Dear Dr Ji-Hyung Park,

Many thanks for all work with our manuscript bg-2019-499, entitled Technical note: Facilitating the use of low-cost methane (CH$_4$) sensors in flux chambers – calibration, data processing, and an open source make-it-yourself logger

We are very grateful to all involved, including the three reviewers, for the very supportive comments that substantially improved the manuscript. Please find below point-by-point comments to all review comments.

With regards to the specific Editorial report comments, we have, as requested by Reviewer #1, added real data from flux chamber measurements on a lake as a figure in the Supplement. Regarding optimum calibration procedures, addressed by Reviewer #3, we added text to clarify that advanced optimum calibration under strictly controlled standardized conditions, which of course is better for sensor comparisons and some applications, were not the aim in this study because we wanted to provide good-enough calibration solutions for the widest possible range of users, most of which does not have access to laboratories where well defined standard calibration conditions can be created. This is key for cost efficiency as the sensors require individual and repeated calibrations over their lifetime.

As requested we uploaded our manuscript and Supplement files file with changes marked (form MS Word Track Changes converted to pdf). We also have a files without track changes ready to send if desired as we could not find space for submitting two manuscript files in the web form. All the line numbers provided in our response below refer to the submitted files with track changes.

We are happy to respond to any emerging questions and again thank you and others involved for all the work with our manuscript.

Best regards,
David Bastviken

Response to comments by Referee #1

Referee comments are provided in grey and author responses in blue italic style text.

In this paper Bastviken and colleagues present details on a low cost sensor for measuring CH4 fluxes in chambers. They also describe a low-cost open source logger. There is a growing interest in development and use of low cost sensors for measuring key biogeochemical processes, and this paper describes a useful new sensor to add to the growing list. The paper is focused on calibration and data processing using this new sensor setup.

One thing that I would have liked to have seen was some real word data using the system - that is a demonstration of field based flux measurements. It is under field conditions where the utility of the sensor needs to be proved. In saying this, I think the paper as it stands is publishable and will make a useful contribution to the scientific literature. The detailed calibration experiments will be extremely useful for the community working on developing similar systems. look forward to seeing "real-world" data collected by the sensor system in the future.

*We thank Referee #1 for all work and are glad that our work is considered valuable and important. We have provided examples of real field based measurements in the revised Supplement (Fig S4).*
Response to comments by Referee #2

The technical note describes comprehensive laboratory tests of a low-cost methane sensor for potential application in flux chamber measurements in aquatic systems. The results are of high relevance for enhancing the spatial and temporal resolution of methane flux measurements and for improving our understanding of their environmental controls. The results and conclusion are comprehensible and well backed-up by data. Moreover, the note provides detailed instructions and procedures for implementing and calibrating such sensor in future applications. It is generally well written and presented. I have a few detailed, minor suggestions for improving the clarity of the note, which are listed below:

We thank Referee #2 for all work and are glad that the manuscript is found relevant and of value in several ways. The detailed comments are addressed below.

- the authors generally refer to “methane levels”, which are reported in ppm. I suggest to clarify at some point what exactly is meant by this – mol fraction, mixing ratio?

We have tried to clarify this in the revised manuscript. In many cases, mol fraction replaced levels when the text was about CH4 in ppm units (many lines throughout the whole text). Levels were kept for text about multiple variables or when discussing relative changes rather than absolute mol fraction numbers.

- similarly, the authors state that the tested sensor is measuring “methane concentration”, however, all results are reported in ppm. Could it be that the sensor responds to the abundance of CH4 molecules, rather than the mixing ratio (as it has been found for humidity in the present manuscript)? The difference between a concentration (as mols or mass per volume) and mol fraction is the temperature and pressure dependence (as it could be described by the ideal gas law).

Referee #2 is correct that the sensors respond to the abundance of the molecules interacting with the sensor surface which is proportional to the mol fraction. The conversion from mol fraction to concentration (mol or mass per volume) via the ideal gas law correct for some of the temperature and pressure effects. On top of this, there can be extra temperature effects on sensor responses if the temperature influence the electronic component performance or the sensor surface characteristics. In this case water vapor also interact with the sensor surface, which explains the need for extra measures to correct for humidity. We have tried to clarify these aspects on row 101 and 227-229.

- the range of relative humidity used in the experiments was 18-70%. Depending on deployment time, humidity in a flux chamber can become much higher than this. Could you add a remark on sensor performance at higher humidity?

The highest absolute humidity reached in our experiments were in the order of 35 000 ppm H2O. This corresponds to approximately 100% humidity at 26 °C which is valid for many conditions. Unfortunately we do not dare to make any statements regarding sensor performance outside our test range, so there will be a need for tests at higher humidity in the future, in e.g. tropical conditions. The highest absolute humidity covered have been clarified in the revised manuscript (lines 86-88).
- the proposed Arduino-based logger includes a humidity/temperature sensor in addition to the CO2 sensor, which already includes sensors for both parameters. What is the reason for adding this additional sensor? Does it have higher accuracy?

We added this extra RH/T sensor just to have a backup to the RH and T sensors at the CO2 sensor. This was done because the CH4 sensor data evaluation (in contrast to the CO2 sensor data) is completely dependent on reliable RH and T information to calculate absolute humidity. We now explain this in the revised supplementary material (section on Hardware setup).

- line 195: “However, results indicate that the relative change of CH4 levels over time, which is the core of flux chamber measurements, can be assessed efficiently with the sensors if calibrated properly.” I do not see how this conclusion can be made is this point. Consider adding a justification.

We agree that this sentence needs clarification. The justification is based on data in Table 2 where the SE and R2 for the slope versus the SE for the intercept of the calibration equations indicated that the relative change in sensor response to increasing CH4 mol fraction was rather consistent and accurate (more accurate than the absolute mol fraction derived). We have clarified this (lines 201-205).

- An important conclusion of the study was that “Sensor-specific calibration is required”. Could you add some information about the stability of the calibration obtained for a specific sensor over extended time periods? What calibration intervals would you suggest?

This is a very important question. We do not yet have data from long-term studies to present, but other studies have addressed this. van den Bossche et al., (2017; cited in manuscript) found no drift over 31 days. Eugster et al (2019) studied results from a very similar type of sensor used for outdoor measurements over 7 years and concluded that the drift was in the order of 4–6 ppb/yr and the variability drifted by –0.24%/yr. We have added this information in the revised study (lines 239-244).

Reference:

- Table 1: the symbol n is used as a coefficient in equation V1 and also for number of samples. I suggest to use separate symbols. The parameter h (listed in the caption) seems not to be used in the table.

Thanks for such detailed reading! We have changed to “N” for number of samples. “h” is used once in Model V2 in Table 1.

Response to comments by Referee #3

Referee comments are provided in grey and author responses in blue italic style text.

The authors are to be commended for working toward affordable instrumentation for trace gas measurement. In addition, information provided for construction of a lowcost datalogger can be useful for other environmental measurements as well. The authors take a primarily empirical approach to the problem of extending the range of usability of a commercial sensor. The goal is to be able to measure low levels that would be of interest in natural ecosystems. Toward this goal they describe a variety of curve-fitting calibrations.
It seems possible that many readers will find the most value in knowing how best to apply these sensors, and what ultimate performance can be achieved. This reviewer suggests that revisions focus mostly on optimum calibration procedures and the performance metrics that can be so obtained. The following are some specific comments addressing individual statements in the manuscript.

