Inter-comparison of two cavity ring-down spectroscopy analyzers for atmospheric $^{13}$CO$_2$/12CO$_2$ measurement

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Submitted to Atmospheric Measurement Techniques (March 2016)
Abstract: The isotope ratio infrared spectroscopy (IRIS) permits in situ and continuous measurements of CO₂ isotopic composition under ambient conditions. Previous studies mainly focused on single IRIS instrument performance, few studies have paid attention to the comparability among different IRIS instruments. In this study, we carried out laboratory and ambient measurements of two Picarro CO₂ δ¹³C analyzers (G1101-i and G2201-i), and evaluated their performance and comparability. The best precision were 0.08 ~ 0.15‰ and 0.01 ~ 0.04‰, the dependence of δ¹³C on CO₂ concentration were 0.46‰ per 100 ppm and 0.09‰ per 100 ppm, the instrument drift ranged from 0.92 ~ 1.09‰ and 0.19 ~ 0.37 ‰. After upgradation of G1101-i, the sensitivity of δ¹³C on water vapor mixing ratio were 0.15 %/‰ H₂O and 0.13‰/‰ H₂O for the G1101-i and G2201-i, respectively. The accuracy after corrected by the two-point mixing ratio gain and offset calibration method ranged from -0.04 ~ 0.09‰ and -0.13 ~ 0.03‰ for G1101-i and G2201-i, respectively. Atmospheric δ¹³C measurements captured the rapidly changing atmospheric δ¹³C signals, with the difference of 0.07 ± 0.24‰ and 0.05 ± 0.30‰ between G1101-i upgraded before and after and G2201-i. Before upgradation of G1101-i, a significant linear correlation was observed between the δ¹³C difference and water vapor concentration, but there is no significant correlation after upgradation of G1101-i. The difference of Keeling intercept values between G1101-i and G2201-i decrease from 1.24‰ to 0.36‰, which indicate the importance of consistency among different IRIS instruments.

Keywords: Isotope Ratio Infrared Spectroscopy (IRIS); Stable isotope; CO₂ concentration dependence; Water vapor sensitivity; Keeling plot.
1 Introduction

The development of stable isotope analyzers and measurement techniques made stable isotope analysis a powerful tool to gain insight into the underlying mechanism of carbon and water cycling in atmospheric, ecological and hydrological studies (Yakir and Sternberg, 2000; Bowling et al., 2003; Griffis, 2013). The isotope ratio infrared spectroscopy (IRIS) permits in situ and continuous isotope measurements under ambient conditions, overcomes the shortcoming of traditional isotope ratio mass spectrometers (IRMS), which is relatively labor-intensive in sample collection and preparation (Bowling et al., 2005; Schaeffer et al., 2008; Wingate et al., 2010; Griffith et al., 2012; Werner et al., 2012; Griffis, 2013). To date, various IRIS techniques are commercially available for measuring stable carbon isotopes, including lead-salt tunable diode laser absorption spectrometer (TDLAS, Campbell Scientific Inc.), wavelength-scanned cavity ring down spectroscopy (WS-CRDS, Picarro Inc.), off-axis cavity output spectroscopy (OA-ICOS, Los Gatos Research), quantum cascade laser absorption spectrometer (QCLAS, Aerodyne research), and difference frequency generation laser spectroscopy (DFG, Thermo Scientific) (Griffis, 2013; Wen et al., 2013). All the data monitored by the IRIS analyzers should capture the δ13C variations of atmospheric CO2 at high precision under ambient condition and can be traceable to standard VPDB scale (Bowling et al., 2005; Schaeffer et al., 2008; Griffis, 2013). Consistency between the isotopic values reported by various IRIS instruments are the precondition of ensuring the comparability among different instruments (Flowers et al., 2012; Griffith et al., 2012; Wen et al., 2013).

Previous studies have shown that temperature dependence, concentration dependence and spectroscopic interferences are among the major sources of errors for IRIS measurements (Griffith et
Instrument long-term drift is another source of error affecting the IRIS performance (Rella, 2012; Vogel et al., 2013). Most of previous studies focus on the methodology of single IRIS instrument (Bowling et al., 2003; Wahl et al.; 2006; Tuzson et al., 2008; Griffith et al., 2012; Guillon et al., 2012; Vogel et al., 2013). It is important guarantee to get accurate measurement results traceable to the international V-PDB standard by improving the measurement precision and constructing proper calibration strategy. Previous laboratory and field experiments showed precisions for IRIS instruments ranged from 0.02‰ to 0.25‰ for δ¹³C (Bowling et al., 2003; Wahl et al., 2006; Schaeffer et al., 2008; Tuzson et al., 2008; Griffith et al., 2012; Guillon et al., 2012; Sturm et al., 2012; Vogel et al., 2013; Wen et al., 2013). Because of the non-linear response of the concentration dependence of the IRIS instruments, it was recommended to used more than 2 standard gas with different CO₂ concentration for the ¹²CO₂ and ¹³CO₂ calibration to eliminate the non-linearity response of the instruments (Bowling et al., 2005; Schaeffer et al., 2008; Tuzson et al., 2008). The accuracy is 0.01 ± 0.03‰ for three-point linear calibration and 0.00 ± 0.01‰ for four-point linear calibration (Bowling et al., 2005). Setting proper calibrate frequency according to the stability of the instrument can eliminate the drift and the environmental sensitivity of the instruments (Griffis, 2013; Wen et al., 2013).

