



1	Inter-comparison of two cavity ring-down
2	spectroscopy analyzers for atmospheric <sup>13</sup> CO <sub>2</sub> / <sup>12</sup> CO <sub>2</sub>
3	measurement
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23	Abstract: The isotope ratio infrared spectroscopy (IRIS) permits in situ and continuous measurements
24	of CO <sub>2</sub> isotopic composition under ambient conditions. Previous studies mainly focused on single IRIS
25	instrument performance, few studies have paid attention to the comparability among different IRIS
26	instruments. In this study, we carried out laboratory and ambient measurements of two Picarro $\mbox{\rm CO}_2$
27	$\delta^{13}C$ analyzers (G1101-i and G2201-i), and evaluated their performance and comparability. The best
28	precision were 0.08 ~ 0.15‰ and 0.01 ~ 0.04‰, the dependence of $\delta^{13}C$ on $CO_2$ concentration were
29	0.46‰ per 100 ppm and 0.09‰ per 100 ppm, the instrument drift ranged from 0.92 ~ 1.09‰ and 0.19
30	$\sim$ 0.37 ‰. After upgradation of G1101-i, the sensitivity of $\delta^{13}C$ on water vapor mixing ratio were
31	0.15 ‰/% $\rm H_2O$ and 0.13‰/% $\rm H_2O$ for the G1101-i and G2201-i, respectively. The accuracy after
32	corrected by the two-point mixing ratio gain and offset calibration method ranged from -0.04 $\sim 0.09\%$
33	and -0.13 ~ 0.03‰ for G1101-i and G2201-i, respectively. Atmospheric $\delta^{13}C$ measurements captured
34	the rapidly changing atmospheric $\delta^{13}C$ signals, with the difference of 0.07 $\pm$ 0.24‰ and 0.05 $\pm$ 0.30‰
35	between G1101-i upgraded before and after and G2201-i. Before upgradation of G1101-i, a significant
36	linear correlation was observed between the $\delta^{13}C$ difference and water vapor concentration, but there is
37	no significant correlation after upgradation of G1101-i. The difference of Keeling intercept values
38	between G1101-i and G2201-i decrease from 1.24‰ to 0.36‰, which indicate the importance of
39	consistency among different IRIS instruments.
40	Keywords: Isotope Ratio Infrared Spectroscopy (IRIS); Stable isotope; CO <sub>2</sub> concentration dependence;

41 Water vapor sensitivity; Keeling plot





# 43 1 Introduction

44	The development of stable isotope analyzers and measurement techniques made stable isotope
45	analysis a powerful tool to gain insight into the underlying mechanism of carbon and water cycling in
46	atmospheric, ecological and hydrological studies (Yakir and Sternberg, 2000; Bowling et al., 2003;
47	Griffis, 2013). The isotope ratio infrared spectroscopy (IRIS) permits in situ and continuous isotope
48	measurements under ambient conditions, overcomes the shortcoming of traditional isotope ratio mass
49	spectrometers (IRMS), which is relatively labor-intensive in sample collection and preparation
50	(Bowling et al., 2005; Schaeffer et al., 2008; Wingate et al., 2010; Griffith et al., 2012; Werner et al.,
51	2012; Griffis, 2013). To date, various IRIS techniques are commercially available for measuring stable
52	carbon isotopes, including lead-salt tunable diode laser absorption spectrometer (TDLAS, Campbell
53	Scientific Inc.), wavelength-scanned cavity ring down spectroscopy (WS-CRDS, Picarro Inc.), off-axis
54	cavity output spectroscopy (OA-ICOS, Los Gatos Research), quantum cascade laser absorption
55	spectrometer (QCLAS, Aerodyne research), and difference frequency generation laser spectroscopy
56	(DFG, Thermo Scientific) (Griffis, 2013; Wen et al., 2013). All the data monitored by the IRIS
57	analyzers should capture the $\delta^{13}C$ variations of atmospheric $\text{CO}_2$ at high precision under ambient
58	condition and can be traceable to standard VPDB scale (Bowling et al., 2005; Schaeffer et al., 2008;
59	Griffis, 2013). Consistency between the isotopic values reported by various IRIS instruments are the
60	precondition of ensuring the comparability among different instruments (Flowers et al., 2012; Griffith
61	et al., 2012; Wen et al., 2013).

