Continuous methane concentration measurements at the Greenland Ice Sheet-atmosphere interface using a low-cost low-power metal oxide sensor system

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Abstract. In this paper, the performance of a low-cost and low-power methane (CH_4) sensing system prototype based on a metal oxide sensor (MOS) sensitive to CH_4 is tested in a natural CH_4 emitting environment at the Greenland Ice sheet (GrIS). We investigate if the MOS could be used as a supplementary measurement technique for monitoring CH_4 emissions from the GrIS with the scope of setting up a CH_4 monitoring network along the GrIS. The performance of the MOS is evaluated on basis of ~~parallel~~simultaneous measurements using a cavity ringdown spectroscopy (CRDS) reference instrument for CH_4 over a field calibration period of approximately 100 h. Results from the field calibration period show that CH_4 concentrations measured with the MOS is in very good agreement with the reference CRDS. The absolute concentration difference between the MOS and the CRDS reference values within the measured concentration range of approximately 2-100 ppm CH_4 were generally lower than 5 ppm CH_4, while the relative concentration deviations between the MOS and the CRDS were generally below 10 %. Calculated ~~mean bias~~ root mean square error (RMSE) for the entire field calibration period was ~~-0.05~~ 1.69 ppm ~~with a standard deviation of ± 1.69 ppm~~ (n = 37,140). The results confirms that low-cost and low-power MOS can be effectively used for atmospheric CH_4 measurements under stable water vapor conditions. The primary scientific importance of the study is that it provides a clear example on how the application of low cost technology can enhance our future understanding on the climatic feedbacks from the cryosphere to the atmosphere.

1. Introduction

Constraining the various sources and sinks in the global methane (CH_4) budget is becoming an increasingly important parameter in mitigating climate change (Saunois et al., 2016). While the Arctic is generally considered a major global emitter of CH_4 to the atmosphere, significant uncertainty exists to the seasonal dynamics and strength of both CH_4 sources and CH_4 sinks from both terrestrial and marine environments, as well as the cryosphere (Callaghan et al., 2011; Emmerton et al., 2014; Juncher Jørgensen et al., 2015; Pirk et al., 2017; Zona et al., 2016). Recently, a previously unknown source of CH_4 emission to the atmosphere was identified where CH_4 is emitted from meltwater originating in the subglacial domain of the Greenland

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Ice Sheet (GrIS) (Christiansen and Jørgensen, 2018; Lamarche-Gagnon et al., 2018; Wadham et al., 2019). The spatiotemporal coverage of the new CH_4 source is yet to be determined and the overall climatic importance of this new component in the Arctic CH_4 budget is still unknown. Future studies are needed in order to assess the overall climatic significance of this source of CH_4 emission from the cryosphere to the atmosphere. The current state of knowledge on the CH_4 exchange from Greenland is inherently limited by the remoteness of many field sites with following high expedition cost and limitations to the spatial coverage and temporal duration of field measurements. Adding to this is the financial and logistical challenges of bringing high precision analyzers into the field, keeping them powered, running and shielded in the harsh environments often encountered in the Arctic. Thus, there is substantial potential and need to develop low-power techniques and measurement systems that can perform reliable autonomous CH_4 concentration measurements. The emergence of low-cost/low-power sensor technology in recent years provides an opportunity to overcome many of current restraints on obtaining continuous field measurements from a wide range of natural CH_4 emitting systems (wetlands, ice sheets, marine gas seeps, lakes, permafrost) and expand the network of continuous measurements in remote areas maximizing our understanding of these systems and minimizing the risk of losing valuable analytical equipment.

Low-cost metal oxide gas sensors (MOS) have been widely used for sensing various gases under atmospheric conditions (Wang et al., 2010). However, MOS sensors have significant obstacles to their direct use as air quality monitors as their output signal is influenced by the concentrations of both the target and interfering gases, as well as the temperature and humidity effects (Masson et al., 2015; Sohn et al., 2008). Other known challenges to the use of MOS are baseline drift over time, caused by either changes in the heat output of the sensing element or due to poisoning of the sensor surface (Peterson et al., 2017).

In recent years, investigations into the performance of CH_4 sensitive MOS sensors for the measurement of atmospheric CH_4 have been made under both natural and controlled conditions (van den Bossche et al., 2017; Eugster and Kling, 2012; Penza et al., 2015). These studies have been prompted by an increased interest in finding effective methods to quantify CH_4 emissions to the atmosphere from both natural systems and man-made systems such as landfills or biogas production plants. Using sensor specific post-processing to compensate for variations in relative humidity and air temperature, the previous studies have demonstrated a high potential for the low-cost and low-power monitoring of CH_4 concentrations above the atmospheric background level for various applications and in sensor networks ~~grids~~. In the current study, we have ~~in situ~~ tested the in situ performance of a CH_4 sensitive MOS (Figaro TGS2611-E00) against a state-of-the-art cavity ring-down spectrometer (CRDS) for CH_4 (Ultra-portable Greenhouse Gas Analyzer, Los Gatos Research Inc.) to measure CH_4 concentrations in the air expelled from a subglacial meltwater outlet at GrIS. This was done to assess the MOS's potential for serving as a sensing element ~~in~~ for future studies of ~~of the important scientific knowledge gap concerning the climatic feedbacks following~~ CH_4 emissions from the subglacial domain under the Greenland Ice Sheet ~~to the atmosphere~~.

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2. Materials and methods

2.1 Field site and instrumentation

The study site is located on the southern flank ~~at the terminus~~ of the Isunnguata Sermia Glacier at the western margin of the GrIS (67°09'16.40''N 50°04'08.48''W) at an elevation of 450 meter above sea level (Fig. 1). At a small subglacial meltwater discharge outlet in this area, we performed measurements of CH_4 concentrations in the subglacial air expelled from naturally occurring caves carved out by meltwater below the ice sheet. The measurements were done in the period between June 22nd and 26th 2018. A more detailed description of the study site at the GrIS is given in (Christiansen and Jørgensen, 2018).

To sample the subglacial air the sampling tube was attached to an aluminum pole inserted approximately 5 meters into an ice cave (Fig. 2a). ~~with t~~The inlet of the sampling tube was connected to a ~~100~~ 120 ml water trap ~~(Fig. 2a)~~. Humidity and temperature of the subglacial air were measured every 10 sec using a combined sensor (S-THB-M008, Onset, USA; resolution 0.02 °C, 0.1 % RH) mounted at the tip of the aluminium pole inserted into the cave. The data were recorded using~~At the end of aluminum pole inside the subglacial cave the humidity and temperature of the subglacial air was measured every 10 seconds with a combined sensor (S-THB-M008, Onset, USA) connected to~~ a datalogger (U30, Onset, USA).

Real-time reference concentration (ppm) measurements of CH_4, carbon dioxide (CO_2) and water vapor (H_2O) was obtained using a CRDS (Ultraportable Greenhouse Gas Analyzer, Los Gatos Research, USA). The inlet port of the CRDS was connected to the subglacial sampling point via a ~~A~~ sampling tube ~~of 50 meter~~ (50 m length, inner diameter of 4 mm and total volume of 630 mL) which was zip-tied to the aluminium pole. Flow of sample gas from the subglacial sampling point to the measurement cell in the CRDS was obtained via the analyzer's internal diaphragm pump (800 mL min^{-1}) ~~was connected to the inlet of the CRDS (Ultraportable Greenhouse Gas Analyzer, Los Gatos Research, USA) for real-time reference concentration analysis of CH_4, carbon dioxide (CO_2) and water vapor (H_2O) (Fig. 2a).~~. The outlet port of the CRDS was connected in series via a 1 m plastic tube to a metal can enclosure (400 mL), where the lid had been removed (Fig. 2b). The prototype CH_4 sensing system (MOS) was placed in the metal enclosure, where the short serial tube connector ensured a rapid flushing of the headspace in which the CH_4 measurements with the MOS were made. Due to the non-destructive sampling principle of the CRDS and the rapid flushing of the headspace volume in the enclosure with the MOS system (2 times per minute), the concentration of CH_4 is estimated to be virtually identical at the same time step for the MOS and the CRDS during the entire field calibration period (22nd to 26th July 2018).

