PARIS

Process Attribution of Regional Emissions

GA 101081430, RIA

High-frequency CH_4 isotope measurements uploaded to ICOS portal

Deliverable D4.1			
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Lead beneficiary: UEDIN	Work package: 4	Nature: Report	Dissemination level: PU
Responsible scientist	T. Arnold (UEDIN)		
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Internal reviewers	S. Walter (UU)		
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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)

The deliverable, belonging to WP4, was due in project month 14. Due to technical reasons some measurements and consequently the upload of data sets was delayed but with no significant impact on the overall tasks.

2. Dissemination and uptake

This deliverable will be of interest to many atmospheric scientists outside the project working on using isotope ratios to understand methane (CH_4) at the European level.

The data has been presented and curated in a way to allow open access through the ICOS Carbon Portal using standardized nomenclature and building on the quality control procedures developed to bring confidence to the dataset.

Within PARIS the new datasets are going to be combined with the network of amount fraction measurements to improve the top-down estimation of emissions from the three main sectors (agriculture, waste and energy).

3. Short Summary of results

One of the aims in WP4 was to create new datasets of stable isotope ratios of methane for input into emissions estimate calculations. Stable isotope ratios help to discern the different sources of methane that contribute to elevated amount fractions at the atmospheric observatories.

This specific deliverable is aimed at making the dissemination of robust datasets for atmospheric scientists to use with confidence. To this aim, the available and ongoing independent datasets have been studied together to assess data quality and comparability. So far data from the Heathfield (UK) and Cluj (Romania) deployments have been packaged into a dataset submitted to the ICOS Carbon Portal and published. We have also published from deployments prior to PARIS to enable these to be used within the same analysis frameworks.

This deliverable report includes work from milestones M12 - Mobile-platform continuous methane isotope measurement campaigns, and M15 - Quality control previous calendar year of methane isotopologue data.

4. Evidence of accomplishment

The digital object identifiers of the dataset at the ICOS Carbon Portal are available here: https://doi.org/10.18160/NXYQ-Y64M. Outputs from the processes leading to this upload of all datasets is provided in section 4.3.

4.1 Introduction | Background of the deliverable | milestone

Methane is emitted to the atmosphere from a complex mixture of sources. There is a focus of PARIS to focus on the use of atmospheric observations of methane isotopic composition ($\delta^{13}C$ and δD) to derive sector-specific flux estimates. Methane emissions in Europe are dominated by anthropogenic sources, primarily agriculture, fossil fuel extraction and use, and waste.

In some countries, one of these sources dominates (e.g., agriculture in Switzerland and Ireland). However, for others (e.g., the UK, Netherlands, and Germany), all three contribute, in ratios that change with time. In these countries, it is difficult to discern the causes of differences with inventory estimates because traditional top-down approaches typically only quantify total emissions.

Measurements of the isotopic composition of methane have the potential to improve our understanding of methane emissions, because different sources emit methane with source-specific stable isotope ratios. Consortium partners have started the first high-frequency $\delta^{13}C$-CH4 and δD-CH_4 observations at European sites, using both isotope ratio mass spectrometry (GC-IRMS) and novel laser-based approaches which have demonstrated that these measurements allow evaluation of regional emission inventories.

PARIS proposed to expand isotope monitoring capabilities across the focus countries using these measurement techniques. In this deliverable report we document the steps taken to make the first submissions of the new datasets to a publicly accessible archive.

4.2 Scope of the deliverable | milestone

High quality datasets of isotope ratio measurements are needed to improve the understanding of atmospheric methane. Further, for inversion models to use the new measurements effectively and ingest the data efficiently, the measurements need to be compiled in a common format. This format should be devised in a way to improve the usability of the measurements, prevent misunderstandings regarding the nature and uncertainty of measurement, and to be able to combine the datasets for single model inversions.

