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Atmospheric Measurement Techniques Discussions

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Interactive comment on "Continuous methane concentration measurements at the Greenland Ice Sheet-atmosphere interface using a low-cost low-power metal oxide sensor system" *by* C. J. Jørgensen et al.

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Dear Anonymous Reviewer #2. Thank you very much for your help in improving the manuscript. Please find our detailed point-by-point to your constructive criticism of our manuscript in the included file "Combined point-by-point responses to reviewer's comments". Additional figure material for reply 32 and 43 is available in the supplement pdf file.

"Anonymous Referee #2 Received and published: 29 February 2020 Review of

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Discussion paper

manuscript amt-2019-468 General aspects:

This is a well-written and interesting study showing how low cost metal oxide semiconductor sensors (MOS) for methane (CH4) can be used to follow CH4 mixing ratios over time in Greenland glacier ice caves. Results convincingly indicate that MOS sensors can perform very well and this is promising for easier and less costly monitoring under such conditions (very stable temperature and relative humidity). These tests are important and I congratulate the authors for their careful and interesting work. The authors are asked to consider the specific comments below in the revision of the manuscript.

Specific comments (numbers refer to line numbers): 15. Please define CRDS in abstract. Some readers may not be familiar with cavity ring-down spectrometry."

⇒ Reply 30: Corrected.

"19-20: What was MBE selected instead of MAE or RMSE? With MBE, positive and negative bias cancel out which is not desirable. Please consider using RMSE or MAE instead."

⇒ Reply 31: This could be an area prone to confusion, and we agree to resolved this in the revised manuscript by including both the mean bias error (MBE), mean absolute error (MAE) and root mean square error (RMSE) in table 1, and replace the MBE in the abstract with the RMSE value.

"97-98. Is it really correct that the conductivity increase with gas concentration as indicated here? Does not the output voltage increase with CH4 mixing ratio due to increasing resistance at higher CH4 levels, which would mean reduced conductivity?"

⇒ Reply 32: In the description of the circuit (https://www.figaro.co.jp/en/product/docs/tgs2611-e00_product%20information%28en%29_rev00.pdf), the output voltage of the sensor (VRL) is measured across a voltage divider with a fixed load resistor. The resistance of the variable resistor (Rs) (i.e. the sensing element itself) can be calculated based on the measured output voltage (VRL) according to the following formula:

[SEE FIGURE IN SUPPLEMENT PDF FILE]

As the reviewer correctly points out, the output voltage (VRL) increased with increasing CH4 concentration. In our setup, we used a load resistor of 10 kOhm and a circuit voltage (VC) of 5 volt.

As argument for why we believe the description in the MS is correct consider the following simplified example: With an output value of say 1.5 volt (arbitrary lower CH4 concentration), the sensor resistance would be Rs: (5V/1.5V – 1) * 10kOhm = 23 kOhm, where a higher output value of say 2.5 volt (arbitrary higher CH4 concentration) would give an sensor resistance of 10 kOhm. In this way, higher CH4 concentrations produce lower sensor resistance or higher sensor conductivity.

“120. Eq.1: What is R0 in Figure 3? Is it equivalent to Rs? If so, please consider using consistent notation in both text, figures and tables.”

⇒ Reply 33: R0 is equal to the sensor resistance Rs under the defined zero gas conditions, to which all other measurements are normalized to (i.e. to calculate the Rs/R0 ratio). Figure 3 only shows the simplified schematic of the electrical circuit, which does not include a notation of the calculated value of sensor resistance at zero gas conditions.

“139-148: Please here explain why the smoothing was needed. An explanation is given later in the text, but it would be good for understanding to provide the explanation here.”

⇒ Reply 34: We have revised the sentence to be: “In order to compensate for potential effects of micro-turbulent mixing of subglacial air with atmospheric air (see also section 3.3), the measured raw time series data from the MOS were smoothed using simple exponential smoothing according to Eq. (2):. . . . . .”

“155-160 and elsewhere. At less stable conditions than in the ice cave studied here, it would be challenging to have zero gas and sample gas with the same water concentrations. Hence, correction to humidity seems needed. Please see doi.org/10.5194/bg-2019-499 for detailed analyses of ways to correct for humidity and temperature to derive more generally applicable calibration curves."

⇒ Reply 35: Thank you for providing the reference to an exciting and very relevant study, which has been published for discussion at a similar point in time as this study. We will include the reference to the list of references and include it in the revised discussion of the potential effect of water vapor and temperature on the sensor measurements.

"163-165- Unclear how the rather poor fit in Figure 6 between MOS and CRDS could be translated into the very close fit in Figure 7. Please clarify this in the manuscript."

