**Atmospheric
Measurement
Techniques
Discussions**

Evaluation of a cavity ring-down spectrometer for in-situ observations of $^{13}CO_2$

F. R. Vogel, L. Huang, D. Ernst, L. Giroux, S. Racki, and D. E. J. Worthy

Environment Canada, Climate Research Division, Climate Chemistry Research Section, 4905 Dufferin St., Toronto, Ontario, M3H 5T4, Canada

Correspondence to: F. R. Vogel (felix.vogel@ec.gc.ca)

AMTD

5, 6037–6058, 2012

Evaluation of a CRDS for $^{13}CO_2$ observations

F. R. Vogel et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

With the emergence of wide-spread application of cavity ring-down spectrometers (CRDS) to monitor $\delta^{13}C$ in atmospheric CO_2 there is a growing need to ensure well calibrated measurements. We characterized a cavity ring-down spectrometer system used for continuous in-situ monitoring of atmospheric $^{13}CO_2$. We found no concentration dependency of the $\delta^{13}C$ ratio within the range of 303–437 ppm. We designed a calibration scheme according to the diagnosed instrumental drifts and established a quality assurance protocol. We find that the repeatability of 10 min measurements is 0.25 ‰ and 0.15 ‰ for 20 min integrated averages. We found the cross-sensitivity to CH_4 in the samples to be 0.42 ± 0.02 ‰ ppm^{-1}. Our ongoing target measurements yield standard deviations of 0.26–0.28 ‰ for 10 min averages. We furthermore estimate the reproducibility of the system for ambient air samples from weekly measurements of a long-term target gas to be 0.18 ‰. We find only a miniscule offset of 0.002 ± 0.025 ‰ of the CRDS and Environment Canada's isotope ratio mass spectrometer (IRMS) results for four target gases used over the course of one year.

1 Introduction

The importance of the carbon cycle in the earth system cannot be overrated as all living organisms participate and rely on it directly or indirectly. Besides understanding the biogenic components of the carbon cycle and its response to future changes in climate, the anthropogenic alterations of the carbon cycle, most prominently observed in the increase in atmospheric CO_2 and the acidification of the oceans have been moving into the forefront of the atmospheric research community (IPCC, 2007). Studies aimed at distinguishing different sources of atmospheric CO_2 and investigating the underlying processes have frequently included carbon isotope analysis. Carbon-13 (^{13}C), the stable isotope of carbon for example, has been used in numerous studies to infer isotopic discrimination by plants during photosynthesis and the isotopic composition of soil and

F. R. Vogel et al.

plant respiration (e.g. Yakir and Wang, 1996; Ekblad and Högberg, 2001; Pataki et al., 2003). The information gathered from ^{13}C observation has also been used to quantify anthropogenic emissions of CO_2 (e.g. Zondervan and Meijer, 1996; Bakwin et al., 1998; Zimnoch et al., 2004; Pataki et al., 2006). Previous studies mostly relied on grab sample measurements and thus provide only limited temporal resolution. Grab sampling tends to also be costly. With the emergence and improvement in optical spectrometers (i.e. cavity ring-down spectroscopy), an affordable and reliable technology appears within reach to conduct studies with quasi-continuous temporal resolution. The aim of this paper is to assess the performance of one type of currently available spectrometer and to suggest a strategy to ensure well calibrated measurements to come as close as possible to the WMO recommendations. We characterize the signal-to-noise ratio, the temporal drift and the cross-sensitivity of this instrument and develop a calibration scheme according to our findings. The performance of our system is evaluated with our quality assurance (QA) routines that include two categories of target gases. The results are evaluated over the course of one year of measurements. Although our current systems cannot fulfill the WMO recommendations in inter-laboratory comparability due to the limited signal-to-noise ratio, our calibration strategy could be applied for future CRDS instruments that will be able to achieve this goal when improving the fundamental signal-to-noise ratio. Although our instrument is capable of measuring CO_2 and H_2O levels as well, this paper addresses ^{13}C in CO_2 only.

2 Instrumental setup

The core of our setup consists of a commercially available cavity ring-down spectrometer (CRDS) (G1101-i+, Picarro, Santa Clara, USA). The effective path length of the cavity is 14 km, and the cell has a volume of 35 ml. This instrument has a built-in wavelength monitor as well as pressure and temperature control systems to ensure high stability of these parameters. One of the advantages of CRDS over other techniques is the little amount of calibration gas needed (c.f. Hammer et al., 2012; Griffith et al.,

2012). For our instrument the abundance of $^{13}CO_2$ and $^{12}CO_2$ are determined independently from two spectral lines in the near-infrared in our system before calculating $\delta^{13}C$ (Zare et al., 2009). Although measuring wet gas streams is possible with this system, we follow the strategy of avoiding negative impacts rather than to correct for these afterwards. We also found that rapid water level changes can slightly affect the retrieved $\delta^{13}C$, when applying the correction.

