Methane Low Cost Sensor (MLCS): 2024 milestone review

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Members of the Linquist Lab, Jack Lamb

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 CH4 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.

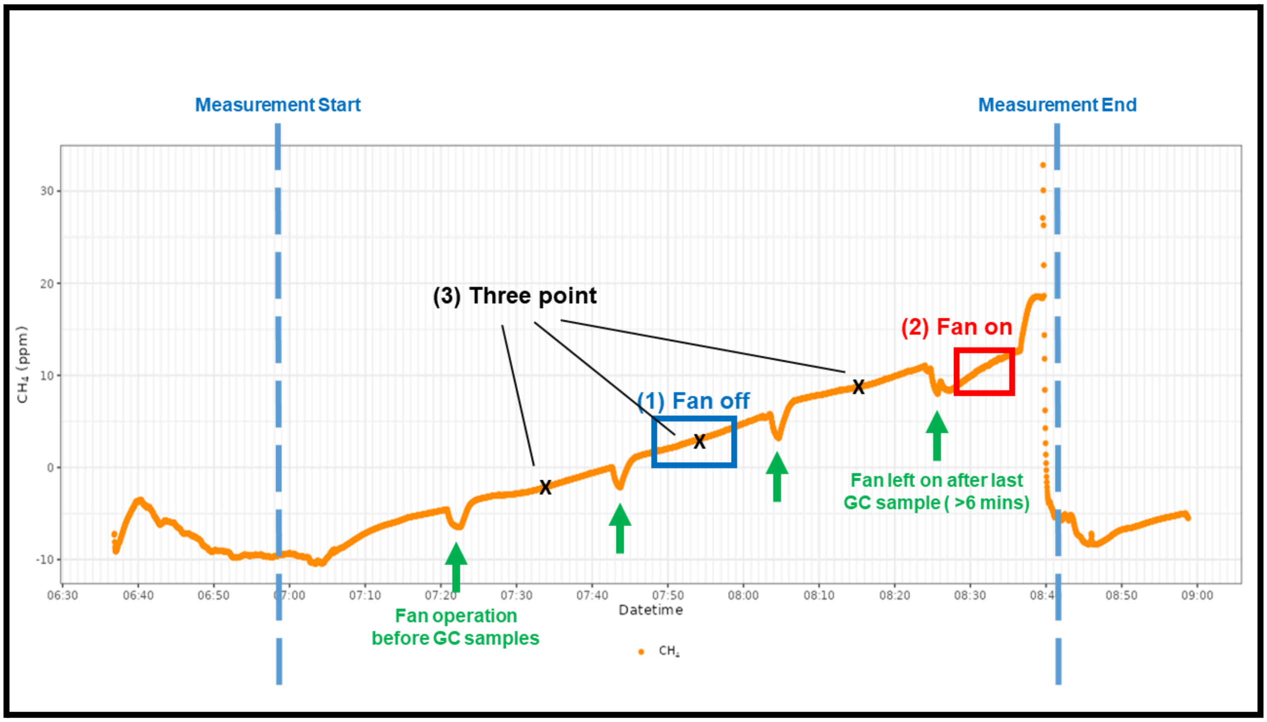
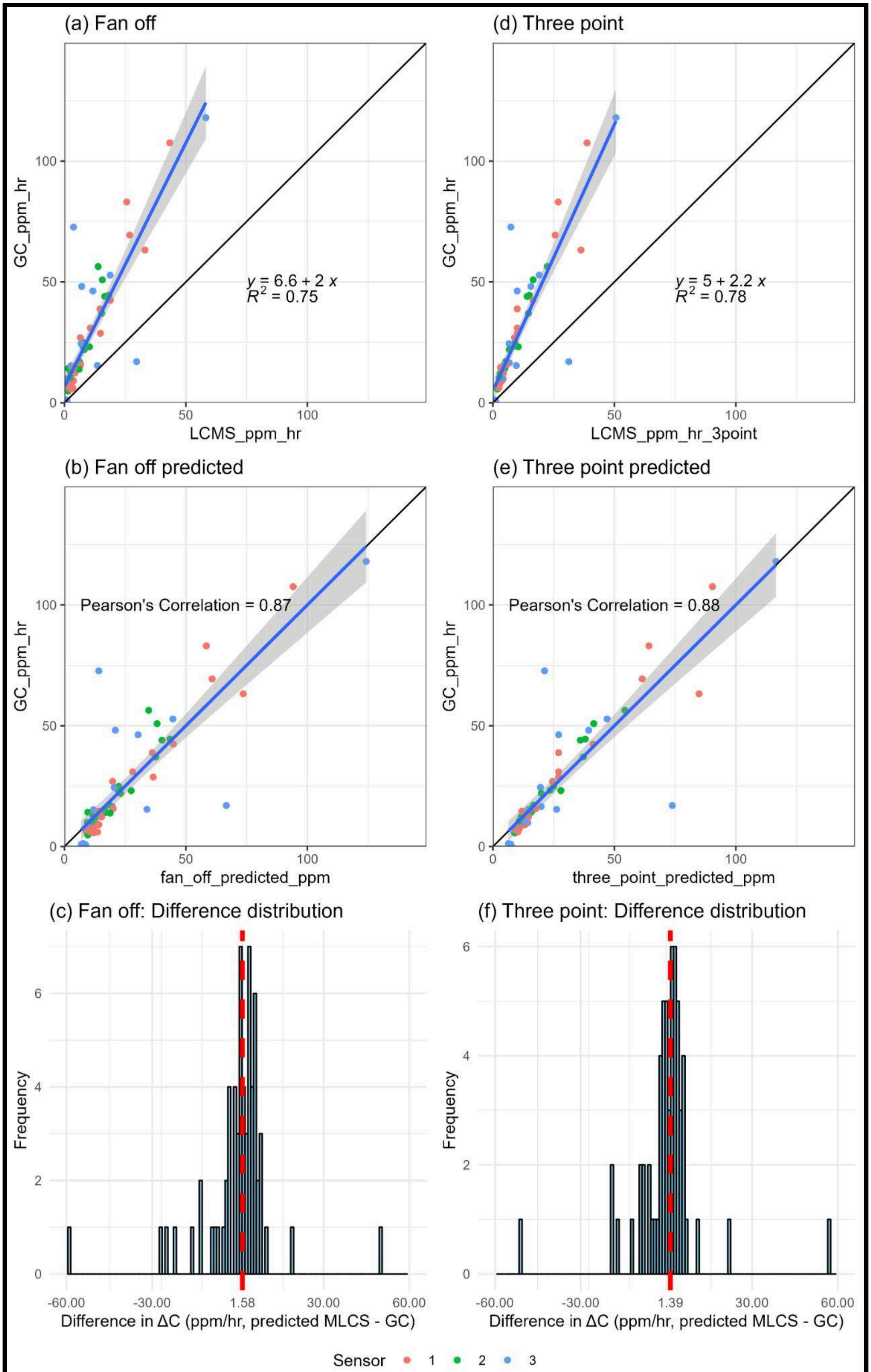


