Methane Low Cost Sensor (MLCS): 2024 milestone review

Written by:
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A note of gratitude

Whilst the findings thus far are not picture perfect, they are however, a testament to the dedication of many amazing individuals. Each data point shown in a plot represented tremendous effort - be it driving out to a field, setting up a greenhouse trial, 3D printing chambers, running samples with the chromatograph, sensor deployment, or the inevitable data crunching once all analytical work had been completed.

A most heartfelt thank you to every single person who gave their time, energy, and expertise to this project.

So they said yes,
And a word turned into seconds and days.

Point by point,
Date by date,
A picture came to life.

Of voltages and resistances,
Soils and puffs of gas.
For a crop that feeds the world,
And a dream to grow it,
Perhaps a little more gently, on our planet.

~ Thank you all, for a labor of love

1. Overview

Low cost metal oxide semiconductor methane sensors are gaining attention as a cheap way to measure ecosystem GHG fluxes. A methane low cost sensor (MLCS) was manufactured by Jonas Stage Sø (MOS; NGM2611-E13, Figaro, USA) and validated in a Lake system (Sø et al., 2024, https://doi.org/10.1029/2024JG008035). Vincent Scholz proposed adapting the MLCS as an alternative and more accessible method to measure CH4 flux in rice systems.

The overall aim of the study was to:

(a) Design MLCS measurement protocols specific to rice systems
(b) Evaluate the accuracy of using MLCS for field CH4 measurements compared to established methods including gas chromatography and Li-Cor 7810.
(c) Exploration of using a custom-built chamber (Octopus) for MLCS measurements

Overall, the study has preliminarily demonstrated the utility of MLCS for CH4 measurements in rice as there were electrical signal responses to concentration changes over time, as well as good correlation between MLCS and GC measurements. We conclude that the MLCS has good potential for field deployment, and more work is required for calibration and field-based protocol development.

Data and analysis repository: https://github.com/XiaoZhangZhangRice/Methane_Insight

2. Field validation of MLCS and protocol development (California field study)

Three unique MLCS were deployed to 9 unique plots for a season-long gas sampling campaign during summer 2024. For each given deployment, change in CH_4 concentration over time (ΔC, ppm/hr) was determined concurrently using (a) gas chromatography (GC, Shimadzu GC-2014), and (b) MLCS in combination with an online R shiny app (https://methaneinsight.shinyapps.io/fluxR/). ΔC (ppm/hr) was chosen as a response variable as it is mathematically associated with flux (g CH4 ha-1 day-1) and allowed the least computation with covariates (e.g. chamber volume) for this initial report.

Gas samples for GC analysis were taken at times 0, 21, 42, and 63 minutes after chamber enclosure. Before samples were taken, a fan was turned on for approximately one minute to mix the air. ΔC_{GC} was determined as the slope from linear regression of CH4 concentration against time.

The MLCS was allowed to warm up for an hour before deployment and fixed to the top of a GHG chamber before chamber closure. A CSV file was generated for each deployment and was subsequently loaded into the R shiny app to determine ΔC_{MLCS}. During initial deployment, it was discovered that fan operations caused rapid drops in CH4 concentrations (Fig 1). Consequently, ΔC_{MLCS} was determined using 3 different methods (Fig 1).

(1) Fan off: ΔC_{MLCS} estimated using a region where no fan was turned on and there was a linear relationship between CH4 (ppm) and time.

(2) Fan on: ΔC_{MLCS} was estimated from the end of a sampling session where the fan was left on for approximately 7 minutes. The region used had a linear relationship between CH4 (ppm) and time. Note: Switching on a fan at the end of a sampling session only started after 19 Jul 2024 after it was discovered that fan operation caused rapid drops in CH4 concentration.

(3) Three point: CH4 concentrations were taken from 3 points where the fan was not in operation along with the associated timestamp. ΔC_{MLCS} was determined as the slope of a 3 point linear regression.