We thank Referee #3 for all work and are glad that the efforts towards affordable trace gas instrumentation are seen as valuable. We have tried to highlight and clarify our approach further, including that we focused on flux chamber use of these sensors and that this use have different calibration requirements than e.g. use in open air to follow atmospheric mol fractions (lines 225-237). In the flux chamber applications, accurate determination of relative changes in gas mol fractions is more important than accuracy in determining absolute mol fraction values. Because of the flux chamber focus, we also calibrated the sensors when positioned in a flux chamber, i.e. at field-like conditions, and we tried to evaluate also simplified calibration procedures as a way to present different acceptable solutions being optimal for field-conditions and various access to laboratory analyses. We are well aware that this is not optimal from the absolute “maximum accuracy and precision” perspective, where it would be desirable to keep a stricter environmental control during calibration. Hence, we need to clarify that we, as also noted by Referee 3, have a more empirical and field-use oriented approach with the aim to facilitate reliable flux chamber measurements by as many sensor users as possible (which is different from assessing the maximum performance of the sensor under stable lab conditions).

Line 59 typo (is are)

Fixed.

L 63 It would be helpful to know what mixing ratios were successfully measured

The mixing ratios of the mentioned reference have been added to the text.

L 77 why were 10 RH sensors used? Was this to provide some averaging?

We had 10 sensors measuring CO2, T and RH in the same chamber as the CH4 sensors to also evaluate our sensor network solution for the CO2/T/RH sensors (separate study). Because we could not link values from any specific CO2/T/RH sensor to each specific CH4 sensors (they all shared the same chamber volume) we decided to just average their values and use this average in the evaluation of the CH4 sensors. We have clarified this in the revised manuscript (lines 78-79 and 88-90).

L 84 How does measured RH compare with the vapor pressure of water at the given temps?

We used absolute humidity in the unit of ppm water vapor, corresponding to vapor pressure in µatm. The study covered a humidity range from 9000 to 35 000 ppm water vapor. At temperatures below 20 ºC the RH was usually 50 - 70 %, while at temperatures > 20 ºC, RH ranged from 18 to 60 % (clarified on lines 86-88). Our result indicates that the absolute humidity was the most important factor, followed by temperature, and therefore we think the absolute ranges in these variables matters more than the RH values for the sensor tests.

L 89 typo (form), superfluous 'before'

Fixed.

L 92 some further discussion of time response is called for, especially if some data points are to be removed from the analysis on the basis of delayed responses
Gas concentrations in the chamber with the sensors were impacting the sensors immediately and recorded at their respective logging frequency. It took some time for this gas to pass of the tubing and flush the measurements cell in the reference instrument. Hence, the reference instrument responded with some delay. When the concentrations were relatively stable or changed at slow constant rates this could be corrected for by considering the time offset. However, when concentrations in the sensor chamber changed rapidly relative to the time off-set, e.g. right after CH4 was added to the chamber or when the chamber was ventilated to reduce gas concentrations, it was not possible to correct for the time off-set. The reference instrument measurement cell was simply large enough to be influenced by CH4 from the chamber over a certain time period (the measurement cell residence time), and if the concentration change in the chamber is more rapid, the data from the reference instrument and sensors become incomparable and need to be omitted to not bias the calibration. We have now tried to clarify this further (line 93-96).

L 92 typo (therefor)

Fixed.

L 108 it is unclear why knowing RL is considered challenging, as 1% resistors are routinely available at low cost.

Referee #3 is correct that most of the variability between sensors are likely to regard the active sensor surface characteristics and that variability regarding RL is less likely. We just did not want to exclude this possibility, but given this comment, we have removed RL from this sentence.

L 123 this reviewer is not in a good position to assess the calibration approaches in detail, as they are mainly empirical and specific to these particular sensors (which this reviewer has not personally used)

Noted. Many thanks for good and important comments overall.

L 168 a few more details of the datalogger would be of interest to readers here. What is input voltage range and resolution (e.g. number of significant bits?). What other parameters would someone wanting to use this device in the field want to know? (see also below)

The Arduino based datalogger has an input voltage range of 7-12 V and a resolution of 10 bits. This has been added to the text (line 177).

There is good documentation regarding logger board specifications on internet (e.g. https://store.arduino.cc/arduino-uno-rev3 and https://learn.adafruit.com/adafruit-data-logger-shield, which has been added to the supplement.

L 176 typo (influence)

Checked but could not find the error.

L 180 self heating is a very interesting issue. How much power is dissipated at the sensor surface, and would it be expected to produce heating that is significant relative to the uncertainty with which sensor temperature is constrained/influenced by environmental conditions?

The heating power consumption of the CH4 sensor is approximately 280 mW. This was not enough to notably change the temperature relative to other factors in the flux chambers tested so far. Not even
under the experimental conditions when we had 20 sensors in a chamber with 7 L gas volume did we see any considerable heating effects.

We added brief information about this (lines 186-187)

L 220 It would be most helpful if the conclusions stated here were expressed more quantitatively, expressed perhaps in terms of accuracy, reproducibility, and long-term stability.

We considered this carefully and in principle agree. However, given that several different calibration models gave acceptable results and may be optimal for different conditions and different users, we would have to repeat rather large amounts of information to provide this information properly. In turn, this would lead to a rather long conclusions section. To try to resolve this situation we refer readers to Table 2 for quantitative information regarding different calibration strategies.

For long-term stability, we have added such information to the manuscript (lines 239-244). Please see the response to the last comment below.

L 234 Good that code is provided for the datalogger!

Thanks.

Supplement
The datalogger may be of interest to many who plan on building their own field instrumentation. A more detailed circuit diagram, perhaps accompanied by a clear and more explicit image of the physical setup, would be helpful to those not experienced with Arduino.

We tried to provide a clear wiring diagram and illustrative images. We realize that the varnish on the CO2 sensor used for moisture protection makes it hard to see all details, but we in the revision tried to improve the visual descriptions of the system by enlarging all images and also provide a link to the CO2 sensor producer web page where very detailed information about the sensor board and connection points can be found.

Fig S1 shows responses over ranges of several hundred ppm. It is suggested to also present data on an expanded scale at the lower end of the usable range.

A similar figure covering the lower end of the range have been added to the revised supplement (new Figure S2).

Fig. S2 what are the units associated with RMSE in this figure. It gives the impression that acceptable results can not be obtained without using 8 or 9 reference samples.

The RMSE units are ppm, which is now clarified in the revised manuscript (Table 2). The impression of Referee #3 is correct. A minimum of 8-9 reference samples are needed for acceptable results. In the text we choose to highlight that 20 reference samples would be preferable to reach even lower RMSE levels, but we have relaxed this conclusion to 10 - 20 reference samples given Fig. S2 as suggested by Reviewer #3.

General: what are the authors’ observations with regard to aging and long-term stability of these sensors?

