CO2MVS RESEARCH ON SUPPLEMENTARY OBSERVATIONS

CORSO
CO2MVS Research on Supplementary Observations

D3.3 Final APO and $^{14}CO_2$ measurement datasets from the 1-year intensive observations in Western Europe

Due date of deliverable	May 31, 2025
Submission date	July 03, 2025
File Name	CORSO-D3-3-V1.3
Work Package /Task	WP3 /3.1b
Organisation Responsible of Deliverable	RUG/UHEI
Author name(s)	I. Luijkx, S. Hammer, L. de Beijl, A. Wenger, P. Jagoda, S. Preunkert
Revision number	1.3
Status	Issued
Dissemination Level / location	Public www.corso-project.eu

Funded by the European Union

The CORSO project (grant agreement No 101082194) is funded by the European Union.
Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the Commission. Neither the European Union nor the granting authority can be held responsible for them.

1 Executive Summary

Work Package 3 in CORSO is dedicated to the assessment of the potential added value of in-situ measurements of $\Delta^{14}CO_2$ and O_2 to the monitoring and verification of fossil fuel CO_2 emissions. Both tracers can provide additional information on separation of the natural and fossil fuel components of the atmospheric CO_2 signal compared to CO_2 mole fraction data alone.

This deliverable presents the results from our intensive sampling year 2024 in Europe funded by CORSO. We expanded the capacity of the ICOS network and laboratory facilities to allow more frequent $\Delta^{14}CO_2$ measurements from ICOS flasks. In total 1363 samples have been measured from 12 sites in Europe. Continuous O_2 and CO_2 measurements (which can be combined into Atmospheric Potential Oxygen (APO)) have been made at Cabauw since September 2024.

This report presents the methods used to obtain these measurements, together with an initial analysis of the quality of the results. The datasets are provided as csv files with the deliverable and will be made available publicly through the ICOS Carbon Portal.

The $^{14}CO_2$ data is available as part of the ICOS Atmosphere Release 2025-1 here:

https://meta.icos-cp.eu/collections/3BKIGVB6Vw3KKlMeYpDEMckb

The data for O_2 from Cabauw is available here:
https://meta.icos-cp.eu/objects/Iq4N2vWXH8aUkmDxiCFL_qNR

Together, we expect that these $\Delta^{14}CO_2$ and continuous O_2 observations will provide a valuable basis for constraining fossil fuel CO_2 emissions in Europe and serve as an input to inversion systems within the Copernicus CO_2 Monitoring and Verification Support (CO_2MVS) framework.

Table of Contents

2 Introduction

2.1 Background

To enable the European Union (EU) to move towards a low-carbon economy and implement its commitments under the Paris Agreement, a binding target was set to cut emissions in the EU by at least 40% below 1990 levels by 2030. European Commission (EC) President von der Leyen committed to deepen this target to at least 55% reduction by 2030. This was further consolidated with the release of the Commission's European Green Deal on the 11th of December 2019, setting the targets for the European environment, economy, and society to reach zero net emissions of greenhouse gases in 2050, outlining all needed technological and societal transformations that are aiming at combining prosperity and sustainability. To support EU countries in achieving the targets, the EU and European Commission (EC) recognised the need for an objective way to monitor anthropogenic CO_2 emissions and their evolution over time.

Such a monitoring capacity will deliver consistent and reliable information to support informed policy- and decision-making processes, both at national and European level. To maintain independence in this domain, it is seen as critical that the EU establishes an observation-based operational anthropogenic CO_2 emissions Monitoring and Verification Support (MVS) (CO2MVS) capacity as part of its Copernicus Earth Observation programme.

The CORSO research and innovation project will build on and complement the work of previous projects such as CHE (the CO2 Human Emissions), and CoCO2 (Copernicus CO2 service) projects, both led by ECMWF. These projects have already started the ramping-up of the CO2MVS prototype systems, so it can be implemented within the Copernicus Atmosphere Monitoring Service (CAMS) with the aim to be operational by 2026. The CORSO project will further support establishing the new CO2MVS addressing specific research & development questions.

The main objectives of CORSO are to deliver further research activities and outcomes with a focus on the use of supplementary observations, i.e., of co-emitted species as well as the use of auxiliary observations to better separate fossil fuel emissions from the other sources of atmospheric CO_2. CORSO will deliver improved estimates of emission factors/ratios and their uncertainties as well as the capabilities at global and local scale to optimally use observations of co-emitted species to better estimate anthropogenic CO_2 emissions. CORSO will also provide clear recommendations to CAMS, ICOS, and WMO about the potential added-value of high-temporal resolution $^{14}CO_2$ and APO observations as tracers for anthropogenic emissions in both global and regional scale inversions and develop coupled land-atmosphere data assimilation in the global CO2MVS system constraining carbon cycle variables with satellite observations of soil moisture, LAI, SIF, and Biomass. Finally, CORSO will provide specific recommendations for the topics above for the operational implementation of the CO2MVS within the Copernicus programme.

2.2 Scope of this deliverable

WP3 is dedicated to the assessment of the potential added value of in-situ measurements of $^{14}CO_2$ and APO. Fossil fuels do not contain radiocarbon (^{14}C), and their combustion releases CO_2 that dilutes the $^{14}C/C$ ratio of the atmosphere compared to other CO_2 sources (e.g., biospheric) that contain $^{14}CO_2$. This dilution induces a depletion of the $^{14}C/C$ isotope ratio in atmospheric CO_2. As outlined by the Green Report from the EC's CO_2 Monitoring Task Force, combined measurement of total atmospheric CO_2 and $^{14}CO_2$ (radiocarbon) concentrations is a well-founded approach for separating natural and anthropogenic (fossil fuel) CO_2, and which inversions can use to estimate fossil fuel CO_2 emissions (see e.g., Levin et al., 2003, 2020; Turnbull et al., 2006; Basu et al., 2016, 2020; Graven et al., 2018).

Combined atmospheric O_2 and CO_2 measurements provide additional information on the contribution of natural and fossil fuel components to CO_2 mole fractions, with the added advantage that they can be measured continuously (e.g., Pickers et al., 2022; Stephens et al., 1998). Fossil fuel combustion consumes atmospheric O_2, and the O_2/CO_2 signal allows different fossil fuels to be distinguished by their oxidative (or exchange) ratio (Steinbach et al., 2011), helping to disentangle the fossil fuel CO_2 ($ffCO_2$) component from the net atmospheric CO_2 signal (Pickers et al., 2022). Atmospheric O_2 and CO_2 can also be combined into the tracer Atmospheric Potential Oxygen (APO), which excludes the biosphere signal by assuming a fixed exchange ratio of 1.1, following the definition by Stephens et al. (1998). APO is primarily sensitive to ocean–atmosphere exchange on large spatial and temporal scales. However, on shorter timescales, the initial study by Pickers et al. (2022) shows that atmospheric O_2 has the potential to provide information on the fossil fuel CO_2 signal, through the deviation from the biospheric exchange ratio of 1.1. The exchange ratio of fossil fuels ranges between 1.2 and 1.9, with the global average fossil fuel mix corresponding to approximately 1.4 (Keeling and Manning, 2014). The use of APO to derive $ffCO_2$ was confirmed by a modelling OSSE study by Rödenbeck et al. (2023). Further research is needed to establish the use of O_2 as a fossil fuel tracer, considering the influence of short-term ocean signals (Chawner et al., 2024) and biosphere ER variability (Faassen et al., 2025).

Task 3.1.b is dedicated to intensifying $^{14}CO_2$ and APO observations in Western Europe throughout the calendar year 2024. To achieve this, the task builds upon the ICOS (Integrated Carbon Observation System) network, a well-established infrastructure of atmospheric stations equipped with continuous greenhouse gas analysers and flask samplers for collecting air samples. While such samples are routinely collected every three days and analysed for greenhouse gases, stable isotopes, and O_2/N_2 ratios, only a limited subset—typically 26 samples per year—is analysed for $^{14}CO_2$ due to cost constraints. Furthermore, continuous O_2 observations are not part of the standard measurements at ICOS stations and were so far only made at two sites in the UK.

For 2024, these limitations were overcome through funding provided by CORSO, enabling 1) the $^{14}CO_2$ analysis of every ICOS flask sample from 10 selected Western European stations (shown in Fig. 1) and 2) continuous O_2 observations at Cabauw in the Netherlands. To further enhance the spatial coverage of $^{14}CO_2$ observations, the Heathfield (HDF) station in the UK and the Białystok Tall Tower (BIK) station in Poland were added, thereby expanding the east–west transect across Central Western Europe. In Białystok, an ICOS flask sampler was installed, and the ICOS Central Analytical Laboratories analysed the samples. In Heathfield, the existing sampling infrastructure from NPL and the University of Bristol (UNIVBRIS) was used. UNIVBRIS, also conducted the $^{14}CO_2$ analysis of the Heathfield samples.

Fig. 1: *Sampling stations for the intensified $\Delta^{14}CO_2$ and O_2 observations in 2024. Stations marked in blue conduct both $\Delta^{14}CO_2$ and O_2 measurements from flasks, while stations in orange are dedicated to APO measurements only. Continuous O_2 observations are made at Cabauw (CBW) as part of CORSO (and were already established at HDF and Weybourne in the UK (not shown)).*

2.2.1 Objectives of this deliverable

The objectives of this deliverable were to:

a) Provide the quality-controlled results of the intensified $^{14}CO_2$ flask observations conducted in the year 2024, along with corresponding uncertainty estimates.
b) Provide high-precision continuous O_2 and CO_2 measurements at Cabauw, the Netherlands for 2024.

Both datasets will be used in subsequent tasks within this work package to support inverse modelling studies aimed at evaluating the regional and large-scale constraints provided by the $\Delta^{14}CO_2$ and O_2 observations.