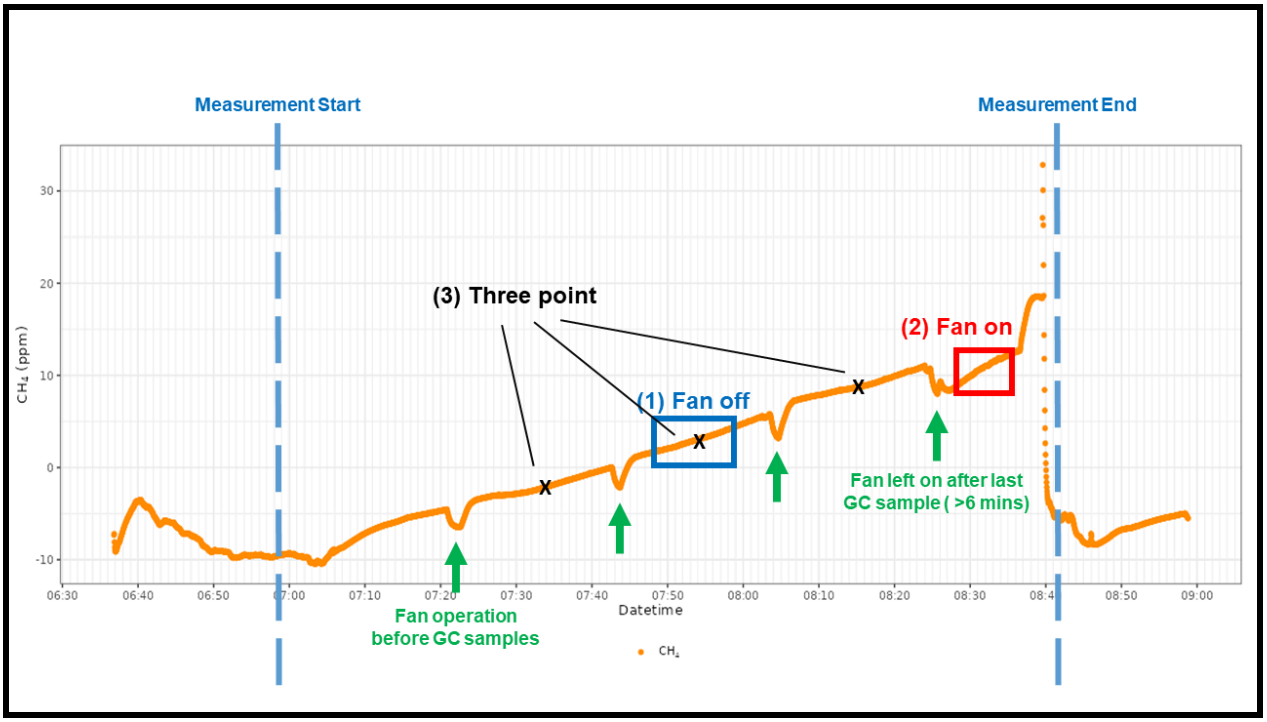

Fig 1. A typical MLCS R shiny output showing change in CH4 concentration over time. Large drops in concentration were observed when the fan was turned on (green arrows). ΔC_{MLCS} was predicted in 3 ways: (1) fan off (blue box), (2) fan on (red box), and (3) three point (black crosses).

All MLCS and GC determined ΔC values were plotted (Fig 2 and 3). Overall, ΔC_{MLCS} determined using the fan on method (Fig 3) was the closest to ΔC_{GC} - points were the closest to the 1:1 line. This might be related to the calibration conditions of the MLCS, whereby there was active airflow (see section 3).

However, for the fan off and three point methods, ΔC_{GC} was almost always higher than ΔC_{MLCS} - evidenced by a large number of points above the 1:1 line (Fig 2). Based on the linear regression, ΔC_{GC} was approximately two times larger than ΔC_{MLCS} for these two methods. However, when raw ΔC_{MLCS} values were transformed using the linear model, there was excellent agreement between ΔC_{GC} and ΔC_{MLCS} (Fig 2b and d). Mathematical transformations are common in the application of low cost sensors, and appear to be a sensible way forward as there is a good prediction ability and eliminates potential inaccuracies caused by fan operation.

