CO2MVS RESEARCH ON SUPPLEMENTARY OBSERVATIONS

Database of existing $\Delta^{14}CO_2$ measurements

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1 Executive Summary

Estimating continental-scale fossil CO_2 emissions from $^{14}CO_2$ observations e.g. over Europe or North America require reliable boundary conditions for the targeted area. These can be defined by global inversions that need to be based on hemispheric (or global) background observations at marine or coastal sites or observations from the free troposphere > 3500 m a.s.l. over the continents. A corresponding database of such $^{14}CO_2$ observations from globally distributed monitoring stations has been compiled within task 3.1, which will be used by the global and regional inversions (tasks 3.3 and 3.4) for the period 2004-2024. The database includes published datasets from the global monitoring programs of NOAA/INSTAAR, SIO/LLNL, SIO/UCI, and GNS/NIWA, as well as published and unpublished data from the UHEI global $^{14}CO_2$ network and from Baring Head, New Zealand. To estimate compatibility of this merged dataset, we revisited inter-laboratory comparison results of the contributing institutions and laboratories, that showed $\Delta^{14}CO_2$ compatibility < 2 ‰. Further comparison of measurements from different monitoring programs conducted in the same latitudinal bands (within ca. 10° lat.) did not reveal any trends of potential offsets between institutions over the last two decades. Comparison of data collected from the 1980s onwards at Baring Head, New Zealand and Cape Grim, Tasmania, Australia shows no offset.

All datasets have been complemented with meta data describing the individual station characteristics, sampling and analysis methods, time period coverage, data sources, and references. For each record, two datasets are delivered. The first contains all measurements from the station. The second contains only those data which have been identified as representing large-scale background conditions. The data are currently openly available, at a server of UHEI. FAIR data principles will be applied to the final data compilations with the data being shared via the ICOS ERIC Carbon Portal.

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 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 CO_2 Human Emissions), and CoCO2 (Copernicus CO_2 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 $^{14}CO_2$ (radiocarbon) and APO (atmospheric potential oxygen) observations as tracers for anthropogenic emissions in both global and regional scale inversions. In addition to this, CORSO will develop coupled land-atmosphere data assimilation in the global CO2MVS system constraining carbon cycle variables using satellite observations of soil moisture, LAI (leaf area index), SIF (solar induced fluorescence), 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 $\Delta^{14}CO_2$ and APO. Fossil fuels do not contain radiocarbon (^{14}C) and their combustion releases CO_2 that dilutes the $^{14}C/C$ ratio of other CO_2 sources (e.g., biospheric) that contain $^{14}CO_2$. This dilution induces a measurable 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).

The global distribution of $\Delta^{14}CO_2$ in background air is a critical boundary condition for atmospheric transport inversions to estimate regional fossil fuel CO_2 emissions using $^{14}CO_2$ observations over continents. While continental-scale $\Delta^{14}CO_2$ observations, such as those conducted over the United States by NOAA (Basu et al., 2020) or within ICOS (Levin et al., 2020; Heiskanen et al., 2021) are generally comparable because they are conducted by one laboratory, global background observations have been measured by several high-precision ^{14}C laboratories distributed world-wide. These laboratories relate their analyses to internationally accepted standards, however, small scale differences between laboratories may still occur (Miller et al., 2013; Turnbull et al., 2015; Hammer et al., 2017) that could compromise the quality of a merged global $\Delta^{14}CO_2$ dataset that aims to quantify hemispheric, inter-hemispheric and regional gradients to be interpreted in atmospheric transport inversions of the $^{14}CO_2$ cycle.

2.2.1 Objectives of this deliverables

The objectives of this deliverable were to gather existing published, and where possible unpublished, high-precision $\Delta^{14}CO_2$ data from globally distributed background stations and to make a first assessment of their quality and compatibility with the final aim of merging them into one single compilation that could be used as boundary conditions for regional estimates of fossil CO_2 emissions in Europe. These data shall also be useful for global inversions that focus on the global carbon cycle and the additional constraints provided by $^{14}CO_2$ observations on that scale (e.g., from global $\Delta^{14}CO_2$ trends and inter-hemispheric gradients (see e.g., Turnbull et al., 2009; Levin et al., 2010, 2021b)). The final product to be delivered would be a publicly available compilation of harmonised $\Delta^{14}CO_2$ observations, including an uncertainty estimate, that could be used within WP3 of CORSO but also by other groups outside Europe for their global carbon cycle modelling studies.

2.2.2 Work performed in this deliverable

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

- Identification of potential data providers that meet the required measurement precision as defined by the WMO Experts for background $^{14}CO_2$ measurements (WMO, 2020).
- Compilation of intercomparison exercises that included the contributing laboratories.
- Gathering and ingestion of published $\Delta^{14}CO_2$ datasets into the ICOS-CRL database.
- Reformatting and harmonisation of the data sets, including their meta data to deliver a unified data compilation in preparation of a background $^{14}CO_2$-ObsPack.
- Flagging of non-representative data by comparison with measurements from similar latitudes (i.e., within ca. 10° latitude bands).
- Preliminary uncertainty assessment based on past inter-comparison exercises (ICP) and comparisons of data from the different laboratories.

2.2.3 Deviations and counter measures

There were no deviations from the original work plan.

2.3 Project partners

This deliverable was conducted by UHEI with the support from CORSO-external data providers/collaborators as listed below:

CORSO Partners / Collaborators /Laboratories	
RUPRECHT-KARLS-UNIVERSITAET HEIDELBERG, Institute of Environmental Physics, Germany	UHEI
Integrated Carbon Observation System Central Radiocarbon Laboratory, Heidelberg University, Germany	ICOS-CRL
GNS Science, National Institute of Water and Atmospheric Research, New Zealand	GNS/NIWA
University of California San Diego, Scripps Institution of Oceanography, U.S.A.	SIO
University of California, Irvine, U.S.A.	UCI
NOAA Global Monitoring Laboratory (CCGG), Boulder, CO, U.S.A.	NOAA
University of Colorado, Institute of Arctic and Antarctic Research, Boulder, CO, U.S.A.	INSTAAR

3 Results

3.1 Background

The current deliverable comprises the compilation of high-precision $\Delta^{14}CO_2$ observations in background air from the past ca. 35 years that have been published by UHEI and collaborating laboratories. They are supplemented by yet unpublished data from the UHEI global collaborative $^{14}CO_2$ network that was established in the 1980s, and from Baring Head, New Zealand. Sampling at most stations continues until today. During the CORSO project, new background $\Delta^{14}CO_2$ data will become available, either through analysis of archived samples from SIO and UHEI as funded by CORSO or from new publications by the collaborating laboratories in the framework of other projects. These new data, when becoming available, will be added to the current compilation and subsequent data releases are planned for the coming years.