The system bias among different IRIS instruments measurement will caused poor measurement comparability (Flowers et al., 2012; Hammer et al., 2013; Griffis, 2013; Wen et al., 2013). Bowling et al. (2003) found a consistent offset of 1.77±0.35‰ between the TDLAS and flask-IRMS measurement (n=82), which was caused by pressure broadening. Schaeffer et al. (2008) compared the TDLAS and portable flask package sampling-IRMS measurement and observed a difference of 0.01 ± 0.45‰.
(n=277) for $\delta^{13}$C. Tuzson et al. (2008) found a difference between QCLAS and flask-IRMS measurement of 0.28 ~ 2‰, which was probably caused by non-linear absorption effect and laser intensity variation. Mohn et al. (2008) observed a mean difference of 0.4‰ (n=81) between FTIR and flask-IRMS measurement. Considering the time resolution difference between IRIS and IRMS sampling technology, clear difference was observed when rapid change in atmospheric CO$_2$ concentration (Schaefeer et al., 2008). Mohn et al. (2008) used a Keeling plot method to eliminate the difference in the sampling time resolution between IRMS and FTIR. The difference of $\delta^{13}$C$_R$ obtained by this method is insignificant (-28.1 ± 0.4‰ and -27.9 ± 0.5‰). Very few studies have focused on the inter-comparison among IRIS instruments (Griffis, 2013; Wen et al., 2013), only Wen et al. (2013) compared two commercially available IRIS instruments, Los Gatos DLT-100 and Picarro G1101-i, which have excellent agreement for atmospheric test with the difference being only -0.02 ± 0.18‰, but the error propagation associated with concentration dependence through the Keeling analysis will caused a difference of 2.44‰ in the Keeling intercept.

The objective of this study is to evaluate the performance and comparability of two Picarro CO$_2$ $\delta^{13}$C analyzers based on CRDS technology (G1101-i and G2201-i). Our goals include: 1) to determine the optimal precision of both analyzers by Allan deviation; 2) to test the dependence of $\delta^{13}$C on CO$_2$ concentration, drift and accuracy by gradient switching experiment; 3) to identify the sensitivity of $\delta^{13}$C on water vapor through a dew point generator, and 4) to examine the compatibility between G1101-i and G2201-i by atmospheric CO$_2$ $\delta^{13}$C measurement.

2 Materials and methods
2.1 Analyzers, sampling, and calibration systems

In this study, the inlets of two \( \text{CO}_2 \delta^{13}\text{C} \) analyzers of the Picarro Inc., Sunnyvale, CA, G1101-i (manufactured in 2010) and G2201-i (manufactured in 2014), were parallel connection and then connected with three three-way solenoid valves, which constitute the sampling and calibration system with one ambient air inlet and three calibration gases inlets. The switch sequence of valves were controlled by the valve sequencer software on the G2201-i analyzer. The built-in pressure and temperature monitor systems of G1101-i and G2201-i maintained the cavity temperature of both systems at 45 °C, and the cavity pressure at 140 Torr and 148 Torr, respectively. A diaphragm pump was used to pump the sample air and calibration gas continuously to the cavity at a flow rate of 0.03Lmin\(^{-1}\)STP, and measurement frequency at approximately 0.3 Hz and 1 Hz. The physical laser arrays and the software of the G1101-i analyzer were upgraded in March 2012 and August 2014, to correct the cross interferences caused by \( \text{CH}_4 \) and water vapor, respectively.

The sample air stream passed through a filter (pore size 2 \( \mu \text{m} \), Swagelok model B-4F-05, Connecticut Valves and Fittings, Norwalk Connecticut) to the analyzers without being dried. In this study, only the water vapor dilution effect was corrected, without considering the water vapor pressure broadening effect and spectral interference effect (Wen et al., 2013). Data from the transitional periods, i.e. the first 3min of each sample measurement cycle after valve switching were discarded (Flowers et al., 2012; Vogel et al., 2013).