~~The diaphragm pump of the CRDS creates a constant flow of 800 mL min^{-1}. Through a 1 meter tube the outlet flow (800 mL min^{-1}) of the CRDS constantly flushed an open-ended enclosure (400 mL) in which the prototype CH_4 sensing system (MOS)~~

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~~was inserted (Fig. 2b). During the field calibration period (22nd to 26th July 2018), the rapid flushing of the air volume in the enclosure with the MOS system (2 times per minute) and the non-destructive sampling principle of the CRDS collectively ensured that the concentration of CH_4 in the above the MOS sensor was identical to the CRDS at the same time step.~~

Following the field calibration test of approximately 100 h, the MOS system was left in the field as an autonomous monitoring system. For this autonomous measurement period, the CRDS was replaced by a 12 volt diaphragm pump (Thomas pumps, 1410VD DC) with a constant air-flow of approximately 3 L min^{-1} attached to the common sample tube with similar connection of the pump inlet and outlet as the CRDS ports. ~~the MOS system was left as an autonomous monitoring system where a constant air-flow of approximately 3 L min^{-1} to the enclosure with the MOS system was supplied by a 12 volt diaphragm pump (Thomas pumps, 1410VD DC) instead of using the outlet from the CRDS.~~ During this period the MOS system was powered by 12V $LiFePO_4$ batteries connected to solar panels and a voltage regulator, ~~. During the autonomous measuring period the MOS system and enclosure was~~ placed in a water-proof case and buried under a pile of rocks to minimize the impact of sunlight induced temperature variations of the sensor system. ~~allowing a direct comparison between CH_4 concentration measurements of the CRDS and MOS systems.~~

2.2 The MOS system

~~-~~The MOS system (Fig. 2c) consists of a microcontroller (Arduino Uno) and datalogger shield (DeekRobot data logging shield V1.0) holding the board-mounted metal oxide CH_4 sensor (Figaro TGS 2611-E00) and an additional temperature/relative humidity micro sensor (GY-21 HTU21). The final prototype was assembled in the laboratory at Aarhus University. Logging frequency of the CRDS and MOS was 1 and 10 seconds, respectively. The CH_4 sensitive MOS consists of a tin(IV)oxide (SnO_2) semiconductor which has low conductivity in clean air. In the presence of CH_4, the sensor's conductivity increases depending on the gas concentration in the air (Kumar et al., 2009). A simple electrical circuit converts the changes in conductivity at the sensing element as the gas concentrations vary to a change in output voltage across the voltage divider (see Fig. 3). Both the heater and the sensing circuit of the MOS ~~was~~ were powered by the 5 volt regulated output of the Arduino Uno. The analogue output of the MOS was connected to the 10-bit analogue input on the Arduino Uno using a 10 kOhm precision load-resistor in the voltage divider.

2.3 Laboratory calibration of the MOS sensor

In preparing for the field test of the CH_4 sensing system prototype, the MOS was performance tested and calibrated in a controlled laboratory environment to evaluate both the response time to variations in methane concentration in the concentration range 0-100 ppm CH_4 at three different levels of relative humidity (37±2 %, 55±3 % and 76±3 %). Synthetic air (80 % N_2 and 20 % O_2) was used as zero gas for the laboratory test to which various concentrations of a CH_4 containing span

gas was mixed in using a HovaCAL calibration gas generator (IAS Gmbh, Germany). After mixing of the zero gas and span gas, the calibration gas was humidified using a water filled impinger ~~similar to~~ (van den Bossche et al., 2017). At each humidity level, the output voltage from the MOS was logged using a Campbell CR1000 datalogger at a 2 second sampling frequency. A pre-programmed calibration step sequence was used for all three humidity levels, consisting of time steps of each 10 minutes in which the sensor was exposed to either zero gas or a calibration gas mixture in the applied the concentration range in an alternating step pattern (Fig. 4). The temperature in the laboratory, zero gas, mixed calibration gas and water in impinger was kept constant around 22 °C throughout the laboratory calibration test.

The sensor resistance (R_{0}) at exposure to the CH_4 free reference gas can be calculated at each of the three different humidity levels according to Eq. (1):

$$R_0 = \frac{V_C * R_L}{V_{OUT}} - R_L \,, \qquad (1)$$

where V_C is the circuit voltage (i.e. 5 volt DC), R_L is the load resistance (10 kOhm) and V_{OUT} is the measured output voltage (see also Eugster and Kling (2012) for further description).

The sensor resistance at various calibration gas concentrations (R_S) at different concentration steps in the calibration sequence can also be calculated using equation 1 for each of the three humidity levels (i.e. Rs replaces R_{0} in equation 1). For the tested type of MOS, the sensor resistance ratio (R_S/R_{0}) between the sensor resistance at a given concentration level (Rs) and the sensor resistance at the reference level (R_{0}) ~~is~~ are inversely proportional to the absolute CH_4 concentration and can be modelled using e.g. a power fit (Fig. 5).

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2.4 Field-calibration of the MOS

Field calibration of the MOS was done at the meltwater outlet at the Greenland Ice Sheet by ~~parallels~~simultaneous measurements of the same air mass by the MOS sensor system and a state-of-the-art CRDS in the configuration described above (section 2.1). For the calculation of the average ambient sensor resistance (R_{0*}) using Eq. 1, the atmospheric background concentration of CH_4 of the air (approximately 1.9 ppm) close to the ice sheet was used, in the absence of a controlled and humidified zero gas. Exact measurements of ~~the~~ temperature and humidity of this air mass is ~~missing~~not available, but T and RH is estimated to fall within the range of 1-4 °C and 90-100 % RH. ~~Since access to a controlled, humidified zero gas was not possible in the field, the atmospheric background concentration of CH_4 (approximately 1.9 ppm) close to the ice sheet was used to calculate the average ambient sensor resistance (R_{0*}) using Eq. 1.~~ The output value of the MOS under these conditions ~~which~~ was then used to establish the resistance ratio (R_S/R_{0*}) vs. CH_4 concentration field calibration function for the MOS (Fig. 6).

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~~the output of the MOS when exposed to ambient air at the atmospheric background concentration of CH_4 (approximately 1.9 ppm) close to the ice sheet was used to calculate the average ambient sensor resistance (R_{0a}) using Eq. 1, which was then used to establish the resistance ratio (R_s/R_{0a}) vs. CH_4 concentration field calibration function for the MOS (Fig. 6).~~

2.5 Data processing

In order to compensate for potential effects of micro-turbulent mixing of subglacial air with atmospheric air observed with the CRDS (Christiansen and Jørgensen, 2018) and which occur at a faster frequency than the 10 s sampling interval of the MOS (see also section 3.3), ~~T~~the measured raw time series data from the MOS were smoothed using simple exponential smoothing according to Eq. (2):

$$s_t = \alpha x_t + (1-\alpha)s_{t-1} \quad \text{for } t>0 \qquad (2)$$

where s_t is the smoothed CH_4 concentration value (ppm), ~~-~~α is the smoothing factor and s_{t-1} is the previous smoothed CH_4 concentration value (ppm). At time zero (t=0), the s_t is equal to the first unsmoothed raw CH_4 value of the MOS. The optimum value for α was determined using Microsoft Excel solver, by minimizing the total average ~~root mean square error (~~RMSE~~)~~ between the raw data from the MOS and the simultaneous concentration measurement of the CRDS. Results show an optimal value of 0.042~~,~~ which ~~for the sake of simplicity was rounded to 0.05, and~~was ~~subsequently~~ used for both the CRDS and MOS data series (Fig. 7).

3. Results and Discussion

3.1 Laboratory calibration test of the MOS

Fig. 3 shows the relationship between the resistance ratio (R_S/R_O) for the step test at three regulated humidity levels, where Ro is calculated for each humidity levels based on the average voltage output of the sensor in the time steps where it was exposed to the CH_4-free synthetic air. It is observed that a near identical response function can be obtained across the three different water vapor concentrations in the air, as long as the water concentration of the zero gas is the same as in the span gas. Based on existing knowledge of the expected air temperature variations at the in situ sampling point at the GrIS (Christiansen and Jørgensen, 2018), the humidity calibration was only carried out at a single temperature in this study. However, variations in the ambient air temperature is also expected to have a linear scaling effect for the type MOS system tested in this study (Bastviken et al., 2020; van den Bossche et al., 2017).

