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Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements

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Abstract. We have developed a method to calculate the fractional distribution of CO_2 across all of its component isotopologues based on measured δ^{13}C and δ^{18}O values. The fractional distribution can be used with known total CO_2 to calculate the amount of substance fraction (mole fraction) of each component isotopologue in air individually. The technique is applicable to any molecule where isotopologue-specific values are desired. We used it with a new CO_2 calibration system to account for isotopic differences among the primary CO_2 standards that define the WMO X2007 CO_2-in-air calibration scale and between the primary standards and standards in subsequent levels of the calibration hierarchy. The new calibration system uses multiple laser spectroscopic techniques to measure mole fractions of the three major CO_2 isotopologues ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, and $^{16}O^{12}C^{18}O$) individually. The three measured values are then combined into total CO_2 (accounting for the rare unmeasured isotopologues), δ^{13}C, and δ^{18}O values. The new calibration system significantly improves our ability to transfer the WMO CO_2 calibration scale with low uncertainty through our role as the World Meteorological Organization Global Atmosphere Watch Central Calibration Laboratory for CO_2. Our current estimates for reproducibility of the new calibration system are ± 0.01 µmol mol^{-1} CO_2, ± 0.2 ‰ δ^{13}C, and ± 0.2 ‰ δ^{18}O, all at 68 % confidence interval (CI).

1 Introduction

Long-term atmospheric monitoring of greenhouse gases relies on a stable calibration scale to be able to quantify small spatial gradients and temporal trends. Small changes in trends and spatial gradients result from realignments in the strengths of emissions ("sources") and removals ("sinks") of greenhouse gases. Inconsistent propagation of the scale to atmospheric measurements would give biased results from one monitoring station or network to the next that would be attributed incorrectly to sources/sinks by atmospheric transport models. Preventing biased results from various national monitoring networks enables improved understanding of the carbon cycle and its response to human intervention and climate change. It has now become even more important as countries have pledged emissions reductions. The capability to independently and transparently verify emission reductions could be helpful for creating trust in the agreements.

The World Meteorological Organization Global Atmosphere Watch (WMO GAW) program facilitates cooperation and data sharing among participating national monitoring programs. Atmospheric data collected over small regional scales are difficult to interpret without global coverage that provides boundary conditions and also insight into influences outside of the region. WMO GAW sets stringent compatibility goals so that measurements from independent laboratories can be combined in scientific studies. This greatly enhances the value of the individual data sets since it allows processes occurring within the region to be better distinguished from processes external to that region. In combining data sets it is imperative that systematic biases between the monitoring networks be small enough that they do not influence scientific interpretation of patterns and strengths of sources and sinks. For CO_2, the consensus of the scientific community is that network biases should be below 0.1 µmol mol^{-1} in the Northern Hemisphere but less than 0.05 µmol mol^{-1} in the Southern Hemisphere, where atmospheric gradients are smaller (WMO, 2016). One initial requirement to accomplishing this network compatibility goal is that measurements be comparable, that is, that each independent laboratory use a single common calibration scale. The use of a single calibration scale makes spatial gradients and temporal changes insensitive to large components in the full uncertainty budget of the scale itself. The calibration scale must be maintained indefinitely to ensure that measurements from various organizations are compatible and that measurements over long timescales can be directly compared to infer rates of changes. The WMO GAW has designated a single laboratory as the Central Calibration Laboratory (CCL), whose mission is to maintain a stable reference scale over time and to disseminate it to other organizations with very low uncertainty (WMO, 2016). The WMO GAW program has two ways to help individual laboratories maintain close ties to the WMO scale. One is a "round-robin" comparison where calibrated cylinders are sent from the CCL to individual laboratories. The values assigned by the CCL are unknown to the laboratories, and they measure them as unknowns. At the end all values are compared with the values assigned by the CCL. This occurs once every few years. The second method is the establishment of several World Calibration Centers (WCCs). Each of them provides assistance in their own region with general quality control of air measurements and calibrations.

The WMO X2007 CO_2 in air calibration scale is maintained and propagated by the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory's Global Monitoring Division in its role as the WMO GAW CCL for CO_2. The scale is defined by 15 primary standards covering the range 250–520 µmol mol^{-1}. The primary standards are modified real-air standards made in the early 1990s by filling cylinders with dried ($H_2O < 2$ µmol mol^{-1}) natural air at Niwot Ridge, CO, USA, a remote site at approximately 3040 m a.s.l. in the Rocky Mountains. It typically is exposed to clean tropospheric air and is only occasionally influenced by local sources. CO_2 abundances of the primary standards were adjusted either by scrubbing CO_2 from a portion of the natural air using a trap with sodium-hydroxide-coated silica to lower the CO_2 or by spiking with a mixture of CO_2 in air (approximately 10 %) to raise it. This differs slightly from the current practice of targeting lower-than-local-ambient CO_2 by diluting with ultrapure air, CO_2 nominally < 1 µmol mol^{-1} (Scott Marrin Inc., Riverside CA, USA) (Kitzis, 2009).

The assigned values of the primary standards come from repeated (approximately every 2 years) manometric determinations of the primary standards. The manometer, described fully in Zhao et al. (1997), essentially measures the CO_2 mole fraction by accurate measurement of pressure and temperature (both traceable to the International System of Units (SI)) of a whole-air sample and then of pure CO_2 extracted from the whole-air sample in fixed volumes. The manometer is enclosed in an oven capable of maintaining a constant temperature (within ±0.01 °C). A 6 L volume borosilicate glass bulb (the large volume) is flushed with the dried whole-air sample (dew point < -70 °C), and the pressure and temperature are measured after the large volume temperature equilibrates with the oven. CO_2 plus N_2O and trace amounts of H_2O are cryogenically extracted from the whole-air sample using two liquid nitrogen cold traps. CO_2 and N_2O are then cryogenically distilled from H_2O and transferred to a ~ 10 mL cylindrical glass vessel (the small volume). Pressure and temperature of the small volume are measured after the oven temperature has stabilized following the transfer. The volume ratio of the small to large volumes, determined by an offline sequential volume expansion experiment, is used with the measured temperatures and pressures to calculate the ratio of moles of CO_2 (corrected for the N_2O) to total moles of air in the sample using the virial equation of state. Uncertainty of the method is approximately ±0.1 µmol mol^{-1} (68 % confidence interval (CI)) at 400 µmol mol^{-1} (Zhao et al., 2006; Hall et al., 2017).

The subject of this paper is the transfer of the scale to lower-level standards and its uncertainty. We do not discuss the total uncertainty of the primary scale itself. It is described in a separate paper (Hall et al., 2017). The transfer of the scale from primary to secondary standards and hence to tertiary standards (which are used as working standards by NOAA and delivered to other organizations) has been done historically using nondispersive infrared absorption (NDIR) spectroscopy. The secondary standards are used to prolong the lifetime of the primary standards. The current primary standards have been in use for nearly 25 years and provide a consistent scale over that time period. All measurements by NOAA and WMO GAW contributing programs are directly traceable to this single set of primary standards through a strict hierarchy of calibration.

The transfer of the scale from primary to secondary standards has typically been done using a subset of three or four primary standards rather than the entire set of 15 primary standards. This was done because we wanted to perform a local curve fit of the nonlinear NDIR response while also minimizing use of the primary standards. The subset of primary standards chosen was a function of the expected CO_2 in the secondary standards and was designed to closely bracket the expected values with a small range of CO_2 in the primary standards. The relatively large uncertainty of the individual manometrically assigned values would potentially introduce significant biases due to the use of subsets of primary standards. To prevent these biases, the individual manometrically assigned values of the primary standards were corrected based on the residuals to a consistency fit of almost all primary standards (usually without the highest and the lowest primary) run on the NDIR instrument. The re-assigned values (average manometer value minus the residual) were assumed to be the best assigned value for the primary standards. This in theory should allow the use of subsets of the primary standards when transferring the scale from primary to secondary. In practice, as will be shown, there are still possible biases due to the grouping of primary standards based on expected CO_2 of the secondary standards. Tertiary standards were calibrated similarly against closely spaced subsets of secondary standards that bracketed the expected values of the tertiary standards.

New analytical methods developed over the last several years have greatly improved the ability of monitoring stations to measure CO_2. These new analytical techniques and improved diligence of monitoring network staff are pushing the uncertainties of measurements lower and improving the network compatibility. Current reproducibility of standards using the NDIR calibration system is 0.03 μmol mol^{-1} (68 % CI) (Carbon Dioxide WMO Scale, 2017). This is a significant component of the targeted 0.1 μmol mol^{-1} (or 0.05 μmol mol^{-1} in the Southern Hemisphere) network compatibility goal (WMO, 2016). Improvements in the scale propagation uncertainty would help monitoring programs achieve the compatibility goals. We have therefore undertaken to improve our calibration capabilities and to address key uncertainty components of the scale transfer. These key components are the reproducibility of the scale transfer, the potential for mole-fraction-dependent biases, and the potential issues we describe in this paper relating to the isotopic composition of the primary standards and subsequent standards in the calibration hierarchy.

2 Isotopic influence on CO_2 measurement

The WMO CO_2 mole fraction scale is defined as the number of moles of CO_2 per mole of dry air, without regard to its isotopic composition. An isotopologue of CO_2 has a specific isotopic composition. The five most abundant CO_2 isotopologues, in order of abundance, are $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, and $^{16}O^{13}C^{18}O$ (referred to in equations in this work by the HITRAN (Rothman, 2013) shorthand notations 626, 636, 628, 627, and 638, respectively). For CO_2 the two oxygen positions are equivalent due to the symmetry of the molecule, so the position of the oxygen isotopes does not matter. The abundance of the radioactive ^{14}C relative to ^{12}C is $\sim 10^{-12}$, which is too small to be of significance in this context. Analysts need to take into account differences in the relative sensitivity of their analyzers to different isotopologues (or isotopomers; see below) as well as differences in the isotopic composition of sample and standard gases.

Isotopic composition is typically measured by isotope ratio mass spectroscopy (IRMS) and is reported as the difference in the minor-isotope-to-major-isotope ratio (i.e., $^{13}C/^{12}C$) from the ratio of an accepted standard reference material. For example, the ^{13}C isotope delta value ($\delta^{13}C$) is defined as

$$\delta^{13}C = \frac{\left(^{13}C/^{12}C\right)_{\text{sample}} - \left(^{13}C/^{12}C\right)_{\text{standard}}}{\left(^{13}C/^{12}C\right)_{\text{standard}}}, \qquad (1)$$

where $(^{13}C/^{12}C)_{\text{sample}}$ and $(^{13}C/^{12}C)_{\text{standard}}$ are the ^{13}C-to-^{12}C isotopic abundance ratios for the sample and the standard reference material, respectively. The internationally accepted scale for ^{13}C is the Vienna Pee Dee Belemnite (VPDB) scale, realized as calcium carbonate. Oxygen isotopic ratios ($^{18}O/^{16}O$ or $^{17}O/^{16}O$) in CO_2 are described with a similar isotope delta notation relative to an accepted reference material. Isotope delta values for carbon and oxygen are typically reported in units of per mil (‰) by multiplying Eq. (1) by 1000. For many applications, the ^{17}O isotope is not actually measured but is assumed to follow a mass-dependent relationship with ^{18}O where $\delta^{17}O \approx 0.528 \cdot \delta^{18}O$. This approximation is adequate for the purpose of defining the oxygen isotopic effects on atmospheric CO_2 measurements. For more detailed descriptions of this relationship see Santrock et al. (1985), Assonov and Brenninkmeijer (2003), Brand et al. (2010), and references therein. Oxygen isotopes can be related to either Vienna Standard Mean Ocean Water (VSMOW) or to VPDB-CO_2, with the latter commonly used in the atmospheric CO_2 community. The VPDB-CO_2 scale relates to the CO_2 gas evolved from the calcium carbonate material itself during the reaction with phosphoric acid and accounts for oxygen fractionation that occurs during the reaction (Swart et al., 1991). In this paper all oxygen isotope values are referenced to the VPDB-CO_2 scale unless otherwise noted.