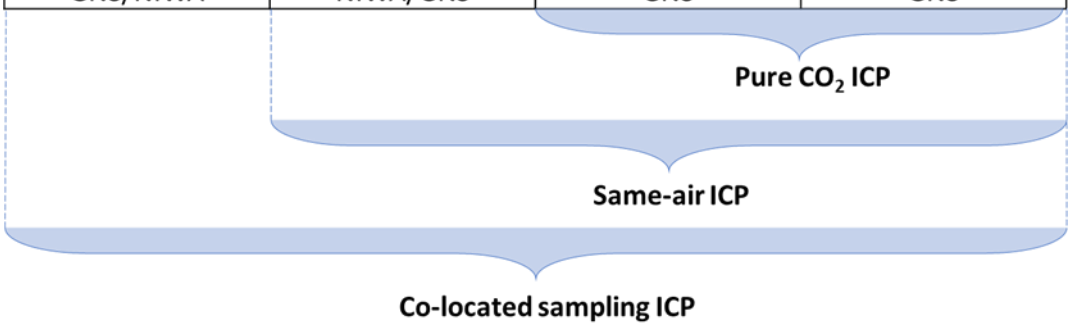
Two types of atmospheric samples are included in this compilation: (1) Integrated samples collected over approximately two weeks by CO_2 absorption in sodium hydroxide (NaOH) solution (UHEI network, Levin et al., 1980), (2) samples collected over several days or weeks by passive absorption in NaOH solution (Baring Head integrated, Turnbull et al., 2017), and whole air spot samples collected into glass flasks (all other networks). UHEI Integrated samples were analysed by low level counting (Kromer and Münnich, 1992). The same is true for most of the integrated Baring Head samples, while whole air samples were analysed by accelerator mass spectrometry (AMS). Details about sampling and analysis methods are referenced in the meta data of the individual data sets.

3.2 Identification of $^{14}CO_2$ laboratories and data providers

The generation of $\Delta^{14}CO_2$ datasets involves four key tasks: sampling, CO_2 extraction, sample preparation, and measurement of ^{14}C activity; these individual tasks are often carried out by different institutions. Of six teams of institutions/laboratories contacted for participation due to their continuous monitoring of global $^{14}CO_2$ background measurements, four are actively engaged in contributing to this merged dataset (listed with their corresponding tasks in Table 1).

Table 1: Overview of the participating research institutions, their responsibilities, and mapping of ^{14}C processing steps to the different types of inter-comparisons.

Sampling	CO_2 extraction	Sample preparation	^{14}C measurements
UHEI	UHEI later ICOS	UHEI later ICOS	UHEI later ICOS
SIO	SIO	LLNL later UCI	LLNL later UCI
NOAA	INSTAAR	INSTAAR	UCI
GNS/NIWA	NIWA/GNS	GNS	GNS



Over the decades, the SIO team has changed. Until the year 2021, sample preparation and ^{14}C measurement were carried out at Lawrence Livermore National Laboratory (LLNL). In later years, both tasks were taken over by UCI. From 2016 onwards, the measurements for the UHEI network were taken over by the ICOS Central Radiocarbon Laboratory, which, however, continued to use the equipment and methods of the former Heidelberg ^{14}C Laboratory.

3.3 Published laboratory inter-comparison exercises

Five $^{14}CO_2$ laboratory inter-comparison (ICP) activities were published previously, involving subsets of the four contributing teams. These studies involve different types of comparison samples, involving all or only a subset of the sample processing steps listed above:

- Co-located sampling covers the entire process from atmospheric sampling to ^{14}C measurement.
- The same-air approach compares CO_2 extraction, sample preparation, and ^{14}C measurement.
- The pure-CO_2 sample type compares only sample preparation and ^{14}C measurement.

Notably, only the pure-CO_2 sample type allows conventional low-level counting $^{14}CO_2$ measurement systems applied in the UHEI background network to participate in the comparison because of the larger sample size required and long integration times when sampling. Collocated sampling at Alert station between UHEI and flasks measured by SIO/UCI during periods of stable weather conditions are being investigated as part of CORSO and will become part of the ICP in updated versions of this report.

In 2013, Graven et al. published results from 22 co-located air samplings at the Barrow station. This ICP involved different sampling, CO_2 extraction, sample preparation systems, and two different Accelerator Mass Spectrometers (AMS) from UCI and SIO/LLNL. Figure 1 illustrates the outcomes of this ICP, showcasing excellent agreement between both laboratories. The $\Delta^{14}CO_2$ bias and standard error were found to be (0.2 ± 0.7) ‰ for all 22 samples collected between 2003 and 2007 (for the definition of the Δ-notation, reporting the $^{14}C/C$ ratio of a sample with respect to the internationally accepted standard in ‰, see Stuiver and Polach

(1977). The formula used by the atmospheric community for reporting atmospheric $\Delta^{14}CO_2$ data is denoted simply Δ in this reference).

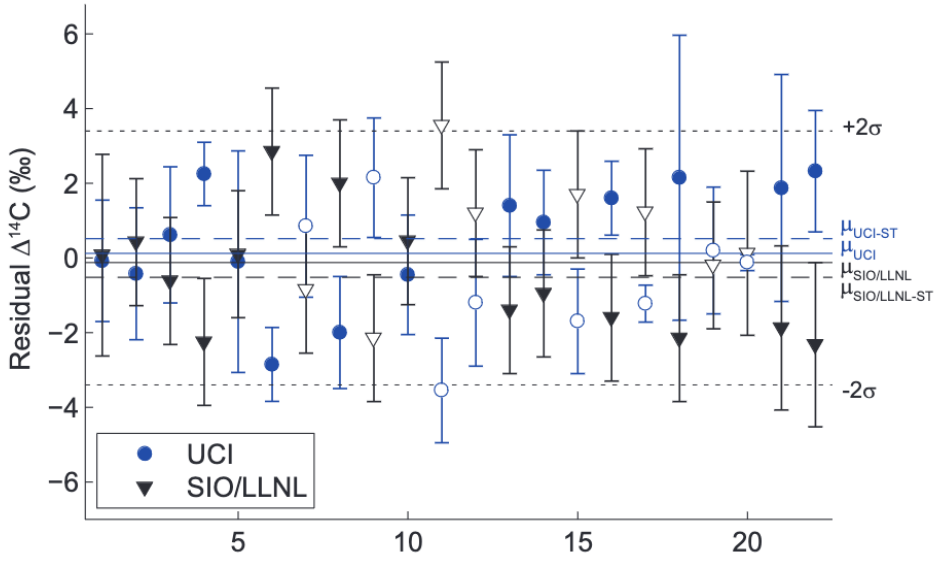


Figure 1: Point Barrow ICP (UCI vs. SIO/LLNL). Residual $\Delta^{14}CO_2$ for 22 individual sample dates. Replicate samples from UCI have been averaged. Error bars show the reported measurement uncertainty or, for UCI, the standard deviation in replicate measurements. The average residuals, μUCI and μSIO/LLNL, are shown by solid lines. The average residuals for samples collected within 1 hr of each other only, μUCI-ST and μSIO/LLNL-ST, are shown by dashed lines. Dotted lines show a $\pm 2\sigma$ envelope around the average reported uncertainty for SIO/LLNL of ±1.7‰.

