ICOS Central Analytical Laboratories

Flask and Calibration Laboratory (FCL)

Quality Control Report 2022

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Jena, April 2023

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Summary

The ICOS Central Analytical Laboratories (CALs) play a central role in assuring the accuracy of atmospheric observations within ICOS. This involves the central provision of reference gases to the ICOS atmospheric network and calibrating these standards based on the World Meteorological Organization (WMO) calibration scales. A quality control strategy for the ICOS atmospheric measurements has been described within the Atmospheric Station Specification document [ATC 2020].

In this report the quality control measures are described that are made by the ICOS-CAL Flask and Calibration Laboratory (FCL) to characterize the performance of their calibration of ICOS reference gases. It updates and replaces the QC 2020 report following the same assessment scheme with only minor changes and some few corrections. The results of these activities of the recent years are presented in detail for each of the ICOS core components for in-situ observations (CO_2, CH_4, CO) and N_2O. The results are then assessed and used to substantiate estimates of the measurement uncertainties of the different tracers and to quantify different uncertainty contributions. This involves an evaluation of the uncertainty of the reference values of calibration standard gases ("scale link uncertainty") and the measurement uncertainty related to the respective analyzer's precision or response stability over time.

The resulting overall measurement uncertainty estimates are summarized in the following table.

Table 1: Summary of total estimated measurement uncertainties
Data taken from sections 5.6, 6.6, 7.6 and 8.6 but expressed as expanded uncertainty (95% confidence level), combined uncertainties are calculated as the square root of the sum of squared uncertainty contributions

	CO_2 [ppm]	CH_4 [ppb]	CO [ppb]	N_2O [ppb]
CCL reproducibility[1)]	0.02	1	0.8	0.22
scale propagation to FCL standards	0.055	0.4	2.3[2)]	0.11
scale link uncertainty	**0.058**	**1.1**	**2.4**[3)]	**0.25**
instrumental precision	0.028	0.4	0.3	0.03
long-term reproducibility	0.02	0.4	1.0[2)]	0.17
estimated FCL reproducibility	**0.034**	**0.5**	**1.1**	**0.17**
estimated overall uncertainty	**0.067**	**1.2**	**2.5**	**0.30**

[1)] WMO Central Calibration Laboratory (CCL)
[2)] both terms include the uncertainty of CO growth in FCL Secondary Standards
[3)] for CO mole fractions at atmospheric background levels

Based on further evidence obtained in 2022 the assumption of a Primary Standard gas set with stable CO_2 appears justified.

This report is a deliverable (D7) of Annex 2 to the Cooperation Agreement between ICOS ERIC and the Max-Planck-Society that is the host organization for the ICOS Flask and Calibration Laboratory (FCL).

1 Introduction

The mission of ICOS is to run a long-term monitoring network that produces harmonized sets of highly precise and accurate observational data. The data should be of a quality to allow for regularly assessing regional carbon fluxes from atmospheric observations using inversion models, to detect changes in emission patterns and to quantify long-term trends. This requires highly consistent experimental records available over decades. The ICOS strategy to ensure best consistency of the entire atmospheric monitoring network includes the central data processing of the measurement data of all instruments at the monitoring stations (done at the Atmospheric Thematic Center ATC) and a central provision of calibrated reference gases by one of the Central Analytical Laboratories, the Flask and Calibration Laboratory (FCL).

This makes it particularly necessary for the FCL to have a comprehensive QA/QC framework with well-defined analytical procedures in place to assure accurate measurements based on WMO calibration scales. The different components of the FCL quality control system described in this report aim to address all requirements for a comprehensive quality control strategy listed in the ICOS Atmospheric Station Specification Document [ATC_2020]. The results of these quality control activities shall document the achieved accuracy, shall allow an assessment of the uncertainty of the assigned values on reference gases and generate credibility by comparing with various external laboratories, including laboratories that are completely independent from ICOS (as the Bureau International des Poids et Mesures (BIPM) and the WMO-CCL).

The aim of this report is to present the results of the measures undertaken by the FCL that contain information on the data quality of its measurement activities for the ICOS community. In the past years the main function requested from the ICOS FCL was the provision of calibrated reference gases for the routine operation of the station measurements, the recalibration of the station standards and to equip stations that have entered the ICOS labeling process. Hence, this report focusses on the quality control of reference gas measurements performed for the ICOS atmosphere observational network. Mole fraction assignments have been made for the core parameters CO_2, CH_4 and CO as well as for N_2O as recommended parameter and are made with the following instrumentation:

- Picarro G2301 Cavity Ringdown Spectrometer (CO_2 and CH_4)
- Los Gatos CO/N_2O Analyzer EP (CO and N_2O)

2 Measurement Methods

Picarro method brief description (see also Annex I)

CO_2 and CH_4 mole fractions of reference standards that are prepared for the station network in high pressure cylinders are assigned by using a Picarro G2301 Cavity-Ring-Down-Spectroscope. The instrument is operated using the software tool GCwerks that exports averaged one minute Level0 data for further processing. Data is migrated in an automated way into an in-house-developed data base on a daily basis for further processing (quality control, calibration, aggregation), before the data is manually validated and finally forwarded to the ATC's data server. The Level0 data is checked and automatically flagged according to predefined criteria for valid data. This includes instrumental readings (cell pressure, sample flow, sampling frequency), the reproducibility within the one minute averages as well as the scatter of the one minute averages, and noise level (standard deviation of the means and 3-sigma excluded outliers (see also Annex III)).

Each measurement (samples as well as references) takes 20 min of gas injection. To avoid cross contamination of succeeding samples and to flush out the pressure regulator, the first five minutes of data at the beginning of each measurement are ignored and the average of the remaining valid 15min data is further processed.

The instrument is calibrated on a daily basis by a dedicated set of four FCL Secondary Reference Standards. These secondary references are calibrated about quarterly against a set of nine FCL Primary Standards with assignments from the WMO Central Calibration Laboratory (CCL).

Los Gatos method brief description (see also Annex II)

CO and N_2O mole fractions of reference standards that are prepared for the station network in high pressure cylinders are assigned using a Los Gatos CO/N_2O Enhanced Performance Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument. The instrument is operated using an in-house built software that controls a multiposition valve for sample provision, collects raw data and delivers averaged 20s Level0 data for further processing. Data are automatically migrated after the termination of the measurement sequence into an in-house-developed data base for further processing (automatic quality control, calibration, aggregation), before the data is manually validated and finally forwarded to the ATC's data server. The Level0 data is checked and flagged automatically according to predefined criteria for valid data. This includes instrumental readings (cell pressure, sample flow, sampling frequency), the repeatability within the one minute averages as well as the scatter of the one minute averages, and noise level (standard deviation of the means and 3-sigma excluded outliers (see also Annex III)).

Each measurement (samples as well as references) involves 20 min of gas injection. To avoid cross contamination of succeeding samples and to flush out the pressure regulator, the first nine minutes of data (27 averages of 20 sec) and the last 20 sec data point of the measurement are ignored and the average of the remaining valid 10 min data is further processed.

Short term drifts of the analyzer are compensated by bracketing every sample analysis by measurements of a working reference standard and normalizing the sample signal to the averaged working standard signal.

The instrument is calibrated by a dedicated set of four FCL Secondary Reference Standards in every series of measurements (at least on a daily basis). These secondary references are calibrated against a set of nine FCL Primary Standards with assignments from the WMO Central Calibration Laboratory (CCL).

GC method description

A gas chromatographic analysis system (GC) has been set up primarily for analysis of flask samples from class1 stations. GC measurements also yield data for the tracers measured by the optical analyzers and thus can be used as an independent check. The GC is equipped with multiple detectors: a Flame Ionization Detector (FID) for CO_2 and CH_4 detection, an Electron Capture Detector (ECD) for N_2O, and a Reduction Gas Detector for CO (HgO Reduction and Hg-UV Detection).

The GC is calibrated for CO_2 and CH_4 by a set of five Secondary Standards dedicated to the GC with currently a bi-weekly to monthly frequency. To calibrate the non-linear detectors for CO and N_2O measurements an extended set of seven Secondary Standards is used. These GC Secondary Reference Gases are calibrated against the set of nine FCL Primary Standards three to four times per year.

3 Calibration gases linking to the WMO Mole Fraction scales

All FCL measurements are traceable to the WMO Mole Fraction Scales. This link is established by a set of standard gases that has been calibrated directly by the WMO Central Calibration Laboratory (CCL). In the WMO/GAW nomenclature these standards are on the level of laboratory tertiary standards (relative to the WMO Mole Fraction scale Primary Standards). However, for the ease of reading they will be referred to throughout this document as FCL Primary Standards. The accuracy of their assignments is an essential prerequisite for the accuracy of the ICOS measurements. Likewise, the knowledge of the stability of the mole fractions of the tracers of interest in these gases is essential for accurate measurements.

Using the set of standards calibrated directly by the CCL as reference (listed in Table 2), additional sets of further working calibration standards (denoted in this document as FCL Secondary Standards) have been derived that are used for daily calibrations of the individual instruments.

All of the FCL Primary Standards have been calibrated at the CCL three times with the most recent recalibration having been made in 2021. This shall allow to verify the stability of the respective trace gases or track the rate of change of their mole fraction. Some tracers have been analyzed using different measurement techniques at the CCL and for CH_4 and CO_2 not all calibration results are considered (see sections 5.1 and 6.1).

Table 2: FCL Primary Standards assignments by the WMO Central Calibration Laboratory

Cylinder ID	Sample ID	Fill date	last CCL calibration	CO_2 (ppm)[1]	CH_4 (ppb)[2]	CO (ppb)[3]	N_2O (ppb)[4]
CB09948	i20140054	07/2013	05/2021	250.13	2933.01	998.13	361.90
CB09944	i20140055	07/2013	05/2021	339.36	1596.74	36.75	317.01
CB09939	i20140056	07/2013	05/2021	365.28	1743.09	84.47	319.93
CB09958	i20140057	07/2013	05/2021	389.77	1896.75	125.03	327.21
CB09983	i20140058	07/2013	05/2021	412.42	2032.96	162.73	330.06
CB09952	i20140059	07/2013	05/2021	433.83	2195.08	203.13	334.57
CB09955	i20140060	07/2013	05/2021	459.17	2343.92	249.93	339.43
CB09957	i20140061	07/2013	05/2021	482.02	2466.23	399.39	343.82
CB09934	i20140062	07/2013	05/2021	515.11	2731.85	697.10	349.14

WMO Mole Fraction scale:	**CCL-reproducibility** (2 sigma) [reference]:
[1] CO_2WMO X2019 (CRDS only)	0.01 ppm [1 sigma, https://gml.noaa.gov/ccl/co2_calsystem.html]
[2] CH_4 WMO X2004A	1 ppb (pers. comm., E. Dlugokencky, Feb. 2018)
[3] CO WMO X2014A	0.8 ppb [CCL_CO 2017]
[4] N_2O WMO X2006A	0.22 ppb [CCL_N_2O 2011]

4 QA/QC Concept

For all measurements made the general approach is the following:

1. *FCL Primary Standards*: To assure compatibility of ICOS observational data all measurements are linked to the WMO calibration scales. For this the set of FCL Primary Standards covers the atmospheric ranges of the trace gases of interest and has been assigned by the Central Calibration Laboratories (CCL). According to the WMO Experts Group for Greenhouse Gases recommendations these assignments should be re-assessed by regular recalibration by the WMO CCL every third year. In order to always have a sufficient set of Primary Standards at the FCL, sub-groups of each three standards have been re-sent to the CCL for recalibration on an annual basis for the first three years. A next batch of re-calibrations is planned for 2024.
2. *FCL Secondary Standards*: All measurements are referenced to daily calibrations using laboratory Secondary Standard gases that have been assigned at the FCL by repeated comparison to the FCL Primary Standards. The FCL Secondary Standard assignments are made a certain point in time and in general kept fixed despite the comparisons to the FCL Primary Standards are being continued. A re-evaluation of these Secondary Standard assignments is commonly not made before they are fully exhausted and thus the record of Primary Standard calibrations has been completed.
3. *Targets*: The performance of daily measurements is characterized by daily analysis of the same gases in high-pressure cylinders over long periods of time that are only used for quality assessment (so-called "Target standards")
4. *Inter-Instrument comparisons*: In cases where additional gas chromatographic measurements have been made these results are compared to the spectroscopic data.
5. *External comparisons* are made routinely. Initially an intensive exchange of samples analyzed at the FCL and the MPI-BGC GasLab was made which is still ongoing with lower frequency. International comparisons with a large group of laboratories are performed in the "Sausage Intercomparison Program" (using flask samples), and within the “MENI” (**M**PI-BGC, **E**MPA, **N**OAA and **I**COS) - Intercomparison that includes among others the NOAA-GML as partner laboratory. Additional such activities that FCL is involved are of more sporadic nature (e.g. WMO Round Robin, BIPM Key Comparison, ATC-Mobile Lab).

All of these steps are evaluated to provide the following information on the FCL data uncertainty (see the respective subsections of chapters 5 to 8 for the respective assessments of the CO_2, CH_4, CO and N_2O measurements):

FCL Primary Standards

- Re-assignments by the CCL provide information on the assignment accuracy or the stability of the specific tracer's mole fraction in the reference gas.
- The observed magnitude of the calibration regression fit residuals contains information on the consistency of the CCL assignments. The persistency of these residuals over time may provide information of the stability of the respective tracers' mole fractions in the Primary Standards.

FCL Secondary Standards

- The consistency of the used Secondary Standards' assigned values with the results obtained from repeated further calibration episodes relative to the FCL Primary Standards is a measure for the uncertainty of the scale transfer and for the stability of the trace gas mole fraction in the reference gases.

- The magnitude of the mean secondary calibration regression fit residuals also contains information on the scale transfer uncertainty.
- The stability of these residuals over time may provide information on the stability of the respective tracers in the Secondary Standards.
- The scatter of the daily residuals is an indicator for the reproducibility of the daily calibration.

Targets

- The reproducibility of the daily mean results of the Targets shall reflect the long-term reproducibility of measurements that the FCL achieves for ICOS station's standard gases (provided that for the respective targets the tracer mole fractions are constant over time).
- Like the FCL Secondary Standards the targets have received an assignment by calibration directly with FCL Primary Standards. The difference of the daily measurement results (based on the daily secondary calibration) and these assigned values serves as another quality control of the actual scale transfer uncertainty.

Inter-Instrument comparison

- The agreement of analysis results of the same sample by different detecting techniques provides the chance to identify and quantify potential analytical biases related to either of the techniques.
- The comparison also involves the cross-check of two different sets of laboratory Secondary Standard gases.

External comparison

WMO compatibility goals aim for achieving consistent atmospheric data from different networks with their associated stations and laboratories. Thus, control of this compatibility requires comparison with external partners. Comparison of analytical data from the same sample provides a check for the success of the overall measurement set-ups, including instrumentation, the accuracy of the reference material, the standardization strategy and data processing.

5 CO_2

5.1 FCL Primary CO_2 Standards

5.1.1 CCL CO_2 assignments

After initial calibration of all FCL Primary Standards in 2014 the first recalibrations of each three of the standards have been made in 2016, 2017 and 2018, respectively. In 2021 the complete set received a recalibration such that three CCL assignments from different years are now available for each standard. The initial calibration was performed using only the NDIR technique. NDIR was also applied for the reassignments in 2016 / 2017, when additional measurements with CRDS analysers were also carried out. From 2018 onwards, recalibrations were made at the CCL only by CRDS (PC1). Hence, two CCL measurements with the CRDS technique are available for all of the nine standards. The revision of the WMO/GAW CO_2 X2007 to an updated X2019 Calibration Scale has been disclosed in February 2021.

The CRDS data confirm the temporal stability of the CO_2 mole fractions in each of these standards (Table 3). Earlier ambiguities related to potentially growing CO_2 in many standards probably were result of inferior reproducibility of NDIR X2007 assignments and different isotopic sensitivities between NDIR and CRDS. The standard approach for X2019 assignments is based on CRDS measurements in combination with the determination of the CO_2 stable isotope composition of the respective standard gas. Therefore, CCL information based on NDIR measurements without consideration of the CO_2 isotopic composition are not further considered any more. Atmospheric observations of CO_2 are performed within ICOS almost exclusively using CRDS instrumentation that is selective for the $^{12}C^{16}O_2$ isotopologue only. The FCL Primary Standards are modified, dried real air. The modification involves addition of pure CO_2 to achieve the wanted composition resulting in standard gases with a CO_2 stable isotope composition that is similar to but not perfectly matching the range of naturally observed atmospheric CO_2. To account for this, the assigned values of the individual standards are adjusted for the offset resulting from the isotopic deviation between standard and atmosphere. The values specified in the last column of Table 3 are those that are currently in use. It has recently been discovered that they are 0.02 µmol/mol too high (see details of the adjustment procedure as described in Annex IV.)

Table 3: CO_2 X2019 assignments for FCL Primary Standards by CCL [ppm].

Sample ID	Cylinder ID	CCL date 1	CCL date 2	CCL date 3	NDIR date1	CCL-CRDS date 2	CCL-CRDS date3	adjusted CRDS used*
i20140054	CB09948	Dec-13	Oct-18	Mar-21	250.129	250.116	250.129	**250.144**
i20140055	CB09944	Mar-14	Jul-17	Mar-21	339.327	339.356	339.360	**339.387**
i20140056	CB09939	Dec-13	Oct-18	Mar-21	365.253	365.277	365.281	**365.306**
i20140057	CB09958	Dec-13	Oct-16	Mar-21	389.762	389.753	389.765	**389.781**
i20140058	CB09983	Feb-14	Oct-18	Mar-21	412.381	412.420	412.424	**412.447**
i20140059	CB09952	Jan-14	Sep-16	Mar-21	433.795	433.830	433.832	**433.853**
i20140060	CB09955	May-14	Jun-17	Mar-21	459.121	459.181	459.173	**459.224**
i20140061	CB09957	Feb-14	Aug-16	Mar-21	481.962	482.010	482.022	**482.068**
i20140062	CB09934	May-14	Jun-17	Mar-21	515.053	515.120	515.113	**515.183**

5.1.2 Regression fit residuals of FCL Primary CO_2 Standards

The time series of the linear regression fit residuals of CRDS calibrations made with these FCL Primary Standards (based on WMO CO_2 X2019 assignments) is presented in the following Figure 1 for calibration events where the *complete* suite of gases was used. The mean residuals of the individual standards range from -0.020 ppm to +0.014 ppm with a standard deviatin of these means of 0.012 ppm. This is a measure of the consistency of the initial CCL assignments confirming the specifications made by the CCL.

Figure 1: Time series of linear regression fit residuals of the CRDS CO2 calibration for FCL Primary Standards

The stability of the regression fit residuals over time provides information on possible drifts in individual standard gases. The values of the residuals do not show significant trends for any of the individual standards (within 0.01 ppm). This supports the finding of a set with stable CO_2 mole fractions.

5.2 FCL Secondary CO_2 Standards

5.2.1 Assignment record

The first set of four reference gases that were used as FCL Secondary Standards for the CRDS measurements had been analyzed within 20 (24) valid calibration episodes together with the *complete* set of FCL Primary Standards between Feb 2015 and Nov 2020. During 2020, the first set of FCL Secondary Standards had to be replaced by a new set because they were consumed. The replacement was done in two steps, with the replacement of the two standards with higher mole fractions made in June and the replacement of the two standards with lower mole fractions made in December.

The stability of CO_2 values for the second set of Secondary Standards had been monitored by repeated measurements against the first set of FCL Secondary Standards for an extended period. The assigned CO_2 X2019 values were based on the records of the CO_2 mole fraction results of the FCL Primary calibration episodes between Aug 2019 and Oct 2021. With a limited number of calibration episodes there seemed to be an annual CO_2 growth of 0.01 ppm and more in all standards of the second set. This impression changed with further calibrations made in 2022. Calibrated results of target standard measurements also showed inconsistent behaviour that pointed to an overestimation of the CO_2 drift. Thus, assigned values of the second set were reassessed and none of the standards is currently assumed to grow CO_2 any more. The FCL CO_2 measurement results from June 2020 to April 2022 are still affected by this preliminary assignment error with maximum biases at the end of this period of 0.02 to 0.03 µmol/mol. While a correction at FCL internally would be a minor effort it is a larger computational work load to reprocess all continuous CO_2 measurements in the ICOS network based on standards assigned by FCL during that time. This requires that the correction needs to be done in collaboration with the ATC in due course. Therefore, these will be rectified latest when this set of Secondary Standards will be replaced at the end of its lifetime. At that point of time the assignment history based on the FCL Primary Standards will be completed.

Such a final assignment revision had been made already for the first set of Secondary Standards.

Table 4: CO_2 assignments of FCL Secondary Standards [ppm]

Sample ID	Cylinder ID	Assigned Value[4]	Drift/yr[1]	*Date of change*	Re-assigned Value[5]	Re-assigned Drift/yr[2]
i20140171[1]	D801336	**359.870**	+0.003	*2020-12-08*		
i20140172[1]	D073384	**393.464**	+0.005	*2020-12-08*		
i20140173[1]	D073392	**424.724**	+0.007	*2020-06-23*		
i20140174[1]	D801331	**454.329**		*2020-06-23*		
i20190708[2]	D761202	**362.751**	+0.014	*2022-04-29*	**362.751**	
i20190803[2]	D073381	**402.078**	+0.010	*2022-04-29*	**402.077**	
i20190709[3]	D761214	**433.119**	+0.016	*2022-04-29*	**433.124**	
i20190438[3]	D073389	**450.779**	+0.017	*2022-04-29*	**450.784**	

Starting dates: [1]1st January 2015; [1]8th December 2020; [3]23rd June 2020

[4]Assigned value at start date; [5]Re-assigned value since date of change

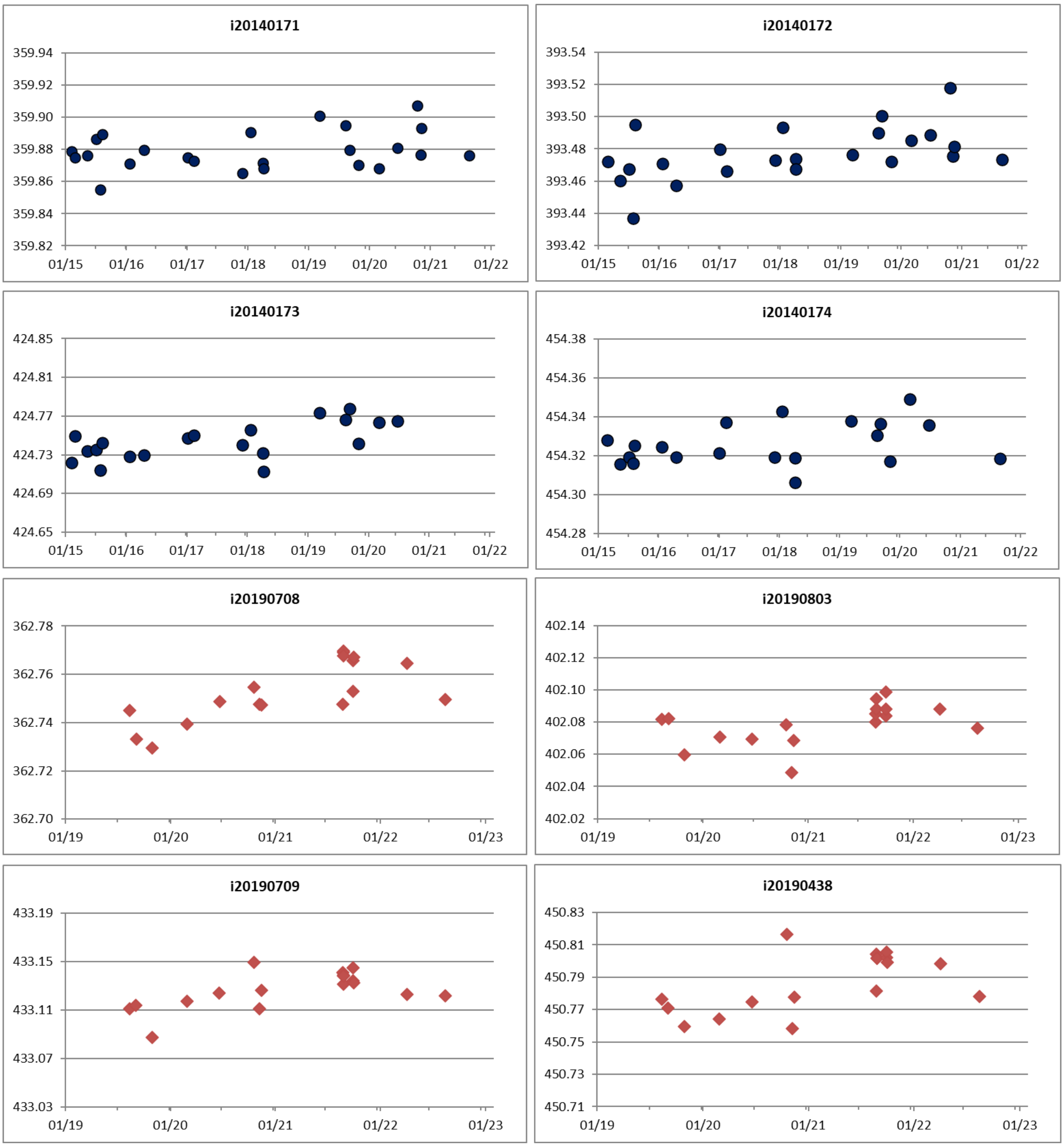


Figure 2: FCL Secondary Standards CO2 assignment time series (all values in [ppm]).
The dark dots represent the data from the first set, the red diamonds display results of the second set of FCL Secondary Standards.

5.2.2 Residual record

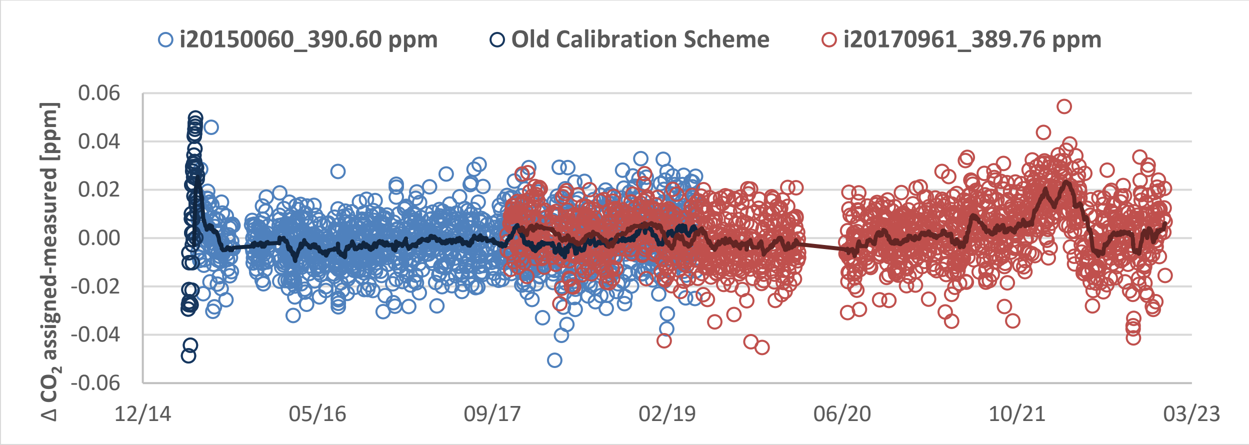
The residuals of the linear regression of the FCL Secondary Standards are given in Figure 3. The mean absolute residuals for the Secondary Standards are on the order of 0.001 ppm and smaller. The standard deviation of the daily residuals for the four individual standard gases in this period amounts to maximum 0.007 ppm. These very small values of the mean residuals of all standards provide evidence for a consistent scale transfer to these FCL Secondary Standards. Trends in the residuals over the periods of the respective Secondary Standard sets do not exceed 0.007 ppm. This documents the long-term internal consistency of the calibration sets throughout their lifetime.

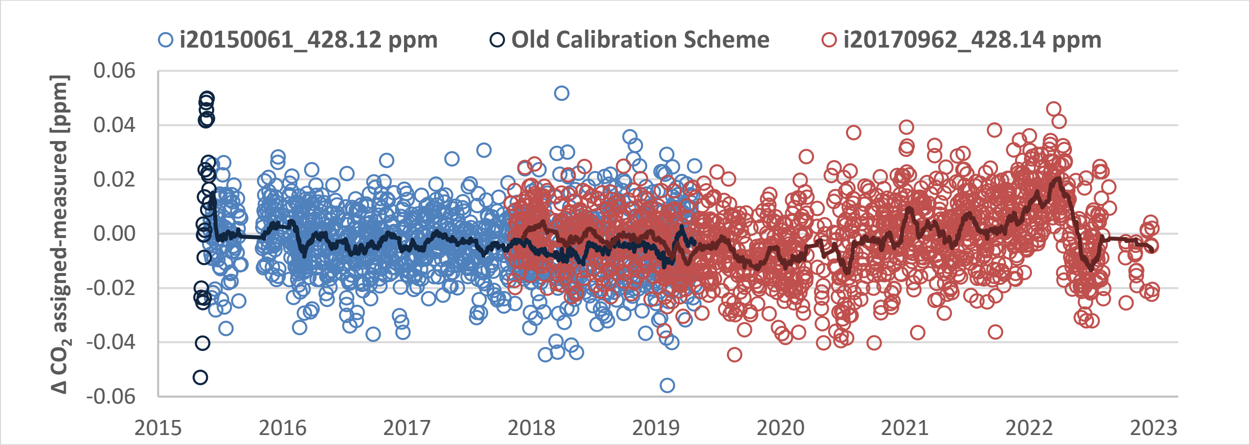
Figure 3: Time series of CO2 linear regression fit residuals of the FCL Secondary Standards.

Blue symbols represent the first set of FCL Secondary Standards, red symbols the second set of FCL Secondary Standards. The dark symbols are indicating the transition phase when only two of the standards were replaced.

5.3 CO_2 Targets

In the period from March 2015 to December 2022 two succeeding sets of each three Target Standards have been in use at the CRDS system. On a regular basis two further targets monitor the long-term stability of the instrument around 360 ppm. The Target Standards' mean measurement results are compared to the assigned values based on the Primary Standard calibrations in Figure 4. In this plot, the daily mean results are compared to the trend line in CO_2 observed in multiple calibrations made with the FCL Primary Standards. No bias is observed except for some minor synoptical patterns and variations of the measured results. The standard deviations of the daily target mean residuals is 0.01 ppm for the respective period. There are two exceptional periods: firstly, the initial period until-May 2015, when the calibration pattern of the CRDS instrument had not yet been in the same strict routine mode as it has been applied ever since. Secondly, Target results are higher by up to 0.02 ppm in the period between June 2020 and April 2022. During this period only preliminary assignment information for the Secondary Standards were available and resulting in incorrect CO_2 growth estimates. While the diverging data in that second period will represent similar deviations of FCL assignments on ICOS standards, this bias will be corrected at a later point in time (see section 5.2).