3.2 Field-calibration of the metal oxide sensor

The measured R_S/R_{O*} ratios per time step over the field calibration period were converted into absolute CH_4 concentrations using the regression statistics of the applied power model (Fig. 6). A total of 37,140 data points ~~are~~is included in the regression model for converting the R_S/R_{O*} ratios to CH_4 concentrations. Inclusion of data points from the micro-turbulent periods produces a noisy visualization of the calibrations data at higher CH_4 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 (R^2 = 0.98; p-value: 0.001). While the same regression model is ~~equations are applied~~ used for ~~in~~ both the laboratory calibration and field calibration, significant deviation in the model parameters are observed between the laboratory calibration as a group and the field calibration. The reason for this difference is unknown, but a possible explanation could be the potential difference in input heater voltage for the MOS sensor (i.e. pin 1 and 4 in Fig. 1), since variations in the input heater voltage have been reported to affect the ~~which has been reported to linearly scale the~~ CH_4 concentration measurements ~~study~~ (van den Bossche et al., 2017). In the laboratory test, the heater circuit of the MOS was supplied by the 5 volt regulated output from the CR1000 datalogger, whereas the heater circuit was supplied from the Arduino Uno's 5 volt regulated output. Future test should aim to investigate if the differences between the results from the laboratory and field calibration can be minimized by using the same type of datalogger and identical power supply (fx. Rechargeable lithium ion battery pack) both in the laboratory and in the field. Results from this type of test could reveal if field calibration for each individual MOS system is needed similar to the approach in Bastviken et al. (2020), or if batch calibrations of several identical MOS-system can be performed in the laboratory without the need for time-consuming field calibration.

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3.3 Time-series plot of CH_4 concentration from reference CRDS and MOS

Due to the dynamic environment at the margin of the GrIS, the physical configuration of the sampling point will vary both over the melt-season as well as on an inter-annual basis. In our previous study, high frequency variations in CH_4 concentrations in the subglacial air were observed in a downward draping curve style where a high concentration plateau was interrupted by rapid decreases in CH_4 concentration (Christiansen and Jørgensen, 2018). This pattern was interpreted to be an effect of micro-turbulent and wind driven dilution of the sample gas in the ice cave by atmospheric air with a CH_4 concentration of approximately 1.9 ppm. In the current study, exponential smoothing of the raw values is used to compensate for the potential effects of physical disturbance of the sample gas caused by wind driven turbulent mixing of atmospheric background air at the subglacial sample point. Also, temporal smoothing can compensate for some of the sensor specific variation in response time improving the pairwise measurement comparability between the CRDS and the MOS. According to the manufacturer, the CRDS is specified to have a response time of less than 1 hz, while the response time of the MOS is expected to be slower. ~~The T_{90} response time for a similar SnO_2 based CH_4 sensor separated with a thin silicone membrane has been reported to be between 1-30 minutes (Boulart et al., 2010), for which the shorter time range is comparable to what is observed in the laboratory calibration of this study (Fig. 4).~~

The time series plot of the raw and exponentially smoothed CH_4 data from the CRDS ($CRDS_{smooth}$) is shown together with the pairwise error between the raw data and the smoothed data (Fig. 7a). Similarly, the time series plot of the raw and exponentially smoothed CH_4 data from the MOS (MOS_{smooth}) is shown together with the pairwise error between the raw data and the smoothed data (Fig. 7b). It is generally observed that over the first 4 days of the calibration test, very low differences are observed between the raw data CH_4 concentration and the smoothed CH_4 concentrations for both $CRDS_{smooth}$ and MOS_{smooth}, with absolute errors below 5 ppm (Fig. 7a & 7b). At the end of the field calibrations, higher errors are observed following the larger spread in CH_4 concentration measurements of both the CRDS and the MOS. CRDS analyzers across different brands and manufacturers generally perform very consistently and have a highly linear measurement response across the effective concentration range without any tendencies for increasing analytical error with increasing gas concentrations (Brannon et al., 2016). Fluctuations in CH_4 concentrations in the subglacial air were also observed in (Christiansen and Jørgensen, 2018) using a CRDS from another manufacturer (G4301 GasScouter, Picarro Inc.). These variations were attributed to the dynamic and micro-turbulent environment in the subglacial cavity where the gas concentrations were measured and are likely produced by both air movement generated by the shear stress of the running meltwater as well as turbulent intrusion of atmospheric air generated by shifting winds speeds at the measurement location at the ice margin.

According to the field notes for the current study, a shift in overall wind regime took place during the 25th of June 2018, where the weather shifted from calm and sunny conditions to more windy conditions dominated by strong catabatic easterly winds

coming off the GrIS. A best estimate of the overall time period where more windy conditions occurred during the field calibration period is indicated with grey background in Fig. 7. Unfortunately, no direct measurements of wind movement were made during the fieldwork period at the location. Measurements of air temperature at the sample inlet point in the subglacial cavity (Fig. 7c) show~~s~~ that an initial period with diurnal temperature variations of approximately 0.1 to 0.2 ^{o}C was followed by a period with more fluctuating temperature variations of up to + 0.6 ^{o}C. The period with higher variability corresponds to the period where higher winds speeds predominate and the deviations between the raw and smoothed CH_4 are the greatest. The higher variability in air temperature measurements during the more windy weather is interpreted as being a product of more turbulent wind conditions right at the margin of the GrIS and opening to the subglacial cavity by which higher amounts of warmer atmospheric air with an approximate CH_4 concentration of approximately 1.9 ppm is introduced into the subglacial cavity. The introduction of these atmospheric air masses results in both short-term temperature increases as well as dilution of the subglacial CH_4 concentration in the cavity producing the more variable CH_4 concentration patterns observed in both the CRDS and MOS raw data. In the absence of direct measurements of wind speed and micro-turbulence at the margin of the ice, rapid variations in air temperature at the sample inlet point with an amplitude greater than the 0.2 ^{o}C appear as a reasonable indicator or proxy for micro-turbulent dilution and physical disturbance of the source signal, which can effectively be filtered out by the application of exponential smoothing.

The relative error between each MOS_{smooth} and $CRDS_{smooth}$ measurement pair can be expressed as the percentage that the difference constitutes compared to the reference CRDS concentration (i.e MOS_{smooth} – $CRDS_{smooth}$/$CRDS_{smooth}$ x 100). It is seen that the pairwise relative error between the MOS_{smooth} and $CRDS_{smooth}$ shows similar non-systematic variations in both the calm weather and windy time period with relative errors typically below ± 10 % (Fig. 7d). This result show both that the accuracy of the CH_4 concentration measured by the MOS are in close agreement with the reference CRDS and that the exponential smoothing effectively compensates for short term physical disturbances at the measurement point. The result also indicate that no systematic drift or over/underestimation is apparent when comparing the MOS_{smooth} to the $CRDS_{smooth}$ over the 100 h field calibration period (Fig. 7b). When considering the magnitude of the absolute errors between the raw and smoothed CH_4 concentration for both the CRDS and the MOS, together with the temporal pattern in the development of the relative error, it shows that the high frequency concentration fluctuations measured with the MOS are most likely the product of physical disturbances at the measurement point (primary sampling error), and not by an analytical error introduced by the MOS itself (secondary sampling error).

As supplement to the pairwise error comparison, average time-series performance statistics for the difference between the MOS_{smooth} and $CRDS_{smooth}$ time series can be calculated for both the full field calibration period, as well for the non-turbulent time period with limited observed physical disturbance at the sampling point (Table 1). RMSE for ~~Mean bias errors for both~~ the non-turbulent and full time series are approximately ~~± 0.01 ppm CH_4 with standards deviations of ±~~ 1.3 to 1.7 ppm CH_4 respectively.