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63 Previous studies have shown that temperature dependence, concentration dependence and64 spectroscopic interferences are among the major sources of errors for IRIS measurements (Griffith et





65	al., 2012; Guillon et al., 2012; Vogel et al., 2013; Wen et al., 2013). Instrument long-term drift is
66	another source of error affecting the IRIS performance (Rella, 2012; Vogel et al., 2013). Most of
67	previous studies focus on the methodology of single IRIS instrument (Bowling et al., 2003; Wahl et al.;
68	2006; Tuzson et al., 2008; Griffith et al., 2012; Guillon et al., 2012; Vogel et al., 2013). It is important
69	guarantee to get accurate measurement results traceable to the international V-PDB standard by
70	improving the measurement precision and constructing proper calibration strategy. Previous laboratory
71	and field experiments showed precisions for IRIS instruments ranged from 0.02‰ to 0.25‰ for $\delta^{13}C$
72	(Bowling et al., 2003; Wahl et al., 2006; Schaeffer et al., 2008; Tuzson et al., 2008; Griffith et al., 2012;
73	Guillon et al., 2012; Sturm et al., 2012; Vogel et al., 2013; Wen et al., 2013). Because of the non-linear
74	response of the concentration dependence of the IRIS instruments, it was recommended to used more
75	than 2 standard gas with different $CO_2$ concentration for the ${}^{12}CO_2$ and ${}^{13}CO_2$ calibration to eliminate
76	the non-linearity response of the instruments (Bowling et al., 2005; Schaeffer et al., 2008; Tuzson et al.,
77	2008). The accuracy is 0.01 $\pm$ 0.03‰ for three-point linear calibration and 0.00 $\pm$ 0.01‰ for four-point
78	linear calibration (Bowling et al., 2005). Setting proper calibrate frequency according to the stability of
79	the instrument can eliminate the drift and the environmental sensitivity of the instruments (Griffis,
80	2013; Wen et al., 2013).

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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  $1.77\pm0.35\%$  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  $0.01 \pm 0.45\%$ 





87	(n=277) for $\delta^{13}$ C. Tuzson et al. (2008) found a difference between QCLAS and flask-IRMS
88	measurement of 0.28 $\sim$ 2‰, which was probably caused by non-linear absorption effect and laser
89	intensity variation. Mohn et al. (2008) observed a mean difference of 0.4‰(n=81) between FTIR and
90	flask-IRMS measurement. Considering the time resolution difference between IRIS and IRMS
91	sampling technology, clear difference was observed when rapid change in atmospheric $\mathrm{CO}_2$
92	concentration (Schaeffer et al., 2008). Mohn et al. (2008) used a Keeling plot method to eliminate the
93	difference in the sampling time resolution between IRMS and FTIR. The difference of $\delta^{13}C_{\text{R}}$ obtained
94	by this method is insignificant (-28.1 $\pm$ 0.4‰ and -27.9 $\pm$ 0.5‰). Very few studies have focused on the
95	inter-comparison among IRIS instruments (Griffis, 2013; Wen et al., 2013), only Wen et al. (2013)
96	compared two commercially available IRIS instruments, Los Gatos DLT-100 and Picarro G1101-i,
97	which have excellent agreement for atmospheric test with the difference being only -0.02 $\pm$ 0.18‰, but
98	the error propagation associated with concentration dependence through the Keeling analysis will
99	caused a difference of 2.44‰ in the Keeling intercept.

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101 The objective of this study is to evaluate the performance and comparability of two Picarro  $CO_2 \delta^{13}C$ 102 analyzers based on CRDS technology (G1101-i and G2201-i). Our goals include :1) to determine the 103 optimal precision of both analyzers by Allan deviation; 2) to test the dependence of  $\delta^{13}C$  on  $CO_2$ 104 concentration, drift and accuracy by gradient switching experiment; 3) to identify the sensitivity of  $\delta^{13}C$ 105 on water vapor through a dew point generator , and 4) to examine the compatibility between G1101-i 106 and G2201-i by atmospheric  $CO_2 \delta^{13}C$  measurement.