2.2.2 Work performed in this deliverable

The following activities have been conducted to achieve the deliverable and are presented in detail in Section 3:

- Develop and implement a flask sampling strategy to minimise the risk of nuclear $^{14}CO_2$ contributions in atmospheric air samples.
- Setup of an ICOS flask sampler at the Białystok station in Poland.
- Collect approximately three-daily flask samples at 10 Western European ICOS stations, plus Heathfield and Białystok.
- Analyse the collected flask samples for their $^{14}CO_2$ activity.
- Improvements to the existing O_2/CO_2 measurement instrument (Faassen et al., 2023), including enhancements to air drying and gas handling, a major software rewrite, the addition of multi-height measurement capability, and extensive testing in the laboratory.

- Installation of the instrument on the Royal Netherlands Meteorological Institute (KNMI) measurement tower in Cabauw, including construction of inlets and tubing at 27 m, 67 m, and 207 m.
- Continuous operation of the instrument since September 2024 and acquisition of raw data, followed by initial analysis, calibration, and correction of the collected data.

2.2.3 Deviations and counter measures

The flask sampler at the ICOS station in Trainou (TRN), France, was installed in mid-2024. The resulting unused $^{14}CO_2$ analysis capacity was utilised to analyse more samples from other ICOS stations.

In Heathfield (HDF), fewer samples were collected than expected; there were two main reasons for this. First, field trips to the site occurred less frequently than desired. The National Physics Laboratory operates the site, aiming to visit it every second week. However, due to staff shortages, this frequency has not been achieved. The second issue for HFD samples arose from severe delays in the $^{14}CO_2$ analysis. The Bristol AMS facility (BRAMS) experienced two long shutdown periods during the project, from January to June 2024 and from January to March 2025. When the BRAMS facility started operating again in mid-2024, the quality control samples measured with each batch of $^{14}CO_2$ flasks were found to have failed. This prompted a lengthy investigation of the UNIVBRIS graphitisation system, resulting in delays in analysis. Sampling of new flasks had to be halted in August 2024, as no flasks could be analysed at that time. As of May 2025, the graphitisation system is operational again, and analysis of the existing samples is proceeding.

The O_2 and CO_2 measurements at Cabauw started later than planned, because of delays in hiring personnel for this project at RUG.

2.3 Project partners:

Partners	
AKADEMIA GORNICZO-HUTNICZA IM. STANISLAWA STASZICA W KRAKOWIE	AGH
RIJKSUNIVERSITEIT GRONINGEN	RUG
RUPRECHT-KARLS-UNIVERSITAET HEIDELBERG	UHEI
UNIVERSITY OF BRISTOL	UNIVBRIS

3 Methods

This section reports on the methods and steps needed to conduct the intensified $^{14}CO_2$ and APO monitoring in 2024.

3.1 Intensified $^{14}CO_2$ Flask Observations in 2024

3.1.1 Flask Sampling Strategy to Minimise Nuclear Contributions

Nuclear facilities emit $^{14}CO_2$, which must be accounted for when using radiocarbon measurements to estimate fossil fuel CO_2 ($ffCO_2$) emissions. ICOS has developed and implemented a dedicated flask sampling strategy for the ICOS stations and BIK to mitigate the influence of nuclear emissions. The ICOS Carbon Portal (CP) conducts near real-time (NRT) FLEXPART (Stohl et al., 1998) footprint calculations for all sampling stations and hours. The footprints are used to estimate the potential nuclear $^{14}CO_2$ contribution from each nuclear facility based on its mean annual emission. As a result, information on the potential nuclear contamination of the samples is available 48 hours after sampling, which was used to select the samples.

We refer to these nuclear contributions as potential contributions since they are based on actual NRT meteorology while using constant $^{14}CO_2$ emissions from previous years. The flask sampling strategy applied in CORSO collects samples approximately every three days, ensuring that the potential nuclear contamination remained less than 0.5‰ in $\Delta^{14}CO_2$, about one-third of the analytical $\Delta^{14}CO_2$ precision. For the first time, this approach enables the minimisation of nuclear $^{14}CO_2$ contamination through sample selection before shipment, allowing for the targeted exclusion of potentially affected air masses. As a result, fewer samples need to be discarded due to high nuclear influence, increasing both the efficiency and scientific value of the radiocarbon dataset.

3.1.2 Setup of an ICOS Flask Sampler at Białystok

The tall tower station at Bialystok (BIK, 53°13'53.4"N 23°01'36.3"E) is located 18 km from the city centre of Białystok (population ~280,000). The tower's main function is radio and television broadcasting. Since 2005, environmental measurements at the BIK tower have been conducted by a team from the Max-Planck-Institute for Biogeochemistry in Jena, Germany. UHEI loaned the ICOS Flask Sampler to AGH. Supervision of the facility was officially transferred to AGH on 1 January 2024. BIK is the easternmost station in the CORSO project and one of the tallest. The total height of the tower is 331 meters. The sampling line used extends to 300 meters. This line is also fitted with an additional pump to minimise the dead volume of the sampling system. The ICOS Flask Sampler was transported to the BIK station in December 2023. Setup and tests of the system lasted until mid-January. With the help of the ICOS Flask and Calibration Laboratory (FCL) team, an issue with the temperature sensors in the drying unit was resolved. The ICOS Flask Sampler became fully operational on 19 January 2024.

3.1.3 Three-Daily Flask Sample Collection

Fig. 2 shows the weekly sampling coverage of the ICOS-related stations and HFD, for 2024. In total, 1363 samples have been collected. All samples, except for HFD, have been selected applying the aforementioned sampling strategy to minimise the influence of the $^{14}CO_2$ emissions from nuclear facilities. For most stations, uninterrupted sampling was achieved. From the ICOS-related stations, only BIK, HTM, and KIT experienced a few weeks without sampling, mainly due to technical issues at BIK and HTM or unfavourable meteorological conditions at the KIT station. The flask sampler at TRN was delayed and was not installed until summer 2024. The unused sample capacity from TRN was distributed among the other ICOS stations to further increase the $^{14}CO_2$ sampling frequency. The HDF station is equipped with a simple automated flask sampling system, which can accommodate a maximum of six flasks. With HFD field trips scheduled for every second week, a sampling frequency of every second day was targeted but could not be achieved due to staff shortages (see Sec. 2.2.3).

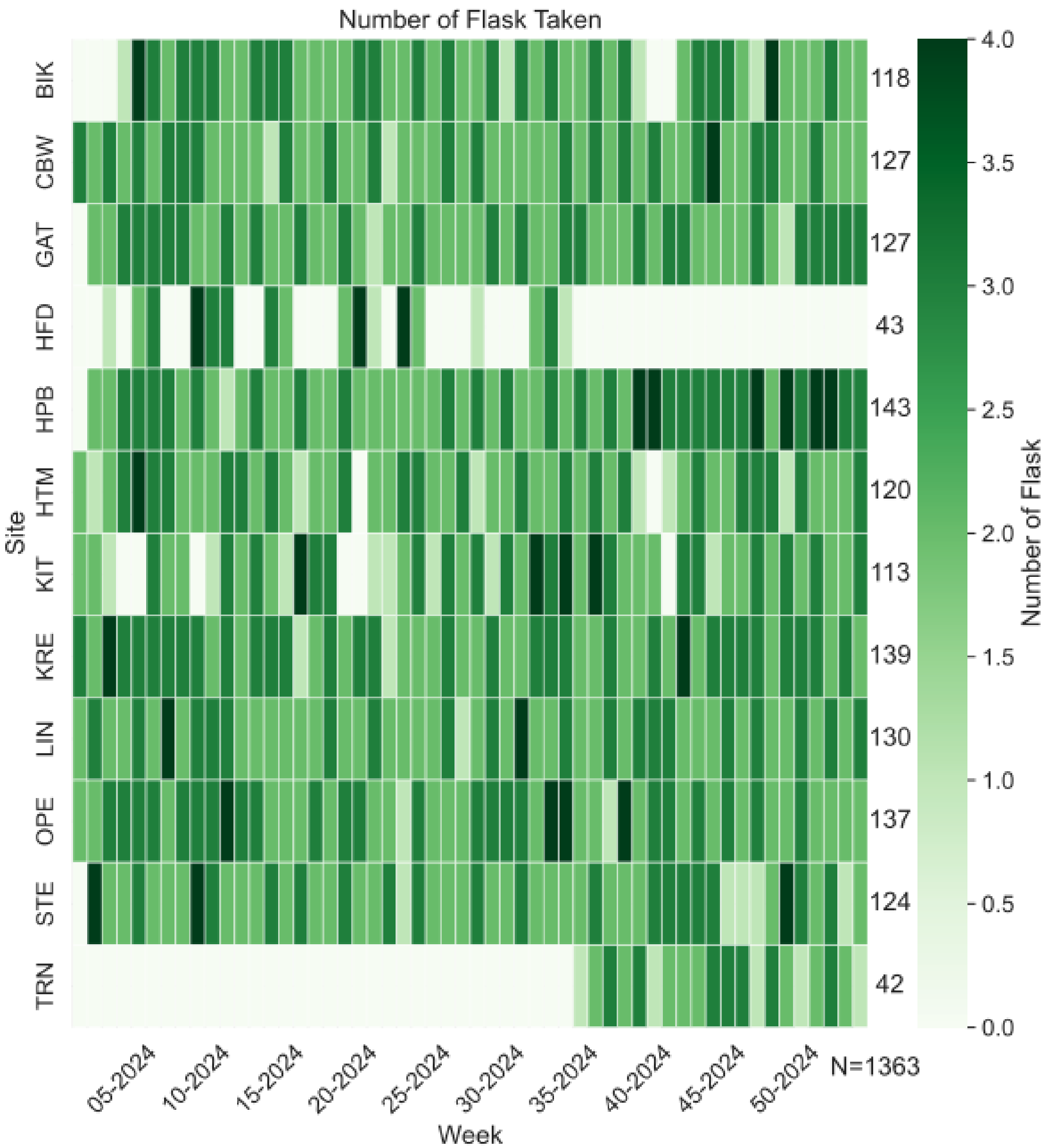

Fig. 2: *Weekly sampling coverage for each CORSO station during the intensified $\Delta^{14}CO_2$ observation year 2024.*

3.2 Intensified APO Observations in 2024

3.2.1 Measurement locations

3.2.1.1 O_2 and CO_2 measurements at Cabauw, the Netherlands

The Cabauw Experimental Site for Atmospheric Research, located near the village of Lopik in the province of Utrecht, the Netherlands, contains a 213-meter tall meteorological tower operated by KNMI. This tower is used for atmospheric research, particularly in observing the lower portion of the atmosphere, the boundary layer.