3.4 Post-correction and cross-interference evaluation

One of the main obstacles previously reported concerning the use of MOS's for monitoring of gases in ambient air is the possible effect of variations in air temperature and humidity in the sampling environment (Bastviken et al., 2020; Eugster et al., 2019; Masson et al., 2015; Sohn et al., 2008). ~~One~~ Different approaches exist to compensate for this potential measurement error and is related to post-correct for variations in temperature and humidity, based on either generic temperature and humidity dependency curves supplied by the sensor company (Eugster and Kling, 2012). This is achieved , ~~or~~ by performing sensor calibrations under controlled levels of temperature and humidity in the laboratory (van den Bossche et al., 2017) or by field calibration (Bastviken et al., 2020).

Measurements from the air-filled cavity under the GrIS document a very stable sampling environment with a relative humidity throughout the sampling period of close to 100 % RH (data not shown) and only minor air temperature variations between approximately 0.05 ^{o}C during the night and 0.25 ^{o}C during mid-day (Fig. 7d). Because of these stable and well-buffered environmental conditions, no post-corrections due to variations in temperature and relative humidity are evaluated to be necessary for this particular sampling environment.

Observed variations in maximum air temperature in the subglacial cavity correspond to field observation of the time of the day when maximum meltwater discharge occurs. We assume that the observed temperature pattern reflects the impact of thermal heat diffusion from this running meltwater to the air immediately above, but would need direct measurements of the daily variations in meltwater temperature to verify this assumption.

The emitted CH_4 may originate from both thermogenic and/or biogenic sources below the GrIS. If the primary source of CH_4 is thermogenic, the emission may also be accompanied by more complex hydrocarbons, including ethane (C_2H_6), while this will not be the case if the source is biogenic (Hopkins et al., 2016). Since the MOS used in the study is non-selective to CH_4 due to its basic principle of operation (Eugster and Kling, 2012; Wang et al., 2010), the presence of other hydrocarbons such as ethanol (C_2H_6O), isobutene (C_4H_{10}) and potentially also other low molecular weight alkanes could potentially cause cross-interference with the CH_4 measurement. It follows, that if the source of the CH_4 that is emitted for the subglacial domain originates in thermogenic natural gas reservoirs under the GrIS, the other non CH_4-hydrocarbons could potentially affect the measurements performed by the MOS, while ~~passing non~~ being undetected by the CRDS. However, since the magnitudes and temporal patterns in CH_4 concentrations are similar in both the CRDS and MOS it is assumed that the gases emitted from the subglacial domain are primarily CH_4 and CO_2 with very limited potential for cross-interference from other hydrocarbon gases. Also, isotopic analysis of the emitted CH_4 and CO_2 in (Lamarche-Gagnon et al., 2018) as well as unpublished data from this study, have shown that the emitted CH_4 is dominantly of microbial origin and has isotopic similarity to CH_4 produced by

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anaerobic decomposition of organic carbon in wetlands. It is therefore assumed that there is no need for any post correction of the CH_4 concentrations measured by the MOS in this type of environment due to lack of cross-interference from other hydrocarbon gases.

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3.5 Autonomous CH_4 monitoring using MOS system

The combined time period in which CH_4 concentrations were measured can be divided into three separate periods depending on the analytical devices used, namely period 1 corresponding to the field calibration period where both the CRDS and MOS were in operation (approximately 100 h), period 2 where only the CRDS was in operation (approximately 24 h) and period 3 where only the MOS was in operation (Fig. 8). Continuous CH_4 data from period 3 exist for the period 27th June to 15th July 2018. When comparing the combined CH_4 concentration curves from all three periods it is observed that the $CRDS_{smooth}$ and MOS_{smooth} follow each other as described above (Fig. 7). $CRDS_{smooth}$ data for period 2 fills the data gap between the MOS measurement of period 1 and 3, where the start concentration data of the MOS_{smooth} ~~concentration data departs very close to~~ are similar to the concentration level where the $CRDS_{smooth}$ measurements end. Due to the nature of the study design and difficult access to the remote field site at the GrIS, the accuracy and precision of the MOS_{smooth} cannot be evaluated for the period 3 where only the MOS system was operating. However, the pattern in which subglacial CH_4 concentrations varied and the estimated minimum and maximum values appear similar to the values of the calibration period. When comparing the complete time period of this study to e.g. Eugster and Kling (2012), no significant sensor drift is expected over the monitoring time period. Additional and extended field work at the GrIS with repeated calibration at the end of the field deployment period is needed to quantify the potential sensor drift, as well as stability range over longer time scales (Eugster et al., 2019). Nonetheless, the observed performance of the MOS during the calibration period with ppm-level accuracies and subsequent trouble-free operation running as an autonomous unit shows that this type of low-cost and low-power CH_4 sensing system holds a great potential for the further development and refinement of a greater sensor network at representative meltwater outlets at the Greenland ice Sheet. ~~The major scientific scope of this performance test is that we can demonstrate a realistic low-cost technical solution for closing one of the most critical knowledge gaps in the Arctic carbon budget, namely the climatic impact of CH_4 emissions to the atmosphere under both current and future warmer climatic conditions.~~

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The next steps and lessons learned from this study deals with the further development of the low-power system for actual CH_4 emission measurements, which involves measurements of air volume and meltwater discharge as well as continuous measurements of the dissolved CH_4 in the meltwater, similar to (Lamarche-Gagnon et al., 2018). Also, optimizing the positioning of gas sensing equipment at the measurement point should be done to reduce the potential physical disturbances due to micro-turbulence and intrusion of atmospheric air in the subglacial cavity. Furthermore, an improved adjustment scheme should be developed to account for the dynamic melt back of the ice margin over the melt season, which requires either manual or automated sample point relocation to keep the sampling point at an optimal physical location. Finally, more work is needed

to test what modification to the systems are needed to establish a universal calibration curve in the laboratory, so that the need for field calibration with the reference CRDS can be eliminated (see also (Bastviken et al., 2020; Eugster et al., 2019)).

4. Conclusions

Recent discoveries at the Greenland Ice Sheet (GrIS) have revealed a so far overlooked cryospheric source of CH_4 from the subglacial domain under the ice to the atmosphere. Development of low-power CH_4 monitoring systems based on low cost metal oxide sensors (MOS) could enable the development of a sensor network at representative meltwater outlets at the GrIS which could significantly ~~could enhance~~ improve the fundamental understanding of the phenomena's climatic importance. In the current study, the performance of a metal oxide sensor sensitive to CH_4 was tested in an air-filled cavity at the edge of the Greenland Ice Sheet over an initial field calibration period of approximately 100 h. ~~using both a reference gas analyzer based on cavity ring-down spectroscopy (CRDS) and a low-cost metal oxide sensor (MOS) followed by a period of autonomous CH_4 concentration monitoring using only the MOS system. Parallel~~Simultaneous measurements by both cavity ring-down spectroscopy (CRDS) and a low-cost metal oxide sensor (MOS) using a common inlet show good agreement between the MOS and the CRDS over time under the stable environmental conditions under the ice. Exponential smoothing of the raw data from both the CRDS and MOS effectively remove high frequency concentration variations induced by physical disturbance of the air in the subglacial cavity under more turbulent wind conditions at the margin of the ice sheet. Based on concentration values of the smoothed CRDS and MOS data, the pairwise measurement errors were generally below ± 5 ppm CH_4 between the MOS and the CRDS reference value. Pairwise relative errors were generally below ± 10 % between the MOS and the CRDS reference value. The ~~mean bias~~RMSE ~~error~~ for the entire field calibration period was ~~0.05 ppm,~~ ± 1.69 ppm CH_4 ~~with a standard deviation of ± 1.69 ppm CH_4~~. If only data for the non-turbulent time period was evaluated, the ~~mean bias error~~ RMSE was reduced to ~~0.09 ppm CH_4 with a standard deviation of~~ ± 1.35 ppm CH_4. Due to the ~~very clean and stable~~ ice buffered sampling environment in the air-filled cavity under the Greenland Ice Sheet, no post-corrections for variations in air temperature, humidity or cross interference from other hydrocarbon gases were needed for the MOS measurements. Combined with measurement of airflow and meltwater discharge, the measurement of CH_4 concentrations can be used for determination of the mass flux of CH_4 to the atmosphere. The study demonstrates a clear potential for expanded monitoring of spatial and temporal variation in CH_4 emissions from the subglacial domain of the Greenland Ice Sheet using low-cost and low-power MOS.

