Data
Models
Inventories

PARIS

Process Attribution of Regional Emissions

GA 101081430, RIA

In-situ methane isotope and ethane sampling established at SOAR

Milestone 14			
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Horizon Europe Cluster 5: Climate, energy and mobility
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1. Changes with respect to the DoA (Description of the Action)

N/A

2. Dissemination and uptake

The results of this milestone will be of direct use to partners within PARIS involved in subsequent WP4 tasks, using high-frequency CH_4, C_2H_6 and $\delta^{13}C(CH_4)$ observations for model–data comparisons and regional inversions for methane source apportionment. The continuous in-situ dataset being produced at SOAR (also designated as IVG) strengthens the spatial coverage of ethane and isotope observations in the UK, enabling improved constraints on fossil-fuel methane emissions in subsequent project tasks. The deliverable will also be integrated into dissemination activities such as conference presentations future peer-reviewed publications addressing improvements in methane source attribution through combined ethane and isotope measurements.

3. Short Summary of results

Close collaboration between the University of Bristol and National Physical Laboratory has resulted in the deployment of an Aerodyne TILDAS-FD-142 to the SOAR tall-tower site (designated IVG) located in Invergowrie, near Dundee, in November 2025, for the purpose of the measurement of methane isotopologues ($^{12}CH_4$, $^{13}CH_4$), ethane (C_2H_6) and calculated methane isotope ratio ($\delta^{13}C$). Long-term precisions for CH_4 and C_2H_6 are in the range of 0.1-0.3 ppb and 10-20 ppt respectively and are dependent on temperature fluctuations between day and night. These values are directly comparable to or better than studies carried out with similar absorption spectrometers (Kostinek et al., 2019; Commane et al., 2023). These values agree with tests prior to deployment. For $\delta^{13}C(CH_4)$, precisions are reported in the range of 0.61-1.5 ‰ which are useful for resolving atmospheric variability in the measurements larger than 10 ‰. Collaboration with the instrument manufacturer is still in progress to ascertain an improvement to this precision.

A preliminary intercomparison was performed against a high-precision reference instrument for CH_4 operating simultaneously with the Aerodyne TILDAS at site. Due to differences in the traceability of the working standard gases the TILDAS generally underrepresents amount fractions with a more noticeable effect at higher amount fractions. This can be corrected in historical and subsequent data. More intercomparisons are scheduled within the next 3-6 months and are dependent on the expected dates of deploying the relevant instruments.

4. Evidence of accomplishment

4.1 Introduction | Background of the milestone

The composition of stable carbon isotopes in emitted atmospheric methane (CH_4) is determined by different microbial, pyrogenic and fossil fuel production mechanisms. These processes cause both carbon and hydrogen in CH_4 to undergo various isotopic fractionation effects which are quantifiable by the relative abundance of heavy $^{13}CH_4$ to light $^{12}CH_4$ isotopes in a sample compared to a standard. This makes resolved isotope ratios a useful tool in the disaggregation of anthropogenic CH_4 emissions. Overlaps in these source signatures between categories can introduce difficulty when attributing sources to a measured plume. Trace gases are used to aid source apportionment as they provide an extra dimension of constraint. Ethane (C_2H_6) is one such gas, emitted predominantly by gas distribution in distinct ratios to CH_4 and thus is used as a vector to constrain fossil fuel methane. Recent work by Ramsden (2022) demonstrates that incorporating atmospheric C_2H_6 measurements into methane inversions substantially improves the ability to quantify UK fossil-fuel CH_4 emissions. Results from these simulated tests in the UK region suggest ethane reduces posterior fossil-fuel CH_4 uncertainties by ~15%

on average and up to 35% compared with CH_4-only inversions. Expanding the spatial coverage of C_2H_6 observations would further improve constraints by providing additional information on regional variations in the ethane:methane emission ratio and refining spatial separation between fossil-fuel and biological CH_4 sources. Therefore, more spatially distributed C_2H_6 measurements enhance the inversion's ability to characterise spatial heterogeneity, reduce dependence on prior assumptions, and improve propagation of uncertainty in the emission ratio hyperparameter.

In this report, we show preliminary results from the recent deployment of a new laser absorption spectrometer, measuring methane isotopologues ($^{12}CH_4$ and $^{13}CH_4$) and C_2H_6 for the purpose of enhanced spatial coverage of ethane emissions and improved source apportionment. These new measurements will be integrated into the inversion modelling systems at a later stage in the project, which will allow estimates of ethane emissions from fossil and non-fossil source categories.

