EGUsphere, author comment AC2
https://doi.org/10.5194/egusphere-2022-545-AC2, 2022

Reply on RC2

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-AC2, 2022

Responses to reviewer 2

We would like to thank the reviewer for their thorough and constructive feedback. We apologize for the flaws in the first version. During the revision, we encountered errors in the calculation of dissolved methane concentrations. These errors were fixed and the results changed in the revised manuscript. We tried to answer and address the reviewer's comments and suggestions as best as possible. Our answers are indicated in italic below.

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*

Review of Vogt et al. (2022)

General comments:

This paper presents atmospheric methane and dissolved methane measurements from a research cruise in Baffin Bay and Davis Strait in summer 2021. The stations where water samples were collected contain several stations with known benthic methane sources (e.g. Scott Inlet) as well as some stations with methane levels more typical of the broader region.

I first want to acknowledge the efforts of the PhD student who led the paper. They have clearly worked hard to prepare this manuscript.

However, the paper contains many major errors that need to be addressed before the paper is published. It is apparent to me that the student has not received sufficient mentorship and guidance on interpretation of the data from scientists with expertise in dissolved gas measurements, sea-air flux measurements, and Arctic Oceanography. The student appears to be working in a research group that focuses on gas emissions from industrial sources. The senior scientist coauthors of the paper who do have oceanographic expertise have clearly not read the paper thoroughly. There are fundamental errors such as the wrong units being used for ocean salinity (figure 4), errors in the gas solubility calculations, flux calculations, and error estimates that will substantially alter the results once corrected.

For this article to be publishable, the coauthors with appropriate expertise need to take an active role in helping the student to correct these errors, and the student and their supervisor may need to establish a collaborative relationship with researcher(s) with expertise in oceanographic sea-air flux calculations who would become coauthor(s) on the manuscript to correct these major errors. A peer reviewer should not be identifying such fundamental issues.

Specific comments:

Errors in calculated methane saturation states (line 158)

Line 158: "Seawater samples showed wide ranges of dissolved CH4 concentrations at the different sample locations and water depths from undersaturated (53%, 0.2 nM) to highly oversaturated (6858%, 272.4 nM, Fig. 3)."

The solubility of methane in Arctic seawater is ~4 nM. A 53% saturation is equivalent to roughly 2 nM , not 0.2 nM,. The highly oversaturated value in this sentence contains a similar error. I am unsure if the saturation states or concentrations are incorrect, and I don't have time to figure out how many similar errors are present in the manuscript and if these errors extend to their flux calculations. The concentrations and saturation states shown in Figure 3 appear to be approximately correct (100% saturation corresponding to 3-4 nM.)

This is a major error that needs to be carefully reviewed throughout the manuscript and underlying calculations.

The reviewer is correct, the numbers were incorrect. Unfortunately, we found mistakes in the calculation of CH4 concentrations in the water sample analysis. We apologize for this flaw. In brief, most CH4 concentrations were wrong and generally numbers were much lower after revision, so that the storyline of the study changed. We revised the text and figures accordingly.

Errors in the gas transfer velocity equation and sea-air flux calculations (line 154)

The flux equation on line 154 requires the wind speed to be U10, the wind speed at 10 m height above sea level. It appears that they have directly used wind speeds from the anemometer which was reported to be 8.1 m above deck (line 82) and likely significantly more than 10 m above sea level based on Fig A1. They need to adjust the wind to 10 m height using one of many published methods.

It is correct that the anemometer was mounted at a location higher than 10 m above sea level, approximately at 14 m above sea level. It should be noted that due to vertical motion of the ship but also depending on the ship's load, the height of the anemometer above sea level was technically not constant. To conform with standard calculations, we

corrected the wind speed to a 10 m above sea level via Power Law.

They also need to correct the fluxes for sea ice cover as they claim on line 64 "The studied region lies within the seasonal sea ice zone and the ocean was partially covered with sea ice in the northernmost regions."

We can confirm that during the water sampling with the CTD-Rosette at the stations in this study no sea ice was present. Sea ice was present at other locations during the cruise, though. We clarified that in the text. We were interested in instantaneous sea-air fluxes and therefore disregarded the fact that there was partial sea ice cover at times when no water was sampled during the cruise.