A multi-laboratory same-air ICP study was published by Miller et al. (2013), with participation from the INSTAAR/UCI, SIO/LLNL, and UCI teams. Over the course of 2007 and 2010, three rounds of comparison samples were distributed, and the results, depicted in Figure 2, demonstrate an agreement between these three teams of approximately 1‰ in $\Delta^{14}CO_2$.

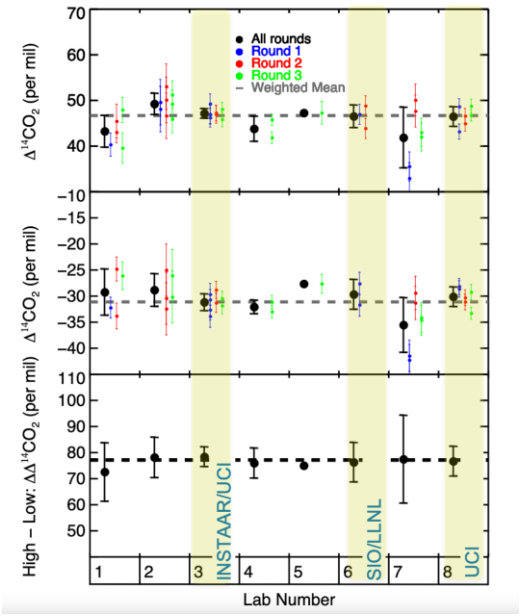


Figure 2: $\Delta^{14}CO_2$ results for ambient (A), depleted (B), and the difference (C) for all groups. For 2A and B, coloured error bars for each sample represent reported uncertainty from each group, while black error bars represent the repeatability (standard deviation) of all measurements. For 2C, error bars are the quadrature-summed standard deviations of the high and low $\Delta^{14}CO_2$ all-round means. The grey dashed lines are the means, weighted by the inverse of the all-round variances. The laboratories participating in the CORSO data compilation are highlighted in yellow.

In 2007, Turnbull et al. reported on a same-air ICP between INSTAAR/UCI and INSTAAR/GNS, yielding a mean difference of only (0.2 ± 0.5) ‰ in $\Delta^{14}CO_2$. This ICP was based on 72 samples and compared two sample preparations and AMS systems and was executed between Nov. 2003 and March 2006.

From 2011 to 2014, Turnbull et al. (2015) conducted bilateral a pure-CO_2 ICP between GNS and INSTAAR/UCI. In total, 69 ICP samples at $\Delta^{14}CO_2$ levels of 43 ‰ and -31 ‰ have been analysed. At both $^{14}CO_2$ levels, the results show a consistent bias of (+1.4 ± 0.3) ‰ and (+1.3 ± 0.3) ‰ for GNS compared to INSTAAR/UCI. The authors recommended applying a mean offset of (-1.4 ± 0.2) ‰ to GNS results when using data sets by INSTAAR and GNS together. Unpublished pure-CO_2 ICP results between ICOS and GNS conducted in 2022 and based on 15 samples found that GNS is (1.1 ± 0.5) ‰ lower compared to ICOS.

Hammer et al. (2017) conducted a pure-CO_2 ICP study comparing the Low-Level-Counting (LLC) laboratory at UHEI to 12 AMS laboratories. The UHEI LLC laboratory shows an average bias of (–0.3 ± 0.5) ‰ with respect to the consensus value of the AMS laboratories. The ICP comprised five pure-CO_2 ICP samples in the atmospheric $\Delta^{14}CO_2$ range of 9.6 ‰ to 40.4 ‰. In Figure 3, the ICP results of the individual laboratories are shown, highlighting the UHEI, GNS and INSTAAR/UCI results in yellow. GNS did split the ICP samples in two targets and reported two independent measurements labelled as GNS a and GNS b. Table 2 summarises the differences between the three laboratories. However, the number of ICP samples was too small to determine whether the measurement biases of the individual AMS laboratories were significant.

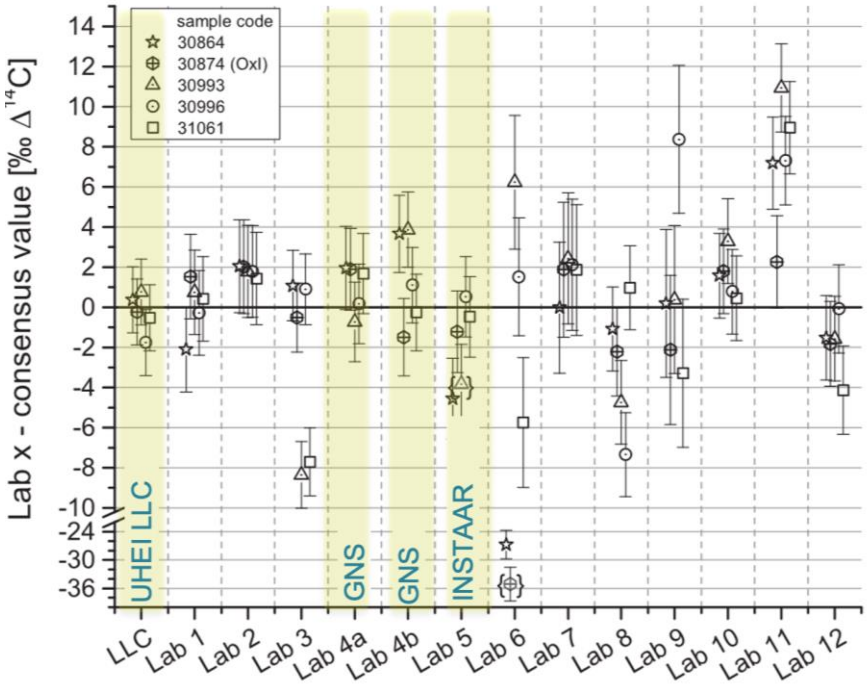


Figure 3: Summary of all pure-CO_2 ICP results. The difference for each sample to the consensus value based on 9 labs is shown. Labs 3, 6, and 11 have been excluded from the calculation of the consensus

value (refer to the original paper for explanations). The measurements in brackets from labs 5 and 6 are subject to sample handling problems. The laboratories participating in the CORSO data compilation are highlighted in yellow.