We could not observe any tendencies of ageing during our studies so far, but we have added information about this based on other studies. van den Bossche et al., (2017; cited in manuscript)
found no drift over 31 days. Eugster et al (2019) studied results from a very similar type of sensor used for outdoor measurements over 7 years and concluded that the drift was in the order of 4–6 ppb/yr and the variability drifted by –0.24%/yr. We have added this information in the revised study to address the drift question (lines 239-244).

Reference:
Technical note: Facilitating the use of low-cost methane (CH$_4$) sensors in flux chambers – calibration, data processing, and an open source make-it-yourself logger

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Abstract. A major bottleneck regarding the efforts to better quantify greenhouse gas fluxes, map sources and sinks, and understand flux regulation, is the shortage of low-cost and accurate-enough measurement methods. The studies of methane (CH$_4$) – a long-lived greenhouse gas increasing rapidly but irregularly in the atmosphere for unclear reasons, and with poorly understood source-sink attribution – suffer from such method limitations. This study present new calibration and data processing approaches for use of a low-cost CH$_4$ sensor in flux chambers. Results show that the change in relative CH$_4$ levels can be determined at rather high accuracy in the 2 – 700 ppm mol fraction range, with modest efforts of collecting reference samples in situ, and without continuous access to expensive reference instruments. These results open for more affordable and time-effective measurements of CH$_4$ in flux chambers. To facilitate such measurements, we also provide a description for building and using an Arduino logger for CH$_4$, carbon dioxide (CO$_2$), relative humidity, and temperature.

1 Introduction

Methane (CH$_4$) is the second most important of the long-lived greenhouse gases (GHGs). Its global 100-year warming potential per mass (GWP$_{100}$) is 28-34 times greater than the GWP$_{100}$ for carbon dioxide (CO$_2$), and its relative increase in the atmosphere since 1750 have been much greater than for other GHGs (e.g., Myhre et al., 2013). The atmospheric CH$_4$ originate from multiple sources including incomplete combustion, natural or biogas gas handling, or microbial CH$_4$ production in agriculture, ruminant digestive tracts, and other anaerobic environments such as wetlands and lakes – the microbial CH$_4$ accounting for approximately two thirds of the total emissions (Saunois et al., 2016). The high diversity of sources, many yielding fluxes that have high spatio-temporal variability, makes it difficult to quantify fluxes and understand flux regulation without a large number of local measurements. At the same time, common methods to measure fluxes rely on expensive equipment or labour-demanding procedures. Consequently, the CH$_4$ flux from various sources are poorly constrained. This is exemplified by the discovery of inland waters and flooded forests as two large global CH$_4$ sources during the last decade (Bastviken et al., 2011; Pangala et al., 2017). Greater availability of measurement approaches that are inexpensive enough to allow many measurements and assessment of both spatial and temporal variability simultaneously, would greatly improve our ability to assess landscape CH$_4$ fluxes and flux regulation.
There is extensive work to develop sensitive, small, and affordable CH$_4$ sensors, but so far the commercially available low-cost CH$_4$ sensors were typically developed for explosion warning systems and thereby for high concentrations (mol fractions at percent levels). CH$_4$ detection at such levels is of high interest for environmental research, including the measurements of CH$_4$ ebullition, and for such applications cost-efficient sensor applications have been presented (e.g. Maher et al., 2019). For measurements of other types of CH$_4$ fluxes, sensors with robust and reliable detection at lower levels (mol fractions in the ppm range) are needed. Previous attempts to use and calibrate such sensors at ppm levels have been promising (Eugster and Kling, 2012), but also reported remaining challenges, and the use of these sensors in environmental research or monitoring has not yet become widespread. The direct monitoring of atmospheric CH$_4$ mol fractions to resolve fluxes, demanding fast and accurate detection of changes in the order of 10ppb, still represents a challenge for low-cost sensors. However, relevant mol fraction ranges for flux chamber studies (2 – ~1000 ppm depending on environment, chamber type, and deployment times) appear within reach.

One commercially available low-cost sensor type, showing promising performance in previous studies, are represented by the TGS 2600 tin dioxide (SnO$_2$) semiconductor sensor family made by Figaro. This type of sensors has been evaluated multiple times at CH$_4$ mol fractions near ambient background air (from 1.8 to 9 ppm; different ranges in different studies; (Eugster and Kling, 2012; Casey et al., 2019; Collier-Oxandale et al., 2018; van den Bossche et al., 2017). Given their low cost, they performed surprisingly well under non-sulphidic conditions (H$_2$S may interfere with the sensors), although it was challenging to generate calibration models with R$^2$ > 0.8, and the reported interferences from e.g. relative humidity (RH) and temperature (T) were large (van den Bossche et al., 2017). We here evaluate one member of this sensor family for a larger CH$_4$ range (2-719 ppm), selected to be appropriate for use in automated and manual flux chambers. We propose further development of the equations suggested by the manufacturer for data processing, and provide guidance on how to address the sensor response to humidity ($H$), $RH$ and $T$ in flux chamber applications. We also describe a simple CH$_4$/CO$_2$/RH/T logger based on the evaluated sensors, an Arduino microcontroller, and a corresponding logger shield.

2 Methods

2.1 The CH$_4$ sensor

The sensor used in this study is the Figaro NGM 2611-E13, which is a factory pre-calibrated module based on the Figaro TGS 2611-E00. The factory calibration is made at 5000 ppm, 20 °C and 65% RH. The CH$_4$ mol fraction in the factory calibration is not relevant for applications near atmospheric concentration, but the NGM 2611-E13 is compact and ready-to-use, facilitating its integration with data loggers and equipment for flux measurements (e.g. automated flux chambers; (Duc et al., 2013; Thanh Duc et al., 2019). The detection range given by the manufacturer is 500-10000 ppm, but the sensor has been used successfully for measuring indoor ambient concentrations of methane (2-9 ppm) (van den Bossche et al., 2017). The potential
of another similar sensor, the Figaro TGS 2600, for atmospheric concentration monitoring have been investigated (Eugster and Kling, 2012; Collier-Oxandale et al., 2018, Eugster et al., 2020). The main difference of the TGS 2611-E00, compared to the TGS 2600, is the presence of a filter that reduce the interference of other combustible gases with the sensor, making it more selective towards CH$_4$ (Figaro_TGS_2611-E00, REV: 10/13). The TGS 2611-E00 is also more than 10 times cheaper than the sensor used in (Duc et al., 2013) and its detection range is wider, allowing for reliable measurements of concentration above 1000 ppm, which makes the sensor potentially useful in both low- and high-emitting environments.

2.2 Calibration setup

The sensor evaluation set-up was designed to resemble real measurement conditions in floating flux chambers in aquatic environments. The sensors were placed in the headspace of a plastic bucket positioned upside down on a water surface in a tank. We used a 7L plastic bucket in which we located 20 TGS 2611-E13 sensors connected to electronic circuitry and sensor signal logging system described in detail separately (Thanh Duc et al., 2019). The chamber headspace was continuously pumped from the chamber, through the measurement cell of an Ultraportable Greenhouse Gas Analyzer (UGGA; Los Gatos Research), and then back to the chamber. The UGGA served as a reference instrument for CH$_4$. The air $T$ and RH inside the chamber were measured with ten K33-ELG CO$_2$ sensors (Senseair), which have an accuracy of ± 0.4°C and ± 3% RH (Bastviken et al., 2015). The large number of K33-ELG sensors was due to a separate test of wireless data transfer (outside the scope of this work) and one K33-ELG sensor would have been enough for this CH$_4$ sensor study. The entire installation was placed in a climate room to allow for varying $T$, and thereby also absolute humidity ($H$) in the chamber headspace. $T$ and $H$ co-vary under field conditions in measurements near moist surfaces, so although $T$ and $H$ were not controlled independently, their variability under this calibration setup was reflecting flux chamber headspace conditions under in situ field conditions.