2.2 Laboratory measurement

Three standard gases (Std1, Std2 and Std3) were produced by Beijing AP BAIF Gases Industry Co., Ltd.
With the \( \text{CO}_2 \) mixing ratio of 368.1 ppm, 451.7 ppm and 550.1 ppm. The \( \delta^{13}\text{C} \) values were measured using an isotope ratio mass spectrometer (Thermo Finnigan MAT 253) at the Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. Since the three standard gases were come from the same gas source, the \( \delta^{13}\text{C} \) values were \(-20.38 \pm 0.06\%\) for all three standard gases.

2.2.1 Allan variance test

Allan variance (Werle et al., 1993) is commonly used to express measurement precision and stability as a function of averaging time. Here the Std1, Std2 and Std3 were connected to the sampling and calibration system were each measured for 24h for conducting the Allan variance analysis.

2.2.2 Gradient switching test

The Std1, Std2 and Std3 connected to the sampling and calibration system and switched sequentially every 40min for a total of 48h. Two of the three standard gases were treated as calibration gases and the other one as target gas, and two-point mixing ratio gain and offset calibration strategy (Bowling et al., 2003; Wen et al., 2013) was used here for each measurement cycle. The measurement data and calibrated data were used to evaluate the dependence of \( \delta^{13}\text{C} \) on \( \text{CO}_2 \) concentration, long-term drift and accuracy of both analyzers.

2.2.3 Water vapor sensitivity test

The water vapor sensitivity of both analyzers were tested by connecting the standard gas (Std1) with a dew point generator (model LI-610, Li-Cor, Inc., Lincoln, NE, USA), and thus creating standard gases.
with various humidity. The first test was conducted during June 2014, the dew point temperature were
set at 5.0, 10.0, 15.0, 20.0, and 25.0 °C, and the corresponding water vapor ranged from 0.87% to 3.15%. After the upgrade of the G1101-i analyzer, a second test was conducted at December 2014, the
dew point temperature were set at 1.0, 5.0, 10.0, 15.0, and 20.0 °C, and the corresponding water vapor ranged from 0.65% to 2.32%. Standard gas at each humidity level was measured for 20 minutes, and a
total of three times.

2.3 Atmospheric measurement

The air sample inlet was located outside the Key Laboratory of Ecosystem Network Observation and Modeling, 10 m above the ground (Wen et al., 2008, 2010, 2012, 2013). The first atmospheric measurement dataset was collected before G1101-i upgraded, from June 15, 2015 to June 23, 2015 (DOY164 ~ 174), and the second dataset was collected after G1101-i upgraded, from December 14, 2014 to December 22, 2014 (DOY348 ~ 356). The first atmospheric measurement sampled Std1 and Std3 for 10 min each, followed by alternate measurements of ambient air (50 min) and Std2(10 min) for 5h. The total duration of the sampling and calibration cycle was 320 min. The second atmospheric measurement sampled Std1, Std3 and Std3 for 10 min each, followed by ambient air measurement for 300min, i.e., a total duration of 330 min. for each sampling and calibration cycle. The atmospheric sample and Std2 was calibrated by Std1 and Std3 for each measurement cycle, and the calibrated atmospheric sample data were used to obtain hourly mean values.

2.4 Calibration procedures

The two-point mixing ratio gain and offset calibration method (Bowling et al., 2003) was used to calibrate the $^{12}$CO$_2$ and $^{13}$CO$_2$ mixing ratio measured by G1101-i and G2201-i. Additional details about
The calibration method can be found in Wen et al. (2013). Following this method, the calibrated mixing ratios of $^{12}\text{CO}_2(x^{12})$ and $^{13}\text{CO}_2(x^{13})$ are calculated as

$$x_{\alpha,t}^{12} = \frac{x_{\alpha,t}^{12} - x_{t}^{12}}{x_{3,m}^{12} - x_{t}^{12}} \left( x_{\alpha,m}^{12} - x_{t}^{12} \right) + x_{t}^{12}$$

$$x_{\alpha,t}^{13} = \frac{x_{\alpha,t}^{13} - x_{t}^{13}}{x_{3,m}^{13} - x_{t}^{13}} \left( x_{\alpha,m}^{13} - x_{t}^{13} \right) + x_{t}^{13}$$

where $m$ and $t$ represent the measured and true mixing ratios, and 1, 3 and a in the subscripts for Std1, Std3 and ambient air, respectively.

The isotopic composition of the CO$_2$ in the ambient air is expressed in the delta notation:

$$\delta^{13}\text{C} = \left( \frac{R_{\text{sample}}}{R_{\text{VPDB}}} - 1 \right) \times 1000$$

Where $R_{\text{sample}}$ is the ratio between $^{13}\text{CO}_2$/$^{12}\text{CO}_2$ ratio of sample, and $R_{\text{VPDB}}$ is the $^{13}\text{C}$/$^{12}\text{C}$ ratio of the reference standard (i.e., the Pee Dee Belemnite).