In our setup (Fig. 1), a mass flow controller (MFC) (Alicat Scientific, Tuczon, USA) delivers a constant flow of 35 ml min^{-1} to the system. Prior to entering the spectrometer, the sample gas is passed through a magnesium perchlorate cartridge (air volume, < 10 ml) to dry the sample gas to a dew point of −80 °C. This design ensures that both the gas standards and the ambient sample air have the same level of moisture. A gas selection valve (Valco instrument, Houston, USA) is used to select between the various sample gas streams. In order to minimize the frequency of changing the chemical dryer, the ambient air is pre-dried to −30 °C by first passing the ambient gas through a Peltier cooler (M&C TechGroup, Ratingen, Germany) located upstream of the selection valve. We determined that a flushing time of 3 min is sufficient to flush the sample cell and ensure no residual sample from the previous stream is present. This was evaluated using two cylinders with differences of isotopic composition of more than 30 ‰. The inlet pressure for all sample lines ranges from 12 to 16 psi. The measurement sequence and valve control is done using the *valve sequencer* software provided by the manufacturer (Picarro Inc. Santa Clara, USA).

3 Characterization of the instrument

3.1 Noise and stability

In order to characterize the noise and the drift behavior of the instrument, we used a cylinder with known $\delta^{13}CO_2$ and monitored the changes of the instrumental output signal over time. For the 2 s high temporal resolution data, we found that the data

displays on average, a standard deviation of around 1.8‰ (c.f. Fig. 2). The noise is governed by the performance of the detector and laser precision, given the high precision needed to determine the $\delta^{13}C$ signal. We find that aggregating the raw data, as expected, decreases the standard deviation and for 5 min averaging intervals, the standard deviation of 0.2‰ is actually better than the specification provided by the manufacturer for this system (i.e. 0.3‰). To achieve a precision level lower than 0.1‰, integration times of 60 min or more are required. We also determined that the WMO recommended precision value of 0.01‰ is not achievable. However, for applications where strong variations of the $\delta^{13}C$ are expected, i.e. in urban measurements or terrestrial forested sites (high diurnal CO_2 signals), such high precision requirements might not be necessary. Given the limitations of the instrument, we have set our target for an accuracy level of 0.2‰, which at current CO_2 concentrations is equivalent to the addition of approximately 5 ppm of CO_2 from, e.g. fossil fuel burning or respiration. Given this goal, we have devised a sampling strategy of measuring ambient air and calibration gases over 20 min intervals. With a 3 min flushing time requirement between gases, this results in 17 min of valid data. Based on the single tank test experiment, as shown in Fig. 2, an average precision (repeatability) of 0.15‰ is achievable.

3.2 Long-term variations

Along with the short-term variations, the instrument also usually displays noticeable long-term drifts which can be as high as 1‰ over one day (Rella A. "Accurate stable carbon isotope ratio measurements with rapidly varying carbon dioxide concentrations using the Picarro d13CO2 G2101-i gas analyzer" Picarro Inc., 17 July 2012, http://www.picarro.com/assets/docs/White_Paper_G2101-i_Transient_Response_for_Isotopic_CO2_Measurements.pdf). Similar tests on our instrument as shown in Fig. 3, typically display less drift and show changes on the order of around 0.3‰ over the course of one day. We monitored the long-term behavior using two cylinders (LTG48-A and TG48-A) that were used to alternatingly flush the system for 10 and 20 min respectively, over several days. As shown in Fig. 3, we found that after

Evaluation of a CRDS for $^{13}CO_2$ observations

F. R. Vogel et al.

subtracting the mean both cylinders display similar drift patterns. Based on these long-term test results, we deduced that calibrating the instrument at least every 10 h and linearly interpolating the instrumental response between bracketing standards is more than sufficient to capture this behavior within 0.1 ‰. We decided to calibrate every 7 h

5 as this ensures that the calibration does not systematically occur at the same time of day. To test the calibration frequency we ran a QA routine to measure a target tank with a known $\delta^{13}C$ every 30 min. We found that monitoring this drift (or lack thereof after calibration) can be achieved using 10 min measurements. This permits the lifetime of the target to last for more than 400 days (~ 7500 l) and provide frequent calibrations. The

10 target can also be used to identify situations of unusual instrument behavior changes within the 7 h calibration interval.

Hence, all our measurement cycles consist of 30 min, beginning with 10 min of a target gas followed by 20 min of another gas and a calibration every 7 h (c.f. Fig. 4). In order to assess the performance of the ambient measurements and to monitor for

15 longer term drifts, we have introduced a second so-called "long-term" target (LTG) that is also measured for 20 min once a week. To increase the precision for the long-term target we measure and average 4 injections. The lifetime of the long-term target is more than 50 yr (~ 7500 l cylinder), much longer than the expected life-time of the instrument. This long-term target also helps to link the measurements over the life-time of several

20 working gases (WG) that are needed to determine the instrumental response and link our measurements to international scales. This is a vital component of the calibration strategy in ensuring long-term stability of the measurements and permit back track corrections of the data due to scale changes or other reasons.