4.2 Scope of the milestone

This milestone will demonstrate installation at the SOAR research station (IVG) in Invergowrie, Scotland in November 2025.

4.3 Content of the milestone

Significant work was undertaken to characterize the Aerodyne TILDAS and develop a sampling methodology for deployment to Invergowrie and is detailed in the M13 report. To summarise, the instrument is operated by a combination of TDLWintel software for spectral acquisition and GCWerks for automated run sequencing. Resulting measurement data is synced to a remote server operated by the University of Bristol ACRG group where a series of Python scripts periodically calibrate and drift-correct the data. This data is planned to be made available to partners after quality control through comparison with similar measurements across the UK tall tower network. The data is not yet publicly available.

Short-term stability testing was repeated after deployment to the SOAR tall-tower site, carried out using Allan-Deviation as a statistical measure, allowing the characterization of noise behaviors over different averaging times (τ). This was to compare performance during lab testing to real operational performance at site. Briefly, a calibration gas with known ambient amount fractions for each species is expanded into the cell and held to be measured for ~6 hours. The square-root of the mean-squared difference between adjacent time-averaged measurements is calculated on the raw data and plotted on a log-log scale against averaging time to identify dominant noise sources. Fig.1 shows the Allan-Deviation analysis carried out for $^{12}CH_4$, $^{13}CH_4$ and C_2H_6 respectively. The performance of the instrument is limited by the presence of "flicker noise" indicated by the black dashed line, which is an expected characteristic and prevalent in all frequency sources such as mid-IR lasers. The averaging times applied to the measurements are given in Table 1, alongside the corresponding short-term noise for each species. The precision analysis shows that each species reaches a well-defined minimum with optimal averaging times ranging from 30s to 190s dependent on species. Raw $^{13}CH_4$ amount fraction and precision is reported at ~95x the true atmospheric value owing to its rarity in ambient air as compared to $^{12}CH_4$. After calibration, the equivalent short-term precision is proportionally smaller than the reported raw value at ~4.6 ppt. The short-term precisions reported here are once again comparable to studies published utilizing similar laser absorption instrumentation (Kostinkek et al., 2019; Commane et al., 2023). Here, short-term precisions across all species are on par with or better than that which was achieved during laboratory testing.