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5. Author contribution

CJJ and JRC designed and carried out the field experiments. CJJ, JMO and KFU planned and carried out the laboratory calibrations. CJJ and JRC prepared the manuscript with contributions from all co-authors.

6. Acknowledgements

This work was supported by a research grant from the "Brødrene Hartsmanns Fond" for the project "Udledning af metan til atmosfæren fra gletchere" and performed as part of the "Arctic Research Centre" and "iClimate" research frameworks at

Aarhus University. Laboratory test of MOS sensors was performed by FORCE Technology through support from the Danish Agency for Innovation as part of the project “Den Danske Renluftsektor”.

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Figure captions

Figure 1: Overview of the sampling location at Isunnguata Sermia Glacier at the western margin of the Greenland Ice sheet during June 2018. (a) Location of sampling region the island of Greenland, (b) regional location of the outlet glacier, (c) location of the meltwater outlet at Isunnguata Sermia and (d) local sample location with investigated subglacial cavity marked with red circle. Source of (a), (b) and (c): Google Earth, earth.google.com/web/.

Figure 2: (a) Close-up of air-filled cavity below the Greenland Ice Sheet next to the lateral meltwater outlet. The aluminum pole extends approximately 5 meters into the cavity and holds the common inlet tube and the temperature and humidity smart sensor. (b) Conceptual diagram of the MOS system which was connected in series to the outlet port of the CRDS analyzer~~The aluminum pole extends approximately 5 meters into the cavity and holds the inlet tube and the temperature and humidity smart sensor. (b) Conceptual diagram of the MOS system placement in an enclosure constantly flushed by the outflow from the CRDS analyzer~~ (c) Close-up of the board mounted MOS and temperature/humidity micro sensor. The MOS system consisted of 1) a microcontroller, 2) Datalogger shield holding metal oxide CH_4 sensor and 3) an additional temperature/relative humidity micro sensor.

Figure 3: Simplified schematic of the metal oxide sensor (MOS) system consisting of a TGS2611-E00 with pin 3 and 4 connected to the 5-volt output of the Arduino Uno, pin 1 connected to ground and pin 2 connected to the analogue input of the Arduino Uno and a 10kOhm load resister, which also connects to ground.

Figure 4: Outlet voltages of the MOS during laboratory step calibration at stabilized levels of relative humidity (37 ± 2 %, 55 ± 3 % and 76 ± 3 %) in both the zero and span gas at alternating concentration of CH_4 in the calibration gas between 10 and 100 ppm CH_4. Each time step lasted 10 min and sequences with grey shadings show time periods where the sensor was exposed to CH_4 free zero gas.

Figure 5: Resistance ratio of MOS as three levels of relative humidity at CH_4 concentration levels between 10 to 100 ppm CH_4 in humidified synthetic air.

Figure 6: Regression plot of calculated MOS resistance ratio R_S/R_{0*} vs. the reference in situ CH_4 concentrations from the CRDS (n = 37,140).

Figure 7: (a) Grey dots show raw CH_4 concentration from the cavity ringdown spectrometer (CRDS). Black line show CRDS CH_4 concentration values following exponential smoothing. Black bars show absolute error between raw and smoothed values. (b) Grey dots show calculated raw CH_4 concentration from metal oxide sensor (MOS). Black line show MOS CH_4 concentration values following exponential smoothing. Black bars show absolute error between raw and smoothed values. (c) Black dots show temperature of air in subglacial cavity. (d) Black bars show the relative error in percentage between the MOS_{smooth} and $CRDS_{smooth}$ divided by the $CRDS_{smooth}$ concentration. Grey background shading indicates period with higher observed turbulence at the margin of the GrIS. Temporal resolution is 10 seconds.
~~Figure 7: (a) Grey dots show raw CH_4 concentration from CRDS. Black line show CRDS CH_4 concentration values following exponential smoothing. Black bars show absolute error between raw and smoothed values. (b) Grey dots show calculated raw CH_4 concentration from MOS. Black line show MOS CH_4 concentration values following exponential smoothing. Black bars show absolute error between raw and smoothed values. (c) Black dots show temperature of air in subglacial cavity. (d) Black bars show the relative error in percentage between the MOS_{smooth} and $CRDS_{smooth}$ divided by the $CRDS_{smooth}$ concentration. Grey background shading indicates period with higher observed turbulence at the margin of the GrIS.~~

Figure 8: Smoothed time series measurements of CH_4 at the Greenland Ice Sheet using both the cavity ring-down spectroscopy (CRDS) reference monitor and the metal oxide sensor (MOS). Temporal resolution is 10 seconds.

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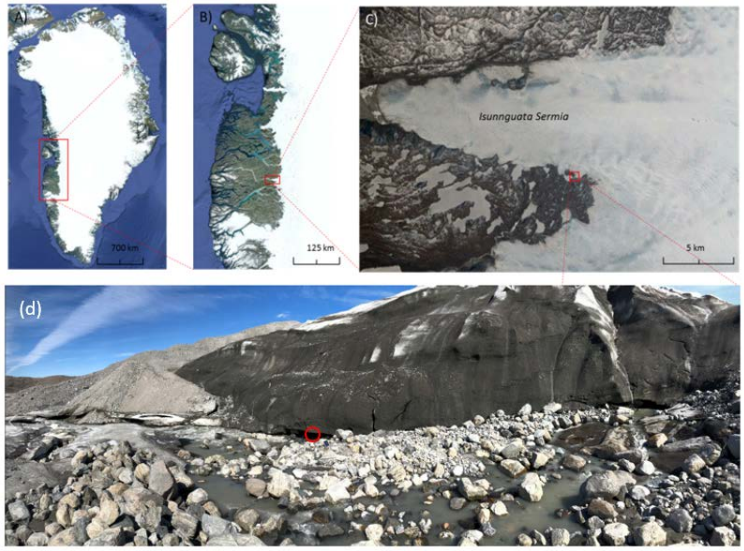

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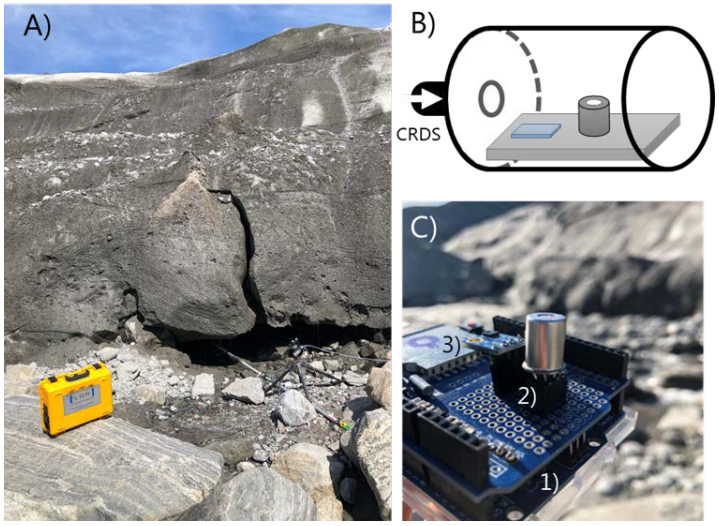

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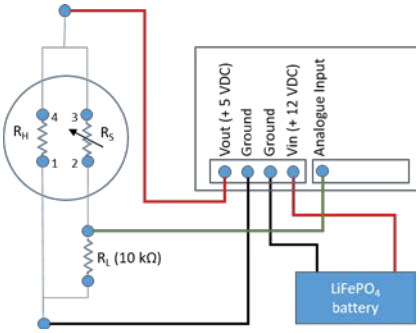

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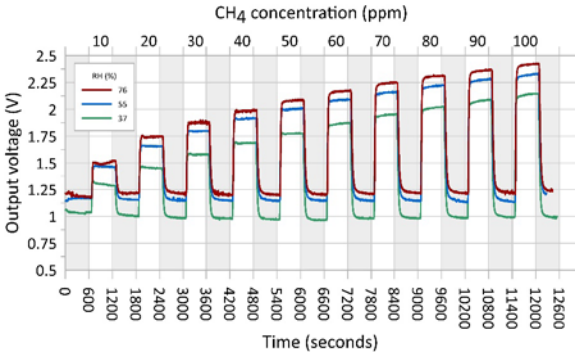

