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Executive Summary

The project centers around a ground-based regional methane sensor developed by the CU/NIST team members under the DOE ARPA-E MONITOR program, and sophisticated aircraft measurement techniques developed by the UCD/Scientific Aviation team (responsible for a recent *Science* publication quantifying the Aliso Canyon storage field release).

The dual frequency-comb spectrometer is an invisible, eye-safe laser capable of measuring atmospheric methane concentrations along beam paths 1+ miles in length with high precision and stability (<1 ppb methane over 1 mile). The CU/NIST team has developed a unique approach to using a single, central spectrometer to locate and size methane emissions as small as 6 scfh from specific gas field structures within the 1+ mile range of the laser. Deployment involves the stationing of small cubic mirrors at strategic locations across the gas storage site. The mirrors direct light from the spectrometer back to a detector, where methane concentrations are recorded based on light absorption at specific wavelengths. The measurements are coupled with high resolution gas transport models based on meteorological measurements (wind, etc.) to determine the precise location and emission rate of methane sources. The calibration-free and continuous nature of dual frequency-comb spectrometer measurements means that a large area can be monitored continuously for temporal variability of emissions over long periods of time.

The aircraft measurements involve spiral flights around storage facilities with a sensitive ethane/methane measurement package. Upwind/downwind concentration comparisons and wind data provide total facility emissions data. During this project, a new micrometeorological package was integrated onto the Scientific Aviation aircraft to provide even greater emissions quantification capability.

In this project, the ground-based measurement system was deployed for 11 months (to capture seasonal variability) at a West Coast storage facility, together with a campaign of twice monthly aircraft total facility emissions flights. The data from these two modalities was combined to quantify the methane emissions from the facility with first-of-its-kind temporal and spatial detail. Concurrent with this deployment, the aircraft team performed flights to quantify emissions at a wider array of previously un-surveyed storage sites.

The ground-based measurement system was then moved to an additional site of differing total storage and delivery capacity. Aircraft mass balance flights continued, repeatedly surveying (twice monthly) this site, as well as surveying a large number of previously un-assessed sites spanning a variety of size, reservoir type and age.

Assessment of ground-based, temporally and spatially detailed methane emissions information alongside aircraft-derived methane total facility emissions information led to an improved understanding of emissions, relevant for inventories of the natural gas storage sector. In particular, this work provided temporal detail (seasonal of emissions and frequency of leaks) to stakeholders and personnel responsible for updates to the EPA's GHGI.

The impact of the proposed work has been a dramatic improvement in the temporal, spatial, and site- and type- specific detail and quantification of emissions inventories for the natural gas storage sector. This work directly benefits the EPA's GHGI, directly ameliorates the environmental impacts and public health and safety of the natural gas storage sector, and aids policymakers and industry to make sound choices with respect to management and regulation.