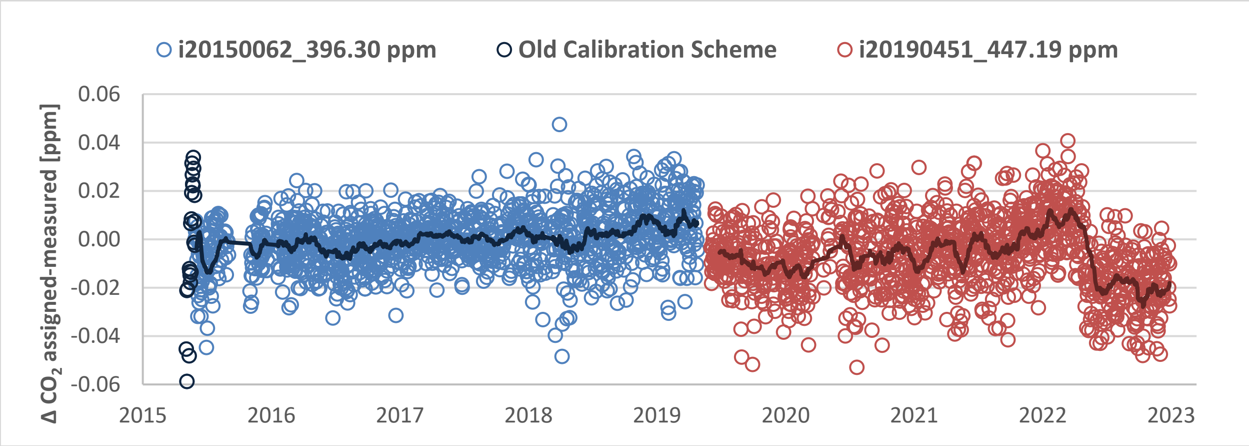
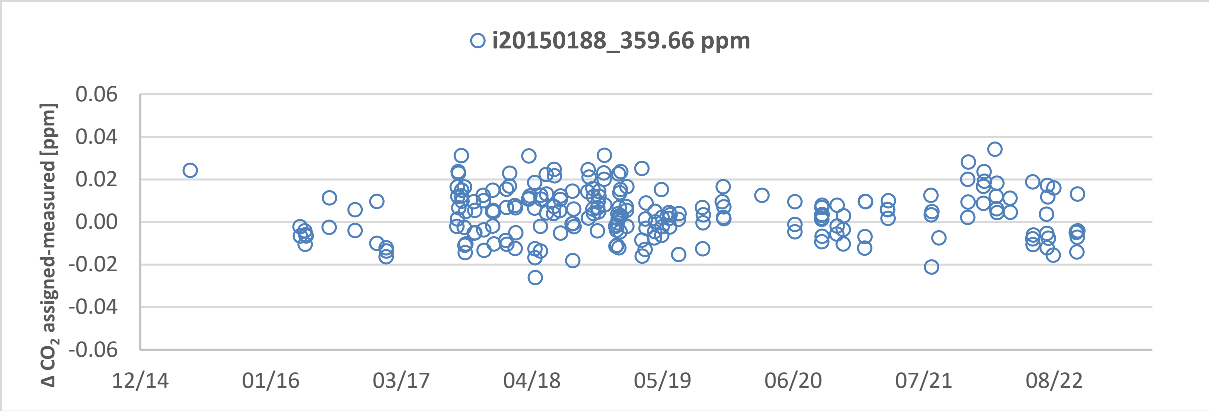


Figure 4: Time series of the offset of CO2 target measurements to their respective assigned values

The dark line represents a 30 points-running mean. (Three outliers in January 2018 and January 2019 have been flagged out for i20150060, i20150061 and i20150062 for a more explicit visualization).



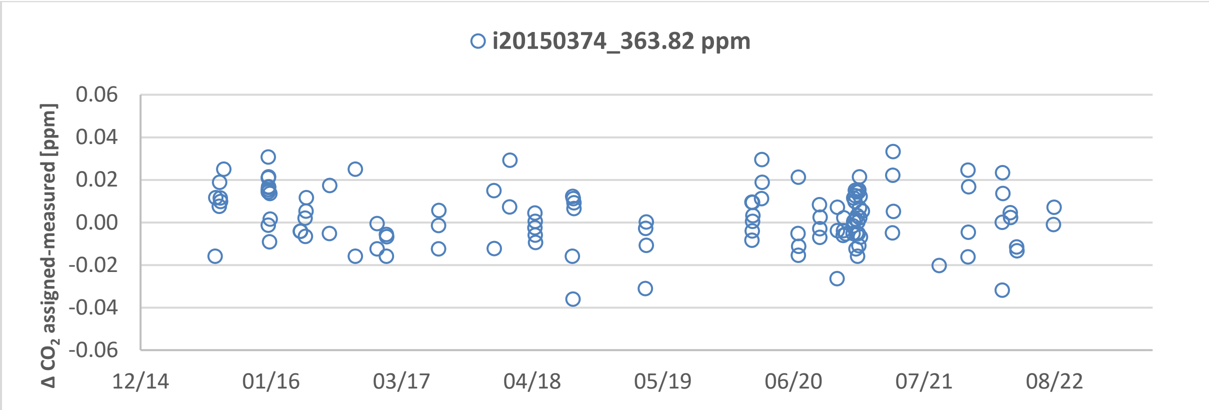


Figure 4: Time series of the offset of CO2 target measurements to their respective assigned values

5.4 Internal CO_2 Comparison: CRDS-GC

Standard gases that are calibrated for CO_2 by CRDS have often also been analyzed by GC. The GC measurements are linked to the same set of FCL Primary Standards but based on a different set of five Secondary Standards. As reproducibility and repeatability of CO_2 measurements using the GC (0.04 ppm and 0.05 ppm, respectively) is in general by a factor of 4-5 worse compared to CRDS (0.01 ppm), only those GC measurements were considered for comparison that have been analyzed on the GC with at least ten injections. The inter-instrumental measurement differences for all standards are depicted in Figure 5 (including only standards within the range defined by the calibration standards). On average there is no offset (-0.006 ppm ± 0.043 ppm), neither any evidence for a trend in time nor a systematic mole fraction dependency of the agreement.

Note that each data point in Figure 5 represents the difference of one CRDS daily mean result relative to the means of GC measurements of the same sample averaged over one calibration episode. Some samples have been analyzed much more frequently on the CRDS system than on the GC giving these latter measurements more weight in the figures which are based on 213 individual samples in total.

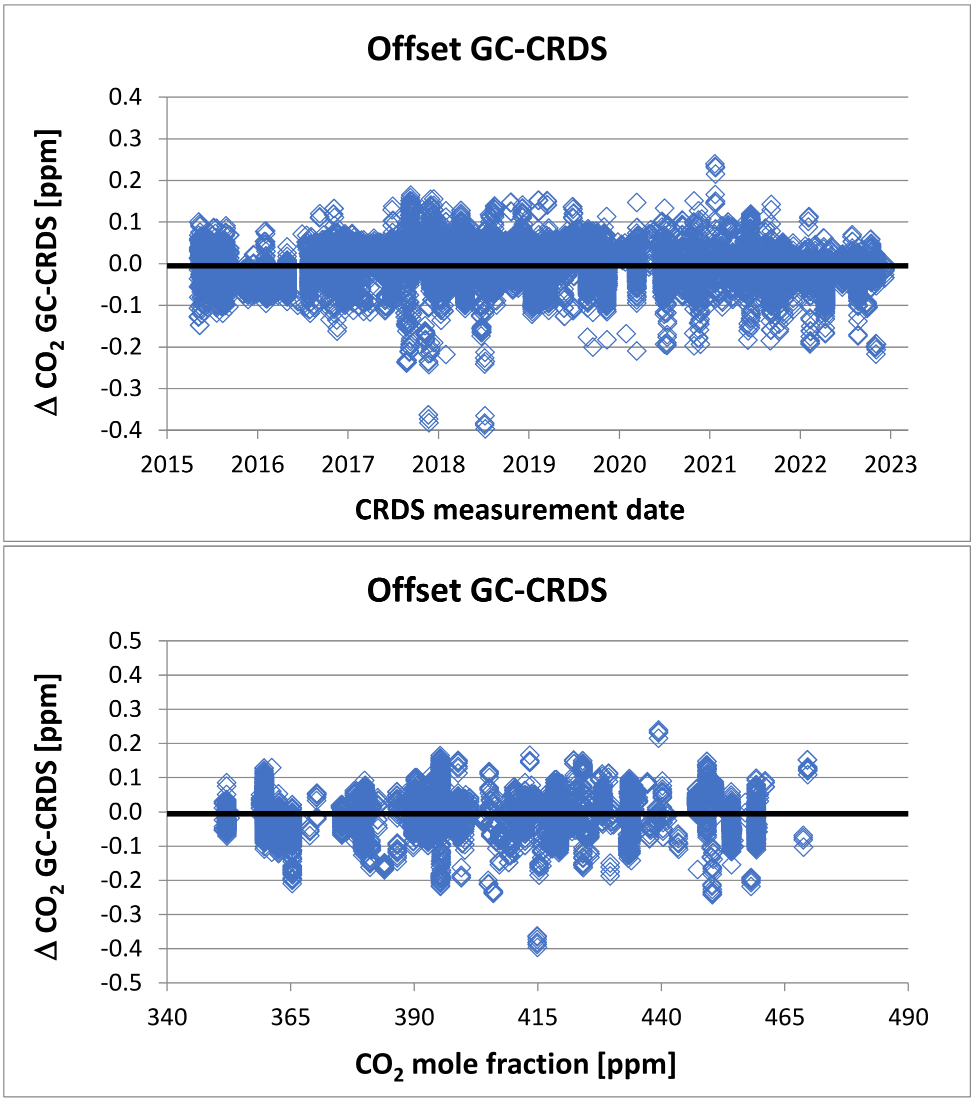


Figure 5: Offsets of daily CRDS CO2 measurements relative to average GC results. Only analyses results made within one year are considered. The black line represents the mean offset.

5.5 External CO_2 Comparisons

5.5.1 CO_2 compatibility ICOS FCL - MPI BGC

The most intensive comparison measurements have been made with the MPI-BGC GasLab. This laboratory is using different instruments (Picarro G1301 through April 2018, G2301 since May 2018) and their measurements are tied to the WMO Mole Fraction scales by an independent set of Lab Primary Standards. These MPI-BGC Primary Standards already have CCL calibration records with multiple measurements in different years for nine individual standards over six to seventeen years.

The MPI-BGC measurements are not relevant for the assignment of the FCL standards and therefore only serve as independent quality control check.

5.5.1.1 Comparison of Primary CO_2 Standards

Basis for an agreement of FCL and MPI-BGC measurements is the compatibility of the respective sets of Primary Standards. As the FCL Primary Standards have been produced at the MPI-BGC they also were thoroughly analyzed at the MPI-BGC in 2013 and 2014 before being used by the FCL. Before or after the shipment to the CCL for recalibration the standards were also analyzed for another time at MPI-BGC. Likewise, MPI-BGC Primary Standards that were simultaneously returned to the CCL for recalibration were also analyzed by the FCL. These data are shown in Figure 6 below.

The results of the MPI-BGC measurements of the complete FCL standard set are on average 0.019 ± 0.025 ppm lower than the CO_2 WMO X2019 PC1 assignments made by the CCL (red symbols) when considering the isotopic composition of CO2 in the standards (see Annex IV). There is an apparent mole fraction dependency of the offset; constraining the compared standards to the four standards in the range of 360-430 ppm results in a mean offset of 0.017 ± 0.017 ppm. The same analysis of FCL measurement results of the MPI-BGC standard set yields a very close match with on average 0.032 ± 0.020 ppm higher values than the CCL PC1 assignments consistent with the mole fraction dependency seen by the MPI measurements (0.024 ± 0.014 ppm within the range of 360-450 ppm) (see Figure 6, blue symbols). Note that the two data sets in Figure 6 are presented on inverse axis because measurements using a set of Primary Standards that are on average carrying too high assignments will detect too little CO_2 in the set of standards that it is analyzing.

Comparison with additional sets of WMO standards could be made by FCL with the WMO Lab Standards of FMI (in 2016) and UBA Zugspitze (in 2021). Whereas the observed offset for the UBA set yields the same small offset there is a consistent offset of opposite sign for the FMI set (FCL CO_2 results 0.065 ppm lower than CCL assignments). While this different offset for the FMI set is not yet understood.

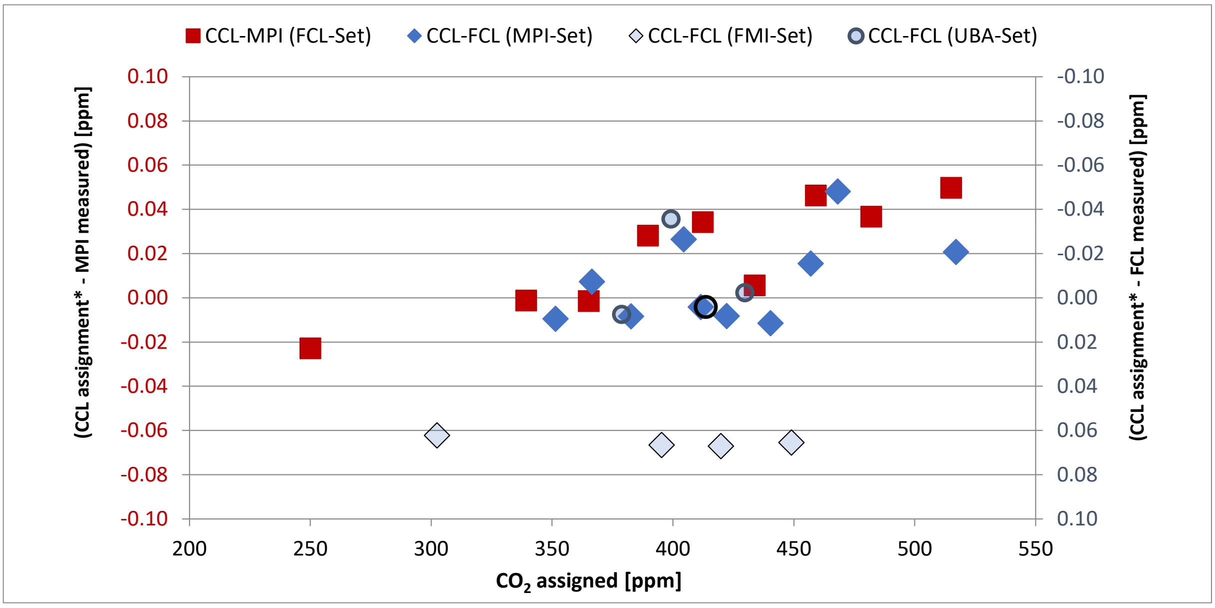


Figure 6: Differences of FCL analysis results of MPI and FMI Primary Standards to CCL CO_2 assignments (blue diamonds) and of MPI-BGC analysis results of the FCL Primary Standards to CCL assignments (red squares).

Note that the data sets with different colors are on axis with opposite sign (see text) and that the assigned values have been adjusted for the isotopic composition of CO_2 in the respective standards (see Annex IV)

5.5.1.2 Comparison of FCL Secondary CO_2 Standards

Three of the four gases from the first set of FCL Secondary Standards have been analyzed at the MPI-BGC in 2013 and 2014. The results show a small offset of about 0.02 ppm for the two lower standards (FCL assignment larger than MPI result) but a 0.1 ppm bias for the 454 ppm standard (see Table 5) which exceeds the increasing offset observed in the primary standards sets. The reason for this is not clearly understood and might reflect limitations of the MPI-BGC reproducibility at that time.

Table 5: Offset of MPI-BGC CO_2 analysis results to FCL Secondary CO_2 Secondary Standard assignments

FSN	Cylinder	FCL	MPI mean	MPI-FCL
i20140171	D801336	359.865	359.845	-0.02
i20140173	D073392	424.721	424.706	-0.015
i20140174	D801331	454.329	454.223	-0.106

5.5.1.3 Target standard CO_2 comparison

The three standard gases that were in use as target standards at the FCL also have been analyzed at the MPI-BGC. The differences of FCL measured means and MPI-BGC measured means given in Table 6 below are as small as expected from the agreement of the Secondary Standards.

Table 6: Comparison of MPI-BGC CO_2 analysis results of FCL Target Standards
FCLmeasured data are based on the daily calibration with FCL lab Secondary Standards; a CO_2 trend has been observed in the targets so FCL values are calculated from this trend function for the specific dates of the MPI analysis

Sample Number (FSN)	Cylinder Code	$FCL_{measured}$	$MPI_{measured}$	ΔMPI-FCL
i20150060	D073381	390.591	390.572	-0.019
i20150061	D073389	428.101	428.071	-0.030
i20150062	D073391	396.290	396.255	-0.035
i20150188	D073398	359.614	359.613	-0.001

5.5.1.4 Sample CO_2 comparison

High pressure standards have been regularly exchanged between MPI-BGC and FCL in earlier years and analyzed in both laboratories. The difference in the results of the two labs for about 2600 daily mean results (involving ca. 90 samples) is presented in Figure 7 below. These comprise all gases that have been analyzed within one year (only samples with CO_2 mole fractions within the calibrated ranges have been considered). The average offset of FCL - MPI for the entire period Mar 2015 through Dec 2022 is 0.021 ppm ± 0.018 ppm is again very similar to the one established in the previous sections. There appears to be a slight mole fraction dependency with FCL results being larger compared to MPI results at higher mole fractions and smaller at lower mole fractions. There also may be a trend in the offset which may have increased by 0.03 ppm within the seven years of comparisons. Note that these differences include the measurement uncertainties of both laboratories and for some samples with growing CO_2 part of the difference will be result of the analysis time delay. As explained in section 5.3 measurements up to May 2015 were not yet made using the same strict procedure that has been adopted since resulting in more noise in the offset. The MPI-BGC precision has been inferior up to May 2018 when a Picarro 1301 analyzer was replaced by a 2301 analyzer. The current MPI-BGC reproducibility is estimated as 0.02 ppm.

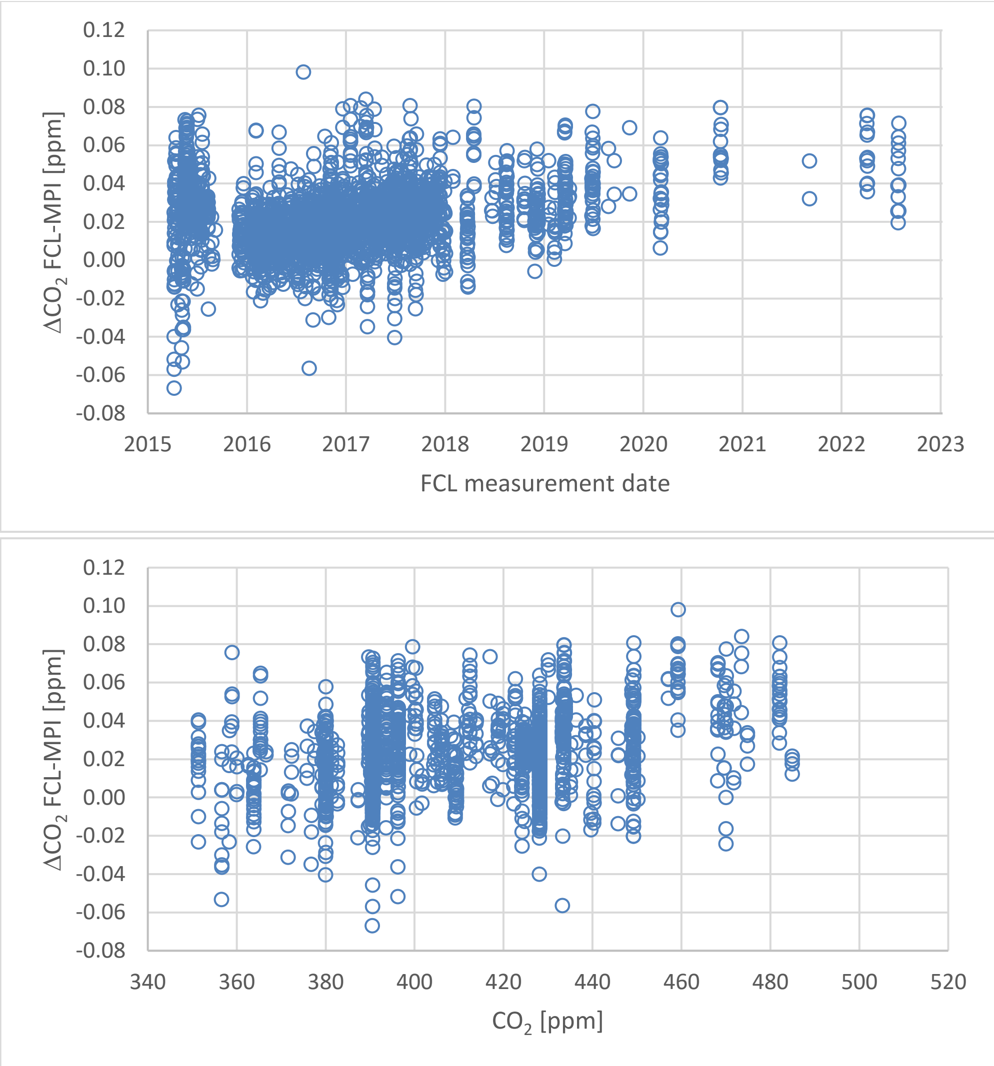


Figure 7: Differences of CO_2 results for samples that have been analyzed at FCL and MPI

Note that there are time lags between the analysis time in both laboratories that can cause biases for gases that are not stable in their CO_2 mole fraction over time in this graph.

5.5.2 CO_2 compatibility ICOS FCL - NOAA

Comparison with the NOAA-GML laboratory (and other laboratories) is routinely made in two independent exercises, the Sausage Flask Intercomparison Program and the MENI (**M**PI – **E**MPA – **N**OAA -**I**COS) high pressure cylinder round robin program.

In the Sausage intercomparison, samples for comparison are prepared by connecting sets of flasks in line and filling them with dry air from a high-pressure cylinder at the FCL. The FCL generally analyzes the composition of the filling air using the normal instrumentation for calibrating standards. Therefore, the results of the flask measurements provided by NOAA can be compared to these high-pressure cylinder measurements. The respective data are compiled in Figure 8. The average agreement of NOAA mean flask results compared to FCL-CRDS filling gas data is NOAA - FCL = - 0.02 ± 0.05 ppm (filled black circles) without any clear mole fraction dependency. Some larger scatter at lower mole fractions may relate to less homogeneous CO_2 isotopic composition for air depleted in CO_2 affecting the isotope sensitive NDIR analysis.

The MENI round robin between NOAA (as WMO-CCL), EMPA (as WMO-WCC), MPI-BGC, FCL and FMI-ATC (ICOS Mobile Lab) has been established to check the ICOS scale link to the WMO mole fraction in a regular manner. In this program a set of three cylinders is prepared and maintained by the FCL. One of these cylinders (D232733) constitutes a blind sample and is modified in its composition after every completed loop. A general small trend in the CO_2 mole fractions has been observed by all labs. To account for the different times of analysis of the comparison samples this trend is defined by the NOAA data record as the reference for the two comparison samples that have been used over several years. The "blind" sample is analysed at different points of time only at the FCL, therefore the CO_2 growth is determined by these measurements and the FCL trend serves as reference. In Figure 9 results of the first four iterations are shown as difference relative to the respective CO_2 trend function. The mean offset FCL-NOAA for the different standards compared is smaller than 0.01 and 0.02 ppm (trend revised) for all standards in the period 2017-2020. and systematically higher for the 2022 data. FCL data suggest an accelerated CO_2 growth at low pressures in the cylinders but it might also point to a real bias.

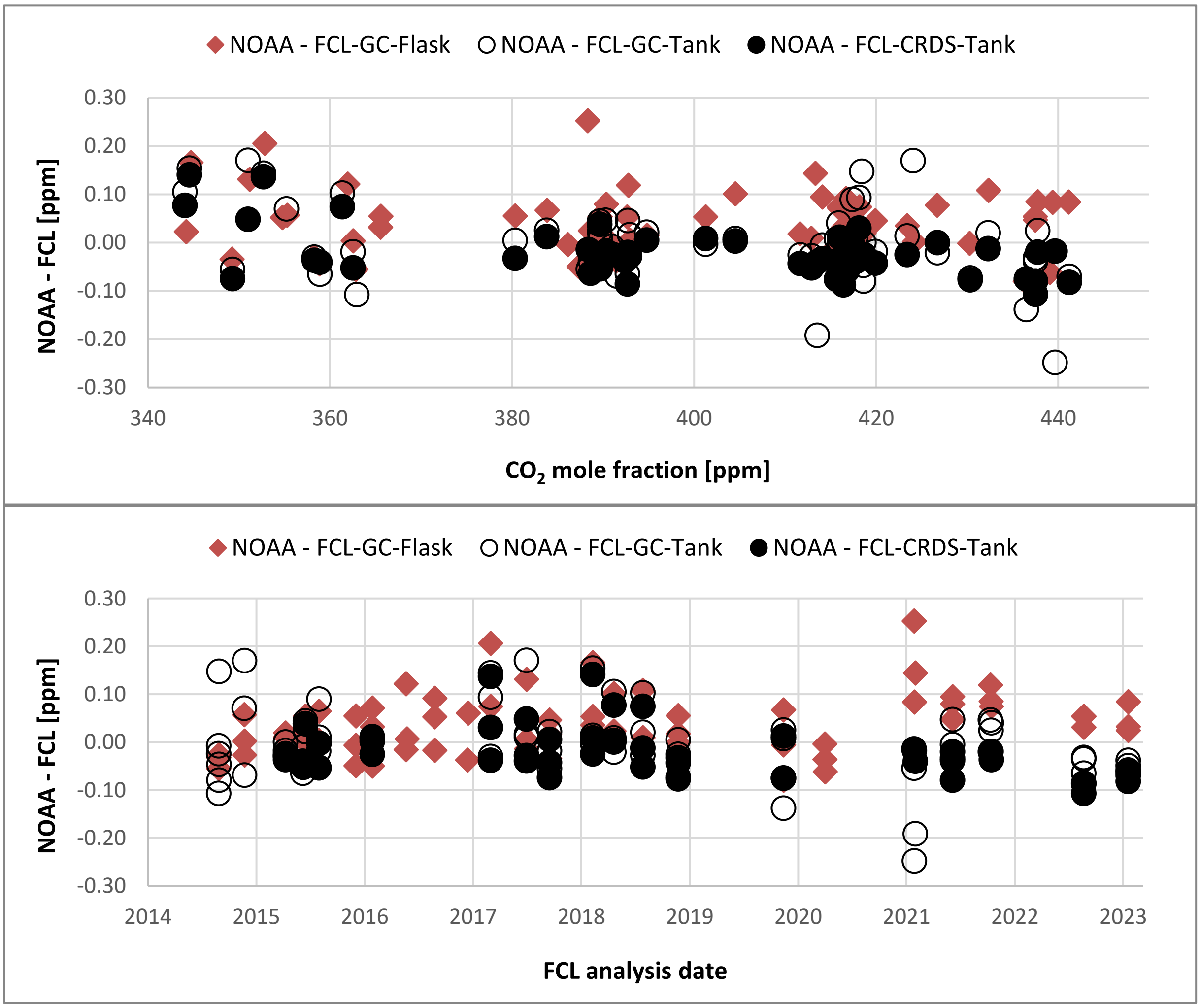


Figure 8: CO2 offset between FCL and NOAA- based on analyses of flask samples (by NOAA), analyses of flask samples by FCL (GC-FID) and their respective source gases from high pressure cylinders (by FCL using CRDS)

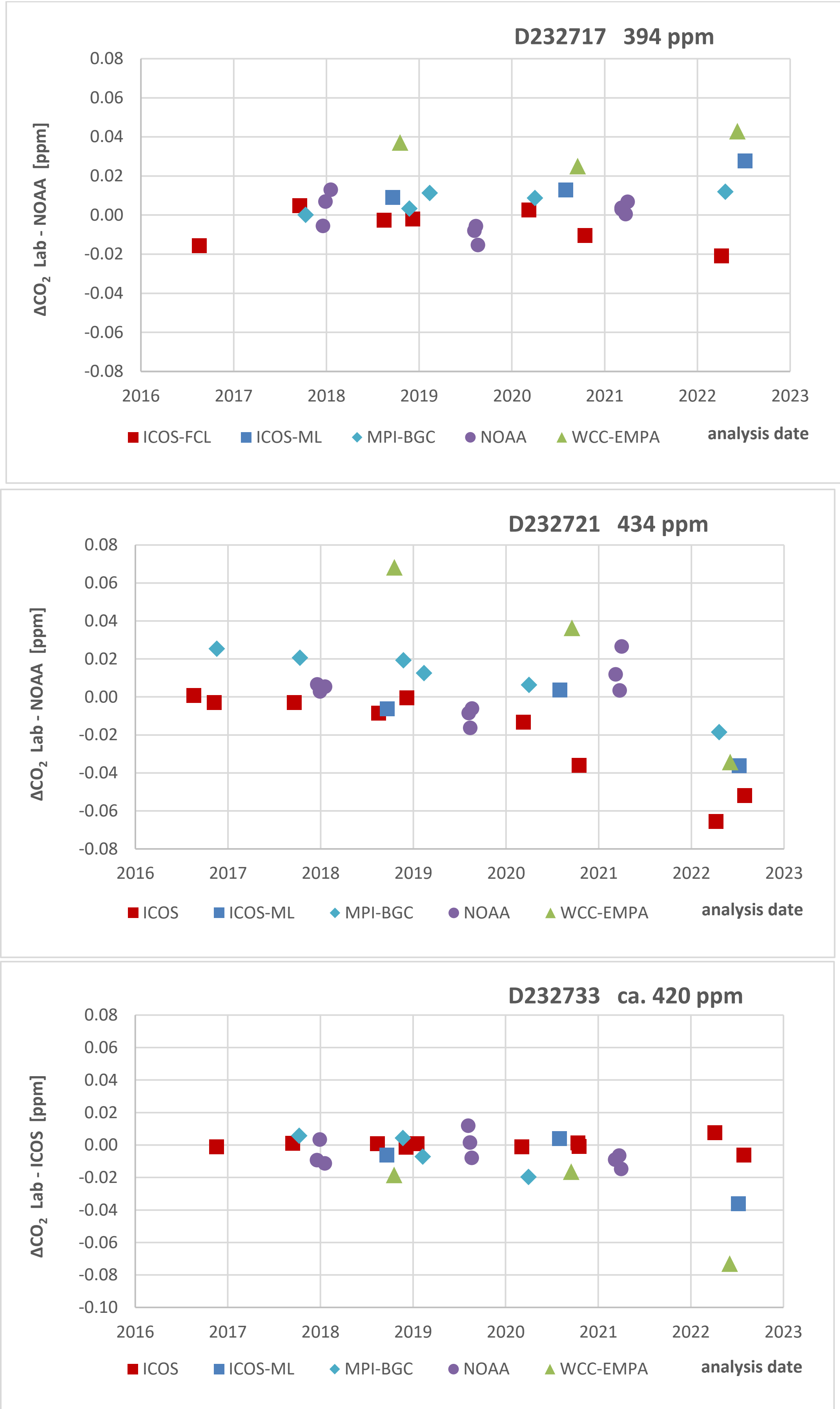


Figure 9: CO2 offset in MENI ICP between FCL, MPI, ICOS MobileLab and WCC relative to NOAA.

5.6 CO_2 uncertainty evaluation

The WMO Expert Group recommendations request investigators to report uncertainty estimates for their data that include all potential sources of error [WMO 2018]. A scheme for a comprehensive uncertainty discussion has been suggested by Andrews et al. 2014. Adapting this scheme, we have made such an overall measurement uncertainty estimate based on a performance assessment of the CRDS system. In this assessment we have considered the following uncertainty contributions and checked them using the quality control data of this report.

5.6.1 FCL Primary CO_2 Standards

The X2019 scale revision has solved earlier ambiguities on the stability of the CO_2 mole fractions in the Primary FCL Standards. There are no signs indicating a significant drift in any of the nine standard gases any more. Regression fit residuals of 0.01 ppm confirm the consistency of the standard assignments.

5.6.2 CO_2 scale transfer uncertainty

The statistics of repeated calibrations of the FCL Secondary Standards by the FCL Primary Standards provide a measure for the uncertainty of their assignments. The average reproducibility of these assignments is 0.015 ppm. With a total of 20 and 24 calibration episodes, respectively, for each of the Secondary Standards of the first set the uncertainty of their assignments is expected to be below 0.005 ppm relative to Primary Standard set. This is consistent with an average daily calibration standard error of 0.006 ppm. The new set of Secondary standards has been calibrated within 10 calibration episodes, but over a shorter period. This increases the uncertainty in the size of the CO_2 growth within the cylinders. The time series of the target standard CO_2 results suggest a potential overestimate of this drift.

The comparison of FCL measurement results of WMO tertiary standards of other groups (MPI, UBA) indicates a slightly larger, mole fraction dependent scale transfer uncertainty on the order of 0.02 ppm at atmospheric mole fractions. This is likely mostly due to to an arithmetic error that has been made in the calculation to account for the differences in the isotopic calculation that amounts to similar bias (see Annex IV). A preliminary assignment of the second set of Secondary Standards based on a limited number of Primary Standard calibrations had suggested a growth of CO_2 in the standards that were not confirmed by further Primary Standard calibrations. While the assignments were adjusted end of April 2022 they have not been rectified for the period before (June 2020 - April 2022). As a result CO_2 results are currently slightly too high for that period with a maximum offset in April 2022 of 0.02 - 0.03 ppm.

The small offset in the Secondary Standard assignments shows consistently up also in the target residuals (comparing results based on Secondary Standard calibrations to those based on the Primary Stand calibrations), as well as all in external comparisons with MPI and NOAA. Therefore, FCL results appear to be slightly biassed by the internal scale-transfer error but consistent within at maximum 0.015 ppm. An adjustment to correct for the erroneous calculation will be made by hindsight.

5.6.3 CO_2 long-term reproducibility

The reproducibility of CO_2 measurements as derived from the target standard measurement record is <0.012 ppm from 2015-2022. Within the scatter of this time series there are minor systematic shifts of mean results occasionally observed over periods of many days to weeks to months that are not cancelled out by the standardization scheme. These typically do not exceed 0.005 ppm and point to small system changes over time that are not always understood.