Fig. 3: *Measurement KNMI-mast Cabauw showing a full view of the tower (TNO, 2024) and the geographical location.*

Cabauw was selected as a measurement site for the continuous O_2 and CO_2 measurements, due to its representative landscape for the Western Netherlands and its relatively stable surroundings, with minimal urban buildings. The location provides a good balance: it lies approximately 50 kilometers inland from the North Sea and is close to Rotterdam, a major industrial and port city that influences local wind patterns, making it a valuable site for studying both natural and anthropogenic atmospheric signals.

Multiple types of meteorological instruments are installed along the height of the tower, positioned on three booms at each level to ensure accurate readings from all wind directions. These instruments continuously record variables such as wind speed and direction, temperature, humidity, and radiation. This setup provides high-resolution vertical profiles of the atmospheric boundary layer (KNMI, n.d.).

3.2.2 The O_2 and CO_2 instrument

The instrument used for continuous atmospheric O_2 and CO_2 measurements applies the electrochemical fuel cell technique, as initially described by Stephens et al. (2007). This system was developed at RUG (van Leeuwen et al., 2015) and most recently used in campaigns in Hyytiälä, Finland, in 2018 and 2019, as detailed by Faassen et al. (2023). The instrument is extensively described in these references.

The instrument setup is designed for ease of transport and remote operation, as it is housed within a robust flight case that simplifies transportation and field installation, visible in Fig. 5. For measurement, ambient air is drawn in through customized inlets (Fig. 4) and directed via a pump through a valve system, allowing alternating sampling from three different heights. Before entering the system, the air is pre-conditioned by a -80°C vapor trap and a 2°C pre-cooler to remove water vapor content, visible in Fig. 5. Oxygen mole fractions are measured using the Oxzilla II (Sable Systems) instrument, a differential electrochemical analyzer that compares sample and reference gases to minimize signal drift. Carbon dioxide mole fractions are determined with an ABB Uras26, which applies non-dispersive infrared (NDIR) absorption spectroscopy. An extensive custom-build gas handling system was designed to stabilize pressure, flow and temperature during the measurements, to achieve high precision measurements. The measurements are made against a continuously measured reference gas, and frequently calibrated using a set of 3 calibration gases.

Since the previous measurements with this system (Faassen et al. 2023), several modifications have been implemented to improve its performance and adapt to specific research requirements. These modifications include improvement of the air drying, using a -80°C vapor trap and a 2°C pre-cooler, and the incorporation of a valve system allowing sampling at three distinct heights. Furthermore, numerous instrument components have been replaced and the software of the system has been completely redeveloped to support these improvements.

Fig. 4: *Air inlets and filters at different heights in the Cabauw tower (27m and 207m).*

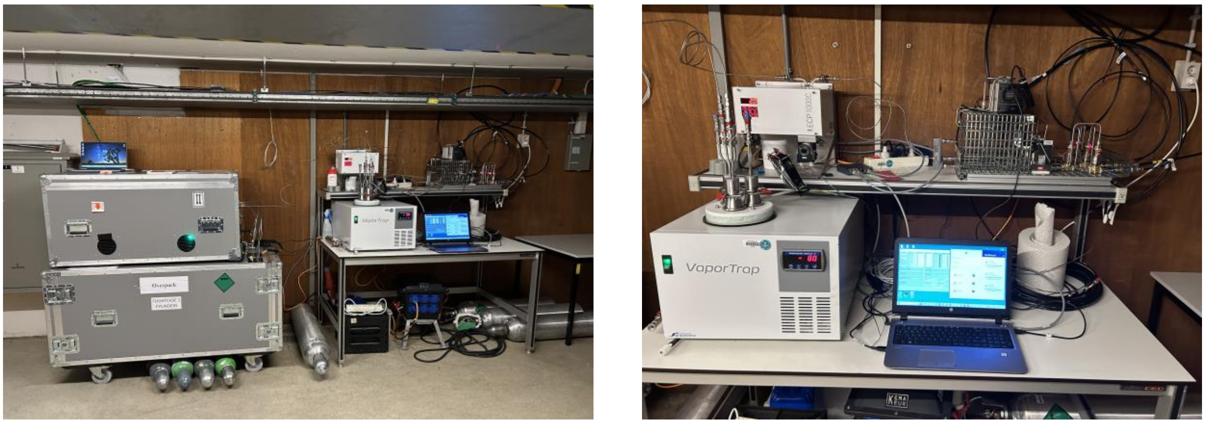

Fig. 5: *O_2 and CO_2 instrument setup. Showing the instrument and cylinder flight case and the vapor trap, cooler and heights valve system.*

3.2.2.1 Measurement information and settings

The air inlets are positioned at heights of 207 m, 67 m, and 27 m. However, from the start of instrument operation on September 17, 2024, until March 9, 2025, measurements were conducted only at the highest level (207 m). This was due to ongoing work required to finalize the valve system and software responsible for switching between sampling heights. As a result, this report presents data from only a single measurement level between September 2024 and March 2025.

Throughout most of this period, a consistent measurement scheme was followed. This included calibration gas measurements approximately every 23 hours. In between these calibrations, target gas measurements were conducted at roughly one-third and two-third intervals. The same calibration and target tanks were used throughout the entire period, while the reference tanks were replaced approximately every three weeks of collected data.

Due to ongoing improvements during this period, as well as changes to the reference tanks and the periodic emptying of the vapor trap, there are several gaps in the data. These gaps occurred either during maintenance activities or when data was discarded due to issues such as insufficient reference tank volume, which prevented accurate measurements, or other technical difficulties that arose.

3.2.2.2 Calibration procedure

The instrument results in 2-minute average O_2 and CO_2 measurements. This raw data was calibrated following the procedures as described by Faassen et al. (2023), but with some differences, which are described here. The calibration tank measurements are used to create calibration lines for every 23-hour period. These are used to calibrate the target tank as well as the outside air measurements. For each 2-minute average measurement (of either outside air or target tank), the measurements from two calibration periods are used. From these two surrounding calibration periods, a time dependent interpolation of the intercept and slope was used to derive a specific calibration line, used to calibrate the measurement at that specific time. Calibration periods during which an issue occurred were not included, in that case the next (or previous) calibration period was used.

3.2.2.3 Pressure fluctuation correction

Based on the resulting target tank measurements, we found that the pressure stabilization of the instrument was not performing optimally. The stability of the measurements was influenced by small remaining pressure fluctuations. The interpolation of the two calibration periods surrounding a measurement (outside air or target tank) assumes smooth pressure transitions between the calibration intervals. However, remaining pressure fluctuations in our setup between these intervals could lead to discrepancies between the interpolated pressure and the actual pressure during the measurement. We saw that these pressure fluctuations resulted in variations in the target tank measurements. We have therefore implemented a correction for these remaining pressure fluctuations, based on half of the target tank measurements. The corrections were then applied to the other half of the target tank measurements, as well as to the outside air measurements. This correction is shown in Fig. 6. For pressure fluctuations close to 0 mbar, no correction was applied.

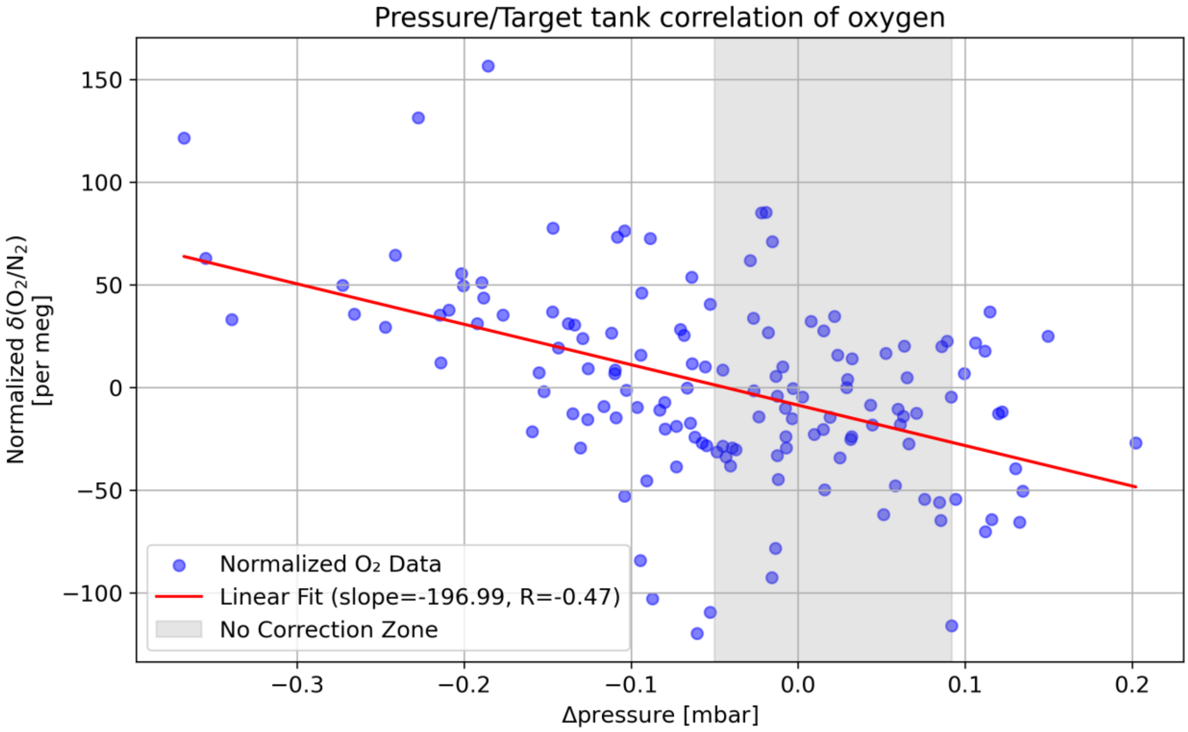

***Fig. 6:** Calibrated target tank measurement correlation to the ΔPressure (difference between interpolated and actual pressure) as used for the correction described in the text. This is based on half of the target tank measurements.*

3.2.2.4 Target tank results

Based on the measurements in the period between September 2024 and March 2025, the second half of the target tank measurements (not used in the correction described above) yielded a measured δ(O_2/N_2) value of –951.74±34.45 per meg (Fig. 8) and a CO_2 value of 416.06±0.03 ppm (Fig. 7). The instrument's sensitivity to pressure fluctuations remains a challenge that we aim to address in future measurements, thereby improving the precision of the target tank measurements.