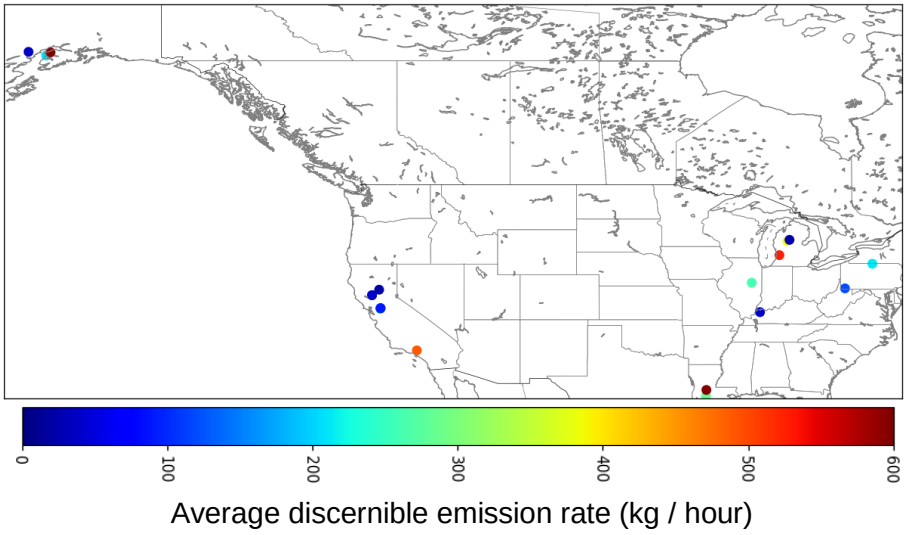
Summary of Project Activities

The overarching goal of the project was to improve the quantification of the temporal characteristics and spatial distributions of sources, volumes and rates of methane emissions from underground natural gas storage fields and wells and improve the quantification of methane emissions reported in the EPA's GHGI. Our aim was to achieve robust and representative emissions estimates for key contributors at underground storage well and field sites.

The specific project goals follow, with findings and results related to each:

1. Quantify the average methane emissions rate at a variety of types of underground storage wells and fields through a combination of long-term, high-sensitivity, and spatially detailed ground-based measurements and aircraft mass balance flights. The objective criterion of success was the ability to cross-validate mass balance fluxes obtained by the two techniques to within a reasonable degree of uncertainty.

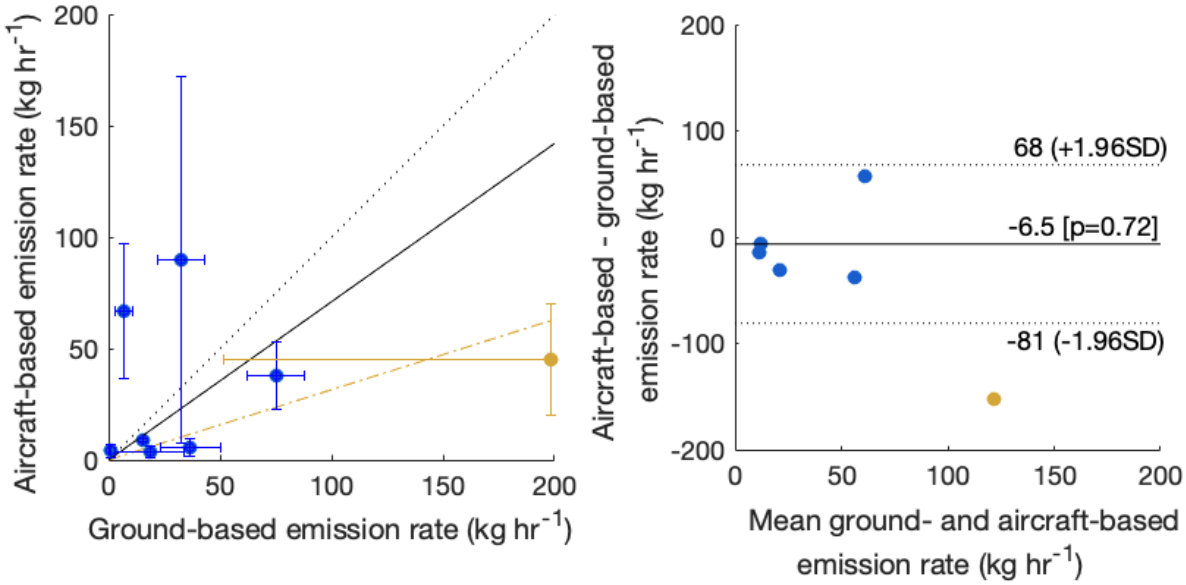
Methane emission rates were estimated at a variety of storage sites via ground- and aircraft-based measurements. Extensive aircraft campaigns documented snapshot-in-time emission rates at a variety of facilities across the continental U.S. and Alaska.



The figure above shows emission rates measured at different facilities, as measured by aircraft mass balance flights.