107

## 108 2 Materials and methods





### 109 2.1 Analyzers, sampling, and calibration systems

- In this study, the inlets of two CO<sub>2</sub>  $\delta^{13}$ C analyzers of the Picarro Inc., Sunnyvale, CA, 110 G1101-i(manufactured in 2010) and G2201-i(manufactured in 2014), were parallel connection and then 111 112 connected with three three-way solenoid valves, which constitute the sampling and calibration system 113 with one ambient air inlet and three calibration gases inlets. The switch sequence of valves were 114 controlled by the valve sequencer software on the G2201-i analyzer. The built-in pressure and 115 temperature monitor systems of G1101-i and G2201-i maintained the cavity temperature of both 116 systems at 45 °C, and the cavity pressure at 140 Torr and 148 Torr, respectively. A diaphragm pump 117 was used to pump the sample air and calibration gas continuously to the cavity at a flow rate of 118 0.03Lmin<sup>-1</sup>STP, and measurement frequency at approximately 0.3 Hz and 1 Hz. The physical laser 119 arrays and the software of the G1101-i analyzer were upgraded in March 2012 and August 2014, to 120 correct the cross interferences caused by CH<sub>4</sub> and water vapor, respectively. 121
- The sample air stream passed through a filter (pore size 2 μm, 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).

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#### 129 2.2 Laboratory measurement

130 Three standard gases (Std1, Std2 and Std3) were produced by Beijing AP BAIF Gases Industry Co.,Ltd.





- 131 With the CO<sub>2</sub> mixing ratio of 368.1 ppm, 451.7 ppm and 550.1 ppm. The  $\delta^{13}$ C values were measured
- 132 using an isotope ratio mass spectrometer (Thermo Finnigan MAT 253) at the Key Laboratory of
- 133 Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural
- 134 Resources Research, Chinese Academy of Sciences. Since the three standard gases were come from the
- 135 same gas source, the  $\delta^{13}C$  values were -20.38  $\pm$  0.06‰ for all three standard gases.
- 136

### 137 2.2.1 Allan variance test

- 138 Allan variance (Werle et al., 1993) is commonly used to express measurement precision and stability as
- 139 a function of averaging time. Here the Std1, Std2 and Std3 were connected to the sampling and
- 140 calibration system were each measured for 24h for conducting the Allan variance analysis.
- 141

### 142 2.2.2 Gradient switching test

- 143 The Std1, Std2 and Std3 connected to the sampling and calibration system and switched sequentially
- 144 every 40min for a total of 48h. Two of the three standard gases were treated as calibration gases and the
- 145 other one as target gas, and two-point mixing ratio gain and offset calibration strategy (Bowling et al.,
- 146 2003; Wen et al., 2013) was used here for each measurement cycle. The measurement data and
- 147 calibrated data were used to evaluate the dependence of  $\delta^{13}$ C on CO<sub>2</sub> concentration, long-term drift and
- 148 accuracy of both analyzers.

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### 150 2.2.3 Water vapor sensitivity test

151 The water vapor sensitivity of both analyzers were tested by connecting the standard gas (Std1) with a

152 dew point generator (model LI-610, Li-Cor, Inc., Lincoln, NE, USA), and thus creating standard gases





153	with various humidity. The first test was conducted during June 2014, the dew point temperature were
154	set at 5.0, 10.0, 15.0, 20.0, and 25.0 $^\circ$ C, and the corresponding water vapor ranged from 0.87% to
155	3.15%. After the upgrade of the G1101-i analyzer, a second test was conducted at December 2014, the
156	dew point temperature were set at 1.0, 5.0, 10.0, 15.0, and 20.0 °C, and the corresponding water vapor
157	ranged from 0.65% to 2.32%. Standard gas at each humidity level was measured for 20 minutes, and a
158	total of three times.
159	2.3 Atmospheric measurement
160	The air sample inlet was located outside the Key Laboratory of Ecosystem Network Observation and
161	Modeling, 10 m above the ground (Wen et al., 2008, 2010, 2012, 2013). The first atmospheric
162	measurement dataset was collected before G1101-i upgraded, from June 15, 2015 to June 23, 2015
163	(DOY164 ~ 174), and the second dataset was collected after G1101-i upgraded, from December 14,
164	2014 to December 22, 2014 (DOY348 ~ 356). The first atmospheric measurement sampled Std1 and
165	Std3 for 10 min each, followed by alternate measurements of ambient air (50 min) and Std2(10 min)
166	for 5h. The total duration of the sampling and calibration cycle was 320 min. The second atmospheric
167	measurement sampled Std1, Std3 and Std3 for 10 min each, followed by ambient air measurement for
168	300min, i.e., a total duration of 330 min. for each sampling and calibration cycle. The atmospheric
169	sample and Std2 was calibrated by Std1 and Std3 for each measurement cycle, and the calibrated
170	atmospheric sample data were used to obtain hourly mean values.

