Data
Models
Inventories

PARIS

Process Attribution of Regional Emissions
GA 101081430, RIA

Methane isotope source signatures uploaded to ICOS portal

Includes work from milestones M12 (Mobile-platform continuous methane isotope measurement campaigns) and M15 (Quality control previous calendar year of methane isotopologue data)

Deliverable D4.2			
Delivery due date Annex I	PM 14 | 28 February 2024		
Actual date of submission	16 December 2024		
Lead beneficiary: UEDIN	Work package: 4	Nature: Report	Dissemination level: PU
Responsible scientist	T. Arnold (UEDIN)		
Contributors	J. van Es (UU), T. Röckmann (UU)		
Internal reviewers	S. Walter (UU)		
Version: 1			

Horizon Europe Cluster 5: Climate, energy and mobility
"This project has received funding from the European Union's Horizon Europe Research and Innovation programme under HORIZON-CL5-2022-D1-02 Grant Agreement No 101081430 - PARIS".

D4.2 – Methane isotope source signatures uploaded to ICOS portal.

Table of content

1. Changes with respect to the DoA (Description of the Action)

Deliverable D4.2 was initially scheduled for submission in project month 14. It was delayed ensuring it was fully interoperable with the continuous dataset. This delay has no significant impact on the overall project tasks.

2. Dissemination and uptake

This deliverable will interest atmospheric scientists both within and beyond the project that work with methane isotope source signature data. The data can be used for comparison with other measurements or as input for atmospheric transport models.

Within PARIS WP4, several groups focus on modelling methane mole fractions and isotopic signatures. For this research, improved source signatures for specific regions will provide them with more accurate isotopic values to assign to the respective emitters that are represented in the emission inventories. This is particularly beneficial for regions where methane source signatures are currently underrepresented in global databases.

3. Short Summary of results

WP4 focuses on investigating methane (CH_4) emissions, using stable isotopes as a valuable tool for source identification. The stable isotopic composition of methane provides insight into its origin. To utilize stable isotopes effectively for source identification, the isotopic signatures of methane sources must be accurately established. This requires direct isotopic measurements of air samples collected from known sources.

Although global databases provide general isotopic compositions for most sources, these values can vary from local isotopic signatures for the same source types.

In Cluj-Napoca, Romania, air was sampled from several known CH_4 sources, including the gas network, a gas station, traffic near a busy intersection, waste, and wetlands. Results showed that the isotopic signatures of the gas station, traffic, and wetlands were consistent with values reported in the literature. However, the isotopic signatures for the gas network and waste sources differed from the established global data, highlighting the importance of localized measurements.

In Debrecen, we sampled several categories that mostly aligned with the global database. We also observed emissions from thermal waters, which were not yet reported in literature.

4. Evidence of accomplishment

The dataset's digital object identifiers at the ICOS Carbon Portal can be accessed here: https://meta.icos-cp.eu/objects/_YoOEP2OSUrbDFovZ3qrWjPG. Details of the processes leading to the upload of all datasets are provided in Section 4.3.

4.1 Introduction | Background of the deliverable

Methane is emitted into the atmosphere from a complex mix of sources. A key objective of the PARIS project is to investigate the methane sources. In Europe, methane emissions are predominantly driven by anthropogenic activities, including agriculture, fossil fuel extraction and usage, and waste management.

The isotopic composition of methane ($\delta^{13}C$ and δD) provides valuable insights into emissions, as different sources emit methane with distinct stable isotope ratios. Consortium partners have initiated the first high-frequency $\delta^{13}C$-CH_4 and δD-CH_4 observations at European sites, utilizing both isotope ratio mass spectrometry (GC-IRMS) and innovative laser-based techniques. These methods have proven effective in evaluating regional emission inventories.