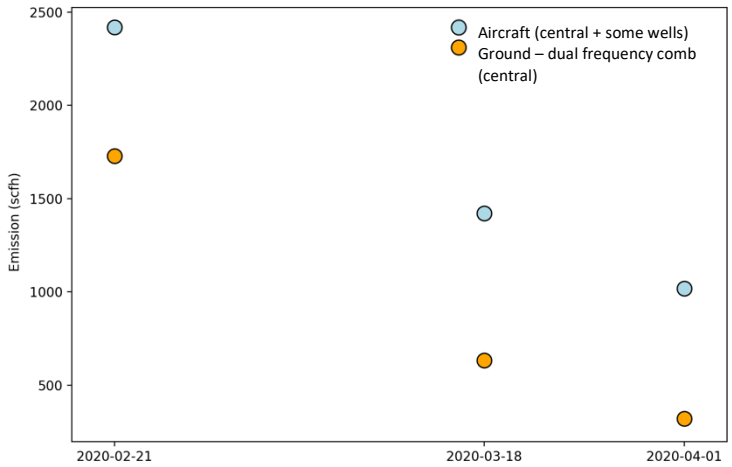
In addition to snap-shot-in-time measurements made by aircraft, long-term emission rates and variability were measured at an underground natural gas storage facility in the EIA's Pacific Region. The results were published in *Environmental Science & Technology*: C. Alden, R. Wright, S. Coburn, D. Caputi, G. Wendland, A. Rybchuk, S. Conley, I. Faloona, G. Rieker, "Temporal variability of emissions revealed by continuous, long-term monitoring of an underground natural gas storage facility", https://doi.org/10.1021/acs.est.0c03175.

In this work, cross-validation of emission rates obtained by the two techniques was shown. The key figure from the manuscript that demonstrates this criterion is reproduced here:



The figure above is a correlation plot of temporally overlapping ground- and aircraft-based emission estimates with black dotted line showing 1:1 and black solid line showing fit (left panel) and Bland-Altman mean-difference plot with dotted lines showing 95% limits of agreement (right panel). Blue points indicate time periods in which 3-hour windows were used, and the yellow points indicate an outlier case in which a 6-hour window was used for some ensemble members. The dash-dotted yellow line indicates the fit when this outlier is included in the correlation analysis.

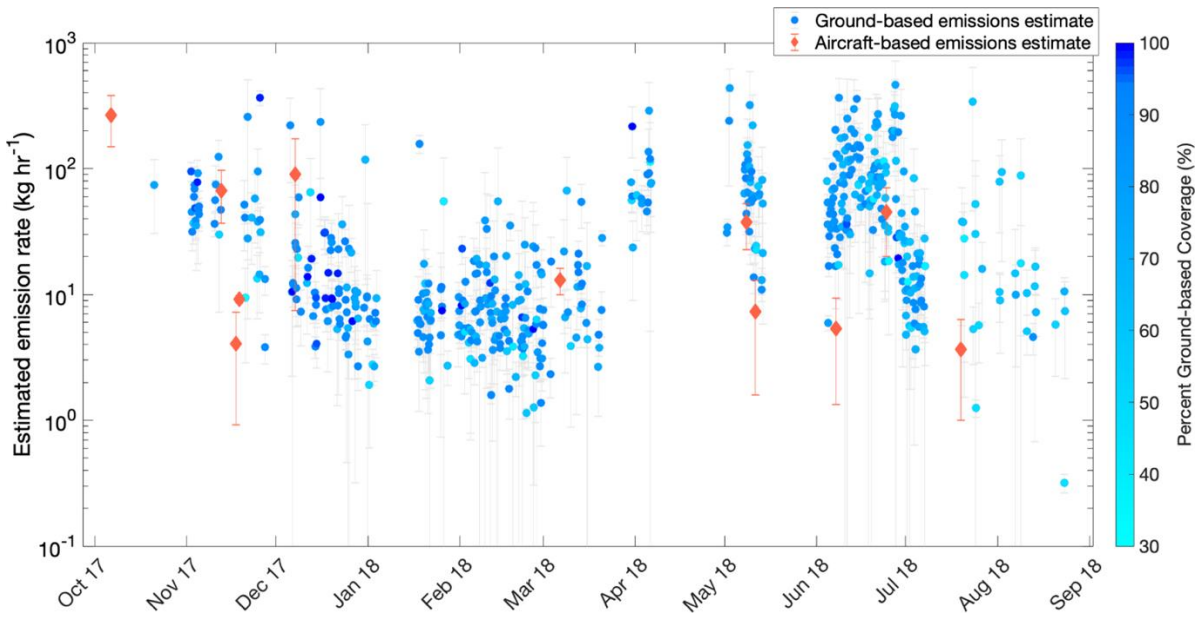
Cross-validation of aircraft- and ground-based emissions estimation was additionally performed at a second storage facility, where the aircraft measurements covered a larger area of infrastructure. Comparisons were made by selecting a subset of ground-based measurements that were closest to the date/time of the flight. Measurements from the two platforms did not always fall within 3 hours (such that differences between emission rates due to temporal variability were expected). Despite this drawback, it is evident from the figure below that emissions follow similar trends and expected offsets based on spatial coverage of the two methodologies.