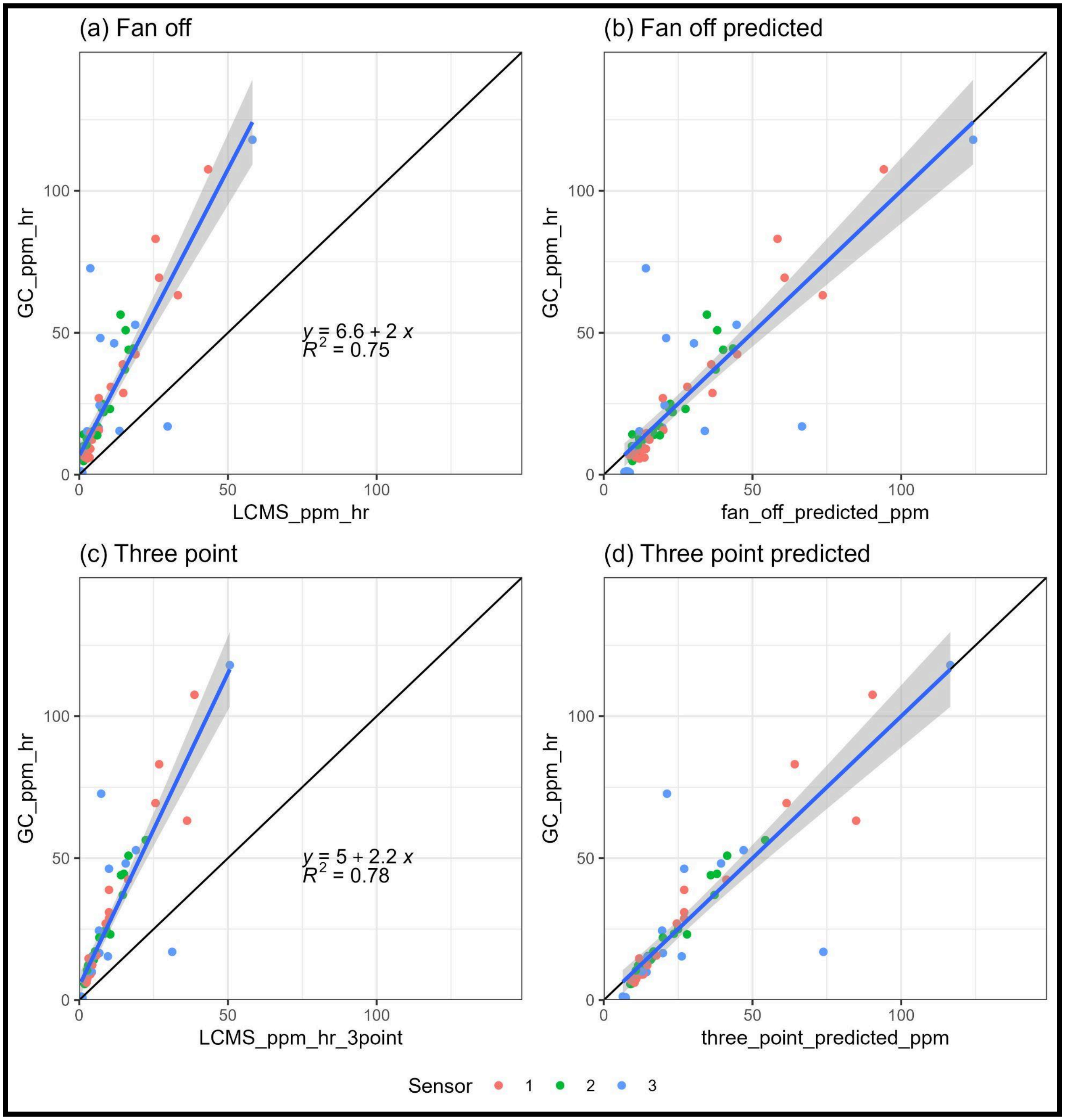

Fig 2. Linear regression of CH4 concentration change (ΔC, ppm/hr) for gas chromatography (GC) measured and MLCS measured values using the fan off and three point methods. The black line represents a 1:1 relationship (i.e. y=x). The equation of the line of best fit and R2 are displayed. Raw ΔC_{MLCS} values were transformed by the linear regressions shown in 2a and c, and are shown on the right (2b and d). The shaded area represents the 95% confidence interval.