3.3 Concentration dependence

25 Instruments are often deployed at measurement sites (Egbert, ON, CA and Toronto, ON, CA) that are both subject to strong anthropogenic and biospheric CO_2 fluxes, large ranges of isotopic compositions and CO_2 mixing ratios will occur. Other measurement techniques such as IRMS are known to display a CO_2 concentration dependency for

F. R. Vogel et al.

the isotopic concentration (Huang et al., 2012). To avoid systemic biases due to such a concentration dependency of the $\delta^{13}C$ observations, we conducted a series of dilution experiments over several days using a cylinder of known $\delta^{13}C$ and CO_2 concentrations. The air stream was split into two with the first stream being completely stripped of CO_2 using two cartridges containing Ascarite II (Fisher Scientific, Hampton, USA). It is vital that this stream be void of CO_2 because the residual CO_2 from this stream could be highly fractionated. We separately analysed the effluent from this stream and found the CO_2 concentration level to be well below our detection limit of less than 0.1 ppm. The second stream was unaltered. The two streams were merged in a static mixing chamber with the contribution from both streams being controlled using two manual needle valves (Swagelok, Solon, USA). All measurements where conducted over 3 days with each day starting off with the measurement of the unaltered gas stream ($[CO_2] = 437$ ppm, $\delta^{13}C = -11.035$ ‰, $[CH_4] = 1972$ ppb) followed with the testing the other stream to evaluated the effectiveness of CO_2 scrubber. Upon ensuring the stability of the two gas streams, the flow of ratio of the two streams were altered and after allowing for settling effects, the $\delta^{13}C$ value was derived over the 20 min measurement interval. Our measurements span a range from around 303 ppm to 437 ppm. The results in Fig. 4 show the uncertainty of the $\delta^{13}C$ values derived from the different dilution steps and clearly demonstrates that there is no significant concentration dependency in this concentration range and that the standard deviation of our measurements to be around 0.2 ‰.

4 Calibration of raw data to Vienna Pee Dee Belemnite

4.1 Scale offset and cross-sensitivity

In order to compare our results to other measurements such as data from the globally available flask networks and in-situ data (http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.

html), the data from our instrument must be calibrated on internationally recognized carbon isotope primary scales (the Vienna Pee Dee Belemnite). From our long-term experiments (cf. Sect. 3.2) we have determined calibrating every 7 h to be sufficient to capture drift patterns. Using multiple cylinders with known $\delta^{13}C$ isotope values, which are all well anchored on the primary scale i.e. VPDBCO$_2$ (Huang et al., 2012) we found that the raw Picarro scale is linearly dependent on the VPDB and has both a mean offset $b = 2.07\permil$ and a slope of $m = 1.075\permil\permil^{-1}$ with inter-quartile ranges of $0.4\permil$ and $0.01\permil\permil^{-1}$, respectively. We therefore measure two working gases high (WGH) and low (WGL) to determine the current instrument response. To reduce the uncertainty of the fit a large isotopic range i.e. $-8\permil$ to $-32\permil$ for the two working gases was chosen. And the (preliminary) $\delta^{13}C_{VPDB^*}$ value can be derived from our raw data using.

$$\delta_i^{13}C_{VPDB^*} = \delta_i^{13}C_{raw} \cdot m + b$$

After applying this correction we found a residual difference, which was identified to be due to a cross-sensitive of the instrument to the CH$_4$ mixing ratio of the sample. This is caused by an overlap of the absorption lines of CH$_4$ and $^{13}CO_2$. This complicates calibrating the instrumental signal (i.e. $\delta^{13}C_{raw}$) as it consists of the response due to the $\delta^{13}CO_2$ levels ($\delta^{13}C_{res}$) and a CH$_4$ concentration ([CH$_4$]) dependent term scaled by a cross-sensitivity factor (X_{sens}).

$$\delta_i^{13}C_{VPDB^*} = \left(\delta_i^{13}C_{res} + [CH]_i \cdot X_{sens}\right) \cdot m + b$$

X_{sens} has been found to be both dependent on the H$_2$O as well as the CO$_2$ concentration (A. van Pelt, Picarro Inc. Santa Clara, USA, personal communication, 2012, "Picarro G2131-i d13C high-precision isotopic CO2 CRDS Analyser" Picarro Inc., 22 July 2012 http://www.picarro.com/isotope_analyzers/co2_ambient). For our application these effects can however be neglected as all samples are dried (to the same level of moisture) and the dependence on the CO$_2$ mixing ratio seems not to be

significant and was not visible in our experiments (cf. Sect. 3.2). The calibrated and cross-sensitivity corrected $\delta^{13}C_{VPDB}$ can thus be derived from

$$\delta_i^{13}C_{VPDB} = \delta_i^{13}C_{res} \cdot m + b = \delta^{13}C_{VPDB^*} - [CH_4]_i \cdot X_{sens} \cdot m$$

To determine X_{sens}, one can use a set of at least three cylinders (A, B, C) with known $\delta^{13}C_{VPDB}$ and known CH_4 concentration to derive the cross sensitivity from a linear regression. Following the equation:

$$X_{sens} = \frac{\Delta_{A-B}\delta^{13}C_{VPDB} \cdot \Delta_{B-C}\delta^{13}C_{res} - \Delta_{B-C}\delta^{13}C_{VPDB} \cdot \Delta_{A-B}\delta^{13}C_{res}}{\Delta_{A-B}[CH_4] \cdot \Delta_{B-C}\delta^{13}C_{VPDB} - \Delta_{B-C}[CH_4] \cdot \Delta_{A-B}\delta^{13}C_{VPDB}}$$

using the convention $\Delta_{i-j}Q = Q_i - Q_j$.