⇒ Reply 36: We are not sure we understand what is meant by poor fit in figure 6 (R2 = 0.98 / p-value = 0.001). However, there is a notable spread in some of the values of under higher concentration levels under more turbulent environmental conditions at the measurement point. However, it is difficult to visualize all of the 37.140 data points in only single figure without a great number of similar data points are visually stacked on top of each other, thereby not being visible in the figure. In this way, the apparent higher degree of spread in the upper CH4 levels are a product of the turbulent data (which are non-dominating for the statistical model) having a visual prevalence over the non-turbulent data points which dominate the statistical model.

The following text has been added to the revised MS in section3.2. to clarify the issue:

"A total of 37,140 data points are included in the regression model for converting the RS/RO* ratios to CH4 concentrations. Inclusion of data points from the micro-turbulent periods produces a noisy visualization of the calibrations data at higher CH4 concentration levels (Fig. 6). However, this apparent noise is primarily a visual artefact that does not have significance for the underlying calibration statistics, which shows excellent statistical agreement between the independent and dependent variables (R2 = 0.98; p-value: 0.001)."

“163-174. Could the deviation between the lab and the field be due to any other factors?”

⇒ Reply 37: It is possible, yes, but further experimental and calibration work would be needed to bring more certainty to this issue.

“239-240. This statement gives the impression that the MOS are accurate to 10 ppb level. Is this really correct? This is orders of magnitude better than others have found. The mean bias error is risky to use because negative and positive errors cancel out. Please consider using RMSE as indicator of MOS performance.”

⇒ Reply 38: We agree to use the RMSE as suggested and have updated the sentence accordingly.

“243-254. Would not field calibration also be an option as done here and suggested in doi.org/10.5194/bg-2019-499? Given the low temperature - what was the absolute humidity which is what influence sensors more than RH?”

⇒ Reply 39: We agree. The original wording was chosen to reflect what has previously been done. The sentence is updated with the inclusion of the suggested reference. The saturated water vapor or absolute humidity in the thermally buffered measurement environment around 0 degrees C is approximately 5 g/m3 (see http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/watvap.html).

“305-307. Some of this is addressed in doi.org/10.5194/bg-2019-499 which could be worth citing.”

⇒ Reply 40: We agree. Citations have been added.

“323-324. Please see previous comments regarding MBE vs RMSE.”

⇒ Reply 41: We have rephrased to focus on the RMSE

“484-485. Please clarify what FIgure 6 shows in relation to Figures 7 and 8. The offset between the sensor and CRDS data are much greater in Figure 6 than in Figure 7 and

8. Figure 6 looks more like what could be expected from theses sensors, while the fit versus the CDRS in Figure 7 and 8 is extremely close (looks fantastic and almost too good to be true, and it is hard to understand how the calibration equations provided could correct all the offset in Figure). Hence, clarifying the differences between Figure 6 vs 7 and 8 seem very important for fully understanding the study and proper sensor use."

⇒ Reply 42: Please see reply 36 for the issue of data fit (Figure 6) and reply 44 for precision issue. In short, our results are in line with the finding of also https://doi.org/10.5194/amt-2019-402, where the authors conclude "... that the TGS 2600 sensor can provide data of research-grade quality if it is adequately calibrated and placed in a suitable environment where cross-sensitivities to gases other than CH4 is of no concern."

"490-496. Legend of Figure 7 has many abbreviations. Please consider to define or spell them out to make it easier to understand the figure independently from the main text? Also it would be of great interest to readers to add humidity to the figure."

⇒ Reply 43: Definitions have been added to captions for Figure 7.

With respect to the relative humidity. The resolution of the used RH sensor (S-THB-M008 from Onset;) is stated by the manufacturer to be 0.1 % RH (https://www.onsetcomp.com/products/sensors/s-thb-m008/). From our measurements, the results show a flat line of 100% relative humidity over the entire measurement period. We therefore chose to only describe this result by means of text (line 251 in original MS) and not show a flat in the figure.

[SEE FIGURE IN SUPPLEMENT PDF FILE]

To accommodate the comment from reviewer 2, we have expanded the description of the relative humidity measurements in the text, to better illustrate that RH was extremely stable in the measurement environment (resolution of sensor has been added in section 2.1 and text has been revised in section 3.4).

“Measurements from the air-filled cavity under the GrIS document a very stable sampling environment with a relative humidity throughout the sampling period showing consistent readings of 100 % RH (data not shown) and only minor air temperature variations between approximately 0.05 oC during the night and 0.25 oC during mid-day (Fig. 7d).”

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2019-468/amt-2019-468-AC2-supplement.pdf

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