The CH$_4$ concentration in the chamber was changed by direct injections of methane into the chamber by syringe via a tube. The CH$_4$ concentrations during the calibration experiments ranged from 2 ppm to 719 ppm. We performed multiple separate calibration experiments at different $T$ and RH levels ranging from 10 to 42 ºC and 18 – 70 %. At temperatures below 20 ºC the RH was usually 50 - 70 %, while at temperatures > 20 ºC, RH ranged from 18 to 60 %. The highest absolute water vapour mol fraction was 35 000 ppm H$_2$O. Values were recorded once per minute. $T$ and RH values form the K33-ELG sensors were averaged among all sensors (because all sensors were in the same chamber and we could not link specific K33-ELG sensors to specific CH$_4$ sensors).

The response time to changing chamber headspace CH$_4$ levels differed between the sensors situated in the chamber (responding rapidly), and the UGGA (delayed response time due to the residence time of the measurement cell and tubing). The reference instrument measurement cell was large enough to be influenced by CH$_4$ from the chamber over a certain time period (the measurement cell residence time), and if the concentration change in the chamber was more rapid, the data from the reference instrument and sensors become incomparable and need to be omitted to not bias the calibration. Therefore data were filtered
to remove periods of rapid changes when the different response times caused data offsets. Some sensor data were lost during parts of the experiments due to power, connection failure, or data communication issues. Altogether on an average, after data filtration, 619 – 930 data points from each sensor and the UGGA, respectively, were used for the evaluation (in total 20 CH₄ sensors evaluated).

### 2.2 Data processing and interpretation

The TGS 2611 SnO₂ sensing area responds to interaction with target gas molecules by exhibiting decreasing resistance (Figaro_Tech_Info_TGS2611, 2012). The sensing area is connected in series with a reference resistor (resistance referred to as Rₗ). The total circuit voltage (Vₖ) is 5V across both the sensing area and the reference resistor. The voltage across the reference resistor (Vₗ) therefore varies in response to how the sensing area resistance (Rₛ) varies. Vₗ is measured and reported as output voltage. The sensor response Rₛ is calculated from the following equation (Figaro_Tech_Info_TGS2611, 2012;Figaro_TGS_2611-E00, REV: 10/13):

\[ Rₛ = \left( \frac{Vₖ}{Vₗ} - 1 \right) \times Rₗ \]  

(1)

The active sensor surface characteristics and Rₗ can differ among individual sensors, which makes individual sensor calibration necessary. Interference by water vapour and T has been previously shown (Pavelko, 2012;van den Bossche et al., 2017). Rₗ is therefore ideally determined in dry air containing no volatile organic compounds or other reduced gases at a standard T. However, it can be challenging to achieve such conditions and determine Rₗ, and Eugster and Kling (Eugster and Kling, 2012) proposed to use the lowest measured sensor output voltage (Vₒ), representing minimum background atmospheric levels, to determine an empirical reference resistance Rₒ, and to calculate the ratio of Rₛ/Rₒ, reflecting the relative sensor response as follows:

\[ \frac{Rₛ}{Rₒ} = \frac{\left( \frac{Vₖ}{Vₗ} - 1 \right)}{\left( \frac{Vₖ}{Vₒ} - 1 \right)} \]  

(2)

This approach allows sensor use without accurate specific determination of Rₗ. Previous attempts to calibrate these type of sensors for environmentally relevant applications have focused on CH₄ mol fractions of 2-9 ppm, and typically considered the influence of T and RH or H (Casey et al., 2019;van den Bossche et al., 2017;Collier-Oxandale et al., 2018;Eugster and Kling, 2012). In these cases, an approximately linear response of the relative sensor response could be assumed due to the narrow CH₄ range. However, the sensor response is non-linear in the range relevant for flux chamber measurements and in this wider range, other approaches are needed. We here present a two-step sensor calibration based on the complete calibration experiment
data. In addition, we tried simplified calibration approaches for situations when full calibration experiments are not feasible and when access to reference instruments is limited. These approaches are described below.

### 2.2.1 Two-step calibration from complete experimental data (Approach I)

The first step (Step1) regards determination of the reference sensor resistance, \( R_0 \). We assumed that \( R_0 \) represented \( R_L + R_{Sbg} \), where \( R_{Sbg} \) is \( R_S \) at the background atmospheric CH\(_4\) level. We first tried the previously suggested approach to determine \( R_0 \) from the minimum \( V_L \), i.e. setting \( V_0 \) to \( V_L \) at the lowest humidity and CH\(_4\) concentrations during all measurements, thereby assuming that \( R_0 \) could be seen as constant. However, \( R_{Sbg} \) may be influenced by \( H \) and \( T \) and could vary even if the CH\(_4\) levels at background atmospheric conditions are constant. Thus, we also tested ways to correct \( R_0 \) to \( RH \) or \( H \) and \( T \). Therefore, after selecting the experiment data at background CH\(_4\) levels but variable humidity and temperature, we tested linear, power, or Michaelis-Menten models, to generate \( V_0 \) values valid for different humidity and temperatures. This allowed estimation of \( R_0 \) values at the humidity and temperature associated with each \( R_S \) value, making the \( R_S/R_0 \) ratio less biased. The background level CH\(_4\) data was selected in two different ways – either as all known CH\(_4\) mol fractions below 2.5 ppm (n = 38-72), or as the minimum \( V_L \) value for each experiment and sensor (n = 6-7).

The second step (Step 2) regards calculation of CH\(_4\) mol fractions from \( R_S/R_0 \). Several models were tested, where the CH\(_4\) mol fraction were estimated as a function of \( R_S/R_0 \), \( H \), \( T \), and a constant to consider offsets that may differ among sensors. We tried several linear and power functions. In line with viewing the sensor surface as an active site where CH\(_4\) and H\(_2\)O compete for space, the \( H \) effect was in some models represented as an interaction with the sensor response.

In all above cases, models were generated by curve-fitting in Python using the scipy.optimize curve_fit function. Predicted CH\(_4\) mol fractions were evaluated by comparison with mol fractions independently measured by the UGGA. The specific model equations are provided in Table 1 and 2. We tested models using \( RH \) or \( H \) (which was calculated from \( RH \) and \( T \); (Vaisala_Technical_Report, 2013). Each evaluation included a combination of both steps above, and generated one set of fitted parameters per sensor used, including the parameters for Step 1 and 2.