The derived cross-sensitivity shows a large standard deviation ($0.29\,‰\,ppm^{-1}$) as the signal-to-noise ratio for the individual terms in the equation is very poor. However, if we combine a large set of over 150 measurements we find that the cross-sensitivity did not show any temporal trends over several months with a mean of $0.42\,‰\,ppm^{-1}$ and a standard error of $\pm 0.024\,‰\,ppm^{-1}$. Therefore a sample with a typical concentration of 2 ppm has to be corrected by $0.84\,‰$ with an uncertainty of $0.048\,‰$ of this correction. Any potential bias introduced by this correction would be the same for both calibrations gases as well as samples. The post-processing correction is done using the concurrent ambient measurements of CH_4 from our in-situ GC system (Worthy, 2003).

4.2 Data processing procedures

The high resolution 2 s raw data is at first averaged over 1 min intervals to reduce storage space requirements. Using a MySQL compatible relational database system (MariaDB), the data is further averaged to 10 min intervals for the target measurements and to 20 min intervals for the ambient air, calibration, long-term target and auxiliary measurements. Each sample switching triggers a flag that invalidates the first 3 min of

each to ensure that the cell has been adequately flushed with the new sample. The data is then flagged according to deviation of the target measurements from the true value that must be less than 0.75‰ and/or 0.15 ppm for the CO_2 mixing ratio. The data is further flagged if water levels exceed 0.1 % in the sample and if the standard deviation of the ambient CH_4 and CO_2 mixing ratios of the averaging interval is above 0.1 ppm or 5 ppm, respectively. This pre-selected data is eventually visually inspected before being ultimately assigned as valid data and used in hourly and longer averaging time steps.

5   Quality assurance and control

5.1   Long-term stability of the target

The long-term stability of the target measurements can be used to assess the long-term performance of the instrument as well as the adequacy of our calibration strategy to capture the changing instrument response and the CH_4 cross-sensitivity. Over the first year of measurements, four different target gas cylinders have been used (TG48-A, TG48-B, TG48-C and TG12-A), over various periods (c.f. Table 1 and Fig. 6). The 29 l aluminum cylinders (Scott Marin, Riverside, USA) were filled with dried ambient air using an oil free Rix compressor (RIX Industries, Benicia, USA). After one year of measurements, we can see in Fig. 6 that the original instrumental output $\delta^{13}C_{raw}$ (in grey) shows significant long-term drifts. This is particularly pronounced in the first episode. We also find that there is a general offset between the "true" and the raw data. After calibrating the data and correcting for the CH_4 cross-sensitivity, we find that the 10 min averaged data still displays a high standard deviation of around 0.25‰ but is stable over long period with a standard error of below 0.01‰ for all episodes. The uncertainty estimate in table 1 of 0.1‰ includes the uncertainty of the X_{sens} and the uncertainty in the assigned values of the working gases.

The daily averaged target data nicely overlaps with the $\delta^{13}C$ isotopes that were determined using Environment Canada's IRMS system (Huang et al., 2012). In the third period (purple) a different set of working gases WGH12-A and WGL12-A was used spanning −9 to −24 ‰. For all other episodes WGH48-A and WGL48-A were used and spanned a range from −32 to −8 ‰. We found that our approach provides consistent results over the four different target gases used and is independent of which set of working gases was used. The standard deviation of target measurement ranges from 0.28 to 0.23 ‰ for all periods and the mean offset between the calibrated CRDS results compared to the IRMS data is 0.002 ‰ and with a standard deviation of 0.025 ‰. This implies, that although a single measurement can be quite imprecise, the CRDS system can provide accurate results if proper calibration procedure are applied.

5.2 Reproducibility and uncertainty estimation for ambient measurements

To assess the reproducibility of our ambient air measurements, we analyzed the measurements of the long-term target. The long-term target is measured once a week (c.f. Fig. 4) and is treated in the same manner as an ambient sample (in the measurement routine as well as during data processing). For the measurements included in this study (November 2011–May 2012) a mean of −12.47 ‰ was determined. This compares well with the independently IRMS calibrated value of $\delta^{13}C$ −12.54 ± 0.03 ‰. The standard deviation (reproducibility) of the long-term target measurements is 0.177 ‰ and follows a distinct Gaussian distribution as shown in Fig. 7. This result is well in line with the expected standard deviation of 0.16 ‰ when including the 0.15 ‰ uncertainty due to the instrumental noise (cf. Sect. 3.1), 0.02 ‰ uncertainty of the $\delta^{13}C$ of the calibration cylinders and 0.048 ‰ uncertainty of the CH_4 cross-sensitivity correction (cf. Sect. 4.1). Even when including all internal sources of error, our system is capable of providing long-term in-situ observations of $\delta^{13}C$ in atmospheric CO_2 better than 0.18 ‰ for 20 min average values.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