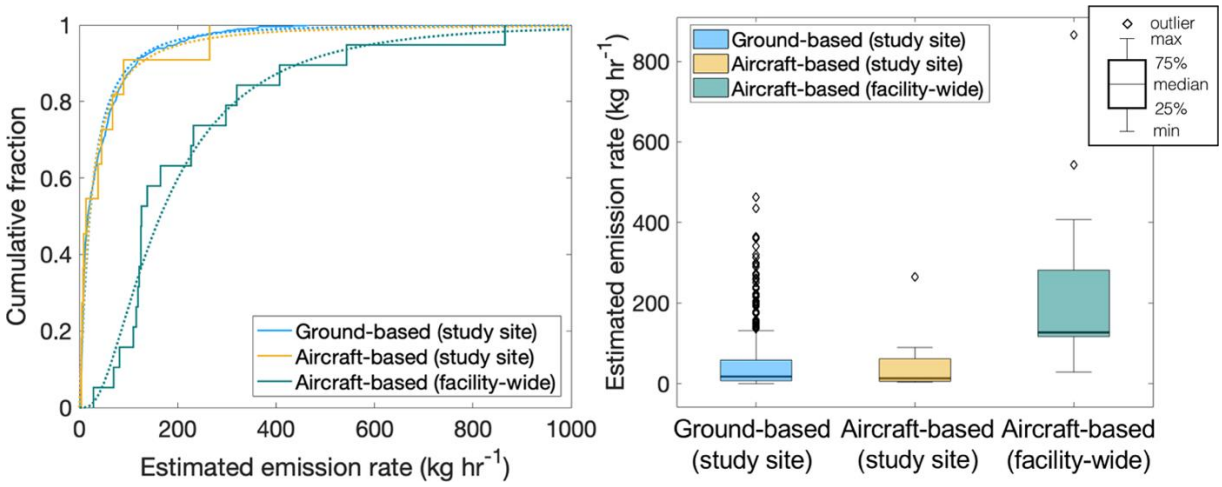
The figure above shows aircraft- (blue circles) and ground-based (orange circles) emissions estimates based on measurements made by both platforms. Aircraft coverage included a central area in addition to wells, and the subset of ground-based measurements selected for comparison covered only the central area.

2. Quantify the time variability (i.e., diurnal-to-seasonal scale emissions and leak frequency) of methane emissions at a variety of underground storage wells and fields through a combination of long-term, temporally and spatially detailed ground-based measurements and aircraft mass balance flights at each ground-monitored site and similar (in size, storage capacity, delivery capacity, facility/infrastructure age, and/or reservoir type) sites. Develop and publish a methane emission inventory that includes quantification of average emissions, seasonal variability of emissions, and leak frequency, through a detailed analysis of data collected at different underground storage wells and fields. This inventory will include scaling relationships to account for site characteristics such as size, storage capacity, delivery capacity, facility/infrastructure age, and/or reservoir type.