PARIS proposed to expand isotope monitoring capabilities, as detailed in deliverable D4.1. However, to accurately assign isotopic values of an unknown air aliquot to a source (as described in D4.1), the isotopic compositions of local sources must be known. While general isotopic signatures for specific sources are available in the literature, previous campaigns have demonstrated that local values can deviate significantly from these reported values. Consequently, establishing isotopic signatures at new measurement locations is essential for accurate source attribution.

4.2 Scope of the deliverable | milestone

High-quality isotope ratio datasets are essential for improving our understanding of atmospheric methane. To ensure that models can effectively utilize these new measurements, the data must be compiled in a standardized format. This format should enhance usability, prevent misunderstandings about measurement nature and uncertainty, and enable integration of datasets for single-model inversions.

1. Sample collection: Air samples are collected using clean, methane-stable, leak-tight bags near identified sources. Additionally, a background air sample is collected daily for correction.
2. Sample measurements: Each sample is measured in duplicate using a suitable system, consistent with that used for deliverable D4.1. Measurements follow published procedures to ensure proper instrument calibration and correction for potential drift (Rennick et al., 2021, and Menoud et al., 2020).
3. Data processing and quality control: Raw data is collected via the instrument's software. Offline data processing scripts are employed to convert raw data into final isotope ratio values, using calibration factors. The final processed files are generated in `.csv` format.
4. Data documentation: All data is documented on the ICOS Carbon Portal. Documentation includes details such as the calculated uncertainties for each measurement, source type, and contact information for the data providers.
5. Data formatting and standardization: Data is provided in `.csv` format following ICOS standards for handling missing values. Metadata is included in the file headers to ensure clarity and consistency.
6. Data submission to ICOS Carbon Portal database: Observation data files are submitted to the ICOS Carbon Portal database following submission procedures and requirements.
7. Accessibility and data sharing: The submitted isotope ratio observation data is publicly accessible through the ICOS Carbon Portal. This includes access for stakeholders and the wider scientific community. Researchers interested in analyzing or publishing the data must first contact the respective data owner(s).

4.3 Content of the deliverable | milestone

Air sampled near various sources was analyzed for methane isotopic composition as part of the Cluj-Napoca continuous measurement campaign (2023). A total of 102 samples were taken at several potential sources and three background locations. At Utrecht University, we measured the methane mole fraction, δ^{13}C, and δD. Methane emissions were detected in the region near sources such as traffic, the gas network, gas stations (fossil fuel), lakes, and waste sites, including those from water treatment plants and solid waste facilities.

Each source was sampled at least three times; however, not all samples showed methane levels elevated above the background. Samples with CH_4 mole fraction below ambient were omitted. Data from the unique sampling locations were used to calculate source signatures via the Keeling plot approach, resulting in 44 source signatures. The results of these calculations are presented in a dual-isotope plot in Fig. 1. These source signature datasets have been uploaded to the ICOS data portal for public access.