171

# 172 2.4 Calibration procedures

The two-point mixing ratio gain and offset calibration method (Bowling et al., 2003) was used to
calibrate the <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> mixing ratio measured by G1101-i and G2201-i. Additional details about





- 175 calibration method can be found in Wen et al.(2013). Following this method, the calibrated mixing
- 176 ratios of  ${}^{12}CO_2(x^{12})$  and  ${}^{13}CO_2(x^{13})$  are calculated as

177 
$$x_{a,t}^{12} = \frac{x_{3,t}^{12} - x_{1,t}^{12}}{x_{3,m}^{12} - x_{1,m}^{12}} \left( x_{a,m}^{12} - x_{1,m}^{12} \right) + x_{1,t}^{12}$$
(1)

178 
$$x_{a,t}^{13} = \frac{x_{3,t}^{13} - x_{1,t}^{13}}{x_{3,m}^{13} - x_{1,m}^{13}} (x_{a,m}^{13} - x_{1,m}^{13}) + x_{1,t}^{13}$$
 (2)

179 where m and t represent the measured and true mixing ratios, and 1, 3 and a in the subscripts for Std1,

- 180 Std3 and ambient air, respectively.
- 181 The isotopic composition of the  $CO_2$  in the ambient air is expressed in the delta notation:
- 182  $\delta^{13}C = (R_{sample} / R_{VPDB} 1) \times 1000$  (3)
- 183 Where  $R_{sample}$  is the ratio between  ${}^{13}CO_2/{}^{12}CO_2$  ratio of sample, and  $R_{VPDB}$  is the  ${}^{13}C/{}^{12}C$  ratio of the
- 184 reference standard (i.e., the Pee Dee Belemnite).

185

#### 186 3 Results

- 187 3.1 Precision
- 188 Figure 1 shows the Allan variance as a function of averaging time of the  $\delta^{13}$ C measurements for Std1,
- 189 Std2 and Std3 measured by G1101-i and G2201-i. The  $\delta^{13}$ C precision improved with the averaging
- 190 time and achieved the optimum values of 0.08‰, 0.15‰ and 0.10‰ for G1101-i at 7600 s, 1900 s and
- 191 1900 s for Std1, Std2 and Std3, respectively, and 0.03‰, 0.04‰ and 0.01‰ for G2201-i at 7600 s,
- 192 3800 s and 7600 s for the three standard gases.
- 193
- The precision of G1101-i and G2201-i for δ<sup>13</sup>C value were comparable with other reported
  performances of the IRIS instruments. The precision of TDLAS instruments ranged from 0.03 to 4‰





- 196 (Bowling et al., 2003, 2005; Griffis et al., 2004; Pataki et al., 2006). Picarro EnviroSense 2050 had a
- 197 precision of 0.08 ‰ at 130 min (Friedrichs et al., 2010). The Picarro G1101-i had a precision of 0.2‰
- 198 at 5 min (Vogel et al., 2013) and the best precision of 0.08‰ at 2000 s (Wen et al., 2013). For Los
- 199 Gatos DLT-100, the optimal precision of 0.04‰ was obtained at 1000 s (Wen et al., 2013). The
- 200 QCLAS typically has a precision of 0.18‰ at 350 ppm CO<sub>2</sub> (McManus et al., 2005), and the best
- 201 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).
- 204