Table 2: Results of the pure-CO_2 ICP for UHEI, GNS and INSTAAR. The bias is given as the difference between the weighted average of the five ICP samples and the consensus value, together with the error of the weighted average.

Laboratory	**$\Delta^{14}CO_2$ bias: weighted average (Lab x minus consensus value)**	**$\Delta^{14}CO_2$ error of weighted average**
UHEI LLC	-0.28 ‰	0.73. ‰
GNS a / Lab 4a	0.96 ‰	0.90 ‰
GNS b / Lab 4a	1.39 ‰	0.85 ‰
INSTAAR / Lab 5	-1.92 ‰	0.90. ‰

Table 3 summarises the interlaboratory differences based on the published ICP studies presented above. These studies show that, in general, the reported inter-laboratory biases are small compared to the inherent uncertainty of single ^{14}C measurements, which is typically between 1.3 and 2.5 ‰. The number of samples in the multi-laboratory ICPs was too small to deduce robust biases. To make reliable assessments of the WMO-GAW inter-laboratory compatibility goal of 0.5‰ (WMO, 2020), approximately 50 comparison samples are required, given the typically achieved ^{14}C precisions. Bilateral ICPs, on the other hand, had a larger data base, which allowed the detection of a significant laboratory bias between INSTAAR and GNS (Turnbull et al., 2015).

Table 3: Compilation of interlaboratory differences based on published ICP studies.

Laboratory Team 1	**Laboratory Team 2**	**ICP Type**	**time span**	**mean $\Delta^{14}CO_2$ bias Lab1 -Lab2**	**error**	**number of samples**	**Reference**
UCI	SIO/LLNL	co-located sampling	2003-2007	0.2 ‰	± 0.7‰	22	Graven et al. (2013)
INSTAAR/ UCI	SIO/LLNL	same air	2007 & 2010	> 1 ‰	n/a	5	Miller et al. (2013)
INSTAAR/ UCI	UCI	same air	2007 & 2010	> 1 ‰	n/a	12	Miller et al. (2013)
INSTAAR/ GNS	INSTAAR/ UCI	same air	2003 to 2006	- 0.2 ‰	± 0.5‰	72	Turnbull et al. (2007)
GNS	INSTAAR/ UCI	pure-CO_2	2011 to 2014	1.4 ‰	± 0.2‰	69	Turnbull et al. (2015)
GNS	UHEI	pure-CO_2	2015	1.5 ‰	± 0.9 ‰	10	Hammer et al., (2017)
INSTAAR/ UCI	UHEI	pure-CO_2	2015	- 1.6 ‰	± 0.9 ‰	5	Hammer et al., (2017)

In 2023 and 2024, a second round of pure-CO_2 ICP with 48 comparison samples is being performed in which all four participating laboratories are taking part. The results of this study will help to determine offsets between all four laboratories better. In addition, co-located

sampling will be carried out at the Mace Head station from 2024 onward as part of the Horizon Europe project NUBICOS. This will establish the first ^{14}C super-site where the four participating laboratories will sample simultaneously with their sampling equipment, allowing a comprehensive comparison from sampling through sample processing to ^{14}C measurement. However, until these new comparison results are available, we have to base the compatibility assessment on the available information. The only significant bias was reported by Turnbull et al., (2015) between GNS and INSTAAR. The authors suggest applying a constant offset of -1.4 ‰ to the GNS AMS measurements. On the other hand, unpublished data of an ICP between GNS and ICOS point towards an offset in the other direction. Between the other laboratories no significant bias can be deduced from the ICP results. As part of CORSO, SIO/UCI will analyse 10 archived samples from Baring Head, New Zealand to add further ICP information. But since ICPs only cover specific periods, it cannot be excluded that systematic biases existed between the laboratories at other times. To investigate this question, background stations located in similar latitudes (within a ca. 10° latitude band) but belonging to different networks are compared with each other in section 3.5.

3.4 Compilation of $^{14}CO_2$ background data from 4 monitoring programs

All $\Delta^{14}CO_2$ data sets shown in Figure 4 and listed in Table 4 have been submitted by the collaborators and ingested into the ICOS-CRL database. If available, also ambient $\delta^{13}CO_2$ and CO_2 mole fractions are included to allow calculating $\delta^{14}CO_2$ from the fractionation-corrected $\Delta^{14}CO_2$ values reported. If not contained in the submitted data sets, further meta data, were added, including sampling sites and methods. For example, integration time of air samples varies between a) CO_2 absorption in sodium hydroxide solution (several days or weeks) and b) glass-flask whole air sampling (instantaneous). A comprehensive header was constructed for each dataset, containing all this and much more information about data ownership, calibration scales, etc., as can be seen in the supplementary material to this report, which contains all individual records as *.csv files.

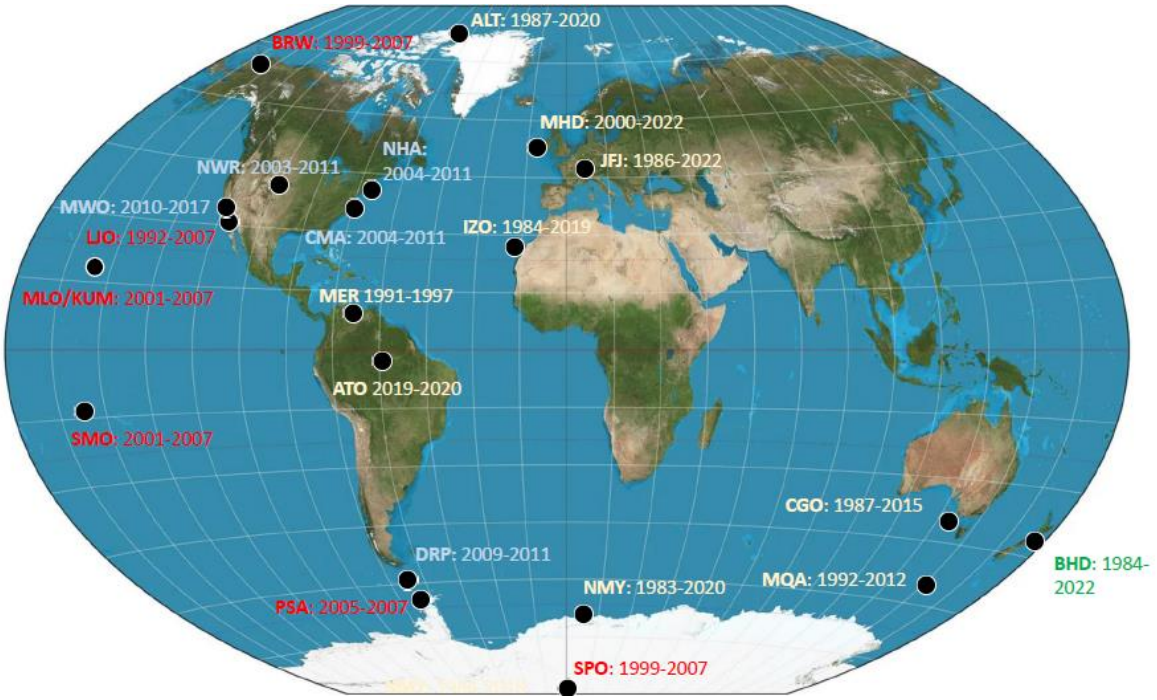


Figure 4: Map of stations from which data are included in the current compilation with the period of data availability (for three-letter station codes see Table 4). The different networks are indicated by different colours, i.e., the Graven et al. (2012 a&b) stations are marked in red, the Turnbull et al. (2017) station