CO_2 analyzers are not equally sensitive to the isotopologues of CO_2. For example, gas chromatography where CO_2 is reduced to CH_4 and detected with a flame ionization detector (GC-FID) (Weiss, 1981) is equally sensitive to all isotopologues, whereas laser-based absorption techniques that measure an absorption line from the single major $^{16}O^{12}C^{16}O$ isotopologue are blind to all of the minor isotopologues. NDIR instruments are much more complicated in their response to the various minor isotopologues of CO_2. Most NDIR analyzers use an optical band-pass filter to limit the wavelengths of light reaching the detectors. These filters often exclude part of the absorption bands of the minor isotopologues (e.g., Tohjima et al., 2009) but are more sensitive to the $^{16}O^{13}C^{16}O$ lines within the passband because absorption of the much stronger $^{16}O^{12}C^{16}O$ lines is partially saturated. The width and shape of the transmission window of the filter are generally not identical between instruments. Tohjima et al. (2009) found significant differences in the sensitivity to the minor isotopologues between three different LI-COR NDIR analyzers. In addition, Lee et al. (2006) found the response of a Siemens ULTRAMAT 6E NDIR analyzer to be almost completely insensitive to the minor isotopologues.

The range of δ^{13}C and δ^{18}O encountered in the background atmosphere (~ -7 to -9 ‰ δ^{13}C and 2 to -2 ‰ δ^{18}O) is too small to cause a significant bias on the total CO_2 measurements with any of these techniques. At 400 µmol mol^{-1} total CO_2, neglecting δ^{13}C values leads to errors of 0.0044 µmol mol^{-1} per 1 ‰, and neglecting δ^{18}O values leads to errors of 0.0018 µmol mol^{-1} per 1 ‰. A problem arises, however, when standards with significantly different isotopic compositions from the atmosphere are used to calibrate instruments that have partial or no sensitivity to the minor isotopologues. This occurs when standards are made from fossil-fuel-sourced CO_2 (such as from combustion of oil or natural gas), which results in significant depletion in ^{13}C and ^{18}O (Andres et al., 2000; Schumacher et al., 2011).

In the past we have neglected the dependency of the NDIR response to isotopic composition during scale transfer. The manometer measurement of the primary standards is not sensitive to isotopic composition; all isotopologues are included in the total. However, the primary standards have a range of δ^{13}C and δ^{18}O values (-7 to -18 ‰ δ^{13}C and 0 to -15 ‰ δ^{18}O), with higher CO_2 standards being more depleted due to the use in the early 1990s of a spike gas that was isotopically depleted. This probably introduced a slight bias in the results when the scale was transferred to secondary standards (often with ambient isotopic values) via NDIR measurements. It was assumed that the bias was small relative to the measurement noise in the NDIR analysis.

We intend to provide standards to the atmospheric monitoring community with isotopic values similar to the background atmosphere by using natural air whenever possible. To adjust the CO_2 content in the natural air standards, the current practice is to dilute using essentially CO_2-free natural air (ultrapure air, Scott Marrin, Inc., Riverside, CA, USA) or enrich using high-CO_2 (10–20 %) spike gases with δ^{13}C ≈ -9 ‰ and δ^{18}O ≈ -30 ‰. The δ^{13}C isotopic composition of the resulting mixture is not significantly different from ambient background air. Currently, urban air highly enriched in CO_2 would have δ^{13}C values lower than the spiked standards of similar CO_2 made by us. However, the WMO scale is designed to track the slow isotopic depletion of background air as the global burden of CO_2 increases over the next decades due to burning of fossil fuels rather than approximate the composition of air influenced by local emission sources. We started using the isotopically correct spike gases in November 2011. Background atmospheric δ^{18}O is not well matched with the current spike gases or the historical spike gases (δ^{18}O ≈ -30 to -40 ‰) and does result in depleted δ^{18}O values in cylinders that are spiked to targeted values above local ambient values. It is also our goal to provide calibration results that incorporate a characterization of the main isotopologues and account for isotopic differences among the primary standards and between the primary standards and measured cylinders through the calibration hierarchy as proposed by Loh et al. (2011). This will ensure that the transfer of the WMO scale by distributing calibrated cylinders is not biased by isotopic differences and will provide users of the distributed cylinders the information required to account for isotopic effects on their own measurement systems.

3 Two different ways to define isotopic ratios and notation conventions

In order to estimate the influence of isotopic composition differences on CO_2 measurements and to develop a precise method for calibration transfer that takes isotopic composition into account, we first introduce the "mole fraction" notation for isotopic ratios in molecules. The conventional definitions of atomic isotopic ratios ($\boldsymbol{r}$) are

$$^{13}\boldsymbol{r} \overset{\text{def}}{=} \frac{^{13}\text{C}}{^{12}\text{C}} \quad ^{18}\boldsymbol{r} \overset{\text{def}}{=} \frac{^{18}\text{O}}{^{16}\text{O}} \text{ etc.}$$

As used here, the symbols ^{13}C, ^{18}O, etc. stand for amounts. It will simplify derivations below if we use isotopic ratios as amount ratios relative to all carbon, oxygen, etc., similar to mole fractions in air. We give these isotope-amount fractions the symbol "$\boldsymbol{x}$" instead of "$\boldsymbol{r}$".

$$^{13}\boldsymbol{x} \overset{\text{def}}{=} \frac{^{13}\text{C}}{^{12}\text{C}+^{13}\text{C}} \quad ^{18}\boldsymbol{x} \overset{\text{def}}{=} \frac{^{18}\text{O}}{^{16}\text{O}+^{17}\text{O}+^{18}\text{O}}$$

$$\longrightarrow {}^{16}\boldsymbol{x} = 1 - \frac{^{17}\text{O}+^{18}\text{O}}{^{16}\text{O}+^{17}\text{O}+^{18}\text{O}}.$$

These definitions lead to the following relationships:

$$^{13}\boldsymbol{x} = \frac{^{13}\boldsymbol{r}}{1+^{13}\boldsymbol{r}} \text{ and } ^{13}\boldsymbol{r} = \frac{^{13}\boldsymbol{x}}{1-^{13}\boldsymbol{x}}. \tag{2}$$

The equivalents for oxygen are

$$^{17}\boldsymbol{x} = \frac{^{17}\boldsymbol{r}}{1+^{17}\boldsymbol{r}+^{18}\boldsymbol{r}} \text{ and}$$

$$^{17}\boldsymbol{r} = \frac{^{17}\text{O}}{^{16}\text{O}} = \frac{^{17}\text{O}/(^{16}\text{O}+^{17}\text{O}+^{18}\text{O})}{^{16}\text{O}/(^{16}\text{O}+^{17}\text{O}+^{18}\text{O})} = \frac{^{17}\boldsymbol{x}}{1-^{17}\boldsymbol{x}-^{18}\boldsymbol{x}} \tag{3}$$

and similarly for $^{18}\boldsymbol{x}$ and $^{18}\boldsymbol{r}$.

From here on we will abbreviate VPDB-CO_2 as VPDB to keep the notation manageable. Using Table 1 and these conventions gives us

$$^{13}\boldsymbol{x}_{\text{VPDB}} = 0.0110564, \tag{4a}$$

$$^{17}\boldsymbol{x}_{\text{VPDB}} = 394.1 \times 10^{-6}, \tag{4b}$$

$$^{18}\boldsymbol{x}_{\text{VPDB}} = 2083.2 \times 10^{-6}. \tag{4c}$$

Isotopic ratio measurements have always been expressed in terms of their (typically) small difference from the standard reference materials, in the so-called delta notation:

$$^{13}\delta \overset{\text{def}}{=} (^{13}\boldsymbol{r}-^{13}\boldsymbol{r}_{\text{VPDB}})/^{13}\boldsymbol{r}_{\text{VPDB}} = ^{13}\boldsymbol{r}/^{13}\boldsymbol{r}_{\text{VPDB}} - 1,$$

$$\text{so that}\,{}^{13}\boldsymbol{r}-{}^{13}\boldsymbol{r}_{\text{VPDB}}={}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\delta \qquad (5)$$

and similarly for ${}^{17}\delta$ and ${}^{18}\delta$.

By analogy we define for the amount fractions $\boldsymbol{x}$

$$\begin{aligned}&{}^{13}\Delta \overset{\text{def}}{=} ({}^{13}\boldsymbol{x}-{}^{13}\boldsymbol{x}_{\text{VPDB}})/{}^{13}\text{x}_{\text{VPDB}}={}^{13}\boldsymbol{x}/{}^{13}\boldsymbol{x}_{\text{VPDB}}-1,\\ &\text{so that}\,{}^{13}\boldsymbol{x}-{}^{13}\boldsymbol{x}_{\text{VPDB}}={}^{13}\boldsymbol{x}_{\text{VPDB}}\,{}^{13}\Delta \qquad (6)\end{aligned}$$

and similarly for ${}^{17}\Delta$ and ${}^{18}\Delta$.

In the above (Eqs. 5 and 6) and the rest of this work we will express δ and Δ as small numbers, not in the "per mil" (‰) notation, in which every delta value is multiplied by 1000. For example $\delta = 0.020$ would normally be written as 20 ‰. To keep the notation economical and the paper more readable, we introduced simplified notations such as ${}^{13}\boldsymbol{r}$ and ${}^{13}\delta$ instead of $\boldsymbol{r}$ (^{13}C / ^{12}C) and δ^{13}C in equations. This produces no ambiguities. In addition, in this paper we need to distinguish between isotope-amount fractions within CO$_2$ (denoted "$\boldsymbol{x}$" above in accordance with Coplen, 2011) of isotopes (and isotopologues) from mole fraction in air. We normally denote mole fraction in air by "$\boldsymbol{x}$" or "$\boldsymbol{X}$", but here we use "$\boldsymbol{y}$" (in accordance with notation recommendations for gas mixtures; IUPAC, 2006) to distinguish mole fraction in air from isotope or isotopologue amount fraction. For example, $\boldsymbol{x}(636)$ is the amount fraction of ^{16}O^{13}C^{16}O to all isotopologues of CO$_2$, whereas $\boldsymbol{y}(636)$ is the mole fraction of the ^{16}O^{13}C^{16}O isotopologue in air.