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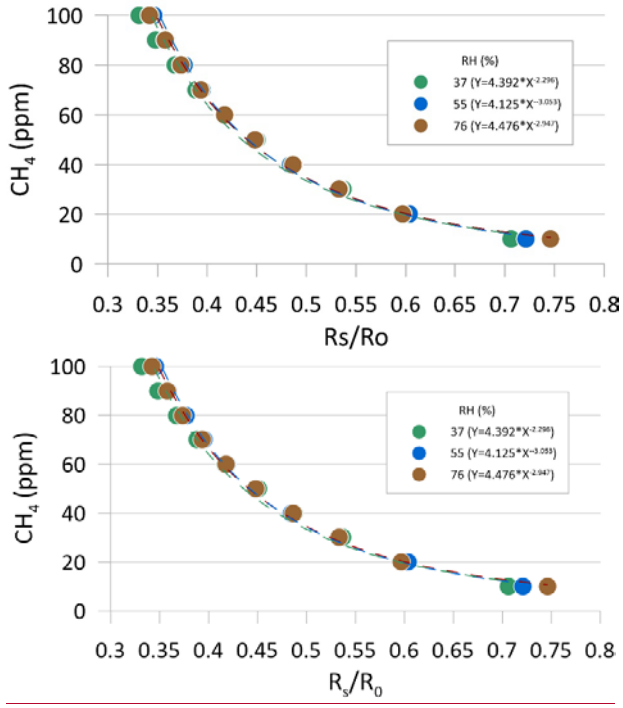

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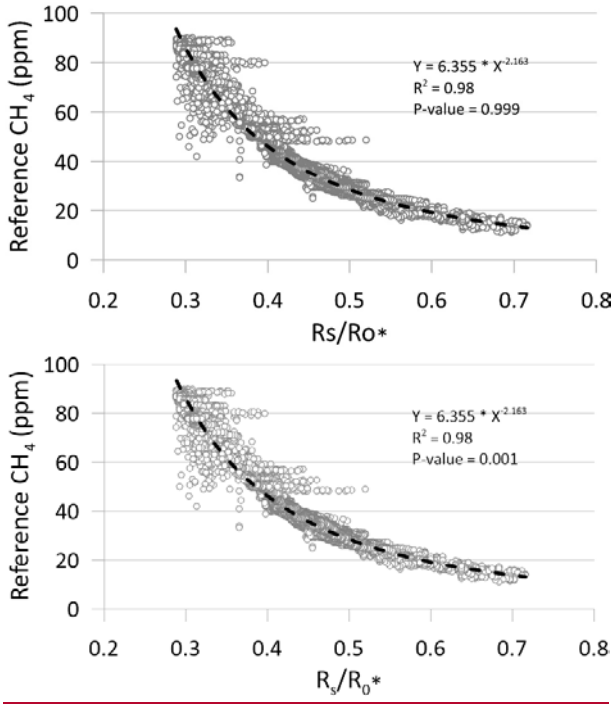

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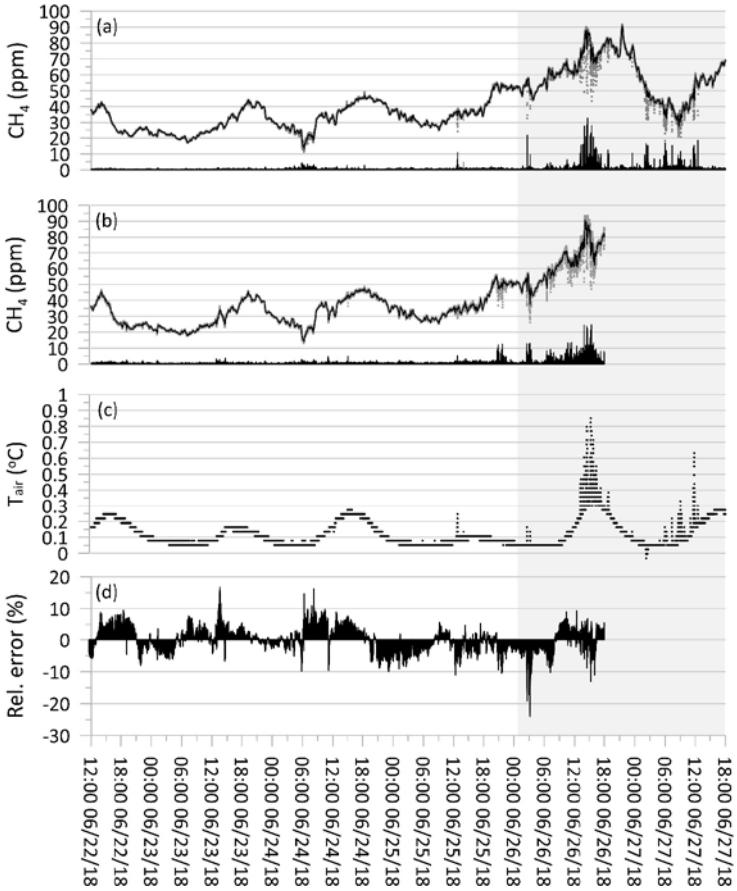

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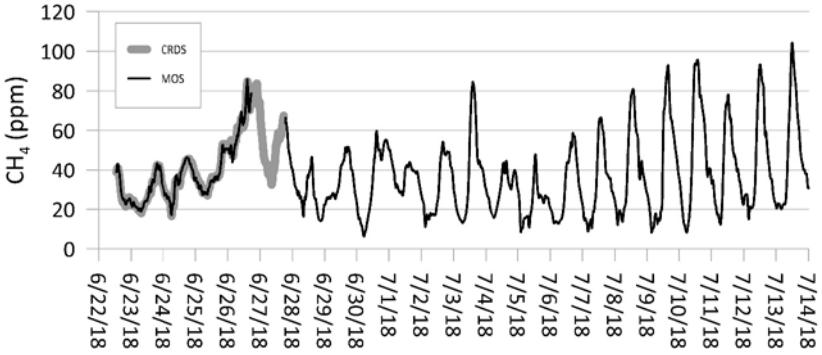

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Tables

Table 1. Statistics for the calculated differences between the smoothed MOS and smoothed CDRS data series in both the non-turbulent time period and full field calibration period. The unit for error and difference values is ppm.

Statistics: MOS_{smooth} - $CRDS_{smooth}$	Non-Turbulent	Full series
Mean bias error (MBE)	0.09	-0.05
Mean absolute error (MAE)	1.08	1.29
Root mean square error (RMSE)	1.35	1.69
Maximum negative difference	-3.96	-11.83
Maximum positive difference	5.04	5.91
Observations	28501	37140

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Point-by-point response to comments by Anonymous Referees #1, #2 and #3 for manuscript "amt-2019-468".

Anonymous Referee #1
Received and published: 16 January 2020

"General comments
This paper presents laboratory and field calibrations of a low-cost MOS for the measurement of methane concentrations in air. Whilst laser spectroscopy is currently the state-of-the-art solution for high-precision measurements of trace gases such as methane, this technology is expensive and ill-suited to remote, hostile environments such as the Greenland Ice Sheet, which is the study site of this paper. There is a great need to develop low-cost, low-power, rugged sensors capable of operating autonomously in remote locations and this is particularly critical for Arctic ecosystems where the effects of climate change on greenhouse gas emissions are believed to
be much larger than at lower latitudes. This paper compares a low-cost MOS with a state-of-the-art Picarro cavity ringdown spectrometer (CRDS), using the latter as a benchmark, and demonstrates the suitability of the prototype for real-time, in situ measurements. The proof-of-concept study is well-designed and generally adequately documented, and the subject matter is a good match for the scope of the journal. The technology is interesting and I hope that it will be developed further. This manuscript should be considered for publication provided that all the comments listed below are addressed."

➔ Reply 1: We appreciate the constructive criticism by Reviewer #1, #2 and #3. We have prepared a point-by-point response to each of the raised issues below, and incorporated appropriate changes to the manuscript, accordingly:

"Specific comments:
The quality of English is acceptable but efforts should be made to shorten sentences throughout the manuscript."