### 2.2.2 Simplified calibration approaches without dedicated calibration experiment data (Approach II and III)

The model combinations from Step 1 and 2 above that generated the best fit with the minimum number of parameters was selected for tests of two simplified calibration approaches. In Approach II we tested if model parameters in Step 2 can be predicted from parameters derived in Step 1, hypothesising that the derived model parameters in both Step 1 and Step 2 reflect the sensor capacity to respond to CH\(_4\) and humidity levels as well as the individual sensor offset. If correct, the parameters in Step 1 should be correlated with parameters in Step 2. If this correlation is strong enough, it may be possible to predict parameters in Step 2 from parameters in Step 1, which can be derived from measurements at background air concentrations under the natural variation in humidity (e.g. the diel variability), as a part of the regular measurements, preferentially using data when the atmospheric boundary layer is well mixed (e.g. windy conditions). Under such conditions atmospheric
background CH₄ concentrations can be relatively accurately assumed. Hence this Approach II would not require access to sensor calibration chambers, nor expensive reference gas analysers, which in turn would make sensor measurements available much more broadly. To test this approach, we searched for the best possible regression equations to predict Step 2 parameters from Step 1 parameters, then used these equations to estimate CH₄ mol fractions, and compared this with the UGGA reference measurements.

In Approach III we evaluated if reasonable accurate Step 1 and 2 equations can be derived from the combination of (i) minimum background atmospheric level \( V_L \) at different humidity, and (ii) a limited number of randomly collected independent manual flux chamber samples. If so, a few manual samples during the regular measurements could replace tedious dedicated calibration experiments. To test this approach the calibration data for each sensor was subsampled randomly and this random subset data were combined with the minimum \( V_L \) data to derive calibration parameters as done in Approach I. Using these parameters, the CH₄ mol fractions for the entire calibration data was estimated and compared with observed values. Monte Carlo simulations were run to test effects of the number of random reference samples (1 – 50) and the methane concentration ranges (3 – 500 ppm, or 3-50 ppm, respectively) in the subset data.

### 2.2.3 A low-cost Arduino-based CH₄/CO₂/RH/T logger

To facilitate use of the sensors and our results, we also gathered instructions for how to build a logger for CH₄, CO₂, RH and \( T \) measurements, using the CH₄ sensor tested here, and the Senseair K33 ELG CO₂/RH/T sensor described elsewhere (Bastviken et al., 2015), a supplementary DHT22 sensor for RH and \( T \), an Arduino controller unit, and an Adafruit Arduino compatible logger shield with a real time clock (input voltage 7-12 V; 10 bit resolution; Figure 2). This development was based on sensor specifications and the open source knowledge generously shared on internet by the Arduino user community. The full description of this logger unit is found in the Supplement.

### 3 Results and Discussion

The results of different Step 1 and Step 2 calibration equations are shown in Tables 1 and 2. The models including \( H \) were equal or superior to models using \( RH \). This is reasonable because it is the absolute water molecule abundance that influence the sensor response. Hence, models using \( H \) were prioritized. In Approach I, several Step 1 models, including a constant minimum \( V_L \), and power, linear and Michaelis-Menten-based equations gave similar \( R^2 \) (0.85 to 0.9) and root mean square error (RMSE) when comparing predicted versus observed results (Table 1). The effect of \( T \) appeared negligible compared to \( H \), which may be related to the built-in heating of the active sensor surface (280 mW; this heating was focused on a small part of the sensor and no self-heating around sensors was detected). It is possible that the Michaelis-Menten equation is superior over the full theoretically possible \( H \) range. However, under our experiment conditions, covering normal field \( H \) levels, the
combination of best fit and minimum number of parameters in Step 1, was found for a simple linear equation with $H$ (Model V4 in Table 1), which was used for later tests of Approach II and III.

The tests of different equations in Approach I, Step 2, showed that power relationships with $H$ and $T$ represented as interactions with the sensor response, performed best (Table 2 Model $\geq 4$). With the exception of Models 10a-c, all these models had in the regression of observed versus predicted, a slope and intercept that was statistically indistinguishable from 1 and 0, respectively ($p < 0.05$) and an $R^2$ of 0.98 – 1.00 (Table 2, Figures S1 and S2). Again, $T$ had a marginal effect and $H$ was clearly most important. Hence, while Model 7 including $T$ in Table 2 had the lowest RMSE (9.8), Model 8 represented a good compromise between minimum number of parameters and low RMSE (10.4) and was used in Approach II and III. The non-linear response of the sensor yielded a stronger and more coherent response at low CH$_4$ levels, and a large part of the uncertainty were generated at the higher CH$_4$ levels in the studied range (Figures S1 and S2). Near the atmospheric background at 2 ppm, the confidence interval for individual sensor response was in the order of $\pm$ 1.1 ppm (Model 7 having lowest RMSE). Hence, the presented calibration equations have a limited accuracy in terms of absolute CH$_4$ mol fractions, and is not optimized for high-precision measurements at atmospheric background levels (as shown by SE for the model intercept corresponding to 0.16-1 ppm; Table 2). However, high $R^2$ and low SE for the slope of several models indicate that the relative change of CH$_4$ levels over time, which is the core of flux chamber measurements, can be assessed efficiently with the sensors if calibrated properly (Table 2).

Approach II, deriving all calibration equations from a small set of minimum $V_L$ values using Models V4 or V5 (Table 1) and 10a-c (Table 2), generated substantially greater RMSE. Most of this RMSE change was due to less accurate prediction of the intercept. The $R^2$ and slope standard error range remained similar to the other models (Table 2), but the actual slope values could deviate substantially from 1 and varied considerably among sensors (in contrast to the models for all other approaches always having slopes close to 1 and similar among sensors; Figures S1 and S2). Thereby, Approach II could lead to a large bias in absolute mol fractions, and this crude generation of calibration equations may be adequate primarily for assessing relative change over time measured by the same sensor, and cross comparisons among sensors should be avoided when using this approach. Examples of equations for the parameter estimation in Approach II is provided in Table S1. Applying Approach II on a smaller concentration range yielded a considerably lower RMSE (Table 2, Model 10c).

Approach III (Model 11a and 11b in Table 2) showed that as few as 10 – 20 reference samples, collected at random occasions during actual measurements, could substantially reduce the RMSE of the calibration models, reaching close to the lowest levels based on the 619 – 930 measurements and the full range up to 719 ppm in Approach I (Table 2 Model 11a; Figure S2S3). The concentrations of the reference samples did not appear important for the RMSE within a given specific data range. However, simulations using data for CH$_4$ levels mol fractions below 50 ppm only, generated much lower RMSE than using all data
This supports the conclusion that the sensors are more sensitive and give a stronger relative response in the low part of the studied concentration range.

An overview of approaches to derive calibration models for this type is shown in Table S21. The challenges found regarding monitoring of background atmospheric levels was confirmed by our study, while use for relative changes of greater magnitudes in flux chambers appear promising based on this study's results, also with a simplified calibration (Approach III). As a general note for all approaches when used under variable environmental conditions, best precision may be achieved by using absolute partial pressure units for both CH₄ and humidity, thereby compensating for variability in atmospheric pressure. In addition, for use above the maximum absolute humidity in this study, extra care is advised to check sensor capacity and behaviour. An example of real field data is provided in Figure S4. This example illustrates that the direct sensor response is heavily influenced by humidity and that the calibration equations shown in Table 1 and 2 is needed to reveal the CH₄ part of the sensor signal. Further, Figure S4 illustrates that sensors can be highly useful in very variable environments with rapid changes in humidity and when using data loggers with 10 bit resolution only. Optimal calibration procedures in stable environments and with higher logger resolution would likely indicate better sensor performance, while we deliberately focused on calibration procedures closely linked to field use with inexpensive equipment to provide information of relevance for as many conditions as possible.