5.6.4 CO_2 measurement uncertainty estimate

Based on these evaluations the following combined standard uncertainty (k=1) is calculated as the square root of the sum of the individual uncertainty squares:

1. Scale link uncertainty = 0.03 ppm:

- The uncertainty from the reproducibility of the CO_2 WMO X2019 CCL CRDS assignments on calibration standards is specified as 0.01 ppm (k=1) [Hall et al. 2021]. This is in agreement with the consistency of the regression fit residuals of the FCL Primary Standards.
- The uncertainty of the FCL internal scale transfer to the Secondary Standard assignments of the first set deduced from the record of the secondary measurement results from FCL primary calibration events results (uncertainty of the regression of the trend line of CO_2 over time) is estimated as 0.015 ppm (2015 to August 2022).
- The assignment error made for accounting of the isotopic composition of CO_2 is 0.024 ppm in the range of 390 to 460 ppm.

2. Measurement uncertainty of daily means = 0.014 ppm:

- mean uncertainty of the daily calibration regression fit = 0.01 ppm
- typical uncertainty of unaccounted detector response drift throughout the validity of the daily calibration = 0.009 ppm
- uncertainty from the repeatability of the daily sample measurements =0.0025 ppm (for 15 min means)

3. Additional long-term variability = 0.01 ppm

The reproducibility derived from the target standard record is consistent with the uncertainty estimate for measurement of daily means.

The accuracy with respect to the WMO scale arises from the root of the sum of squares of the scale link uncertainty, the measurement uncertainty and additional long-term variability amounting to 0.02 ppm for calibration data before July 2020 and 0.03 ppm for calibration data since July 2020.

6 CH_4

6.1 FCL Primary CH_4 Standards

6.1.1 CCL CH_4 Assignments

After initial calibration of all FCL Primary Standards in 2014, the first recalibrations of each three of the standards have been made in 2016, 2017, and 2018, respectively. In 2021 the complete set was recalibrated again, such that three CCL assignments from different years are available for each standard. In 2017 the CCL has changed instrumentation now using CRDS instead of GC-FID. With the recalibration in 2021, two CRDS measurements are now available for the entire set. For the tanks, the difference in mole fractions between the CRDS and the initial values measured with GC-FID lies within the range of the standard deviations specified by the CCL for the individual measurements (range of CRDS-GC-FID difference is -0.28 to 0.57 ppb).

Table 7: CH_4 assignments for FCL Primary Standards by the CCL [ppb]

Sample ID	Cylinder ID	CCL date 1	CCL date 2	CCL date 3	mean GC data	mean CRDS data*	Assignment used **
i20140055	CB09944	Dec-13	May-17	Mar-21	1596.76	1596.68	**1596.64**
i20140056	CB09939	Feb-14	Oct-18	Mar-21	1743.13	1743.11	**1743.13**
i20140057	CB09958	Dec-13	Aug-16	Mar-21	1896.80	***1896.90***	**1896.82**
i20140058	CB09983	Dec-13	Oct-18	Mar-21	2032.92	2032.93	**2032.92**
i20140059	CB09952	Feb-14	Aug-16	Mar-21	2195.27	***2195.06***	**2195.34**
i20140060	CB09955	Dec-13	Jun-17	Mar-21	2344.03	2343.90	**2344.05**
i20140061	CB09957	Dec-13	Aug-16	Mar-21	2466.60	***2466.60***	**2466.72**
i20140062	CB09934	Jan-14	Jun-17	Mar-21	2731.47	2731.84	**2731.28**
i20140054	CB09948	Jan-14	Oct-18	Mar-21	2932.82	2933.04	**2932.82**

* values in bold and italics are indicating results from measurements performed only at date 3

** Corresponds to initial CCL GC assignment

Thus, the recalibrations by the CCL have not changed the assignments significantly and the signs of the update terms for the various standards are such that they largely compensate in sum. Therefore, there was no need for an update of the assigned values and the initial assignment is still used (last column in Table 7).

6.1.2 Regression fit residuals of FCL Primary CH_4 Standards

The time series of the linear regression fit residuals is presented in Figure 10 for calibration events where the *complete* FCL Primary Standard gas suite was used.

CH_4 mole fractions are known to be generally very stable in aluminium high pressure cylinders. Accordingly, the regression fit residuals do not show significant trends over time for any of the individual standards (generally within 0.2 ppb), which is supporting the assumption of a stable set.

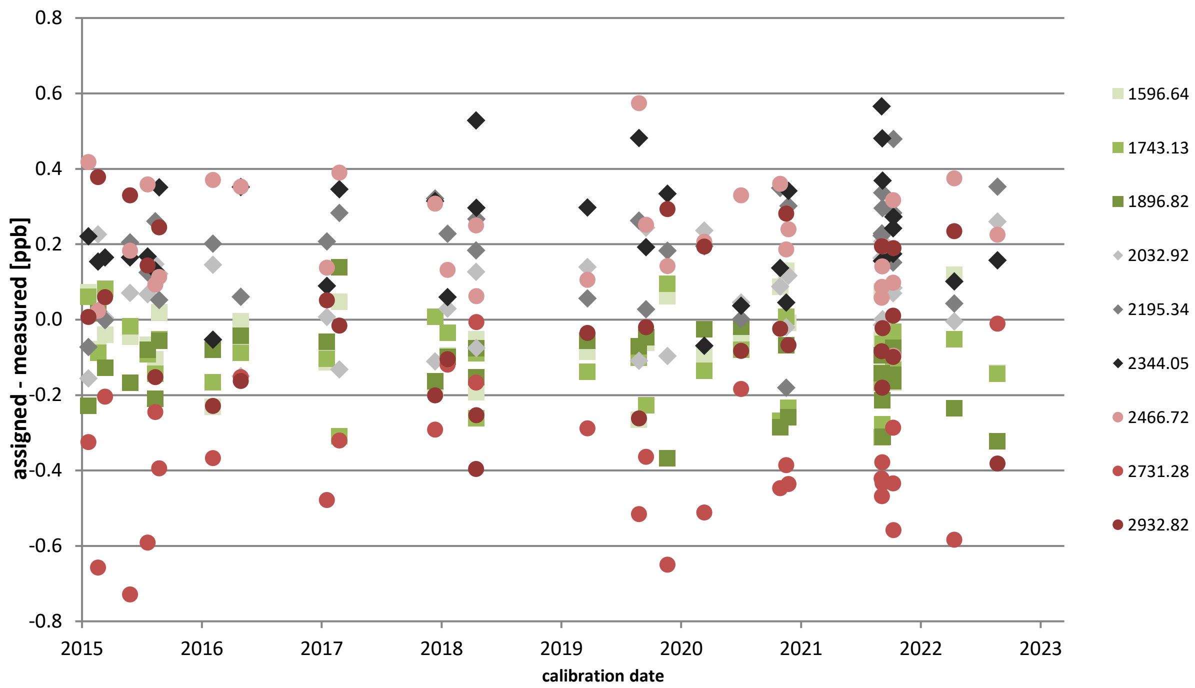


Figure 10: Time series of linear regression fit residuals of CRDS CH4 calibrations for FCL Primary Standards

6.2 FCL Secondary CH_4 Standards

6.2.1 Assignment record

The four reference gases that were used as initial set of FCL Secondary Standards for the CRDS measurements have been analyzed within 20-24 valid calibration episodes together with the FCL Primary Standards between Feb 2015 and either July2020 or Sep2021, respectively. During 2020, the first set of FCL Secondary Standards had to be replaced by a new set due to consumption. The replacement was done in two steps, with the replacement of the two standard gases with higher mole fractions in June and the replacement of the two standard gases with lower mole fractions in December.

The assigned values for the new standards were determined by repeated measurements against the FCL Primary Standards (n=10). The assigned values are listed for comparison with the first set in Table 8.

The record of the CH_4 mole fraction results of these FCL primary calibration episodes is displayed in the graphs below. The measured values for the first set of FCL Secondary Standards are shown with dark dots, those for the subsequent second set, which is currently in use, with red diamonds

For the initial set of Secondary Standards used until June 2020 the initial assigned values (indicated by open symbols) have not yet been replaced by the mean of the complete set of calibrations given the marginal difference. However, after the replacement of the first two of the initial Secondary Standards in June 2020, updated assigned values were used for the two remaining Secondary Standards of the initial set for the period until their replacement in December 2020.

Table 8: CH_4 assignments of FCL Secondary Standards

Sample ID	Cylinder ID	Assigned Value	Re-assigned*	*Date of exchange*	Sample ID	Cylinder ID	Assigned Value
i20140171	D801336	**1795.46 ppb**	1795.56 ppb	*2020-12-08*	i20190708	D761202	**1799.01 ppb**
i20140172	D073384	**1960.24 ppb**	1960.54 ppb	*2020-12-08*	i20190803	D073381	**1949.24 ppb**
i20140173	D073392	**2288.57 ppb**		*2020-06-23*	i20190709	D761214	**2296.10 ppb**
i20140174	D801331	**2092.46 ppb**		*2020-06-23*	i20190438	D073389	**2098.41 ppb**

* Re-assignments used from 2020-06-23 to 2020-12-07

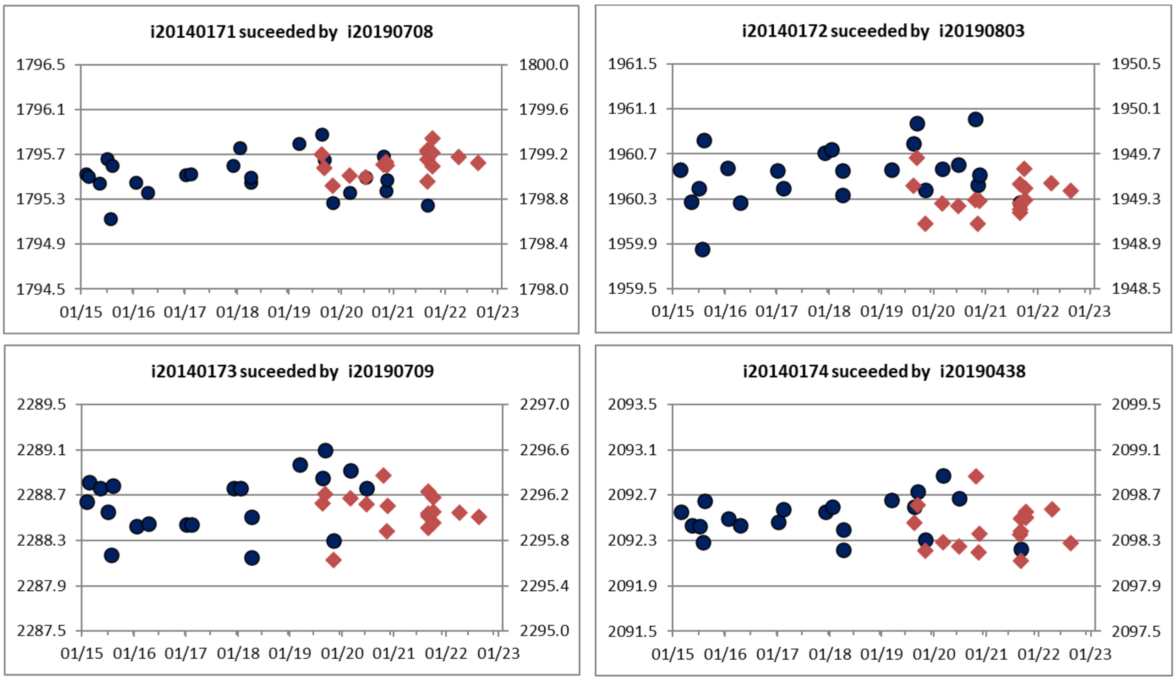


Figure 11: FCL Secondary Standards CH4 assignment time series (all values in [ppb]).

Dark blue dots represent the assignments for the first set of FCL Secondary Standards, the red diamonds display the four new FCL Secondary Standards.

6.2.2 Residual record

The record of the residuals of the linear regression fit of the Secondary Standard calibrations are given in Figure 12. The scatter of the residual time series for the individual standards is mostly < 0.1 ppb without any trend in the residuals being apparent. This documents the long-term internal consistency of the calibration set over time. The internal consistency of the new FCL Secondary Standard set expressed as the standard deviation of the mean residuals is ~0.02 ppb compared to 0.12 ppb for the first FCL Secondary Standard set. This reflects the small bias in the initial assignments of the first set of standards but still indicates the overall very little scale transfer uncertainty.

Figure 12: Time series for CH4 linear regression fit residuals of the FCL Secondary Standards.

Dark symbols indicate the transition phase when only the first part of the standards was replaced

6.3 CH_4 Targets

In the period from March 2015 to December 2021 two succeeding sets of each three target standards have been in use for the CRDS system. The replacement was made in 2019 with two of the succeeding targets having been analyzed in parallel for more than 200 analysis days to characterize the transition. On a regular basis two additional Targets monitor the long-term stability of the instrument for mole fractions below the calibrated range (1600 ppb and 1700 ppb). The consistent step of 0.2 ppb after changing the Secondary Standard calibration sets apparent in Fig. 13 complies with the small initial assignment bias of the Secondary Standards made in 2015 (see section above). Since the exchange of the secondary set, the offset has decreased to <0.07 ppb for all targets. This confirms that very little uncertainty contribution results from the scale propagation.

Table 9: Target standards for the CRDS CH_4 analyses

sample ID	tank ID	measured CH_4 [ppb]*	std.dev. [ppb]*	Primary Calibration CH_4 mean [ppb]	std.dev. Calibration mean [ppb]	n calibration values
i20150062	D073391	1914.71	0.17	1914.94	0.16	29
i20150061	D073389	2043.05	0.19	2043.30	0.11	32
i20150060	D073381	1947.18	0.17	1947.37	0.13	82
i20170961	D761211	**1943.21** *1943.40*	**0.12** *0.19*	1943.41	0.12	31
i20170962	D801332	**2032.71** *2032.91*	**0.12** *0.20*	2032.94	0.14	25
i20190451	D073391	**2085.97** *2086.18*	**0.12** *0.21*	2086.27	0.12	19
i20150188	D073398	**1595.55** *1595.73*	**0.10** *0.19*	1595.72	0.10	26
i20150374	CA05755	**1703.32** *1703.51*	**0.10** *0.19*	1703.53	0.11	31

*For Targets i20170961, i20170962, i20190451, i20150188 and i20150374 the mean values for the period from start until 23.06.2020 (change of the FCL Secondary Standards) are displayed in bold, for the period since then in italics

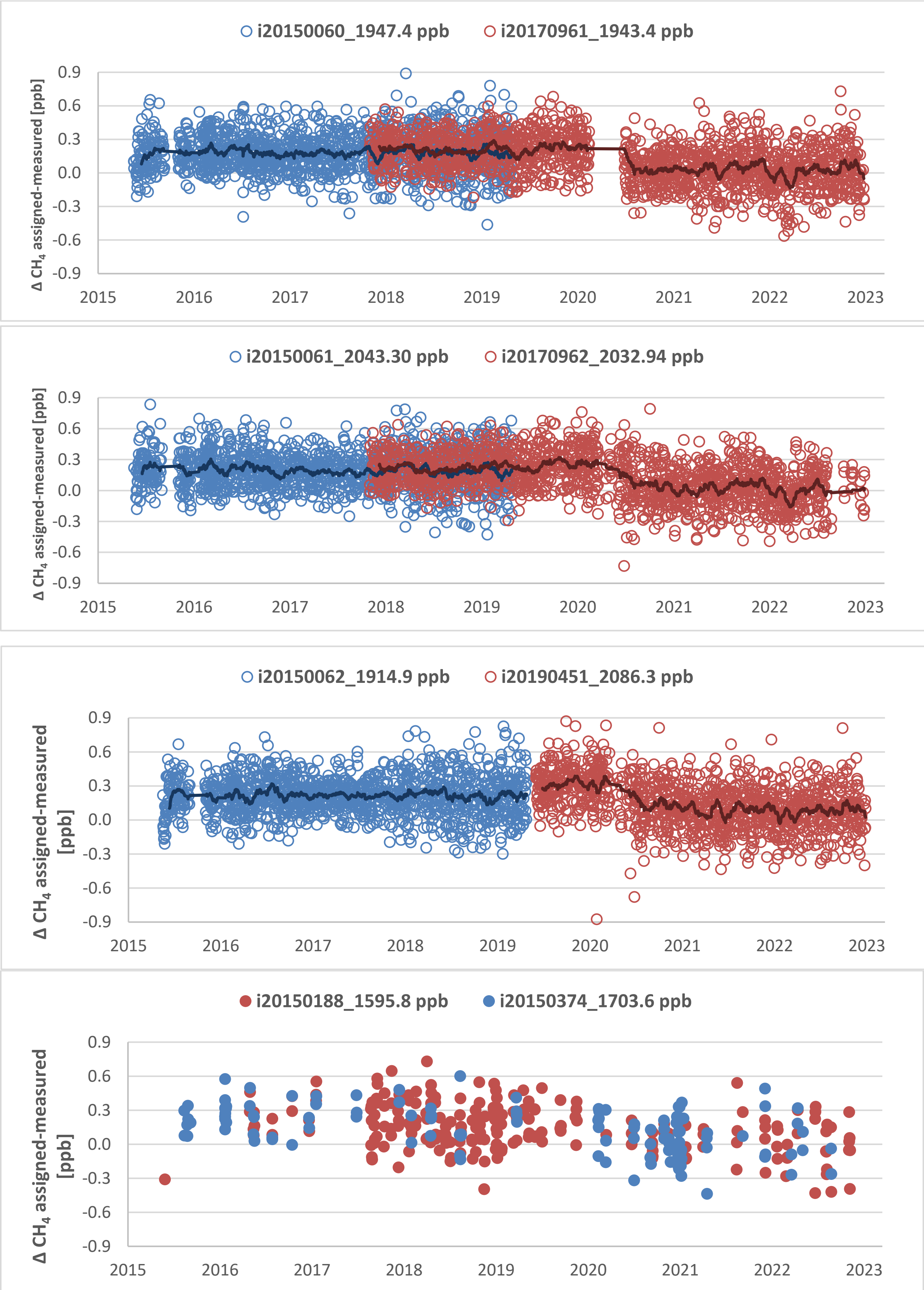


Figure 13: Time series of the CH4 offset of target measurements to their respective assigned values.

The dark line represents a 30 points-running mean.

6.4 Internal CH_4 Comparison: CRDS-GC

Standard gases that are calibrated for CH_4 using CRDS have often also been analyzed by GC-FID. The GC measurements are linked to the same set of Primary FCL Reference Standards but based on a different set of five Secondary Standards. As the reproducibility and typical repeatability of the GC-FID (0.4 ppb and 0.8 ppb, respectively) is approximately by a factor of 3-5 worse than that of the CRDS instrument, only GC measurements have been considered that have been analyzed on the GC on more than one day with at least ten injections. The inter-instrumental measurement differences for all samples are depicted in Figure 14 (only standards within the range defined by the calibration standards were considered). The average offset is 0.23 ppb ± 0.35 ppb for the initial phase until the change of the FCL Secondary Standards on 23rd June 2020, from that date onwards about 0.12 ppb ± 0.35 ppb, which again reflects the small bias of the initial CRDS Secondary Standard assignments.

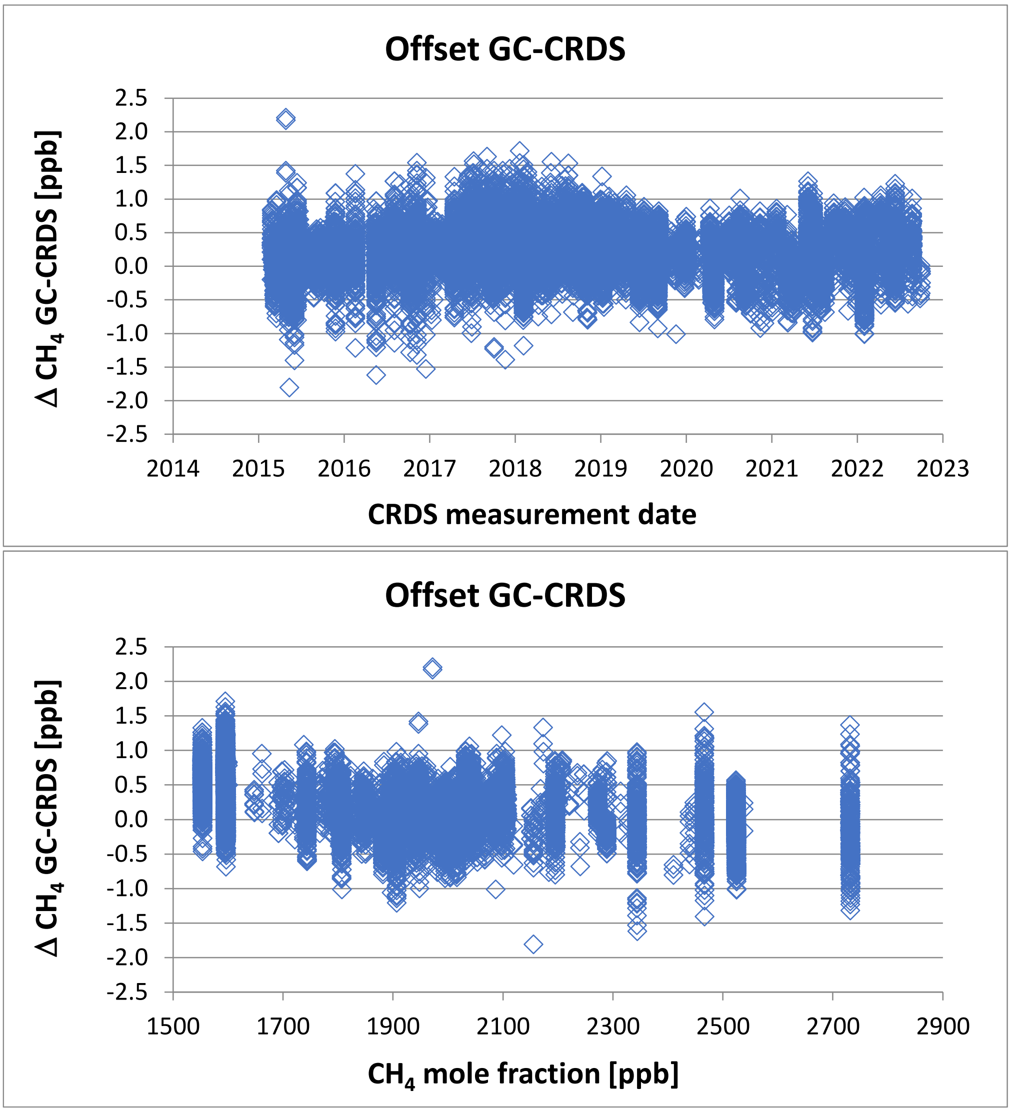


Figure 14: Offset of CRDS daily mean CH4 results relative to GC average results of the same sample.

Note that each data point in Figure 14 represents the difference of one CRDS daily mean result relative to the annual means of all GC measurements of the same sample. Some samples have been analyzed much more frequently than others (e.g. target standards) which explain the occurrence of many clustered data points in the Figure. Overall, the comparison with the independent GC measurements does not indicate any significant error in the CRDS measurements that might have been missed.

6.5 External CH_4 Comparisons

6.5.1 CH_4 compatibility ICOS FCL - MPI-BGC

The most intensive external comparison measurements have been made with the MPI-BGC GasLab. This laboratory is using different instrumentation (Picarro G1301 through April 2018, G2301 since May 2018) and their measurements are tied to the WMO Mole Fraction scales by an independent set of Primary Standards. These MPI-BGC Primary Standards already have CCL calibration records with multiple measurements in different years for nine individual standards over six to seventeen years.

The MPI-BGC measurements are not relevant for the assignment of the FCL standards and are therefore completely independent.

6.5.1.1 Comparison of CH_4 Primary Standards

Basis for an agreement of FCL and MPI-BGC measurements is the compatibility of the respective sets of Primary Standards. As the FCL Primary Standards have been produced at the MPI-BGC they also were thoroughly analyzed at the MPI-BGC in 2013 and 2014 before being used by the FCL. Before or after the shipment to the CCL for recalibration of sub-sets of this FCL Primary Standard gas suite these standards were also analyzed for a third time. Likewise, MPI-BGC Primary Standards that were simultaneously returned to the CCL for recalibration were also analyzed by the FCL. These data are shown in Figure 15.

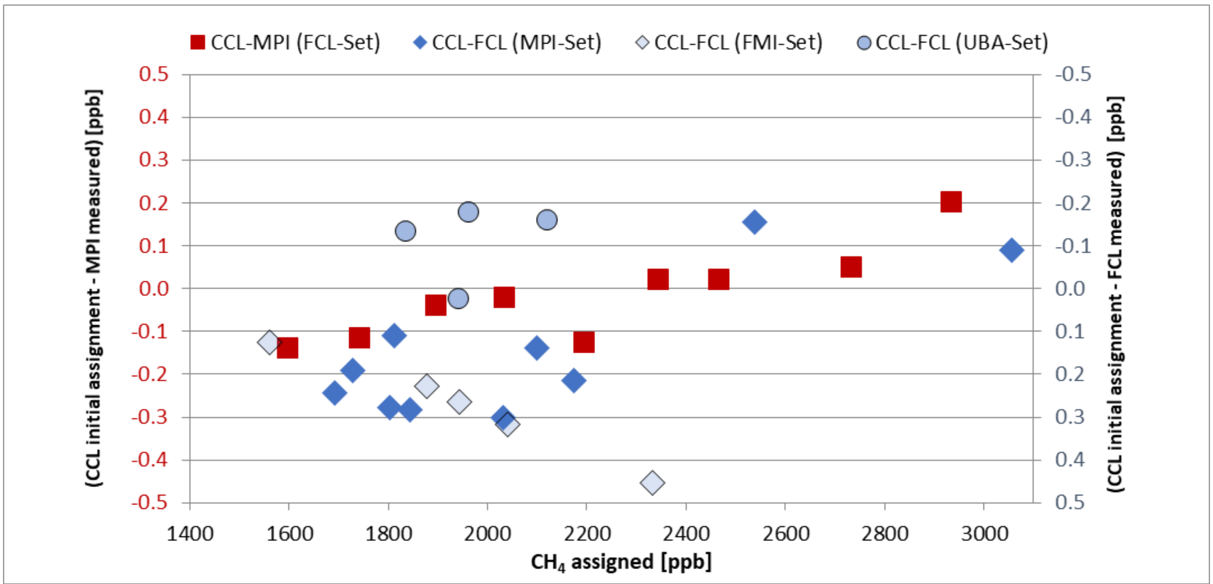


Figure 15: Differences of measured CH4 results to CCL assigned values for FCL Primary CH4 Standards.

The mean difference of the MPI-BGC measurement results relative to the CCL assignments is <0.02 ppb and the differences for the individual standards closely follow the regression fit residuals observed with the FCL Picarro CRDS instrument (see section above). The mean difference of the FCL measurement results relative to the CCL assignments has been 0.19 ppb before June 2020 (using MPI-Set and FMI-Set) and 0.11 ppb in 2021 (using the

UBA set). This is fully consistent with the findings in the previous sections and confirms the excellent accuracy of the CH_4 CCL assignments.

6.5.1.2 Comparison of FCL Secondary CH4 Standards and Target standards

Three of the four gases from the first set of FCL Secondary Standards have been analyzed at the MPI as well as three of the target standards. The differences between MPI-BGC measurement results and FCL assignments (Figure 16, blue symbols) are very consistent to the difference of FCL measurement results of the MPI-BGC Primary CH_4 Standards.

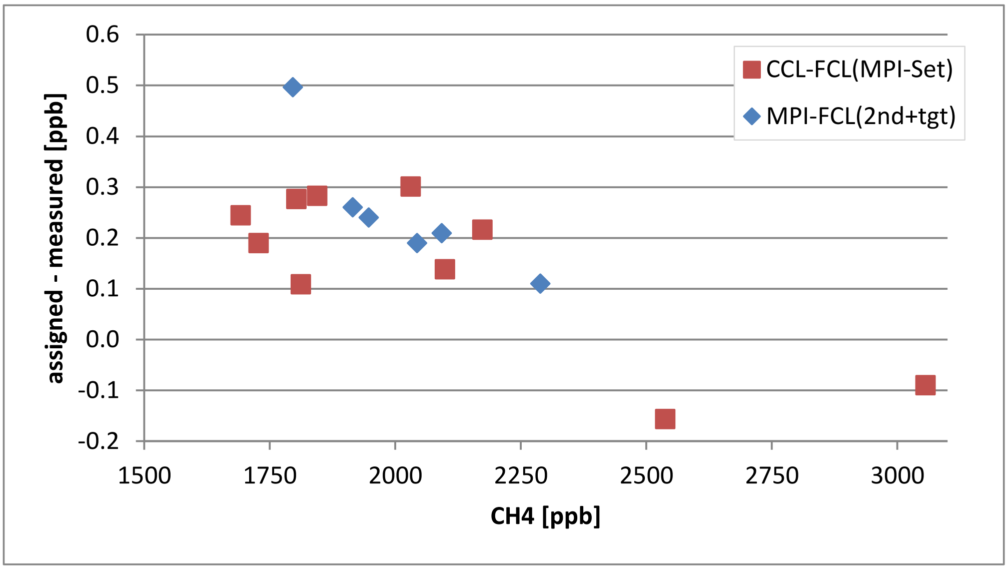


Figure 16: Differences of MPI-BGC measured results to FCL Secondary Standard assigned CH4 values (blue diamonds) compared to the differences of FCL measured results relative to CCL CH4 assignments of MPI-BGC Primary Standards (red squares)

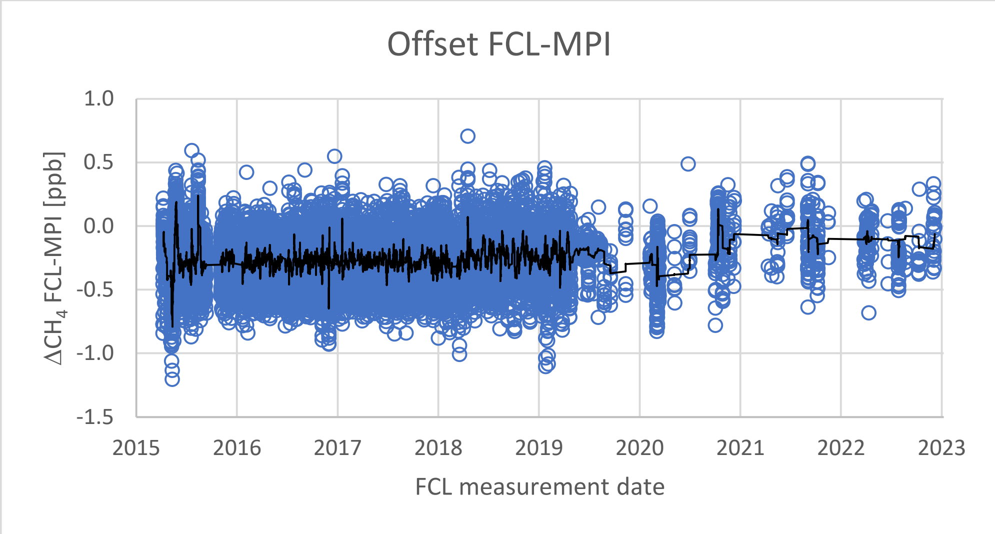
The mean differences of FCL-assigned values (based on the initial calibrations with the FCL Primary Standards for the secondaries but accounting for all calibrations of the targets), the FCL measured means and the MPI-BGC measured means are given in Table 10. As seen in Fig. 16 MPI-BGC measurement results show a difference on average 0.2 ppb to the assigned values of the Secondary Standards and the measured values of the targets. However, they do not show any difference to the FCL assignments (0.0 ± 0.1 ppb).

Table 10: CH_4 Comparison of MPI-BGC analysis results and FCL for Target standards

FSN	Cylinder	$FCL_{assigned}$	$FCL_{measured}$	$MPI_{measured}$	$MPI\text{-}FCL_{assigned}$	$MPI\text{-}FCL_{measured}$
i20140171	D801336	1795.46		1795.93	0.47	
i20140173	D073392	2288.57		2288.72	0.15	
i20140174	D801331	2092.46		2092.70	0.24	
i20150060	D073381	1947.37	1947.18	1947.42	0.05	0.24
i20150061	D78910	2043.30	2043.05	2043.24	-0.06	0.19
i20150062	D073391	1914.94	1914.71	1914.97	-0.03	0.26

6.5.1.3 Sample CH_4 comparison

High pressure standards have been regularly exchanged between MPI-BGC and FCL and analyzed in both laboratories. The difference in results for about 280 comparisons is presented in Figure 17. The average offset of all MPI-FCL sample comparisons amounts to 0.22 ppb ± 0.18 ppb. This difference confirms the observed offset in the Secondary Standard assignments.



