Reply on RC2
Knut Ola Dølven et al.

Author comment on "Autonomous methane seep site monitoring offshore western Svalbard: hourly to seasonal variability and associated oceanographic parameters" by Knut Ola Dølven et al., Ocean Sci. Discuss., https://doi.org/10.5194/os-2021-85-AC2, 2021

Reply to referee #2

Thank you for your positive comments and for acknowledging the importance of this study. We are also thankful for the comments and suggestions on improving the manuscript. Please see below our replies regarding the suggested changes.

Regarding Figure 2

The figure is now extended to the limits of the template, fonts are homogenized (to helvetica) and the different axis and issue at $O_{246}$ are pointed out in the figure caption. Figure 2d shows a continuous 24-hour measurement (obtained every 21 days) followed by 1-hour measurement (obtained every day) on 2-3 Aug. Figure 2d is meant to show both a 24-hour and a 1-hour time-series in the same figure for clarity and has no missing data.

Methane sensor

First we would like to point out a couple of general changes we made regarding this topic (also partly based on the review comment). Firstly, we have now clarified what detector, membrane, and pump system we used. This important information is now added in the method section of the manuscript (line 86-91). Additionally, since Dølven et al. (2021) is now openly available to the public, we found it appropriate to shorten the description of the response time correction method and merge Appendix C into Appendix B. Appendix B now contains all instrument/measurement related information not crucial to understand the content of the manuscript. Furthermore, we address all concerns mentioned by the reviewer in the reply/explanations below and have implemented corresponding changes/additions in the manuscript.

- **Low selectivity**: This might have been an issue in previous versions of the sensor relying on NDIR, but Tunable Diode Laser Absorption Spectroscopy (TDLAS) detectors such as the one used in the Contros HydroC CH$_4$ have relatively good selectivity (see Figure R1 and e.g. Shemshad et al., 2012). This information is added in line 386-387.
- The accuracy of the data is described in Appendix B. We used the ISO 5725-1 definition of accuracy which includes both random and systematic errors (sometimes referred to
as precision (random errors) and accuracy (systematic errors). Appendix B describes both instrument accuracy and accuracy of the response time corrected data, which we use in the results and discussions of the manuscript (Table B1). We agree that these uncertainties could have been more elaborately described, and have therefore added more detailed information on this in line 408-412 in the revised manuscript and a figure showing the distribution of expected errors in the response time corrected data (Figure B1b, see also Dølven et al., 2021). We have also added an explicit address of the uncertainty in the methods part of the main text of the manuscript (line 105-107). Additionally, we added the 95% uncertainty range for all discrete (i.e. not averages) concentrations mentioned in the text.

- **Strong dependency to changes in the physical conditions**
  - **Biofouling:** We observed little to no biofouling on the instruments and observatories upon recovery (probably due to cold water and local environment). Figure R2 shows the pumps from the HydroC CH₄ and CO₂ directly after recovery, i.e. after 10 months in the water. We added a sentence stating that there was only minimal biofouling and no other indications of problems with the sensors other than the electrical malfunction at O₂ and the conductivity sensor (all sensors, not only the HydroCs) at retrieval in line 388-391.
  - **Hydrostatic pressure:** The change in hydrostatic pressure during the deployment was small, i.e. between 1.2 and 1.5 dbar over the course of one tidal cycle (~12 hours). The pressure fluctuations in the measuring chamber were also small (R<0.05 dbar) and had a statistically negligible relationship with concentration (which could also be related to other environmental processes, cf. Figure R3).
  - **Water temperature:** The bottom water temperature varied with less than ~3 °C and the internal temperature was kept constant at correct instrument operating temperature for data recorded and used in analysis (we discarded measurements obtained during instrument warm-up). Water temperature indeed affects the response time of the instrument due to changes in membrane permeability, we now explicitly address the effect of temperature changes and how we accounted for this in the response time correction procedure in line 397-399 (see also Dølven et al., 2021).
  - **Salinity:** The relatively small changes in salinity observed at the measurement sites should only have a negligible effect on membrane permeability (Robb, 1968). This is now also mentioned in Appendix B (line 399-400).
  - **Dissolved oxygen content:** This should have no effect on the measurements unless there is a complete depletion of oxygen which is not the case at the observatory sites (Figure 2 in manuscript). Dissolved oxygen can influence sensors relying on metal dioxide detectors (Boulart et al., 2010), but should not affect the TDLAS used in the HydroC CH₄. We added this information in line 387-388.