4 Fractional abundances of isotopologues in molecules

Converting measured δ^{13}C and δ^{18}O values into ^{16}O^{13}C^{16}O and ^{16}O^{12}C^{18}O isotopologue abundances is not straightforward due to the rare ^{17}O^{12}C^{16}O and doubly substituted isotopologues. IRMS determines δ^{13}C and δ^{18}O values by measuring molecular mass 45/44 and 46/44 ratios, with appropriate corrections for interfering masses, relative to a standard reference material. These mass ratios can be used with the accepted isotopic ratios of the standard reference materials to *approximate* the abundance as amount fraction ($\boldsymbol{x}$) of the three main isotopologues in CO$_2$ using

$$\begin{aligned}&\boldsymbol{x}(636)\cong{}^{13}\boldsymbol{x},\;\; \boldsymbol{x}(628)\cong 2\cdot{}^{18}\boldsymbol{x},\;\; \text{and}\\ &\boldsymbol{x}(626)\cong 1-\boldsymbol{x}(636)-\boldsymbol{x}(628). \qquad (7)\end{aligned}$$

The oxygen abundance ratio is multiplied by a factor of 2 in Eq. (7) to convert the amount fractions from atomic abundance (i.e., ^{18}O / ^{16}O) into molecular abundance. The approximations in Eq. (7) ignore the contribution of the oxygen isotopes to $\boldsymbol{x}(636)$ and of ^{13}C to $\boldsymbol{x}(628)$, as well as the portion of the total composed of the rare isotopologues. Depending on the level of uncertainty desired, this may or may not be acceptable. As the WMO GAW CCL for CO$_2$, we feel obligated to minimize biases in the CO$_2$ calibration scale, and therefore we will correctly account for the apportionment of CO$_2$ through all isotopologues. The same technique was developed independently by Flores et al. (2017) for use in calibrating spectroscopic instruments for δ^{13}C and δ^{18}O measurements. Here our focus is on total CO$_2$ measurements that account for isotopic differences between standards.

We start by assuming a purely statistical distribution of ^{13}C, ^{18}O, and other atoms when putting together a molecule starting from atomic amount fractions as given for standard reference materials (Table 1), namely, that the probability of picking a particular isotope is not affected by what is picked before or later. In general the other picks can affect the probability a little (called "clumped" isotopes), so that the thermodynamic abundances are slightly different from the statistical distribution. We will ignore that for now and construct a purely statistical baseline distribution for the reference. It is important to note that thermodynamic and kinetic fractionation effects are reflected in actual measured delta values and fractionation factors relative to the agreed-upon reference material. Thus the probability of picking a ^{13}C atom for a carbon position is defined as simply ${}^{13}\boldsymbol{x}$. However, a molecule may have more than one position for C, O, N, etc. For example, suppose there are N chemical positions for a particular atom in a molecule and we want to define the probability of M of those positions being filled with one particular isotope (denoted isotope a). If the locations of the M, as a subset of N, do not matter, as is the case for symmetrical molecules like CO$_2$ and CH$_4$, we could call the N positions equivalent. In that case the probability is

$$P = \binom{\text{N}}{\text{M}}\cdot \boldsymbol{x}_a^M \cdot \boldsymbol{x}_b^{N-M}. \qquad (8)$$

$\boldsymbol{x}_a$ is the amount fraction of isotope a; $\boldsymbol{x}_b$ is the amount fraction of other isotopes ($\boldsymbol{x}_b = 1-\boldsymbol{x}_a$). The first term in Eq. (8) is the statistical weight, which equals the number of combinations (a statistical term, the order of picking the M does not matter) of M out of N, given as

$$\frac{N!}{M!(N-M)!} \overset{\text{def}}{=} \binom{\text{N}}{\text{M}}. \qquad (9)$$

$N!$ is the factorial notation, $N! \overset{\text{def}}{=} 1\cdot 2\cdot 3\cdot \ldots\ldots (N-1)\cdot N$, with the special case $0! \overset{\text{def}}{=} 1$

For example, there are two equivalent positions for a single ^{18}O in CO$_2$, namely ^{18}O^{12}C^{16}O and ^{16}O^{12}C^{18}O, jointly denoted as "628" (one ^{16}O, one ^{12}C, one ^{18}O), so that the statistical weight is

$$\binom{2}{1} = \frac{2!}{1!\cdot(2-1)!} = 2.$$

Or for methane, a single or double substitution of deuterium (^{2}H) for ^{1}H has respective statistical weights:

$$\binom{4}{1} = \frac{4!}{1!\cdot(4-1)!} = 4 \quad \binom{4}{2} = \frac{4!}{2!\cdot(4-2)!} = 6.$$

It should be noted that whether positions can be considered equivalent depends on the symmetry of the molecule and the

Table 1. Isotopic ratios of international standard reference materials.

Reference material	Ratio	Reference
$(^{18}O\,/\,^{16}O)_{VSMOW}$	0.0020052	Baertschi (1976)
$(^{17}O\,/\,^{16}O)^{a}_{VSMOW}$	0.00038672	Assonov and Brenninkmeijer (2003)
$(^{18}O\,/\,^{16}O)_{VPDB-CO_2}$	0.00208835	Allison et al. (1995)
$(^{17}O\,/\,^{16}O)^{b}_{VPDB-CO_2}$	0.00039511	Assonov and Brenninkmeijer (2003)
$(^{13}C\,/\,^{12}C)^{c}_{VPDB}$	0.011180	Zhang et al. (1990)
$(^{2}H/^{1}H)_{VSMOW}$	0.00015576	Hagemann et al. (1970)
$(^{15}N\,/\,^{14}N)_{air\text{-}N2}$	0.0036765	Junk and Svec (1958); Coplen et al. (1992)

[a] In the literature, it is possible to find different $^{17}O\,/\,^{16}O$ ratio values for these standard reference materials than those given here. However, for the determination of ^{17}O isotopic effects on atmospheric CO_2 measurements, differences from the values given in this table are insignificant. [b] This $^{17}O\,/\,^{16}O$ ratio of VPDB-CO_2 is consistent with $[(^{17}O\,/\,^{16}O)_{VPDB-CO_2}\,/\,(^{17}O\,/\,^{16}O)_{VSMOW}] = [(^{18}O\,/\,^{16}O)_{VPDB-CO_2}\,/\,(^{18}O\,/\,^{16}O)_{VSMOW}]^{0.528}$. [c] We used the revised value of Zhang et al. (1990). For the determination of ^{13}C isotopic effects on atmospheric CO_2 measurements the difference between this value and the original value (0.0112372; Craig, 1957) is insignificant.

measurement method. For example for nitrous oxide the two positions for N in NNO would be equivalent when mass 45 (one ^{14}N, one ^{15}N, one ^{16}O) is measured in a mass spectrometer, but they are not when an optical absorption method is used because the spectrum of $^{14}N^{15}N^{16}O$ is different from $^{15}N^{14}N^{16}O$. In the latter case we need to keep separate track of the probabilities, denoted below as "P", of these two isotopomers. Isotopomers have the same number of specific isotopes, but they differ in their position in the molecule.

The probability for any particular CO_2 isotopologue is the product of the probability of picking the carbon isotope and the probability of picking the oxygen isotopes. Each of these probabilities is determined using Eq. (8). For example, the probability for the $^{16}O^{13}C^{18}O$ isotopologue is the probability of picking one ^{13}C isotope for one carbon position times the probability of picking one ^{18}O isotope for one of the two oxygen positions and one ^{16}O for the other.

The equations below give the probabilities for individual CO_2 isotopologues. When the isotopic compositions of the standard reference materials (VPDB in Table 1) are filled in, we obtain the numbers after the "⟶" sign.

$$P(626) = (1-{}^{13}\boldsymbol{x}) \cdot (1-{}^{17}\boldsymbol{x}-{}^{18}\boldsymbol{x})^2 \longrightarrow 0.98404985 = 1 - 0.01595015 \tag{10}$$

$$P(636) = {}^{13}\boldsymbol{x} \cdot (1-{}^{17}\boldsymbol{x}-{}^{18}\boldsymbol{x})^2 \longrightarrow 0.011001688 \tag{11}$$

$$P(628) = (1-{}^{13}\boldsymbol{x}) \cdot 2 \cdot {}^{18}\boldsymbol{x} \cdot (1-{}^{17}\boldsymbol{x}-{}^{18}\boldsymbol{x}) \longrightarrow 0.0041101273. \tag{12}$$

The sum of the above three major abundances is $0.99916166 = 1 - 0.00083834$.

$$P(627) = (1-{}^{13}\boldsymbol{x}) \cdot 2 \cdot {}^{17}\boldsymbol{x} \cdot (1-{}^{17}\boldsymbol{x}-{}^{18}\boldsymbol{x}) \longrightarrow 0.000777554. \tag{13}$$

The sum of the above four major abundances is $0.99993922 = 1 - 0.00006078$.

$$P(638) = {}^{13}\boldsymbol{x} \cdot 2 \cdot {}^{18}\boldsymbol{x} \cdot (1-{}^{17}\boldsymbol{x}-{}^{18}\boldsymbol{x}) \longrightarrow 4.59513 \times 10^{-5}$$

and so on, with progressively smaller probabilities. The sum of all probabilities equals 1, which was verified digitally in double precision. This example was for VPDB, but in any population of CO_2 molecules (i.e., in a sample or standard cylinder) probabilities determined from the isotope-amount fractions of the population equate to the fractional abundance of each isotopologue.

