# PARIS

**Process Attribution of Regional Emissions**

GA 101081430, RIA

# One growing season of quality-controlled isotope measurements

| **Milestone 19** | | | |
|---|---|---|---|
| Delivery due date Annex I | 31/08/2024 | | |
| Actual date of submission | 1/05/2025 | | |
| Lead beneficiary: Empa | Work package: 5 | Nature: R | Dissemination level: PU |
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| Internal reviewers | J. Mohn | | |
| Version: 1 | | | |

# Table of content

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

The milestone was initially planned for the growing season 2024. This was extended to increase the data set and measurements were prolonged into the winter season 2024.

# 2. Dissemination and uptake

The methodologies and output data provided by this work will enhance the quantification of $N_2O$ source attributions in agricultural ecosystems. The output data includes weekly integrated fluxes of $N_2O$, $CH_4$, and $CO_2$ as well as the isotopic composition of the emitted N2O. These data will serve as key inputs for tuning the iso-tope-enabled version of the LandscapeDNDC model (SIMONE) and the DAYCENT model (Task 5.3 and D5.3), supporting more accurate simulation of soil biogeochemical processes. The improved model outputs will feed into Task 5.4 (Objective 5.3) and will be aligned with the time period covered by atmospheric $N_2O$ observations for validation and comparison. The obtained dataset of source signatures is available from the ICOS carbon portal (https://doi.org/10.18160/ANQW-32YY).

# 3. Short Summary of results

Greenhouse gas fluxes and microbial $N_2O$ isotopic source signatures were determined weekly using air samples from an automatic time-integrating chamber (ATIC) system. Chambers were closed for 15 minutes every 4 hours, during which four headspace samples were sequentially collected into 5 L gas bags at 3.50, 7.25, 11.50, and 14.25 minutes post-closure. Gas concentrations ($N_2O$, $CH_4$, $CO_2$) and $N_2O$ isotopologues ($\delta^{15}N\alpha$, $\delta^{15}N\beta$, $\delta^{18}O$) were analysed using Picarro G2401-m and G5131-I instruments. Raw data were corrected for spectral interferences, instrumental drift, and calibrated against WMO GAW and international isotope standards (Havsteen et al., 2025). Fluxes were calculated using linear regression ($R^2 \geq 0.7$) of concentration changes over time, adjusted for temperature-dependent molar volume based on data from the Tänikon NABEL (national Swiss air quality network) station. Microbial $N_2O$ isotopic signatures were estimated using Keeling plot analysis, where isotopologue values were regressed against reciprocal $N_2O$ concentrations. The intercept indicated the isotopic composition of the soil-emitted $N_2O$. Data quality was classified based on the agreement between observed and Keeling-derived ambient values: Class 1 (≤2 ‰), Class 2 (≤4 ‰), and Class 3 (≤6 ‰). Results where the Keeling line deviated >6 ‰ or the $N_2O$ flux was <75 µg m$^{-2}$ h$^{-1}$ were excluded from further iso-topic source quantification analysis.

# 4. Evidence of accomplishment

## 4.1 Introduction | Background of the milestone

Nitrous oxide is a potent greenhouse gas with significant contributions from both microbial and abiotic sources. Unlike $CO_2$ and $CH_4$, its sectorial attribution remains more uncertain due to multiple co-occurring source processes. To quantify the microbial N2O emission pathways in agricultural soils we measured $N_2O$ isotopologues ($\delta^{15}N\alpha$, $\delta^{15}N\beta$, and $\delta^{18}O$), since they provide a powerful tool for disentangling microbial pro-duction pathways. Within the PARIS framework, a chamber-based field system was deployed to obtain $N_2O$ fluxes and isotopic source data. Weekly averaged fluxes were calculated from automated chamber measurements, and microbial source signatures were derived using a Keeling plot approach.

This work thus supports both quantification of the total flux and the microbial pathway(s) responsible, which advances integration of isotopic constraints into top-down emissions evaluation.