1. Data collection: To measure in-situ atmospheric isotope ratios of methane quasi-continuously at a frequency of a single measurement every 1-2 hours. These measurements are based on published procedures to ensure continued instrument calibration and drift corrections (see Rennick et al, 2021 and Menoud et al., 2020).

2. Data processing and quality control: The instrument software collects raw data and offline data processing scripts convert this to final isotope ratio values based on calibration factors. All files produced are .csv format.

3. Data documentation: data is documented on the ICOS Carbon Portal website. Details include site location and time period, calculated uncertainties of individual measurements and contact information for the data providers.

4. Data formatting and standardization: data is provided as .csv files using ICOS format for missing values. Metadata is included in the file header.

5. Data submission to ICOS Carbon Portal database: Observation data files are submitted to the ICOS Carbon Portal database following submission procedures and requirements.

6. Accessibility and data sharing: The submitted meta isotope ratio observation data is fully accessible to the public, including stakeholders and the broader scientific community, through the ICOS Carbon Portal. Researchers considering data analysis and publication must contact the data owner(s) before use.

4.3 Content of the deliverable | milestone

High-frequency measurements of $\delta^{13}C$-CH^4 and δD-CH^4 are continuing at Heathfield under PARIS and data has been uploaded to the ICOS Carbon Portal following a period of analysis and development of quality procedures (see Fig. 1 for the complete data set of stable isotope ratio measurements from 2021 to 2024). Some gaps in the timeseries have occurred due to instrument component failures. The most recent breakdown occurred early in 2024 when a trap overheated and destroyed the packing material used to trap methane from large sampling volumes. This was replaced, however, owing to the different properties of the new trap some time was needed to understand how well it was functioning and to optimise the methane trapping and elution.

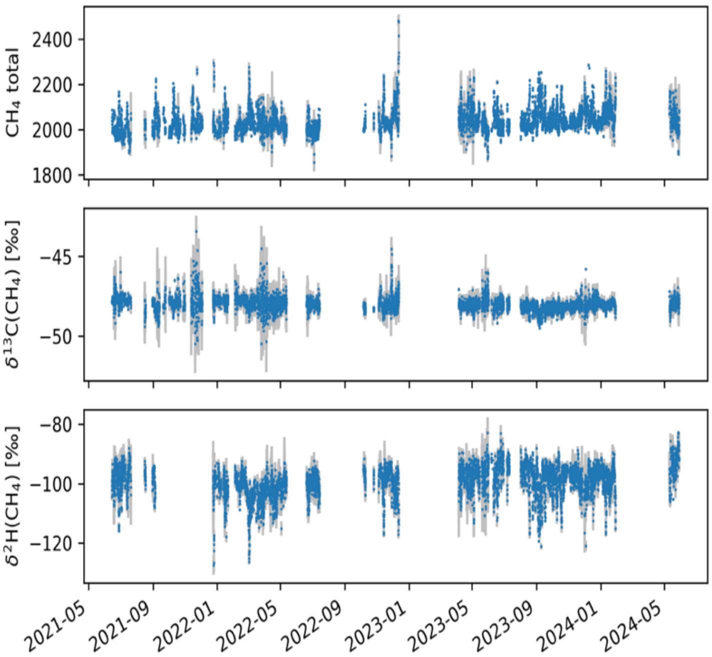

Fig. 1: Showing results from Heathfield of stable isotope ratios and amount fractions of methane, following developed quality procedures. These data are in the process of being uploaded to the ICOS Carbon Portal for dissemination.

A GC-IRMS was deployed at Cluj (Romania) from the start of PARIS, January 2023, however, prior to this several other European locations were explored. This data is used to investigate the emissions in several locations throughout Europe. The obtained data will be used in the Paris project for comparison with other systems. This included Cabauw, Lutjewad, Krakow, Hamburg, and Cluj. Following deployment to Cluj the GC-IRMS system was due to go to the Hungarian site Hegyhátsál (HUN), however, technical problems prevented the start of measurements and since the instrument has been under repair ready for deployment to Monte Cimone (Italy).