6 Discussion and outlook

We characterized a cavity ring-down spectrometer system used for continuous in-situ monitoring of ^{13}C in atmospheric CO_2. We found no concentration dependency of the $\delta^{13}C$ ratio within the range of 303–437 ppm and determined a cross sensitive to CH_4 in the sample of 0.42 ± 0.024 ‰ ppm^{-1}. We designed a calibration scheme according to the found instrumental drifts and established a QA protocol. We find that the repeatability of 10 min measurements is 0.25 ‰ and 0.15 ‰ for 20 min integrated averages over the course of one year. We determine the reproducibility of the system for ambient air measurements from weekly measurements of a long-term target gas to be 0.18 ‰. This is consistent with the theoretical prediction. We find that the uncertainty is dominated by the instrumental noise of 0.15 ‰ and less by the uncertainty of the calibration and the cross-sensitivity. Analysing our target measurement performed for QA reasons we find a neglectable offset of 0.002 ± 0.025 ‰ between our CRDS and IRMS scales. Our calibration strategy is suited for this instrument, but was already developed bearing in mind that future instruments will show better signal-to-noise characteristics and a thorough cross-sensitivity correction might be even more important. Recently developed instruments are reported to having a three-fold improved fundamental signal-to-noise ratio ("Data Sheet G2131-i" 17 July, http://www.picarro.com/isotope_analyzers/co2_ambient), which, theoretically would allow for an accuracy of below 0.1 ‰ for 15 min integrals using this calibration. Assuming that the cross-sensitivity can be determined with a higher precision even measurements with an accuracy of the order of 0.05 ‰ is in reach.

The fundamental approach presented here is applicable to other CRDS systems as well as other spectrometers and comprises the following steps: (I) quantification of fundamental signal-to-noise ratio. (II) Determine short-term and long-term drift of the instrument responses by measuring known cylinders. (III) Determining the calibration frequency needed to ensure the needed precision for the planned measurements. (IV) Identify external drivers and cross-sensitivities to other species (e.g. CH_4) and

check for any concentration dependencies. (V) Establishing a link of the instrumental scale to internationally recognized standards. (VI) Most importantly a thorough QA routine using at least two target cylinders should be implemented. The value of frequent target gas measurements to monitor the instrumental drift on short time-scales to iden-
5 tify erroneous situations and to flag bad data, in addition to a long-term monitoring scheme to determine the reproducibility of the system, as well as check for any drifts in the scale established through the working gas cylinders, cannot be overestimated.

References

Bakwin, P. S., Tans, P. P., Hurst, D. F., and Zhao, C.: Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program, Tellus B, 50, 401–415. doi:10.1034/j.1600-
20 0889.1998.t01-4-00001.x, 1998.
Ekblad, A. and Högberg, P.: Natural abundance of ^{13}C in CO_2 respired from forest soils reveals speed of link between tree photosynthesis and root respiration, Oecologia, 12, 305–308, 2001.
Griffith, D. W. T., Deutscher, N. M., Caldow, C. G. R., Kettlewell, G., Riggenbach, M., and Ham-
25 mer, S.: A Fourier transform infrared trace gas analyser for atmospheric applications, Atmos. Meas. Tech. Discuss., 5, 3717–3769, doi:10.5194/amtd-5-3717-2012, 2012.
Hammer, S., Griffith, D. W. T., Konrad, G., Vardag, S., Caldow, C., and Levin, I.: Assessment of a multi-species in-situ FTIR for precise atmospheric greenhouse gas observations, Atmos. Meas. Tech. Discuss., 5, 3645–3692, doi:10.5194/amtd-5-3645-2012, 2012.

Huang, L., Chivulescu, A., Ernst, D., Zhang, W., and Lee, Y.-S.: Maintaining consistent traceability in high precision isotope measurements of CO_2: verifying atmospheric trends of δ^{13}C, Atmos. Meas. Tech. Discuss., 5, 4003–4040, doi:10.5194/amtd-5-4003-2012, 2012.

Pataki, D. E., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R., Still, C. J., Buchmann, N., Kaplan, J. O., and Berry, J. A.: The application and interpretation of Keeling plots in terrestrial carbon cycle research, Global Biogeochem. Cy., 17, 1022, doi:10.1029/2001GB001850, 2003.

Pataki, D. E., Alig, R. J., Fung, A. S., Golubiewski, N. E., Kennedy, C. A., McPherson, E. G., Nowak, D. J., Pouyat, R. V., and Romero Lankao, P.: Urban ecosystems and the North American carbon cycle, Glob. Change Biol., 12, 2092–2102, doi:10.1111/j.1365-2486.2006.01242.x, 2006.

Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M. M., Miller, H. L., and Chen, Z.: Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007 – The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC, Cambridge University Press, Cambridge, 2007.

Worthy, D. E. J. and Meteorological Service of Canada, Atmospheric and Climate Science Directorate: Canadian Baseline Program: Summary of Progress to 2002, Environment Canada, Meteorological Service of Canada, http://books.google.de/books?id=3g_8NAAAACAAJ (last access: August 2012), 2003.

Yakir, D. and Wang, X.-F.: Fluxes of CO_2 and water between terrestrial vegetation and the atmosphere estimated from isotope measurements, Nature, 380, 515–517, doi:10.1038/380515a0, 1996.

Zare, R. N., Kuramoto, D. S., Haase, C., Tan, S. M., Crosson, E. R., and Saad, N. M. R.: High-precision optical measurements of ^{13}C/^{12}C isotope ratios in organic compounds at natural abundance, P. Natl. Acad. Sci. USA, 106, 10928–10932, doi:10.1073/pnas.0904230106, 2009.

