace by increase

We followed the reviewer's suggestion.

L310 Please split this sentence in 3 to enhance readability. Further, the lack of a correlation between water concentration and air mole fraction is not an indication "that CH4 released from seeps at the seafloor alone did not directly increase atmospheric CH4 mixing ratios". Surely the situation is similar to dimethyl sulfide where highest air mole fractions are not observed above areas of highest seawater concentrations, because air parcels move much faster than water parcels and other complexities (differences in lifetime in air and water, air-water interface acting as a barrier and thus the two are decoupled, different sources and sinks in air and water as the authors discuss in the manuscript etc.). E.g.
https://bg.copernicus.org/articles/19/701/2022/bg-19-701-2022.pdf, page 710

We split the sentence, revised the text with updated fluxes and incorporated the reviewer's suggestion and reference.

L313 "Furthermore, linear correlations of CH4 mixing ratios with available data were not found, suggesting more complex relationships at sea." Change to: "Furthermore, simple linear correlations of CH4 mixing ratios with available atmospheric auxiliary data were not found, suggesting more complex relationships." Maybe briefly mention what atmospheric auxiliary data was tested for here.

We followed the reviewer's suggestion and elaborated on which data was used for the linear regression.

L315: Why is the n number so low here? Was there data excluded from the fit?

The number n is so low because atmospheric pressure and dew point temperature data from the ship's own measurement system had large gaps. For the GAM, we used hourly averages, which already reduced the number of datapoints to 510. Therefore, only data where atmospheric pressure, dew point temperature and methane mixing ratios were present could be used for this model.

L317: "In this study, small increments of atmospheric CH4 levels in proximity to seep locations were observed, whereas at other locations where substantial fluxes of CH4 from the sea to the atmosphere were determined locally atmospheric concentrations were not noticeably affected" – replace by "In this study, small increases of atmospheric CH4 levels in proximity to seep locations were observed. At other locations where substantial fluxes of CH4 from the sea to the atmosphere were determined local atmospheric concentrations were not noticeably affected" Did the sea-to-air flux correlate with methane air mixing ratios? "small increments of atmospheric CH4 levels in proximity to seep locations" – this is not very clear from figure 3. The air mixing ratios do not show a clear trend because air parcels travel fast and the sampling location (upwind or downwind from seep) also plays a role as well as the air sea flux. The authors should be more clear what data they are referring to which supports this claim.

We removed this paragraph after updating the sea-air fluxes. Sea-air fluxes and atmospheric methane mixing ratios did not correlate.

L323 “Continuous measurements of atmospheric CH4 levels in remote marine regions of the northern Labrador Sea and Baffin Bay made this study unique.” Suggest changing this sentence. Are the seawater measurements, depth profiles and flux calculations of value as well? Especially since they represent measurements near methane seep sites. Additionally, the year-on-year comparisons in Fig. 3 are probably of value as well. Personally I am quite impressed with the large methane fluxes from the seeps. The fact that these fluxes are so large, probably warrants monitoring indeed, as the authors suggest. The authors could review the conclusion from their manuscript to better highlight the importance of their manuscript.

We adjusted the conclusion to better highlight the importance of the manuscript.

Appendix A. Great picture.

Thank you!