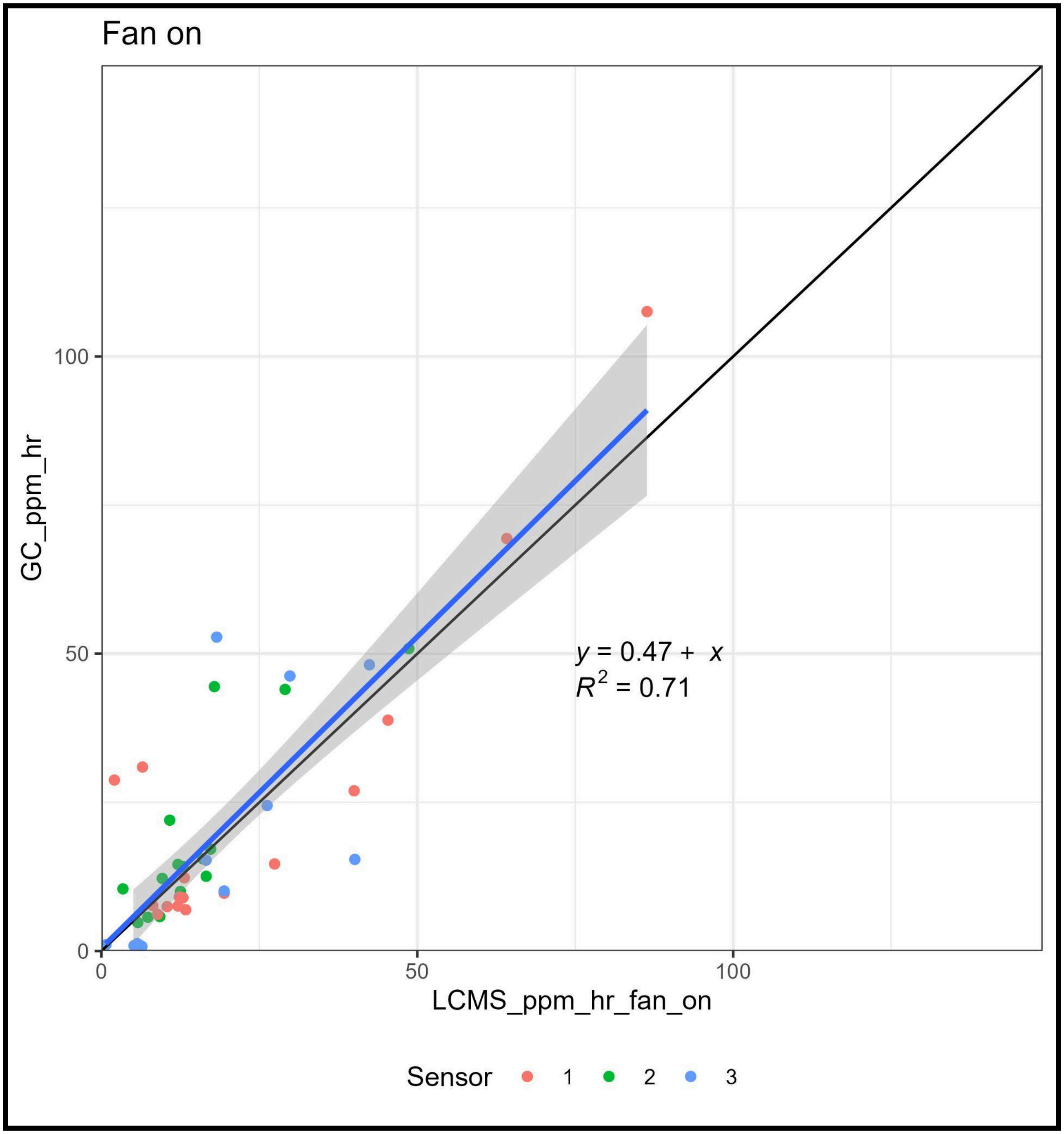

Fig 3. Linear regression of CH4 concentration change (ΔC, ppm/hr) for gas chromatography (GC) measured and MLCS measured values using the fan on method. The black line represents a 1:1 relationship (i.e. y=x). The equation of the line of best fit and R2 are displayed. The shaded area represents the 95% confidence interval.