in New Zealand in green, the Basu et al. (2020) stations in light blue and the UHEI stations with published data from Levin et al. (2010, 2021) and additional unpublished data are displayed in white (map from Wikimedia).

These files are available for download on the UHEI data repository (https://heibox.uni-heidelberg.de/d/1f481155f63c46a8aaf0/). In the coming weeks all these files will be transferred to the ICOS ERIC Carbon Portal (https://www.icos-cp.eu/) receiving individual landing pages and dois/pids, with the original data providers listed as authors. The entire compilation as well as this report will also receive dois with all co-authors being listed. Within the next months, i.e. until the beginning of 2024, the ICOS ERIC CP will generate the first $\Delta^{14}CO_2$ ObsPack from this compilation, as an extra service for the CORSO modelling community and other users.

Table 4: Laboratory and station information for the data sets included in the $\Delta^{14}CO_2$ background data compilation.

Laboratory	Station	Code	Lat	Long	m a.s.l.	Period
UHEI/ICOS	Alert, Canada	ALT	82.5	-62.34	185	1987-2020
SIO/UCI	Point Barrow, Alaska	BRW	71.38	-156.47	11	1999-2007
UHEI/ICOS	Mace Head, Ireland, marine	MHD	53.33	-9.90	8.4	2000-2022
UHEI/ICOS	Jungfraujoch, Switzerland	JFJ	46.55	7.99	3450	1986-2022
NOAA/INSTAAR	Offshore Portsmouth, U.S.A., aircraft	NHA	42.95	-70.63	4000	2004-2011
NOAA/INSTAAR	Niwot Ridge, U.S.A.	NWR	40.05	-105.58	3523	2003-2021
NOAA/INSTAAR	Offshore Cape May, U.S.A., aircraft	CMA	38.83	-74.32	4000	2005-2011
NOAA/INSTAAR	Mount Wilson, U.S.A.	MWO	34.22	-118.06	1729	2011-2017
SIO/UCI	La Jolla, U.S.A., marine	SIO	32.90	-117.30	10	1992-2007
UHEI/ICOS	Izaña, Tenerife	IZO	28.31	-16.50	2373	1984-2019
SIO/UCI	Mauna Loa, Hawaii	MLO	19.50	-155.60	3397	2001-2007
SIO/UCI	Kumukahi, Hawaii	KUM	19.5	-154.82	3	2001-2007
UHEI/ICOS	Mérida Obs., Venezuela	MER	8.78	-70.87	3600	1991-1997
UHEI/ICOS	Amazon Tall Tower, Brasil	ATO	-2.15	-59.90	120	2019-2020
SIO/UCI	Cape Matatula, Samoa	SMO	-14.25	-170.57	30	2001-2007
UHEI/ICOS	Cape Grim, Australia	CGO	-40.68	144.69	94	1987-2015
GNS/NIWA	Baring Head, New Zealand	BHD	-41.41	174.87	75	1984-2022
UHEI/ICOS	Macquarie Isl., Australia	MQA	-54.5	158.94	6	1992-2012
NOAA/INSTAAR	Drake Passage, shipboard	DRP	-59.02	-66.98	10	2009-2011
SIO/UCI	Palmer Station, Antarctica	PSA	-64.9	-64.00	5	2005-2007
UHEI/ICOS	Neumayer, Antarctica	NMY	-70.65	-8.25	17	1983-2020
SIO/UCI	South Pole, Antarctica	SPO	-89.98	0.00	2835	1999-2007

3.5 Data flagging and selection of non-representative data

Flagging of non-representative (for background conditions) data within the data sets is an important part of this deliverable. Each individual dataset included flags to mark analytical errors or unexpected errors. For example, continental flask records from Niwot Ridge, which have been locally or regionally influenced by fossil CO_2 (as indicated by elevated CO concentrations in the flask samples) have been flagged. Here samples were flagged if the CO measurement deviated by more than 15 ppb from the fitted smooth curve through all data. In our compilation we added another flag column to the data sets marking "unexpected deviations of the data from the long-term trend". This flag is aimed to indicate outliers that are not obviously locally contaminated but that may still not be representative for background air on the scale of hundreds to thousands of kilometres.

We deliver two data compilations with different DOI's, one set of records that contains **all** measurements with the corresponding flags and another "clean" compilation, where we have removed all flagged data, providing, for the less experienced users, a ready-to-use record of only validated background values. All individual measurements have analytical measurement uncertainties added, which correspond to 1-σ errors and generally lie within ±2-3 ‰. Only the early (pre-2000) data from BHD and CGO have sometimes larger uncertainties.

In the following, we present figures from a selection of the data sets comparing measurements from stations located in similar latitudes (within a ca. 10° latitude band), but belonging to different networks. This gives an impression of the comparability of the data from the four measurement programs while also illustrating the very small gradients of $\Delta^{14}CO_2$ we have monitored in global background air over the last decades (see e.g., Levin et al. (2021), for the size of current north-south differences).