## 4.2 Scope of the milestone

This milestone delivers N₂O emission estimates and pathway attributions for the Agricultural field site (Reckonholz, Agroscope, Zürich, CH), based on continuous automated chamber measurements and high-precision isotopic analysis. The results will support improvements in forward biogeochemical models such as DAYCENT (Switzerland) and LandscapeDNDC (Switzerland, Germany), and will also contribute to policy-relevant reporting by providing data for inverse modelling systems used in national emission inventory verification efforts.

## 4.3 Content of the milestone

Significant progress has been made towards obtaining reliable, high-precision N₂O isotopic data from agricultural field sites through collaboration between multiple institutions, including Empa, Agroscope, ETH, KIT, VTT, and PTB. A customized post-processing pipeline has been developed to extract N₂O isotopologue data from Cavity Ring-Down Spectroscopy (CRDS) analysers, incorporating corrections for spectral interferences, N₂O non-linearity, instrumental drift, and calibration in a seamless, automated workflow (Fig. 1). This methodology was documented in a manuscript submitted for publication to EGUsphere (Havsteen et al., 2025).

In parallel, a data reduction framework has been established for identifying microbial N₂O source endmembers, which will underpin the calibration of soil-process models (PARIS deliverable D5.3) as exemplified for the DEMO site at Agroscope Reckonholz during a field campaign in 2024 (Figs 2 and 3). These will focus on integrating isotopic constraints into the DAYCENT and LandscapeDNDC models to refine their representation of soil biogeochemical processes. Additionally, the data have been applied in targeted cow-urine fertilisation experiments to differentiate between nitrification and denitrification-driven N₂O production under such treatment conditions.
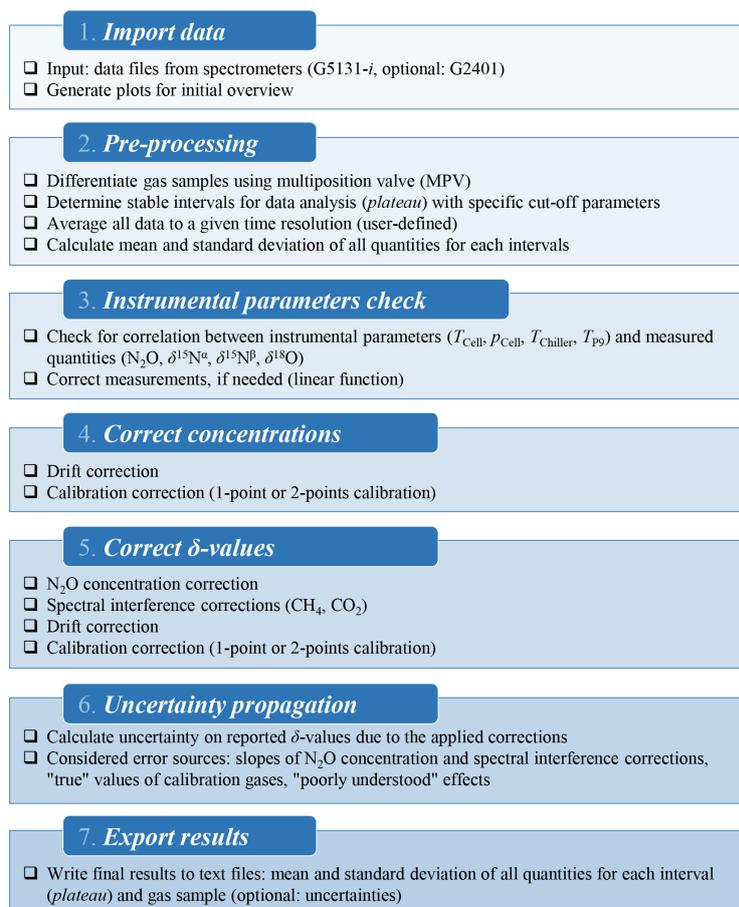
**1. *Import data***
- ❑ Input: data files from spectrometers (G5131-*i*, optional: G2401)
- ❑ Generate plots for initial overview