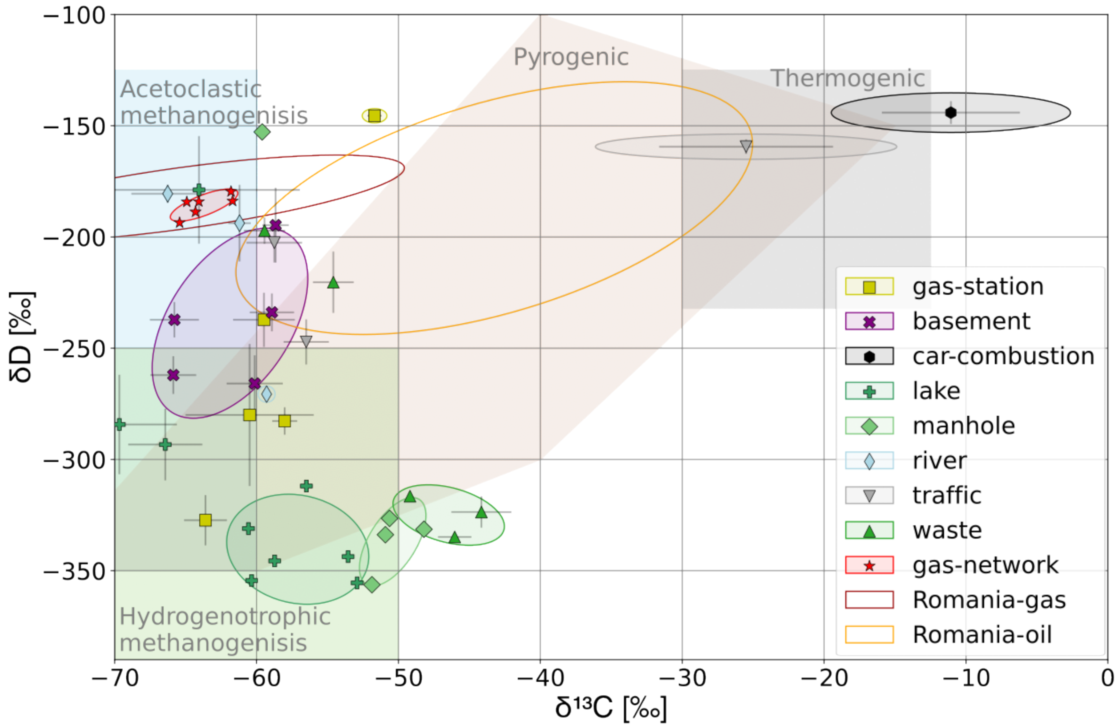

Fig. 1: Dual isotope plot with the source signatures of sampling locations established via the keeling plot approach (dots). For all the accepted samples in the unique categories, ellipses were estimated by fitting the points in an ellipse with 95% certainty for several source types. The open ellipses are from previous investigations, displaying oil and gas mining in Romania. The filled zones are the main methane production pathways. Comparison of the Cluj measurements with the literature indicates an offset for the waste samples. Furthermore, the production processes show that the measured gas originates from microbial reduction, instead of the typical thermogenic pathway.

Comparison of the source signatures from these samples with global databases reveals that the isotopic signatures of wetlands and pyrogenic emissions are consistent with literature values. However, the waste samples show greater enrichment in ^{13}C compared to reported global values.

The gas network, typically characterized as a thermogenic source in the literature, is depleted in ^{13}C, suggesting that the gas network in this region contains biogenic methane. This strong depletion was also observed during the ROMEO campaign in Transylvania (2019, Fig. 1, dark-red ellipse), indicating that the gas supply in Cluj-Napoca likely originates from the same region in Transylvania.

These findings underscore the importance of δD measurements, as distinguishing between the gas network and wetland sources would be infeasible using $\delta^{13}C$ values alone. It also highlights the need for local sampling to improve the continuous dataset evaluation, as the leakage from the gas network may have been misidentified as a biogenic emission.

As it is highly important that is data is comparable with the continuous dataset (D4.1), we decided to keep the data for this deliverable in a similar format, for the best interoperability. These headers are shown in Fig. 2 and differ mainly in the mole fraction data, as this variable is not available for source signatures.

Therefore, the Cluj-Napoca data is uploaded to the ICOS portal with the FAIR principals:

- *Findability:* The dataset can be accessed via the ICOS Carbon Portal database. Users can locate the dataset by specifying Cluj-Napoca in the ICOS carbon portal data search function. 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.csv files using a comparable to ICOS data format, facilitating interoperability with other datasets and platforms. Our goal is to continue this format in the future for similar samples.
- *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.

```
# Total LINES: 68
# HEADER LINES: 24
# title = Isotope source signatures d13C and d2H of methane sources in Cluj-Napoca, Romania in 2022
# data_owner = Carina van der Veen; Thomas Röckmann; Jacoline van Es
# data_owner_email = c.vanderVeen@uu.nl; t.roeckmann@uu.nl; j.d.vanes@uu.nl
# comment = Methane isotope ratio source signatures from samples taken during a mobile campaign. The source signatures are established from repeated location samplings and background samples vi
approach.
# conditions_of_use = Ensure that you contact the data owner before considering data analysis and publication.
# Source = Isotope source signatures derived from Keeling plot results of air samples from CH4 sources.
# file_created = 2024-09-16
# processed_by = j.d.vanes@uu.nl; c.vanderVeen@uu.nl
# species = ch4
# d13c_ch4:standard_name = isotope_source_signature_delta_13C-CH4_to_12C-CH4_relative_to_VPDB
# d13c_ch4:units = 1e-3
# d13c_ch4:ancilliary_variables = d13c_ch4_standard_deviation
# d13c_ch4_standard_deviation:standard_name = isotope_source_signature_delta_13C-CH4_to_12C-CH4_relative_to_VPDB standard_deviation
# d13c_ch4_standard_deviation:units = 1e-3
# d13c_ch4_standard_deviation:comment = standard deviation of the Keeling plot intercept
# d2h_ch4:standard_name = isotope_source_signature_delta_2H-CH4_to_1H-CH4_relative_to_VSMOW
# d2h_ch4:units = 1e-3
# d2h_ch4:ancilliary_variables = d2h_ch4_standard_deviation
# d2h_ch4_standard_deviation:standard_name = isotope_source_signature_delta_2H-CH4_to_1H-CH4_relative_to_VSMOW standard_deviation
# d2h_ch4_standard_deviation:units = 1e-3
# d2h_ch4_standard_deviation:comment = standard deviation of the Keeling plot intercept
# source;d13c_ch4;d13c_ch4_standard_deviation;d2h_ch4;d2h_ch4_standard_deviation;
```

Fig. 2: Header information for the Cluj-Napoca sampling, uploaded to the ICOS portal.

Furthermore, samples were taken in and around Debrecen, Hungary (2024). This included points samples at 47.542615 N, 21.623797 E and mobile samples at several locations.

The point samples were collected over the course of two-week sampling campaigns conducted during winter (February), spring (June) and summer (August-September) at specific and dedicated daily time points in the morning (AM, 08:30 LST) and in the afternoon (PM, 15:30 LST). We identified a significant biological source contribution that persisted through winter. During this season, methane mole fractions consistently exceeded 2040 ppb, reaching a maximum of 2458 ppb, alongside low carbon and hydrogen isotope ratio source signatures of approximately -52 $\delta^{13}C_{CH4}$ and -259 $\delta^{2}H_{CH4}$ (Fig. 3).