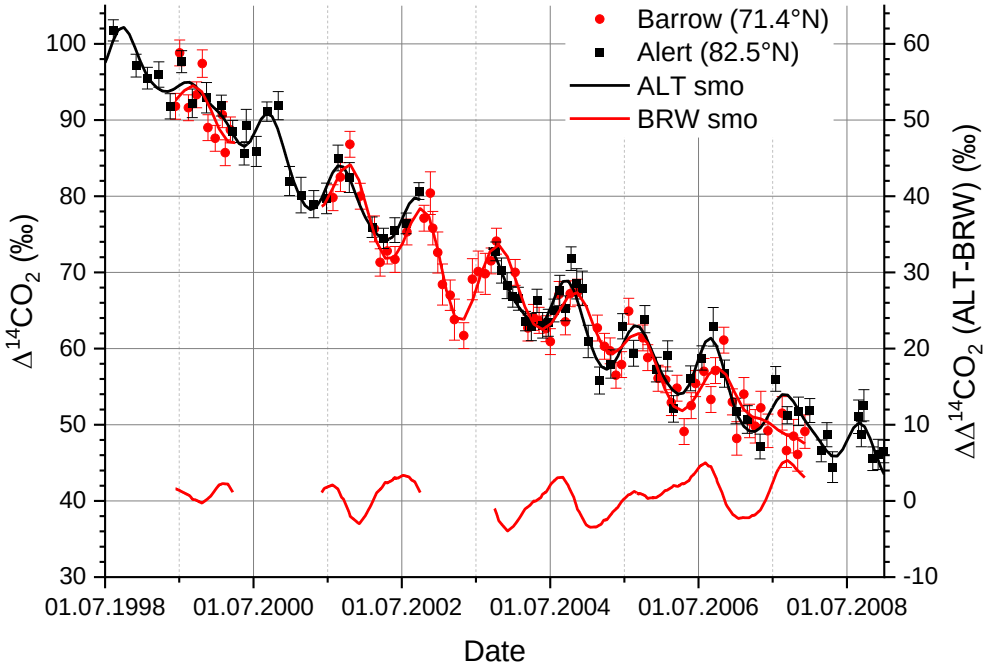


Figure 5: Comparison of $\Delta^{14}CO_2$ measurements at Alert, Canadian Arctic (UHEI program, two-week integrated) and Point Barrow, Alaska (SIO program, flasks). The solid lines are harmonic fit curves calculated through the data using the ccgcrv algorithm from NOAA GMD (Thoning et al., 1989). The

difference between the two smooth fit curves (Alert – Point Barrow) is varying around (0.7±2.3) ‰ (scale at right axis)

Both records from the Arctic (Figure 5) show significant seasonal cycles with similar amplitudes but a small phase shift of about 1-2 months. This is the reason for a bi-modal distribution of the differences between the two fit curves that has a mean value of about 0.7‰ and a standard deviation of 2.3‰. The slightly lower average $\Delta^{14}CO_2$ values at Barrow compared to Alert may be due to a slightly larger influence from North American fossil emissions at Barrow.

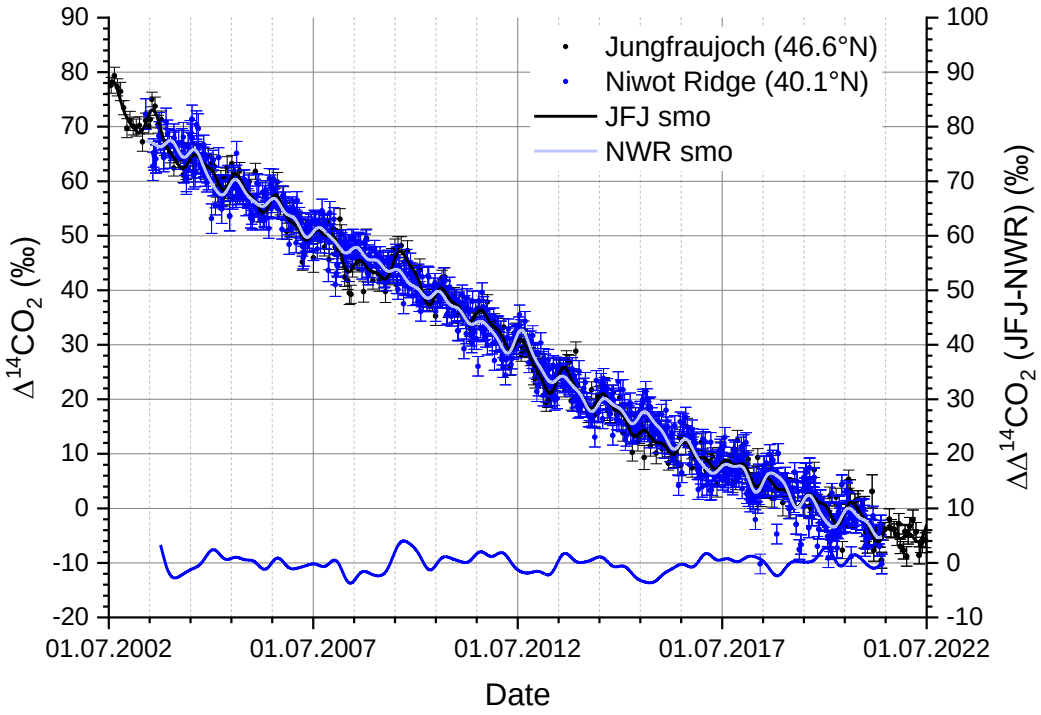


Figure 6: Comparison of $\Delta^{14}CO_2$ measurements from two continental high-altitude stations, Niwot Ridge, U.S.A. (NOAA/INSTAAR program, selected flasks) and Jungfraujoch, European Alps (UHEI/ICOS program, two week integrated). The solid lines are harmonic fit curves calculated through the data using the ccgcrv algorithm from NOAA GMD (Thoning et al., 1989). The difference between the two smooth fits (Jungfraujoch – Niwot Ridge) is varying around (0.1±1.5) ‰ (scale at right axis).

The two $\Delta^{14}CO_2$ records from high-altitude sites in North America (Niwot Ridge) and in the European Alps (Jungfraujoch) show surprisingly good agreement in their mean level and in their seasonal cycle amplitude (Figure 6). The air collected at both stations at altitudes above 3500m a.s.l. seems to be representative of the free troposphere at mid-latitudes in the Northern Hemisphere. No differences are observed in the long-term trend of the two smoothed curves calculated through the two datasets. This can be seen as an indication that both laboratories deliver consistent $\Delta^{14}CO_2$ results with possible laboratory offsets not having changed over time (here from 2002 – 2020).

Figure 7 shows data comparisons from three sampling stations at the Antarctic coast and in the Drake Passage between 59°S and 71°S. Here we see small latitudinal differences with slightly higher $\Delta^{14}CO_2$ at Neumayer and mean depletions towards Palmer Station of (1.2±1.4) ‰ (from 2006 - 2007) and towards Drake Passage of (0.9±1.3) ‰ (from 2009 - 2011). A

$\Delta^{14}CO_2$ depletion of on average 3.5‰ from Neumayer towards the open ocean around 50°S (Macquarie Island, UHEI program, marine air selection) indicates that the differences between Neumayer and the two other Antarctic stations from the SIO and the NOAA programs are most likely a real signal of atmosphere-ocean ^{14}C disequilibrium and not caused by laboratory offsets.