3. MLCS stability and fan operation (Greenhouse study)

Fan operation was a subject of interest for MLCS usage protocol development. The first reason was to understand the effect of fan operation on ΔC_{MLCS} measurements. A GHG chamber for rice has a large headspace (often >20L in volume), and it was normal practice to mix the air with a fan. Spatial heterogeneity of gas concentrations within the gas chamber may lead to inaccurate quantification of ΔC_{MLCS}. Importantly, it was shown during the growing season that fan operation would cause a sharp decrease in measured CH4 concentration (Fig 1).

A key point was that the calibration for MLCS was done in the environmental chamber in Y2E2 (Stanford). These chambers had airflow due to a large fan in the back, and were markedly different from fan off measurement conditions. Insights from the Hoyt lab's low cost sensor projects and other catalytic sensor experiences showed that the MLCS was likely very sensitive to airflow. Airflow may affect the operational temperature (usually around 250-300 °C) of the catalytic sensor on the MLCS, leading to inaccurate, if not at least fluctuating readings.

Nonetheless, a greenhouse test was set up to evaluate the effect of airflow on MLCS measurements. Two MLCS units were placed into a chamber with concurrent Li-Cor 7810 measurements as a reference to obtain ΔC. Unfortunately, the results show that variability amongst MLCS was a far larger issue - evidenced by the lack of clustering of sensor 3 and 13 dots (Fig 4). Thus, the replicability of measurements across different MLCS units need to be resolved in tandem with airflow considerations before further validation steps. Having said that, it did appear that with a fan turned on, ΔC_{MLCS} was larger (points shifted to the right), agreeing with the findings of the California field study. We duly acknowledge that this study was conducted when CH4 fluxes were low, and may have been a contributing factor to this finding.

Results from both the field and greenhouse studies show that ΔC_{MLCS} was strongly affected by airflow, likely due to alteration of sensor operation temperature (e.g. Fig 1). This points to important decision-making pertaining to hardware calibration, hardware characteristics, and intended measurement conditions during deployment. Future work would need to keep airflow constant in both calibration and deployment phases (recording or eliminating airflow rate) to ensure congruence.

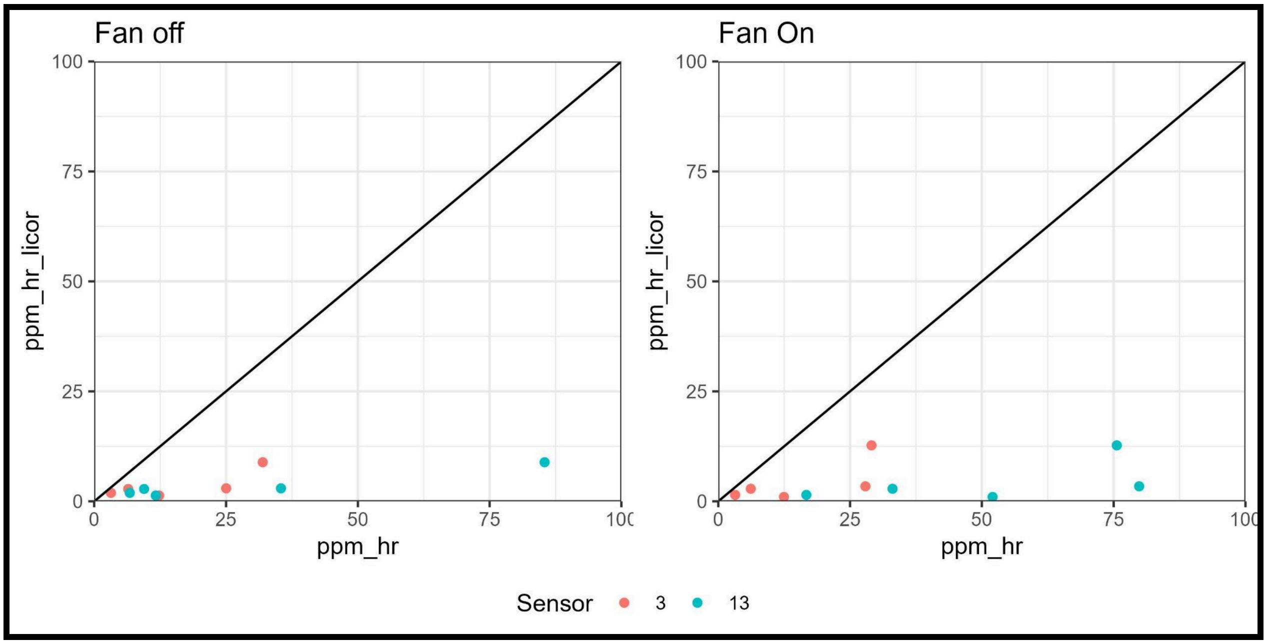

Fig 4. Scatter plot of (ΔC, ppm/hr) for Li-Cor 7810 measured (y) and MLCS measured values (x). The black line represents a 1:1 relationship (i.e. y=x).