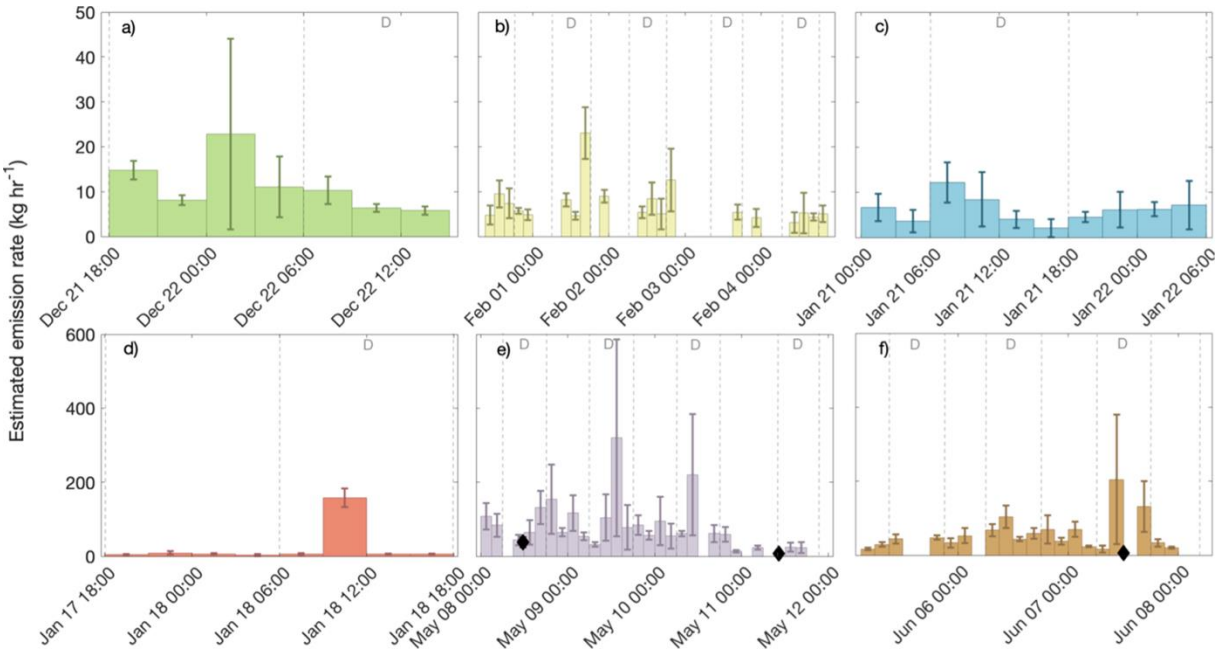
In Alden et al., (2020) (the manuscript described above), we quantified the variability of methane emissions using ground- and aircraft-based methods. Given the high degree of variability observed at the onset of the long-term ground-based campaign, we chose to extend the length of the monitoring period (rather than remove the system to re-station it at a different storage facility).



The figure above shows 3-hourly emission estimates (blue dots) of the ground-based dual frequency comb observing system and aircraft-based mass balance emission estimate (red diamonds) on a log scale. Gradation of color for the ground-based dual frequency comb observing system emission estimates represents the percent of equipment on site covered by observations in each 3 h period (color bar). Uncertainty bars are 1σ.



The 2-panel figure above shows empirical (solid step lines) and fitted (dotted curves) cumulative distribution functions (left panel) for the ground-based rates for the study site (blue), aircraft-based rates for the study site (yellow), and aircraft-based rates for the entire facility (teal). Box and whisker plots showing range, variability, and outliers for the estimated emission rates (right panel) for ground-based rates for the study site (blue, left box), aircraft-based rates for the study site (yellow, middle box), and aircraft-based rates for the entire facility (teal, right box).