#### 205 **3.2** Concentration dependence

Figure 2 shows the dependence of  $\delta^{13}$ C on CO<sub>2</sub> concentration for the G1101-i and G2201-i. The 206 207 dependence of  $\delta^{13}$ C on CO<sub>2</sub> concentration is the non-linearity of the analyzer response to CO<sub>2</sub> concentration variance (Griffith et al., 2012; Guillon et al., 2012; Wen et al., 2013). The  $\delta^{13}$ C values of 208 209 Std1, Std2 and Std3 measured by G1101-i were -23.46  $\pm$  0.26‰, -22.99  $\pm$  0.28‰ and -22.62  $\pm$  0.27‰, 210 with average value of  $-23.02 \pm 0.27$ %. The  $\delta^{13}$ C values measured by G2201-i were  $-21.65 \pm 0.07$ %, 211  $-21.51 \pm 0.08\%$  and  $-21.49 \pm 0.05\%$ , with average value of  $-21.55 \pm 0.07\%$  (Fig. 2). In the range of 212 368.1 ~ 550.1 ppm,  $\delta^{13}$ C values measured by G1101-i and G2201-i showed an increase with the 213 increase of CO<sub>2</sub> concentration at 0.46 ‰ per 100 ppm and 0.09‰ per 100 ppm, respectively, and the 214 peak-to-peak amplitudes were 1.75‰ and 0.47‰, respectively.

215

The concentration dependence of the measured  $\delta^{13}$ C values is the main error source affecting IRIS measurements. Guillon et al. (2012) found that the DLT-100 based on ICOS technology had a





218	non-linearity concentration dependence in the range 300 $\sim$ 2000 ppm, and after corrected the
219	concentration dependence by a fifth order polynomial calibration curve, the accuracy improved from
220	2.7‰ to 1.3‰ for $\delta^{13}C.$ The picarro G1101-i analyzer based on CRDS technology showed no
221	significant concentration dependence of $\delta^{13}C$ with the standard deviation of ~0.2‰ in the range
222	303~437 ppm (Vogel et al., 2013). Griffith et al. (2012) used a series of different CO <sub>2</sub> mixing ratio at
223	constant $\delta^{13}C$ and found a residual curvature against the reciprocal of $\text{CO}_2$ was caused by a small
224	nonlinearity response of the analyzer.
225	
226	3.3 Stability and Accuracy
227	Based on the same data measured in section 3.2, the temporal drift and accuracy of $\delta^{13}C$ values of Std1,
228	Std2 and Std3 measured by G1101-i and G2201-i is shown in Fig. 3. Two-point mixing ratio gain and
229	offset calibration method (Bowling et al., 2003) was used to calibrate measured $\delta^{13}C$ value. During the
230	48 h measuring period, the standard deviation of $\delta^{13}C$ values of Std1, Std2 and Std3 measured by
231	G1101-i were 0.26‰, 0.28‰ and 0.27‰, with the temporal drift of 0.92‰, 1.09‰ and 0.93‰; the
232	standard deviation of $\delta^{13}C$ values of Std1, Std2 and Std3 measured by G2201-i were 0.07‰, 0.08‰
233	and 0.05‰, with the temporal drift of 0.23‰, 0.37‰ and 0.19‰. The differences between the CRDS
234	and IRMS measurements were -3.08 $\pm$ 0.26‰, -2.61 $\pm$ 0.28‰ and -2.24 $\pm$ 0.27‰ for the G1101-i, and
235	-1.27 $\pm$ 0.07‰, -1.13 $\pm$ 0.08‰ and -1.11 $\pm$ 0.05‰ for the G2201-i . After calibration, the differences
236	reduced to 0.09 $\pm 0.34$ ‰, 0.04 $\pm 0.20$ ‰ and 0.06 $\pm 0.21$ ‰ for the G1101-i, and -0.13 $\pm 0.21$ ‰, 0.03 $\pm$
237	0.08‰ and -0.10 $\pm0.14\%$ for the G2201-i, respectively. A much better accuracy was obtained when
238	the calibration is interpolated (Std2) than extrapolated (Std1 and Std3).