4. Alternative chamber designs using MLCS (Greenhouse study by Anthony Macias)

Alternative designs to the static chamber method were tested for the MLCS. The development of these designs was halted after initial data collection and further analysis of sensor behavior was required.

4.1 Octopus chamber design

The Octopus Prototype was a proposed chamber setup to measure ΔC in rice. The setup involved embedding eight thin-walled silicone tubes in rice soils, which were left in the field for eight hours to collect data. The goal was for methane in the soil to diffuse into semi-permeable silicone tubes, eventually filling the chamber with methane until the chamber concentration equilibrated with that of the soil. However, the prototype's battery life limited deployment to eight hours. The data followed an anticipated trend, with methane levels gradually increasing throughout the day until it reached a horizontal asymptote upon equilibrating with the soil. However, the data lacked reliability in representing absolute soil methane concentrations, given the limitations of low cost sensors in measuring true methane levels. With a longer battery life, it may be possible to capture the diurnal cycle of soil methane, offering insights into changes in soil methane concentration over time. An additional concern raised by Alison Hoyt and Klaus Koren was the risk of oxygenating deep rice clay via the Octopus prototype. They were concerned that ambient oxygen entering the clay through the tubes could alter methane production. In response, we explored using deoxygenating packets, similar to silica gel packets, to limit oxygen exposure. Ultimately, the project was put on hold.

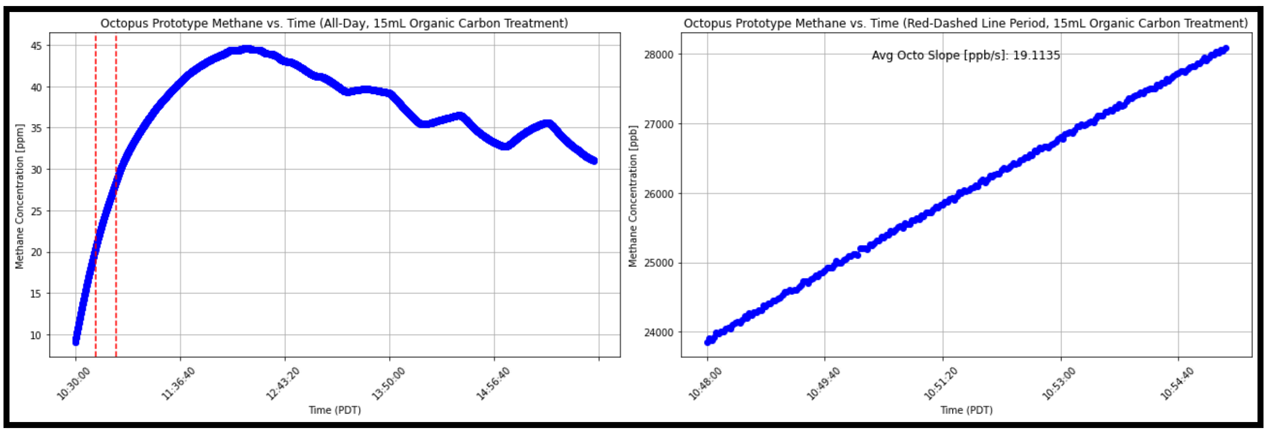

Fig 5. Plots of Low Cost Methane Sensor Data from inside the Octopus Chamber. The left subplot shows the behavior during a day-long deployment, while the right subplot zooms into a 10-minute section marked by the two red vertical lines.