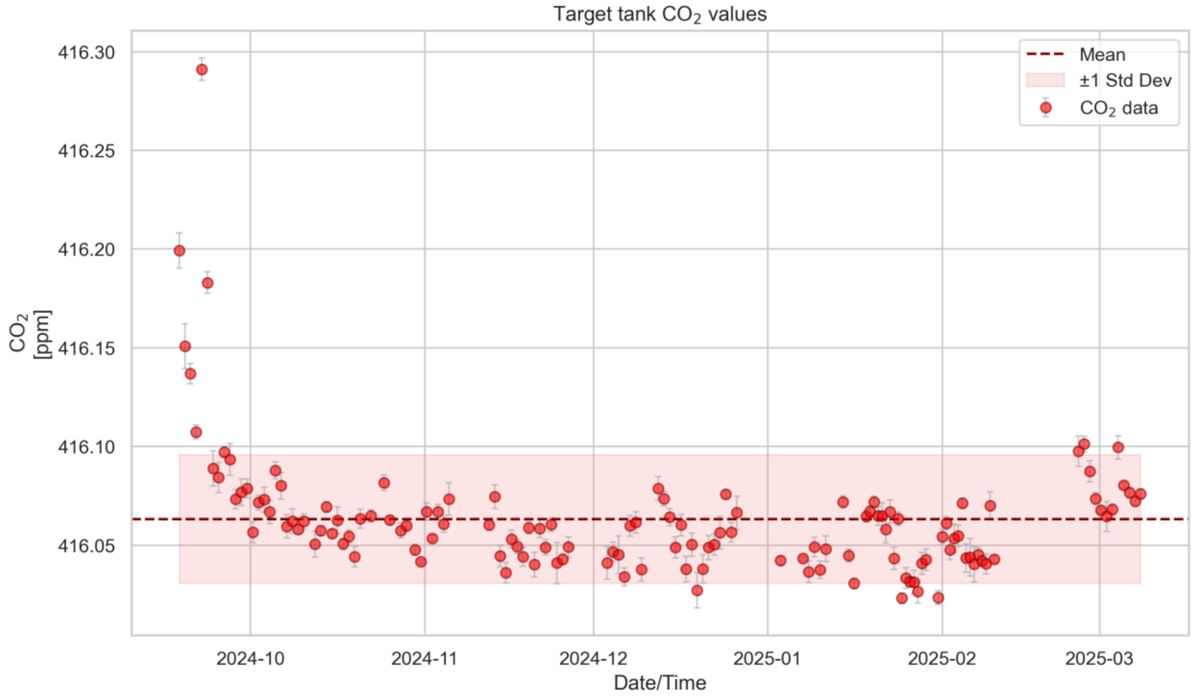

Fig. 7: Calibrated and corrected CO_2 target tank measurements.

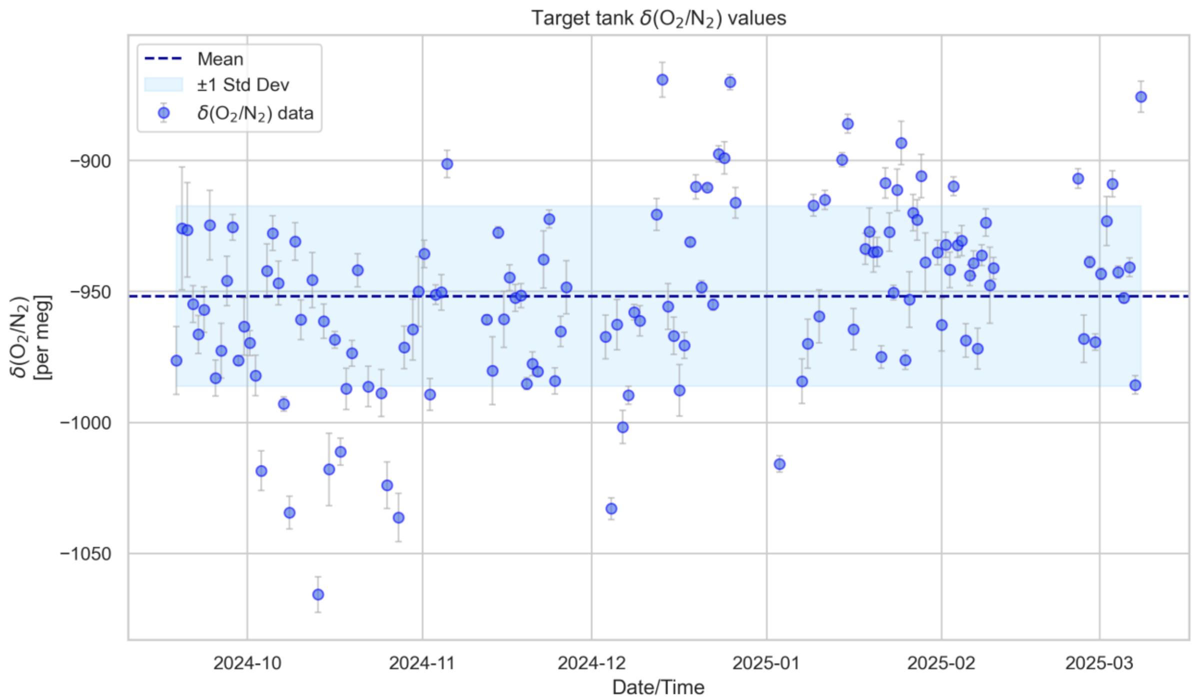

Fig. 8: Calibrated and corrected O_2 target tank measurements

4 Results

4.1 $\Delta^{14}CO_2$ results for flask samples collected in 2024

The $\Delta^{14}CO_2$ results from the flask samples collected in 2024 are included in an accompanying CSV file. This dataset contains measurements from 1,301 individual flasks, as not all collected flasks were analysed for $^{14}CO_2$ (refer to Sec.2.2.3 for deviations from the work plan). The complete CORSO Δ^{14}CO2 dataset for the ICOS stations is included in the L2 ICOS Atmosphere Release 2025-1, published on 1 July 2025. This part of the dataset is consistently curated over the long term and is made available in accordance with FAIR principles through these ICOS Atmosphere Data Releases. The CSV file provided here serves to fulfil Deliverable 3.3 and contains the HFD results as well.

4.1.1 $\Delta^{14}CO_2$ data format of the CSV file

The $\Delta^{14}CO_2$ flask results, along with their related metadata, are included in the accompanying file *CORSO_L2_Flask_Release_Multi_Station.14CO2*. The file header contains references, contact information, and descriptions of the dataset. Table 1 describes the CSV columns and their corresponding units.

Table 1: *Column names and description of the CSV version of the CORSO $\Delta^{14}CO_2$ data set.*

Column Name	Unit	Description
Site	–	Station code where the sample was collected (e.g., BIK, HFD, KIT).
intake height	m (agl)	Height above local ground level at which the flask sample was collected.
CRL/BRAMS_ Flask_Identifer	–	Internal identifier of the flask used, assigned by either ICOS Central Radiocarbon Lab (CRL) or BRAMS laboratory.
CAL_flask_id	–	Internal flask identifier of the ICOS Calibration Laboratory
SamplingStart	–	Start time of the air sampling (UTC), excluding flushing period.
SamplingEnd	–	End time of the air sampling (UTC)
Δ14CO2	‰ (per mil)	Radiocarbon content of CO_2 in per mil deviation from the modern standard, according to the “Δ“ definition in Stuiver & Polach (1977).
MeasUnc	‰ (per mil)	Measurement uncertainty (σ_{meas}) from the accelerator mass spectrometer (AMS), including counting statistics, calibration, and current dependencies.
EstRep.	‰ (per mil)	Estimated reproducibility (σ_{LT}) based on long-term QC data. Including the measurement uncertainty of the QC samples.
CombUnc.	‰ (per mil)	Combined uncertainty (σ_{comb}) calculated from MeasUnc and EstRep.
Measurement_Flag	–	Quality control flag indicating issues or special conditions during measurement.
Sampling_Flag	–	Quality control flag indicating issues or special conditions during sampling.

4.1.2 $\Delta^{14}CO_2$ data example

Fig. 9 illustrates an example of the $\Delta^{14}CO_2$ data collected at Cabauw station in the Netherlands, along with the derived ^{14}C-based estimates of the fossil fuel CO_2 concentration enhancements for these flasks ($\Delta ffCO_2$). The $\Delta^{14}CO_2$ results from the individual flasks are represented as blue symbols, accompanied by their 1σ uncertainty range. The green line depicts the extrapolated marine clean air $\Delta^{14}CO_2$ background level at the Mace Head station in Ireland. Only two flask samples exhibit higher $\Delta^{14}CO_2$ activity concentrations compared to the marine background. This suggests that the sampling strategy designed to avoid air masses significantly affected by $^{14}CO_2$ emissions from nuclear facilities has generally been effective, particularly considering Cabauw's location downwind from major nuclear $^{14}CO_2$ emitters in the UK. The lower panel of Fig. 9 displays the estimated $\Delta ffCO_2$ concentration enhancements relative to the marine background for these flask samples. The $\Delta ffCO_2$ concentration enhancements have been calculated following Maier et al. (2023).