3 Results

3.1 Precision

Figure 1 shows the Allan variance as a function of averaging time of the $\delta^{13}\text{C}$ measurements for Std1, Std2 and Std3 measured by G1101-i and G2201-i. The $\delta^{13}\text{C}$ precision improved with the averaging time and achieved the optimum values of 0.08‰, 0.15‰ and 0.10‰ for G1101-i at 7600 s, 1900 s and 1900 s for Std1, Std2 and Std3, respectively, and 0.03‰, 0.04‰ and 0.01‰ for G2201-i at 7600 s, 3800 s and 7600 s for the three standard gases.

The precision of G1101-i and G2201-i for $\delta^{13}\text{C}$ value were comparable with other reported performances of the IRIS instruments. The precision of TDLAS instruments ranged from 0.03 to 4‰.
(Bowling et al., 2003, 2005; Griffis et al., 2004; Pataki et al., 2006). Picarro EnviroSense 2050 had a precision of 0.08 ‰ at 130 min (Friedrichs et al., 2010). The Picarro G1101-i had a precision of 0.2‰ at 5 min (Vogel et al., 2013) and the best precision of 0.08‰ at 2000 s (Wen et al., 2013). For Los Gatos DLT-100, the optimal precision of 0.04‰ was obtained at 1000 s (Wen et al., 2013). The QCLAS typically has a precision of 0.18‰ at 350 ppm CO₂ (McManus et al., 2005), and the best precision of 0.16‰ was obtained at 500 s (Tuzson et al., 2008). Nicolet Avatar 370 (Thermo Electron, USA) based on FTIR technology obtained the best precision of 0.15‰ at 16 min (Mohn et al., 2007), and an improved version had a precision of 0.02‰ at 10 min (Griffith et al., 2012).

3.2 Concentration dependence

Figure 2 shows the dependence of δ¹³C on CO₂ concentration for the G1101-i and G2201-i. The dependence of δ¹³C on CO₂ concentration is the non-linearity of the analyzer response to CO₂ concentration variance (Griffith et al., 2012; Guillon et al., 2012; Wen et al., 2013). The δ¹³C values of Std1, Std2 and Std3 measured by G1101-i were -23.46 ± 0.26‰, -22.99 ± 0.28‰ and -22.62 ± 0.27‰, with average value of -23.02 ± 0.27‰. The δ¹³C values measured by G2201-i were -21.65 ± 0.07‰, -21.51 ± 0.08‰ and -21.49 ± 0.05‰, with average value of -21.55 ± 0.07 ‰ (Fig. 2). In the range of 368.1 ~ 550.1 ppm, δ¹³C values measured by G1101-i and G2201-i showed an increase with the increase of CO₂ concentration at 0.46 ‰ per 100 ppm and 0.09‰ per 100 ppm, respectively, and the peak-to-peak amplitudes were 1.75‰ and 0.47‰, respectively.

The concentration dependence of the measured δ¹³C values is the main error source affecting IRIS measurements. Guillon et al. (2012) found that the DLT-100 based on ICOS technology had a...
non-linearity concentration dependence in the range 300 ~ 2000 ppm, and after corrected the
concentration dependence by a fifth order polynomial calibration curve, the accuracy improved from
2.7‰ to 1.3‰ for \( \delta^{13}C \). The picarro G1101-i analyzer based on CRDS technology showed no
significant concentration dependence of \( \delta^{13}C \) with the standard deviation of \( \sim 0.2‰ \) in the range
303~437 ppm (Vogel et al., 2013). Griffith et al. (2012) used a series of different CO\(_2\) mixing ratio at
constant \( \delta^{13}C \) and found a residual curvature against the reciprocal of CO\(_2\) was caused by a small
nonlinearity response of the analyzer.