Fig 1. A typical MLCS R shiny output showing change in CH4 concentration over time. Large drops in concentration were observed when the fan was turned on (green arrows). ΔC_{MLCS} was predicted in 3 ways: (1) fan off (blue box), (2) fan on (red box), and (3) three point (black crosses).

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 2a and d). 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 predicted ΔC_{MLCS} (Fig 2b and d) - evidenced by the high correlation value. The majority of predicted ΔC_{MLCS} values also have a small difference compared ΔC_{GC} and the majority of differences lie close to the median difference value (Fig 2c and f). 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.



(a) Fan off
GC_ppm_hr
LCMS_ppm_hr
y = 6.6 + 2 x
R2 = 0.75
(d) Three point
LCMS_ppm_hr_3point
y = 5 + 2.2 x
R2 = 0.78
(b) Fan off predicted
Pearson's Correlation = 0.87
fan_off_predicted_ppm
(e) Three point predicted
Pearson's Correlation = 0.88
three_point_predicted_ppm
(c) Fan off: Difference distribution
Frequency
1.58
Difference in ΔC (ppm/hr, predicted MLCS - GC)
(f) Three point: Difference distribution
1.39
Sensor 1 2 3

Fig 2. Linear regression, 2a and d, 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 d (predicted values), and are shown in the middle two rows (2b and e). The shaded area represents the 95% confidence interval. 2c and f are histograms of differences between predicted MLCS and GC ΔC measurements. The median value is indicated by a red vertical dashed line.