240	As for the drift of IRIS instruments, Vogel et al. (2013) monitored two gas cylinders sequentially for 3
241	days with 10 min and 20 min for each cylinder, the drift of G1101-i was around 0.3‰ day <sup>-1</sup> . Hammer et
242	al. (2013) measured a target gas continuously for 6 days, the FTIR instrument showed a drift of $0.02\%$
243	day <sup>-1</sup> for $\delta^{13}$ C after sensitivity correction. Tuzson et al. (2008) measured an identical air samples 1 min
244	every 15 min for 7 h, the standard deviation of the $\delta^{13}C$ measured by QCLAS was 0.14‰ (n=28).
245	Schaeffer et al. (2008) monitored two quality control tanks in the field over 2.44 year, and the standard
246	deviation of the difference between actual and measured values were $0.31\%$ and $0.33\%$ (n=2318 and
247	n=2254). Wehr et al. (2008) monitored a CSIRO standard gas over a period of 30 min, and the standard
248	deviation for integration times of 20s and 120s were 0.71‰ and 0.64‰. in this study, during the period
249	of 48 h, the standard deviation of $\delta^{13}C$ measured by G1101-i and G2201-i are 0.26 $\sim$ 0.28‰ and 0.05 $\sim$
250	0.08‰, and the drift are 0.92 $\sim$ 1.09‰ and 0.19 $\sim$ 0.37‰, respectively.

252	As for the accuracy of IRIS instruments, Guillon et al. (2012) found in the range $300 \sim 2000$ ppm, the
253	accuracy of $\delta^{13}C$ value measured by DLT-100 was 2.7‰ for raw measurements and improved to 1.3‰
254	after correction. Over the entire 2.44 year period, two quality control gas measured by TDLAS in the
255	field showed agreement between actual and measured values of -0.17 $\pm$ 0.33‰ and -0.14 $\pm$ 0.4‰ for
256	tank 1 and tank 2 (Schaeffer et al., 2008). Over a period of 30 min measurement, the $\delta^{13}C$ values
257	measured by CEAS showed a systematic error of 0.9% between the measured and IRMS values (Wehr
258	et al., 2008). Used the optimized PLS algorithm, the accuracy of $\delta^{13}C$ measured by FTIR was 0.4‰
259	with CO <sub>2</sub> concentrations in the range 364 ~ 530 ppm (Mohn et al., 2007). Over one year period, Vogel
260	et al. (2013) found although a single measurement was imprecise, the G1101-i $\delta^{13}C$ analyzer provided a
261	mean accuracy of $0.002 \pm 0.025\%$ after proper calibration. In this study, the accuracy of G1101-i and





- 262 G2201-i  $\delta^{13}$ C analyzer are -3.06 ~ -2.22‰ and -1.25 ~ -1.09‰ before calibration and improved to
- $-0.02 \sim 0.11$  and  $-0.11 \sim 0.05\%$  after calibration over a measurement course of 48 h.
- 264
- 265 3.4 Sensitivity of  $\delta^{13}$ C on water vapor concentration

The sensitivity of  $\delta^{13}$ C on water vapor concentration of G1101-i and G2201-i before and after 266 267 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  $\delta^{13}$ C values measured by G1101-i and G2201-i 268 were  $-20.64 \pm 0.72\%$  and  $-21.60 \pm 0.19\%$ , the sensitivity of  $\delta^{13}$ C on water vapor mixing ratio at 269 270 0.86 ‰/% H<sub>2</sub>O and 0.20‰/% H<sub>2</sub>O, respectively, and the peak-to-peak amplitudes were 1.96‰ and 0.45‰, respectively. After upgradation of G1101-i, the mean  $\delta^{13}$ C values measured by G1101-i and 271 G2201-i were -22.34  $\pm$  0.09% and -22.27  $\pm$  0.18%, the sensitivity of  $\delta^{13}$ C on water vapor mixing ratio 272 273 at 0.13 ‰/% H<sub>2</sub>O and -0.27‰/% H<sub>2</sub>O, respectively, and the peak-to-peak amplitudes were 0.22‰ and 0.46‰. With dew point in the range 5 ~ 20 °C, the mean  $\delta^{13}$ C value measured by G1101-i and G2201-i 274 were -20.84  $\pm$  0.66‰ and -21.68  $\pm$  0.07‰ before upgradation of G1101-i and -22.34  $\pm$  0.10‰ and 275 276  $-22.34 \pm 0.08\%$  after upgradation of G1101-i. The sensitivity to water vapor mixing ratio of  $\delta^{13}$ C at 277 1.01 ‰/% H<sub>2</sub>O and 0.09‰/% H<sub>2</sub>O, respectively, and the peak-to-peak amplitudes were 1.47‰ and 278 0.14 ‰ before upgradation of G1101-i, and at 0.15 ‰/% H<sub>2</sub>O and 0.13‰/% H<sub>2</sub>O, respectively, and the 279 peak-to-peak amplitudes were 0.22‰ and 0.19‰ after upgradation of G1101-i.