It is surprising to me that they "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" and would like to see this data for both CO2 and CH4. I also recommend they contact other researchers who have made atmospheric CO2 and other gas measurements from the flux tower on the CCGS Amundsen in prior years and inquire if they observed contamination from the ship's exhaust and how they detected it.

Methane contamination from the exhaust, if present, was not sufficient 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 to procedures used in other studies. A supporting figure was added in the Appendix.

They claim the Schmidt numbers were taken from Wanninkhof (2014). Did they correct the Schmidt numbers for salinity? The values should be interpolated from the the freshwater (S=0) and seawater (S=35) values, based on the salinity of the sample (often significantly less than S=35 in Arctic surface waters). Also, note that Wanninkhof recommends authors cite and consult the original sources for the Schmidt numbers.

The Schmidt numbers were not corrected for salinity in the first version of this study. After revision of the methane concentrations, fluxes were re-calculated using code examples from Manning & Nicholson (2022), which consider a correction for salinity according to Jähne et al. (1987).

Furthermore, I believe it is very misleading to calculate an annual flux over the whole study region based on their data, which is based on a 3-minute shipboard measurement of wind speed and has significantly higher concentrations than prior studies at similar stations, and is from a cruise where more than half of the surface samples were specifically targeting known methane seeps or otherwise had elevated levels.

As discussed in Wanninkhof et al. (2009) and other studies, due to the nonlinear dependence of gas flux on wind speed, flux estimates based on instantaneous winds will be systematically biased compared to longer-term winds. Furthermore they calculate a flux "Considering all measurements from 2021 and an area of 1,123,000 km² for the Baffin Bay and Davis Strait" but this seems inappropriate when the majority of stations were from known methane seeps and 5 out of 13 measurements were collected within 5 km of a known methane seep (if I am understanding their methods correctly); these sites are extreme outliers (as shown in Manning et al., 2022 and Punshon et al. 2019 among others). They also calculate a flux "if samples with high concentrations were excluded" but don't explain how 'high concentrations' were defined, and this likely brings the number of stations down to a very small number (perhaps 5 stations) which is not appropriate to extrapolate over a larger region.

As they do not account for seasonal and annual variability in the gas transfer velocity (due

to ice and wind speeds), their annual fluxes based on 3 minutes of wind speed data are very unlikely to be accurate. Their surface concentrations are much higher than reported in previous studies at the same/similar stations (e.g. Cramm et al., 2021, Manning et al., 2022, Punshon et al., 2019, etc.) which I believe makes it even less appropriate to calculate a flux based on their data only.

We understand this concern and excluded the calculation of annual fluxes from the analysis in the manuscript.

Uncertainty estimates are 1-2 orders of magnitude too small (line 130)

The authors need to clarify whether any duplicate samples were collected. It appears the answer is no. They claim "Uncertainty in dissolved CH4 was ±0.08% (Punshon et al., 2014, 2019)." World-leading labs typically report combined uncertainty (incorporating accuracy and precision of replicate measurements) of one to several percent for dissolved methane analysis in seawater. I took the time to review Punshon's 2019 paper which claims "Analytical precision, determined by repeated analysis of air equilibrated seawater, was ± 0.80% for methane." Analytical precision of air equilibrated water samples prepared in the lab is not the same as the combined/propagated uncertainty of field samples.

It is misleading to claim in the abstract (line 20) that "Dissolved CH4 concentrations in the near-surface water peaked at 56.58±0.05 nM" – this appears to be based on erroneously applying an accuracy of 0.08% (0.05 nM) to a single bottle measurement. If there were no repeat measurements during this cruise, then in my opinion they should be upfront about this and not apply an uncertainty that does not account for all sources of error.

We did not collect repeat measurements during the cruise (with one exception) and corrected the uncertainty statement in the Methods and refrain from using uncertainties for the individual methane concentrations in the revised version.

Technical comments and recommendations:

Figure 4: Salinity is incorrectly labeled as "permil"

We corrected the units to psu.