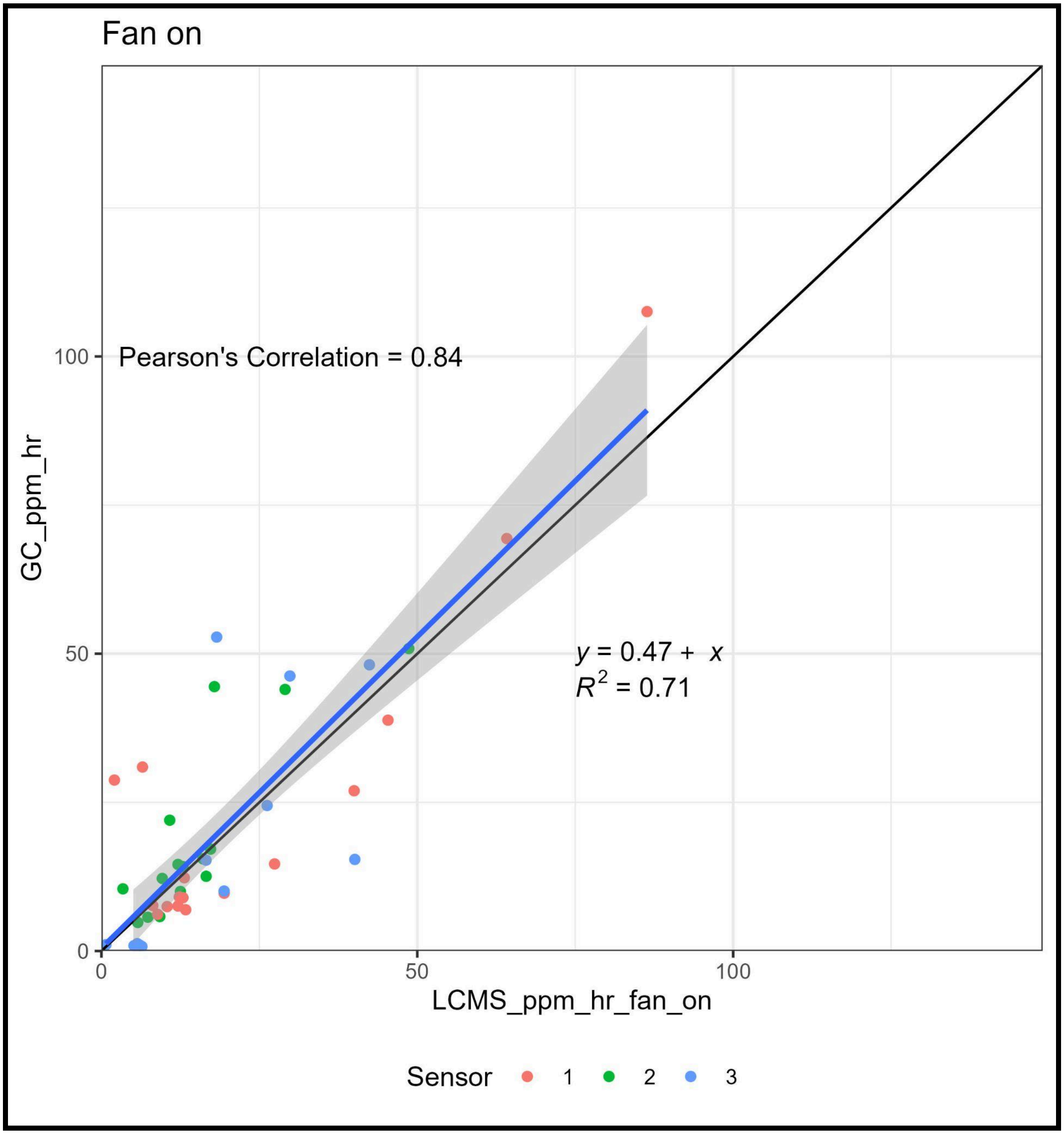


Fig 3. Linear regression of CH4 concentration change (ΔC, ppm/hr) for gas chromatography (GC) measured and MLCS measured values using the fan on method. The black line represents a 1:1 relationship (i.e. y=x). The equation of the line of best fit and R2 are displayed. The shaded area represents the 95%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