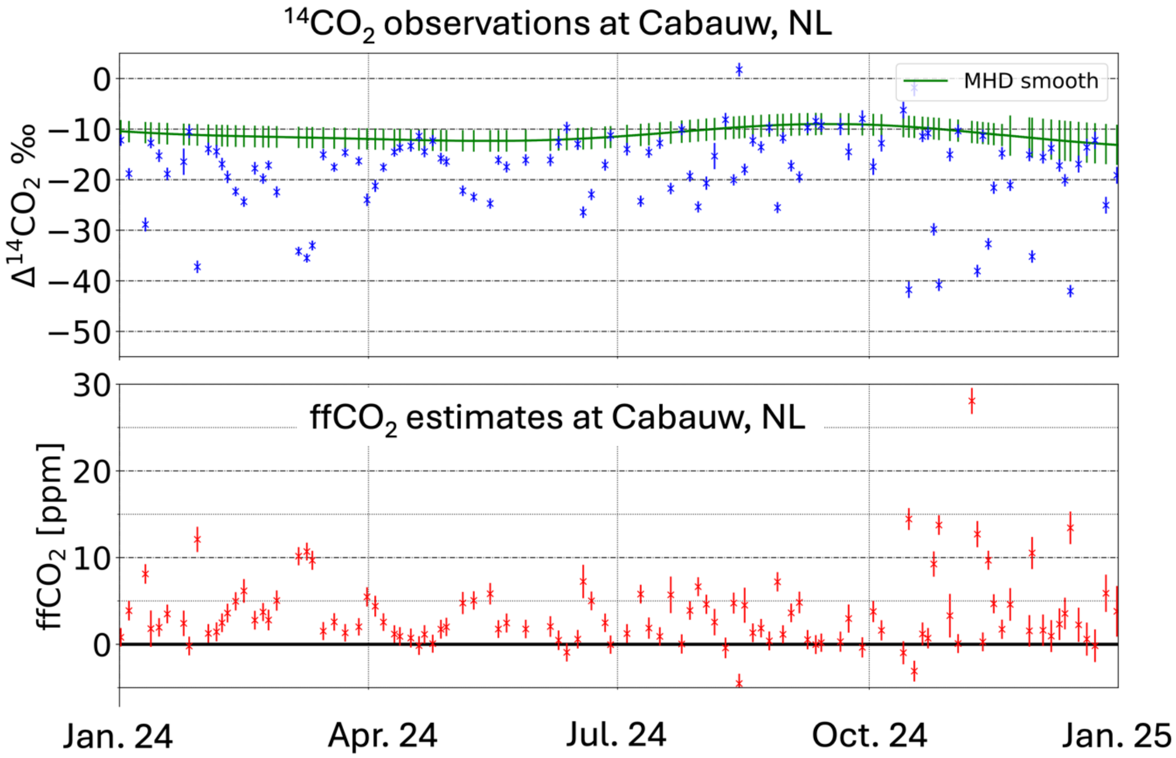

***Fig. 9**: Upper panel: $\Delta^{14}CO_2$ results for Cabauw station (Netherlands) and corresponding ^{14}C-based estimates of fossil fuel CO_2 enhancements ($\Delta ffCO_2$). Blue symbols represent individual flask values with 1σ uncertainty; the green line indicates the marine clean air background from Mace Head (Ireland). The lower panel displays the corresponding $\Delta ffCO_2$ enhancements, calculated following Maier et al. (2023).*

4.1.3 $\Delta^{14}CO_2$ data quality control and uncertainty assessment

Both laboratories, ICOS-CRL and BRAMS, analyse quality control samples alongside the flask samples to determine and document the long-term reproducibility of their $\Delta^{14}CO_2$ measurements. The quality control results are shown in Fig. 10 and Fig. 5, respectively.

ICOS CRL uses three different QC samples: Oxalic Acid I (OX I, NIST SRM 4990B), and two atmospheric air samples QC1 and QC2, with different $^{14}CO_2$ activity concentrations. The results of the individual quality control measurements, together with a 30-point moving average for the period from January 2024 to April 2025, are summarised in the left column of Fig. 10. The CORSO samples from the ICOS-related stations were analysed over this period. The median of the OX I samples deviates by 0.05‰ from the nominal value of OX I, thus confirming a tight link to the international $\Delta^{14}CO_2$ scale. Note, that the scale link was provided via OX II standards, while OX I was measured as an unknown, normalised to $\delta^{13}C$ = -25‰.

The three ICOS CRL quality control samples exhibit no consistent drift over the relevant period, confirming good long-term stability of the ICOS flask analyses. In the right-hand column of Fig. 10, the deviations of the individual measurements from their respective nominal value are displayed as histograms. For the pure-CO_2 sample OX I, we obtain a standard deviation of 1.48‰. The two ambient air quality control samples, QC1 and QC2, exhibit slightly higher standard deviations of 1.57‰ and 1.62‰, respectively. The somewhat lower reproducibility of the ambient air QC samples is likely due to the additional sample preparation steps required to extract the CO_2 from the air sample.

From the QC1 and QC2 results, we deduce a long-term reproducibility σ_{LT} of approximately 1.6‰ for ambient air samples. σ_{LT} includes the measurement uncertainty σ_{meas} of the individual QC samples, which is typically 1‰. As the long-term reproducibility σ_{LT} comprises the independent uncertainty contributions of the measurement uncertainty σ_{meas} and the inter-magazine uncertainty σ_{inter}, σ_{inter} can be estimated to be 1.25‰. The σ_{inter} uncertainty and the flask-specific measurement uncertainty σ_{meas} are added quadratically to form the combined measurement uncertainty σ_{comb}, which is provided for each ICOS-related flask sample in the CORSO dataset (see Table 1).

Fig. 11 shows the ambient air quality control (QC) measurement results from the BRAMS laboratory in 2024. As detailed in Section 2.2.3, the BRAMS AMS experienced several breakdowns in 2024 and 2025. Additionally, the flask sample preparation line at BRAMS was not operating as expected. This resulted in poor reproducibility of the quality control (QC) samples, which ultimately led to the flagging of all HFD flask samples analysed in 2024.

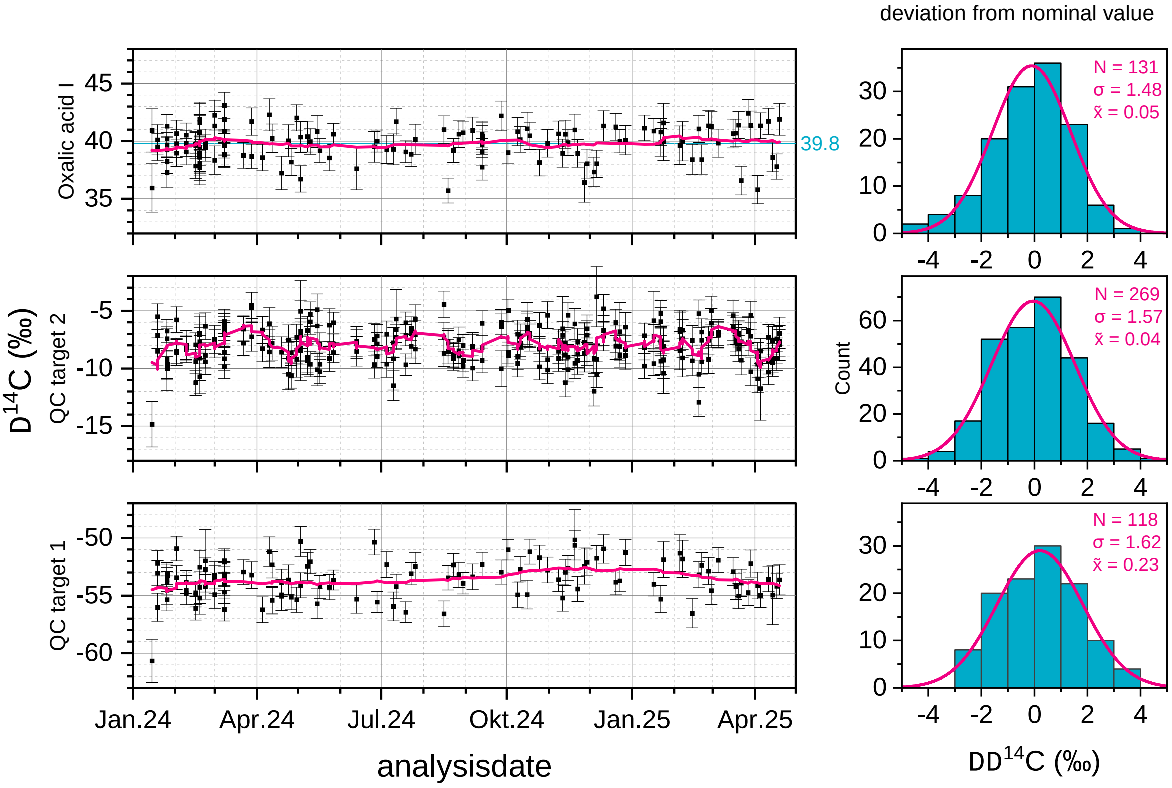

Fig. 10: *Results of ICOS-CRL quality control measurements from January 2024 to April 2025 for three QC materials: Oxalic acid I (OX I), and two atmospheric air samples (QC1, QC2). Left: individual $\Delta^{14}CO_2$ values with 1σ uncertainties and 30-point moving averages. Right: histograms showing deviations from nominal values. Each histogram depicts the number of samples N, their 1σ standard deviation and median deviation from the nominal value x̃.*