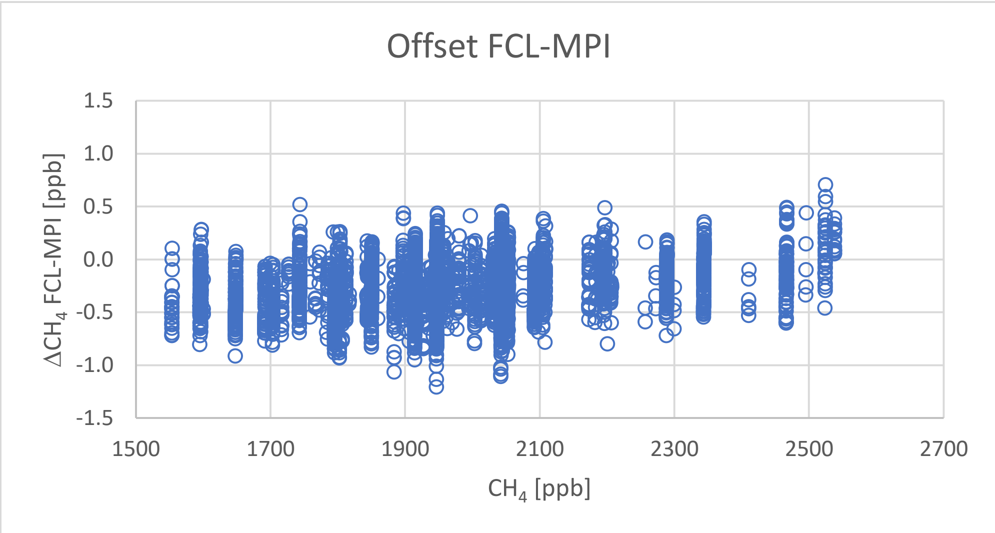


Figure 17: Differences of CH4 results for samples that have been analyzed at FCL and MPI-BGC

6.5.2 CH_4 compatibility ICOS FCL - NOAA

Comparison with the NOAA-GML laboratory (and other laboratories) is routinely made in two independent exercises, the Sausage Flask Intercomparison Program and the MENI high pressure cylinder program. In the Sausage intercomparison samples for comparison are prepared by connecting sets of flasks in line and filling them with dry air from a high-pressure cylinder at the FCL. The FCL generally analyzes the composition of the filling air using the normal instrumentation for calibrating standards. Therefore, the results of the flask measurements provided by NOAA can be compared to these high-pressure cylinder measurements. The respective data are compiled in the following figures. The CH_4 offset of all samples is NOAA - FCL = 0.37 ppb ± 0.52 ppb. In 2019 NOAA has changed the instrumentation for flask analysis to a CRDS system; constraining the comparisons to data since 2021 (after the change in the FCL Secondary Standards) results in a CH_4 offset of NOAA - FCL = -0.06 ppb ± 0.19 ppb.

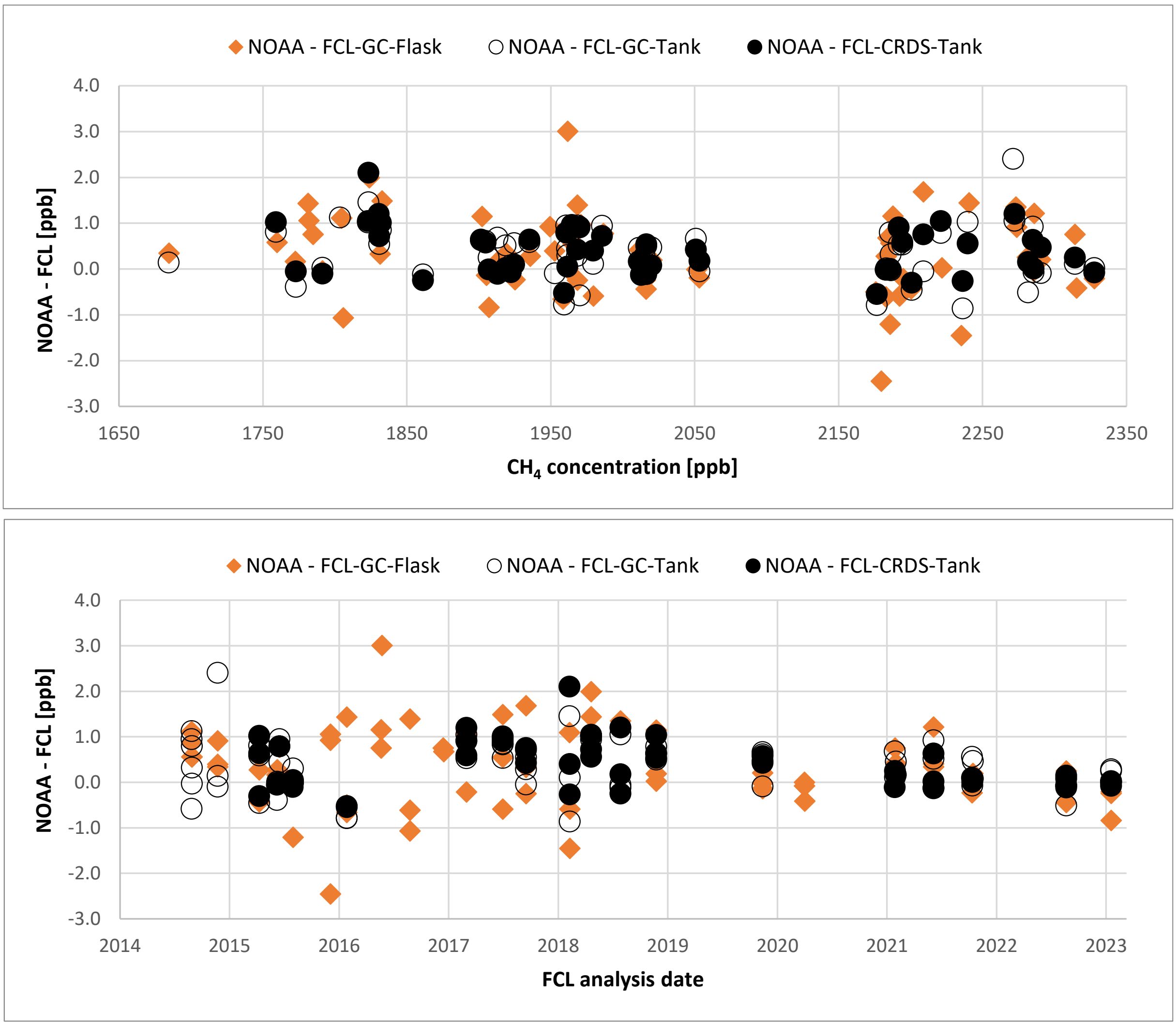


Figure 18: CH4 offset between FCL and NOAA based on analyses of flask samples (by NOAA), analyses of flask samples by FCL (GC-FID) and their respective source gases from high pressure cylinders by FCL (CRDS)

The MENI round robin between NOAA (as WMO-CCL), EMPA (as WMO-WCC), MPI-BGC, FCL and FMI-ATC (ICOS Mobile Lab) has been established to check the ICOS scale link to the WMO mole fraction in a regular manner. In this program a set of three cylinders is prepared and maintained by the FCL. One of these cylinders constitutes a blind sample and is modified in its composition after every loop completed. In Figure 19 results of the first four circulations are shown. The observed offset between CCL and FCL is 0.15 ± 0.10 ppb.

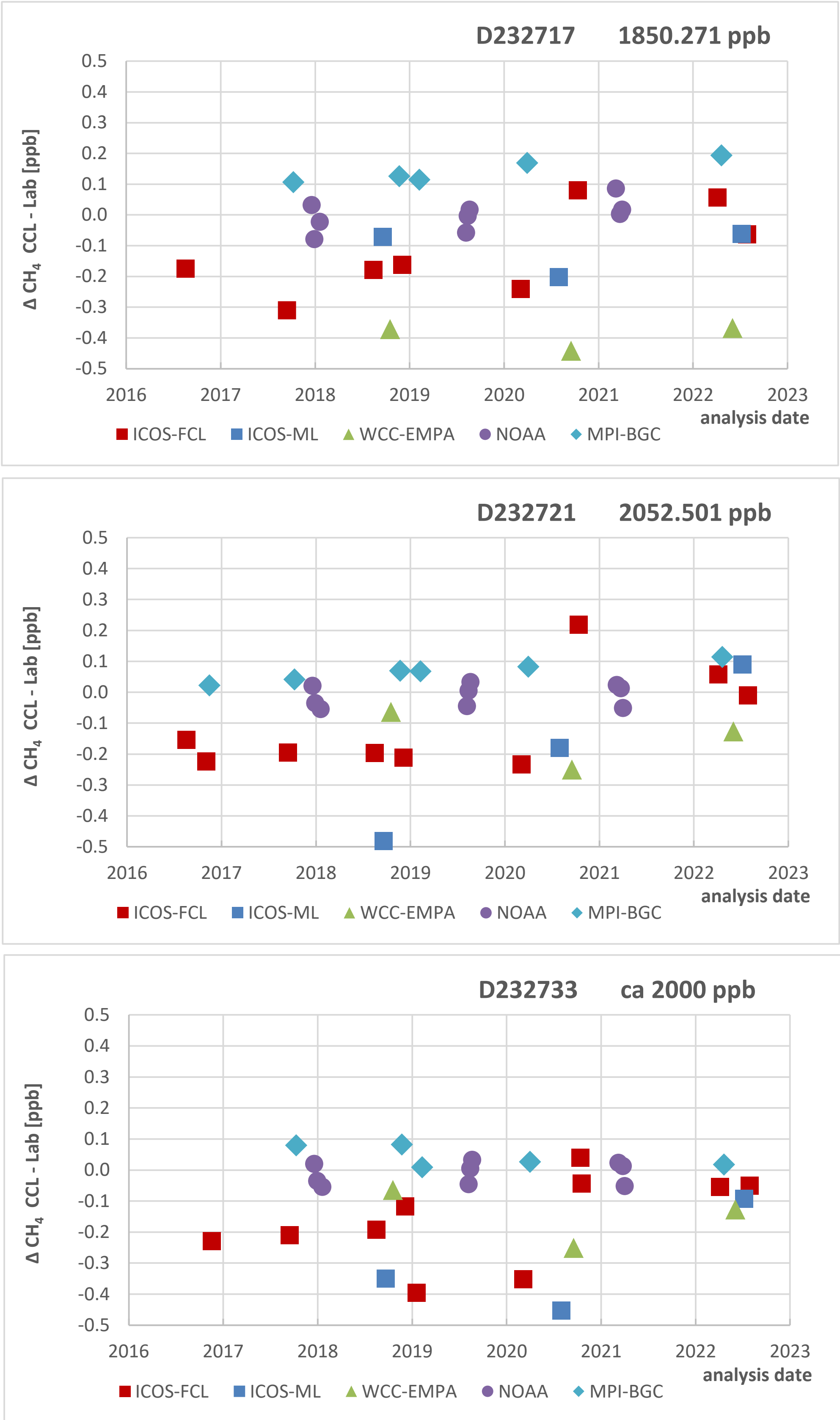


Figure 19: CH4 offset in MENI ICP between FCL, MPI, ICOS MobileLab and WCC relative to NOAA

6.6 CH_4 uncertainty evaluation

The WMO Expert Group recommendations request investigators to report uncertainty estimates for their data that include all potential sources of error [WMO 2018]. A scheme for a comprehensive uncertainty discussion has been suggested by Andrews et al. 2014. Adapting this scheme we have derived an overall measurement uncertainty based on a performance assessment of the CRDS system. In this assessment we have considered the following uncertainty contributions and checked them using the quality control data of this report.

6.6.1 FCL Primary CH_4 Standards

According to all available evidence CH_4 mole fractions within the FCL Primary Standards are accurately assigned and stable with all metrics (re-calibration by the CCL, repeated analysis by the MPI-BGC, consistency of regression fit residuals) pointing to a consistency of 0.2 ppb. For this evaluation, however, we consider the uncertainty specification of the scale propagation to individual standard gases at the CCL as 0.5 ppb (k=1)(pers. comm. E. Dlugokencky, Feb. 2018).

6.6.2 CH_4 scale transfer uncertainty

The statistics of repeated calibrations of the FCL Secondary Standards by the FCL Primary Standards provide a measure for the uncertainty of their assignments. The reproducibility of these assignments is 0.2 ppb. However, the initial assignments in 2015 have been based on a set of calibration events that turned out to be all lower by 0.1 - 0.3 ppb than the mean results from all calibration episodes. This finding of such a marginal offset in the FCL Secondary Standards' CH_4 mole fractions is quantitatively confirmed by the comparison FCL measurement results of standard sets assigned by the CCL for other laboratories (MPI-BGC and FMI). It is also consistent with the offsets observed up to 2020 in various comparisons including the MENI intercomparison with NOAA. With the replacement of the FCL Secondary Standard set when the first set from 2014 was exhausted this offset has been remedied. It could be considered to update the initial assignments as all gases of this Secondary Standard set have received their final calibration in 2021. However, the update terms are very minor. This will be discussed with ICOS ATC and ICOS Atmosphere MSA.

6.6.3 CH_4 long-term reproducibility

The reproducibility derived from the target standard measurement record is 0.2 ppb (standard deviation of daily means). Within the scatter of this time series there are occasional systematic shifts of mean results observed over periods of many days to weeks to months that are not cancelled out by the standardization scheme. These typically do not exceed about 0.2 ppb and point to additional uncertainty arising from small system sensitivity changes that are not always understood.

6.6.4 CH_4 measurement uncertainty estimate

Based on these evaluations the following combined standard uncertainty (k=1) is calculated as the square root of the sum of the individual squared uncertainty contributions:

1. Scale link uncertainty = 0.54 ppb

- uncertainty of the FCL Primary Standards set based on CCL assignments =0.5 ppb
- uncertainty of the FCL internal scale transfer to FCL Secondary Standard assignments =0.3 ppb (first Secondary Standard set) and 0.2 ppb (second Secondary Standard set), respectively.

2. Measurement uncertainty of daily means = 0.18 ppb

- mean uncertainty of the daily calibration regression fit = 0.1 ppb
- uncertainty of the detector response drift throughout the validity of a daily calibration ≈ 0.15 ppb
- uncertainty from the repeatability of the daily sample measurements = 0.03 ppb (for 15 min means)

3. Additional long-term variability = 0.2 ppb

The accuracy with respect to the WMO Mole Fraction scale arises from the root of the sum of squares of the scale link uncertainty, the measurement uncertainty and additional long-term variability amounting to 0.6 ppb.

The internal reproducibility is estimated to be 0.3 ppb which is consistent with the results from the target standard record.

7 CO

7.1 FCL Primary CO Standards

7.1.1 CCL CO assignments

After initial calibration of all FCL Primary Standard gases in 2014 the first recalibrations of each three of the standards have been made in 2016, 2017, and 2018. In December 2020 the complete set of FCL Primary Standards was sent to the CCL for the third calibration, performed in March 2021.

The CCL calibration record of the FCL Primary Standards is summarized in Table 11 indicating that the increase in CO exhibits a mole fraction dependency with standards with lower CO mole fraction having a larger increase in CO. While all initial CCL assignments have been made based on measurements with the LGR2 instrument, not all of the first recalibration measurements were made using this instrument but one third was re-assigned using the V3 Aerolaser VURF analyzer only. For the last recalibration both instruments were used for all standard gases. Figure 20 shows that systematically larger CO values result from the LGR2 measurements for all standards with CO below 400 ppb compared to VURF results. The effect is under investigation at the CCL [CCL_CO 2018].

Growth of CO in high pressure aluminium cylinders is a known limitation for accurate CO measurements that has to be accounted for. To account for the increasing CO mole fractions in FCL Primary Standards we applied a linear interpolation between the initial and the second calibration data point for every standard where the increase exceeded the analytical uncertainty of the CCL calibrations. This includes all standards with CO below 210 ppb. Based on these new, drifting assigned values, the calibration results of the FCL Secondary Standards were recalculated. Lab-internally, all data sets have been updated to take the CO growth in the reference standards into account. Data presented here are therefore also compensated for this drift.

A further refinement of the CO growth in the Primary Standards would be possible with the third CCL assignment. However, this has not been performed because a re-assignment would not only entail a re-processing of all FCL-CO calibration measurements but also require a re-computation of all ICOS atmospheric CO data. At this point this effort appears not justified as Fig. 20 shows that the FCL measurement results of the Primary Standards (blue squares) are generally well in line with the trend arising from the second and third CCL calibration with differences not exceeding the offset between the results from different instruments used at the CCL (LGR (grey diamonds) and Aerolaser (light blue circles)).

Table 11: CO assignments for FCL Primary Standard gases by the CCL (WMO X2014A scale)

Sample ID	Cylinder ID	CCL date 1	CCL date 2	CCL date 3	CO-date1	CO-date 2	CO-date 3	drift [ppb/yr.]*	Assignment used**
i20140055	CB09944	Dec-13	Jun-17	Mar-21	31.31	34.41	36.92	**0.767**	32.20
i20140056	CB09939	Feb-14	Oct-18	Mar-21	80.14	82.73	84.27	**0.582**	80.62
i20140057	CB09958	Dec-13	Sep-16	Mar-21	120.69	122.36	124.70	**0.546**	121.32
i20140058	CB09983	Dec-13	Oct-18	Mar-21	158.92	161.28	162.19	**0.450**	159.47
i20140059	CB09952	Feb-14	Sep-16	Mar-21	199.47	200.77	202.69	**0.448**	199.92
i20140060	CB09955	Dec-13	Jul-17	Mar-21	247.14	247.88	249.48	**0.331**	247.37
i20140061	CB09957	Dec-13	Sep-16	Mar-21	397.06	396.19	398.75	**0**	397.90
i20140062	CB09934	Jan-14	Jun-17	Mar-21	697.56	697.72	697.07	**0**	697.30
i20140054	CB09948	Jan-14	Oct-18	Mar-21	998.63	999.40	999.21	**0**	999.06

* Drift calculated based on period CCL date3 – CCL date1; ** On 1/1/2015, calculated based on the corresponding drift

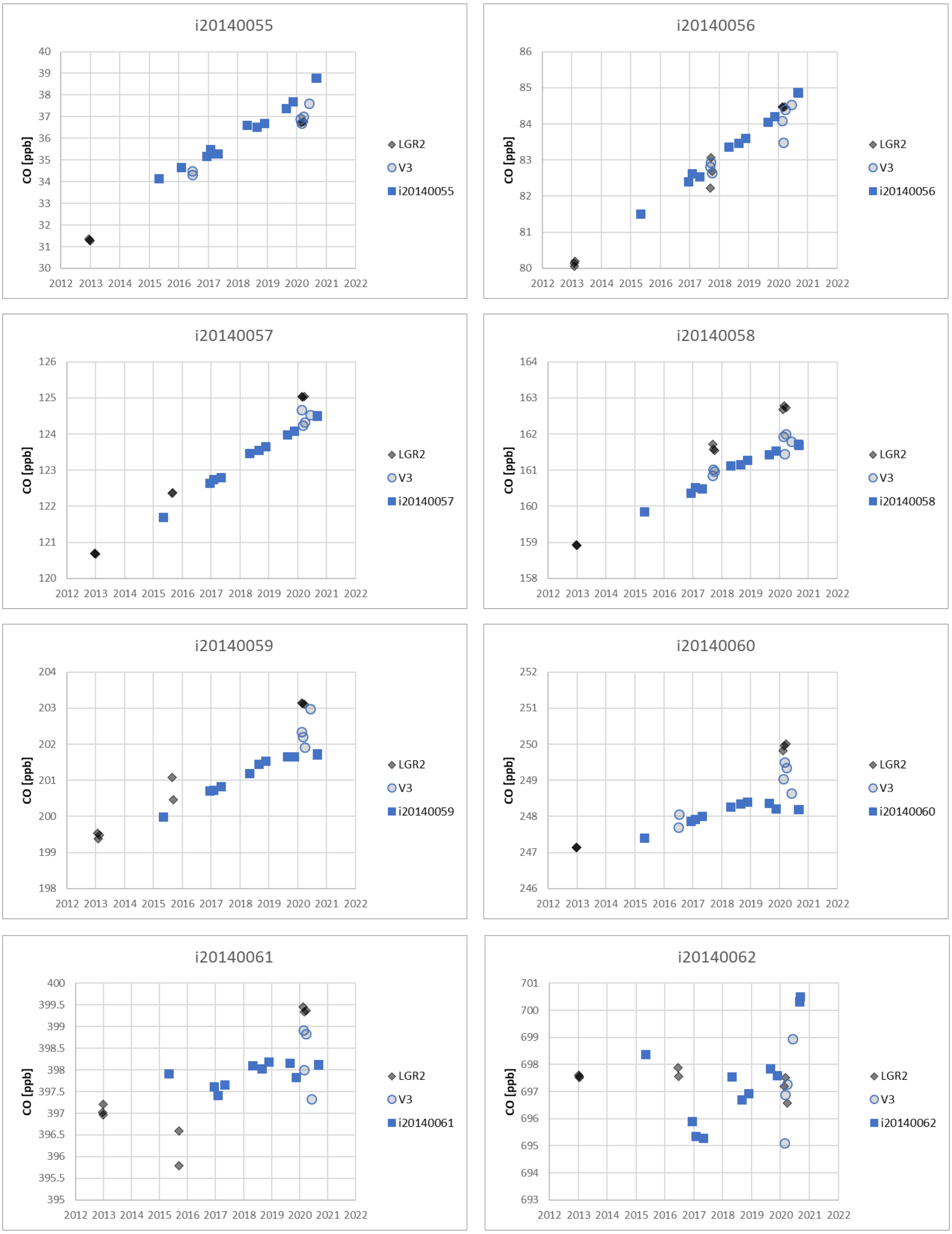


Figure 20: CO Primary Standards, measured at the FCL (blue squares) and at the CCL.

CCL analysers: LGR (grey diamonds) and Aerolaser (light blue circles)

7.1.2 Regression fit residuals of FCL Primary CO Standards

The time series of the regression fit residuals displayed in Figure 21 shows consistent results but with trends on the order of 0.05 – 0.2 ppb/yr for the individual standard gases. This reflects the limited accuracy of the applied trend functions. This is partly result from only two CCL calibration results having been available to assign the trend lines. On the one hand, information has been presented by the CCL that the WMO Mole Fraction scale Primary Standards drift at a different rate as the values used for calibrating tertiary standards (https://www.esrl.noaa.gov/gmd/ccl/co_scale_update.html). Whereas this drift may be overcorrected at low CO mole fractions, it is below the CCL defined significance level for the high CO standards.

Figure 21: Time series for CO quadratic regression fit residuals of LGR FCL Primary Standard calibrations

7.2 FCL Secondary CO Standards

7.2.1 Assignment record

The four reference gases that are used as FCL Secondary Standards for the daily LGR calibration have been analyzed within 24 to 25 calibration episodes together with the complete set of FCL Primary Standards between May 2016 and August 2022. In May 2018 one of the Secondary Standard gases was exhausted (i20150251; five calibration episodes together with FCL Primary Standards) and was succeeded by a new standard with a similar CO mole fraction (i20170889; 21 calibration episodes together with FCL Primary Standards). The three remaining tanks were replaced when they were exhausted in July 2021. For the three replacements, the assigned values and drift rates were determined by measurements against the old set of FCL Secondary Standards (the number of comparison measurements is: i20201308 (n=114), i20201254 (n=114), i20201255 (n=117)). Table 12 summarizes the initial assignment values and the CO growth rates for all tanks.

In Figure 22 the record of the Secondary Standards' CO mole fraction results of these FCL primary calibration episodes is presented based on time dependent assigned values for the FCL Primary CO Standard gases. It appears that the two high standards are relatively stable in CO in the currently used set of Secondary Standards.

Table 12: CO assignments for FCL Secondary Standard gases (WMO X2014A scale)

Sample ID	Cylinder ID	Assigned Value[1]	drift/yr[1]	*Date of exchange*	Sample ID	Cylinder ID	Assigned Value[2]	drift/yr[2]
i20150251	CA05640	**78.52 ppb**	**+0.76 ppb**	*2018-05-03*	i20170889	D557226	**79.63 ppb**	**+1.28 ppb**
i20150189	D073397	**150.79 ppb**	**+0.97 ppb**	*2021-07-26*	i20201308	D753834	**149.53 ppb**	**+0.25 ppb**
i20150191	D073395	**305.80 ppb**	**+0.72 ppb**	*2021-07-26*	i20201254	D753835	**293.54 ppb**	**-0.16 ppb**
i20150544	D073396	**433.52 ppb**	**+0.51 ppb**	*2021-07-26*	i20201255	D753836	**423.90 ppb**	**-0.07 ppb**

[1] Starting date: 1st November 2015
[2] Starts for i20170889 on 1st October 2017, for the other three tanks on 26th July 2021

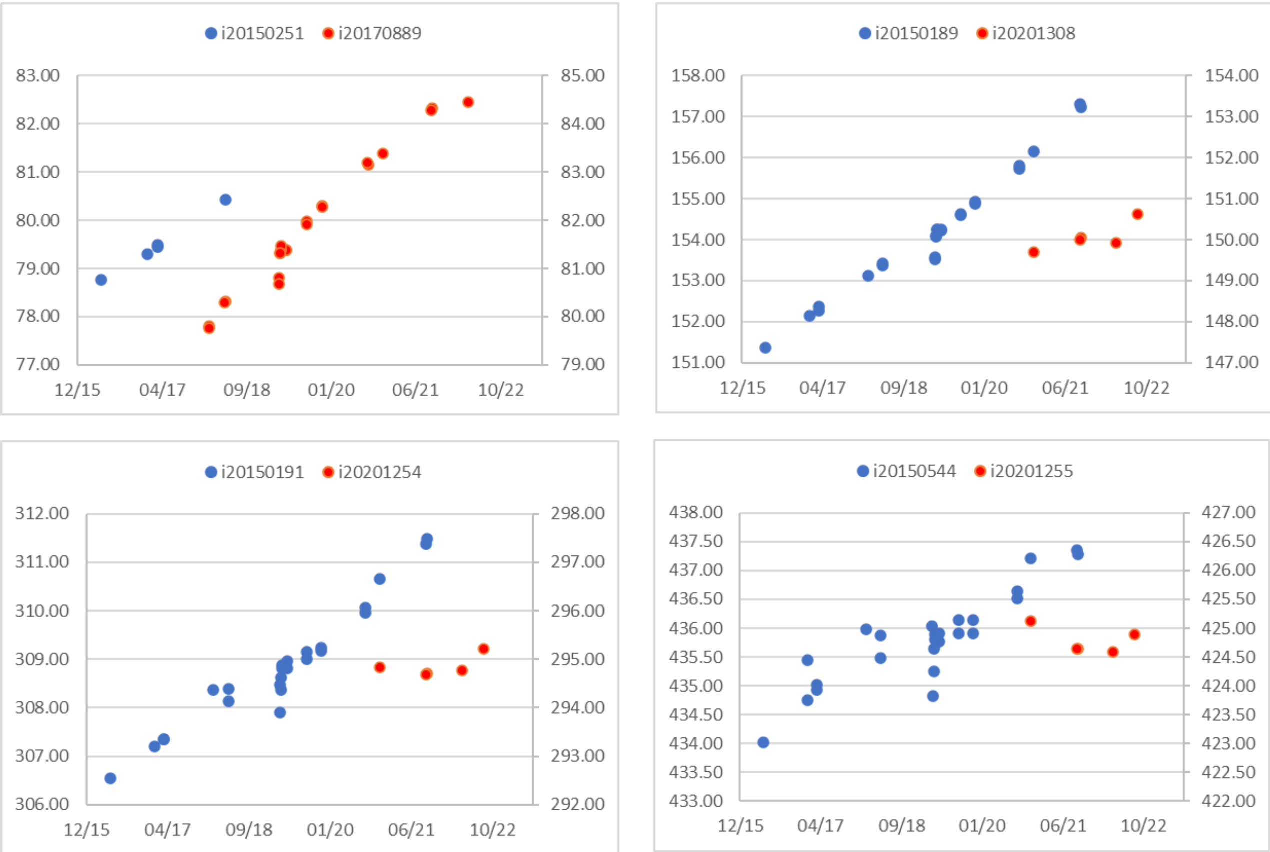


Figure 22: Secondary CO standard assignment record (values in [ppb]).

7.2.2 Residual record

The residuals of the quadratic regression of the FCL Secondary Standards are displayed in Figure 23. These residuals document an excellent consistency of this reference gas set. The time series also illustrates that the reproducibility is not at all limited by the instrumental precision capability. Note, though, that the changes in these plots only reflect the relative changes between the FCL Secondary Standards and do not allow deducing any absolute trends.

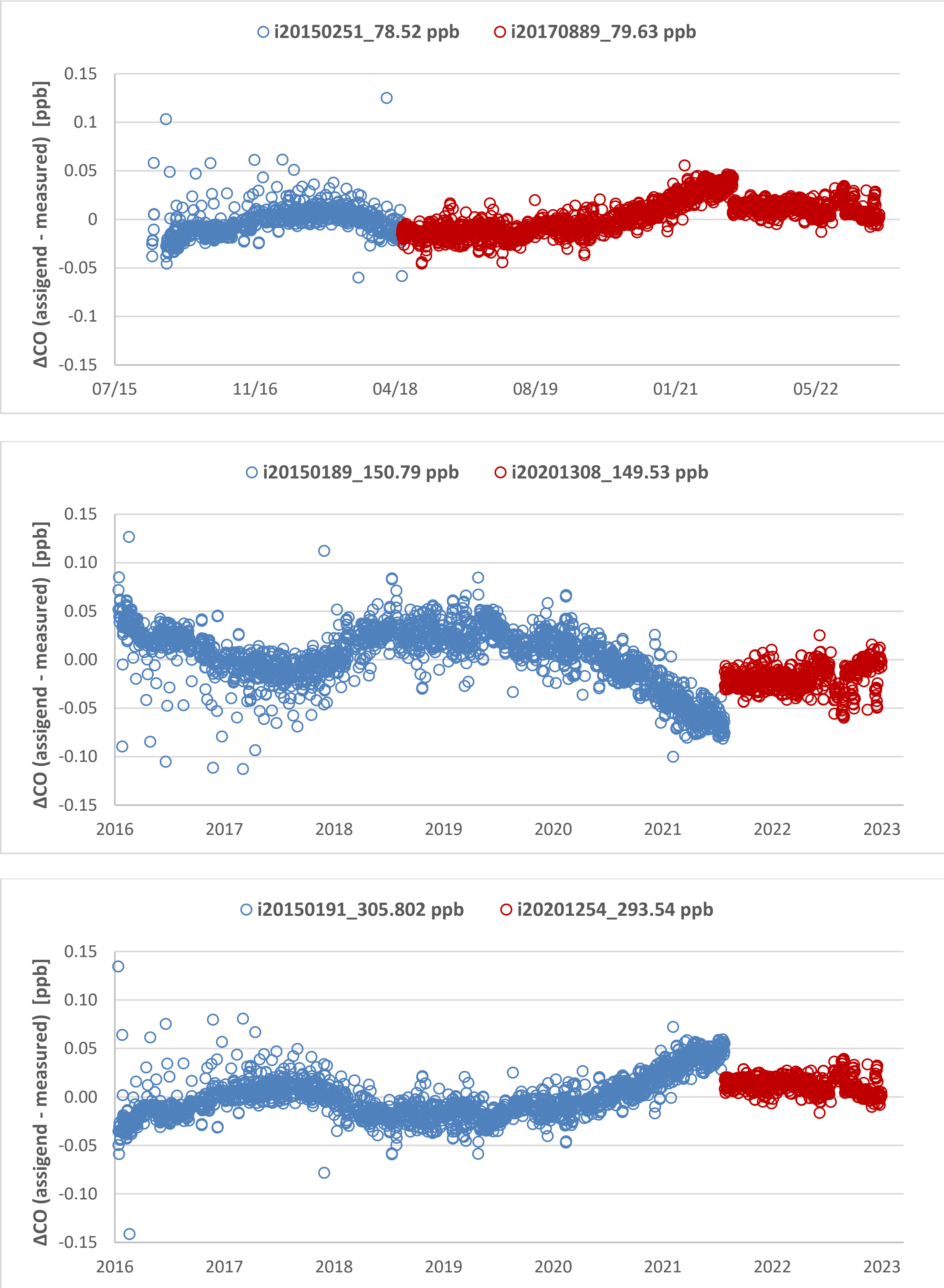


Figure 23: Time series of quadratic regression fit residuals of LGR CO FCL Secondary Standards calibrations

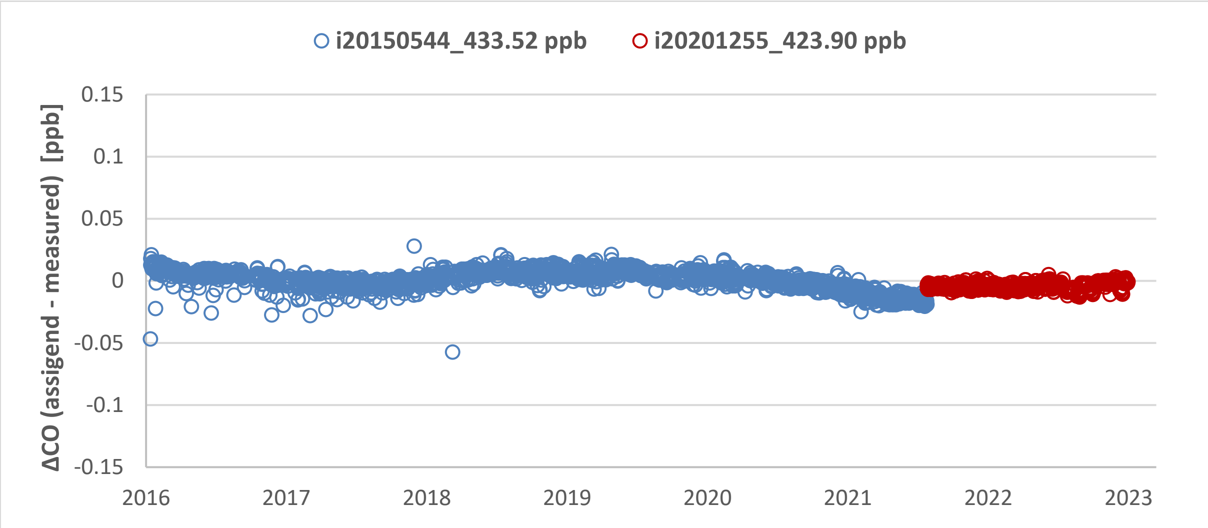


Figure 23: Time series of quadratic regression fit residuals of LGR CO FCL Secondary Standards calibrations

7.3 CO Targets

In the period from Feb 2016 to December 2022 two targets have been in use on the LGR system. They are complemented by three Long Term Targets (also Archive Quality Control). These are currently being measured less frequently after an initial phase of daily analysis frequency to maintain a long-term link of succeeding targets in future. As for the reference standards also the target standards exhibit a steady increase of CO. This is more pronounced at low mole fractions and only minor at 390 ppb. The record of the residuals of daily measurement results relative to the assigned trend based on Primary Standard calibrations is presented in in Figure 24. There are trends and offsets apparent in the residuals of most of these targets of up to 1.5 ppb. These are probably result of the limited accuracy of the drift assignment for the standards of the primary and secondary calibration sets involved.