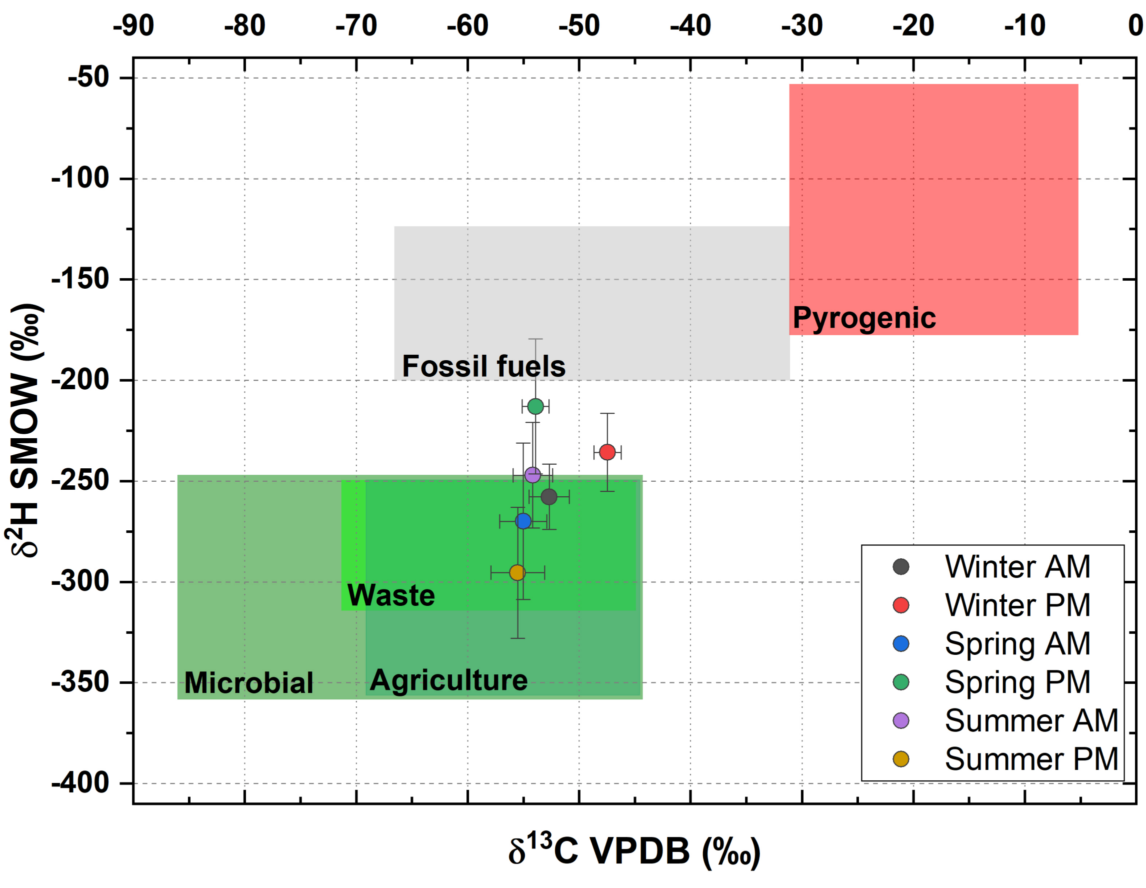

Fig. 3: Results of the fixed location isotopic measurements in Debrecen, Hungary (2024)

The mobile samples were collected from 25 different locations, which included a variety of sources such as landfill sites, sewage pipelines, car exhaust emissions, combusted gas from chimneys, thermal water, and other origins. The source signatures were determined using the Keeling plot method. These samples were then categorized in thermogenic, pyrogenic, and biogenic sources and are shown in Fig. 4. Note: the thermal water is added to the natural gas, though it is uncertain where this belongs as there are no previous studies performed on thermal water.