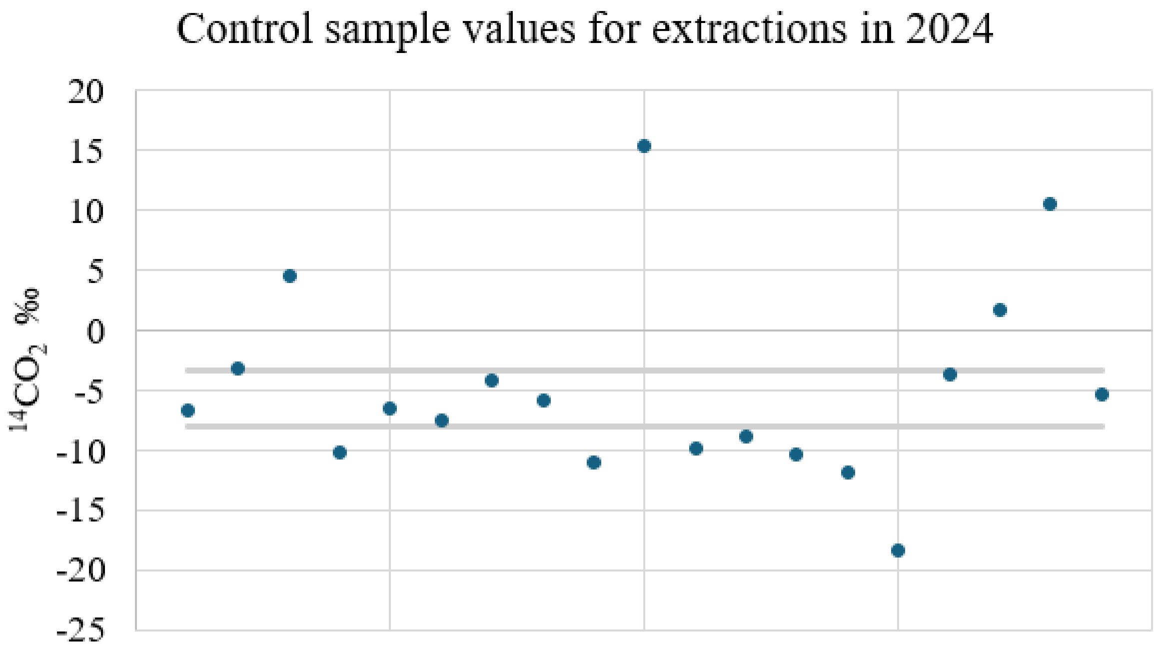

Fig. 11: *Results of BRAMS quality control measurements from 2024 for one ambient air quality control sample.*

4.2 O_2 and CO_2 measurements

Ambient air measurements of O_2 and CO_2 were averaged into hourly means of the 2-minute measurements of calibrated and corrected $\delta(O_2/N_2)$ values, reported in per meg (Fig. 12). For clarifications of $\delta(O_2/N_2)$ values and its unit, see Keeling and Manning (2014). Calibration is based on the 2023 Scripps scale (https://scrippso2.ucsd.edu). The hourly averages in the data file are accompanied by standard deviations, which reflect the variability within each hour, as well as the measurement uncertainty. The hourly values are flagged when fewer than 9 individual measurements contribute to the hourly average. Time-averaged values are assigned to the beginning of their respective averaging intervals in the data file. The CO_2 measurements are also provided as hourly averages and are also used in the $\delta(O_2/N_2)$ calculation. The CO_2 measurements are calibrated to the WMO 2019A scale and reported in ppm. The dataset spans the period from September 17, 2024, to March 9, 2025.

Fig. 12: *Cabauw measurements (17/09/2024 until 09/03/2025) of O_2, CO_2 and constructed APO.*

Additionally, this section includes plots that visualizes the measured data. Fig. 12 displays the complete dataset of calibrated CO_2, $\delta(O_2/CO_2)$, and APO measurements. APO (expressed in per meg) is calculated using Equation 1 (Stephens et al. 1998).

$$\delta APO = \delta(O_2/N_2) + 1.1 \cdot (CO_2 - 350) \qquad [1]$$

Fig. 13 focuses on a shorter time span of a few days to highlight an example of the diurnal cycles of atmospheric carbon dioxide and oxygen. The figure illustrates the characteristic anti-correlation between CO_2 and $\delta(O_2/CO_2)$, with both signals showing similar magnitudes. $\delta(O_2/CO_2)$ is expressed in ppm equivalents.

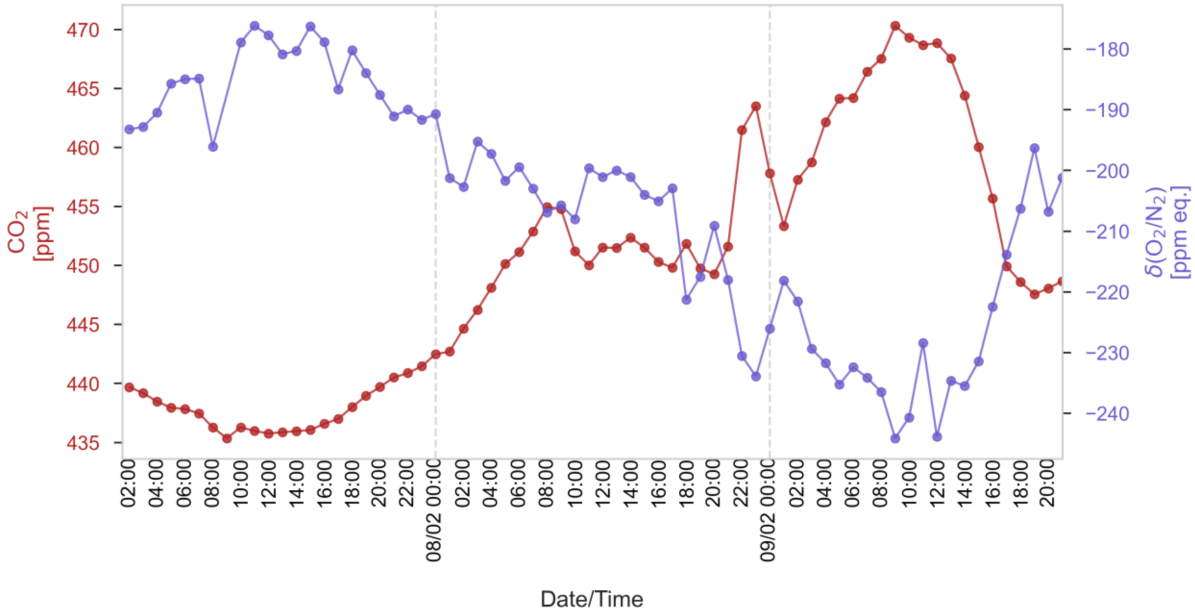

***Fig. 13:** Subsection (07/02/2025 until 09/02/2025) of O_2 and CO_2 data showing a diurnal cycle.*

Fig. 14 presents approximately four days of data, showing calibrated CO2, δ(O_2/CO_2), and APO measurements from both Cabauw and the Weybourne Atmospheric Observatory (WAO) in the United Kingdom. The WAO measurements, conducted by the University of East Anglia (UEA), were obtained using a similar instrument. The main differences are that the WAO site is located in a coastal setting and measurements are sampled at a height of 10 meters. The figure shows that the O_2 and CO_2 signals from both sites have comparable magnitudes, consistent with calibration to the same reference scale. Additionally, CO_2 data from a height of 207 meters at Cabauw, conducted by ICOS, is included to demonstrate the consistency and precision of the CO_2 signals. The APO comparison shows a larger variability at Cabauw compared to Weybourne, which is partially driven by the difference between the stations, and the larger influence of local sources at Cabauw, but could potentially also indicate limited precision of the Cabauw measurements. This will be further investigated in future measurements of calibration tanks that are to be exchanged between the UEA and RUG laboratories.

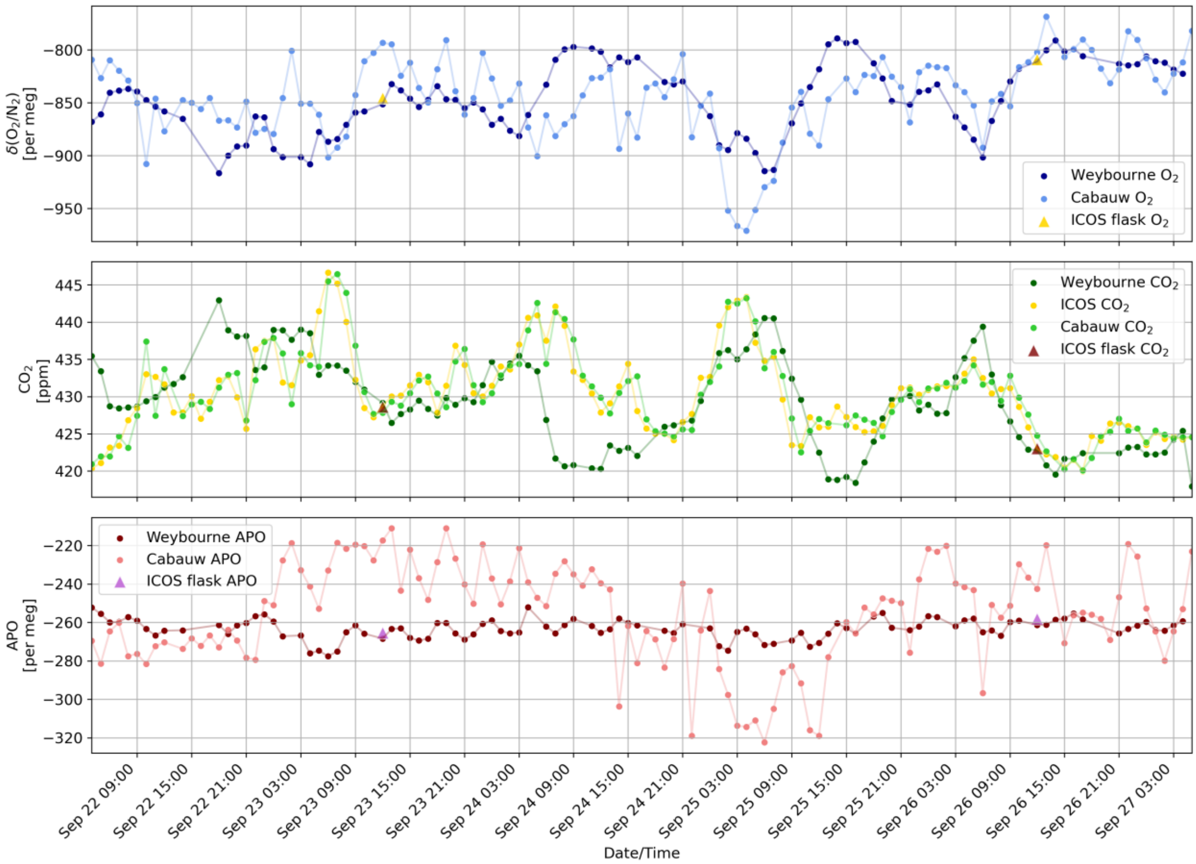

Fig. 14: *Subsection (18/09/2024 till 20/09/2024) of O_2, CO_2 and APO data of Cabauw and in comparison to Weybourne measurements.*

Fig. 15 presents the full set of CO_2 measurements from Cabauw at 207m, alongside continuous and flask-based CO_2 data from ICOS at the same height. The two continuous datasets are closely aligned, as illustrated more clearly in Fig. 16, which displays their difference over the overlapping time period shown in Fig. 15. The differences remain small throughout this period, with a mean of −0.14 ppm and a standard deviation of 2.5 ppm.