5 An expression for potential effects of isotopic mismatches on measurements of CO_2

In this section we derive some practical expressions for biases and corrections, resulting from isotopic mismatches if they are ignored, for the case of CO_2. Similar considerations apply to other greenhouse gases such as CH_4 and N_2O. Such corrections can be generally applied to CO_2 measurements if desired. The unknown quantity of CO_2 in air that we intend to measure is called "measurand". It can be a real-air sample or an intermediate transfer standard. Here we give an example for an instrument that quantifies the mole fraction of total CO_2 in air, denoted $\boldsymbol{y}_{CO_2}$, by measuring only one isotopologue, namely $^{16}O^{12}C^{16}O$. We assume that the instrument is calibrated by a CO_2 standard with amount fractions $^{13}\boldsymbol{x}_{VPDB}$ and $^{18}\boldsymbol{x}_{VPDB}$ of the two main isotopologues, corresponding to the international VPDB reference points for ^{13}C and ^{18}O. In almost all cases deviations of $^{17}\boldsymbol{x}$ from VPDB are tightly correlated with deviations of $^{18}\boldsymbol{x}$ from VPDB. The deviation of total CO_2 from being proportional to $P(626)$ due to inconsistencies of $^{13}\boldsymbol{x}$, $^{17}\boldsymbol{x}$, and $^{18}\boldsymbol{x}$ between the measurand and VPDB, using Eq. (10), is

$$\Delta P(626) \overset{\text{def}}{=} P(626) - P_{VPDB}(626) =$$

$$\frac{\partial P\,(626)}{\partial^{13}\boldsymbol{x}}\left({}^{13}\boldsymbol{x}-{}^{13}\boldsymbol{x}_{\mathrm{VPDB}}\right)+\frac{\partial P\,(626)}{\partial^{17}\boldsymbol{x}}\left({}^{17}\boldsymbol{x}-{}^{17}\boldsymbol{x}_{\mathrm{VPDB}}\right)$$
$$+\frac{\partial P\,(626)}{\partial^{18}\boldsymbol{x}}\left({}^{18}\boldsymbol{x}-{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}\right). \qquad (14)$$

The above are the first terms of a Taylor expansion around $P_{\mathrm{VPDB}}(626)$. Inserting the first derivatives and using Eq. (6) gives

$$\Delta P\,(626)=-\left(1-{}^{17}\boldsymbol{x}_{\mathrm{VPDB}}-{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}\right)^{2}\left({}^{13}\boldsymbol{x}_{\mathrm{VPDB}}{}^{13}\Delta\right)$$
$$-2\left(1-{}^{13}\boldsymbol{x}_{\mathrm{VPDB}}\right)\left(1-{}^{17}\boldsymbol{x}_{\mathrm{VPDB}}-{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}\right)$$
$$\left({}^{17}\boldsymbol{x}_{\mathrm{VPDB}}{}^{17}\Delta+{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}{}^{18}\Delta\right). \qquad (15)$$

If ${}^{13}\Delta$ is positive, the air to be measured has a higher ${}^{13}\mathrm{C}\,/\,{}^{12}\mathrm{C}$ ratio than VPDB. Therefore $P(626)$ is slightly lower than it is for VPDB, and the relative correction in the mole fraction assigned to the measured air will have to be positive, of opposite sign to the relative error of $P(626)$:

$$\frac{\Delta \boldsymbol{y}_{\mathrm{CO_2}}}{\boldsymbol{y}_{\mathrm{CO_2}}}=-\frac{\Delta P\,(626)}{P\,(626)}=\frac{{}^{13}\boldsymbol{x}_{\mathrm{VPDB}}{}^{13}\Delta}{\left(1-{}^{13}\boldsymbol{x}_{\mathrm{VPDB}}\right)}$$
$$+\frac{2\left({}^{17}\boldsymbol{x}_{\mathrm{VPDB}}{}^{17}\Delta+{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}{}^{18}\Delta\right)}{\left(1-{}^{17}\boldsymbol{x}_{\mathrm{VPDB}}-{}^{18}\boldsymbol{x}_{\mathrm{VPDB}}\right)}. \qquad (16)$$

We note here that we could have used a ${}^{16}\mathrm{O}{}^{13}\mathrm{C}{}^{16}\mathrm{O}$ line for quantifying $\boldsymbol{y}_{\mathrm{CO_2}}$, but an analogous derivation for $\Delta P(636)/P(636)$ shows that it is 90 times more sensitive to isotopic errors or mismatches.

Using Eqs. (2) and (3) gives

$$\frac{\Delta \boldsymbol{y}_{\mathrm{CO_2}}}{\boldsymbol{y}_{\mathrm{CO_2}}}={}^{13}\boldsymbol{r}_{\mathrm{VPDB}}{}^{13}\Delta+2\left({}^{17}\boldsymbol{r}_{\mathrm{VPDB}}{}^{17}\Delta+{}^{18}\boldsymbol{r}_{\mathrm{VPDB}}{}^{18}\Delta\right). \qquad (17)$$

Generally, one is not making atmospheric CO$_2$ measurements with standards that have isotopic abundances for C and O exactly like VPDB. Because the linear Eq. (17) applies to the measurement of a transfer standard itself as well as to an air sample, we can give an expression for corrections to be made when the standard (subscript "st") has an isotopic composition different from air but not equal to VPDB:

$$\frac{\Delta \boldsymbol{y}_{\mathrm{CO_2}}}{\boldsymbol{y}_{\mathrm{CO_2}}}={}^{13}\boldsymbol{r}_{\mathrm{VPDB}}\left({}^{13}\Delta_{\mathrm{air}}-{}^{13}\Delta_{\mathrm{st}}\right)$$
$$+2\left[{}^{17}\boldsymbol{r}_{\mathrm{VPDB}}\left({}^{17}\Delta_{\mathrm{air}}-{}^{17}\Delta_{\mathrm{st}}\right)\right.$$
$$\left.+{}^{18}\boldsymbol{r}_{\mathrm{VPDB}}\left({}^{18}\Delta_{\mathrm{air}}-{}^{18}\Delta_{\mathrm{st}}\right)\right]. \qquad (18)$$

In the Appendix we derive the following very close approximation to Eq. (18) in which the Δ values have been replaced by the familiar δ values:

$$\Delta \boldsymbol{y}_{\mathrm{CO_2}}=\boldsymbol{y}_{\mathrm{CO_2}}\left[0.01106\left({}^{13}\delta_{\mathrm{air}}-{}^{13}\delta_{\mathrm{st}}\right)\right.$$
$$\left.+2\cdot 0.00230\left({}^{18}\delta_{\mathrm{air}}-{}^{18}\delta_{\mathrm{st}}\right)\right]. \qquad (19)$$

This is an expression for CO$_2$ corrections when only the ${}^{16}\mathrm{O}{}^{12}\mathrm{C}{}^{16}\mathrm{O}$ isotopologue is used to measure $\boldsymbol{y}_{\mathrm{CO_2}}$, and we are using VPDB scales. As an example, if we use a standard with CO$_2$ made from natural gas, it could have ${}^{13}\delta_{\mathrm{st}}=-0.045$ and ${}^{18}\delta_{\mathrm{st}}=-0.017$ on the VPDB scales, whereas air has ${}^{13}\delta_{\mathrm{air}}\cong-0.008$ and ${}^{18}\delta_{\mathrm{air}}\cong 0.000$. Assuming $\boldsymbol{y}_{\mathrm{CO_2}}=400\,\mu\mathrm{mol\,mol^{-1}}$, then $\Delta\,\boldsymbol{y}=0.164+0.031=0.195\,\mu\mathrm{mol\,mol^{-1}}$. ${}^{13}\delta_{\mathrm{air}}$ is higher than ${}^{13}\delta_{\mathrm{st}}$, so that the ${}^{16}\mathrm{O}{}^{12}\mathrm{C}{}^{16}\mathrm{O}$ abundance of the standard is higher than assumed, resulting in the air measurement being too low. Therefore an upward correction is needed for ${}^{13}\mathrm{C}$ and likewise for ${}^{18}\mathrm{O}$.

6 Practical calculations for definition and propagation of the CO$_2$ calibration scale

Equations (18) and (19) give the correction required when only the ${}^{16}\mathrm{O}{}^{12}\mathrm{C}{}^{16}\mathrm{O}$ isotopologue is used to determine $\boldsymbol{y}_{\mathrm{CO_2}}$ as a function of the isotopic differences between the sample and a single standard. However, most CO$_2$ measurements are made vs. a suite of standards that may have various isotopic compositions, and the isotopic compositions may be a function of CO$_2$ (as is the case for the primary CO$_2$ standards used by the WMO GAW CCL). In this case the calibration curve that defines the response of the analyzer may incorporate a systematic error, making the idea of a simple "correction" impractical. Equations (18) and (19) can be used to estimate the potential offsets due to sample–standard isotopic differences but are not practical for making corrections when multiple standards are used. Therefore, we must instead use a calibration approach that fully accounts for the isotopic composition of the standards rather than using a post-measurement correction.

We have taken the approach of decomposing the total CO$_2$ in the primary standards, as defined by manometric measurements, into individual isotopologue mole fractions in air based on measured $\delta^{13}\mathrm{C}$ and $\delta^{18}\mathrm{O}$ values. The $\delta^{13}\mathrm{C}$ and $\delta^{18}\mathrm{O}$ values are determined by IRMS by the Stable Isotope Laboratory, Institute of Arctic and Alpine Research, University of Colorado, Boulder (INSTAAR), on their own realization of the VPDB scales. The current scales used by INSTAAR were set using NBS-19 and NBS-20 (carbonates) and VSMOW, GISP, and SLAP (waters) (Trolier et al., 1996). These isotopologue-specific mole fractions in air of the standards are used to calibrate laser spectroscopic instruments for the three major CO$_2$ isotopologues (${}^{16}\mathrm{O}{}^{12}\mathrm{C}{}^{16}\mathrm{O}$, ${}^{16}\mathrm{O}{}^{13}\mathrm{C}{}^{16}\mathrm{O}$, and ${}^{16}\mathrm{O}{}^{12}\mathrm{C}{}^{18}\mathrm{O}$) individually. The three major isotopologues in unknown cylinders are measured relative to these isotopologue-specific calibration curves. The isotopologue mole fractions in air of the unknowns are then recombined into total CO$_2$, conventional $\delta^{13}\mathrm{C}$, and $\delta^{18}\mathrm{O}$ values while properly accounting for the non-measured rare isotopologues.

A great advantage of our method is that it uses multiple standards covering a range of values to create a scale. "Scale contraction" can result from extrapolating from a single standard reference, and mass spectrometer measurements have suffered from that. We do not have such "contraction" because we calibrate with multiple standards over the full range of interest instead of using a single point. Having such isotopologue-specific response curves over a large range also opens the intriguing possibilities of making CO_2 isotopic scales that are traceable to SI and improving our understanding of VPDB and its relation to LSVEC. This may be beyond the scope of our laboratory, but we offer it as an interesting aside.

Suppose we have one or more instruments measuring each isotopologue ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{18}O$, and perhaps also $^{16}O^{12}C^{17}O$) individually. The response of the instrument(s) for each of the isotopologues needs to be calibrated separately. How often such calibrations need to be repeated depends on the instrument. For this purpose we need to have a series of reference gas standards with well-defined total CO_2 ($\boldsymbol{y}_{CO_2}$) and with known conventional δ values for the isotopic ratios. Equations (10)–(13) can be used to convert that information to the fractional abundances of the isotopologues, by first writing them in terms of conventional delta values by using relations (2) and (3) and then writing $\boldsymbol{r}_{\text{sample}}$ as $\boldsymbol{r}_{\text{VPDB}}(1+\delta)$ (see Eq. 5).

$$P\,(626) = \frac{1}{1+{}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta)} \times \frac{1}{\left[1+{}^{17}\boldsymbol{r}_{\text{VPDB}}(1+{}^{17}\delta)+{}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta)\right]^2} \quad (20)$$

$$P\,(636) = \frac{{}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta)}{1+{}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta)} \times \frac{1}{\left[1+{}^{17}\boldsymbol{r}_{\text{VPDB}}(1+{}^{17}\delta)+{}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta)\right]^2} \quad (21)$$

$$P\,(628) = \frac{1}{1+{}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta)} \times \frac{2 \cdot {}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta)}{\left[1+{}^{17}\boldsymbol{r}_{\text{VPDB}}(1+{}^{17}\delta)+{}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta)\right]^2} \quad (22)$$

$$P\,(627) = \frac{1}{1+{}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta)} \times \frac{2 \cdot {}^{17}\boldsymbol{r}_{\text{VPDB}}(1+{}^{17}\delta)}{\left[1+{}^{17}\boldsymbol{r}_{\text{VPDB}}(1+{}^{17}\delta)+{}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta)\right]^2}. \quad (23)$$

If $\delta^{17}O$ has not been measured, we approximate $\delta^{17}O = 0.528 \cdot \delta^{18}O$ to determine the fractional abundances above.