A first 'data meeting' was conducted for instruments run by project participants Utrecht University and Edinburgh University with all data presented within the same software GCCompare (see Fig. 2 below that allows measurements to be compared efficiently on the same flexible visual output). NPL as associated partner was invited for sharing data and experience.

The meeting highlighted a need for improvements in harmonization needed between datasets, particularly in the traceability for calibration, which is a known issue in the measurement of methane stable isotope ratios by separate groups. Nonetheless, these calibration 'offsets' don't prevent dissemination of the data while a solution is found on harmonizing all measurements across institutes.

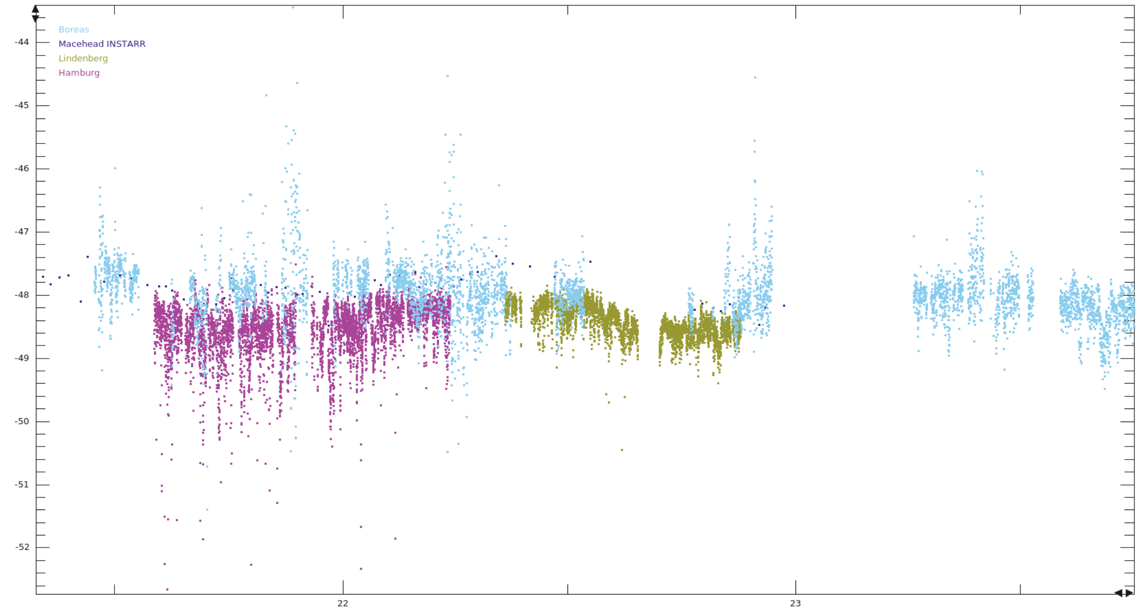

Fig. 2: GCCompare output for comparison of data that will be used in the PARIS project – Boreas (Heathfield optical measurements run by NPL/Edinburgh University), Mace Head (NOAA/INSTAAR flask measurements) and Lindenberg (most recent Utrecht University mass spectrometry in situ measurements)

Following the qualitative comparison of datasets a final data flagging a processing protocol for the Heathfield optical data was finalized (Fig. 3). This was written in Python and allows for the code to be rerun following any changes in values assigned to standards and for the same methods of processing to be applied across a timeseries as it continues to grow. Finally, the data was processed into csv files for upload to the ICOS Carbon Portal.

Our efforts for curating the isotope ratio datset follow the FAIR principals:

Findability: The dataset can be accessed via the ICOS Carbon Portal database. Users can locate the dataset by specifying δ^{13}CH4 in the ICOS carbon portal data search function. This is also easily found in the drop-down menu. The PARIS website also links to the data sets on the ICOS carbon portal.

Accessibility: The dataset is publicly accessible through the ICOS Carbon Portal database, ensuring that stakeholders and the broader scientific community can easily access and utilize the data for their research and applications.