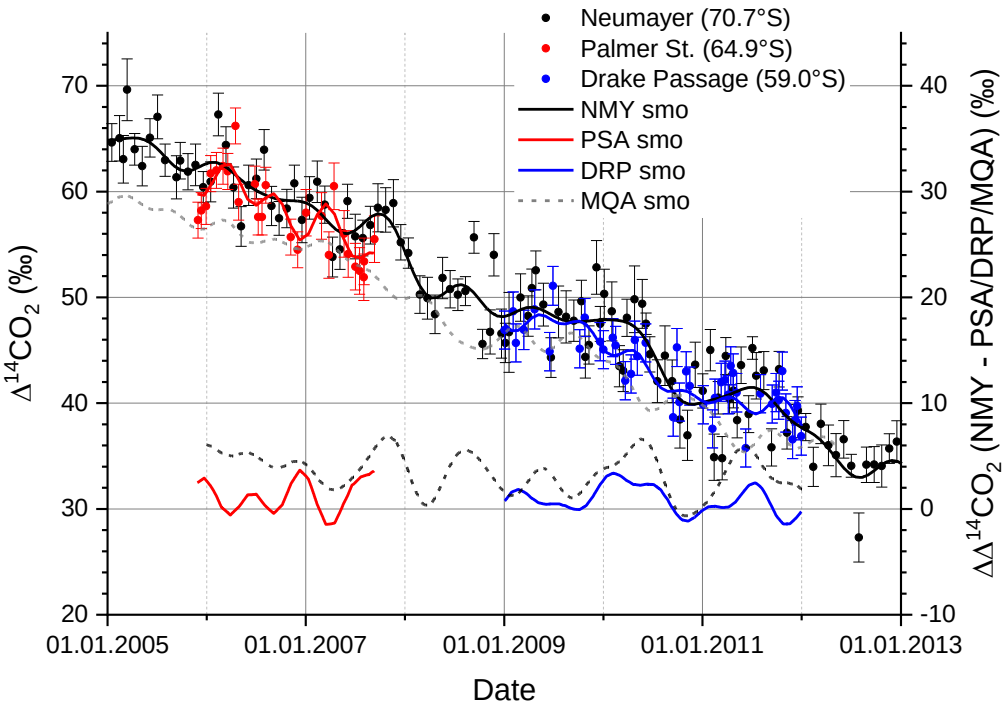


Figure 7: Comparison of $\Delta^{14}CO_2$ measurements at three stations in high southern latitudes, Neumayer, Antarctica (UHEI program, two week integrated), Palmer Station, Antarctic Peninsula (SIO program, flasks) and Drake Passage (NOAA program, flasks). The solid lines are harmonic fit curves calculated through the data using the ccgcrv algorithm from NOAA GMD (Thoning et al., 1989). The differences between the smooth curve fits through the individual data sets are displayed in the lower part of the figure (scale at right axis). The harmonic fit curve through data from Macquarie Island (UHEI program, 54.5°S, two week integrated, marine air selected) has been added to this graph to illustrate the significant $\Delta^{14}CO_2$ draw-down due to the disequilibrium flux with the ^{14}C-depleted surface ocean water around Antarctica (e.g. Levin et al., 2010; 2021; Graven et al., 2012b).

The comparison of Baring Head (New Zealand, GNS) and Cape Grim (Australia, UHEI) $^{14}CO_2$ data in Figure 8 goes back to the 1980s. Earlier portions of the record have lower precision. This is due to analytical capabilities but also the importance of high precision for $\Delta^{14}CO_2$ analyses was not as obvious as today, when we see only very small spatial gradients in global background air (e.g. Levin et al., 2021). Moreover, in the BHD record of integrated samples there occurred a period (1995 – 2005), where excess noise and apparent bias exists in the record, believed to be due to inappropriate fractionation correction; these data are not shown in Figure 8. After 2005, online AMS ^{13}C measurement allowed for appropriate fractionation correction (Turnbull et al., 2017; Zondervan et al., 2015). But also, the Cape Grim measurements showed more variability in the early part of the record than in recent years, so that the differences between the two smooth curves fitted through the data sets showed larger variability than at other stations from the 2000s onwards, as displayed in Figures 5-7. The BHD record of integrated samples shows a significant positive excursion in 2010, which is not observed in the Cape Grim data. We thus flagged the BHD data (red dots in Figure 8) during

the period when the smooth curve difference was larger than 6 ‰, i.e., deviating by more than 3σ from the inter-laboratory agreement of better than 2 ‰. In the five years from 2011-2015, where data from both stations are available, the records agree well with a mean difference of 0.5‰ and a standard deviation of ±1.3‰. During this same period, we observe a significant offset between the BHD flask and the integrated sample data, with the flasks data being higher by about 2 ‰. This difference may be a real signal as the BHD flasks are collected only during marine conditions, while during integrated NaOH sampling the station could also occasionally be influenced by fossil CO_2 emissions, e.g., from the city of Wellington. All-in-all, however, we can conclude that also the comparison between CGO and BHD data does not indicate any long-term change in station offsets with improved compatibility in the last part of the CGO record.