**2. *Pre-processing***
- ❑ Differentiate gas samples using multiposition valve (MPV)
- ❑ Determine stable intervals for data analysis (*plateau*) with specific cut-off parameters
- ❑ Average all data to a given time resolution (user-defined)
- ❑ Calculate mean and standard deviation of all quantities for each intervals

**3. *Instrumental parameters check***
- ❑ Check for correlation between instrumental parameters ($T_{Cell}$, $p_{Cell}$, $T_{Chiller}$, $T_{P9}$) and measured quantities (N₂O, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$)
- ❑ Correct measurements, if needed (linear function)

**4. *Correct concentrations***
- ❑ Drift correction
- ❑ Calibration correction (1-point or 2-points calibration)

**5. *Correct δ-values***
- ❑ N₂O concentration correction
- ❑ Spectral interference corrections (CH₄, CO₂)
- ❑ Drift correction
- ❑ Calibration correction (1-point or 2-points calibration)

**6. *Uncertainty propagation***
- ❑ Calculate uncertainty on reported *δ*-values due to the applied corrections
- ❑ Considered error sources: slopes of N₂O concentration and spectral interference corrections, "true" values of calibration gases, "poorly understood" effects

**7. *Export results***
- ❑ Write final results to text files: mean and standard deviation of all quantities for each interval (*plateau*) and gas sample (optional: uncertainties)

**Figure 1:** Flowchart illustrating the data post-processing workflow, including data import, plateau identification, co-averaging, parameter-based and drift corrections, calibration, uncertainty assessment and final output.

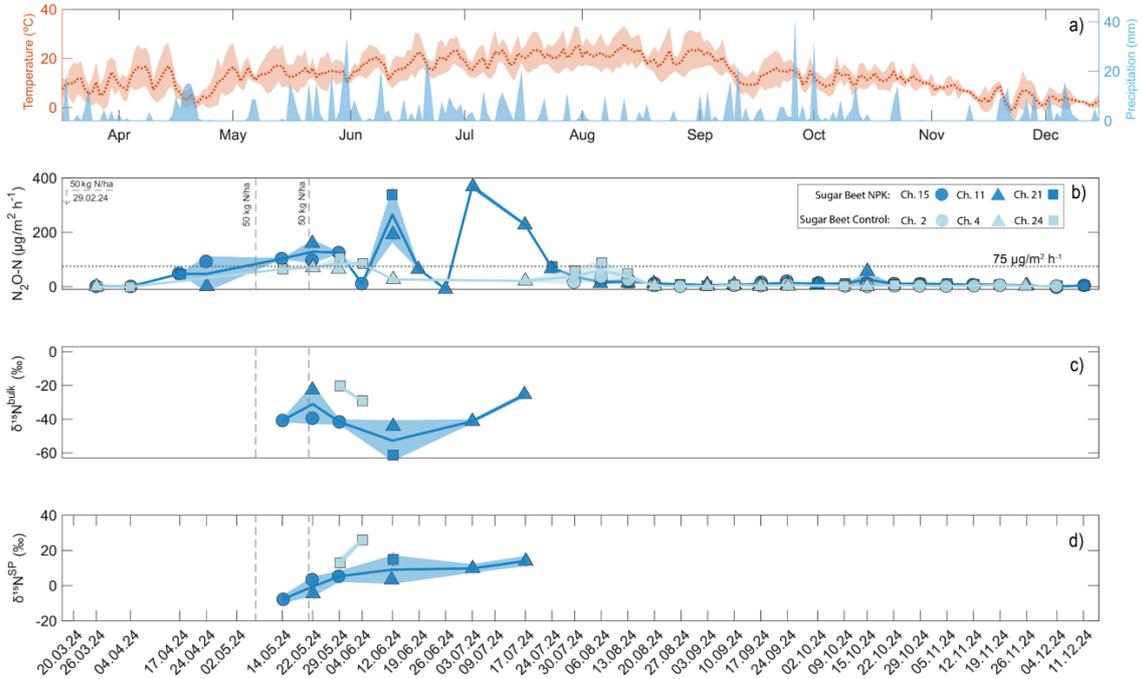M19 – One growing season of quality-controlled isotope measurements