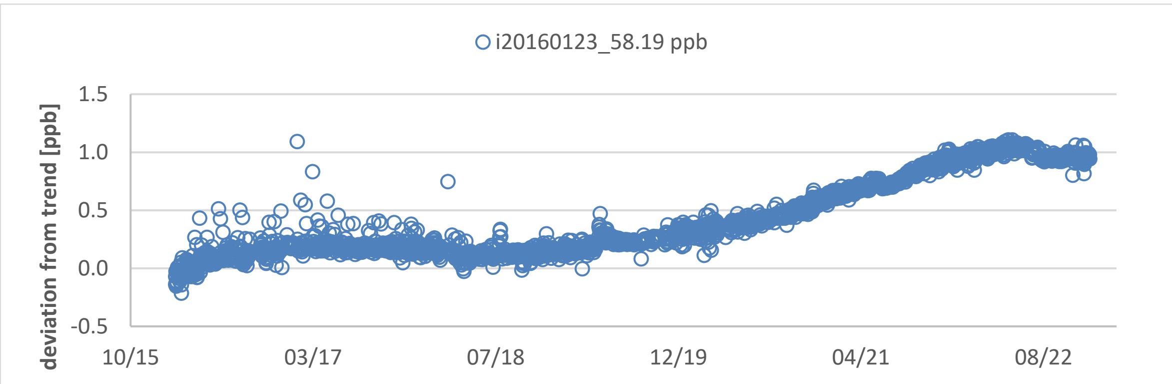


Figure 24: Time series of daily CO residuals data of target standards analyzed on the LGR instrument

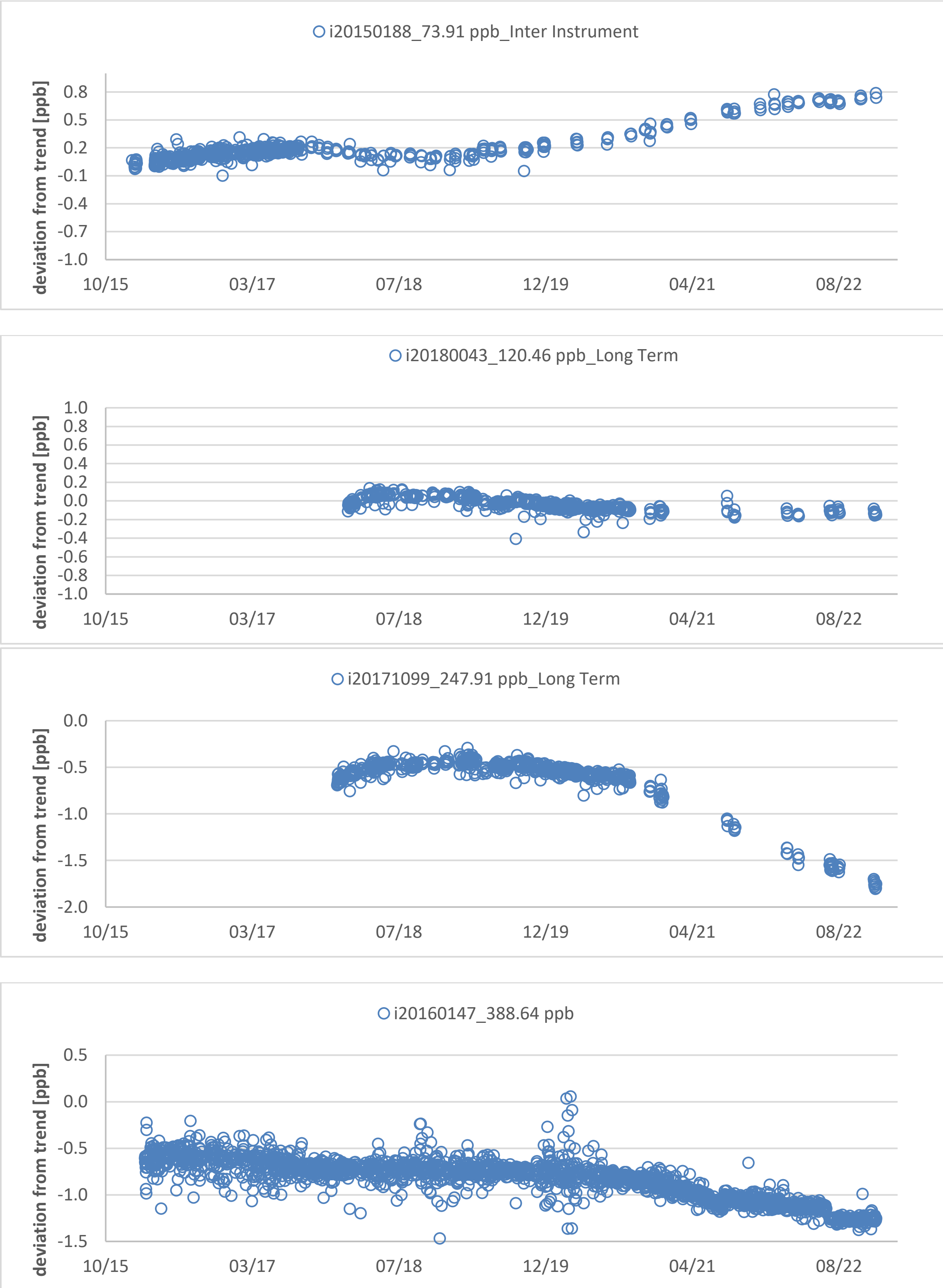


Figure 24: : Time series of daily CO residuals data of target standards analyzed on the LGR instrument

7.4 Internal CO Comparison: LGR-GC

Standard gases that are calibrated for CO by the LGR have often also been analyzed by GC. The GC measurements are linked to the same set of Primary FCL Standards but are based on a different set of seven Secondary Standards. The inter-instrumental measurement differences for all standards that have been analyzed within the same month (in order to avoid any overlaying CO growth in the lag period) are depicted in Figure 25 (only standards within the range defined by the calibration standards were considered).

GC results for the intercomparison samples are on average slightly higher (LGR-GC = -0.4 ± 0.6 ppb). There is a small mole fraction dependency in the offset between the instruments. It has changed only a little over time but offsets in 2021 have increased a bit. Note, that the GC-RGA precision in general is by a factor of 10 worse than the LGR, and the scatter and most likely mean biases of the data can primarily be attributed to the GC analysis.

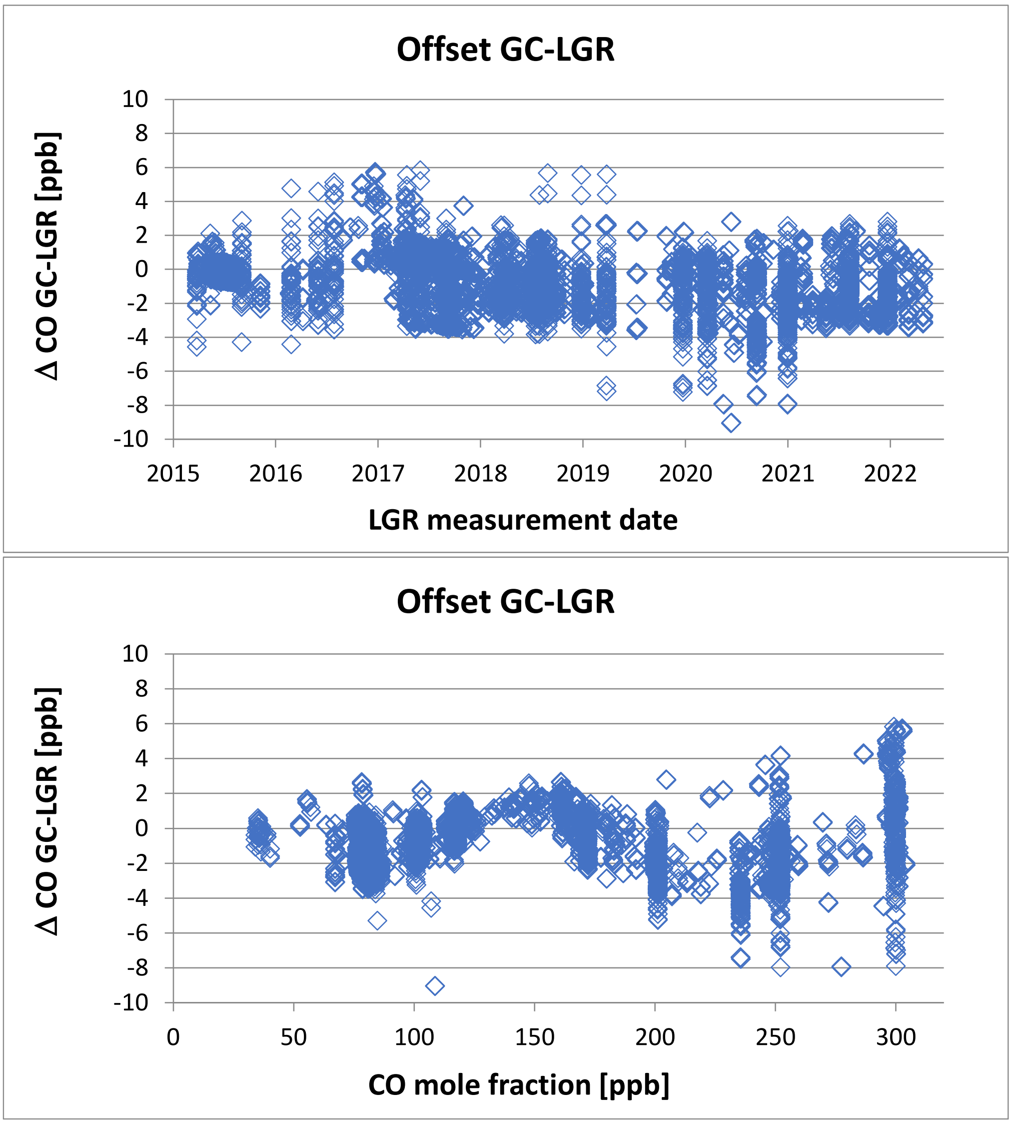


Figure 25: Time series of LGR-GC CO differences of measurement results of the same samples

7.5 External CO Comparisons

7.5.1 CO compatibility ICOS FCL - MPI-BGC

The most intensive comparison measurements have been made with the MPI-BGC GasLab. This laboratory is using different analytical technology (Aerolaser AL5002) and their measurements are tied to the WMO Mole Fraction scales by an independent set of Primary Standards. These MPI-BGC Primary Standards already have CCL calibration records with multiple measurements in different years for nine individual standards over six to seventeen years, partly with established drift rates and partly with apparently stable composition. In contrast to the other trace gases covered by this report calibrations made by the CCL before 2011 are not tied to the same WMO primary standards. The comparability of these old calibrations to calibrations since 2012 is therefore inferior. The assessment of the drift of MPI-BGC CO standards based on the old calibrations therefore may be not as accurate as the assessment of the drift of FCL Standards.

The MPI-BGC measurements are not relevant for the assignment of the FCL standards and therefore are completely independent.

7.5.1.1 Comparison of CO Primary Standards

Basis for an agreement of FCL and MPI-BGC measurements is the compatibility of the respective sets of Primary Standards. Before or after the shipment to the CCL for recalibration of sub-sets of the respective Lab Primary Standard suites these standards were mutually exchanged between MPI-BGC and FCL and analyzed. This allows a direct comparison with the CCL.

The comparison data of the measurement results relative to the CCL assignments are shown in the Figure 26 also including the set of FMI standards that had been calibrated by the CCL. Note that the two data series in the plot are on inverted y-axes. FCL CO data for MPI-BGC Primary Standards within the calibrated range of the FCL measurements are on average 0.5 ± 0.5 ppb lower than the CCL assignments, the offset of MPI-BGC results relative to CCL assignments is 0.2 ± 0.8 ppb,

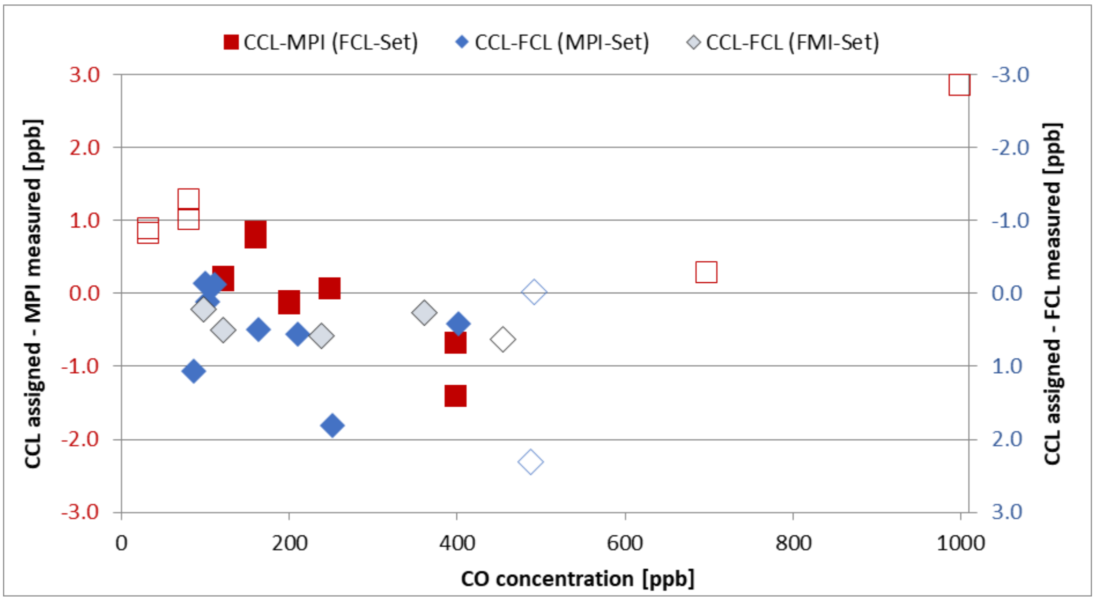


Figure 26: Difference of measured CO data to CCL assignment of the WMO standards of partner labs (unfilled symbols for mole fractions beyond the calibrated range)

7.5.1.2 Sample CO comparison

High pressure standards have been regularly exchanged between MPI-BGC and FCL in earlier years and analyzed in both laboratories. To make sure that the comparison is not affected by growing CO in the comparison standards only comparisons are taken into consideration where the analysis was done within six months. The difference in results based on 68 sample measurements using the VURF instrument is presented in Figure 27 and Figure 28. The average offset of FCL-MPI amounts to -0.1 ppb ± 0.7 ppb. The difference exhibits a clear mole fraction dependence. This in accordance with the different patterns of mole fraction dependent offsets to the CCL shown in Figure 26. It is also result of the different calibration approaches: for the LGR a multi-point quadratic fit follows the primary scale more closely than the one-point calibration of the linear VURF instrument.

Plotting the inter-laboratory differences against the analysis date at the FCL reveals a trend in the offset. This trend is explainable by an overestimate of the CO increase in the FCL references [Crotwell 2019] or an underestimate of a CO growth in MPI-BGC reference standards or a combination of both.

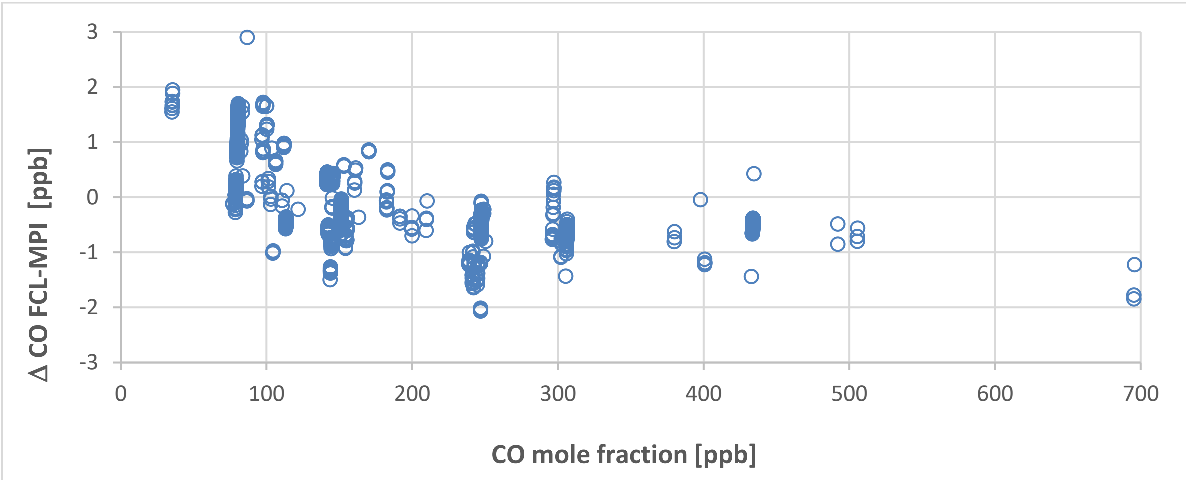


Figure 27: Mole fraction dependence of CO offsets for samples analyzed at FCL and MPI-BGC

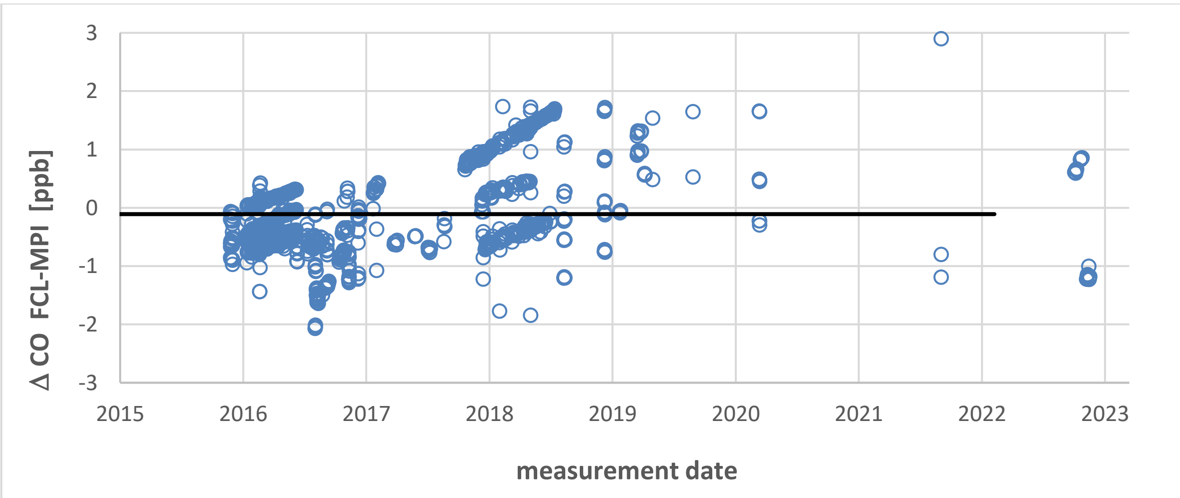


Figure 28: Differences of CO results for samples that have been analyzed at FCL and MPI-BGC

7.5.2 CO compatibility ICOS FCL - NOAA

A comparison with the NOAA-GML laboratory (and other laboratories) is routinely made in the Sausage Flask Intercomparison program. In this program samples for comparison are prepared by connecting sets of flasks in line and filling them with dry air from a high-pressure cylinder at the FCL. The FCL is generally analyzing the composition of the filling air using the normal instrumentation for calibrating standards. Therefore, the results of the flask measurements provided by NOAA can be compared with these high-pressure cylinder measurements. The respective data are compiled in Fig. 29 and 30. The difference between FCL and NOAA increases with increasing CO, the mean CO offset for of all tank samples (black symbols) is FCL-NOAA = -1.3 ± 0.9 ppb.

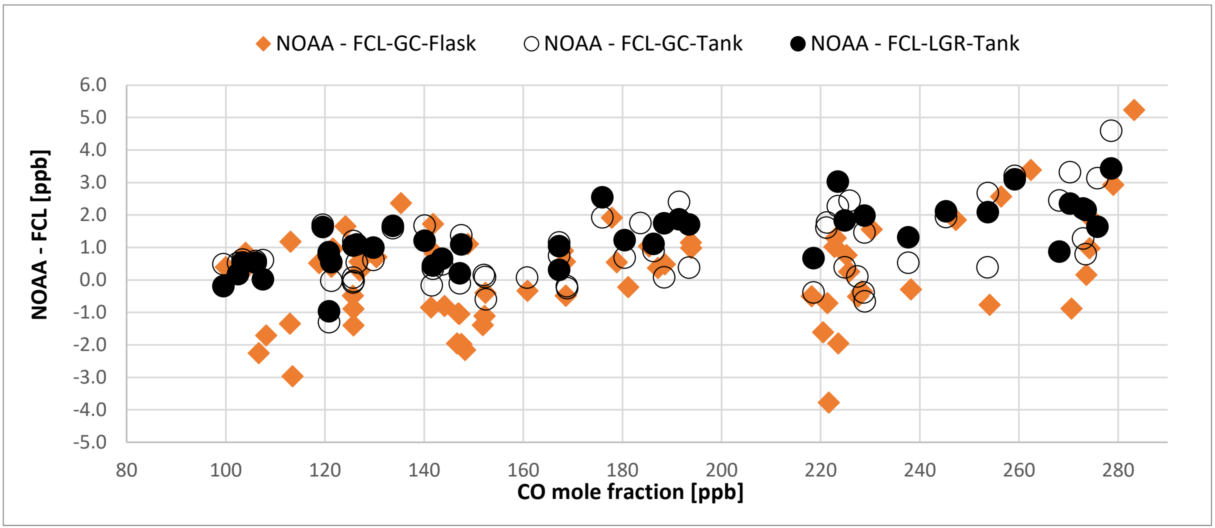


Figure 29: CO offset between NOAA Sausage flask data and FCL data.
Black dots represent FCL's analysis of the Sausage fill gas (filled symbol: LGR measurement; unfilled symbol: GC); orange diamonds represent GC flask sample analysis

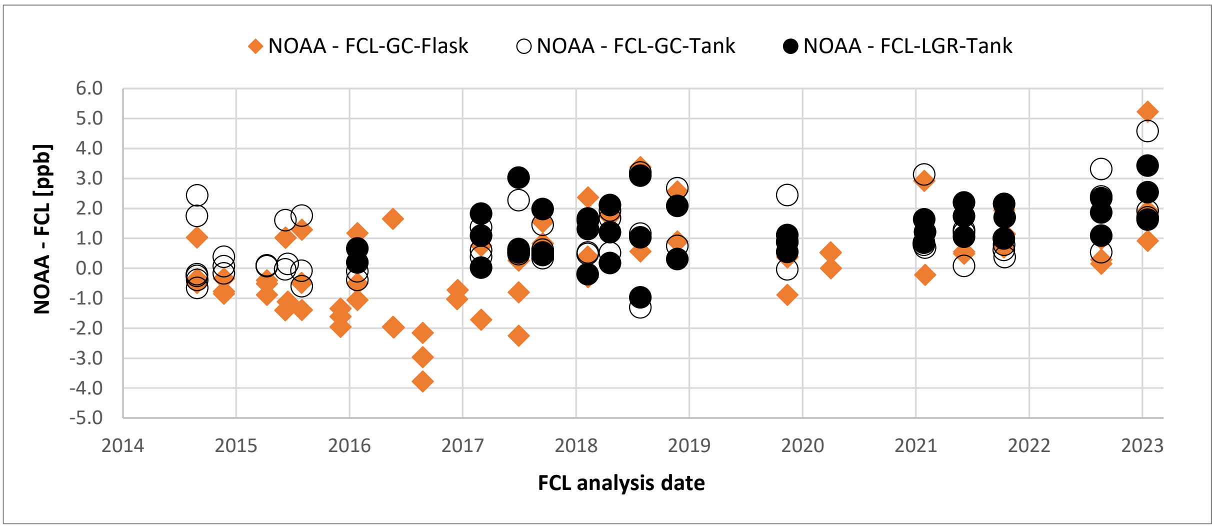


Figure 30: Record of CO offsets of NOAA Sausage flask data compared with FCL data.
(symbols as in Fig. 30)

A complementary round robin test between NOAA (as WMO-CCL), EMPA (as WMO-WCC), MPI-BGC, FCL and FMI-ATC (ICOS Mobile Lab) (called "MENI" program) has been established. In this program a set of three cylinders is prepared and maintained by the FCL. One of these cylinders constitutes a blind sample and is modified in its composition after every completed loop. In Figure 31 results of the first iterations are shown. It turned out that the CO mole fractions in the cylinders were growing over the time of the experiment. This needs to be taken into consideration when comparing data from measurements made at different points of time. Therefore, in Figure 31 the CO grow rate is assessed based on the CCL measurement records. The displayed offset takes the trendline of the CCL measurements as reference. On average there is no offset (FCL - CCL = - 0.1 ± 0.7 ppb) but there may be a drift of 0.5 ppb/yr in the offset of the high comparison sample.

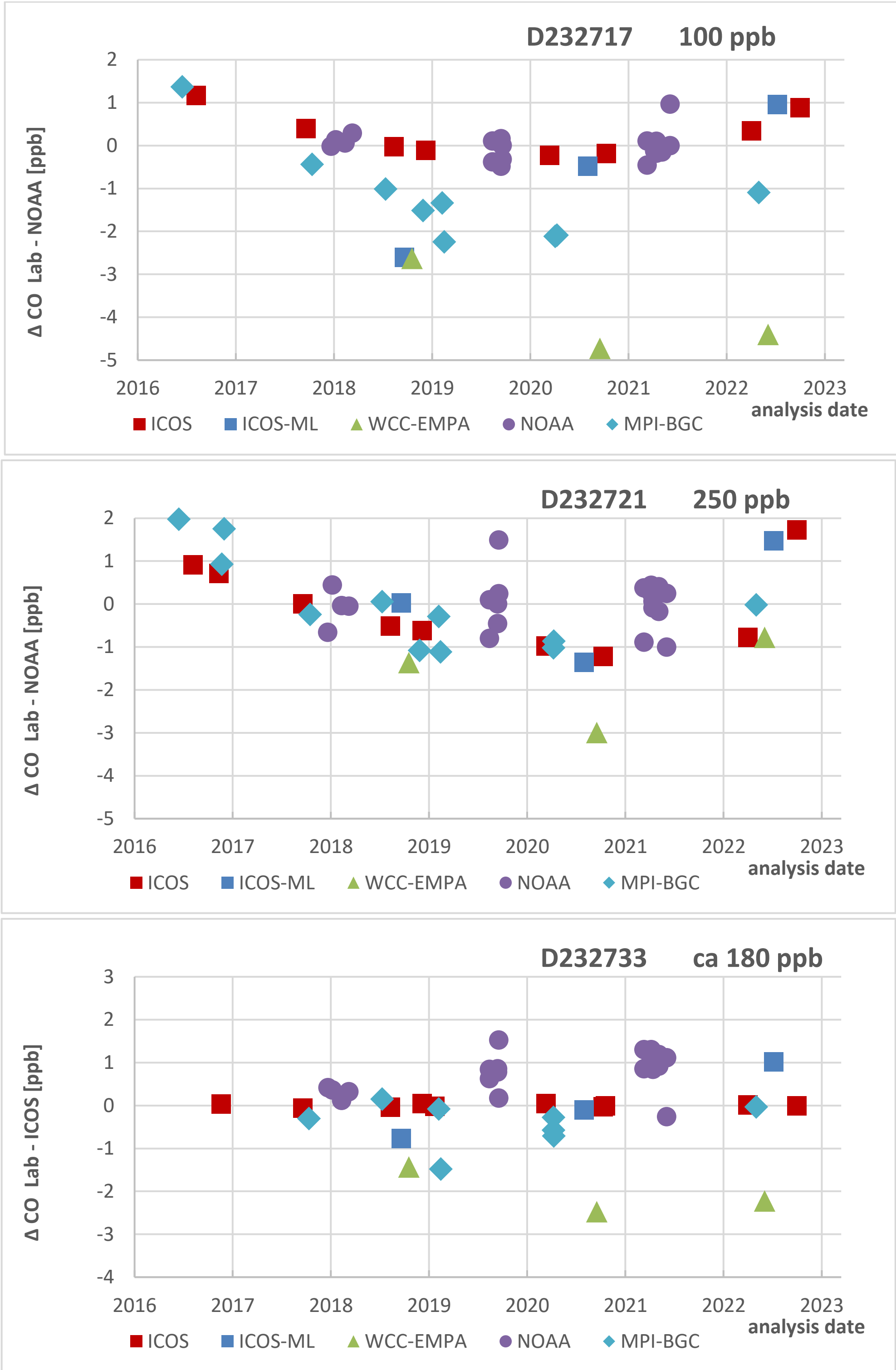


Figure 31: CO offset in MENI ICP between FCL, MPI, ICOS ML and EMPA relative to NOAA (adjusted for CO growth)

7.6 CO uncertainty evaluation

The WMO Expert Group recommendations request investigators to report uncertainty estimates for their data that include all potential sources of error [WMO 2018]. A scheme for a comprehensive uncertainty discussion has been suggested by Andrews et al. 2014. Adapting this scheme we have tried to derive such an overall measurement uncertainty based on a performance assessment of the LGR system and an evaluation of the consistency of CO assignments in the reference gases. The latter is as well the dominant source of uncertainty and at the same time the most difficult to quantify reliably.

In this assessment we have considered the following uncertainty contributions and checked them using the quality control data of this report.

7.6.1 FCL Primary CO Standards

The CCL specifies a scale transfer uncertainty of 0.4 ppb (k=1) in the range up to 400 ppb increasing (in particular for LGR assignments) to 2 ppb at 700 ppb and 4 ppb at 1000 ppb. The CCL has pointed to systematic differences they have observed between the OA-ICOS (LGR) and VURF measurement data that causes a mole fraction dependent bias in results between the analytical techniques of 0.5 – 1.5 ppb (LGR-VURF). All initial assignments had been made using the LGR instrument whereas recalibrations in 2017 were all made using the VURF instrument. While this may suggest a larger uncertainty than specified above, the quadratic regression fit residuals of the calibrations using the FCL Primary Standards are consistent with the above quote.