- **Long-term drift/calibration:** Standard calibration procedures (for relevant conditions) were followed prior to deployment. While long-term stability might be an issue with NDIR detectors, post/intermittent calibration was neither recommended by the manufacturer nor found necessary (the latter also practically very difficult) due to the high stability of the TDLAS unit and PDMS membranes which are almost unaffected by cold water (this is also the case for teflon membranes). We added this information in line 385-389. This is supported by 4h-Jena (and previously Contros) who have aggregated and cross-checked data from sensors that have been returned after long-term deployments over several years and found that any drift or changes are insignificant (<1 ppm both for low and high concentrations) (pers. comm. Jack Triest, 4h-Jena GmbH).
  - **The power-on-off-cycles:** As previously mentioned, all measurements obtained during the instrument warm-up period were discarded; in practice, the instrument was turned on approximately 35 minutes before used data was recorded (the 1- and 24-hour periods therefore vary slightly by 1-2 minutes in length). The sensor operation should therefore not be affected by the length of the measuring periods. We added this
Even though modern HydroC CH$_4$s with our pump/membrane/detector setup can give decent accuracy and be applicable in a wide range of settings, it might still be relevant to acknowledge that the analysis and discussions in the current manuscript mainly concerns large changes and high concentrations. Considering this, we believe the response time corrected Contros HydroC CH$_4$ data should be more than sufficient to support the scientific results and inferences described in our manuscript. Additionally, the data show that the sensor can produce high variability, high concentration, and low concentration data throughout the time-series and also produce a stable minimum (background) concentration at around 10 nmol L$^{-1}$ (Figures 2, 4, 6, and Appendix B). Based on this and what iterated above, we found no apparent reason to question the reliability of the sensor for the purpose of the study and believe the additions in the method section and in Appendix B, as well as addition of uncertainty ranges for concentrations mentioned in the results/discussion sections should be sufficient to address this.

**Discrepancy with results in Gentz et al. (2014):** We trust that the text reflects that we emphasize high spatiotemporal variability and sparse sampling as a possible explanation for the discrepancy in concentrations when comparing with data from Gentz et al. (2014). Taking the spatiotemporal variability into account, and the fact that O$_2$ was deployed around 30 m from an intense seep, we believe the measurements aligns reasonably well with Gentz et al., (2014). It should also be noted that the data in Gentz et al. (2014) was obtained with discrete water samples (not the underwater mass spectrometer, which was only used a 10 m water depth), greatly limiting data coverage compared to a continuous measurement. We also find that the comparison with the concentrations reported in Silyakova et al. (2020) (the doi should be correct) seems reasonable taking the above perspectives into account and the similarities in distribution of values (see added Figures showing distributions in Appendix D).

**Methane inventory**

We agree that more details on the implications for inventory/budget estimates would improve the manuscript. We address this by using a statistical approach where we find the expected error from unresolved short-term variability for a hypothetical discrete water sampling survey seeking to estimate seep site averages, where the short-term variability is represented by the 24-hour time-series of the observatories. This exercise also explicitly describes the expected errors for single measurements. We compare with the results presented in Silyakova et al. (2020) who performed discrete water sampling surveys in the O$_9$1 area every summer from 2014-2016. The content is added via a remodulation and extension of the last part of section 4.1 (“CH$_4$ variability”, lines 202 to 239), Appendix D (lines 414-460), Figure 4, D1 and D2. We concluded that a budget estimate would provide unreliable results since we are monitoring CH$_4$ only at a single location. We believe the added result strengthens the manuscript and at the same time addresses the reviewers concern about being too unspecific on implications for budget estimates. This addition also led to a slight reformulation and addition in the abstract, introduction, and conclusion of the manuscript (i.e. adding one sentence describing the results).

We appreciate the suggestion to add a boxplot and agree that this could illustrate certain aspects of the data in an elegant way. However, in addition to the above reasoning on not including inventory estimates based on our data (which such a boxplot might have shown), we believe that the addition of a boxplot would not add any new information to what is already shown in Figures 2,3,4,6, and Appendix C, which all concern dissolved CH$_4$ data.

Figures R1, R2, and R3 referred to in the reply is in pdf "Figures_for_AC_R2.pdf"
References

Shemshad, J., Aminossadati, S. M., Kizil, M. S.,: A review of developments in near infrared methane detection based on tunable diode laser, Sensors and Actuators B: Chemical, 171-172, 77-92, 2012. https://doi.org/10.1016/j.snb.2012.06.018

Boulart, C., Connelly, D. and Mowlem, M.: Sensors and technologies for in situ dissolved methane measurements and their evaluation using technology readiness levels. Trends in Analytical Chemistry, 29(2), 186-195, 2010.

Dølven, K. O., Vierinen, J., Grilli, R., Triest, J., and Ferré, B.: Response Time Correction of Slow Response Sensor Data by Deconvolution of the Growth Law Equation. Geoscientific Instrumentation, Methods, and Data Systems Discussion, 1-22, https://doi.org/10.5194/gi-2021-28, 2021.

Robb, W. L.: Thin silicone membranes – Their permeation properties and some applications, Annals of the New York Academy of Sciences, 146, 119-137, https://doi.org/https://doi.org/10.1111/j.1749-6632.1968.tb2077.x, 1968.

Please also note the supplement to this comment: https://os.copernicus.org/preprints/os-2021-85/os-2021-85-AC2-supplement.pdf