### 3.3 Stability and Accuracy

Based on the same data measured in section 3.2, the temporal drift and accuracy of \( \delta^{13}C \) values of Std1,
Std2 and Std3 measured by G1101-i and G2201-i is shown in Fig. 3. Two-point mixing ratio gain and
offset calibration method (Bowling et al., 2003) was used to calibrate measured \( \delta^{13}C \) value. During the
48 h measuring period, the standard deviation of \( \delta^{13}C \) values of Std1, Std2 and Std3 measured by
G1101-i were 0.26‰, 0.28‰ and 0.27‰, with the temporal drift of 0.92‰, 1.09‰ and 0.93‰; the
standard deviation of \( \delta^{13}C \) values of Std1, Std2 and Std3 measured by G2201-i were 0.07‰, 0.08‰
and 0.05‰, with the temporal drift of 0.23‰, 0.37‰ and 0.19‰. The differences between the CRDS
and IRMS measurements were -3.08 ± 0.26‰, -2.61 ± 0.28‰ and -2.24 ± 0.27‰ for the G1101-i, and
-1.27 ± 0.07‰, -1.13 ± 0.08‰ and -1.11 ± 0.05‰ for the G2201-i. After calibration, the differences
reduced to 0.09 ± 0.34‰, 0.04 ± 0.20‰ and 0.06 ± 0.21‰ for the G1101-i, and -0.13 ± 0.21‰, 0.03 ±
0.08‰ and -0.10 ± 0.14‰ for the G2201-i, respectively. A much better accuracy was obtained when
the calibration is interpolated (Std2) than extrapolated (Std1 and Std3).
As for the drift of IRIS instruments, Vogel et al. (2013) monitored two gas cylinders sequentially for 3240 days with 10 min and 20 min for each cylinder, the drift of G1101-i was around 0.3‰ day\(^{-1}\). Hammer et al. (2013) measured a target gas continuously for 6 days, the FTIR instrument showed a drift of 0.02‰ day\(^{-1}\) for \(\delta^{13}\)C after sensitivity correction. Tuzson et al. (2008) measured an identical air samples every 15 min for 7 h, the standard deviation of the \(\delta^{13}\)C measured by QCLAS was 0.14‰ (n=28). Schaeffer et al. (2008) monitored two quality control tanks in the field over 2.44 year, and the standard deviation of the difference between actual and measured values were 0.31‰ and 0.33‰ (n=2318 and n=2254). Wehr et al. (2008) monitored a CSIRO standard gas over a period of 30 min, and the standard deviation for integration times of 20s and 120s were 0.71‰ and 0.64‰. In this study, during the period of 48 h, the standard deviation of \(\delta^{13}\)C measured by G1101-i and G2201-i are 0.26 ~ 0.28‰ and 0.05 ~ 0.08‰, and the drift are 0.92 ~ 1.09‰ and 0.19 ~ 0.37‰, respectively.

As for the accuracy of IRIS instruments, Guillon et al. (2012) found in the range 300 ~ 2000 ppm, the accuracy of \(\delta^{13}\)C value measured by DLT-100 was 2.7‰ for raw measurements and improved to 1.3‰ after correction. Over the entire 2.44 year period, two quality control gas measured by TDLAS in the field showed agreement between actual and measured values of -0.17 ± 0.33‰ and -0.14 ± 0.4‰ for tank 1 and tank 2 (Schaeffer et al., 2008). Over a period of 30 min measurement, the \(\delta^{13}\)C values measured by CEAS showed a systematic error of 0.9‰ between the measured and IRMS values (Wehr et al., 2008). Used the optimized PLS algorithm, the accuracy of \(\delta^{13}\)C measured by FTIR was 0.4‰ with CO\(_2\) concentrations in the range 364 ~ 530 ppm (Mohn et al., 2007). Over one year period, Vogel et al. (2013) found although a single measurement was imprecise, the G1101-i \(\delta^{13}\)C analyzer provided a mean accuracy of 0.002 ± 0.025‰ after proper calibration. In this study, the accuracy of G1101-i and...
G2201-i δ¹³C analyzer are -3.06 ~ -2.22‰ and -1.25 ~ -1.09‰ before calibration and improved to -0.02 ~ 0.11 and -0.11 ~ 0.05‰ after calibration over a measurement course of 48 h.

3.4 Sensitivity of δ¹³C on water vapor concentration

The sensitivity of δ¹³C on water vapor concentration of G1101-i and G2201-i before and after upgradation of G1101-i are shown in Fig. 4. Before upgradation of G1101-i, the dew point temperature of standard gas ranged from 5 to 25 °C, and the mean δ¹³C values measured by G1101-i and G2201-i were -20.64 ± 0.72‰ and -21.60 ± 0.19‰, the sensitivity of δ¹³C on water vapor mixing ratio at 0.86‰/% H₂O and 0.20‰/% H₂O, respectively, and the peak-to-peak amplitudes were 1.96‰ and 0.45‰, respectively. After upgradation of G1101-i, the mean δ¹³C values measured by G1101-i and G2201-i were -22.34 ± 0.09‰ and -22.27 ± 0.18‰, the sensitivity of δ¹³C on water vapor mixing ratio at 0.13‰/% H₂O and -0.27‰/% H₂O, respectively, and the peak-to-peak amplitudes were 0.22‰ and 0.46‰. With dew point in the range 5 ~ 20 °C, the mean δ¹³C value measured by G1101-i and G2201-i were -20.84 ± 0.66‰ and -21.68 ± 0.07‰ before upgradation of G1101-i and -22.34 ± 0.10‰ and -22.34 ± 0.08‰ after upgradation of G1101-i. The sensitivity to water vapor mixing ratio of δ¹³C at 1.01‰/% H₂O and 0.09‰/% H₂O, respectively, and the peak-to-peak amplitudes were 1.47‰ and 0.14 ‰ before upgradation of G1101-i, and at 0.15‰/% H₂O and 0.13‰/% H₂O, respectively, and the peak-to-peak amplitudes were 0.22‰ and 0.19‰ after upgradation of G1101-i.