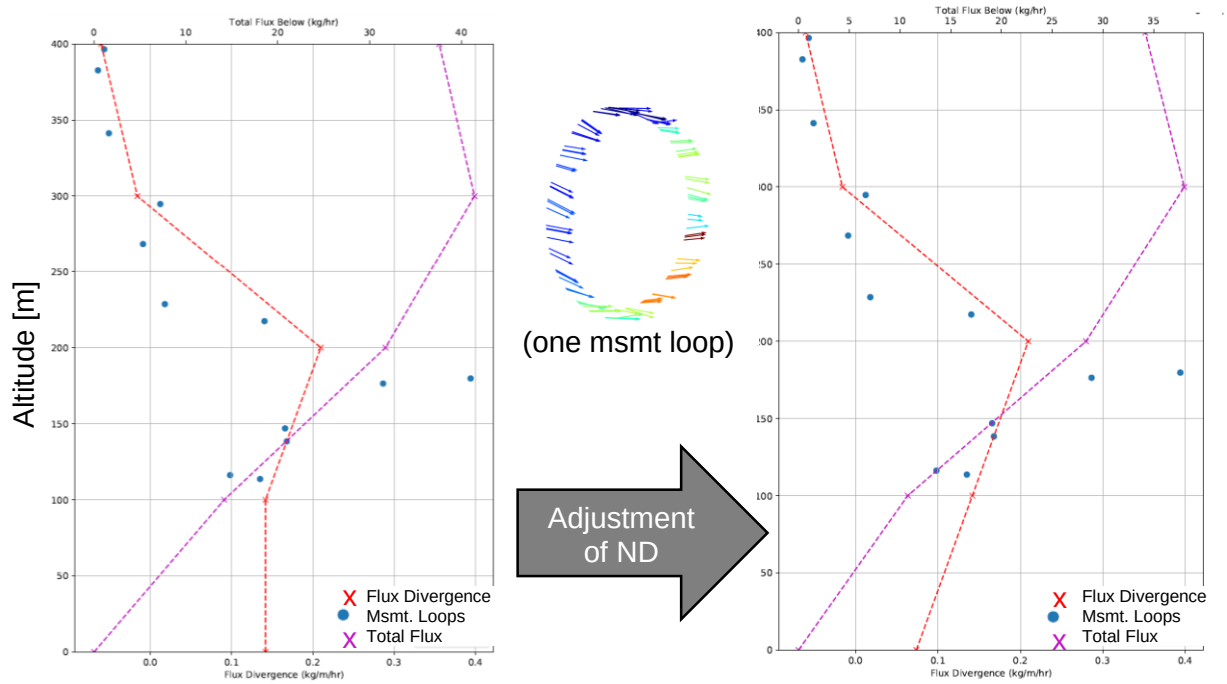
The 6-panel figure above shows ground-based dual frequency comb observing system emission estimates (bars) and aircraft-based mass balance emission estimates (black diamonds) for six time periods. (a−c) show time periods during which the variability in 3 h estimated emission rates is low, compared with time periods shown in (d− f) in which variability is high. Note the change in the y-axis from (a−c) to (d−f). Uncertainty bars are 1σ, and the width of each bar is 3 h. Dashed vertical gray lines distinguish day (6:00−18:00, labeled "D") from night.

Finally, an additional manuscript will be submitted soon to *Applied Optics*, with the author list and title: S. Coburn, C. Alden, R. Wright, G. Wendland, A. Rybchuk, N. Seitz, I. Coddington, G. Rieker, "Long distance continuous methane emissions monitoring with dual frequency comb spectroscopy: deployment and blind testing in complex emission scenarios". This work also demonstrates emission rates from underground storage facilities and hourly variability.

3. Collect new aircraft-based micrometeorological measurements and use them to improve models for how emissions are transported across and from natural gas storage fields. The models will improve the ability to locate and size above-ground methane emissions from ground and aircraft methane measurements at underground natural gas storage wells and fields. Micrometeorological measurements will also be used for validation of atmospheric modeling. The metrics for success in meeting this objective include LES model validation, or the demonstration of model improvement and/or model confirmation with aircraft-based atmospheric and meteorological observations. Increased scientific understanding of the advantages of including new micrometeorological observations will be gained as part of the model validation effort. Such metrics will serve as important contributions to the existing scientific knowledgebase.

New measurements and new methodologies were developed to improve models used in interpreting aircraft-based measurements for emissions estimation. In particular, past work had demonstrated methods to select the optimal non-dimensional distance (ND) at which aircraft mass