The fractional abundances (Eqs. 20–23) are converted into mole fractions in dry air by multiplying with the total mole fraction of CO_2 in dry air ($\boldsymbol{y}_{CO_2}$). The isotopologue mole fractions in air are written as $\boldsymbol{y}(626)$, $\boldsymbol{y}(636)$, etc. In other words, we have $\boldsymbol{y}(626) = \boldsymbol{y}_{CO_2} \cdot P(626)$ and similar for all isotopologues.

A series of standards can in this way be used to calibrate the instrument response for each isotopologue individually. With these response functions we can then assign mole fractions in air to the isotopologues of the unknown gas mixtures that are being measured, $\boldsymbol{y}(626)_{\text{unk}}$, $\boldsymbol{y}(636)_{\text{unk}}$, etc.

Then we need to convert the measured isotopologue mole fractions of the unknown ($\boldsymbol{y}(626)_{\text{unk}}$, $\boldsymbol{y}(636)_{\text{unk}}$, and $\boldsymbol{y}(628)_{\text{unk}}$) back to standard delta notation using Eqs. (20)–(23) as follows:

$$\frac{\boldsymbol{y}(636)_{\text{unk}}}{\boldsymbol{y}(626)_{\text{unk}}} = \frac{P\,(636)}{P\,(626)} = {}^{13}\boldsymbol{r}_{\text{VPDB}}(1+{}^{13}\delta) \longrightarrow {}^{13}\delta = \frac{\boldsymbol{y}(636)_{\text{unk}}}{{}^{13}\boldsymbol{r}_{\text{VPDB}} \cdot \boldsymbol{y}(626)_{\text{unk}}} - 1 \quad (24)$$

$$\frac{\boldsymbol{y}(826)_{\text{unk}}}{\boldsymbol{y}(626)_{\text{unk}}} = \frac{P\,(826)}{P\,(626)} = 2 \cdot {}^{18}\boldsymbol{r}_{\text{VPDB}}(1+{}^{18}\delta) \longrightarrow {}^{18}\delta = \frac{\boldsymbol{y}(826)_{\text{unk}}}{2 \cdot {}^{18}\boldsymbol{r}_{\text{VPDB}} \cdot \boldsymbol{y}(626)_{\text{unk}}} - 1 \quad (25)$$

and similarly for $\delta^{17}O$. If $\delta^{17}O$ has not been measured, we assume that $\delta^{17}O = 0.528 \cdot \delta^{18}O$.

The total CO_2 in dry air is given by

$$y_{CO_2,\text{unk}} = \frac{\boldsymbol{y}(626)_{\text{unk}} + \boldsymbol{y}(636)_{\text{unk}} + \boldsymbol{y}(628)_{\text{unk}} + \boldsymbol{y}(627)_{\text{unk}}}{P(626)_{\text{unk}} + P(636)_{\text{unk}} + P(628)_{\text{unk}} + P(627)_{\text{unk}}}. \quad (26)$$

Dividing by the sum of the probabilities (P) corrects the sum of the measured isotopologues for the unmeasured rare isotopologues. The sum of the probabilities in Eq. (26) would equal 0.99993922 if the isotopic ratios were equal to the standard reference materials for carbon and oxygen. This adds $0.024\,\mu\text{mol mol}^{-1}$ to the sum of the measured isotopologues, assuming $\boldsymbol{y}_{CO_2} \sim 400\,\mu\text{mol mol}^{-1}$. The correction in Eq. (26) that applies for actual unknowns will in general be *very* slightly different from 0.99993922 (the sum of the four major molecular abundances assuming VPDB values). We calculate actual P values for the unknown using Eqs. (20)–(23) with the δ values from Eqs. (24)–(25) and then use those in Eq. (26) instead of the standard reference material values to account for this small discrepancy, but it is not necessary in most cases.

7 Analytical methods

NOAA's new CO_2 calibration system is based on multiple laser spectroscopic techniques. It uses a combination of cavity ring-down spectroscopy (CRDS, Picarro, Inc., $CO_2/CH_4/H_2O$ analyzer, model number G2301) (O'Keefe and Deacon, 1988; Crosson, 2008), off-axis integrated cavity output spectroscopy (ICOS, Los Gatos Research, Inc., carbon dioxide isotope analyzer, CCIA-46-EP, model number 913-0033-0000) (Paul et al., 2001; Baer et al., 2002), and quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS, Aerodyne Research, Inc., carbon dioxide isotope analyzer, model QC-TILDAS-CS) (Tuzson et al., 2008; McManus et al., 2015).

The CRDS instrument measures a single absorption line from the $^{16}O^{12}C^{16}O$ isotopologue at 1603 nm (Crosson, 2008). For most of the data presented here, the instrument operated in an enhanced CO_2 mode where it did not measure CH_4 and instead focused exclusively on the CO_2 absorption line with periodic measurements of H_2O as a diagnostic. However, we have since determined this enhanced CO_2 mode does not improve the reproducibility of CO_2 measurements. We are currently testing the ability to do CH_4 calibrations at the same time as the CO_2 calibrations using the standard operating mode of the CRDS.

The ICOS and QC-TILDAS analyzers both measure absorption lines of $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, and $^{16}O^{12}C^{18}O$ isotopologues individually (using lines at 2309 cm^{-1}). Both analyzers also measure the $^{16}O^{12}C^{17}O$ isotopologue, but we cannot independently calibrate this measurement because our standards have not been measured for $\delta^{17}O$. We assume that $\delta^{17}O$ follows the mass-dependent fractionation relative to $\delta^{18}O$. Deviations from this relationship would be small and be insignificant when calculating total CO_2. The two analyzers have comparable performance and serve as backups for each other since only one is installed and used at a time. In the following discussion they are designated collectively as the CO_2 isotope analyzer. The $^{16}O^{12}C^{16}O$ measurement in the isotope analyzers uses a weak absorption line to match the measured absorption with the low-abundance minor isotopologues. They are therefore not as precise as the measurement on the CRDS. The $^{16}O^{12}C^{16}O$ measurement from the isotope analyzer is not used to calculate total CO_2 but is used as $\boldsymbol{y}(626)_{\text{unk}}$ in the calculation of $\delta^{13}C$ and $\delta^{18}O$ (see Eqs. 24 and 25 in the discussion above). Using this "internal" $\boldsymbol{y}(626)_{\text{unk}}$ measurement gives slightly more precise $\delta^{13}C$ and $\delta^{18}O$ results than using the "external" $\boldsymbol{y}(626)_{\text{unk}}$ measurement from the CRDS instrument since it accounts for some instrument bias common to both the $^{16}O^{12}C^{16}O$ and the $^{16}O^{13}C^{16}O$ and $^{16}O^{12}C^{18}O$ isotopologue measurements. $\boldsymbol{y}(626)_{\text{unk}}$ from the CRDS system is used in Eq. (26) to calculate total CO_2.

Figure 1 is a plumbing diagram for the CO_2 calibration system. The system uses the CRDS analyzer plus one of the CO_2 isotope analyzers. All measurements on the system are relative to a reference tank of compressed, unmodified natural air. A four-port, two-position switching valve (Valco Instruments Co, Inc. (VICI), model EUDA-24UWE) is used to send sample and standard gas to one analyzer while the other analyzer simultaneously measures the reference tank. Sample and standard tanks are introduced to the system via two identical sample manifolds composed of 16-port multi-position selection valves (VICI, model EUTA-2CSD16MWE). A four-port multi-position stream selection valve (VICI, model EUTA-2SD4MWE) is used to select either manifold A or B, or, optionally, for expansion to a third manifold C. A plugged port on the manifold selection valve is used as a safe off port during shutdown. Sample/standard and reference gas pressures are controlled at 760 ± 1 torr by two electronic pressure controllers with integrated mass flow meters (MKS Instruments, type 649B electronic pressure controller, model number 649B00813T13C2MR). The analyzers themselves control their internal cell pressures. However, controlling the inlet pressure prevents large inlet pressure swings due to inconsistent cylinder regulator set points and allows the internal pressure control to be more consistent. All three instruments are continuous-flow instruments, so an idle gas is provided through a three-way solenoid valve (Parker, model 009-0143-900) just upstream of the instrument inlet. This idle gas is partially dried room air drawn through a Nafion drier (Perma Pure LLC.) for extended system idle time (e.g., on weekends) but is a cylinder of dried ambient natural air (dew point $\sim -80\,°C$) for short idle times during and just prior to actual calibrations. This cylinder ensures that the system downstream of the water traps does not get exposed to elevated levels of water vapor during short idle times between analyses. Each analyzer has a H_2O trap upstream of the inlet that normalizes any differences in water content among cylinders analyzed. These traps are 3.2 mm OD stainless-steel tubing loops immersed in a $-78\,°C$ ethanol bath (SP Scientific Inc., MultiCool, model number MC480A). Both analyzers have individual sampling pumps to pull gas through the sample cell at partial vacuum. All tubing in the system is 3.2 or 1.6 mm OD stainless steel.

The flow rates are set to 130–150 mL min^{-1} by using a critical flow orifice downstream of the isotope analyzer cell or by partially closing the upstream solenoid valve in the CRDS instrument and relying on a stable pressure at the instrument inlet. The analysis sequence starts with a 4 min flush of the sample/standard regulator (and sample/standard electronic pressure controller) and then alternates reference and sample through the two analyzers for eight cycles before moving to the next sample or standard. Each measurement cycle is 2.5 min of flushing and a 30 s signal average.