The dilution and pressure broadening effect are the two major factors leading to the dependence of the measured δ¹³C on water vapor concentrations (Chen et al., 2010; Nara et al., 2012). The variations of sample water vapor significantly affect the mixing ratio of ¹²CO₂ and ¹³CO₂ via dilution effect. In
addition, the variability of water vapor also introduce broadening effect on spectroscopic line, which includes Lorentzian line broadening and Dicke line narrowing effect. The CRDS instruments measured $^{12}$CO$_2$ and $^{13}$CO$_2$ concentration by the peak height of the absorption peak whose baseline and shape can be interfered by the absorption peaks of water (Nara et al., 2012; Rella et al., 2013). As for the CO$_2$, the systematic errors caused by the broadening effects would be 40% of the dilution effects if it is not corrected (Chen et al., 2010). The transferability of water correction function among multiple instruments also bias the measurement data among different instruments. Rella et al., (2013) found the transferability meet the GAW quality extend to ~2% water vapor for both CO$_2$ and CH$_4$. But for 3 instruments based on CRDS technology, the residual errors of CO$_2$ showed substantially large values with increasing water vapor concentration (Nara et al., 2012). These incompatibility results indicate the need of more precise experiments to evaluate the transferability of water correction function. Moreover, potential long-term drift of the water vapor correction coefficients of individual instrument need to assess with water vapor correction (Nara et al., 2012; Rella et al., 2013).

In this study, the standard deviation of $\delta^{13}$C measured by G2201-i under different water vapor concentration (0.07‰ and 0.08‰) are smaller than the precision given by manufacturer (0.15‰), and the standard deviation of $\delta^{13}$C measured by upgraded G1101-i (0.10‰) is smaller than the specified precision, too. These results indicate that the water corrections embedded in the instruments’ software work sufficiently within the dew point range of 5 ~ 20 °C.

3.5 Atmospheric measurement

Before and after G1101-i upgraded, the $\delta^{13}$C of atmospheric CO$_2$ was measured continuously by G1101-i and G2202-i analyzers. The temporal variations of atmospheric $\delta^{13}$C, the difference between
G1101-i and G2202-i analyzers, and the distribution of differences are shown in Fig. 5. The measured atmospheric δ^{13}C values were calibrated by Std1 and Std3, and the Std2 used here as quality control gas to assess the accuracy of atmospheric sample measurement (Fig. 6).

Atmospheric δ^{13}C measured by G1101-i and G2201-i showed good agreement and both of them captured the rapidly changing atmospheric δ^{13}C. Before G1101-i upgraded (DOY164 ~ 174), atmospheric δ^{13}C measured by G1101-i and G2201-i ranged from -13.24‰ to -7.47‰ and -13.41‰ to -7.62‰, with average value of -9.49 ± 1.22‰ and -9.42 ± 1.17‰, respectively. The difference of δ^{13}C measured by G1101-i and G2202-i analyzers ranged from -0.62‰ to 0.76‰, with average value of 0.07 ± 0.24‰. The difference exhibits a Gaussian distribution. A significant systematic bias of δ^{13}C values were identified between these two analyzers (t-test, p<0.01). After G1101-i upgraded (DOY348-356), atmospheric δ^{13}C measured by G1101-i and G2201-i ranged from -14.08‰ to -8.64‰ and -13.89‰ to -9.06‰, with average value of -10.61‰ and -10.56‰. The difference of δ^{13}C measured by G1101-i and G2202-i analyzers ranged from -0.57‰ to 0.85‰, with average value of 0.05 ± 0.30‰. A significant systematic bias of δ^{13}C values still existed between these two analyzers (t-test, p=0.018). In addition, field measured values of Std2 during atmospheric measurement period (DOY164 ~ 174 and DOY348 ~ 356) were used to assess the stability and accuracy of both analyzers (Fig. 6). During the first atmospheric measurement period, the average δ^{13}C values of Std2 were -21.32 ± 0.51‰ and -21.91 ± 0.12‰ for G1101-i and G2201-i. After calibration, the average δ^{13}C values were -20.30 ± 0.40‰ and -20.56 ± 0.17‰, respectively. The accuracy (the difference between calibration and actual values) ranged from -0.70‰ to 0.91‰ and -0.42‰ to 0.19‰, with average values of 0.09 ± 0.40‰ and -0.17 ± 0.17‰. During the second atmospheric measurement period, the average δ^{13}C values were...
values of Std2 were $-24.37 \pm 0.59\%\text{o}$ and $-21.92 \pm 0.18\%\text{o}$ for G1101-i and G2201-i. After calibration, the average $\delta^{13}\text{C}$ values were $-20.56 \pm 0.23\%\text{o}$ and $-20.57 \pm 0.09\%\text{o}$, respectively. The accuracy ranged from $-0.60\%\text{o}$ to $0.30\%\text{o}$ and $-0.42\%\text{o}$ to $0.02\%\text{o}$, with average values of $-0.17 \pm 0.23\%\text{o}$ and $-0.18 \pm 0.09\%\text{o}$. These results indicate that the stability of G2201-i is better than G1101-i, which is consistent with the Allan variation result.