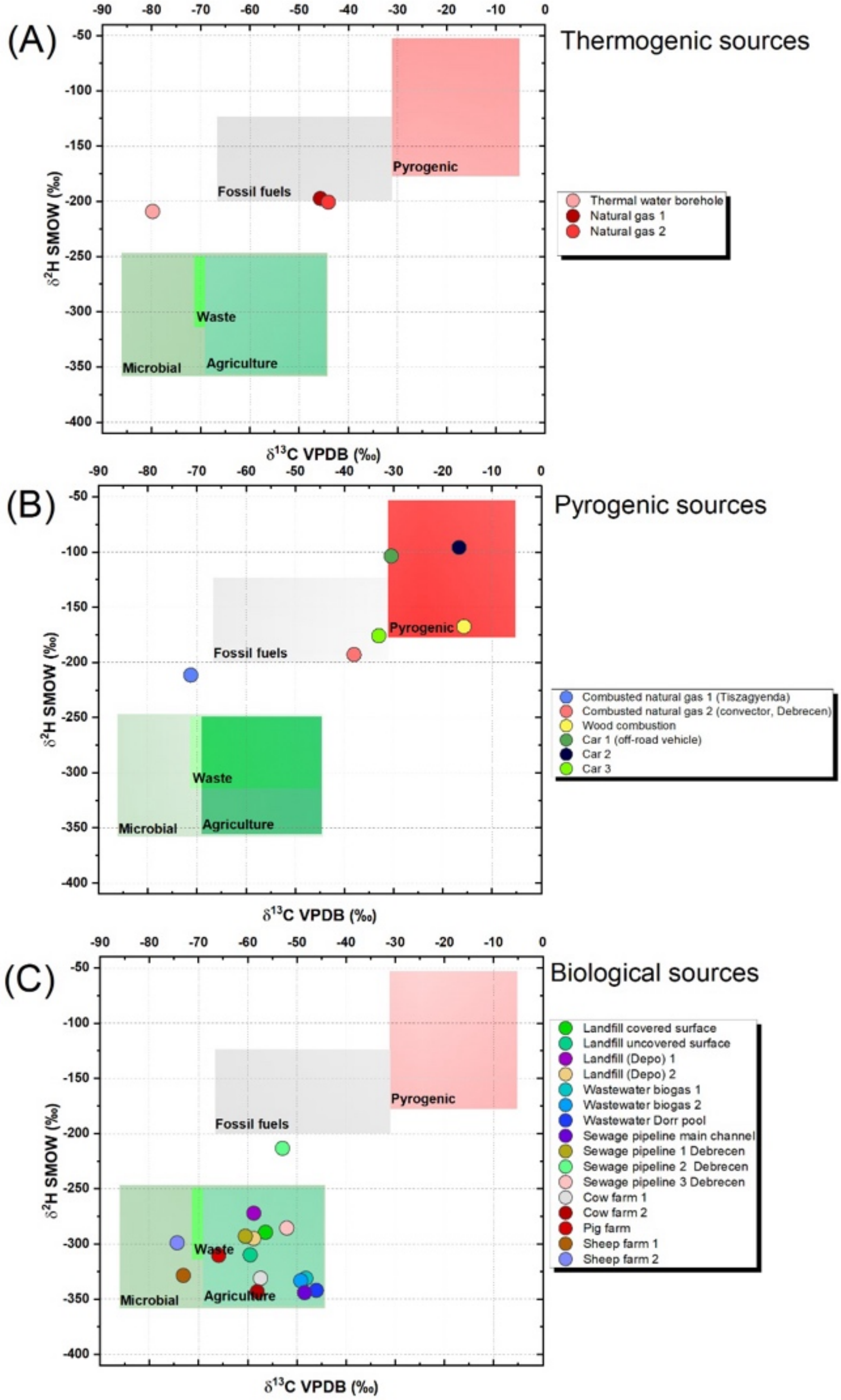

Fig. 4: Results of the local sources in Debrecen

In the thermogenic sources plot, the natural gas emissions from these sources align well with existing literature. The thermal water is more depleted in ^{13}C than the fossil fuels because the production process is unknown. The pyrogenic sources likely involve some leakage alongside combustion processes, causing their isotopic composition to be representative for fossil fuels. The biogenic sources are generally accurate, except for one instance where the sewage pipe samples showed a slight enrichment in ^{2}H. The reason for this anomaly is currently unknown.

4.4 Conclusion and possible impact

We obtained 44 source signatures for major methane sources in Cluj-Napoca. This included the gas network, a gas station, traffic, waste, and wetlands. The wetlands, gas stations and traffic presented source signatures comparable to the international databases. The gas network measurements show that the gas in Cluj-Napoca is produced by microbial reduction, rather than a thermogenic process. The source signatures obtained from samples taken near wastewater treatment plants and solid waste disposal were more enriched in ^{13}C than the values in the literature.

In Debrecen, we found that, with the exception of a few outliers, the samples were in good agreement. The new thermal water source did not fit into any specific category. However, additional sampling of this source type would be required to obtain a more accurate representation.

These samples improve evaluation of the continuous measurements and count as input for methane isotopic models.

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	J. van Es	21 June 2021	
1.1	T. Arnold	17 Oct 2024	Added link to ICOS Carbon Portal
		Nov./Dec.	Feedback rounds
1.2	J. van Es, T. Röckmann	14 Jan 2025	Thorough revision following addition of new results
	S. Walter	21 Jan 2025	Finalising and submission