➔ Reply 2: Ok.

"Line 61: the MOS would not directly inform on climatic feedbacks. Please shorten the sentence to ": : : sensing element for future studies into CH4 emissions from the subglacial domain under the Greenland Ice Sheet.""

➔ Reply 3: Suggestion has been followed. The revised sentence is: "*This was done to assess the MOS's potential for serving as a sensing element for future studies CH_4 emissions from the subglacial domain under the Greenland Ice Sheet. "*

"Line 80: what is an open-ended enclosure? (**A**)"

"Lines 85-91: Where/how was the air fed to the MOS sampled from? Through a 50 m tube, independently of the CRDS? If so, the sampling rate, and hence flushing rate of the MOS enclosure, would have been > 3 times that of the CRDS. My interpretation of this is that the autonomous setup would have been different from the calibration one and you would no longer compare like for like (direct comparison?). Please explain. (**B**)"

"Line 131: also refers to comment above. "Parallel measurements: : :"; the setup is still

unclear to me. Did you use separate sampling lines for the CRDS and the MOS? (**C**)"

➔ Reply 4: A combined reply has been prepared for the three above reviewer comments (**A,B,C**)

Two different configurations were used depending on the measurement period:

1) Field calibration period where parallel measurements were done with the CRDS and MOS **connected in series**. In this configuration, a 50 meter plastic tube connected the subglacial sampling point to the inlet of CRDS. Here, the sample gas passed through the internal pump of the CRDS to the measurement cell before exiting the outlet port of the CRDS. The outlet port was connected via 1 meter tube to enclosure where the MOS was placed.
2) Autonomous measuring period where the CRDS was replaced by a small 12 volt diaphragm pump (inlet of pump connected to the sampling point and outlet of pump connected to bottom of enclosure).

In order to make this more clear as well as to accommodate the general advise of shortening sentences. the 2nd and 3rd paragraph of section 2.1 has been revised to the following:

"*Real-time reference concentration measurements of CH_4, carbon dioxide (CO_2) and water vapor (H_2O) was obtained using a CRDS (Ultraportable Greenhouse Gas Analyzer, Los Gatos Research, USA). The inlet port of the CRDS was connected to the subglacial sampling point via a sampling tube (50 m length, inner diameter of 4 mm and total volume of 630 mL) which was zip-tied to the aluminium pole. Flow of sample gas from the subglacial sampling point to the measurement cell in the CRDS was obtained via the analyzer's internal diaphragm pump (800 mL min^{-1}). The outlet port of the CRDS was connected in series via a 1 m plastic tube to a metal can enclosure (400 mL), where the lid had been removed (Fig. 2b). The prototype CH_4 sensing system (MOS) was placed in the metal enclosure, where the short serial tube connector ensured a rapid flushing of the headspace in which the CH_4 measurements with the MOS were made. Due to the non-destructive sampling principle of the CRDS and the rapid flushing of the headspace volume in the enclosure with the MOS system (2 times per minute), the concentration of CH_4 is estimated to be virtually identical at the same time step for the MOS and the CRDS during the entire field calibration period (22nd to 26th July 2018).*

Following the field calibration test of approximately 100 h, the MOS system was left in the field as an autonomous monitoring system. For this autonomous measurement period, the CRDS was replaced by a 12 volt diaphragm pump (Thomas pumps, 1410VD DC) with a constant air-flow of approximately 3 L min^{-1} attached to the common sample tube with similar connection of the pump inlet and outlet as the CRDS ports. During this period the MOS system was powered by 12V $LiFePO_4$ batteries connected to solar panels and a voltage regulator, placed in a water-proof case and buried under a pile of rocks to minimize the impact of sunlight induced temperature variations of the sensor system. "

Figure caption of Fig.2 has also been updated for improved clarity.

Also, the wording "***Parallel measurements***" has been changed throughout the manuscript to "***simultaneous measurement***" to avoid the potential ambiguity of whether the CRDS and MOS were connected in series using a common sample tube (as were the case) or in parallel using different sample tubes (which were not the case).

“Line 147: I don’t understand why 0.042 is more complicated than 0.05. What uncertainty does rounding up (why not round down to 0.04 which is nearest?) add?”

➔ Reply 5: In a sense, the reviewer could be right that it defies its own purpose to do an optimization for a best values, and then round it up afterwards. We have revised the data smoothing with 0.42 for both dataseries, and updated the figures accordingly.

“Line 165: a graph illustrating the differences in model parameters would be useful. How significant are the differences between lab and field calibrations? In line 115 (lab calibration) you mentioned that the temperature was kept constant at around 22 _C. Was there a temperature effect in the field calibrations? Please, comment.”

➔ Reply 6: The environmental conditions between the controlled atmosphere of the laboratory and the uncontrolled field conditions in Greenland are of course significantly different, which is one of the reasons why field calibration of the MOS seems necessary, unless we work out a better way to do a generic standard calibration. During the field measurements used for the calculation of the R_0*, air with a CRDS confirmed CH_4 concentration of the atmospheric background (approx. 1.9 ppm CH_4) was sampled within 10 meters of the ice margin where meltwater and CH4 emission was absent. The exact temperature and relative humidity of this air mass is unknown, but likely within the range between 1-4 C^o and above 90 % RH. The text in section “2.4 Field calibration of the MOS” has been revised to include this information.

“Lines 187-189: I do not understand the relevance of discussing the response time of a similar MOS, unless by similar you mean same model, different unit. Furthermore, the response time range (1-30 minutes) is massive compared to the CRDS (< 1 Hz). Considering the large differences in response times, you would have to take into consideration the temporal buffering introduced by the pumping rate, particularly where the Picaro is concerned (_ 47 seconds to flush the 50 m sampling tube @ 800 mL/min).”

➔ Reply 7: Since we cannot be absolutely sure that the model used in the reference is identical to the TGS2611 used in this study, we have followed the advice to remove this part of the discussion.

“Lines 220-222: Re. filtering out the fluctuations attributed to micro-turbulence/ dilution of cavity air by influx of ambient air. If the purpose of the exercise is to study the emissions of CH4 from the cavity, then filtering out such perturbations is justified.

However, this paper is concerned with a field assessment of a MOS sensor, and in this context, characterizing the response of the 2 sensors to these perturbations is of great interest. This ties in with the comment above (response time and temporal buffering). Looking at Fig. 7a, the outliers in the turbulent period are further from the smoothed line for the CRDS than for the MOS. This might be an effect of the faster response time of the CRDS. It would be interesting to choose a longer averaging time (>= sample line flush rate + sensor response time) and plot the time series of Fig. 7a and b again. I would like to see this analyzed and discussed rather than just smooth it out.”

➔ Reply 8: We understand the point raised by the reviewer, and agree that a better understanding of especially the response of the MOS to fluctuation conditions would be great. In the current dataset, we unfortunately have no data to actually quantify the amount and rate of dilution by microturbulens to

support such an analysis. Since the ultimate aim of this study is to develop a low-cost low-power system specifically designed to study subglacial CH4 emissions, we feel more comfortable with proceeding the data smoothing as presented, and thereby avoiding the risk of over-analyzing a dataset with respect to parameters which are uncontrolled.

“Line 284: “very close”; please quantify this statement.”

➔ Reply 9: See revised sentence under reply 24.

“Lines 295-297: Please tone down this statement. Your study evaluates a low-cost sensor for the measurement of CH4 in a hostile environment with the potential to lead to a better understanding and quantification of CH4 emissions from GrIS and similar locations.”

➔ Reply 10: OK. The sentence has been removed in the revised MS.

“Technical comments

Line 57: “: : : and in sensor network grids.” This might require clarification.”

➔ Reply 11: text has been changed to “…sensor networks.”

“Line 57: change “we have in situ tested: : :” to “we have tested in situ: : :”.”

➔ Reply 12: Corrected.

“Line 67: “: : :southern flank: : :” of what?. Terminus does not seem to be the right term.”

➔ Reply 13: “… *at the terminus*…” has been removed in the revised MS.