8 Calibration and system performance

Analyzers are calibrated approximately every 2 weeks in an offline calibration mode using a suite of 14 secondary standards, covering the range 250 to 600 $\mu mol\,mol^{-1}$ total CO_2. The system is calibrated routinely to 600 $\mu mol\,mol^{-1}$ in expectation of a scale expansion in 2017. Each isotopologue is calibrated independently after decomposing the standard's total CO_2 into its component isotopologue mole fractions using the method discussed above. The secondary standards have assigned total CO_2 values by calibration against the entire set of primary standards (plus two additional standards that will extend the scale to 600 $\mu mol\,mol^{-1}$) in an analogous manner as described here. This is a significant change from our previous NDIR calibration system where subsets of standards were used. It makes the new calibration system less

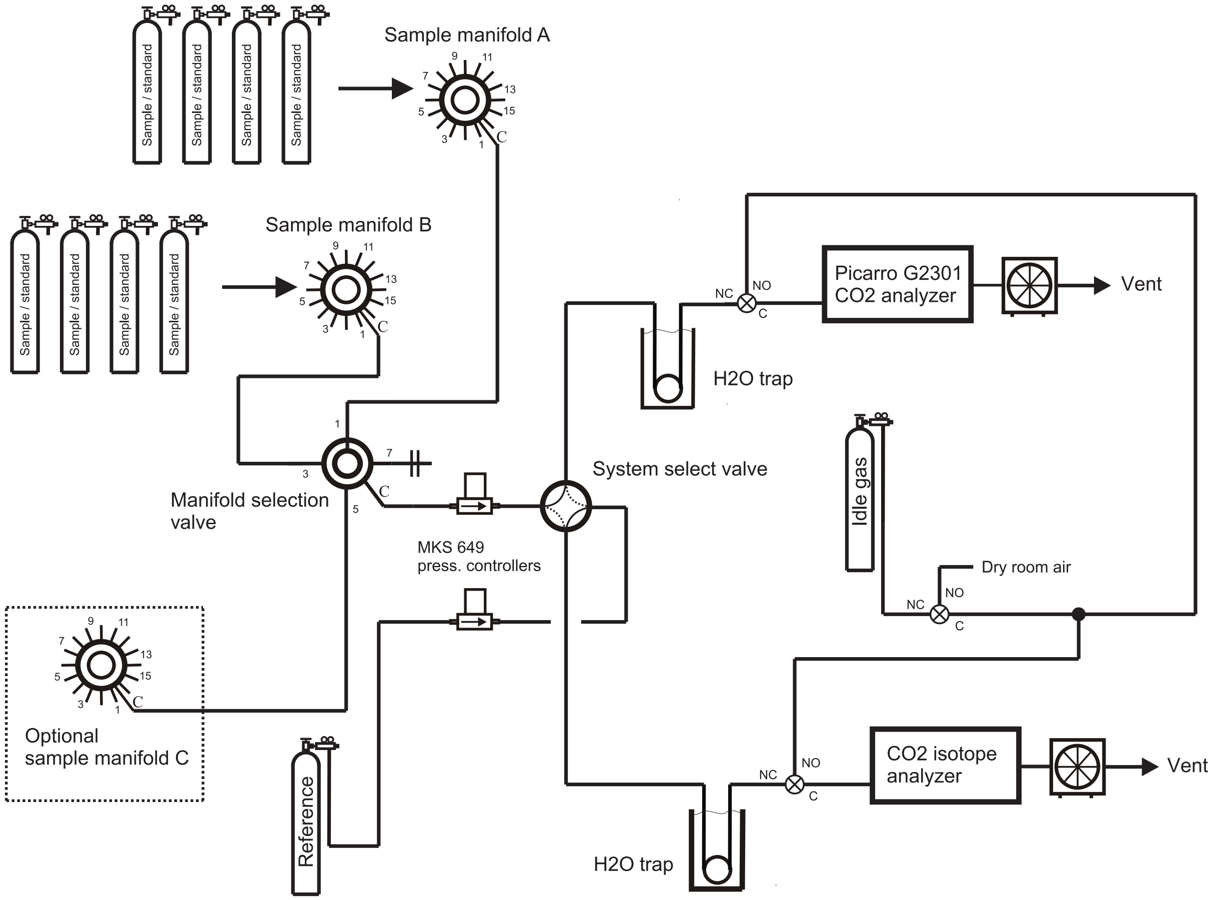

Figure 1. Schematic for the NOAA laser spectroscopic CO_2 calibration system. The CRDS analyzer is used with one of the CO_2 isotope analyzers, which are interchangeable.

likely to have CO_2-dependent biases. The secondary standard's $\delta^{13}C$ and $\delta^{18}O$ values were assigned by IRMS measurement at INSTAAR. Primary standards also have $\delta^{13}C$ and $\delta^{18}O$ values assigned by INSTAAR, which we use when primary standards are used to calibrate secondary standards. The use of INSTAAR $\delta^{13}C$ and $\delta^{18}O$ assigned values on the secondary standards rather than the values from measurement vs. the primary standards shortens the traceability of the delta measurements to a true IRMS measurement. A comparison of the INSTAAR assignments with the NOAA measured isotopic values for the secondary standards is discussed below.

As mentioned in section 6, INSTAAR $\delta^{13}C$ and $\delta^{18}O$ measurements are relative to their own realization of the VPBD scales rather than on the WMO GAW scale for isotopic measurements of CO_2 (Jena Reference Air Set (JRAS-06) maintained by the Max Planck Institute for Biogeochemistry, Jena, Germany) (Wendeberg et al., 2013). INSTAAR has scale contraction issues relative to JRAS. The relationships between INSTAAR and JRAS published by Wendeberg et al. (2013) indicate that, while the offsets are significant for isotopic studies, the use of the INSTAAR realization for accounting for isotopic differences when determining total CO_2 will not add significant bias. When we use primary standards to calibrate secondary standards, the apportionment of the total CO_2 into component isotopologues will be slightly off. However, this is partially corrected when we recombine the resulting measured isotopologue mole fractions of the secondary standards into total CO_2. Using approximate JRAS values for our primary standards based on the Wendeberg et al. (2013) relationships, we see changes in the apportionment of the $^{16}O^{12}C^{16}O$ isotopologues on the order of 0.000 to 0.004 $\mu mol\,mol^{-1}$ with corresponding but opposite sign changes in the other isotopologues.

The instrument readings are absorption measurements corrected for cell pressure and temperature and converted into nominal mole fraction units. However, we treat them purely as an instrument response in arbitrary units. They could also be a voltage or a current. The responses from the analyzers are subsequently used in an offline calibration of each instrument. We do not use the internal calibration capabilities of the instruments; this ensures that the measurements are directly traceable to the WMO primary standards and can be reprocessed for future scale revisions. Each standard is measured relative to a reference cylinder to correct for slow drift of the analyzers. For the CRDS and ICOS analyzers the instrument response to each standard is divided by the average instrument response of the bracketing reference aliquots. For the QC-TILDAS, the difference between the response to the standard and the reference is used. In both cases we term the resulting values "response ratios". The choice of division vs. subtraction is made due to the characteristics of the drift in each analyzer. For example, the division operation does a better job when there is a slow span drift (perhaps due to variations in cell temperature and pressure) causing relative changes that are proportional to CO_2, whereas the difference operation is more appropriate when the majority of the drift is caused by a uniform shift in the output that is not proportional to CO_2. Rather than characterize the source of drift in each analyzer, we use the reproducibility of target tank measurements to empirically determine which method gives more consistent results between calibration episodes.

The calibration curves are CO_2 isotopologue mole fractions as a function of response ratios. The CRDS instrument response is linear within the uncertainty of the standards (typical uncertainty of the primary standards is $\pm 0.1\,\mu\text{mol mol}^{-1}$ 68 % CI). However, both isotope analyzers are slightly nonlinear in their response and are fit with a quadratic polynomial. Nonlinearity in the isotope analyzers may be partially due to incomplete flushing of the sample cell, caused by unswept dead volumes, as the system switches from reference to standard. Residual reference gas (ambient air from Niwot Ridge, $\sim 400\,\mu\text{mol mol}^{-1}$ CO_2) in the sample cell influences the standards on the ends of the scale more than those close to the reference gas value, potentially leading to a slight nonlinear response. The difference in $^{16}O^{13}C^{16}O$ calibration curve residuals at $600\,\mu\text{mol mol}^{-1}$ using a quadratic fit ($0.0005\,\mu\text{mol mol}^{-1}$) and a linear fit ($0.003\,\mu\text{mol mol}^{-1}$) indicates the memory effect is small in terms of total CO_2. Since standards and samples are treated identically and measured against the same reference gas, small memory effects should cancel out. Longer flushing times would reduce the memory effect but would decrease the lifetime of the standards.

Sample measurements are made relative to the same reference tank to account for drift in the analyzers between calibration episodes. The sample response ratios are used with the isotopologue-specific calibration curves to determine isotopologue mole fractions for the sample cylinder which are combined into total CO_2, $\delta^{13}C$, and $\delta^{18}O$ values using the method discussed above. These values (total CO_2, $\delta^{13}C$, and $\delta^{18}O$) are stored in the NOAA database and are reported to the user via certificates and the Web interface. Isotopologue-specific mole fractions are not provided; however the equations described in this paper can be used to regenerate them.

Performance of the new calibration system has been evaluated over approximately 1 year by repeated measurements of target tanks (cylinders repeatedly measured as a diagnostic of system performance). Figure 2 shows the time series of total CO_2 measured for four target tanks with CO_2 ranging from 357 to $456\,\mu\text{mol mol}^{-1}$. Standard deviations of the measurements are approximately $\pm 0.007\,\mu\text{mol mol}^{-1}$. Reproducibility of the target tanks close to the reference tank (typically $\sim 400\,\mu\text{mol mol}^{-1}$ CO_2) is a little better than reproducibility of those farther out on the ends of the calibration range, but the difference is small. While 1 year is not a long enough time series to fully quantify the reproducibility of the system, we estimate it to be $\pm 0.01\,\mu\text{mol mol}^{-1}$ (68 % CI) based on these target tank measurements. This is a significant improvement over the NDIR system where reproducibility is $\pm 0.03\,\mu\text{mol mol}^{-1}$ (68 % CI) (Carbon Dioxide WMO Scale, 2017).

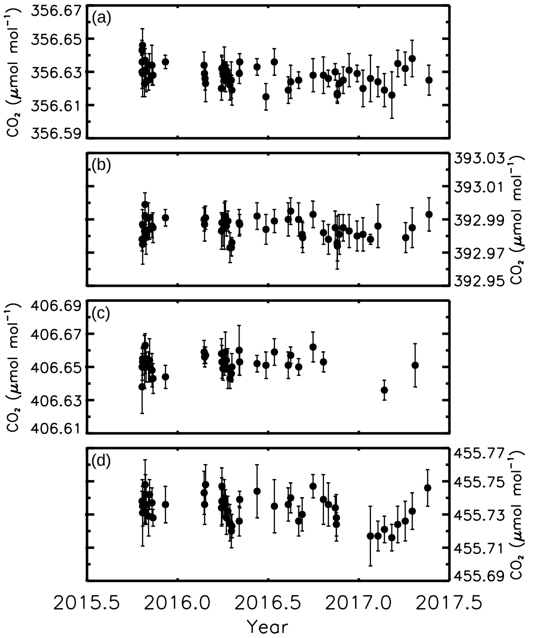

Figure 2. Total CO_2 calibration results for four target tanks measured on the laser spectroscopic CO_2 calibration system over approximately 1 year. Error bars are the standard deviation of eight measurements per calibration episode. The results span multiple gas handling system modifications. Values since April 2016 are on the final design. Average and standard deviations of the four target tanks results are **(a)** CC71624 $356.628 \pm 0.007\,\mu\text{mol mol}^{-1}$, **(b)** CB11127 $392.985 \pm 0.006\,\mu\text{mol mol}^{-1}$, **(c)** CA05008 $406.652 \pm 0.006\,\mu\text{mol mol}^{-1}$, and **(d)** CB10826 $455.734 \pm 0.008\,\mu\text{mol mol}^{-1}$.