Fig 6. Picture of Octopus Prototype after several deployments in Stanford Greenhouse

4.2 Pump design

The pump design was a 3D-printed prototype similar to the Octopus, developed to use a low cost methane sensor in a small fixed volume. Unlike the Octopus, which recorded soil methane levels through gas diffusion in silicone tubing, the pump design aimed to extract pore water into the chamber using a peristaltic pump, agitate the water to release methane, and then measure methane levels with the low cost sensor (MLCS). In lab tests, the pump successfully transferred water into the chamber, but in field deployments, it failed to draw enough pore water from the soil. Following this limitation, the project was put on hold.

Several challenges remain for the pump design. First, low cost methane sensors lack the precision needed for measuring absolute methane concentration, meaning the initial methane levels in the chamber must be known for accurate readings. Second, proper agitation and volume control are essential. At the time of design, I (Anthony) was unaware that standard pore water sample preparation involves two minutes of vigorous shaking to release dissolved methane. Since the MLCS records methane changes over time, variations in mixing would impact data accuracy. To advance this project, adding a sensor to verify a consistent volume of pore water in each sample and incorporating a motorized stirrer or similar mechanism to ensure thorough mixing would significantly improve methane measurement reliability.

The pump prototype was initially conceived with additional functionality in mind: the potential to dispense acids and bases into a series of chambers to measure soil carbonate levels. Although this application was ultimately deemed out of scope, the development of a reliable pump and chamber setup could be valuable if soil carbonate measurement becomes a future research goal.

5. Lessons learned and areas for improvement

5.1 Explicit instructions

Explicit expectations should also be set for all collaborators, especially for a multi-research group endeavor. Ideally, the role each individual plays and when specific deliverables should be achieved should be set out before data acquisition. This is especially important for agronomic experiments because there are limited cropping seasons and thus sampling opportunities.

For the application of a "novel" technique, providing a clear set of instructions for researchers, specifically field-based protocols, would have been helpful. For the UC Davis collaborators, an initial deployment protocol was issued to researchers obtaining field data. After discovering that fan operation affected senor functionality, a protocol update was issued to researchers (Fig 7). Such a practice helped to eliminate ambiguities in data acquisition - which is fundamental to obtaining good data and allows standardization of experimental techniques across individuals.

The authors of this milestone review were unaware of how instructions were handled for other research groups in this project. However, we strongly feel that the provision of explicit instructions was a catalyst in ensuring the progress we have achieved thus far.

5.2 Data management

There were no standardized data management procedures for all collaborators. When data was collected, it was stored based on what the collaborators thought was best. For example, UC Davis collaborators utilized Google Drive as the database, and made use of standardized naming conventions for uploading CSV files (Fig 7).

However, the authors of this milestone review were unaware of the data management protocols of collaborators from other regions (Asia and Arkansas). For future collaborations, data management strategies, including but not limited to naming conventions, database selection and setup (e.g. Google Drive), data types, and explicit experiment procedures, ideally should be discussed and implemented prior to research initiation.

We are adjusting the protocol a little bit. Please see updated instructions in red. Essentially, we leave the fan on after sampling is done until we pack up. There will be no adjustments to the Linquist Lab's sampling protocols.

1) Folder link:
https://drive.google.com/drive/folders/1UFozFQIAnJhreNu4pKEe6X4Zmpp2pNP_?usp=drive_link

Alternatively it can be accessed Linquist Lab > GC Files > VincentxZhang > 2024 > LCMS Logs

All should have access. If not, please let me know.

2) Plot and LCMS allocations

LCMS Number	Telha	Nawal_Plot
1	301	14
2	302	12
3	306	11

Note that all LCMS have a number on the side (i.e. UC Davis 1,2,3). Only 3 lids will carry LCMS this season.

3) Naming and file uploading
Please name all files in the following format:

Plot()_Name(Telha/Nawal/Vincent)_LCMS(1/2/3)_Date(27Jun2024)

E.g. 301_Telha_LCMS1_2Jul2024

In practice, only the date needs to be changed. Files should be uploaded after each sampling session to avoid data loss. Please upload all log files into the folder corresponding to the main researcher.