The growth of CO in most FCL Primary Standards is clearly documented by results from the recalibration of these standard gases by the CCL. Its results suggest a mole fracion dependent CO increase: standards with low mole fractions exhibit a large drift and standards with high CO mole fractions a minor to no drift. The trend function for the CO assigned values had been defined in 2019 by the first two CCL calibration events only and is currently being extrapolated beyond the time of the recalibration. This also contributes to the uncertainty. The average difference in the CO growth rates of the FCL Primary Standards when considering the 2021 recalibration compared to when ignoring it is -0.06 ppb/year for all standards < 200 ppb and +0.3 ppb/yr for the two standards at 250 ppb and 400 ppb. Based on this an additional extrapolation uncertainty of 0.5 ppb at standards < 200 ppb is assumed and an uncertainty of 1.5 ppb at larger CO values. A slowly degrading consistency of the Primary Standard set is also indicated by the steadily growing regression fit uncertainty (rising from 0.3 ppb to 0.6 ppb from 2016 to 2021).

7.6.2 CO scale transfer uncertainty

Knowledge of the CO mole fractions in the individual FCL Secondary Standards is based on the record of repeated calibrations using the FCL Primary Standards. The additional uncertainty arising from the FCL internal scale transfer measurements is expressed by the scatter of the individual calibration episode results relative to the trend line of increasing CO. The mean absolute residuals of the up to 15 assignment periods are mole fraction dependent between 0.2 and 0.3 ppb for the low and high FCL Secondary Standard, respectively.

7.6.3 CO long-term reproducibility

Any long-term reproducibility limitations beyond the random errors in daily measurements can be derived from discontinuities in the Target Standard measurement record (Figure 25). The comparison of daily Target Standards measurements to the trends established by the measurements calibrated by the FCL Primary Standard set results in residuals that vary between the individual Target Standards but amount up to 1 ppb. Whereas the record of the FCL Primary Standards appears as steady trend the CO growth rate of the Target

Standards appears to change over time look at the daily measurement results results. This likely points to limitations in the accuracy of the actually assigned CO trend of the FCL Secondary Standards.

7.6.4 CO measurement uncertainty estimate

Based on the above considerations the following combined standard uncertainty (k=1) is calculated as the square root of the sum of the individual uncertainty squares:

1. Scale link uncertainty = 0.9 ppb (standards with CO < 200 ppb)

   = 1.7 ppb (standards with CO > 200 ppb)

- The scale link uncertainty estimate is derived from the specified CCL assignment uncertainty (0.4 ppb below 400 ppb) and the CO growth function uncertainty (0.5 ppb below 200 ppb).
- Uncertainty of the FCL internal scale transfer to FCL Secondary Standard assignments (0.2 ppb).
- Uncertainty in the CO growth rate of the second set of FCL Secondary Standards (1 ppb)

2. Measurement uncertainty of daily means = 0.15 ppb

- mean uncertainty of the daily calibration regression (0.07 ppb)
- uncertainty of the detector response drift throughout the validity of a daily calibration (0.01 ppb)
- uncertainty from insufficient sample flushing and instrumental repeatability of the daily sample measurements (0.05 ppb, for 10 min means)
- uncertainty based on observed inter-instrument bias: 0.1 ppb

3. Additional long-term variability = 0.2 ppb

The accuracy with respect to the WMO Mole Fraction scale is limited by the uncertain knowledge of the current assigned values in the drifting reference standards. It calculates as the root of the sum of squares of the scale link uncertainty and the measurement uncertainty and amounts to 0.7 ppb for samples with CO < 200 ppb and 1.6 ppb for samples with larger CO. The internal reproducibility is estimated to be 0.5 ppb.This is consistent with observed external comparison results.

The CCL by definition provides the link to the WMO Mole Fraction scale but it has announced that the way the growth of CO in the WMO Scale Primary References was prescribed likely overcompensated this drift for low concentrated standards. The evaluation of the scale is ongoing at the CCL. All uncertainty estimates made here refer to the uncertainty of the measurements and assignments relative to the current scale and do not include a term for any potential mole fraction dependent scale error.

8 N_2O

8.1 FCL Primary N_2O Standards

8.1.1 CCL N_2O assignments

After initial calibration of all FCL Primary Standard gases in 2014 the first recalibrations of each three of the standards have been made in 2016 and 2017, and 2018. In December 2020 the complete set of FCL Primary Standards was sent to the CCL for the third calibration, performed in May 2021.The reassignments by the CCL have generally been within the uncertainty of the initial assignment and have not caused a systematic shift of the entire set. (Δ = -0.01 ±0.06 ppb) see Table 13. However, there is a slight mole fraction dependent difference for the FCL Primary Standards < 320 ppb having probably been determined too low initially.

Table 13: N_2O assignments for FCL Primary Standards by the CCL (WMO X2006A scale, [ppb])

Sample ID	Cylinder ID	CCL date 1	CCL date 2	CCL date 3	N_2O date 1	N_2O date 2	N_2O date 3	Assignment used*
i20140055	CB09944	Jan-14	Jul-17	May-21	316.77	316.90	317.01	**316.893**
i20140056	CB09939	Jan-14	Feb-19	May-21	319.86	319.97	319.93	**319.92**
i20140057	CB09958	Jan-14	Oct-16	May-21	327.12	327.02	327.21	**327.12**
i20140058	CB09983	Jan-14	Jan-19	May-21	329.92	329.89	330.06	**329.96**
i20140059	CB09952	Apr-14	Nov-16	May-21	334.60	334.52	334.57	**334.56**
i20140060	CB09955	Jan-14	Jul-17	May-21	339.48	339.52	339.43	**339.48**
i20140061	CB09957	Jan-14	Nov-16	May-21	343.95	343.88	343.82	**343.88**
i20140062	CB09934	Mar-14	Jun-17	May-21	349.13	349.18	349.14	**349.15**
i20140054	CB09948	Jan-14	Jan-19	May-21	362.13	362.12	361.90	**362.05**

* Represents the mean of WMO X2006A date 1-date 3

8.1.2 Regression fit residuals of FCL Primary N_2O Standards

The time series of the quadratic regression fit residuals is presented in Figure 32 for calibration events where the complete FCL Primary Standard suite was used.

N_2O mole fractions are known to be generally stable in aluminium high pressure cylinders. The assumption of a stable standard set is supported by the fact that the regression fit residuals do not show significant trends for any of the individual standards (within 0.03 ppb).

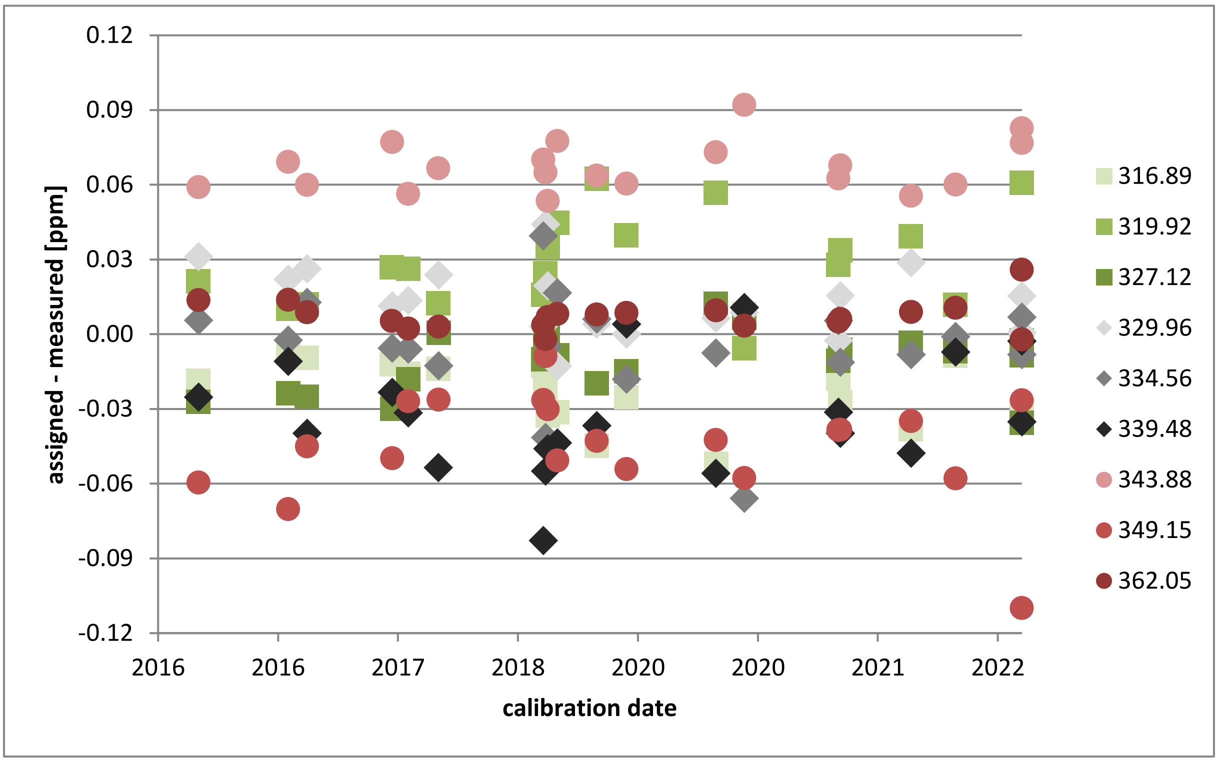


Figure 32: Time series of N2O quadratic regression fit residuals of LGR FCL Primary Standard calibrations

8.2 FCL Secondary N_2O Standards

8.2.1 Assignment record

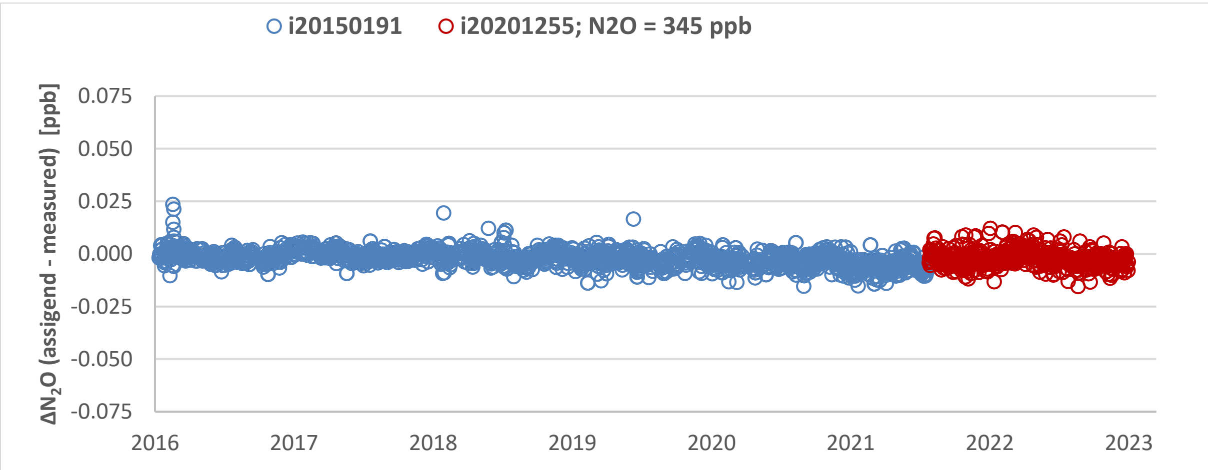
The four reference gases that have been used as FCL Secondary Standards for the daily LGR calibration have been analyzed within 24 to 25 calibration episodes together with the complete set of FCL Primary Standards between May 2016 and Sep 2021. In May 2018 one of the Secondary Standard gases was exhausted (i20150251; five calibration episodes together with FCL Primary Standards) and was succeeded by another standard with a similar N_2O content (i20170889; 18 calibration episodes together with FCL Primary Standards). The three remaining tanks were replaced when they were exhausted in July 2021. For the three replacements, the assigned values were determined by measurements against the old set of FCL Secondary Standards (the number of comparison measurements is: i20201308 (n=114), i20201254 (n=114), i20201255 (n=117)). As explained in the section above the initial CCL assignments for standards with N_2O < 320 ppb were lower than for both recalibration results. Therefore, for the assignment of all new Secondary Standards (including the standard i20170889) the assigned values of the initial Secondary Standard set have been adjusted and are based on the mean of all three CCL calibrations (not only the initial CCL assignment). This results in a new assigned value for i20170889 that is about 0.10 ppb higher than the one used between 3rd May 2018 and 26th July 2021. As indicated in the previous section the update is very minor for ambient atmospheric N_2O mole fractions (< 0.03 ppb).

Table 14: N_2O assignments for FCL Secondary Standards ([ppb] WMO X2006A scale)

Sample ID	Cylinder ID	Assigned Value	*Date of exchange*	Sample ID	Cylinder ID	Assigned Value
i20150251	CA05640	**316.923 ppb**	*2018-05-03*	i20170889	D557226	**315.682**
i20150189	D073397	**324.506 ppb**	*2021-07-26*	i20201308	D753834	**324.395**
i20150544	D073396	**334.201 ppb**	*2021-07-26*	i20201254	D753835	**339.360**
i20150191	D073395	**344.970 ppb**	*2021-07-26*	i20201255	D753836	**348.730**

8.2.2 Residual record

The residuals of the quadratic regression fit of the FCL Secondary Standard daily calibration are given in Figure 33. The absolute values are all extremely small, the average scatter of the individual standard's residual time series is generally smaller than 0.01 ppb, containing random noise but also systematic variations that last for several weeks to months. No steady trend is apparent in the residuals. This is good supporting evidence for the assumption that all FCL Secondary Standards are stable in their N_2O mole fractions.



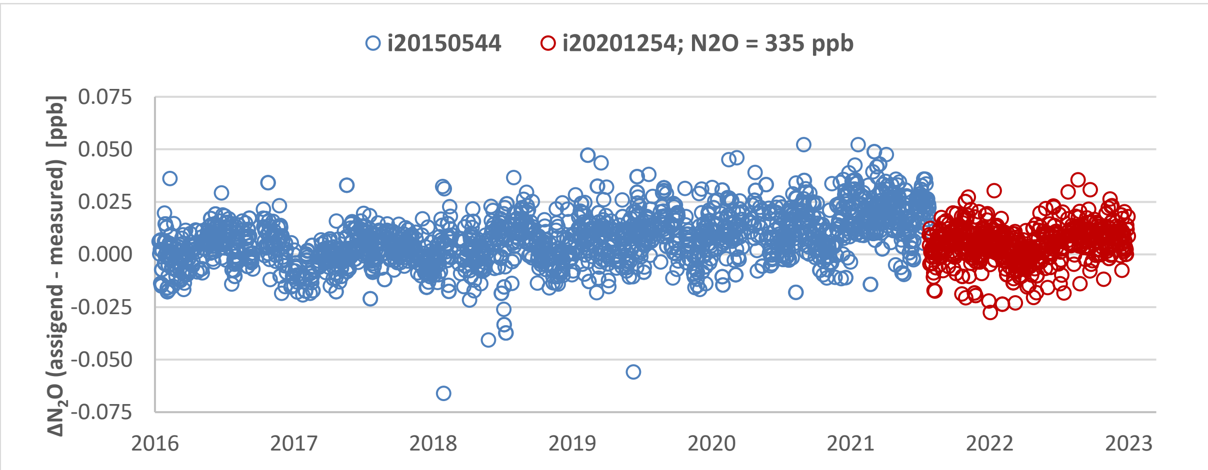
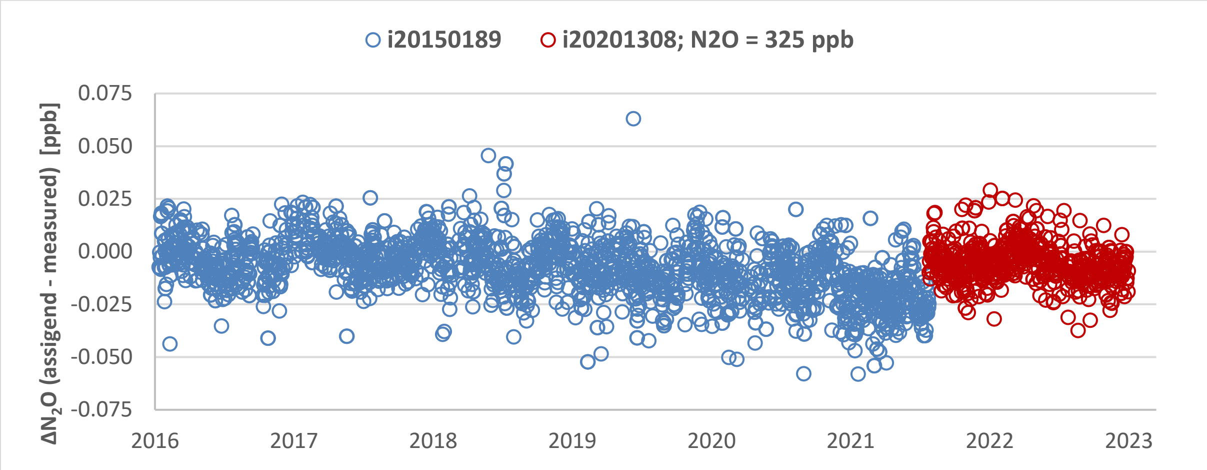


Figure 33: Quadratic regression fit residuals of the daily LGR N2O calibration with FCL Secondary Standards



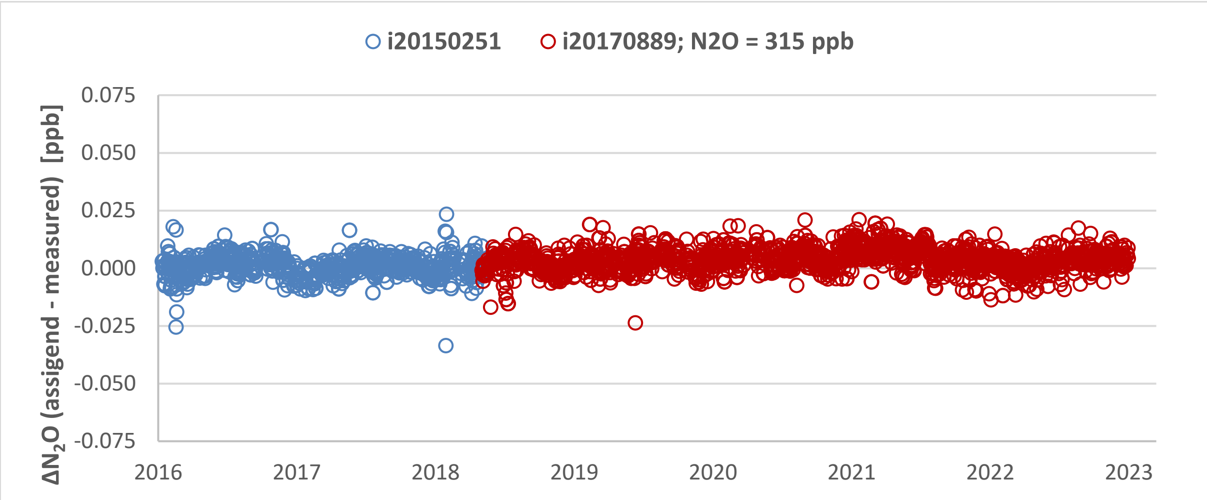


Figure 33: Quadratic regression fit residuals of the daily LGR N2O calibration with FCL Secondary Standards

8.3 N_2O Targets

In the period from March 2016 to December 2020 two targets have been constantly in use for the LGR system. They are complemented by additional Long Term Targets (also known as Archive Quality Control). This shall maintain a long-term link of succeeding (short term) targets. After an initial phase of daily analysis, they have been assessed on a regular, less frequent basis since 2020 to extend their lifetime.

In Table 15 the daily mean target results based on the LGR daily calibration are compared to the assignment by calibration directly with FCL Primary Standards. The adjustment of the assigned value for i20170889 in the course of the replacement of the three emptied tanks from the first set of FCL Secondary Standards, the daily mean target results were split into two tables, for the period before the change (26th July 2021) and after.

One standard is slightly above currently ambient atmospheric mole fractions (336 ppb) while the other two targets contain 308 ppb and 313 ppb N_2O, respectively. The reproducibility over time gets worse when the mole fractions are below the calibrated range and also the offset between the Primary Standard calibration results and the regular (Secondary Standard based) analysis results increases the further the N_2O mole fraction is away from the calibrated range. The low target therefore rather serves as an early indicator for problems with the system and is not considered as a measure for the performance of the measurements.

Table 15a: Target reference standards for N_2O

sample ID	tank ID	measured N_2O mean [ppb]	std.dev. of mean [ppb]	Primary Calibration N_2O mean [ppb]	std.dev. Calibration mean [ppb]	n calibration events
i20160123	D073388	308.732	0.046	308.94	0.05	24
i20150188	D073398	313.460	0.025	313.60	0.04	17
i20180043	D557243	324.163	0.020	324.21	0.02	13
i20171099	D557242	333.719	0.025	333.73	0.03	13
i20160147	D801333	335.768	0.018	335.79	0.03	20

Table 15b: Target reference standards for N_2O (since 26.07.2021)

sample ID	tank ID	measured N_2O mean [ppb]	std.dev. of mean [ppb]	Primary Calibration N_2O mean [ppb]	std.dev. Calibration mean [ppb]	n calibration events
i20160123	D073388	308.893	0.044	308.94	0.05	24
I20150188	D073398	313.566	0.044	313.60	0.04	17
I20180043	D557243	324.179	0.051	324.21	0.02	13
I20171099	D557242	333.725	0.033	333.73	0.03	13
i20160147	D801333	335.783	0.035	335.79	0.03	20

The upper table contains the values up to the adjustment of the scale link on 26th July 2021, the lower table the subsequent period.

The time series of the Target Standard N_2O measurement residuals is depicted in Figure 34 (the adjustment of the assigned value for i20170889 is reflected in the graphs). For mole fractions within the calibrated range, the agreement between assigned and mean measured value is generally very good (mean residuals ≤0.04 ppb). The record of the low standard reveals different periods where the mean results are stable for weeks to months on different levels that are different by up to 0.1 ppb. This provides some estimate for the uncertainty of measurements beyond the calibrated range. There are step changes in the records for the low targets (<325 ppb) when the Secondary Standard set was changed due to a revision of the low Secondary Standard (i20170889). In July 2022 the time series of both targets also exhibit a small 0.05 ppb drop. This is result of an exchange of the analyzer. The cause for the small bias between the instruments is not yet understood.

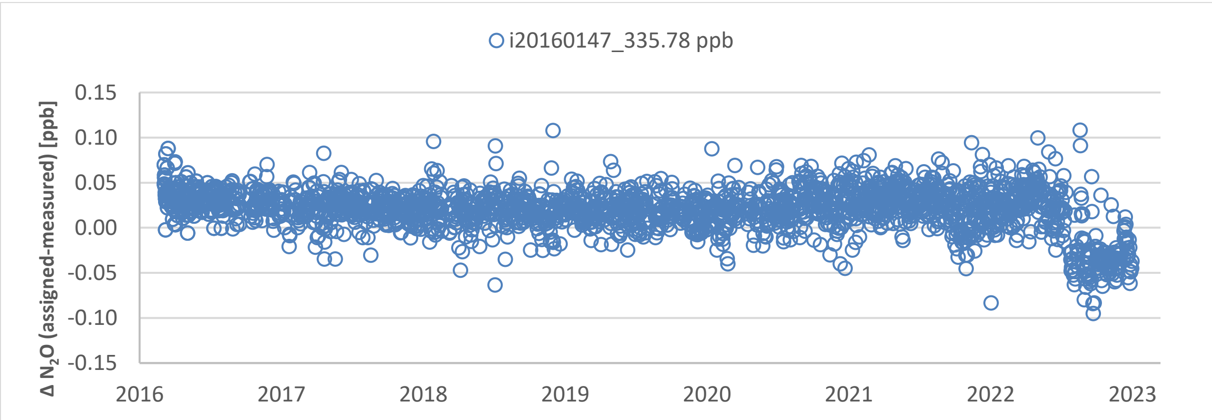
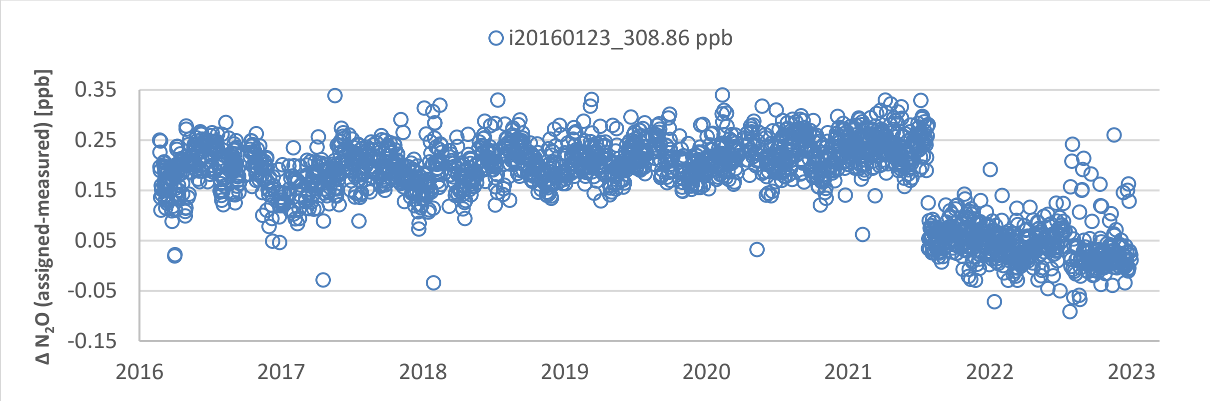
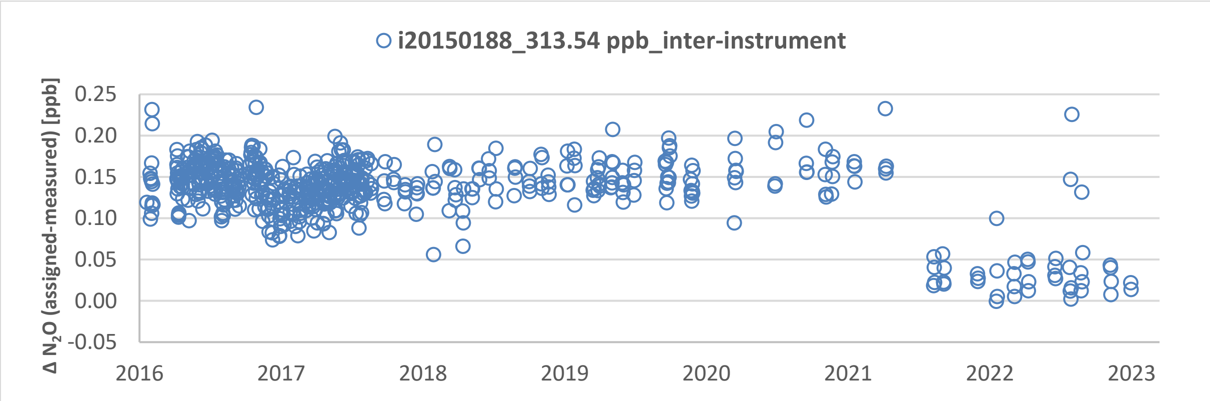
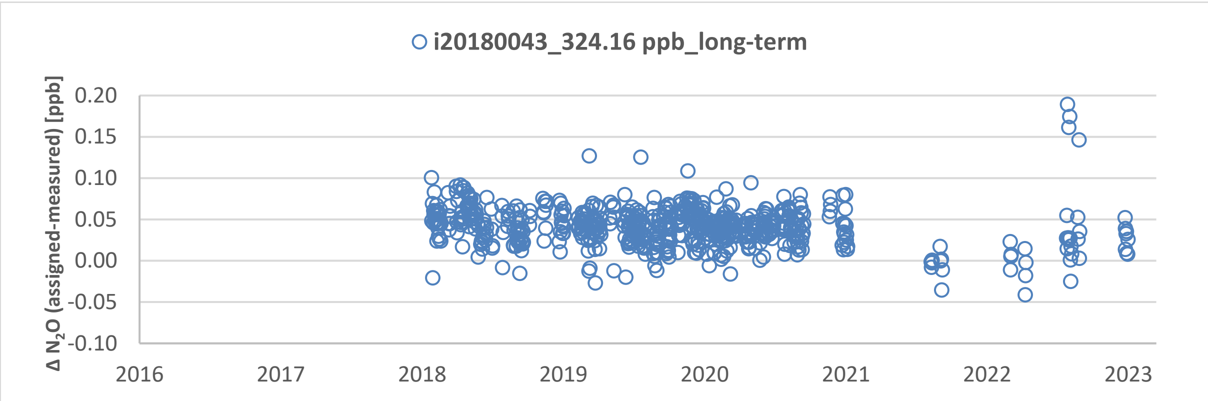


Figure 34: Time series of the offset of the ambient N2O target measurements to its assigned values.







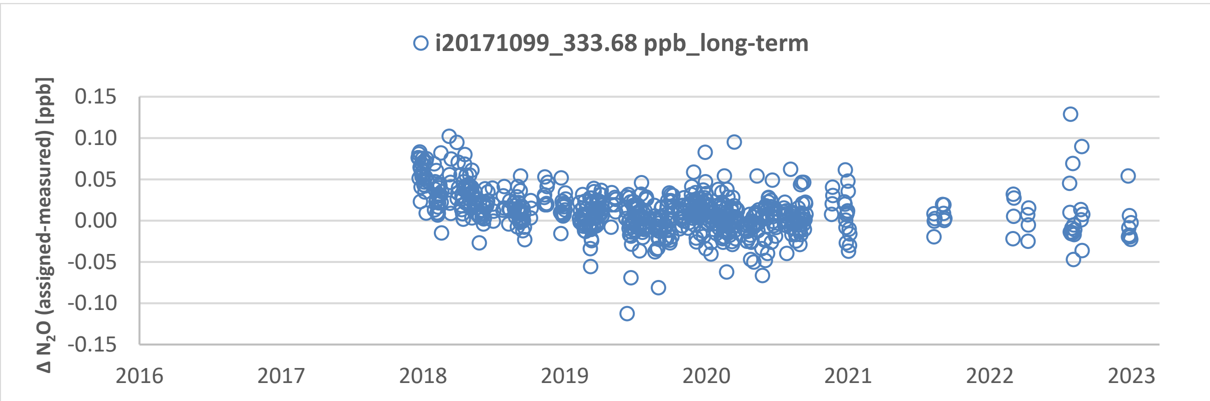


Figure 34: Time series of the offset of the ambient N_2O target measurements to its assigned values.

8.4 Internal N_2O Comparison

8.4.1 N_2O comparison of two LGR instruments

A failure of the LGR analyzer in July 2022 required an exchange of the instrument. The replacement analyzer was operated until the end of 2022 when the original instrument was repaired. Several standards had been analyzed on both instruments, simultaneously and with time lags of up to 20 months. Figure 35 shows the offsets of the mean results for each sample with a total average of 0.05 ± 0.06 ppb. These biasses remain constant over time without any underlying cause yet having been identified.

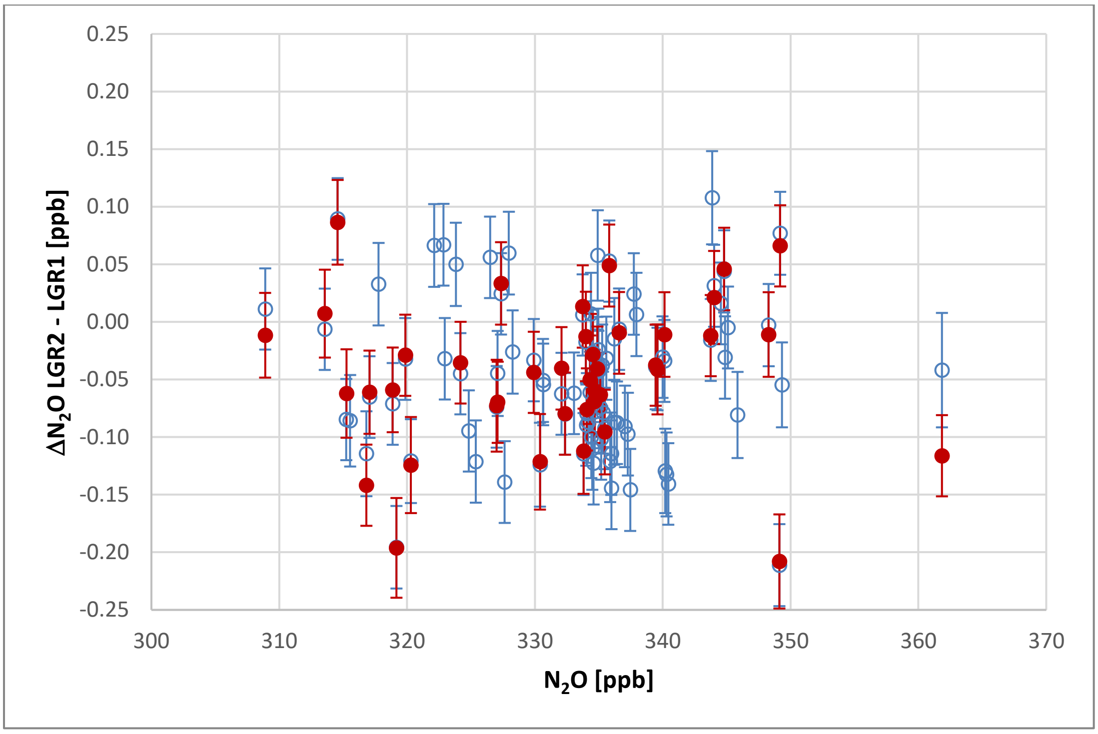


Figure 35: N2O offset of two LGR instruments for the same samples

Blue symbols represent offsets of total means of all measurement days, red symbols represent data analysed on the same day. Samples within 308 - 362 ppb are considered, both analyzers are operated in the same way and based on the same set of FCL Secondary Standards; error bars are combied uncertainties assessed in section 8.6.4 2. and 3.