Prior to this new CO_2 calibration system, NOAA provided informational isotopic values for tertiary standards delivered to outside organizations by taking discrete samples from cylinders in flasks and having them measured by INSTAAR. This continued during the 6-month period when both calibration systems were run in parallel. Comparisons of these measurements with the isotopic results from the new calibration system are show in Figs. 3 and 4. The top plot in each figure is differences of measured delta values (NOAA–

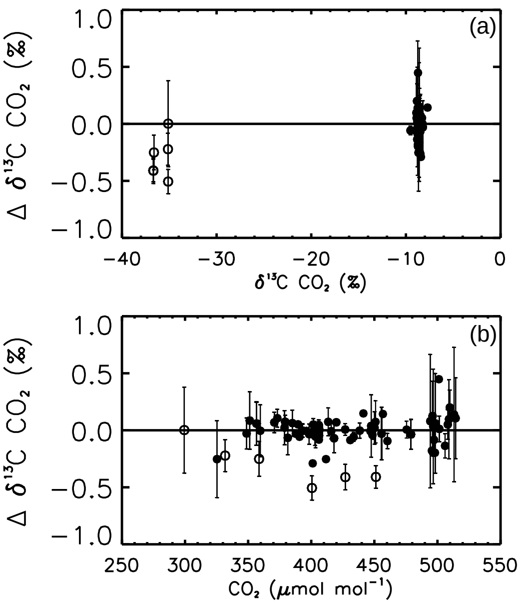

Figure 3. Discrete samples from tertiary standards were collected in flasks and measured by INSTAAR. The average INSTAAR flask δ^{13}C result is compared to the average δ^{13}C tank calibration result on NOAA's laser spectroscopic CO_2 calibration system. **(a)** is the difference (NOAA–INSTAAR) as a function of the INSTAAR δ^{13}C value, and **(b)** is the difference vs. total CO_2. Error bars in both plots are the standard deviation of multiple calibration episodes by NOAA. INSTAAR uncertainties are typically ±0.03 ‰ (68 % CI) (Trolier et al., 1996) but do not account for problems with the collection of the discrete air sample. Highly depleted cylinders ($\delta^{13}C < -20$ ‰) are shown with open circles in each panel.

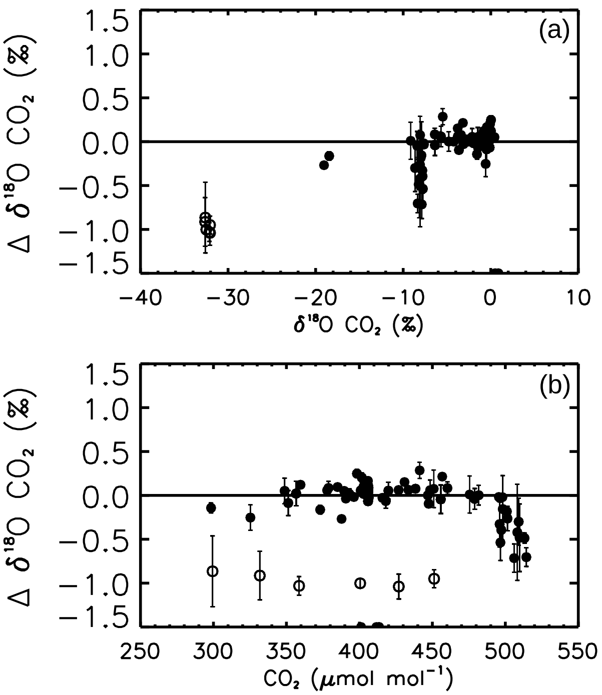

Figure 4. The same as Fig. 3 **(a, b)** but for δ^{18}O. INSTAAR uncertainties are typically ±0.05 ‰ (68 % CI) (Trolier et al., 1996) but again do not account for problems with the collection of the discrete air samples. Differences greater than 1.5 ‰ are assumed to be caused by problems during discrete sample collection. These results are shown but are not included in the statistics. Highly depleted cylinders ($\delta^{18}O < -20$ ‰) are shown with open circles.

INSTAAR) vs. INSTAAR values, and the bottom plot in each figure is differences as a function of total CO_2 measured by NOAA. There is no systematic bias between the NOAA and INSTAAR measurements for either species except for highly depleted cylinders (δ^{13}C or δ^{18}O less than −20 ‰, shown by open symbols in both figures) and δ^{18}O in very high CO_2 cylinders (> 490 µmol mol^{-1}). The average offset (NOAA–INSTAAR) of non-depleted tanks is 0.0 ± 0.1 ‰ δ^{13}C and 0.0 ± 0.2 ‰ δ^{18}O. The offset in the highly depleted cylinders most likely occurs as a result of the large extrapolation in the INSTAAR IRMS measurements from the working standard at ambient δ^{13}C and δ^{18}O. These offsets are roughly consistent with the INSTAAR JRAS offsets (Wendeberg et al., 2013) which are attributed to scale contraction issues at INSTAAR. The secondary standards used to routinely calibrate the NOAA system have isotopic assignments made by direct measurement by INSTAAR and are all relatively close to ambient (see Figs. 5 and 6), where the INSTAAR scale contraction is very small. By using these standards and calibrating our measurements in mole fraction space, we are not sensitive to the scale contraction issues in the INSTAAR measurement of depleted tanks. The δ^{18}O data do show a pronounced "hook" above ∼ 490 µmol mol^{-1}. This is thought to be due to issues when sampling air from cylinders into flasks and not to the measurements either at INSTAAR or NOAA. A tertiary standard with 497 µmol mol^{-1} CO_2 showed excellent agreement when measured directly by both NOAA ($\delta^{18}O = -8.92 \pm 0.04$ ‰) and INSTAAR ($\delta^{18}O = -8.94 \pm 0.1$ ‰). A comparison can also be made using the secondary standards which were calibrated directly by INSTAAR and by NOAA vs. the primary standards. The assigned values of the secondary standards (as measured directly by INSTAAR) and the NOAA-minus-INSTAAR differences are shown in Figs. 5 and 6 for δ^{13}C and δ^{18}O, respectively. Agreement is very good, but there is a loss of precision on the NOAA calibration system near the wings of the CO_2 scale. NOAA measurements show some decrease in performance as total CO_2 moves away from the reference cylinder, which is always an ambient CO_2 cylinder. However, even on the wings of the range the performance is more than adequate for the purpose of correcting total CO_2 for isotopic differences. The reproducibility of δ^{13}C (±0.2 ‰, 68 % CI) and δ^{18}O (±0.2 ‰, 68 % CI) measurements is again estimated from target tanks measurements. The uncertainty of the δ^{13}C and δ^{18}O measurements is dependent on the uncertainty of the total CO_2 values of the standards in addition to the reproducibility of the measurement system (Flores et al., 2017). This will be treated in an upcoming publication describing the CO_2 scale revision (Hall et al., 2017). The uncertainties of our measurement results for $\delta^{13}C$ and $\delta^{18}O$ are more than adequate for correcting atmospheric CO_2 measurements for standard vs. sample isotopic differences. However, we caution against using them as standards for high-precision CO_2 isotopic measurements.

The new calibration system was run in parallel with the NDIR system from April 2016 through October 2016. Agreement between the two systems near ambient CO_2 is good, but there are significant offsets from 300 to 360 and 430 to 500 µmol mol^{-1} (Fig. 7). These offsets can be traced primarily to the effects of calibrating the NDIR system with subsets of the primary standards when transferring the scale to secondary standards. Using subsets in this way makes the results from the NDIR system sensitive to uncertainty in the assigned values of the individual primary standards. Additional manometric determinations have been made since the assignments were made in 2007. Also the use of the new calibration system for correcting the average manometer values for residuals of a fit to the entire set will help to improve the consistency of the individual assignments and thus reduce the CO_2 dependency of the NDIR measurements. These improvements, as well as two additional subtle bias corrections in the manometer calculations, will be incorporated in an upcoming scale revision (scheduled for mid-2017). The revised scale should remove most of the CO_2-dependent bias between the two analysis systems. However, there may be a component due to gas handling issues on the NDIR system that cannot be resolved. This is still under investigation and will be addressed in a forthcoming paper discussing the scale revision (Hall et al., 2017). After the scale revision all past calibrations of tertiary standards will be revised to the new scale. Calibrating the new system by fitting all primary standards makes the new system very insensitive to the assignment of individual cylinders. Thus results from the new system are more accurate than from the NDIR; however, caution should be used when evaluating cylinders for drift when comparing historical results from the NDIR system and new measurements from the new calibration system as these systematic differences could be incorrectly interpreted as drift.

Figure 7 also has results from highly depleted tanks ($\delta^{13}C$ < −20 ‰) that show a greater NDIR-minus-laser system difference. This is consistent with the NDIR having reduced sensitivity to the minor isotopologues. Quantifying the sensitivity of the current NDIR (LI-COR 6252) is difficult due to the CO_2-dependent biases and would not be possible for historical NDIR analyzers used on the NDIR CO_2 calibration system. Measurements of isotopically depleted cylinders by NOAA via NDIR need to be considered more uncertain due to this unknown isotope sensitivity of NDIR's used for CO_2 calibrations.

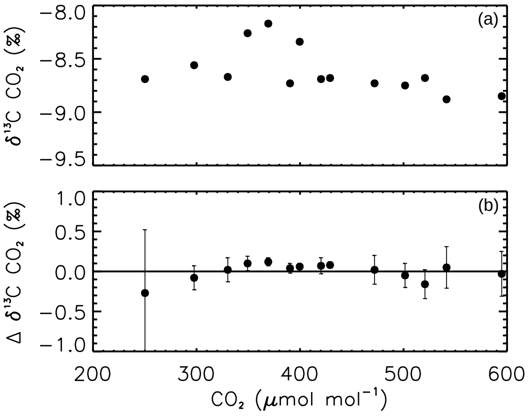

Figure 5. Secondary standards used to calibrate the laser spectroscopic system have $\delta^{13}C$ and $\delta^{18}O$ values from direct measurement by INSTAAR, and they have measured $\delta^{13}C$ and $\delta^{18}O$ from calibration on the laser spectroscopic system against the primary CO_2 standards. **(a)** shows the INSTAAR $\delta^{13}C$ values as a function of CO_2. Uncertainties on the INSTAAR values (less than 0.02 ‰) are not visible. **(b)** shows the difference between the NOAA and INSTAAR measurements of the secondary standards (NOAA–INSTAAR) also as a function of CO_2. Error bars are the standard deviation of four calibration episodes of the secondary standards vs. the primary standards on the NOAA CO_2 calibration system.

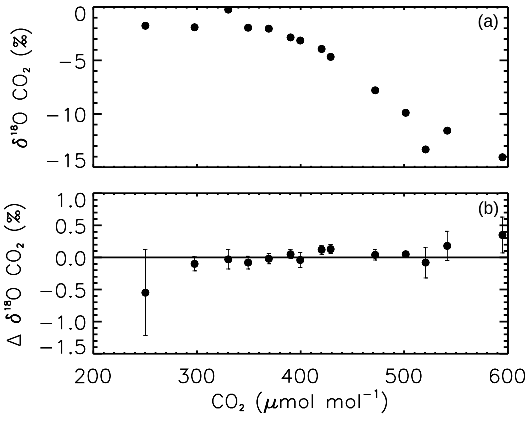

Figure 6. The same as Fig. 5 **(a, b)** but for $\delta^{18}O$. The CO_2-dependent depletion of $\delta^{18}O$ in cylinders above ambient CO_2 results from the depleted $\delta^{18}O$ of the spike gas.