Interoperability: The dataset is formatted into standardized .csv files using the ICOS data format, facilitating interoperability with other datasets and platforms. We standardize this output across many sites and measurements from two different research groups utilizing distinct methods

Reusability: The dataset includes a calculation of uncertainty and a description of how this is calculated, providing a comprehensive view of the observed atmospheric methane isotope ratio measurements.

Following the data quality and processing procedures developed by the teams in the project, the other datasets are due for upload to the ICOS Carbon Portal in the coming years.

```
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# HEADER LINES: 43
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# data_owner = Chris Rennick; Tim Arnold
# data_owner_email = chris.rennick@npl.co.uk; tim.arnold@ed.ac.uk
# inlet_height_magl = 100.0
# comment = Methane isotope ratio and amount fraction from Boreas preconcentrator and laser spectrometer. datetimeISO represents the start of an integrated sample of air, collected for the
duration given in the sampling_duration column, which is subsequently processed and measured by a laser spectrometer in situ. The reported uncertainties of d13c_ch4_standard_deviation and
d2h_ch4_standard_deviation are the standard deviation of approximately four samples of a compressed air working standard treated in an identical manner to the air sample. These measurements
are taken within 12 hours of the air sample measurement and are also used to correct for short term instrument drift. Full sampling, sample processing, detection and calibration procedures
are provided by Rennick et al., 2021 https://doi.org/10.1021/acs.analchem.1c01103. As described in Rennick et al., 2021, for d13C measurements traceability to the VPDB scale is via
measurement of the the compressed air standards by Royal Holloway, University of London. The mole fraction data reported here is from the the isotope ratio spectrometer given for purposes of
anaytical interpretation. For methane modelling purposes please refer to the methane amount fraction data measured simultaneously by a separate high precision instrument and published
separately via WDCC or ICOS obspacks.
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Fig. 3: Header information submitted alongside the isotope ratio measurement data of >12,000 new measurements from the Heathfield tall tower in the UK from June 2021 to June 2024.

4.4 Conclusion and possible impact

The groups creating these new datasets have worked together towards a common reporting format. More work is needed to fully harmonise the measurements, particularly for the hydrogen isotope ratio measurements where robust traceability chains for standards for instrument calibration are lacking. These datasets provide the first widely available output of ambient air measurements of isotope ratios of methane within Europe. The aim is now for these measurements to be taken up by the project's inverse modelling teams. We will also make sure that other projects know of the new datasets for use in their own emissions calculations. We will do this by including reference to the uploaded data in our own publications in preparation and during conferences such as the European Union General Assembly that are attended by many scientists in this research area.

4.5 References

Rennick, C., T. Arnold, E. Safi, A. Drinkwater, C. Dylag, E. M. Webber, R. Hill-Pearce, D. R. Worton, F. Bausi, and D. Lowry, Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision In Situ Analysis of δ13C and δ2H from Ambient Air Methane, Analytical Chemistry, 2021. doi: 10.1021/acs.analchem.1c01103

Menoud, M., van der Veen, C., Scheeren, B., Chen, H., Szénási, B., Morales, R. P., … Röckmann, T. (2020). Characterisation of methane sources in Lutjewad, The Netherlands, using quasi-continuous isotopic composition measurements. Tellus B: Chemical and Physical Meteorology, 72(1), 1–20. https://doi.org/10.1080/16000889.2020.1823733

5. History of the document

Version	Author(s)	Date	Changes
1.0	T. Arnold, J. v. ES, C. Rennick, S. Defratyka, E. Chung	18th June 2024	First set-up
1.1	T. Arnold	19th September 2024	Updated following submission of multiple datasets to the CP
1.2	T. Arnold	17th Oct 2024	Update links to Carbon Portal
		November 2024	Feedback rounds report
1.3	T. Arnold	5 Dec 2024	Improvements to align descriptions with deliverable.
		January 2025	Feedback rounds report
	S. Walter	21 January 2025	Finalise and upload