4) LCMS Usage

- Please ensure that LCMS are turned on approx 1 hr before putting on lids.
- Attach firmly to the lids before sampling, making sure velcro is in maximum contact area
- Light should be blinking
- At T42 or earlier, prep 2 extra batteries, making sure that by T63, all LCMS plots have a 12v battery.
- After taking the last GC sample for a given chamber at T63, turn on the fan before proceeding to the next plot. Enclose for at least 6 mins with the fan turned on.
- Turn off LCMS after field sampling
- Encouraged to bring along extra batteries

Fig 7: Data collection workflow and naming conventions for UC Davis collaborators

5.3 Additional pointers for improvement

As this was a collaborative effort across various research groups and geographic regions, due diligence should be taken to ensure higher precision of measurements and success of the research studies. Listed here are some situations that could have been better handled by multiple stakeholders.

- For the usage of new measurement techniques, pilot studies to ensure reproducibility and precision should be done in controlled settings before field deployment. Protocols for MLCS deployment should have also been standardized and instructions should have been sent out to all collaborations prior to sensor deployment in the field.
- Clock Issues on Circuit Boards: Notably, circuit boards on MLCS 03 and 13 now have clock signals running a few minutes fast, indicating a possible increase in clock signal frequency. This could mean other components, like sensors, are operating at faster frequencies, possibly corrupting data. Since the black circuit boards differ from those used by Jonas, a more experienced PCB (printed circuit board) designer should carefully review these boards before any further assembly.
- A key lesson learned from this project was the importance of replicating established calibration methods early on. If we had initially tried to replicate the successful calibration from Jonas' paper using the new sensor batch, any calibration-related issues could have been identified and potentially resolved before the rice-growing season ended. Starting with lab tests in a controlled environment, ideally without a fan, would have provided a clearer baseline for methane flux measurements.
- Regular discussions with stakeholders such as Jack Lamb and Alison Hoyt might have helped establish an early objective of recalibrating sensors specifically for rice field applications, testing in the greenhouse to optimize measurement setups, and developing a tool for consistent flux calculations (beyond manual calculation or using an R Shiny app).
- Sensor Labeling: For the sensors used by UC Davis collaborators, labeling caused confusion. Although labeled 1-3 on stickers (matching UC Davis data as MLCS1-3), their actual serial numbers were 01, 04, and 05. This confusion underscores the importance of assigning a single identifier to each sensor to avoid mix-ups in future deployments.

6. Conclusions and future directions

Based on the results of the California field study, we conclude that the MLCS has the potential to be developed for field measurements of CH4 concentration change in rice. Importantly, there was a good correlation between ΔC_{MLCS} and ΔC_{GC} (Fig 3) for the fan-on method. Additionally, when raw ΔC_{MLCS} values were transformed, there was excellent agreement between ΔC_{MLCS} and ΔC_{GC} (Fig 2). However, due to a lack of replicability between sensors (Fig 4) as well as inconsistencies between calibration and deployment conditions, more validation work needs to be done before the end goal of an "open source guide" for usage and measurements can be attained.

There are two main steps forward, including engineering validation, and protocol development.

First, for the engineering validation step, airflow needs to be standardized during calibration and deployment. It may have been by chance that the airflow from FAN ON intervals in the California field study mimicked the airflow experienced when calibrating the sensors in the environmental chamber (Stanford), and allowed us to get a reasonable correlation to GC data for the “fan on” method (Fig 3). Additionally, the “fan off” and “three point” methods were excellent predictors of ΔC_{GC} when raw ΔC_{MLCS}values were transformed, but airflow was present during calibration and is a point of concern.

We believe that both fan on and off methods can potentially be feasible, especially when considering the need for air mixing within chambers to obtain concentration homogeneity. Should mathematical transformations of raw ΔC_{MLCS} values be a way forward, the transformation method and model parameters need to be robustly investigated. The baseline for both approaches: calibration and deployment conditions need to be congruent.

Second, for protocol development, there need to be clear instructions and documentation of MLCS operation, including but not limited to field deployment, chamber air mixing, chamber enclosure duration, and subsequent ΔC or flux calculations.

To conclude, the application of Figaro’s low cost methane sensor in rice field methane emission remains feasible. The experiment so far was an important first step in troubleshooting hardware, and identifying calibration and deployment challenges, providing a clear forward for improving sensor precision and protocol development.

Climate change is real, and we truly hope that we can continue to work towards our overall mission of using MLCS to make GHG flux measurements more financially and operationally accessible for researchers, legislators, farmers, and other stakeholders across the global rice industry.