8.4.2 N_2O comparison LGR-GC

Standard gases that are calibrated for N_2O by the LGR instrument have often also been analyzed by GC. The GC measurements are linked to the same set of FCL Primary Standards but are based on a different set of six Secondary Standards. The GC detection of N_2O by an Electron Capture Detector (ECD) can be influenced by SF_6 mole fractions if they differ significantly from the atmospheric air abundance. Therefore, only samples have been included in the comparison that contain 8-30 ppt SF_6 at ambient N_2O mole fractions of 319-350 ppb. As the reproducibility and repeatability of the GC-ECD (0.1 ppb and 0.14 ppb, respectively) are in general by a factor of 7 inferior to that of the LGR, only GC measurements have been considered that have been analyzed on the GC on more than one day with at least 10 injections. The averaged inter-instrumental measurement difference for all comparison samples is -0.02 ppb ± 0.12 ppb (see Figure 36). This includes the marginal bias of the initial LGR Secondary Standard assignments for measurements before July 2021 and does not provide indication for any other bias in either of the instruments.

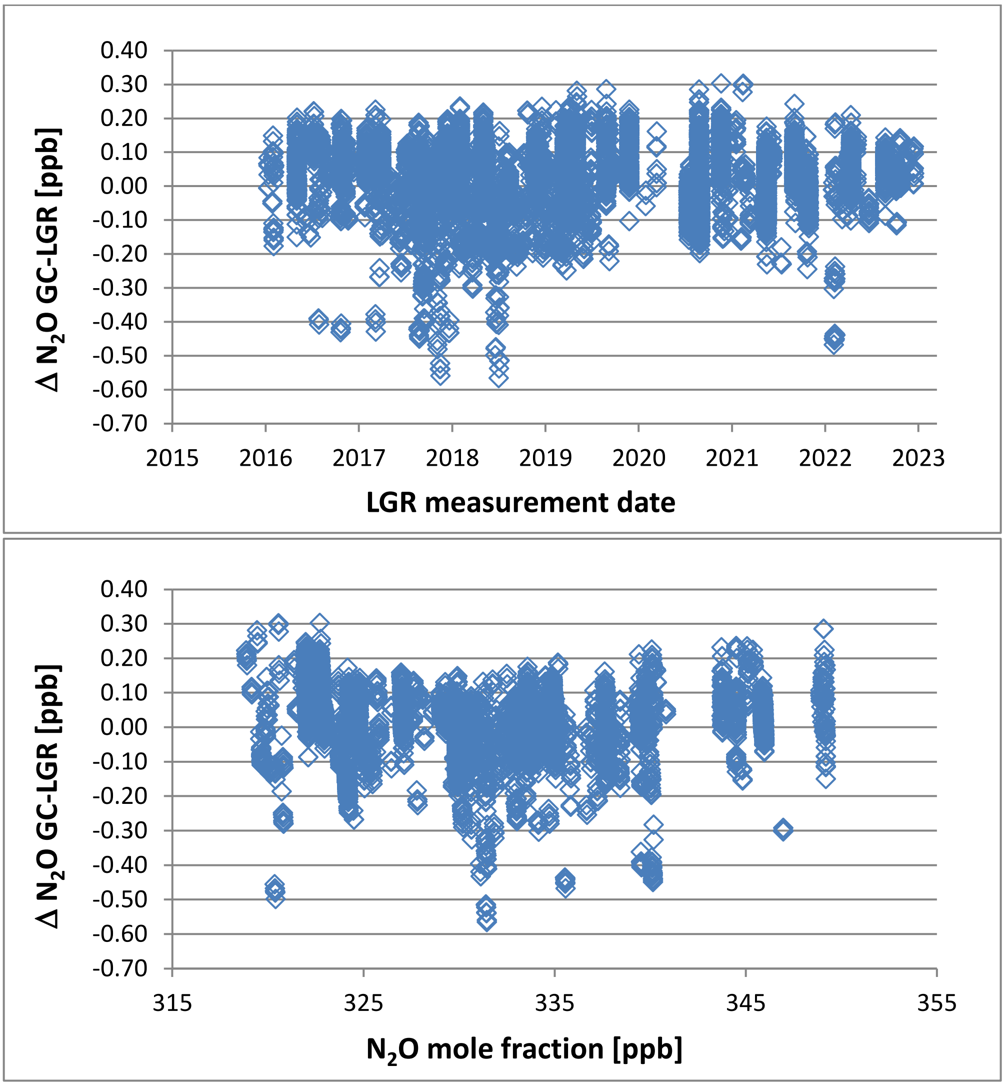


Figure 36: Offsets of daily LGR N2O measurements relative to the annual mean of GC results

8.5 External N_2O Comparisons

8.5.1 N_2O compatibility ICOS FCL - MPI BGC

The most intensive comparison measurements have been made with the MPI-BGC GasLab. This laboratory is using different instrumentation (Agilent 6890 GC-ECD) and their measurements are tied to the WMO Mole Fraction scales by an independent set of Primary Standards. These MPI-BGC Primary Standards already have CCL calibration records with multiple measurements in different years for fifteen individual standards assigned over 14 years. The MPI-BGC measurements are not relevant for the assignment of the FCL standards and therefore are completely independent.

8.5.1.1 Comparison of N_2O calibration standards

Basis for an agreement of FCL and MPI-BGC measurements is the compatibility of the respective sets of calibration standards. As the FCL Primary Standards have been produced at the MPI-BGC they also were thoroughly analyzed at the MPI-BGC in 2013 and 2014 before being used by the FCL. In addition, these standards were also analyzed for a third time before or after the shipment to the CCL for the first recalibration of subsets of this FCL Primary Standard suite. Likewise, MPI-BGC Primary Standards that were simultaneously returned to the CCL for recalibration were also analyzed by the FCL. Measurements at MPI-BGC have started 15 years earlier and thus the mole fraction range of the Primary Standards is about 15 ppb lower compared to the FCL Primary Standards. Therefore, the high FCL standard and low MPI-BGC standard are far beyond the calibrated ranges of the other lab and the bias for these standards is largely due to an extrapolation error. For the remaining standards a small, consistent offset between CCL-assignments and MPI-BGC measurements of the FCL Primary Standard set of -0.06 ± 0.04 ppb is observed whereas an offset between CCL-assignments and FCL measurements of the MPI-BGC Primary Standard set of 0.17 ± 0.07 ppb is apparent which also shows up with 0.15 ± 0.05 ppb in the CCL-FCL difference for the FMI set in that range. However, these offsets are reduced to 0.12 ppb when changing the basis of the N_2O assignments of the FCL Secondary Standards from the initial CCL assignment values of the FCL Primary Standards to the average value of all CCL calibration results up to 2021 (see section 8.2.1). Including the measurements of the UBA standard set in October 2021 an overall offset of 0.08 ppb ± 0.08 ppb is observed for all standards in the range relevant for atmospheric measurements (325 - 350 ppb). This is consistent with the standard assignment uncertainty of 0.11 ppb specified by the CCL and very similar to the corresponding CCL-MPI offset for the FCL Primary Standards as shown in Figure 37.

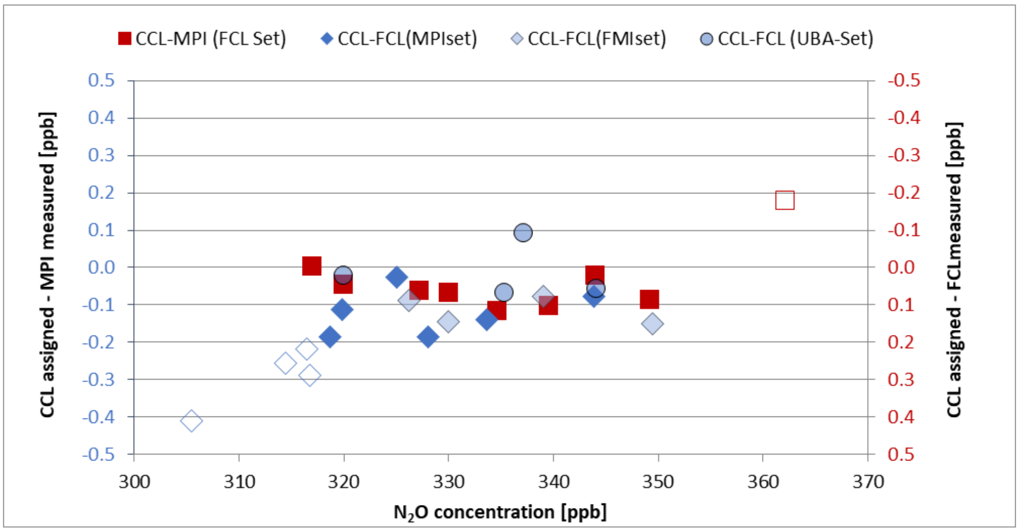
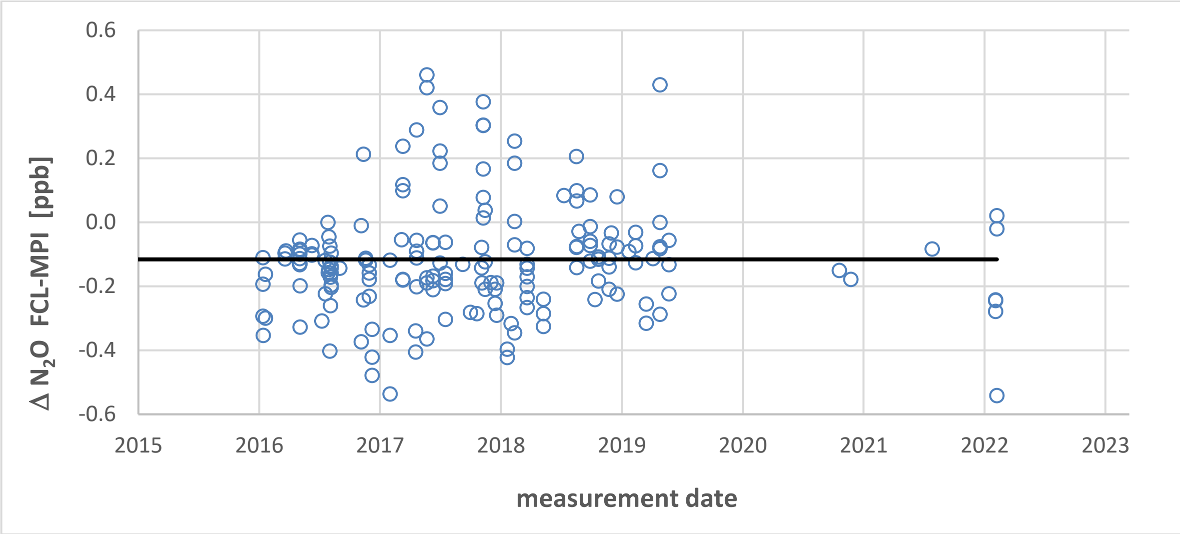


Figure 37: Differences of Primary Standard measured N2O results to CCL assigned values

MPI-BGC measurements of FCL Primary set (red squares- right y axis) and FCL measurements of MPI-BGC (blue diamonds, open symbols represent values extrapolated beyond the calibrated range set by Secondary Standards), ATC-MobileLab Primary set (grey diamonds) and UBA Schneefernerhaus (bluish dots)   (Note that the two axes have opposite signs)

8.5.1.2 Sample N_2O comparison FCL

High pressure standards have been regularly exchanged between MPI-BGC and FCL and analyzed in both laboratories. The resulting differences for about 180 comparisons (for FCL LGR values only) are presented in Fig 38. The average offset of MPI-FCL within the Secondary Standards' range amounts to 0.09 ppb ± 0.17 ppb. This corresponds to the offset established in the preceding section and confirms the mole fraction dependence.



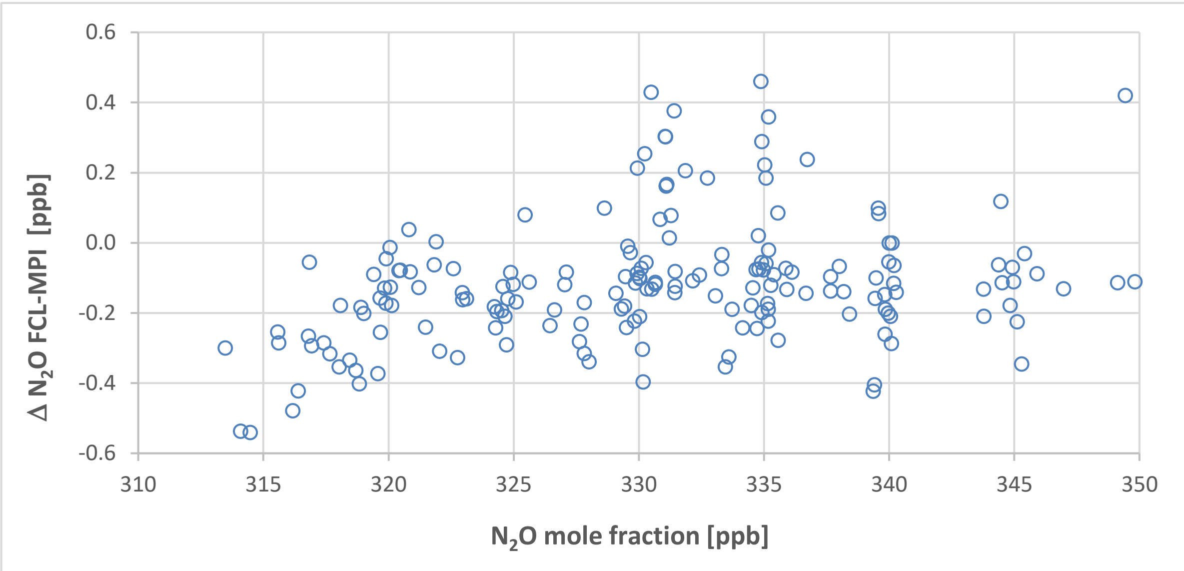


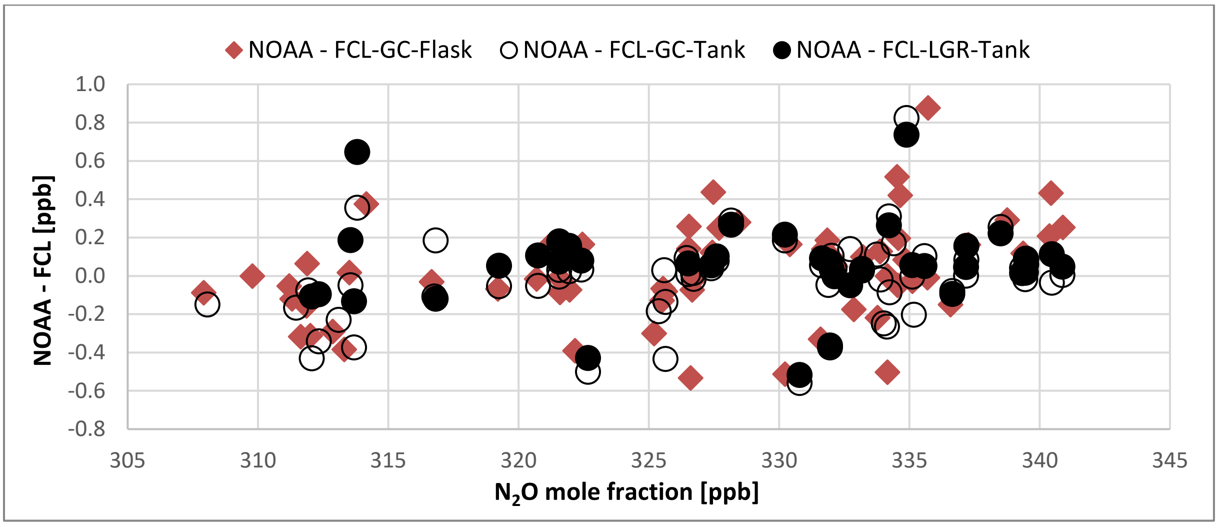
Figure 38: Difference of N2O results for samples that have been analyzed at FCL and MPI-BGC

All MPI-BGC GC measurements since 2015 with minimum 6 injections within the range of 313 - 350 ppb are considered in aggregated means

8.5.2 N_2O compatibility ICOS FCL - NOAA

Comparison with the NOAA-GML laboratory (and other laboratories) is routinely made in two independent exercises, using the Sausage Flask Intercomparison Program and MENI high pressure cylinder program. In the Sausage Program, samples for comparison are prepared by connecting sets of flasks in line and filling them with dry air from a high-pressure cylinder at the FCL. The FCL is generally analyzing the composition of the filling air using the normal instrumentation for calibrating standards. Therefore, the results of the flask measurements provided by NOAA can be compared with these high-pressure cylinder measurements (see Figure 39). The agreement of all valid samples (defined by a flask pair agreement within 0.3 ppb) yields a difference of NOAA - FCL = 0.07 ppb ± 0.09 ppb. In summer 2019 the NOAA laboratory has changed instrumentation which did not change the offset but the standard deviation of the difference has been reduced to 0.08 ppb.

The MENI round robin test between NOAA (as WMO-CCL), EMPA (as WMO-WCC), MPI-BGC, FCL and -ATC (ICOS Mobile Lab) has been established to check the ICOS WMO mole fraction scale link in a regular manner. In this program a set of three cylinders is prepared and maintained by the FCL. One of these cylinders constitutes a blind sample and is modified in its composition after every completed loop. Results of the first iterations are shown in Figure 40. The observed offset between CCL and FCL is 0.04 ± 0.05 ppb. This small offset is in line what has been revealed by the comparison of other standards assigned by the CCL and the Sausage Program.



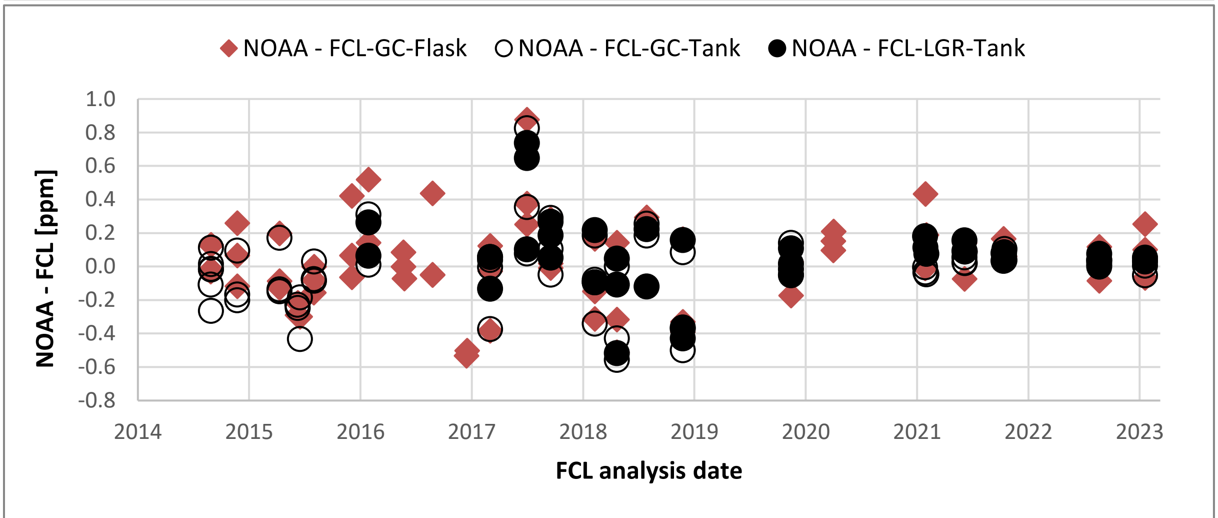


Figure 39: N2O offset between NOAA and FCL based on flask samples

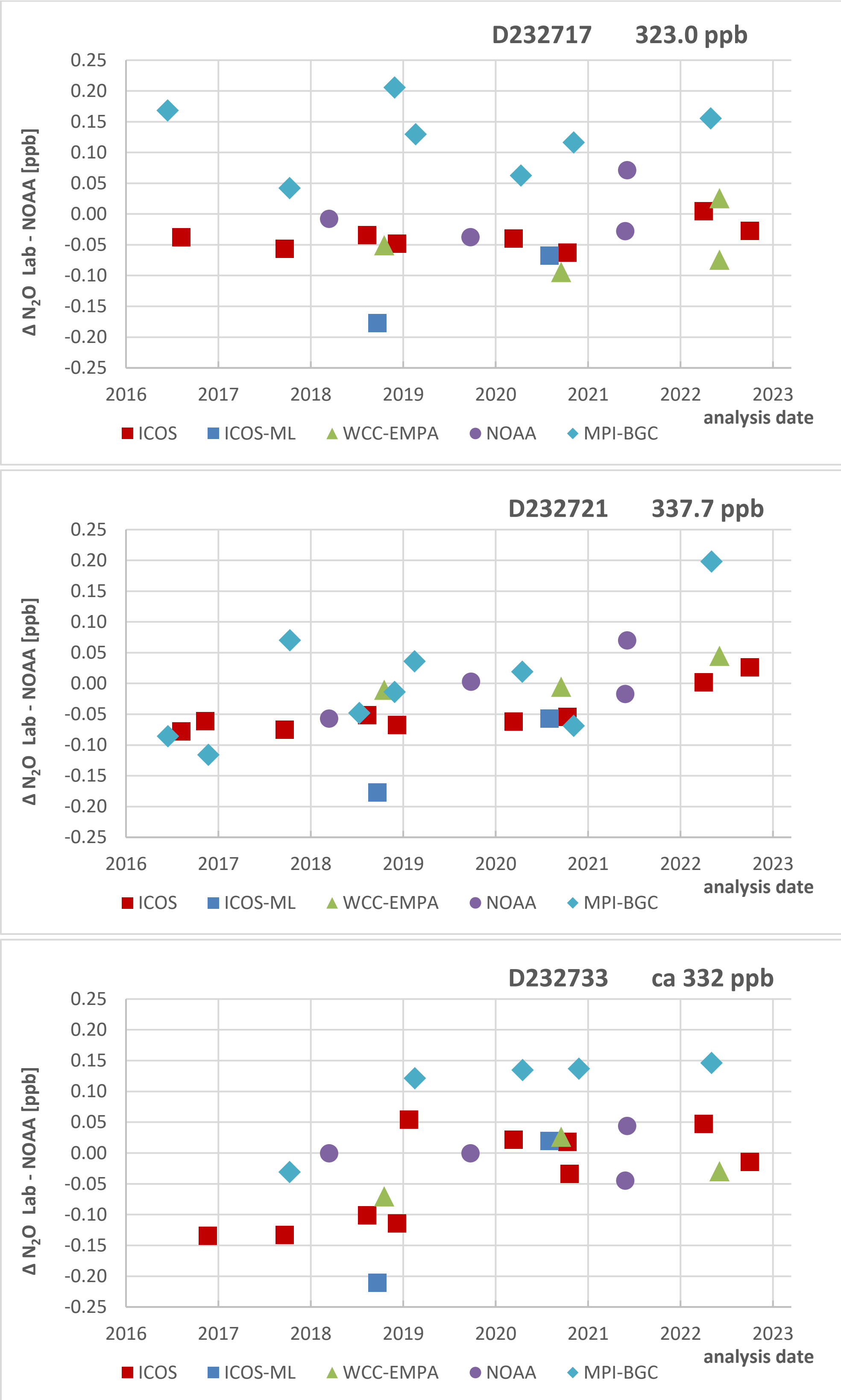


Figure 40: N2O offset in MENI ICP between FCL, MPI, ICOS MobileLab and WCC relative to NOAA

8.6 N_2O uncertainty evaluation

According to the WMO Expert Group recommendations investigators must report uncertainty estimates for their data that include all potential sources of error. A scheme for a comprehensive uncertainty discussion has been suggested by Andrews et al. 2014. Following this scheme we have derived an overall N_2O measurement uncertainty based on a performance assessment of the LGR system. In this assessment we have considered the following uncertainty contributions:

8.6.1 FCL Primary N_2O Standards

The CCL specifies reproducibility for N_2O calibrations of 0.11 ppb (68% confidence level). This CCL uncertainty quote is in line with the assessment of the FCL Primary Standard set. The initial absolute residuals of the FCL Primary Standard set are on average 0.05 ppb and the differences from the succeeding CCL recalibrations relative to the first were also within this range with the exception of a systematic increase of the assignments of the N2O assignments in the two standard gases with the lowest N_2O. The compatibility of the FCL Primary Standard set with other CCL calibrated standards (held by MPI-BGC, FMI, UBA) yield a systematic offset of 0.08 ppb on average lower than the CCL assignments of the respective standards for gases with $N_2O \geq 320$ ppb. The reverse assessment of FCL Primary Standards by the MPI-BGC laboratory results in a very similar mean offset of 0.06 ppb. This offset includes the assignment uncertainties of each calibration gas set.

8.6.2 N_2O scale transfer uncertainty

The assigned values of the first set of LGR Secondary Standards was defined by the first calibration using the FCL Primary Standards. Repeated calibrations of the FCL Secondary Standards using these FCL Primary Standards indicated that these initial assignments were slightly too low in the atmospheric mole fraction range (≈ 0.03 ppb in the range 330 - 340 ppb) with a larger offset for the low Secondary Standard (0.11 ppb). As the LGR instrument is characterized by a quadratic curve this introduced a more significant extrapolation error for samples with N_2O outside the calibrated range. The second Secondary Standard set, which is in use since July 2021, is based on multiple Primary Standard calibrations. The reproducibility of these assignments is ranging between 0.018 ppb and 0.036 ppb. The absolute mean values of the regression fit residuals of the daily calibration using the Second Standards are on average < 0.005 ppb for all individual standards. This suggests very small uncertainties for the FCL internal scale transfer based on 18 - 25 calibration points using the FCL Primary Standard Set (initial Secondary Standard set) and more than 110 measurement days to assign the current Secondary Standard set using the initial FCL Secondary set.

A comparison of the FCL Primary Standard set with other CCL calibrated standards (held by MPI-BGC, FMI, UBA) was made. On average a systematic offset of FCL - CCL of - 0.09 ± 0.075 ppb for gases with $N_2O \geq 317$ ppb was established. The reverse assessment of FCL Primary Standards by the MPI-BGC laboratory results in a similar mean offset of 0.06 ppb.

8.6.3 N_2O long-term reproducibility

The time series of the target standard and the calibration fit residuals, respectively, indicate periods where the result stabilizes on varying levels within a very minor range. While the reason for this variability is not understood it is used to deduce an additional uncertainty of 0.02 ppb for long-term system changes that are not cancelled out by the standardization scheme.

An exchange of the LGR analyzer in July 2022 brought to light persistent biasses between the two instruments that the calibration does not cancel out. This additional uncertainty is estimated as 0.08 ppb based on comparison of common samples measurement results.

8.6.4 N_2O measurement uncertainty estimate

Based on the above considerations the following combined standard uncertainty (k=1) is calculated as the square root of the sum of the individual uncertainty squares:

1. Scale link uncertainty = 0.12 ppb

- uncertainty of the CCL assignments for individual FCL Primary Standards (0.11 ppb)
- uncertainty of initial Secondary Set assignments (0.05 ppb)
- uncertainty of the FCL internal scale transfer to Secondary Standard assignments (0.026 ppb)

2. Measurement uncertainty of daily means = 0.082 ppb

- mean uncertainty of the daily calibration regression fit (0.011 ppb)
- uncertainty of the detector response drift throughout the validity of a daily calibration (0.01 ppb)
- uncertainty from the repeatability of the daily sample measurements (0.004 ppb)
- uncertainty based on instrument bias: 0.08 ppb

3. Additional long-term variability = 0.02 ppb

In sum the accuracy with respect to the WMO Mole Fraction scale arises from the root of the sum of squares of the scale link uncertainty, the long-term reproducibility and the measurement uncertainty which amounts to 0.12 ppb (k=1). The FCL reproducibility is estimated to be 0.03 ppb.

The reproducibility derived from the target standard record is consistent with the uncertainty estimate for measurement of daily means.

The analytical precisions of many instruments that are involved in comparison activities are considerably inferior to the FCL LGR system. Therefore, the time series of these comparisons are mostly dominated by this scatter and contain little information on the LGR's reproducibility but the consistently small mean offsets support the uncertainty estimate. The mean offset relative to NOAA based on measurement results for CCL assigned standards from partner labs and the MENI comparison samples are compatible with this uncertainty estimate.

References

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[CCL_CO_2 2017] Information published at CCL's webpage: https://gml.noaa.gov/ccl/co2_scale.html (accessed March 2022)

[CCL_N_2O 2011] Information published at CCL's webpage: https://gml.noaa.gov/ccl/n2o_scale.html (accessed March 2022)

[Crotwell 2017] Presentation by A. Crotwell at the WMO meeting GGMT2017: https://wmoomm.sharepoint.com/sites/wmocpdb/eve_activityarea/Forms/AllItems.aspx?id=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c%2FGGMT2017%5FT05%5FCrotwell%2Epdf&parent=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c&p=true (accessed March 2022)

[Crotwell 2019] Presentation by A. Crotwell at the WMO meeting GGMT2019: https://wmoomm.sharepoint.com/sites/wmocpdb/eve_activityarea/Forms/AllItems.aspx?id=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c%2FMeetings%2F2019%2FGGMT2019%2FOral%2FT5%5Fcrotwell%5Fggmt%5F2019%2Epdf&parent=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c%2FMeetings%2F2019%2FGGMT2019%2FOral&p=true (accessed march 2022)

[Hall 2017] Presentation by B. Hall at the WMO meeting GGMT2017: https://wmoomm.sharepoint.com/sites/wmocpdb/eve_activityarea/Forms/AllItems.aspx?id=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c%2FGGMT2017%5FT04%5FHall%2Epdf&parent=%2Fsites%2Fwmocpdb%2Feve%5Factivityarea%2FGlobal%20Atmosphere%20Watch%20Programme%20%28GAW%29%5F63452102%2D7575%2De911%2Da98e%2D000d3a44bd9c&p=true (accessed March 2022)

[Hall et al. 2021] Hall, B. D., Crotwell, A. M., Kitzis, D. R., Mefford, T., Miller, B. R., Schibig, M. F., and Tans, P. P.: Revision of the WMO/GAW CO_2 Calibration Scale, https://doi.org/10.5194/amt-2020-408

[WMO 2018] Crotwell, A., & Steinbacher, M. (Eds.). (2018). *19th WMO/IAEA meeting on carbon dioxide, other greenhouse gases and related measurement techniques (GGMT-2017). GAW Report: Vol. 242. 19th WMO/IAEA meeting on carbon dioxide, other greenhouse gases, and related measurement techniques (GGMT-2017)*. Feb. 2019 retrieved from https://library.wmo.int/index.php?lvl=notice_display&id=20698#.W_5gRvJgifE; Section 1.5 a General recommendations for the quality control of atmospheric trace gas measurements, p. 12

[CCQM-P188] International comparison-Report of the Pilot study CCQM-P188 (in parallel with CCQM-K120.a and b): Carbon dioxide in Air (380-800) µmol/mol; Draft B; Edgar Flores*1, Joële Viallon1, Tiphaine Choteau1, Philippe Moussay1, Faraz Idrees1, Robert I. Wielgosz1, C. Meyer2, Daniel Rzesanke 3.; 2018

Annex I

Analysis of CO_2 and CH_4 mole fractions in reference standard mixtures at near-ambient mole fraction levels

Instrumentation:

Analysis of dried atmospheric air samples, pressurized in high pressure cylinders is performed by a Picarro Inc. G2301 CO_2/CH_4 Cavity Ringdown Spectroscopy (CRDS) Analyzer. The instrument (S/N CFADS2193) retrieves mole fractions by analyzing the characteristic absorption of light of infrared-active molecules (near-IR spectroscopy).