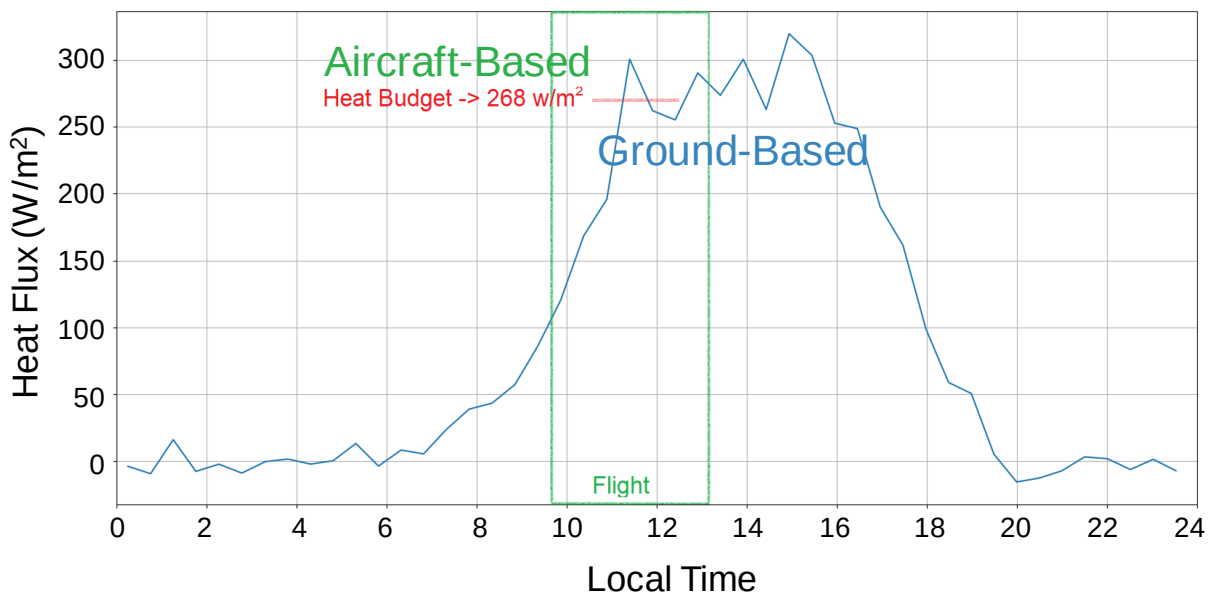
balance flights should be located with reference to the measured source area. Generally, an optimal ND of 0.4 was previously shown to balance the horizontal flux divergence to be roughly constant from the lowest flight leg to the ground level. However, this method required many assumptions to be made if direct measurements of turbulence were not possible.



The figure above shows how, by estimating and adjusting for non-dimensional distance, emission estimation can be improved. On the left, a constant flux to the surface below the lowest flight circle is assumed. On the right, ND is >0.4 and the slope of the flux in the lowest bins is consistent with a further than optimal measurement. Here, the slope is extrapolated to the surface, which affects the emission estimate. Improvements of up to 40% were shown in this work.

This work was published in: Caputi, S. D. Meteorological Conditions Surrounding California's Central Valley High Ozone Events: An Integrative Approach. Ph.D. Dissertation, University of California Davis, 2019.

Separately, two independent methods for estimating convective velocity scale and heat flux, important micrometeorological parameters, were validated. Excellent agreement was shown between the aircraft- and ground-based estimates using the scalar budget method (see figure below).