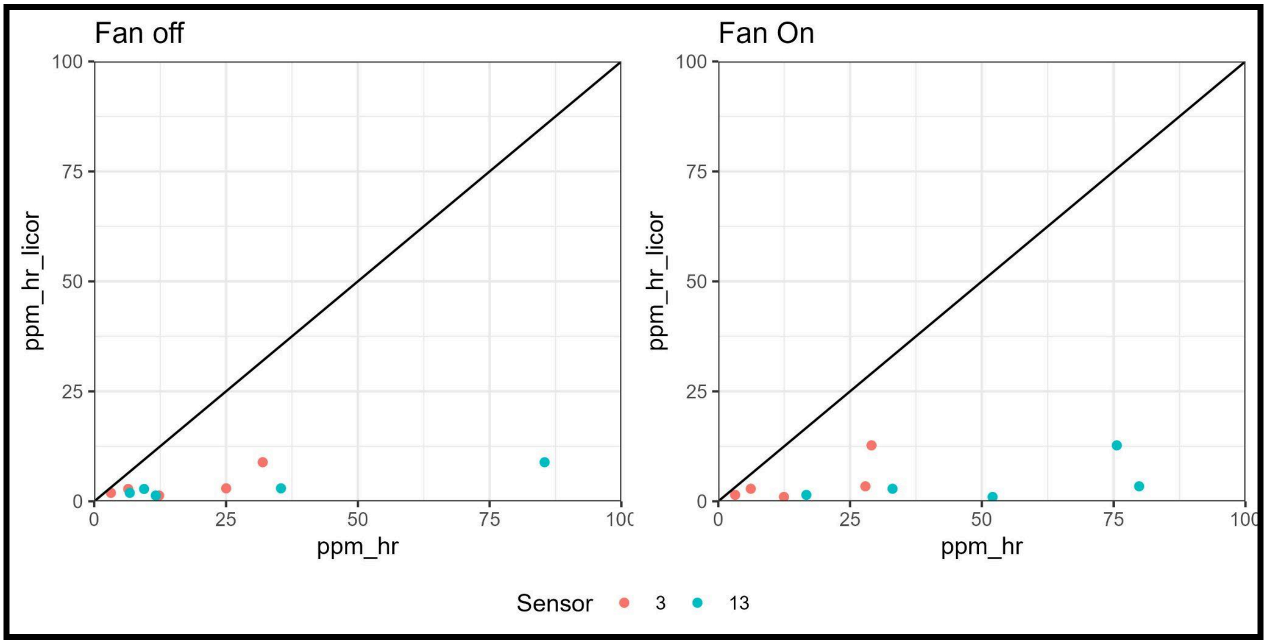


Fig 4. Scatter plot of (ΔC, ppm/hr) for Li-Cor 7810 measured (y) and MLCS measured values (x). The black line represents a 1:1 relationship (i.e. y=x).

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.

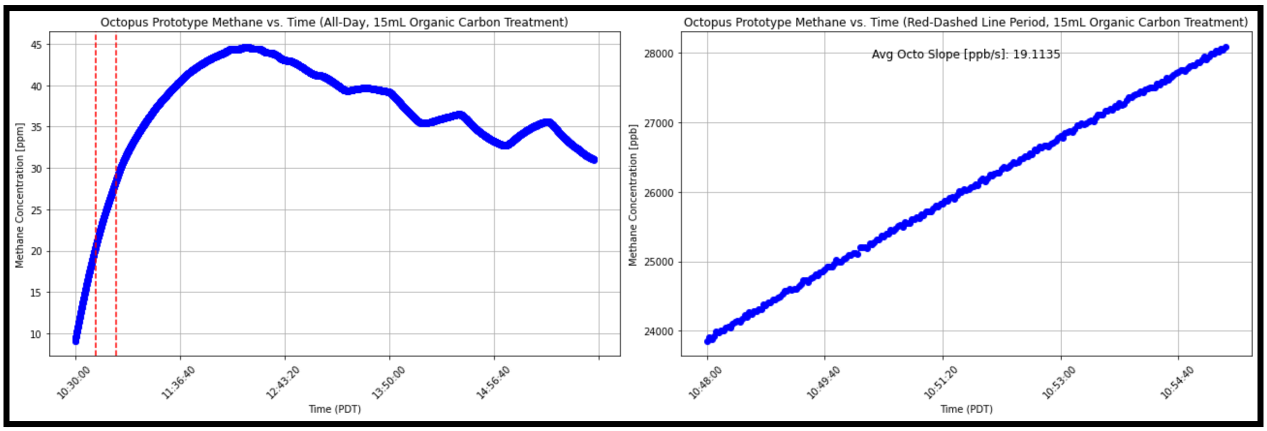


Fig 5. Plots of Low Cost Methane Sensor Data from inside the Octopus Chamber. The left subplot shows the behavior during a day-long deployment, while the right subplot zooms into a 10-minute section marked by the two red vertical lines.

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. 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 obtained from three-point and fan-off methods 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.