280

The dilution and pressure broadening effect are the two major factors leading to the dependence of the measured  $\delta^{13}$ C on water vapor concentrations (Chen et al., 2010; Nara et al., 2012). The variations of sample water vapor significantly affect the mixing ratio of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> via dilution effect. In





284	addition, the variability of water vapor also introduce broadening effect on spectroscopic line, which
285	includes Lorentzian line broadening and Dicke line narrowing effect. The CRDS instruments measured
286	$^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentration by the peak height of the absorption peak whose baseline and shape can
287	be interfered by the absorption peaks of water (Nara et al., 2012; Rella et al., 2013). As for the CO <sub>2</sub> , the
288	systematic errors caused by the broadening effects would be 40% of the dilution effects if it is not
289	corrected (Chen et al., 2010). The transferability of water correction function among multiple
290	instruments also bias the measurement data among different instruments. Rella et al., (2013) found the
291	transferability meet the GAW quality extend to ~2% water vapor for both $\mathrm{CO}_2$ and $\mathrm{CH}_4.$ But for 3
292	instruments based on CRDS technology, the residual errors of $\mathrm{CO}_2$ showed substantially large values
293	with increasing water vapor concentration (Nara et al., 2012). These incompatibility results indicate the
294	need of more precise experiments to evaluate the transferability of water correction function. Moreover,
295	potential long-term drift of the water vapor correction coefficients of individual instrument need to
296	assess with water vapor correction (Nara et al., 2012; Rella et al., 2013).
297	In this study, the standard deviation of $\delta^{13}C$ measured by G2201-i under different water vapor
298	concentration (0.07‰ and 0.08‰) are smaller than the precision given by manufacturer (0.15‰), and
299	the standard deviation of $\delta^{13}C$ measured by upgraded G1101-i (0.10‰) is smaller than the specified
300	precision, too. These results indicate that the water corrections embedded in the instruments' software
301	work sufficiently within the dew point range of $5 \sim 20$ °C.
302	

# 303 3.5 Atmospheric measurement

304 Before and after G1101-i upgraded, the  $\delta^{13}C$  of atmospheric CO<sub>2</sub> was measured continuously by

305 G1101-i and G2202-i analyzers. The temporal variations of atmospheric  $\delta^{13}C$ , the difference between





- 306 G1101-i and G2202-i analyzers, and the distribution of differences are shown in Fig. 5. The measured
- 307 atmospheric  $\delta^{13}$ C values were calibrated by Std1 and Std3, and the Std2 used here as quality control gas
- 308 to assess the accuracy of atmospheric sample measurement (Fig. 6).
- 309

310	Atmospheric $\delta^{13}C$ measured by G1101-i and G2201-i showed good agreement and both of them
311	captured the rapidly changing atmospheric $\delta^{13}$ C. Before G1101-i upgraded (DOY164 ~ 174),
312	atmospheric $\delta^{13}C$ measured by G1101-i and G2201-i ranged from -13.24‰ to -7.47‰ and -13.41‰ to
313	-7.62‰, with average value of -9.49 $\pm$ 1.22‰ and -9.42 $\pm$ 1.17‰, respectively. The difference of $\delta^{13}$ C
314	measured by G1101-i and G2202-i analyzers ranged from -0.62‰ to 0.76‰, with average value of
315	$0.07\pm0.24\%$ . The difference exhibits a Gaussian distribution. A significant systematic bias of $\delta^{13}C$
316	values were identified between these two analyzers (t-test, p<0.01). After G1101-i upgraded
317	(DOY348-356), atmospheric $\delta^{13}$ C measured by G1101-i and G2201-i ranged from -14.08‰ to -8.64‰
318	and -13.89‰ to -9.06‰, with average value of -10.61‰ and -10.56‰. The difference of $\delta^{13}C$
319	measured by G1101-i and G2202-i analyzers ranged from -0.57‰ to 0.85‰, with average value of
320	0.05 ± 0.30‰. A significant systematic bias of $\delta^{13}C$ values still existed between these two analyzers
321	(t-test, p=0.018). In addition, field measured values of Std2 during atmospheric measurement period
322	(DOY164 ~ 174 and DOY348 ~ 356) were used to assess the stability and accuracy of both analyzers
323	(Fig. 6). During the first atmospheric measurement period, the average $\delta^{13}C$ values of Std2 were -21.32
324	$\pm$ 0.51‰ and -21.91 $\pm$ 0.12‰ for G1101-i and G2201-i. After calibration, the average $\delta^{13}C$ values were
325	-20.30 $\pm$ 0.40‰ and -20.56 $\pm$ 0.17‰, respectively. The accuracy (the difference between calibration
326	and actual values) ranged from -0.70‰ to 0.91‰ and -0.42‰ to 0.19‰, with average values of 0.09 $\pm$
327	0.40‰ and -0.17 $\pm$ 0.17‰. During the second atmospheric measurement period, the average $\delta^{13}C$