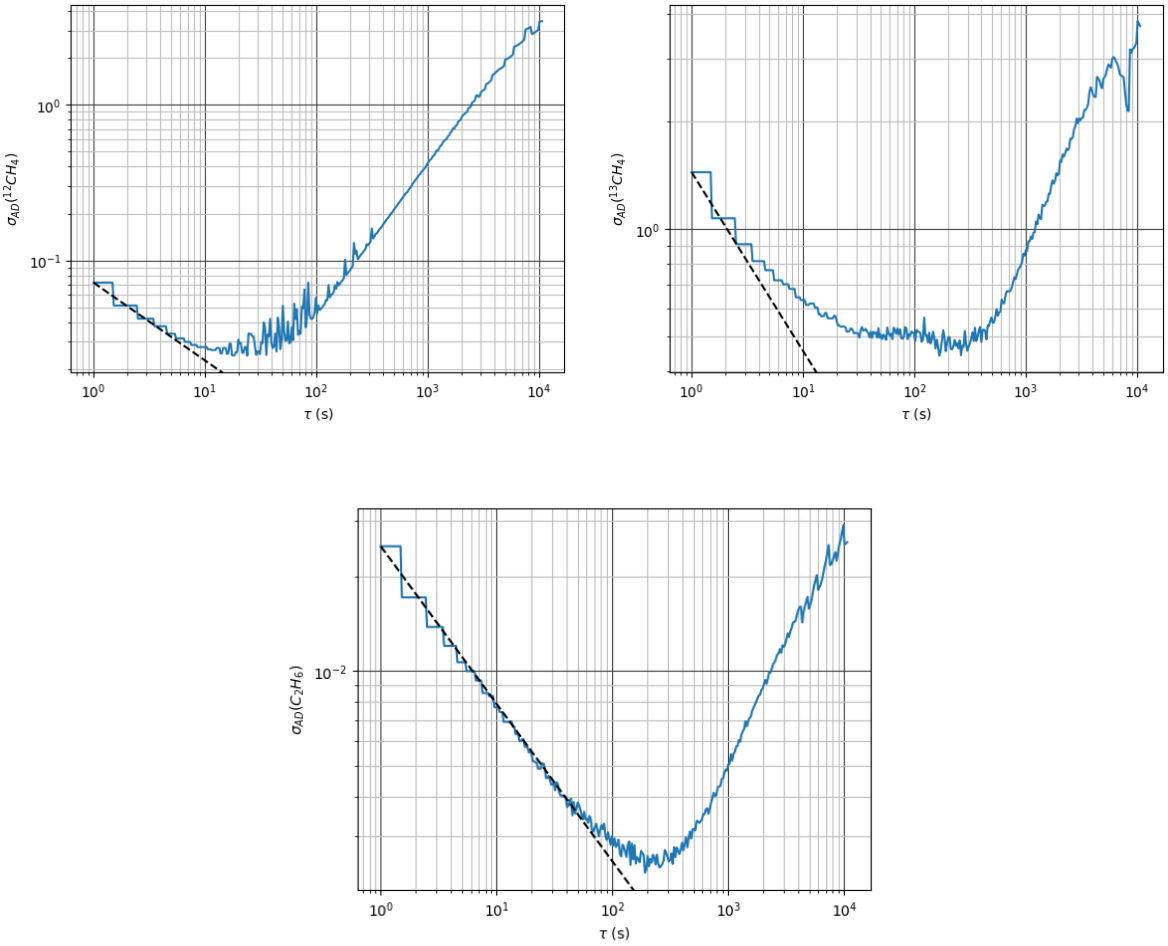

Fig. 1: Allan-Deviation plot for carbon-12 methane (upper left), carbon-13 methane (upper right) and ethane (lower centre). The minimum of the curve (blue) represents the optimal averaging time and corresponding short-term precision. The dashed black line denotes flicker noise as the dominant noise type.

Table 1: Optimal averaging time per measurement period applied to the methodology. The minimum AD at the corresponding averaging time gives the short-term precision, encompassing all noise sources.

Species	Optimal averaging time τ (s)	Minimum σ(AD)
$^{12}CH_4$	30	0.02 ppb
$^{13}CH_4$	60	0.44 ppb
C_2H_6	190	2.3 ppt

Fig. 2 gives the calibrated and drift-corrected timeseries for the instrument stationed at Invergowrie. A noticeable drop in performance is noted from 16/12/2025 onwards due to maintenance carried out on the instrument. This is attributed to temperature changes pertaining to the disruption of temperature control within the field enclosure while opened for maintenance, after which the instrument is subject to a period of thermal stabilization for ~2 weeks. Here, worsening precisions in the calculated isotope ratio is attributed to the sensitivity of the $^{13}CH_4$ absorption line as compared to that of $^{12}CH_4$, making it considerably more sensitive to pressure or temperature broadening effects during spectral acquisition. Hence, changes in these variables affect the absorption lines disproportionately and are exasperated by the ratio within the calculation of δ^{13} C(CH_4). Communication with the instrument manufacturer is ongoing to resolve precision issues. However, the performance of the individual species is within expectations.

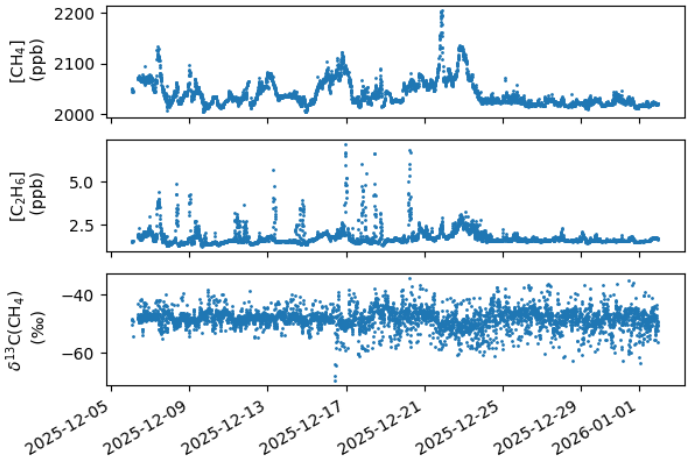

Fig. 2: Calibrated and drift-corrected timeseries data for methane (upper), ethane (centre) and carbon-13 isotope ratio (lower). Performance issues are noted from 16/12/2025 onwards after instrument maintenance was performed and which serve as an example of the thermal stabilization period needed after maintenance is performed.

The long-term precisions are calculated by evaluating the 4-hour rolling standard deviations of a calibrated tank of whole air. We report the long-term precisions of each species as follows:

- CH_4: ~0.1-0.3 ppb
- C_2H_6: 10-20 ppt
- $\delta^{13}C(CH_4)$: 0.61-1.5 ‰

The range of values encompasses the precisions experience due to natural variation in temperature between the day and the night. Here, amount fraction measurements are sufficient for evaluating measurements from background to large enhancements. Enhancements in the isotope ratio above 10 ‰ are expected to be resolved reliably at this stage which correspond to the attribution of major source categories (microbial, fossil fuel). We expect an improvement in this outcome after a full review in collaboration with the instrument manufacturer which is still ongoing. However, the instrument continues to make useful high-precision, high-frequency amount fraction measurements of CH_4 and C_2H_6.