Zimnoch, M., Florkowski, T., Necki, J. M., and Neubert, R. E. M.: Diurnal variability of δ^{13}C and δ^{18}O of atmospheric CO_2 in the urban atmosphere of Kraków, Poland, Isot. Environ. Healt. S., 40, 129–143, 2004.

Zondervan, N. A. and Meijer, H. A. J.: Isotopic characterisation of CO_2 sources during regional pollution events using isotopic and radiocarbon analysis, Tellus B, 48, 601–612. doi:10.1034/j.1600-0889.1996.00013.x, 1996.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

F. R. Vogel et al.

Table 1. Comparison of CRDS and IRMS values of target gas measurements (c.f. Fig. 6). The standard error for the target measurements of the CRDS ($\delta^{13}C_{cal}$) are all below 0.01‰, yet the uncertainty is given as (< 0.1‰) as other sources of error have to be included (see text and c.f. Fig. 6).

		CRDS				IRMS
Target ID	$\delta^{13}C_{raw}$	$\delta^{13}C_{cal}$ (uncertainty)	$\delta^{13}C_{cal}$ std.dev.	N	Working gas range	$\delta^{13}C_{MS}$ (uncertainty)
TG48-A	−10.96‰	−9.94 (< 0.1)‰	0.22‰	> 5400	−32‰ to −8‰	N/A
TG48-B	−9.62‰	−8.47 (< 0.1)‰	0.23‰	> 2600	−32‰ to −8‰	−8.495 (± 0.03)‰
TG12-A	−9.51‰	−8.58 (< 0.1)‰	0.23‰	> 2200	−24‰ to −9‰	−8.585 (± 0.02)‰
TG48-B	−9.39‰	−8.52 (< 0.1)‰	0.26‰	> 5000	−32‰ to −8‰	−8.495 (± 0.03)‰
TG48-C	−10.56‰	−9.48 (< 0.1)‰	0.26‰	> 1500	−32‰ to −8‰	−9.445 (± 0.03)‰
TG48-B	−9.55‰	−8.47 (< 0.1)‰	0.28‰	> 1500	−32‰ to −8‰	−8.495 (± 0.03)‰
TG48-C	−10.49‰	−9.43 (< 0.1)‰	0.27‰	> 900	−32‰ to −8‰	−9.445 (± 0.03)‰
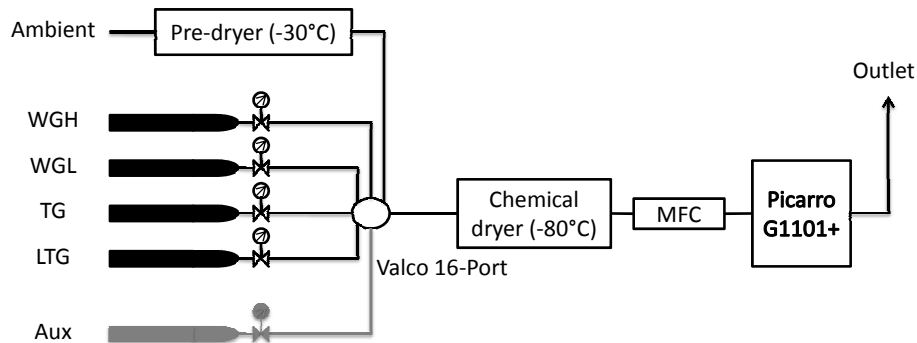
Fig. 1. Schematic setup of the in-situ $^{13}CO_2$ monitoring system: The working gases high (WGH) and low (WGL) as well as the target gases (TG and LTG) are connected to a rotary valve. After this all gases share the same path with the pre-dried ambient air through a chemical dryer ($Mg[ClO_4]_2$) and a mass-flow controller (MFC) before entering the cavity ring-down spectrometer.
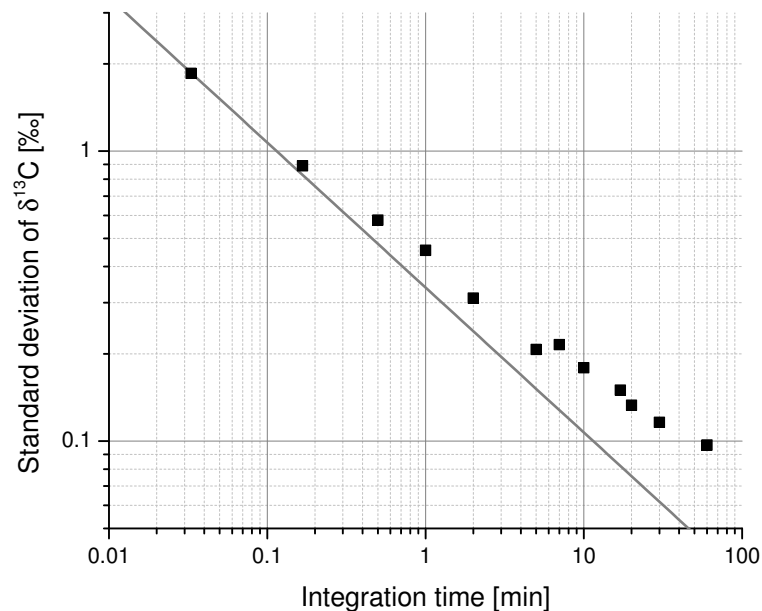
Fig. 2. Allan-Variance plot for the measurements of CBDS-48 using constant flow from a single cylinder using different integration times. The grey line gives the theoretical predication for random (white) noise.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
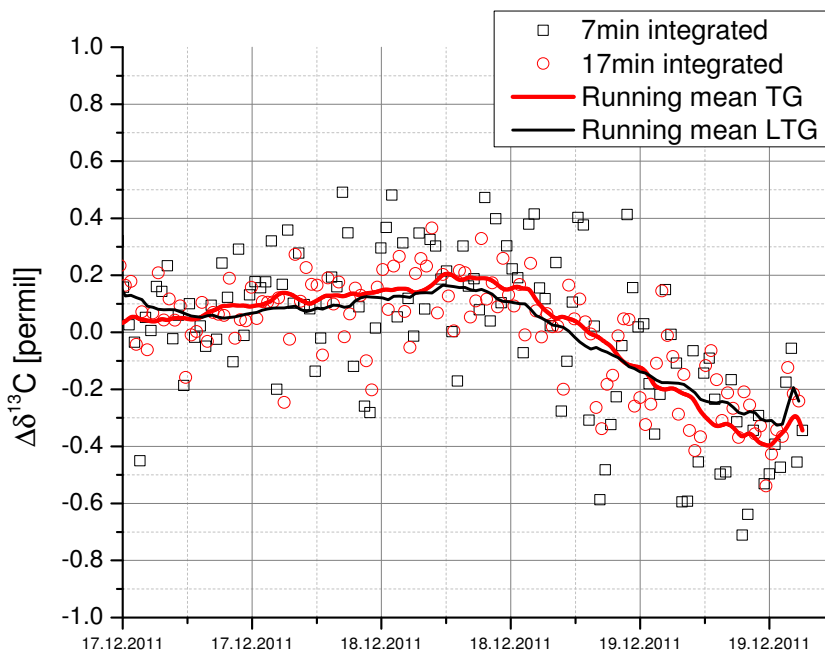
Fig. 3. Instrumental drift of the Picarro $\delta^{13}C_{raw}$ monitored over 2 days using two gas cylinders TG48-A (black) and LTG48-A (red) measured twice per hour. To highlight the trend a running mean (6 h window) is given in the solid lines.