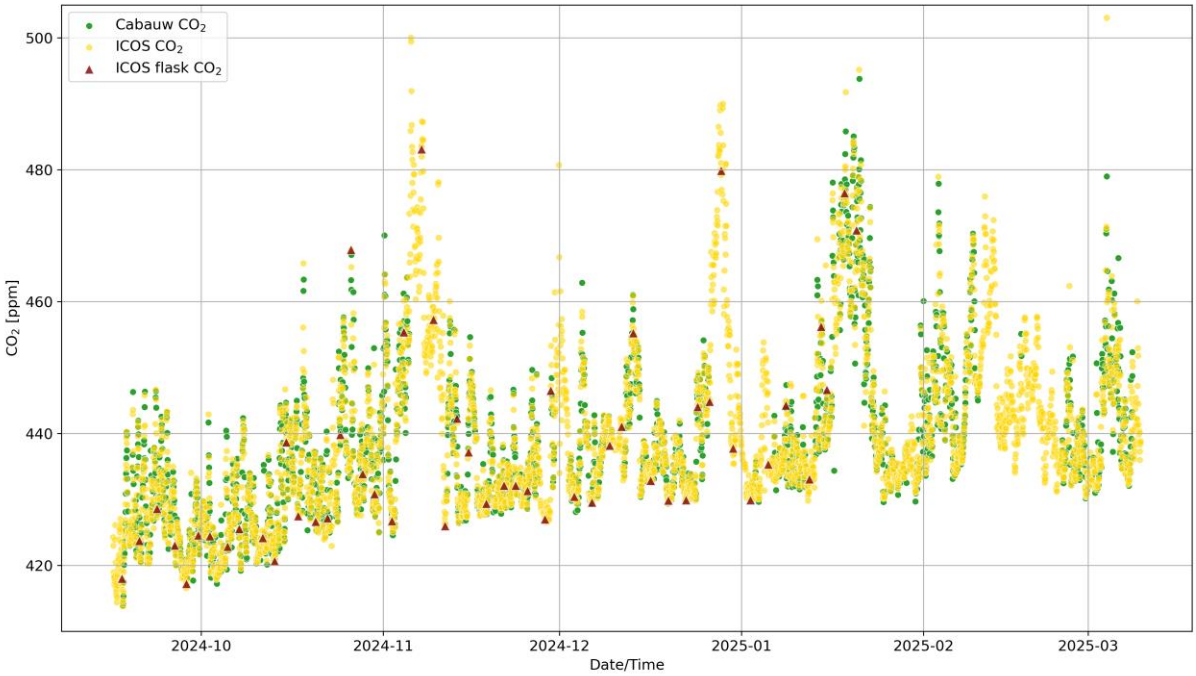

***Fig. 15:** Cabauw CO_2 measurements (17/09/2024–09/03/2025) compared with calibrated ICOS CO_2 data at 207m (continuous and flask).*

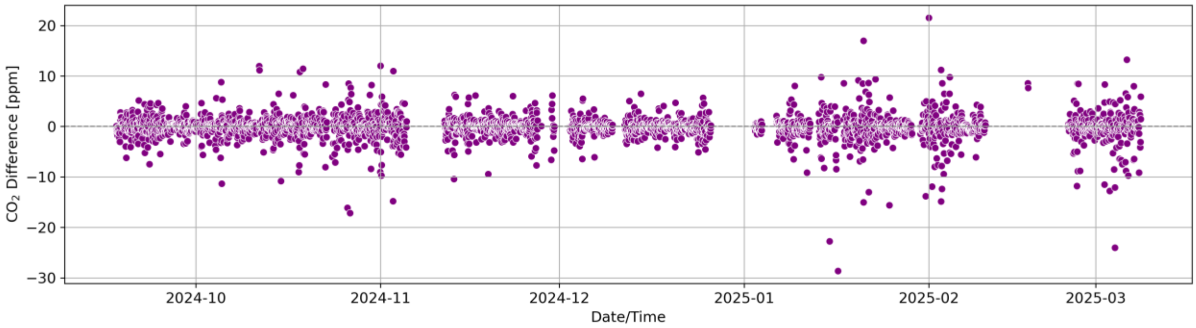

***Fig. 16:** Difference between CO_2 values from the Cabauw measurements and the ICOS Cabauw data at 207m height (Cabauw CO_2 − ICOS CO_2).*

Fig. 17 shows the O_2 measurements from the full available Cabauw dataset (207m), alongside the flask O_2 values published by ICOS at the same height. The difference for O_2 has a mean of 44.6 per meg and a standard deviation of 14.8 per meg and the difference for CO_2 has a mean of 0.14 ppm and a standard deviation of 1.5 ppm as illustrated in Fig. 18.

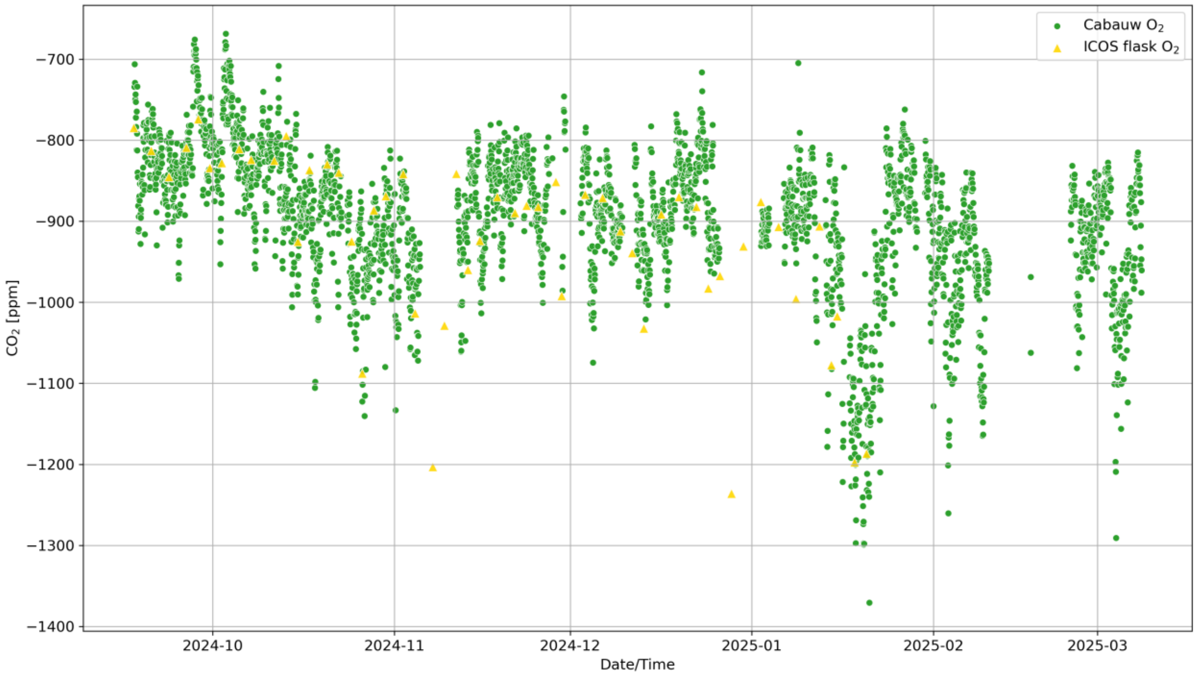

Fig. 17: *Cabauw O_2 measurements (17/09/2024–09/03/2025) compared with calibrated ICOS flask O_2 data at 207m.*

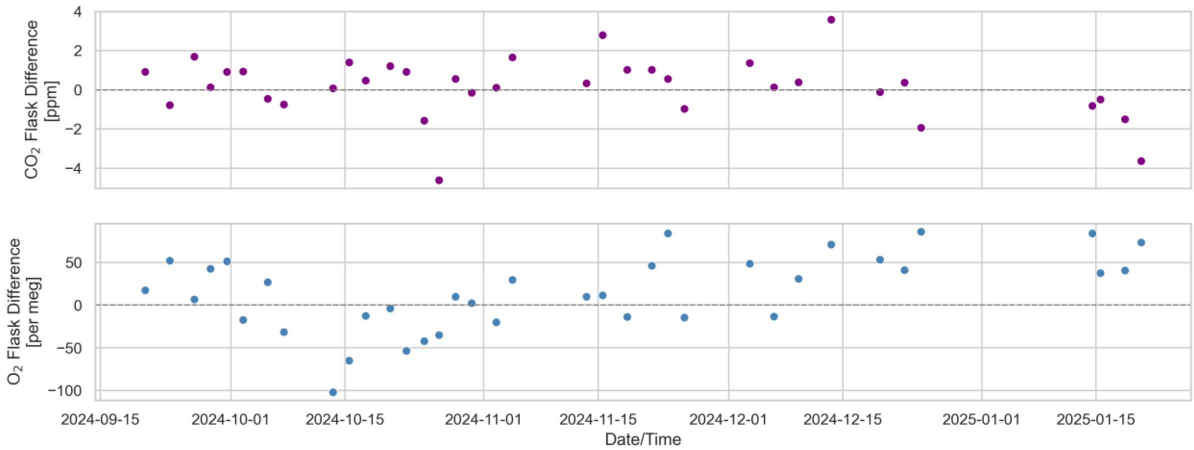

Fig. 18: *Difference between O_2 and CO_2 values from the Cabauw measurements and the ICOS flask Cabauw data at 207m height (Cabauw O_2 − ICOS O_2).*

5 Conclusions

The intensified $\Delta^{14}CO_2$ flask analysis conducted within the CORSO project in 2024 has successfully expanded the observational coverage of $\Delta^{14}CO_2$ in Western Europe. By leveraging the ICOS infrastructure and deploying additional capacity at the Białystok and Heathfield stations, a fivefold increase in the temporal frequency of radiocarbon observations was achieved. The dedicated sampling strategy based on near-real-time footprint modelling effectively reduced the risk of nuclear $^{14}CO_2$ contamination in the collected air samples, as evidenced by the small number of above-baseline samples thereby increasing the scientific usefulness of the dataset.