At the time of submission of this report, the SOAR tall-tower site houses three instruments: the Aerodyne TILDAS, a Picarro G2401 (CRDS) and a Picarro 5310 (CRDS). The Picarro G2401 takes minute-averaged measurements of CH_4, carbon monoxide (CO) and water vapour (H_2O), and was chosen to perform a preliminary intercomparison against the Aerodyne to assess their agreement of CH_4 amount fraction within their known limitations. The result is detailed in Fig. 3. In general, the Aerodyne TILDAS underestimates amount fraction with an average bias of ~10 ppb across the full reported concentration range. This bias is attributed to a combination of scale difference between instruments and poor matching of measurement timestamps between instruments owing to the complex nature of sampling with the Aerodyne.

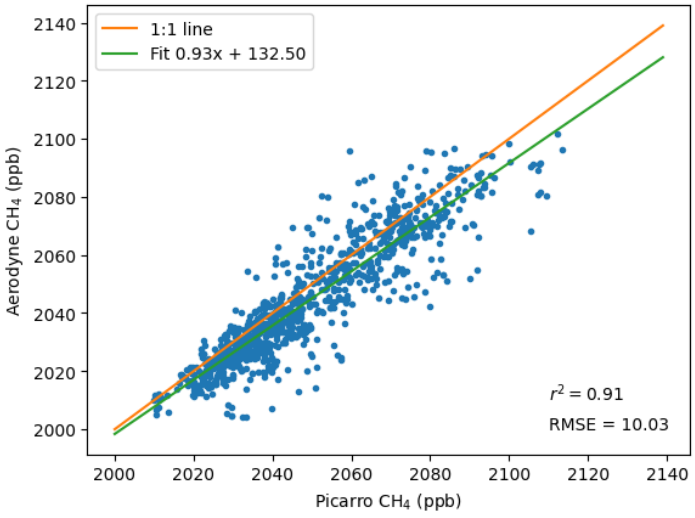

Fig. 3: Comparison of measurements made by the Aerodyne TILDAS system (y-axis) and the Picarro G2401 system (x-axis).

This result can be used to correct historical and subsequent data. Despite this, the TILDAS shows good agreement ($r^2 = 0.91$) with the reference instrument. This work is ongoing as validation needs to be carried out for C_2H_6 and $\delta^{13}C(CH_4)$ which is constrained by the deployment of the relevant reference instruments to site. This is expected to be carried out within the next 3-6 months.

We expect to make the dataset publicly accessible after one-year of data has been procured via publication and upload to a database such as the ICOS

Carbon Portal. This is to ensure the dataset will be substantial enough to determine variables such as seasonality and to allow for a thorough validation, not only for CH_4 but against other instruments for C_2H_6 and $\delta^{13}C(CH_4)$.

4.4 Conclusion and possible impact

The deployment and initial characterization of the Aerodyne TILDAS at the SOAR site represents a significant step toward expanding high-frequency, in-situ capability for CH_4 isotopologues and C_2H_6 measurements. The instrument has demonstrated strong short- and long-term performance for CH_4 and C_2H_6, and although challenges remain for $\delta^{13}C(CH_4)$ precision, these are understood and currently being addressed in collaboration with the manufacturer. The system is fully operational and already producing high-frequency amount fraction data suitable for regional emissions modelling.

The new dataset will enable improved inversion constraints on fossil-fuel versus microbial methane sources in the UK, directly supporting the project's goal of advancing process-level attribution of emissions. The expanded spatial coverage of ethane will enhance the robustness of inversion frameworks by supplying an additional tracer for distinguishing fossil-fuel contributions. The deployment demonstrates contributes valuable evidence to ongoing efforts to harmonize mid-IR spectroscopic techniques across laboratories and supports improved national greenhouse-gas inventories. Three publications are expected to be made based on the use of this dataset as part of a PhD project at the University of Bristol, including the publication of a one-year timeseries and the use of the dataset in an inversion study investigating the effects of spatially-improved ethane observations on inversion-modelled uncertainties as compared to synthetic tests carried out by Ramsden (2022).

4.5 References

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5. History of the document

Version	Author(s)	Date	Changes
1.0	Yeo, Ganesan, Rennick	25 January 2025	First draft