Dataset– I downloaded the data and noted they have put both the dissolved data and atmospheric data into the same file. There are 1826786 rows in the file and only 13 of them contain dissolved gas and flux data. I recommend they make a separate file that contains the dissolved gas data only. They also need to archive the exact depth/pressure, salinity, temperature data corresponding to each dissolved gas sample to ensure reusability of the data and reproduce figures in the manuscript. Currently they have only archived the concentration and approximate/target depth, e.g. 10 m.

We split the dataset into atmospheric and dissolved methane measurements, and added relevant CTD data.

The final sentence of the manuscript is misleading: they state "the Arctic Ocean does not contribute significantly to the global CH4 budget." This manuscript does not prove or disprove this statement; the authors only collected instantaneous data in one small region of the Arctic and subarctic. In the intro, line 42, they report the very high CH4 fluxes reported from the East Siberian Arctic Shelf as a motivation for this study.

We clarified that this statement was not based on findings from this study.

Line 87: Where were the calibration gases obtained? What was the accuracy of the cylinder actually used in the field?

For calibration, we used Ameriflux standard gas. The cylinder used in the field was filled with CO2 mixed with ambient air, so that methane concentrations were not determined, but amounted to ~5 ppm with unknown uncertainty. Using this cylinder in the field was not planned, but due to some logistical issues, it was the only option for benchmarking. However, the analyzer was calibrated before using it in the field, and the benchmarking serves the purpose of detecting analyzer drift, which can be determined from any gas containing methane as long as its concentration does not change over time. The uncertainty of the gas is not crucial in this case.

They need to clarify throughout manuscript and in published dataset if the atmospheric mixing ratios are based on dry mole fraction or include the water vapor pressure.

We used dry mixing ratios and clarified that in the Methods section.

Latitudes and longitudes require a degree symbol. Longitudes reported as W do not need a negative sign.

We revised that.

Fig 3: Are the profiles from 2012 and 2016 the CH4 saturation or CH4 concentration? I suggest making an updated legend that would show each line type, the year, and whether it is concentration or saturation.

We added a legend for clarification and included more nearby stations to account for all stations within 50 km of those visited in 2021.

Fig 5: Add a legend to accompany the caption.

We added a legend.

I do not have expertise in atmospheric modeling, and I am not qualified to comment on whether there are errors in these aspects of the manuscript.

Final notes

I want to again commend the PhD student on their strong (and likely quite independent) effort. I again emphasize that I believe the issues with this manuscript arise from a lack of engagement from the more senior coauthors and/or lack of collaboration with researchers with necessary expertise. Early career researchers require this mentorship and collaboration to develop advanced level scientific knowledge.

References

Cramm, M. A., Neves, B. de M., Manning, C. C. M., Oldenburg, T. B. P., Archambault, P., Chakraborty, A., et al. (2021). Characterization of marine microbial communities around an Arctic seabed hydrocarbon seep at Scott Inlet, Baffin Bay. Science of The Total Environment, 762, 143961. https://doi.org/10.1016/j.scitotenv.2020.143961

Manning, C. C. M., Zheng, Z., Fenwick, L., McCulloch, R. D., Damm, E., Izett, R. W., et al. (2022). Interannual Variability in Methane and Nitrous Oxide Concentrations and Sea-Air Fluxes Across the North American Arctic Ocean (2015–2019). Global Biogeochemical Cycles, 36(4), e2021GB007185. https://doi.org/10.1029/2021GB007185

Punshon, S., Azetsu-Scott, K., Sherwood, O., & Edinger, E. N. (2019). Bottom water methane sources along the high latitude eastern Canadian continental shelf and their effects on the marine carbonate system. Marine Chemistry, 212, 83–95. https://doi.org/10.1016/j.marchem.2019.04.004

Punshon, S., Azetsu-Scott, K., & Lee, C. M. (2014). On the distribution of dissolved methane in Davis Strait, North Atlantic Ocean, 161(C), 20–25. https://doi.org/10.1016/j.marchem.2014.02.004

Wanninkhof, R., Asher, W. E., Ho, D. T., Sweeney, C., & McGillis, W. R. (2009). Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing. Annual Review of Marine Science, 1(1), 213–244. https://doi.org/10.1146/annurev.marine.010908.163742

Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. Limnology and Oceanography: Methods, 12(6), 351–362. https://doi.org/10.4319/lom.2014.12.351