**Figure 2:** Seasonal course of N₂O fluxes and isotopic composition for sugar beet under NPK fertilisation vs. control of the Demo experiment at Agroscope Reckonholz: (a) daily air temperature and precipitation, (b) N₂O flux (µg N2O-N m⁻² h⁻¹), (c) δ¹⁸O, δ¹⁵Nbulk and (d) site preference (δ¹⁵NSP). The stippled line in the N2O flux graph represents the 75 µg m-2 h-1 threshold for isotope flux analysis.
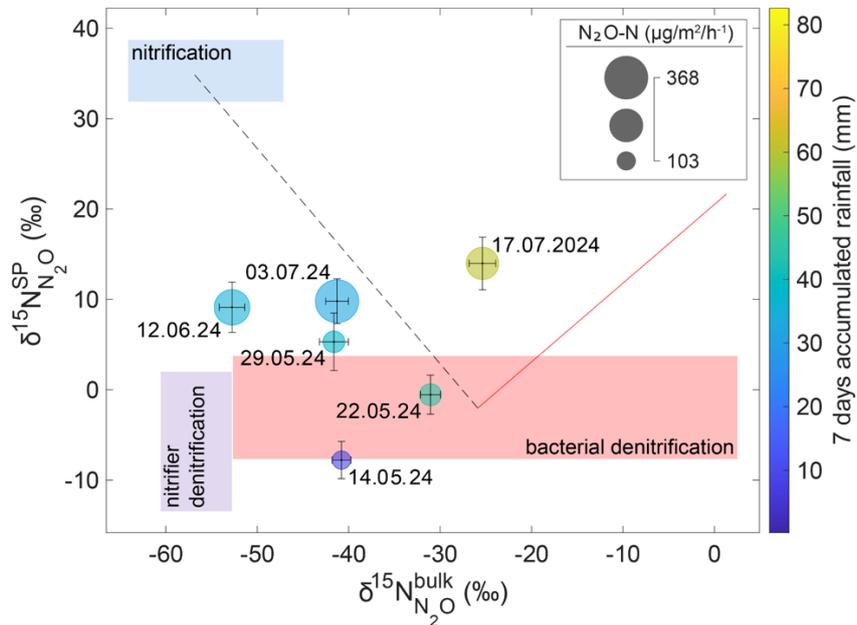


**Figure 3:** Dual isotope plot of site preference (SP) 〚δ¹⁵N〛_(N_2 O)^SP = (δ¹⁵Nα - δ¹⁵Nβ) versus 〚δ¹⁵N〛_(N_2 O)^bulk = (δ¹⁵Nα + δ¹⁵Nβ)/2 for N2O emitted from the NPK-fertilized sugar beet plot. The points are colour-coded by 7-day accumulated rainfall (mm) and scaled by N₂O flux (µg N/m² h⁻¹). The coloured boxes indicate ranges of isotopic signatures reported for prominent microbial N2O production pathways in literature (Yu et al., 2020).

## 4.4 References

Havsteen, J. C., Fatima, M., Brunamonti, S., Pogány, A., Hausmaninger, T., Wolf, B., Well, R., and Mohn, J.: Correction and Calibration Protocol for Isotope Data via CRDS: A Study Case for N2O and Other Isotope Systems, EGUsphere, 2025, 1–37, doi: 10.5194/egusphere-2025-4954, 2025.

Yu, L., Harris, E., Lewicka-Szczebak, D., Barthel, M., Blomberg, M. R., Harris, S. J., ... & Mohn, J. (2020). What can we learn from N2O isotope data?–Analytics, processes and modelling. *Rapid Communications in Mass Spectrometry*, *34*(20), e8858.

## 5. History of the document

| Version | Author(s) | Date | Changes |
|---|---|---|---|
| 1.0 | J. Havsteen | 12.05.2025 | First draft |
| | J. Mohn | 13.05.2025 | Second draft |
| | J. Havsteen | 16.05.2025 | Final report and uploaded |