Long-term stability of the sensors were not addressed here but is important for environmental use. Other studies of the same type of sensors show promising results. For example, van den Bossche et al. (2017) found no drift over 31 days. Eugster et al. (2020) using the similar Figaro TGS 2600 sensor for outdoor measurements over 7 years, concluded that the drift was in the order of 4–6 ppb/yr and the variability drifted by −0.24%/yr. This suggest that the sensors drift is modest even when exposed to variable weather over long time. However, it is possible that drift can be faster under some conditions and regular drift checks are therefore advised.

4 Conclusions

The main conclusions can be summarized by the following:

- The tested CH₄ sensors are suitable for use in flux chamber applications if there are simultaneous measurements of relative humidity and temperature (or humidity).
- Sensor-specific calibration is required.
- Occasional independent reference samples during regular measurements, is an alternative to designated calibration experiments. Background atmospheric levels in combination in the order of 10–20 in situ reference samples at other CH₄ levels, can yield rather accurate calibration models.
• For highest accuracy regarding absolute CH₄ concentrations, careful designated calibration experiments covering relevant environmental conditions are needed.

• These results, together with the increased accessibility of low-cost sensors and data logger systems (one example described in the Supplement), open supplementary paths toward improved capacity for greenhouse gas measurements in both nature and society.

5 Code and data availability

Python code for data evaluation and the calibration experiment data is available from the main author upon request. Please note that both the code and the data are specific for the experimental setup. The Python code needs modifications for use with other data, and the CH₄ sensor data cannot represent results from other sensors as sensor specific calibration is needed. The Arduino code for the CH₄/CO₂/RH/T logger described in the supplement is available at http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-162780.

6 Author contribution

DB and NTD designed and supervised the study. NTD designed and built the experimental setup, the sensor units and the data logging system. JN and NTD performed the calibration experiment. The analysis of the sensor data was led by DB with contributions from NTD, JS, and JN. DB and NTD developed the logger units presented in the supplementary material. RP helped to build and test logger units and drafted a user manual. DB wrote the first complete draft of the manuscript and led the manuscript development, with contributions from NTD, JS, RP, and JN.

7 Competing interests

There are no competing interests.

8 Acknowledgements

This work was funded by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 725546), and the Swedish Research Councils VR and FORMAS (grant no. 2016-04829 and 2018-01794, respectively). We thank Sivakiruthika Balathandayuthabani, Magnus Gålffalk, Balathandayuthabani Panneer Selvam, Gustav Pajala, David Rudberg, Henrique Oliveira Sawakuchi, Anna Sieczko, Jimmy Sjögren, and Ingrid Sundgren, for stimulating discussions regarding sensor use.
References


Table 1: Model results for Step 1 of sensor calibration - i.e. the correction of reference output voltage ($V_0$ in the unit mV) in background air to humidity and temperature. $V_{0\text{min}}$, $H$, and $T$, represent the minimum $V_0$ for each sensor (mV), absolute humidity (ppm), and temperature ($^\circ$C) during measurements in open air. The model parameters $g$, $h$, $S$, $m$ and $n$ are constants for each sensor derived by curve fitting. The model $R^2$ is the adjusted coefficient of determination (mean, minimum and maximum for the 20 sensors tested), and RMSE is then root mean square error. Equivalent models using relative humidity ($RH$; %) instead of $H$, returned lower $R^2$ and higher RMSE and are not shown.

These Step 1 models were combined with the Step 2 models as noted in Table 2. **N denotes number of values used.** See text for details.

<table>
<thead>
<tr>
<th>Model for $V_0$</th>
<th>Data</th>
<th>$N$</th>
<th>Observed vs. Predicted</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No.</strong></td>
<td><strong>Equation</strong></td>
<td><strong>Minimum $V_0$</strong></td>
<td><strong>$R^2$</strong></td>
<td><strong>RMSE</strong></td>
</tr>
<tr>
<td>V1</td>
<td>$V_{0\text{min}}$ (constant)</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V2</td>
<td>$V_0 = gH^h + mT^n + S$</td>
<td>All $&lt; 2.5$ ppm $CH_4$</td>
<td>38 - 72</td>
<td>0.85</td>
</tr>
<tr>
<td>V3</td>
<td>$V_0 = gH + mT + S$</td>
<td>All $&lt; 2.5$ ppm $CH_4$</td>
<td>38 - 72</td>
<td>0.88</td>
</tr>
<tr>
<td>V4a</td>
<td>$V_0 = gH + S$</td>
<td>All $&lt; 2.5$ ppm $CH_4$</td>
<td>38 - 72</td>
<td>0.88</td>
</tr>
<tr>
<td>V4b</td>
<td>$V_0 = gH + S$</td>
<td>Min $V_0$ for each exp.</td>
<td>6 - 7</td>
<td>0.90</td>
</tr>
<tr>
<td>V5a</td>
<td>$V_0 = gH/(S + H)$</td>
<td>All $&lt; 2.5$ ppm $CH_4$</td>
<td>38 - 72</td>
<td>0.88</td>
</tr>
<tr>
<td>V5b</td>
<td>$V_0 = gH/(S + H)$</td>
<td>Min $V_0$ for each exp.</td>
<td>6 - 7</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Table 2: Model results for Step 2 of the data evaluation, i.e. the determination of methane (CH₄) levels (mol fractions) (ppm) from the sensor response expressed as \( R \) (corresponding to \( R_s/R_0 \)) using different calibration models. \( (RH) \), \( H \), and \( T \) as defined in Table 1. The model parameters \( a, b, c, d, e, f \) and \( K \) are constants for each sensor derived by curve fitting. The models were evaluated via a linear regression of Observed versus Predicted CH₄ levels (mol fractions), where \( k \) and \( M \) are the slope and the intercept, respectively. SE denote standard error, \( R^2 \) the adjusted coefficient of determination (mean and minimum to maximum for the 20 sensors tested), and RMSE is the root mean square error (ppm). The table show the most successful subset of all models tested. N = 619 – 930 per sensor in total and 203-313 for the data subset with CH₄ levels (mol fractions) < 50 ppm. See text for details.