“Line 74-75: this sentence is clumsy and needs re-structuring. Suggestion “Humidity and temperature of the subglacial air were measured every 10 s using a combined sensor (: : :) mounted at the tip of the aluminium pole inserted into the cave. The data were recorded using: : :””

➔ Reply 14: Good suggestion. Text has been replaced as suggested.

“Section 2.2: could you specify whether the MOS setup was built by your lab?”

➔ Reply 15: The following has been added: “The final prototype was assembled in the laboratory at Aarhus University.”

“Line 99: “electrical circuit converts” not convert.”

➔ Reply 16: Corrected.

“Line 100: “were powered” not was.”

➔ Reply 17: Corrected.

“Line 127: “are inversely” not is.”

➔ Reply 18: Corrected.

“Lines 132-136: long sentence, difficult to read. Split into 2 parts.”

➔ Reply 19: Sentence now reads: “Access to a controlled and humidified zero gas was not available in the field. Instead the atmospheric background concentration of CH_4 of the air (approximately 1.9 ppm) close to the ice sheet was used to calculate the average ambient sensor resistance (R_{0*}) using Eq. 1. The output value of the MOS under these conditions was then used to establish the resistance ratio (R_S/R_{0*}) vs. CH_4 concentration field calibration function for the MOS (Fig. 6).”

“Line 168: “which has been reported to scale linearly: : :”?”

➔ Reply 20: Sorry, incomplete sentence. The revised wording is:

The reason for this difference is unknown, but a possible explanation could be the potential difference in input heater voltage for the MOS sensor (i.e. pin 1 and 4 in Fig. 1), since variations in the input heater voltage have been reported to affect the CH_4 concentration measurements (van den Bossche et al., 2017).

“Line 177: “at the margin of the: : :” not if.”

➔ Reply 21: Corrected.

“Line 211: “Measurements: : : show: : :” not shows.”

➔ Reply 22: Corrected.

“Line 268: “: : : while being undetected: : :””

➔ Reply 23: Corrected.

“Line 284: “departs” means leaves. Use a more appropriate verb.”

➔ Reply 24: The sentence has been reformulated: “$CRDS_{smooth}$ data for period 2 fills the data gap between the MOS measurement of period 1 and 3, where the start concentration data of the MOS_{smooth} concentration data are similar to the concentration level where the $CRDS_{smooth}$ measurements end

“Line 313: “: : : which could significantly improve: : :””

➔ Reply 25: Corrected.

“Lines 314-317: this sentence is too long. Please divide it into two.”

➔ Reply 26: Corrected.

“Line 325: Remove “very clean” unless you can substantiate its meaning.”

➔ Reply 27: Corrected.

“Fig. 7: please indicate the temporal resolution of each plot.”

➔ Reply 28: Temporal resolution is 10 seconds. Info has been added to the figure caption.

“Fig. 8: as in Fig. 7, what is the time step?”

➔ Reply 29: Temporal resolution is 10 seconds. Info has been added to the figure caption.

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

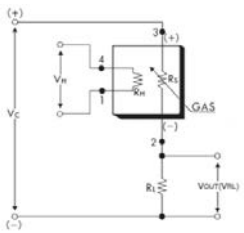
➔ Reply 31: This could be an area prone to confusion, and we agree to resolved this in the revised manuscript by including both the mean bias error (MBE), mean absolute error (MAE) and root mean square error (RMSE) in table 1, and replace the MBE in the abstract with the RMSE value.

"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 (V_{RL}) 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 (V_{RL}) according to the following formula:

Sensor resistance (Rs) is calculated with a measured value of V_{OUT}(V_{RL}) by using the following formula:

$$R_S = \left(\frac{V_C}{V_{RL}} - 1\right) \times R_L$$



As the reviewer correctly points out, the output voltage (V_{RL}) increased with increasing CH4 concentration. In our setup, we used a load resistor of 10 kOhm and a circuit voltage (V_C) 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: R_0 is equal to the sensor resistance R_s under the defined zero gas conditions, to which all other measurements are normalized to (i.e. to calculate the R_s/R_0 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 (R^2 = 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/m^3 (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."

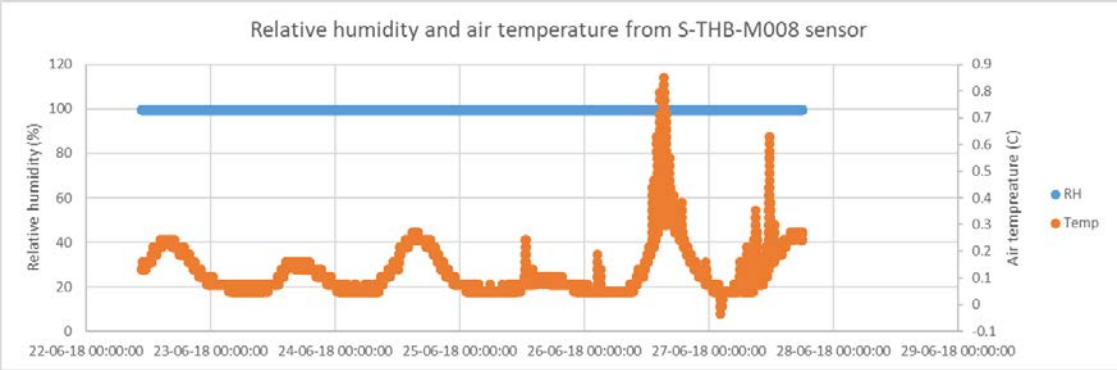
➔ Reply 42: Please see reply 36 for the issue of data fit (Figure 6) and reply 44 for precision issue. In short, our results are in line with the finding of also https://doi.org/10.5194/amt-2019-402, where the

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 CH_4 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.



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 °C during the night and 0.25 °C during mid-day (Fig. 7d)."

"Anonymous Referee #3

Received and published: 30 March 2020

In this paper, the authors studied the performance of a low-cost and low-power methane (CH4) sensing system prototype based on a metal oxide sensor (MOS) sensitive to CH4. The sensor was tested in a natural CH4 emitting environment at the Greenland Ice sheet (GrIS). The primary scientific importance of the study is that it provides a clear example on how the application of low cost technology can enhance our future understanding on the climatic feedbacks from the cryosphere to the atmosphere. The present study fits within the aim of this journal and the results are promising and interesting for future applications of low cost sensors.

The reviewer think that the paper can be published for open discussion and a main lack has been observed: - Low costs sensors from past studies show a 'drift' of the sensors response over the time. The authors do not cite this problem and neither they have tested it because a short experiment has been performed. This should be underline and future studies should include long term comparison between reference instrument and low cost sensor kit. The correction for the drift of the sensor will increase the final uncertainty related to the measurement and will also increase the cost of the field campaign because of the need of in situ continuous calibrations. The reviewer suggests to perform a study on the sensor drift over the months."

➔ Reply 44: We agree with #R3 that sensor drift may be an issue which potentially can limit the long-term applicability for the specific sensor, and that this issue should be addressed in our future research.

Another study has been published for discussion in AMT during the time period where our manuscript has been in review, namely [https://doi.org/10.5194/amt-2019-402] "*Long-term reliability of the Figaro TGS 2600 solid-state methane sensor under low Arctic conditions at Toolik lake, Alaska*" by Eugster et al., 2019. In this study, the authors evaluated the long-term stability of a similar CH_4 sensitive metal oxide sensor and conclude the following:

- Quotations from the abstract of amt-2019-402*:*

"At weekly resolution the two sensors showed a downward drift of signal voltages indicating that after 10–13 years a TGS 2600 may have reached its end of life…."

"Weekly median diel cycles tend to agree surprisingly well between the TGS 2600 and reference measurements during the snow-free season, but in winter the agreement is lower."

"We 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 CH_4 is of no concern."

- Quotation from amt-2019-402, ll. 208-210:

"They [TGS 2600 sensors] provide encouraging results suggesting that with occasional (infrequent) calibration against a high-quality standard, e.g. using a traveling standard operating during a few good days with adequate coverage of the near-surface diel cycle of CH_4, TGS 2600 measurements might be suitable for the monitoring of CH_4 concentrations also in other areas."

We have added this reference to the manuscript in section 3.5, where the issue of potential drift is discussed.