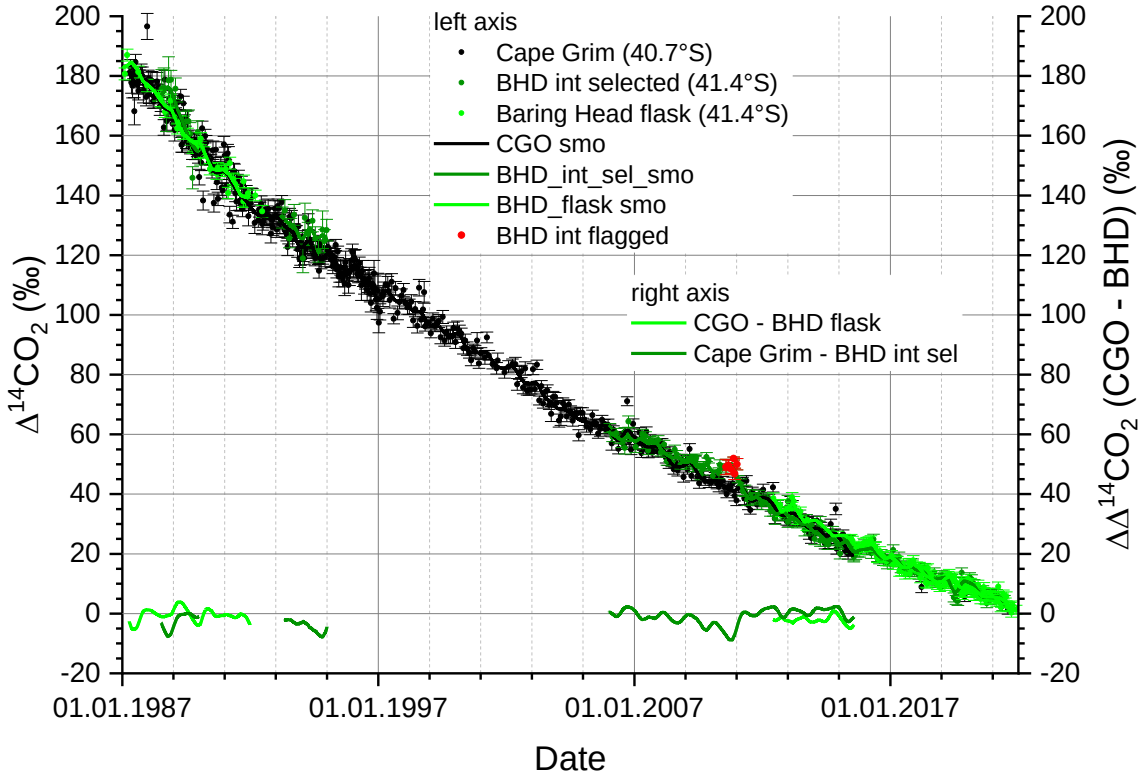


Figure 8: Comparison of $\Delta^{14}CO_2$ measurements at Cape Grim Observatory (CGO, UHEI program, two week integrated) with those at Baring Head (BHD, GNS program). Two different sample types have been analysed from BHD, integrated and flask samples shown in different green colours. The solid lines are harmonic fit curves calculated through the data using the ccgcrv algorithm from NOAA GMD (Thoning et al., 1989). The differences between the corresponding smooth curve fits from that fitted through the CGO data are shown in the lower part of the graph (scale at right axis).

3.6 Preliminary uncertainty assessment of the $^{14}CO_2$ data compilation

Each individual data point in the submitted records has its associated 1-σ measurement uncertainty reported. However, this uncertainty does not include possible additional uncertainties related to the imperfect compatibility of measurements from different laboratories, which may result from different sampling and analysis methodologies as well as calibration histories. To quantify this uncertainty, we can principally use the inter-comparison

(ICP) exercises reported in Section 3.3. All these ICPs resulted in inter-laboratory agreements of better than ±2‰. Due to the statistical uncertainty of ^{14}C measurements, the reported biases between laboratories decrease as the number of comparison samples increases. Based on the ICP results, no systematic bias correction between the different laboratories is required.

However, these few ICPs represent only episodic evaluations and cannot inform about the long-term compatibility over the course of the last two decades. When inspecting the comparisons between stations in similar latitudes (Sec. 3.5), we also did not observe any persistent long-term trends in these differences. As all evaluated records represent large-scale atmospheric background conditions and because the troposphere mixes within a few months on the hemispheric scale and on the global scale within one to two years, any trend in interstation differences could either be due to changes in regional disequilibrium fluxes or, interpreted as an indication of a trend in an individual laboratory calibration scale. We did not find such persistent trends. This gives us rather good confidence that inter-laboratory biases did not significantly change over time, but also shows that subtle regional changes need to be interpreted with great care.

The total uncertainty of the ^{14}C data sets comprise potential uncertainties in sampling, sample preparation, statistical ^{14}C measurement uncertainty, and the uncertainty of the calibration of the measurements. The statistical 1σ measurement uncertainties for the ^{14}C analyses are provided within each data set. Based on the ICP information we conclude that, to the best of our current knowledge, although in some of the ICPs significant biases in sample preparation or calibration have been identified, these are inconclusive and need further comprehensive ICP programs; these are currently underway or prepared. Potential uncertainties related to sampling have only been included in the one co-located sampling ICP by Graven et al. (2013), which yielded excellent agreement. Generally, sampling artefacts are less likely to occur in $^{14}CO_2$ collection compared to sampling for CO_2 mole fractions or $\delta^{13}CO_2$, as “only” the $^{14}C/C$ ratio is measured, and potential fractionation is corrected through $\delta^{13}CO_2$ normalization. Therefore, we conclude that the error contributions related to sampling, sample preparation and calibration might be of the same order compared to the statistical measurement uncertainty of the individual samples. As long as no better ICP data is available, we suggest using the individual measurement uncertainties as uncertainty of the $\Delta^{14}CO_2$ data compilation.

4 Conclusion

All objectives of Task 3.1 have been achieved: i.e., compiling a database of published and partly unpublished (from the UHEI global network and Baring Head, New Zealand) globally distributed high-precision $\Delta^{14}CO_2$ observations. We provide an initial evaluation of uncertainty of this compilation, which consists of measurements from four international monitoring programs. No significant inter-laboratory biases have been reported, except for the AMS analyses of GNS, which however are of opposite sign between INSTAAR – GNS and ICOS-GNS. This reflects the current state of the ^{14}C ICP data basis and thus calls for further improvements in determining potential inter-laboratory biases. At the current stage, the overall uncertainty is, thus, best represented by the uncertainty contribution of the individual $^{14}CO_2$ measurements provided with each observation. It needs, however, to be emphasised that it is generally difficult - if not impossible - to make retrospective quality assessments of a data compilation, if only sporadic information on inter-laboratory compatibility measures is available. In CORSO we analyse samples from the SIO archive for Alert and Baring Head to generate further co-located sampling ICP information, however the number of potential co-located samples is limited. These results will be included in the ICP section once the samples are measured. We want to stress the requirement of regular ongoing ICPs if global datasets are to be merged, to use them as constraints in global studies such as atmospheric transport inversions for estimates of CO_2 sources and sinks. This underlines the importance of the establishment of co-located sampling that will be carried out at the European Mace Head

station from 2024 onwards, as part of the Horizon Europe project NUBICOS. Within NUBICOS, the first ^{14}C super-site will be established and the four participating monitoring programs will sample simultaneously with their dedicated equipment. This will allow for an ongoing comprehensive comparison from sampling methods through sample processing to ^{14}C measurement.

The datasets compiled here have undergone rigorous quality control by the providing laboratories and individual data have been flagged if sampling or analytical errors were identified. Additionally, samples at Niwot Ridge that were identified as non-background, have been flagged. But comprehensive evaluations of representativeness could not be accomplished e.g., in the case of integrated sampling. Still, in the case of the coastal stations Mace Head and Macquarie Island, integrated sampling was only conducted from the marine sector and at Neumayer, Antarctica, integrated sampling was automatically stopped when the aerosol level at the site exceeded a certain threshold.

During the CORSO project, this background data set will be extended with more recent $^{14}CO_2$ data from the SIO archive, which are currently being analysed and quality controlled by SIO/UCI. Also, Alert, Mace Head and Izaña data sets will be extended as part of the CORSO project.

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