High-precision analytical performance and long-term stability were demonstrated by the ICOS-CRL, as evidenced by quality control results from three reference materials. The median deviation of Oxalic Acid I from its nominal value was only 0.05‰, confirming the laboratory's close alignment with the international $^{14}CO_2$ scale. Ambient air QC samples demonstrated an excellent long-term reproducibility of 1.6‰, supporting the reliability of the reported uncertainties in the CORSO $\Delta^{14}CO_2$ dataset.

While the analysis of Heathfield samples suffered delays due to technical issues at the BRAMS laboratory, the remaining network delivered robust data, which is now available as a CSV file and as part of the ICOS Atmosphere Data Releases, thereby complying with FAIR principles.

For O_2, the measurement capacity in Europe was expanded through the installation and operation of the setup at Cabauw in the Netherlands. This is the third site in Europe providing these continuous O_2 measurements after Weybourne and Heathfield in the UK. The measurements started later than initially planned, in September 2024, but will be continued beyond the CORSO period.

Together, these $\Delta^{14}CO_2$ and continuous O_2 observations provide a new basis for constraining fossil fuel CO_2 emissions in Europe and can serve as input to inversion systems also within the CO2MVS framework.

6 References

Basu, S., Lehman, S. J., Miller, J. B., Andrews, A. E., Sweeney, C., Gurney, K. R., Xue, X., Southon, J., and Tans, P. P.: Estimating US fossil fuel CO_2 emissions from measurements of ^{14}C in atmospheric CO_2, *Proc. Natl. Acad. Sci. USA*, 117(24), 13300–13307, https://doi.org/10.1073/pnas.1919032117, 2020.

Basu, S., Miller, J. B., and Lehman, S.: Separation of biospheric and fossil fuel fluxes of CO_2 by atmospheric inversion of CO_2 and $^{14}CO_2$ measurements: Observation System Simulations, *Atmos. Chem. Phys.*, 16, 5665–5683, https://doi.org/10.5194/acp-16-5665-2016, 2016.

Chawner, H., Adcock, K. E., Arnold, T., Artioli, Y., Dylag, C., Forster, G. L., Ganesan, A., Graven, H., Lessin, G., Levy, P., Luijkx, I. T., Manning, A., Pickers, P. A., Rennick, C., Rödenbeck, C., & Rigby, M. Atmospheric oxygen as a tracer for fossil fuel carbon dioxide: a sensitivity study in the UK. *Atmos. Chem. Phys,* 24, 4231–4252, https://doi.org/10.5194/acp-24-4231-2024, 2024.

Faassen, K. A. P., Nguyen, L. N. T., Broekema, E. R., Kers, B. A. M., Mammarella, I., Vesala, T., Pickers, P. A., Manning, A. C., Vilà-Guerau de Arellano, J., Meijer, H. A. J., et al.: Diurnal variability of atmospheric O_2, CO_2, and their exchange ratio above a boreal forest in southern Finland, *Atmos. Chem. Phys.*, 23(2), 851–876, https://doi.org/10.5194/acp-23-851-2023, 2023.

Faassen K.A.P., van der Woude, A., Hooghiem, J.D., Kaushik, A., Hilman, B., Peters, W., Luijkx, I.T., Impact of the variability of O_2 and CO_2 biosphere exchange on O_2-based fossil fuel estimations, in prep. 2025.

Graven, H., Fischer, M. L., Lueker, T., Jeong, S., Guilderson, T. P., Keeling, R. F., Bambha, R., Brophy, K., Callahan, W., Cui, X., Frankenberg, C., Gurney, R. K., LaFranchi, B. W., Lehman, S. J., Michelsen, H., Miller, J. B., Newman, S., Paplawsky, W., Parazoo, N. C., Sloop, C., and Walker, S. J.: Assessing fossil fuel CO_2 emissions in California using atmospheric observations and models, *Environ. Res. Lett.*, 13, 065007, https://doi.org/10.1088/1748-9326/aabd43, 2018.

Keeling, R. F., and Manning, A. C.: Studies of recent changes in atmospheric O_2 content, in: *Treatise on Geochemistry: Second Edition*, 385–404, Elsevier, https://doi.org/10.1016/B978-0-08-095975-7.00416-8, 2014.

KNMI: Meetmast Cabauw, https://www.knmi.nl/kennis-en-datacentrum/uitleg/meetmast-cabauw, accessed: 15 April 2025.

Levin, I., Karstens, U., Eritt, M., Maier, F., Arnold, S., Rzesanke, D., Hammer, S., Ramonet, M., Vítková, G., Conil, S., Heliasz, M., Kubistin, D., and Lindauer, M.: A dedicated flask sampling strategy developed for ICOS stations based on CO_2 and CO measurements and STILT footprint modelling, *Atmos. Chem. Phys.*, 20, 11161–11180, https://doi.org/10.5194/acp-20-11161-2020, 2020.

Levin, I., Kromer, B., Schmidt, M., and Sartorius, H.: A novel approach for independent budgeting of fossil fuel CO_2 over Europe by $^{14}CO_2$ observations, *Geophys. Res. Lett.*, 30(23), 2194, https://doi.org/10.1029/2003GL018477, 2003.

Maier, F., Levin, I., Gachkivskyi, M., Rödenbeck, C., and Hammer, S.: Estimating regional fossil fuel CO_2 concentrations from $^{14}CO_2$ observations: challenges and uncertainties, *Philosophical Transactions of the Royal Society A*, 381(2261), 20220203, https://doi.org/10.1098/rsta.2022.0203, 2023.

Pickers, P. A., Manning, A. C., Le Quéré, C., Forster, G. L., Luijkx, I. T., Gerbig, C., Fleming, L. S., and Sturges, W. T.: Novel quantification of regional fossil fuel CO_2 reductions during

COVID-19 lockdowns using atmospheric oxygen measurements, *Sci. Adv.*, 8(16), eabl9250, https://doi.org/10.1126/sciadv.abl9250, 2022.

Rödenbeck, C., Adcock, K. E., Eritt, M., Gachkivsky, M., Gerbig, C., Hammer, S., Jordan, A., Keeling, R. F., Levin, I., Maier, F., Manning, A. C., Moossen, H., Munassar, S., Pickers, P. A., Rothe, M., Tohjima, Y., & Zaehle, S. (2023). The suitability of atmospheric oxygen measurements to constrain Western European fossil-fuel CO_2 emissions and their trends. *Atmos. Chem. Phys.*, 23, 15767-15782, https://doi.org/10.5194/acp-23-15767-2023, 2023.

Steinbach, J., Gerbig, C., Rödenbeck, C., Karstens, U., Minejima, C., and Mukai, H.: The CO_2 release and oxygen uptake from fossil fuel emission estimate (COFFEE) dataset: effects from varying oxidative ratios, *Atmos. Chem. Phys.*, 11(14), 6855–6870, https://doi.org/10.5194/acp-11-6855-2011, 2011.

Stephens, B. B., Bakwin, P. S., Tans, P. P., Teclaw, R. M., and Baumann, D. D.: Application of a differential fuel-cell analyzer for measuring atmospheric oxygen variations, *J. Atmos. Oceanic Technol.*, 24(1), 82–94, https://doi.org/10.1175/JTECH1941.1, 2007.

Stephens, B. B., Keeling, R. F., Heimann, M., Six, K. D., Murnane, R., and Caldeira, K.: Testing global ocean carbon cycle models using measurements of atmospheric O_2 and CO_2 concentration, *Global Biogeochem. Cycles*, 12(2), 213–230, https://doi.org/10.1029/98GB00736, 1998.

Stohl, A., Hittenberger, M., & Wotawa, G. (1998). Validation of the Lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data. *Atmospheric Environment*, *32*(24), 4245-4264.

TNO: Cabauw atmospheric supersite: 50 years of measuring for clean air and climate, https://www.tno.nl/en/newsroom/insights/2024/01/cabauw-atmospheric-supersite/, accessed: 15 April 2025.

Turnbull, J. C., Miller, J. B., Lehman, S. J., Tans, P. P., Sparks, R. J., and Southon, J. R.: Comparison of $^{14}CO_2$, CO and SF_6 as tracers for determination of recently added fossil fuel CO_2 in the atmosphere and implications for biological CO_2 exchange, *Geophys. Res. Lett.*, 33, L01817, https://doi.org/10.1029/2005GL024213, 2006.

van Leeuwen, C.: Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from carbon capture and storage sites, M.Sc. thesis, 2015.

Document History

Version	Author(s)	Date	Changes
1.0	Samuel Hammer	May 14^{th} 2025	Initial 14CO2 part
1.1	Ingrid Luijkx, Samuel Hammer, Lois de Beijl	May 23th	Full first draft
1.2	Ingrid Luijkx	30 June 2025	Revised draft after review
1.3	Samuel Hammer	02 July 2025	Revised draft after review

Internal Review History

Internal Reviewers	Date	Comments
Matthew Rigby (Univ Bristol)	5/6/25	This is an excellent overview of these exciting new datasets. My comments are provided throughout the document. (MR)
Marya el Malki (TNO)	11/06/2025	Well-written report that clearly outlines the novel work carried within the deliverable. Minor comments / suggestions included in the doc.