Time	10 min	20 min	10 min	20 min
1 hr	Target	Ambient	Target	Ambient
...	...	...	...	...
6 hr	Target	Ambient	Target	Ambient
7 hr	Target	WG high	Target	WG low
8 hr	Target	Ambient	Target	Ambient
...	...	...	...	...
168 hr	Target	Ambient	Target	Ambient
169 hr	Target	Long-term target	Target	Long-term target
170 hr	Target	WG high	Target	WG low
1 hr	Target	Ambient	Target	Ambient
...	...	...	...	...

Fig. 4. Measurement cycle of the CRDS system for target, ambient air, working gases and long-term target. Note that the first 3 min of each measurement is neglected to ensure an adequate flushing of the optical cell.
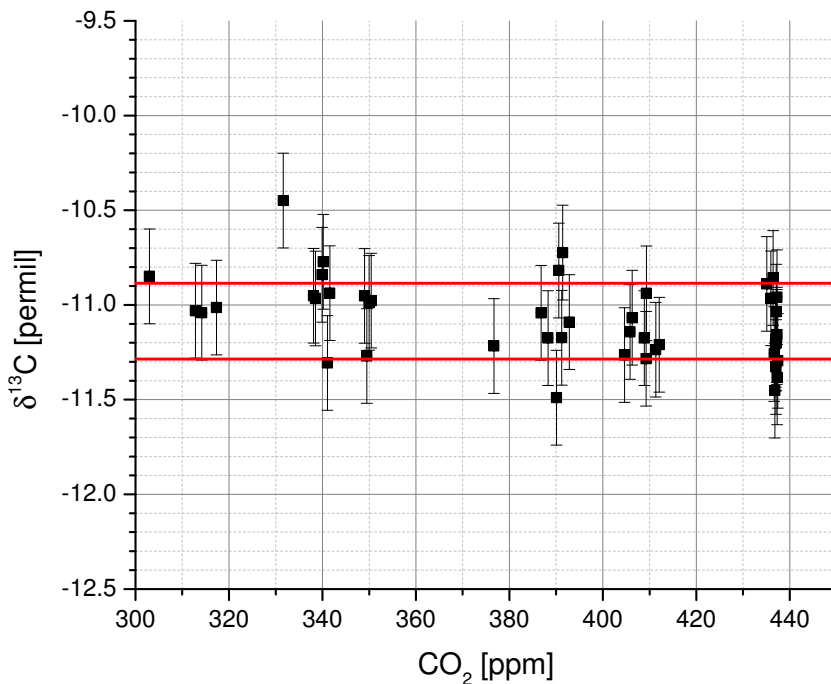
Fig. 5. Dilution experiment using two gas streams to vary the CO_2 concentration while maintaining a constant $\delta^{13}C$ to infer potential CO_2 concentration dependency.