Procedure:

Sample flow and cell pressure are controlled in an automated way and protocolled by the instrument.

The sample is provided via an external multi-position valve (VICI Valco, EMT2C16UWE; MPV) to the instrument's inlet. Commonly up to 16 high pressure cylinder air samples are analyzed within a sequence.

For data collection and synchronization of the MPV position and detector data an additional, external PC supervises the setup (see Fig.A1.1). The resulting data and .log files are compiled by this PC and provided to the lab internal data management and data storage system. Following the automated migration of the raw data into the central data base quality checks and calibration of the instrument are self-controlled performed.

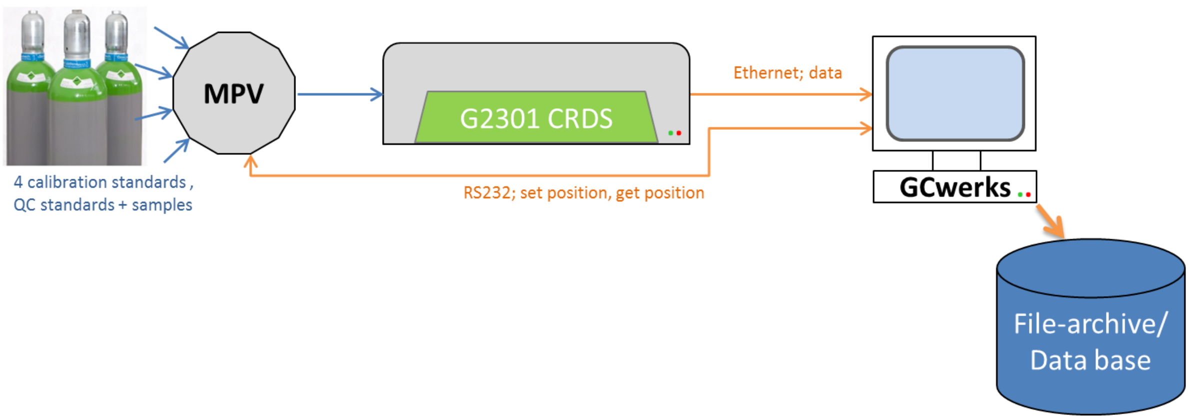

Figure A1.1: Schematics of the instrumental setup, blue lines= sample, orange lines=data/commands

Mode of Operation:

The operator defines the sequence of analysis using the GCwerks software at the supervising PC. Required information is shown in Table A1.1 and includes the date and time of initial connection, a MPV port number, sample identifier and meta information like the specific regulator mounted or the type of the sample. This information is stored in a *ports.log*-file, that supplies identifiers for the GCwerks-internal data base and sequencing as well as meta information for later summary purposes.

In a second step, the operator sets up the sequencing of the sampling ports stored as **.sequence*-file (as shown in Table A1.2). This list contains the port to be addressed and the residence time at this position as well as the runfile, that specifies the parameter set for this sample analysis. In the subsequent results file, both input files are merged with the raw data to automatically link the data collected during a specific port position to the respective sample identifier.

To keep the optical cell dry and maintain the instrument in a defined state the default sequence terminates with continuous analysis of a purge gas. The analyzed sample gas is discarded.

Date	Time	# port	Sample	Regulator	Type
170711	1200	6	i20150060	Tes1-021	qc
170711	1440	4	i20150062	Sco2-005	qc
170711	1440	3	i20150062	Sco2-005	qc
170711	1440	1	i20140171	Tes1-009	cal
170711	1440	5	i20140172	Sco2-001	cal
170711	1440	9	i20140173	Sco2-002	cal
170711	1440	13	i20140174	Tes1-004	cal
170711	1440	12	i20170017	Tes1-007	tank
170711	1440	14	i20170205	Sco3-008	tank

Table A1.1: Exemplary *ports.log* meta look-up table

While preparing the schedule, the operator has to make sure, that every sequence contains at least one Quality Control Standard (Target) and that for each calendar day the four FCL Secondary Calibration Standards have to be analyzed once at least.

Table A1.2 shows an exemplary analysis sequence containing 3 target samples (qc), 4 calibration gases (cal), a sample (tank) and the closing purge gas (for 60 minutes).

Duration [min]	Procedure	Type	# port
20	picarro.runfile	qc	6
20	picarro.runfile	qc	3
20	picarro.runfile	qc	4
20	picarro.runfile	cal	1
20	picarro.runfile	cal	5
20	picarro.runfile	cal	9
20	picarro.runfile	cal	13
20	picarro.runfile	tank	12
60	picarro.runfile	tank	14

Table A1.2: Exemplary sampling sequence

Every sample is fed to the analyzer for 20 minutes. During the initial 5 minutes the results are discarded with respect to running-in effects, like purging of the tube and allows for equilibration in pressure regulators, thermal equilibration and settling of the regulating loops. The instrument itself runs up to 0.2 Hz analysis frequency but raw data is aggregated in 60 s integration intervals to reduce the data volume. This leaves the opportunity to observe the sampling time series for subsequent flagging and averaging.

The optical cell is evacuated to 140 Torr, so the sample has not necessarily to be provided at over pressure. Pressure regulators (either and most common Tescom 64 series regulators or Scott Specialties 14C series brass regulators) are mounted on the cylinders at least the day before the analysis, flushed and stored pressurized with closed cylinder head valves. Before analysis this pressure is released and a slight overpressure of about 100mbar is generally adjusted to purge the regulators. This purging step, with pressurization followed by pressure release at closed cylinder head valve is performed three times.

The instrument is calibrated on a daily basis. The operator has to ensure that an analysis of the FCL Secondary Calibration Standards occurs within each calendar day. If it is more frequent the raw results of these standards are averaged for a daily mean. During data processing the daily mean calibration standard data are fitted by a regression function to their assigned mole fraction values to calculate the calibration coefficients of this day. For calibration of CO_2 and CH_4 a linear equation is applied.

Five dedicated samples, called Targets are regularly analyzed for quality control of the instrument's performance including the daily calibrations. Two of them are included within every sequence. They have CO_2 and CH_4 mole fractions close to the boundaries set by the range of the calibration gases to give a conservative assessment that is meaningful for all mole fractions. The two additional targets are analyzed less frequently (at least four times a year) as "long term targets" to assess long term variability and potential drifts of the instrument's calibration suite. A fifth QC standard is shared between different instruments in the laboratory to assess the link of their respective results on a regular basis.

Instrument calibration:

Measurement data are calibrated relative to the current WMO Mole Fraction Scales for all reported gas mole fractions. The current scales that are maintained by NOAA ESRL as Central Calibration Laboratory (CCL) are: WMO CO_2 X2007 and WMO CH_4 X2004A. For spring 2021 a revision of the WMO/GAW CO_2 Calibration Scale is announced (X2019).

The traceability to these scales is realized by a suite of high pressure standard gases calibrated by the WMO Central Calibration Laboratory. The link is actively maintained by regular re-calibrations of subgroups of these laboratory calibration standards. The respective standard cylinders are listed in Table A1.3 with the currently used assigned values. These values may change due to scale revisions by the Central Calibration Laboratory or additional measurements done by the CCL. The updated data is available in the internet (http://www.esrl.noaa.gov/gmd/ccl/refgas.html).

With this CCL-calibrated reference suite (FCL Primary Calibration Standards) the daily used FCL Secondary Calibration Standards were calibrated/assigned at the same instrument.

Cylinder ID	Fill date	CO_2 [ppm]	CH_4 [ppb]	Last CCL analysis
CB09944	07/2013	339.24	1596.64	06/2017
CB09939	07/2013	365.12	1743.13	10/2018
CB09958	07/2013	389.53	1896.82	09/2016
CB09983	07/2013	412.21	2032.92	10/2018
CB09952	07/2013	433.58	2195.34	11/2016
CB09955	07/2013	458.92	2344.05	07/2017
CB09957	07/2013	481.75	2466.72	09/2016
CB09934	07/2013	514.79	2731.28	06/2017
CB09948	07/2013	250.08	2932.82	10/2018

Table A1.3: Calibration standards assigned by the WMO Central Calibration Laboratory

Data evaluation:

The detector response function and the mole fractions of the various trace species in the FCL Secondary Standard are determined by analysis of a suite of laboratory standard gases measured by the WMO Central Calibration Laboratory (see Table A1.3). Measurements of these highest level laboratory calibration standards are generally repeated four times a year to capture small changes in the composition of the FCL Secondary Standards or in cases where quality control measurements suggest sudden changes.

To evaluate the validity of the analytical results the following is regularly checked:

- Instrumental parameters during analysis (sampling frequency; cell temperature as well as pressure level and variability).
- Baseline drift and noise when the instrument is purged with a constant sample;
- The measurement results of the target standards relative to their known composition
- The regression fit residuals of the associated daily calibration and their time series.

Measurements are flagged invalid in cases where instrumental variables indicate a system malfunctioning or if the sample flow points to insufficient supply.

Annex II

Analysis of CO and N_2O mole fractions in reference standard mixtures at near-ambient mole fraction levels

Instrumentation:

Analysis of dried atmospheric air samples, pressurized in high pressure cylinders is performed by a Los Gatos Research Inc. CO/N_2O-analyzer Enhanced Performance (LGR). The instrument (S/N 15-0140) retrieves mole fractions by analyzing the characteristic absorption of light of infrared-active molecules (near-IR spectroscopy). The instrument's uses the technical principle of Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) is implemented (see Fig.A2.1).

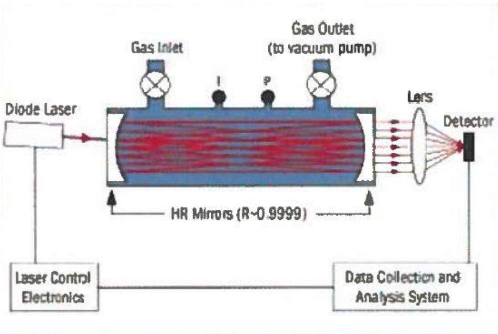

Figure A2.1: Schematic diagram of an OA-ICOS analyzer

Data retrieval is performed with tunable-laser absorption-spectroscopy (TDL) by scanning a narrowband wavelength across the absorption band of a target species to record the loss in the emitted light (ref. Fig.A2.2). Under knowledge of the gas temperature, pressure in the cell, effective path length and known line strength the mole fraction can be calculated from the integrated loss-signal following Lambert-Beer's-Law.

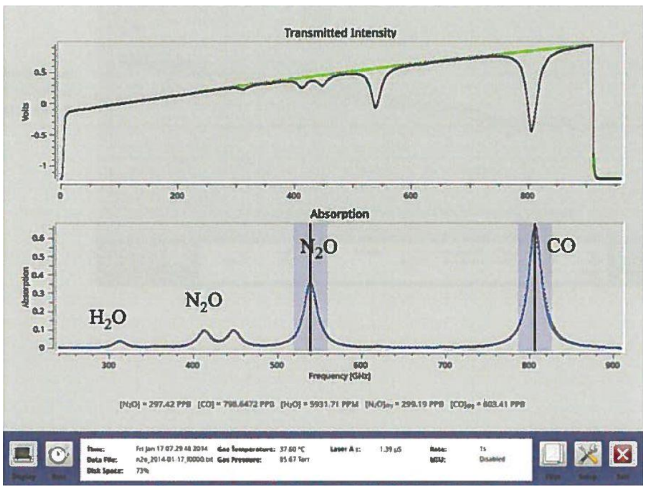

Figure A2.2: Screen shot of spectrum display, upper panel shows photo detector voltage, lower panel shows optical absorption of species of interest.

Instrumental Setup:

Sample flow and cell pressure are controlled and protocolled automatically. Figure A2.3 gives an overlook of the sample flow and meta information retrieval within the instrument.

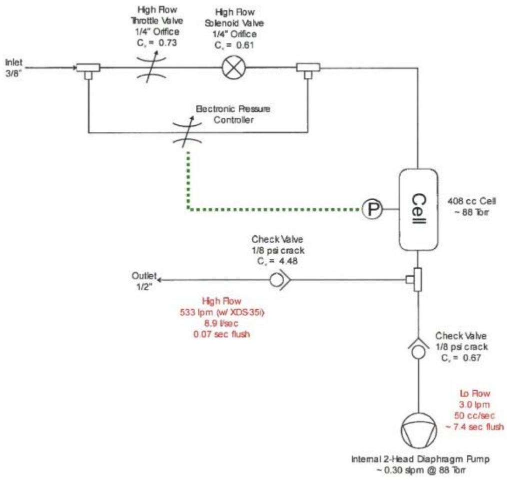

Figure A2.3: Internal flow schematics of the LGR instrument

The sample is provided via an external multi-position valve (MPV; VICI Valco EMT2C16UWE) to the instrument's inlet. Commonly up to 16 high pressure cylinder air samples are analyzed within a sequence. The analyzed sample gas is discarded.

For data collection, synchronization of the MPV and merging of position and detector data an additional, external PC supervises the setup (see Fig. A2.4). The resulting data and .log files are compiled by this PC and provided to the lab internal data management and data storage system. Following the automated parsing process to migrate the raw data into the central data base the data processing includes a short term stability correction, automated quality checks and automated calibration of the instrument.

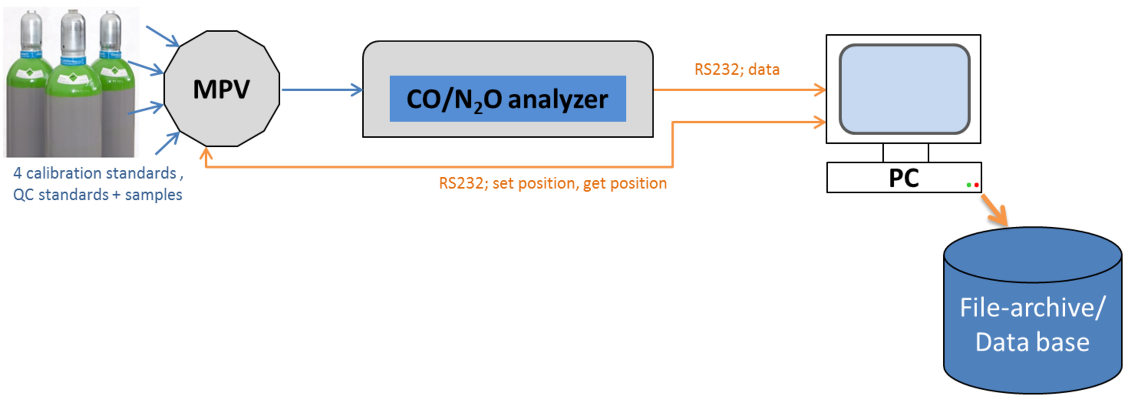

Figure A2.4: Schematics of analysis station, blue lines= sample, orange lines=data/commands

Mode of Operation:

The operator defines the analysis sequence using an in-house programmed software at the supervising PC. Required information to be entered is shown in Table A2.1 and includes the sample identifier, measurement duration, and the port number of the multi position valve.

The mandatory structure of the sample sequence scheme is:

1. *Every* sample analysis has to be bracketed by analysis of the Working Standard (WT) that is used for short term drift correction.

2. The first samples in the sequence have to be the calibration gases for the automated data processing.

3. Every sequence has to include the analysis of minimum one Target Standard that is analyzed for quality control purposes.

4. Samples described as "purging" are ignored and not transferred to the database.

Table A2.1 shows an exemplary analysis sequence containing 4 Calibration Standards, a sample, 3 Target Standards (QC) and the periodic Working Standard (WT). To keep the optical cell dry and maintain the instrument in a defined state the default sequence terminates with continuous analysis of a dried purge gas.

Duration [min]	# port	Sample	Description
20	10	i20160515	WT
20	2	i20150251	Cal1_CA05640
20	10	i20160515	WT
20	3	i20150189	Cal2_D073397
20	10	i20160515	WT
20	6	i20150544	Cal3_D073396
20	10	i20160515	WT
20	5	i20150191	Cal4_D073395
20	10	i20160515	WT
20	1	i20160123	QClow_D073388
20	10	i20160515	WT
20	11	i20170274	sample_D073386
20	10	i20160515	WT
20	13	i20150188	QCinter_D073398
20	10	i20160515	WT
20	4	i20160147	QChigh_D801333
20	10	i20160515	WT
720	15	i20170299	purging

Table A2.1: Exemplary sampling sequence

Every sample is fed to the analyzer for 20 minutes. During the initial 10 minutes the results are discarded due to running-in effects like sample purging of and equilibration in pressure regulators, thermal equilibration and settling of the regulating loops. The instrument itself runs up to 1 Hz analysis frequency but raw data is aggregated in 20 s integration intervals to reduce the data volume. This leaves the opportunity to observe the sampling time series for later flagging and averaging. This 20 s averaging interval set by the LGR instrument is not synchronized with the valve switch schedule set by the controlling software such that there is the possibility that the last data point combines the signals of two subsequent samples. Therefore, the very last data point is generally discarded. The remaining 20s-data points are the raw reading of this analysis.

The optical cell is evacuated to 85 Torr, so the sample has not necessarily to be pressurized. Pressure regulators (either and most common Tescom 64 series regulators or Scott Specialties 14C series brass regulators) are mounted on the cylinders at least the day before the analysis, flushed and stored pressurized with closed cylinder head valves. Before analysis this pressure is released and a slight overpressure of about 100mbar is generally adjusted at the inlet to purge the regulators.

Every sample analysis (including the Calibration Standards) is bracketed by analysis of the Working Standard (WT_{prior}, WT_{after}). Thus short term drifts of the analyzer are accounted for by normalization to the Working Standard's raw signal in the same way for unknown samples as for Calibration Standards:

$$C_{corr} = 2\frac{C_{raw}}{\left(\frac{WT_{prior}}{WT_{ref}}+\frac{WT_{after}}{WT_{ref}}\right)},$$

with C_{raw} – raw signal of sample, C_{corr} – the normalized sample and WT_{ref} - assigned value of the Working Standard Tank.

Every sequence has to be started by the set of the four FCL Secondary Calibration Standards. If all 16 available ports are occupied with bracketing by the WT and sampling time of 20min, an analysis takes no longer than 11 hours. Therefore, the instrument is practically calibrated on a daily basis.

During data processing the normalized calibration standard data are fitted by a regression function to their assigned mole fraction values to calculate the calibration coefficients of this run. For calibration of CO a linear and for N_2O a quadratic equation is applied.

Three dedicated standards, called Targets are regularly analyzed for quality control the instrument's performance including the daily calibrations. Two of them are included within every sequence. They have CO and N_2O mole fractions close to the boundaries set by the range of the calibration gases to allow a conservative assessment that is meaningful for all mole fractions. The third QC is shared between different instruments in the laboratory to assess the link of their respective results on a regular basis. It serves as "long term target" to assess long term variability and potential drifts of the calibration suite.

Instrument calibration:

Measurement data are calibrated relative to the current WMO Mole Fraction Scales for all reported gas mole fractions. The current scales that are maintained by NOAA ESRL as Central Calibration Laboratory (CCL) are: WMO CO X2014A and WMO N_2O X2006A.

The traceability to these scales is realized by a suite of nine high pressure standard gases calibrated by the WMO Central Calibration Laboratory. The link is actively maintained by regular (annual) re-calibrations of subgroups of these FCL Primary Calibration Standards by the CCL. The respective standard cylinders are listed in Table A2.2 with the currently used assigned values. These values may change due to scale revisions by the Central Calibration Laboratory or additional measurements done by the CCL. The updated data is available in the internet (http://www.esrl.noaa.gov/gmd/ccl/refgas.html).

With this CCL assessed reference suite the FCL Secondary Calibration Standards (used on a daily basis) are calibrated at the same instrument. Measurements of the FCL Primary Calibration Standards are generally repeated four times a year.

Cylinder ID	Fill date	CO [ppb]	N2O [ppb]	Last CCL analysis
CB09944	07/2013	31.31	316.77	06/2017
CB09939	07/2013	80.14	319.86	02/2019
CB09958	07/2013	120.69	327.12	09/2016
CB09983	07/2013	158.92	329.92	01/2019
CB09952	07/2013	199.47	334.60	11/2016
CB09955	07/2013	247.14	339.48	07/2017
CB09957	07/2013	397.06	343.95	09/2016
CB09934	07/2013	697.56	349.13	06/2017
CB09948	07/2013	998.63	362.13	01/2019

Table A2.2: Calibration standards assigned by the WMO Central Calibration Laboratory

Data evaluation:

A regular analysis sequence consists of alternate measurements of the Working Standard and Target Standards that are used for quality control assessment. Raw data of any sample measurement is normalized to the raw data of the Working Standard to cancel out instrumental drifts within hours (triggered e.g. by variations in atmospheric pressure or other laboratory environment variations). The detector response function and the mole fractions of the various trace species in the Working Standard are determined by analysis of the FCL Secondary Calibration Standards.

To evaluate the validity of the analytical results the following is regularly checked:

- Instrumental parameters during analysis (sampling frequency; cell temperature as well as pressure level and variability),
- Baseline drift and noise when the instrument is purged with a constant sample;
- Every Working Standard raw data 10 min mean relative to the means of the preceding and subsequent Working Standard measurements,
- Measurement results of the Target Standards relative to their known composition,
- Regression fit residuals of the associated daily calibration.

Measurements are flagged invalid in cases where instrumental variables indicate a system malfunctioning or if the sample flow points to insufficient supply. In cases of an invalid Working Standard measurement it is checked if this individual reference point can be replaced by the next Working Standard measurement result. However, it is also checked if this failed standard measurement indicates a problem that makes the sample measurement also invalid and has to be flagged accordingly.

Annex III

Overview of flagging parameters for measurements performed with Picarro and Los Gatos analyzers

Picarro:

Flag	description
NSigma	NSIGMA with a sigma factor of 3
RI	RUNNINGIN with a running in duration of 300 seconds
P	PCavity with range 139.99 ... 140.01
MISS CO2	Missing value in CO2 related measurements
MISS CH4	Missing value in CH4 related measurements
OPV	OutletProportinalValve Flag 28800 … 34000
SDMinRaw CO2	Standard deviation of MinRaw data, range 0 … 0.035
SDMinRaw CH4	Standard deviation of MinRaw data Flag, range 0 … 0.3
INMinRaw CO2	Insufficient number (of MinRaw values)
INMinRaw CH4	Insufficient number (of MinRaw values)
RC	Insufficient number of calibration gases, <4
CO2_DYN_sd	static dynamic upper bound: 0.070 threshold: 450
CH4_DYN_sd	static dynamic upper bound: 0.6 threshold: 2300

Los Gatos:

Flag	description
NSigma	NSIGMA with a sigma factor of 3
RI	RUNNINGIN with a running in duration of 540 seconds (28 measurement points)
RO	RUNNINGOUT with a running out duration of 5 seconds (1 measurement point)
Gas pressure	with range 85.17 ... 85.28
Gas pressure sd	with range 0 ... 0.006
MISS CO	Missing value in CO related measurements
MISS N2O	Missing value in N2O related measurements
H2O	leakage on the basis of water signal
H2O sd	leakage on the basis of water signal stdev
CO sd	Standard deviation of CO out of range, -1.0 … 0.00014
N2O sd	Standard deviation of NO2 out of range, -1.0 … 0.0001
RC	Insufficient number of calibration gases, <4
N2O_DYN_sd	Dynamic upper bound, Minimum: 4.0e-04 dyn_poly: 6.357375e-04
CO_DYN_sd	Dynamic upper bound, Minimum: 2.2e-04 dyn_poly: 1.074092e-03

Annex IV

CO_2 mole fraction measurement calibrations using an isotopolgue selective analyzer

The analyzer for CO_2 calibration used in the FCL as well as in the ICOS observational network is applying the CRDS technique. This method is selective only for the $^{12}C^{16}O_2$ isotopologue. However, the standard gases to calibrate the analyzers have CO_2 mole fraction assignments from the WMO-CCL for total CO_2 that account for the complete suite of all CO_2 isotopologues. *Measurand is not what is assigned.* So in principle, this calibration approach is working without bias only if the CO_2 isotopic composition of the standard gases is similar to the one observed in the atmosphere. *FCL task is to provide assignments to stations tht they can use* Figure A4.1 displays the relationship between the measured CO_2 mole fraction and $\delta^{13}C$ and $\delta^{18}O$ data for the FCL Primary Standard gases and background atmosphere, respectively. The atmospheric values represent data points from Northern Hemispere background stations from the MPI-BGC flask sampling network (namely ALT, CVO, JFJ, OXK, SIS, ZOT [Heimann et al. 2021]).

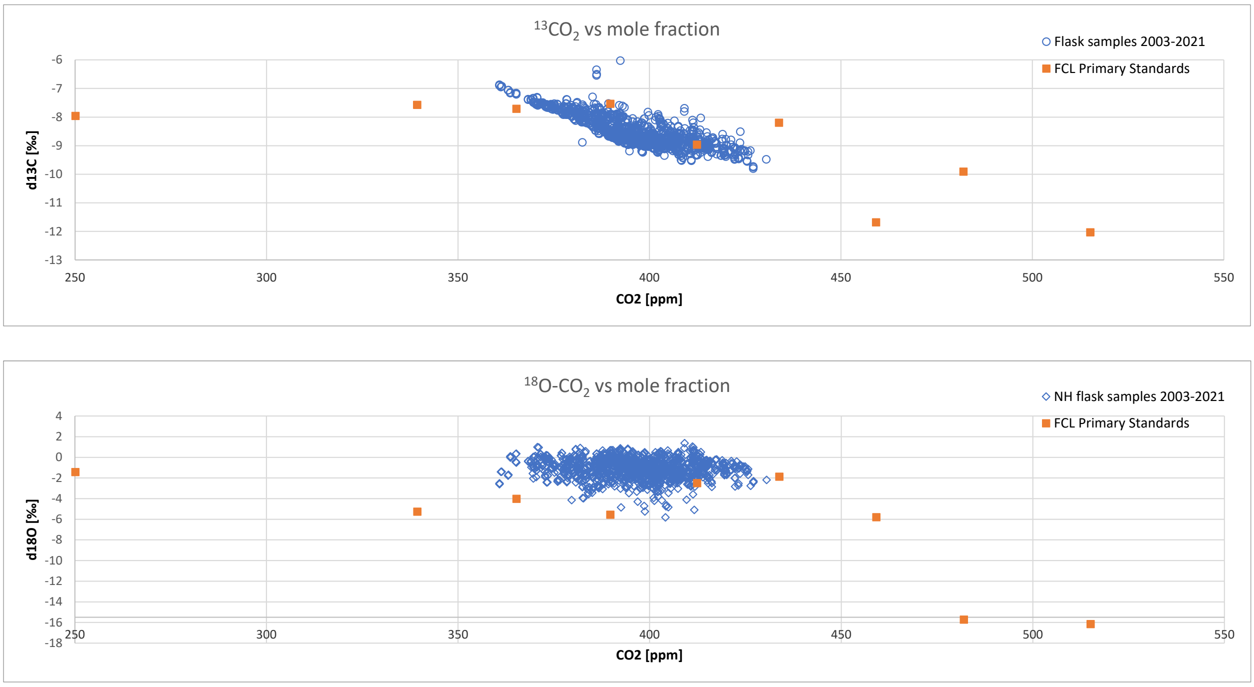

Figure A4.1: CO_2 isotope vs. CO_2 mole fraction relationship in standard gases and atmospheric samples

Modification of CO_2 isotopic composition resulting from preparation of standard gases

Standard gases are prepared at FCL on the basis of compressed, dried real air collected at the roof tops of either the MPI-BGC building at the South-Western edge of Jena city or the FCL building close to Jena city centre. To prepare standard gases with sub-atmospheric mole fractions of CO_2 and other trace gases (CH_4, CO, N_2O; in the case of the FCL primaries also SF_6) the CO_2 is partly taken out using molecular sieve as scrubber which is mostly followed by an addition of pure CO_2 to achieve the wanted composition. other standards only undergo the spiking step. For this spiking there are two pure CO_2 gases available with ^{13}C either depleted or enriched relative to atmospheric CO_2 ($\delta^{13}C$ = -2 ‰ and -38 ‰, respectively). The spiking is generally made such that the selected relative amounts of each of the two CO_2 that are added result in a $\delta^{13}C$-CO_2 value that is expected to match the range of typically observed $\delta^{13}C$-CO_2 in atmospheric CO_2. Fig A4.1a shows that this is relatively well achieved for $\delta^{13}C$. In contrast the $\delta^{18}O$ value of both CO_2 spike gases is more negative than in the atmosphere (??‰) in either spike gas causing spiked standards to exhibit too negative ^{18}O (and associated ^{17}O) values. This is similar to the situation described by the WMO-CCL [Tans et al. 2017].

Mole fraction adjustments accounting for standard - atmosphere isotope mismatch

Table A4.1 lists the CO_2 mole fractions of the FCL Primary Standards and their measured isotope delta values relative to the VPDB-CO_2 scale. For each standard gas the isotope amount-fraction ($x^{12}C^{16}O_2$) of the main isotopologue $^{12}C^{16}O_2$ relative to total CO_2 is calculated. This calculation is based on the $\delta^{13}C$- and $\delta^{18}O$- CO_2 measurement results by the CCL, $\delta^{17}O$- CO_2 data that are deduced from a $\delta^{17}O$ to $\delta^{18}O$ relationship of 0.5281 [Assonov and Brenninkmeijer 2003] and the isotope-amount fractions for the VPDB reference as compiled by Tans et al 2017:

$^{13}x_{VPDB}$ = 0.010564 (eq. 4a [Tans et al. 2017]), $^{17}x_{VPDB\text{-}CO2}$ = 0.0003941 (eq. 4b [Tans et al. 2017]), $^{18}x_{VPDB\text{-}CO2}$ = 0.0020832 (eq. 4c [Tans et al. 2017]).

The resulting $x^{12}C^{16}O_{2\,std}$ of the standard gas is then compared to the $x^{12}C^{16}O_{2\,atm}$ that is expected to be observed in the atmosphere at the respective mole fraction based on the trend line through the data points presented in Figures 1a and 1b. The ratio of x_{std}/x_{atm} indicates if a larger fraction of CO_2 is detectable by the analyzer in either the standard gas or the atmosphere and therefore serves as adjustment factor assigned values for total CO_2 by the WMO-CCL. The correction term is insignificant for the FCL Primary Standards at current atmospheric background CO_2 mole fractions (<0.01 µmol/mol) but increases between 459 and 515 µmol/mol to 0.04 µmol/mol. However, for other standard gases ssigned by the WMO-CCL the ratio of x_{std}/x_{atm} can deviate differently from 1. Most standard gases of the WMO tertiary set held by the MPI-BGC GasLab, for example, has adjustment factors < 1. If not accounted for this would amount to a bias of 0.08 ppm at higher CO_2 mole fractions.

Table A4.1:

FSN	UCN	CO_2 [ppm]	$\delta^{13}C$ [‰]	$\delta^{18}O$ [‰]	$x^{12}C^{16}O_{2\,std}$	$x^{12}C^{16}O_{2\,atm}$	adj.factor	CO_2 [ppm] $_{iso\_adjusted}$
i20140054	CB09948	250.12	-7.96	-1.43	0.984141	0.984101	1.000041	250.126
i20140055	CB09944	339.36	-7.58	-5.27	0.984154	0.984127	1.000028	339.365
i20140056	CB09939	365.28	-7.71	-4.04	0.984150	0.984135	1.000016	365.283
i20140057	CB09958	389.75	-7.54	-5.57	0.984155	0.984142	1.000014	389.757
i20140058	CB09983	412.42	-8.97	-2.52	0.984157	0.984148	1.000009	412.423
i20140059	CB09952	433.83	-8.20	-1.88	0.984146	0.984155	0.999991	433.829
i20140060	CB09955	459.18	-11.69	-5.82	0.984202	0.984162	1.000040	459.200
i20140061	CB09957	482.01	-9.92	-15.74	0.984227	0.984169	1.000060	482.043

i20140062	CB09934	515.12	-12.03	-16.17	0.984253	0.984178	1.000075	515.158

In order to avoid any such measurement bias the assigned values by the CCL are adjusted to the value specified in the last column of Table A4.1.

Erroneous initial X2019 mole fraction assignments

The used CO_2 mole fractions listed in Table A4.1 are 0.02 µmol/mol lower than those listed in the QC-Report Tables 2 and 3. This is a result from an arithmetic error made when initially calculating the $x^{12}C^{16}O_2$ amount fraction that was discovered recently. While an update of this error internally in the CAL database is a moderate work effort it is a big computational work load to reprocess all continuous CO_2 measurements in the ICOS network. This requires that the correction needs to be done in collaboration with the ATC in due course.