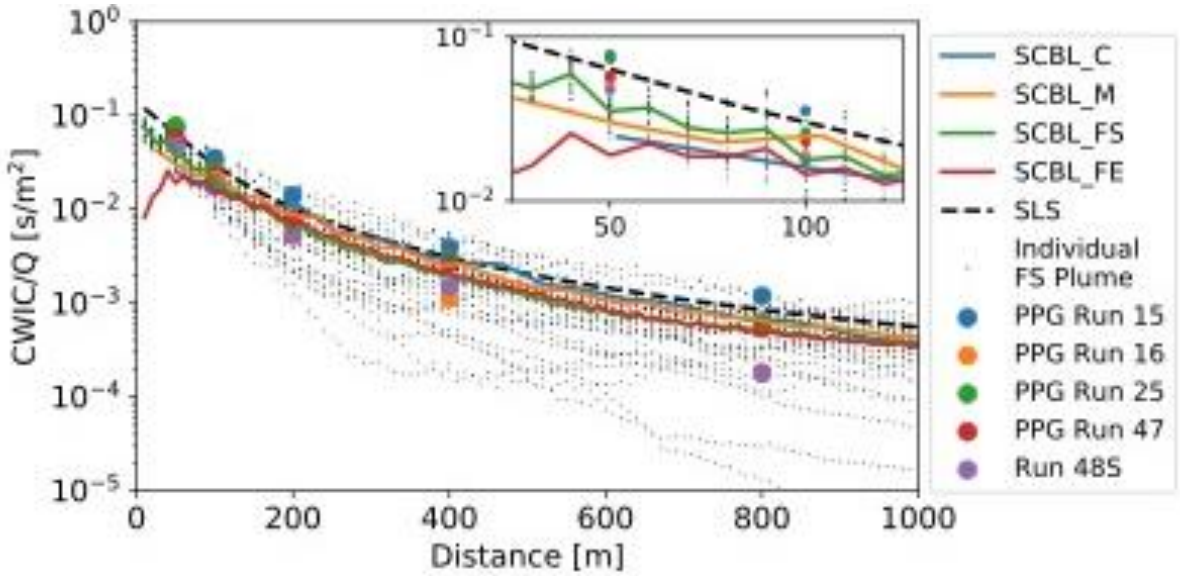
In the above figure, the blue curve is a time-series of the surface heat flux as measured by a sonic anemometer on the ground. The scalar budget method from the aircraft estimated a heat flux of 268 W/m^2 during this flight, which showed excellent agreement with the sonic anemometer data from the same time period.

Additional LES validation is discussed in the final objective 4 (below).

4. Integrate ground- and aircraft-based observations at co-located measurement sites. The ground-based methods will generate highly sensitive, temporally and spatially resolved estimates of methane emissions at several sites over long periods (i.e., emissions explicitly delineated by location and time within the storage field). Modeling of emissions from the ground- and aircraft-based measurements of the same site at the same time will enable characterization of uncertainties and biases among methods and will be used to improve the fidelity of subsequent aircraft sampling at a large number of sites. Metrics for success in meeting this objective will include demonstration of model ability to incorporate data from one or all measurement platforms (i.e., aircraft or ground-based) into a single inversion for storage site emissions. The success criteria will include the determination of *a posteriori* emissions uncertainties, particularly with respect to data inclusion and exclusion and to comparison of methodologies. A major advantage of this effort is the gain of new scientific and technical knowledge regarding the capabilities and uncertainties inherent in the ground-based, aircraft-based, and combined emissions estimation techniques.

A test platform was built for the integration of ground- and aircraft-based measurement approaches into a single model framework, using WRF-LES modeling of emissions. As a necessary precursor step, an extensive validation was undertaken of the use of the WRF-LES model for simulation of emissions near the ground in various (strongly convective, weakly convective, neutral) boundary layer conditions. This work demonstrated important strengths and critical limitations of WRF-LES for the assessment of ground- and aircraft-based emissions estimation methods.

That work is accepted and in proof for publication in *Monthly Weather Reviews*: A. Rybchuk, C. Alden, J.K. Lundquist, G. Rieker, “A Statistical Evaluation of WRF-LES Dispersion Against Project Prairie Grass”.



In the figure above, strongly convective boundary layer (SCBL) observations from the Project Prairie Grass (PPG) field campaign and WRF-LES model predictions (C, M, FS and FE refer to course, moderate, fin-surface and fine-elevated simulations) show good agreement for a horizontal array of concentrations downwind of a point source. Cross-wind integrated concentrations (CWIC) per flux (Q) are shown with distance downwind from the source. Ensemble-average LES concentrations are shown as solid lines. Surface Layer Similarity theory (SLS) concentrations are calculated using $u*$ and L from SCBL_FS.

The next step of the WRF-LES modeling is to simulate synthetic dual frequency comb (ground-based) and aircraft mass balance estimates of emissions. This work will be published under the working author list, title and journal of: A. Rybchuk, C. Alden, I. Faloona, J.K. Lundquist, G. Rieker, "LES-Simulated Trace Gas Emissions Estimates from Concurrent Ground-Based Lasers and Aircraft Measurements", currently In Prep for submission to *Environmental Science & Technology*.