4 Discussion

The isotopic composition of source CO$_2$ ($\delta^{13}\text{C}_S$) was used to gain insight into the potential local CO$_2$ sources and underlying mechanisms at different temporal and spatial scales. In this study, $\delta^{13}\text{C}_S$ was calculated using the calibration dataset of $\delta^{13}\text{C}$ and CO$_2$ by the Keeling plot intercept method (Fig. 7).

During the first measurement period, the $\delta^{13}\text{C}_S$ values were $-24.80 \pm 0.39\%\text{o}$ and $-23.98 \pm 0.30\%\text{o}$ for G1101-i and G2201-i, the mean difference between G1101-i and G2201-i was 0.82\%o. If used the nighttime data (22:00 ~ 04:00) only for the Keeling analysis, the $\delta^{13}\text{C}_S$ values were $-28.35 \pm 1.34\%\text{o}$ and $-27.11 \pm 1.02\%\text{o}$ for G1101-i and G2201-i, with a mean difference of 1.24\%o. The $\delta^{13}\text{C}_S$ value deduced from nighttime data was a mixed value of various local CO$_2$ sources, including the combustion of natural gas, gasoline and coal, and the respiration of plant and soil (Pang et al., 2016).

During the second measurement period after G1101-i upgraded, the $\delta^{13}\text{C}_S$ values were $-25.90 \pm 0.28\%\text{o}$ and $-25.97 \pm 0.12\%\text{o}$ with a mean difference of 0.07\%o. If used the nighttime data (22:00 ~ 04:00) only for the Keeling analysis, the $\delta^{13}\text{C}_S$ values were $-26.05 \pm 0.16\%\text{o}$ and $-25.69 \pm 0.41\%\text{o}$ for G1101-i and G2201-i, with a mean difference of 0.36\%o. After G1101-i upgraded, the systematic bias of $\delta^{13}\text{C}$ between G1101-i and G2201-i decreased from $0.07 \pm 0.24\%\text{o}$ to $0.05 \pm 0.30\%\text{o}$, and the difference of
$\delta^{13}C_s$ decreased from 1.24‰ to 0.36‰. The results confirm that we should pay attention to the measurement difference among different IRIS instruments and this difference will cause an error propagation through Keeling plot analysis (Wen et al., 2013).

Figure 8 shows the dependence of the $\delta^{13}C$ difference between G1101-i and G2201-i on water vapor concentration and CO$_2$ mixing ratio. Before and after upgradation of G1101-i, there were no significant correlation between the $\delta^{13}C$ difference and CO$_2$ mixing ratio (Fig. 8a and 8b). Before upgradeation of G1101-i, a significant linear correlation was observed between the $\delta^{13}C$ difference and water vapor concentration (P<0.01, Fig. 8c), after upgraded of G1101-i, there was no significant correlation between the $\delta^{13}C$ difference and water vapor concentration (P>0.05, Fig. 8d), this relationship mainly due to the upgradation of G1101-i, which excluded $\delta^{13}C$ measurement errors came from water vapor variation, and improved the accuracy of $\delta^{13}C$ measurement. This result was consistent with the sensitivity of $\delta^{13}C$ on water vapor concentration test. In addition, the second measurement was conducted in winter when the atmospheric water vapor concentration was relatively low and the water vapor interferences were small.

5 Conclusion

In this study, the performance and comparability of Picarro G1101-i and G2201-i CO$_2\delta^{13}C$ analyzers was evaluated. The main conclusions are as follows:

1) The Allan variation test indicate that the best precision of 0.08 ~ 0.15‰ and 0.01 ~ 0.04‰ measured by G1101-i and G2201-i can be obtained with averaging time of 1850 ~ 7400 s and 3700 ~ 7400 s with the CO$_2$ ranged from 368.1 to 550.1 ppm.