9 Conclusions

We describe here the expected distribution of isotopologues of CO_2 based on measured $\delta^{13}C$ and $\delta^{18}O$ and its application in calibrating cylinders for total CO_2, $\delta^{13}C$, and $\delta^{18}O$. The distribution accounts for all isotopologues, including rare doubly substituted isotopologues. The methods are applicable to CO_2 or any other molecule where isotopologue (or isomer)-specific values are required to reach desired precision goals.

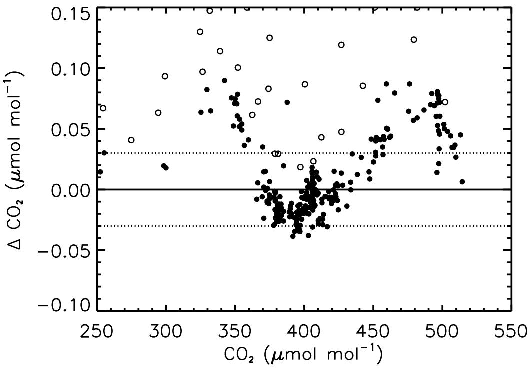

Figure 7. The laser spectroscopic CO_2 calibration system was run in parallel with the NDIR CO_2 calibration system for approximately 6 months. The differences (average NDIR−average laser spectroscopic system) are plotted as a function of CO_2. Typical reproducibility of the NDIR measurements (±0.03, 68 % CI) is shown with dashed lines. Highly depleted cylinders ($\delta^{13}C < -20$ ‰) are shown by open circles. These clearly indicate enhanced offsets due to the NDIR being somewhat sensitive to the isotopic composition differences between the samples and the standards used to calibrate the instrument.

The new calibration system provides total CO_2 values that are insensitive to isotopic differences between standards and provides to users of the standards a characterization of the isotopic composition of the standards. The isotopic values are not intended for propagating the isotopic standard scales. They are only to be used to make corrections to atmospheric CO_2 measurements made by instruments that have selective sensitivities to the isotopologues. For CO_2 isotopic measurements we encourage users to continue to have standards calibrated by dedicated isotope measurement facilities where the isotopic scales can be propagated with lower uncertainty.

The performance of the new calibration system improves our ability to propagate the CO_2 scale and is expected to lead to improvements in the compatibility of measurement networks provided laboratories maintain tight connection with the CCL. Although the system has not run long enough to fully evaluate the reproducibility of the scale transfer, it is expected to be approximately ±0.01 $\mu mol\,mol^{-1}$ (68 % CI). Comparison of the new calibration system with the historical NDIR-based system shows significant CO_2 dependence in the NDIR measurements. This results from a combination of errors in the assigned values of the primary standards and the use of small subsets of the primary standards when the scale is transferred to secondary standards. This is under further investigation, and we expect to resolve the issue with an upcoming revision to the CO_2 in air scale.

Code availability. Available upon request.

Data availability. Cylinder calibration results presented in this work include those used by laboratories outside of NOAA. We can provide results in anonymous form upon request.

Appendix A

We will derive expressions for Δ in terms of conventional δ values because we currently supply standards to users within the greenhouse gas measurement community with their δ values as information in addition to the total $\boldsymbol{y}_{\text{CO}_2}$ calibration.

$$\begin{aligned}{}^{13}\Delta &= \frac{{}^{13}\boldsymbol{x}}{{}^{13}\boldsymbol{x}_{\text{VPDB}}} - 1 = \frac{{}^{13}\boldsymbol{r}}{{}^{13}\boldsymbol{r}_{\text{VPDB}}}\,\frac{1+{}^{13}\boldsymbol{r}_{\text{VPDB}}}{1+{}^{13}\boldsymbol{r}} - 1 = (1+{}^{13}\delta)\\ &\quad(1+{}^{13}\boldsymbol{r}_{\text{VPDB}})(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2) - 1,\end{aligned}$$

where we have used the first three terms of the series expansion $(1+\boldsymbol{r})^{-1} = 1-\boldsymbol{r}+\boldsymbol{r}^2-\boldsymbol{r}^3+\ldots$ and the definitions of $\boldsymbol{r}$, $\boldsymbol{x}$, δ, and Δ. Expanding,

$$\begin{aligned}{}^{13}\Delta &= (1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2)+{}^{13}\boldsymbol{r}_{\text{VPDB}}(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2)\\ &\quad+{}^{13}\delta(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2)+{}^{13}\delta\,{}^{13}\boldsymbol{r}_{\text{VPDB}}(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2) - 1,\end{aligned}$$

and rearranging, we get

$$\begin{aligned}{}^{13}\Delta &= (-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2) + ({}^{13}\boldsymbol{r}_{\text{VPDB}}+{}^{13}\delta)(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2)\\ &\quad+{}^{13}\delta\,{}^{13}\boldsymbol{r}_{\text{VPDB}}(1-{}^{13}\boldsymbol{r}+{}^{13}\boldsymbol{r}^2).\end{aligned}$$

Neglecting the smallest terms,

$$\begin{aligned}{}^{13}\Delta &= {}^{13}\delta - ({}^{13}\boldsymbol{r}-{}^{13}\boldsymbol{r}_{\text{VPDB}})+{}^{13}\boldsymbol{r}({}^{13}\boldsymbol{r}-{}^{13}\boldsymbol{r}_{\text{VPDB}})\\ &\quad-{}^{13}\delta({}^{13}\boldsymbol{r}-{}^{13}\boldsymbol{r}_{\text{VPDB}})-{}^{13}\delta\,{}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\boldsymbol{r}.\end{aligned}$$

Then, using Eq. (5),

$$\begin{aligned}{}^{13}\Delta &= {}^{13}\delta-{}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\delta+{}^{13}\boldsymbol{r}\,{}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\delta-{}^{13}\delta\,{}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\delta\\ &\quad-{}^{13}\delta\,{}^{13}\boldsymbol{r}_{\text{VPDB}}\,{}^{13}\boldsymbol{r}.\end{aligned}$$

The third and the last term cancel, and then, keeping only the two leading terms, we obtain

$${}^{13}\Delta = {}^{13}\delta(1-{}^{13}\boldsymbol{r}_{\text{VPDB}}). \tag{A1}$$

Equation (A1) is an excellent approximation. Using the values for ${}^{13}\boldsymbol{r}_{\text{VPDB}}$ in Table 1 and assuming that ${}^{13}\delta = -0.00800$ (-8.00 ‰, an approximate value for CO$_2$ in air), we calculate both ${}^{13}\boldsymbol{x}$ for the air sample and ${}^{13}\boldsymbol{x}_{\text{VPDB}}$; using the definition (Eq. 6) for ${}^{13}\Delta$, we obtain ${}^{13}\Delta = -0.0079122$. Equation (A1) gives us -0.0079106.

A very similar derivation holds for ${}^{17}\Delta$ and ${}^{18}\Delta$, but it is a bit more complicated because the terms for ${}^{17}\boldsymbol{x}$ and ${}^{18}\boldsymbol{x}$ get mixed.

$$\begin{aligned}{}^{17}\Delta &= \frac{{}^{17}\boldsymbol{r}}{{}^{17}\boldsymbol{r}_{\text{VPDB}}}\,\frac{1+{}^{17}\boldsymbol{r}+{}^{18}\boldsymbol{r}}{1+{}^{17}\boldsymbol{r}_{\text{VPDB}}+{}^{18}\boldsymbol{r}_{\text{VPDB}}} - 1\\ &= \frac{{}^{17}\boldsymbol{r}}{{}^{17}\boldsymbol{r}_{\text{VPDB}}}\,\frac{1+{}^{78}\boldsymbol{r}}{1+{}^{78}\boldsymbol{r}_{\text{VPDB}}} - 1\end{aligned}$$

To keep the notation simpler and stressing the analogy with the derivation for ${}^{13}\Delta$, we have written in the above ${}^{78}\boldsymbol{r} = {}^{17}\boldsymbol{r}+{}^{18}\boldsymbol{r}$ for the air sample and ${}^{78}\boldsymbol{r}_{\text{VPDB}} = {}^{17}\boldsymbol{r}_{\text{VPDB}}+{}^{18}\boldsymbol{r}_{\text{VPDB}}$ for the standard.

After keeping only the leading terms, we have

$$\begin{aligned}{}^{17}\Delta &= {}^{17}\delta - ({}^{78}\boldsymbol{r}-{}^{78}\boldsymbol{r}_{\text{VPDB}})\\ &= {}^{17}\delta-{}^{17}\boldsymbol{r}_{\text{VPDB}}\,{}^{17}\delta-{}^{18}\boldsymbol{r}_{\text{VPDB}}\,{}^{18}\delta.\end{aligned} \tag{A2}$$

Similarly for ^{18}O,

$${}^{18}\Delta = {}^{18}\delta-{}^{17}\boldsymbol{r}_{\text{VPDB}}\,{}^{17}\delta-{}^{18}\boldsymbol{r}_{\text{VPDB}}\,{}^{18}\delta. \tag{A3}$$

These are the equivalents of Eq. (A1) for ${}^{13}\Delta$. Because ${}^{17}\boldsymbol{r}$ and ${}^{18}\boldsymbol{r}$ are significantly smaller than ${}^{13}\boldsymbol{r}$, we approximate further ${}^{17}\Delta \cong {}^{17}\delta$ and ${}^{18}\Delta \cong {}^{18}\delta$. Since ${}^{17}\delta$ is not usually measured and also is often very closely related as ${}^{17}\delta = 0.53\ {}^{18}\delta$, we can write for the oxygen correction terms in Eq. (17) (after substituting for ${}^{17}\delta$ and ${}^{18}\delta$ and using $\boldsymbol{r}_{\text{VPDB}}$ values from Table 1)

$$\begin{aligned}{}^{17}\boldsymbol{r}_{\text{VPDB}}\,{}^{17}\delta+{}^{18}\boldsymbol{r}_{\text{VPDB}}\,{}^{18}\delta &= (0.53\cdot{}^{17}\boldsymbol{r}_{\text{VPDB}}+{}^{18}\boldsymbol{r}_{\text{VPDB}})\,{}^{18}\delta\\ &\longrightarrow\cong 0.00230\cdot{}^{18}\delta\end{aligned} \tag{A4}$$

Now we return to Eq. (18) in the main text, applicable when the isotopic composition of measured air is different from the standard that is used. We restate it as

$$\begin{aligned}\Delta\boldsymbol{y}_{\text{CO}_2} &= \boldsymbol{y}_{\text{CO}_2}[0.01106\left({}^{13}\delta_{\text{air}}-{}^{13}\delta_{\text{st}}\right)\\ &\quad+2\cdot 0.00230\left({}^{18}\delta_{\text{air}}-{}^{18}\delta_{\text{st}}\right)].\end{aligned} \tag{A5}$$

Author contributions. PT derived the equations used to apportion total CO_2 into component isotopologues and their application. AC designed and built the calibration system. KT wrote software for operating the calibration system and managing the data.

Competing interests. The authors declare that they have no conflict of interest.

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