<table>
<thead>
<tr>
<th>Model No.</th>
<th>Equation</th>
<th>( V_0 )</th>
<th>CH₄</th>
<th>( Observed = k \times Predicted + M )</th>
<th>( V_0 )</th>
<th>CH₄</th>
<th>( Observed = k \times Predicted + M )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mod</td>
<td>max</td>
<td>( k )</td>
<td>( M )</td>
<td>( R^2 )</td>
<td>RMSE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppm</td>
<td></td>
<td>SE (min-max)</td>
<td>SE (min-max)</td>
<td>mean (min-max)</td>
<td>mean (min-max)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>( CH_4 = aR + b(RH) + cT + K )</td>
<td>V1</td>
<td>719</td>
<td>0.024-0.036</td>
<td>-3.2 \times 10^{-7} to 3.5 \times 10^{-7}</td>
<td>5.8-8.2</td>
<td>0.58</td>
</tr>
<tr>
<td>2</td>
<td>( CH_4 = aR^b + c(RH)^d + eT + K )</td>
<td>V1</td>
<td>719</td>
<td>0.006-0.010</td>
<td>-8.8 \times 10^{-7} to 4.2 \times 10^{-7}</td>
<td>1.6-2.6</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>( CH_4 = aR^b + c(RH)(aR^b) + dT(aR^b) + K )</td>
<td>V1</td>
<td>719</td>
<td>0.003-0.006</td>
<td>-6.8 \times 10^{-7} to 9.3 \times 10^{-7}</td>
<td>0.72-1.44</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>( CH_4 = aR^b + cH(aR^b) + dT(aR^b) + K )</td>
<td>V1</td>
<td>719</td>
<td>0.002-0.003</td>
<td>-4.3 \times 10^{-7} to 3.2 \times 10^{-7}</td>
<td>0.43-0.90</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>As No. 4</td>
<td>V2</td>
<td>719</td>
<td>0.001-0.003</td>
<td>-3.3 \times 10^{-7} to 4.1 \times 10^{-7}</td>
<td>0.38-0.87</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>As No. 4</td>
<td>V3</td>
<td>719</td>
<td>0.001-0.003</td>
<td>-4.1 \times 10^{-7} to 3.6 \times 10^{-7}</td>
<td>0.37-0.82</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>As No. 4</td>
<td>V4a</td>
<td>719</td>
<td>0.001-0.003</td>
<td>-2.2 \times 10^{-7} to 2.8 \times 10^{-7}</td>
<td>0.37-0.82</td>
<td>0.99</td>
</tr>
<tr>
<td>8</td>
<td>( CH_4 = aR^b + cH(aR^b) + K )</td>
<td>V4a</td>
<td>719</td>
<td>0.001-0.003</td>
<td>-5.6 \times 10^{-7} to 1.3 \times 10^{-7}</td>
<td>0.37-0.84</td>
<td>1.00</td>
</tr>
<tr>
<td>9a</td>
<td>As No. 8 with equation V4b to determine ( V_0 )</td>
<td>V4b</td>
<td>719</td>
<td>0.001-0.003</td>
<td>-7.8 \times 10^{-7} to 1.4 \times 10^{-6}</td>
<td>0.37-0.84</td>
<td>1.00</td>
</tr>
<tr>
<td>9b</td>
<td>As No. 9a with lower max CH₄ level.</td>
<td>V4b</td>
<td>50</td>
<td>0.007-0.014</td>
<td>-4.1 \times 10^{-8} to 8.1 \times 10^{-8}</td>
<td>0.16-0.33</td>
<td>0.98</td>
</tr>
<tr>
<td>10a</td>
<td>As No 8. Parameters $a$, $b$, $c$ and $K$ estimated from relationships with parameters in V4b; see text.</td>
<td>V4b</td>
<td>719</td>
<td>0.001-0.012</td>
<td>-108 to 1.1</td>
<td>0.39-1.62</td>
<td>1.00</td>
</tr>
<tr>
<td>-----</td>
<td>------------------------------------------------------------------------------------------------</td>
<td>-----</td>
<td>-----</td>
<td>-------------</td>
<td>------------</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>10b</td>
<td>As No 8. Parameters $a$, $b$, $c$ and $K$ estimated from relationships with parameters in V5b; see text.</td>
<td>V5b</td>
<td>719</td>
<td>0.001-0.024</td>
<td>-122 to 1.9</td>
<td>0.43-2.80</td>
<td>0.99</td>
</tr>
<tr>
<td>10c</td>
<td>As No. 10a with lower max CH$_4$ level.</td>
<td>V4b</td>
<td>50</td>
<td>0.006-0.021</td>
<td>-51 to -14</td>
<td>0.30-0.87</td>
<td>0.98</td>
</tr>
<tr>
<td>11a</td>
<td>As No. 8. Parameters $a$, $b$, $c$, and $K$, derived from 6-7 minimum $V_L$ values at different $H$, and 20 samples at random CH$_4$ levels-mol fractions between 3 and 500 ppm.**</td>
<td>V4b</td>
<td>719</td>
<td>0.002-0.004</td>
<td>-6.5 to 7.1</td>
<td>0.41-0.96</td>
<td>1.00</td>
</tr>
<tr>
<td>11b</td>
<td>As No. 11a with the 20 random samples at CH$_4$ levels-mol fractions between 3 and 500 ppm.**</td>
<td>V4b</td>
<td>50</td>
<td>0.008-0.017</td>
<td>-0.7 to 0.5</td>
<td>0.17-0.41</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*Minimum and maximum mean intercepts for the group of 20 sensors. The confidence interval around the mean intercept was ± 1.1 ppm in Model 7 (having lowest RMSE). ** Monte Carlo simulations with 1000 runs generating random data subsets used for deriving the model parameter ranges.
Figure 1. Sensor output voltage ($V_L$; mV), $R_s/R_0$ ratio, and predicted CH$_4$ mixing ratio (predCH$_4$; ppm) using Model 9a, 10a and 11a in Table 2, respectively, versus observed CH$_4$ mixing ratio (obsCH$_4$; ppm), for one of the studied sensors. See text for details and Figures S1 and S2 for similar graphs regarding all sensors.
Figure 2. Photo of the CH₄/CO₂/RH/T logger described in the supplementary information.
Supplement

This supplement contains supplementary tables and figures, and a description of a CH₄/CO₂/RH/T make-it-yourself logger.

Table S1: Best identified relationships between parameters \( g \) and \( S \) in Model V4b (Table 1) and parameters \( a \), \( b \), \( c \), and \( K \) (Model 10a in Table 2). \( R^2 \) is the adjusted coefficient of determination, and SD denote standard deviation. Please note that the relationships are examples derived for the specific sensors used only, and the verification of their application to other sensors requires more tests.

<table>
<thead>
<tr>
<th>Response variable</th>
<th>Best predictor</th>
<th>Relationship</th>
<th>( R^2 ) or SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) ( g ) ( S ) ( y )</td>
<td>( x )</td>
<td>( y = 6.98 \times 10^{-2} \cdot x - 3.55 )</td>
<td>( R^2 0.90 )</td>
</tr>
<tr>
<td>( b ) ( a ) ( S ) ( y )</td>
<td>( - )</td>
<td>Constant value for all sensors: -2.36</td>
<td>SD 0.24</td>
</tr>
<tr>
<td>( c ) ( g/S ) ( S ) ( y )</td>
<td>( x ) ( y = 1.37 \cdot 10^4 \cdot x^2 - 8.94 \cdot 10^{-2} \cdot x - 1.02 \cdot 10^{-5} )</td>
<td>( R^2 0.96 )</td>
<td></td>
</tr>
<tr>
<td>( K ) ( S ) ( y )</td>
<td>( x ) ( y = -7.15 \cdot 10^{-2} \cdot x + 0.95 )</td>
<td>( R^2 0.85 )</td>
<td></td>
</tr>
</tbody>
</table>