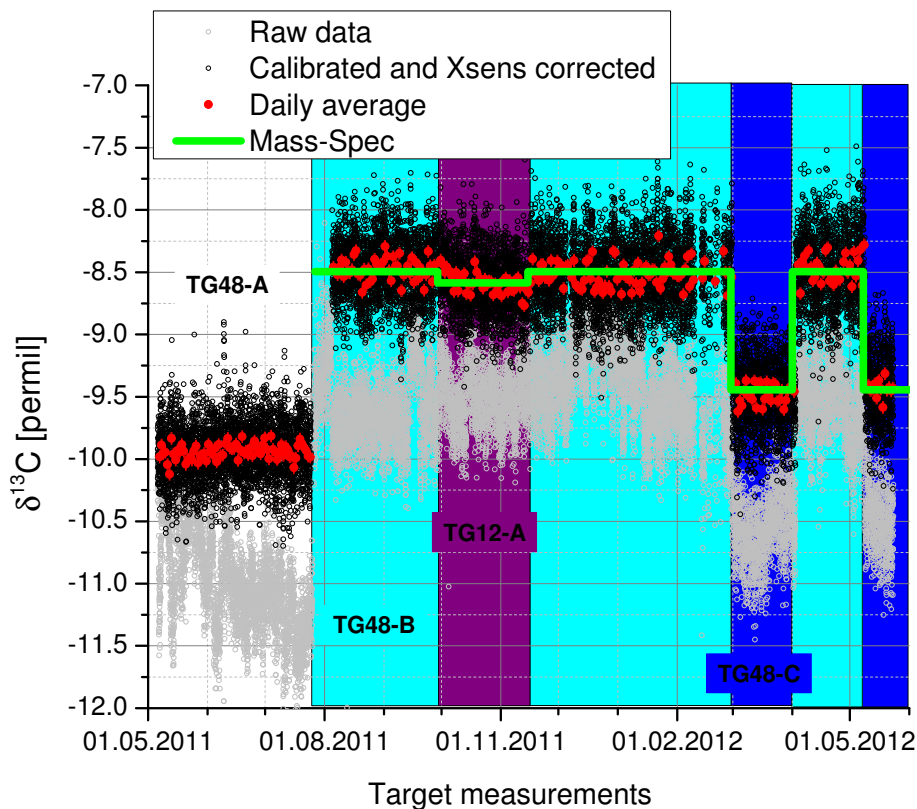
Fig. 6. Time series of the 10 min averaged target measurements passed through the system every 30 min. The Picarro raw data is shown in grey. The calibrated data is in black and daily averages of the $\delta^{13}C_{TG}$ are shown in red. The externally calibrated $\delta^{13}C$ values (using the EC IRMS system) are shown in green. Periods in which different sets of target gases are used are indicated by the background coloring (c.f. Table 1).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

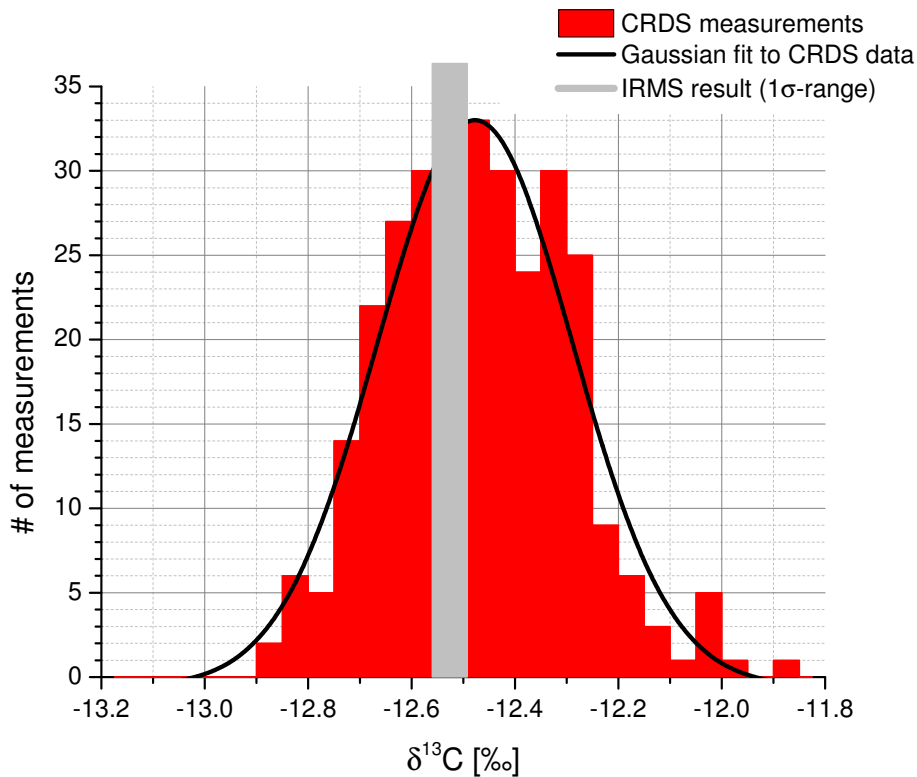Printer-friendly Version

Interactive Discussion

Fig. 7. Histogram of long-term target (LTG-48A) values between November 2011 and May 2012 from three consecutive measurements once per week in red and the IRMS value for LTG-48A in grey.