2) With the gradient switching test lasted 48h, the dependence of $\delta^{13}C$ on CO$_2$ concentration were
0.46‰ per 100 ppm and 0.09‰ per 100 ppm for G1101-i and G2201-i in the range of 368.1 ~ 550.1 ppm, and the instruments drift ranged from 0.92‰ to 1.09‰ and 0.19‰ to 0.37 ‰. After calibrated by the two-point mixing ratio gain and offset calibration method, the average δ¹³C values were -20.34 ± 0.07‰ and -20.45 ± 0.09‰, similar with actual value measured by IRMS (-20.38 ± 0.06‰).

3) With dew point temperature in the range 5 ~ 20 °C, the sensitivity of δ¹³C on water vapor mixing ratio measured by G1101-i and G2201-i were 1.01 ‰/% H₂O and 0.09‰/% H₂O during the first test and 0.15 ‰/% H₂O and 0.13‰/% H₂O during the second test. The standard deviation of δ¹³C measured by G2201-i and upgraded G1101-i were ~ 0.08‰ and ~ 0.10‰, which were smaller than instrument precision(0.15‰). These results indicate that the water corrections embedded in the instruments’ software work sufficiently within the dew point range of 5 ~ 20 °C.

4) Atmospheric δ¹³C measured by G1101-i and G2201-i captured the rapidly changing of atmospheric δ¹³C. Before G1101-i upgraded (DOY164 - 174), the difference of δ¹³C measured by G1101-i and G2202-i analyzers ranged from -0.62‰ to 0.76‰, with average values of 0.07 ± 0.24‰. After G1101-i upgraded (DOY348-356), the difference of δ¹³C measured by G1101-i and G2202-i analyzers ranged from -0.57‰ to 0.85‰, with average value of 0.05 ± 0.30‰. This difference exhibits a Gaussian distribution. Before upgradation of G1101-i, a significant linear correlation was observed between the δ¹³C difference and water vapor concentration (P<0.01), but there is no significant correlation (P>0.05) after upgradation of G1101-i. this is mainly due to the upgradation of G1101-i improved the interference of water vapor on δ¹³C measurement. The difference of Keeling intercept value between G1101-i and G2201-i decrease from 1.24‰ to 0.36‰, which indicate the importance of consistency among different IRIS instruments.
Acknowledgments

This study was supported by the National Natural Science Foundation of China (41571130043, 31290221 and 31470500).

Reference


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Tables and Figures:

Figure 1: Allan deviation of the $\delta^{13}$C for the (a) G1101-1 and (b) G2201-1 analyzers with 3 different CO$_2$ concentrations with same $\delta^{13}$C standard gases.

concentration with same $\delta^{13}$C standard gases.
Figure 2: Dependency of the measured $\delta^{13}$C of G1101-i and G2201-i analyzers on the measured CO$_2$ concentration with 3 different CO$_2$ concentration with same $\delta^{13}$C standard gases.
Figure 3: Time variations of $\delta^{13}$C of the 3 different CO$_2$ concentration with same $\delta^{13}$C standard gases (Std1, Std2 and Std3) of G1101-i (a, c, e) and G2201-i (b, d, f) analyzers. (a) and (b) are data from Std1, (c) and (d) are data from Std2, and (e) and (f) are data from Std3.
Figure 4: Sensitivity of the measured $\delta^{13}C$ by G1101-i and G2201-i on water vapor mixing ratio. (a) measured before G1101-i upgraded and (b) measured after G1101-i upgraded.
Figure 5: Time variations of (a) and (d) hourly atmospheric δ\textsuperscript{13}C, (b) and (e) difference between the Picarro G1101-i and G2201-i analyzers and (c) and (f) histogram of the differences. The left panels (a, b, and c) were measured before G1101-i upgraded (DOY 164 - 174) and the right panels (d, e, and f) were measured after G1101-i upgraded (DOY348 - 356).
Figure 6: Time series of the 10 min averaged $\delta^{13}$C of quality control gas (std2) monitored by (a) G1101-i analyzer and (b) G2201-i analyzer.
Figure 7: Keeling plot of the calibrated atmospheric δ\(^{13}\)C against the reciprocal of the calibrated CO\(_2\) concentration for the Picarro (a, b) G2201-i and (c, d) G1101-i analyzers. (a) and (c) was measured before G1101-i upgraded (DOY 164 - 174), and (b) and (d) was measured after G1101-i upgraded (DOY 348 - 356). Both daytime and nighttime data were used.
Figure 8: Dependence of the atmospheric δ13C difference between the Picarro G1101-i and G2201-i analyzers on the CO2 and H2O concentration. (a) and (c) was measured before G1101-i upgraded (DOY 164-174), and (b) and (d) was measured after G1101-i upgraded (DOY 348-356).