Table S2: Examples of previous studies addressing calibration and performance of the Figaro TGS 2600-type sensors for CH₄. All studies included consideration of humidity and temperature influence on the sensor response. Please see Reference list in main text for full references.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sensor model</th>
<th>Range (ppm)</th>
<th>Notes</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eugster and Kling, 2012</td>
<td>Figaro TGS 2600</td>
<td>1.8 - 2</td>
<td>Ambient air. Linear models in focus.</td>
<td>0.19 (^a)</td>
</tr>
<tr>
<td>Casey et al., 2019</td>
<td>Figaro TGS 2600</td>
<td>1.8 - 4.5</td>
<td>Linear, inverted linear, and artificial neural network models based on two Month training data tried.</td>
<td>0.66 (^a)</td>
</tr>
<tr>
<td>Collier-Oxandale et al., 2018</td>
<td>Figaro TGS 2600</td>
<td>1.8 - 5</td>
<td>Linear and inverted linear models.</td>
<td>0.6 to 0.8 (^a)</td>
</tr>
<tr>
<td>van den Bossche et al., 2017</td>
<td>Figaro TGS 2611-E00</td>
<td>2 - 9</td>
<td>Linear models. Accuracy of 0.8-2.7 ppm.</td>
<td>No ( R^2 ) reported.</td>
</tr>
<tr>
<td>This study</td>
<td>NGM 2611-E13</td>
<td>2 - 719</td>
<td>Multiple models tested (see Table 1 and 2).</td>
<td>0.51-1.00 all models considered</td>
</tr>
</tbody>
</table>

\(^a\) The highest reported \( R^2 \) values selected.
**Figure S1**: Observed CH₄ levels (measured by Los Gatos instrument) versus Rs/R₀ ratio, and predicted CH₄ levels from each tested sensor. “all”, “V” and “R” for predicted CH₄ denote that parameters were estimated in different ways (Approach I, II and III, and Model 9a, 10a and 11a in Table 2, respectively; see main text for details.)
Figure S2: Observed CH₄ levels (measured by Los Gatos instrument) versus sensor output ($V_L$), $R_s/R_0$ ratio, and predicted CH₄ levels from each tested sensor at CH4 mol fractions < 50 ppm. Results from three calibration models representing Approach I, II and III (model 9b, 10c, and 11b in Table 2, respectively) are shown.
Figure S3: Root mean square error (RMSE) obtained during Monte Carlo simulations in the simplified calibration Approach III, using 4-20 reference samples above the atmospheric background level. See text for details.
**Figure S4:** Real data from a flux chamber on a lake in June 2019 with 14 automated chamber open-closure cycles over 30 hours. The upper, central and bottom panels show calibrated CH$_4$ mol fractions based on this study, untreated sensor output signal, and absolute humidity.
Example of an Arduino controlled CH₄/CO₂/RH/T logger

Read first

Please note that this description is intended as an example to give inspiration and facilitate extended use for greenhouse gas measurements. What is described below has been working for us but small differences in electronic components among brands or even batches, may generate a need of modifications, so we cannot guarantee full functionality based on this description. Users should be prepared for some own development time and trouble shooting. The authors are interested in learning from issues and improvements and would appreciate communication with users to the extent time allows.

Hardware setup

The parts list is given in Table S2 and the wiring is illustrated in Figure S3. The total material cost in Sweden, November 2019, was in the order of 200 Euro. We made a small interface board to which the CH₄ and DHT (measure RH and T) sensors were soldered (Figure S3). This interface board was on one side attached to the CO₂ sensor via a connection and on the other side to the cable via another connector. The other end of the cable was attached to the Arduino connectors via connectors soldered onto the SD card logger board. This setup provides capacity to measure humidity and temperature both by the DHT sensor and by the humidity sensor on the CO₂ sensor board – a setup described to give the option to exclude the CO₂ sensor if only CH₄ is of interest, and to have backup measurements as humidity is critical to interpret the CH₄ sensor data. Details regarding the Arduino and the logger shield can be found at https://store.arduino.cc/arduino-uno-rev3 and https://learn.adafruit.com/adafruit-data-logger-shield).
Figure S5. Wiring diagram for the CH₄/CO₂/RH/T logger described here. See detailed information about the CO₂ sensor board at www.senseair.com.

Table S3. Parts used to make the CH₄/CO₂/RH/T logger described here.

<table>
<thead>
<tr>
<th>Type</th>
<th>Part</th>
<th>Brand</th>
<th>MFG Part No</th>
<th>Qty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>Arduino Uno Rev3 SMD;</td>
<td>Arduino</td>
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<td>Datalogging</td>
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<td><a href="http://www.adafruit.com/product/1141">www.adafruit.com/product/1141</a></td>
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SD Memory Card 2 GB; www.elfa.se/Web/Downloads/et/_1/Transcend_TSDC_Datasheet_1.pdf?pid=11074864

| Sensors                  | Methane Sensor Module; www.figarosensor.com/product/entry/ngm2611.html | Figaro | NGM2611-E13 | 1 
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<td>DHT22 Temperature Humidity sensor; <a href="http://www.adafruit.com/product/385">www.adafruit.com/product/385</a></td>
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| K33 ELG Carbon dioxide sensor; www.senseair.com/products/flexibility-counts/k33-elg/ | Senseair | 033-8-0007 | 1  

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<th>Cable</th>
<th>Data Cable PVC 8x 0.22mm²; 1.5m used here.</th>
<th>Alpha Wire</th>
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**Software**

An Arduino code was developed by combining and adapting publicly available information from sensor producers and the generous open source Arduino community contributions on internet. The code is available at http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-162780. For basic Arduino software use knowledge if needed, there are many excellent open source tutorials on the internet.
Power supply

The CH$_4$/CO$_2$/RH/T logger described here was primarily tested and calibrated using 12V power supply or acid lead battery of 12V and 7Ah with a solar panel. For about 8h measurement, it is possible to use a set of two 9V batteries (connected in parallel) or 8 AA batteries using battery holder. A risk of using such small sets of battery is that the CH$_4$ sensor signal may be less stable (more noisy), but the system still works. Note that with our setup, there is no error indication or alarm, when battery is low.
General use

1. Load the software onto the Arduino board.
2. Connect the sensors with the controller and logger boards. The measurement cell of the CO₂ sensor (white part) should be facing the same direction as the methane sensor.
3. Insert the SD card to the SD card holder (logger shield on the Arduino board).
4. Connect the power source via the power cable.
5. Connect the power cable to the main board and **NOTE THE REAL CLOCK TIME**. This is important as the logger real time clock and associated time stamps logged is not always reliable and may be drifting.
6. The main board should now start, and a LEDs should be blinking every 2 seconds (or other selected interval) when data is logged to the SD card.
7. After about one minute, the CO₂ sensor LED in the measurement cell should start blinking (visible through the white membrane).
8. The CO₂ sensor LED will keep blinking once per minute (or at other selected time intervals for CO₂ measurements).
9. **To turn off the device, unplug the power cable from the main Arduino board. Again **NOTE THE REAL CLOCK TIME to enable drift correction.**
10. Download the data to computer, and reformat the SD card using SD formatter program before using again to minimize the risk of time stamp recording errors.