- 328 values of Std2 were -24.37 ± 0.59‰ and -21.92 ± 0.18‰ for G1101-i and G2201-i. After calibration,
- 329 the average  $\delta^{13}$ C values were -20.56  $\pm$  0.23‰ and -20.57  $\pm$  0.09‰, respectively. the accuracy ranged
- 330 from -0.60% to 0.30% and -0.42% to 0.02%, with average values of -0.17  $\pm$  0.23% and -0.18  $\pm$
- 331 0.09%. these results indicate that the stability of G2201-i is better than G1101-i, which is consistent
- 332 with the Allan variation result.
- 333
- 334 4 Discussion

The isotopic composition of source CO<sub>2</sub> ( $\delta^{13}C_8$ ) was used to gain insight into the potential local CO<sub>2</sub> 335 sources and underlying mechanisms at different temporal and spatial scales. In this study,  $\delta^{13}C_8$  was 336 calculated using the calibration dataset of  $\delta^{13}$ C and 1/CO<sub>2</sub> by the Keeling plot intercept method (Fig. 7). 337 During the first measurement period, the  $\delta^{13}C_s$  values were -24.80 ± 0.39‰ and -23.98 ± 0.30‰ for 338 339 G1101-i and G2201-i, the mean difference between G1101-i and G2201-i was 0.82‰. If used the nightime data (22:00 ~ 04:00) only for the Keeling analysis, the  $\delta^{13}C_s$  values were -28.35 ± 1.34 ‰ 340 and -27.11  $\pm$  1.02‰ for G1101-i and G2201-i, with a mean difference of 1.24‰. The  $\delta^{13}C_s$  value 341 342 deduced from nighttime data was a mixed value of various local CO<sub>2</sub> sources, including the 343 combustion of natural gas, gasoline and coal, and the respiration of plant and soil (Pang et al., 2016).

344

During the second measurement period after G1101-i upgraded, the  $\delta^{13}C_s$  values were -25.90 ± 0.28‰ and -25.97 ± 0.12‰ with a mean difference of 0.07‰. If used the nighttime data (22:00 ~ 04:00) only for the Keeling analysis, the  $\delta^{13}C_s$  values were -26.05 ± 0.16‰ and -25.69 ± 0.41‰ for G1101-i and G2201-i, with a mean difference of 0.36‰. After G1101-i upgraded, the systematic bias of  $\delta^{13}C$ between G1101-i and G2201-i decreased from 0.07 ± 0.24‰ to 0.05 ± 0.30‰, and the difference of





350

351 measurement difference among different IRIS instruments and this difference will caused an error 352 propagation through Keeling plot analysis (Wen et al., 2013). 353 Figure 8 shows the dependence of the  $\delta^{13}$ C difference between G1101-i and G2201-i on water vapor 354 355 concentration and CO2 mixing ratio. Before and after upgradation of G1101-i, there were no significant correlation between the  $\delta^{13}$ C difference and CO<sub>2</sub> mixing ratio (Fig. 8a and 8b). Before upgradation of 356 G1101-i, a significant linear correlation was observed between the  $\delta^{13}$ C difference and water vapor 357 358 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 359 due to the upgradation of G1101-i, which excluded  $\delta^{13}C$  measurement errors came from water vapor 360 variation, and improved the accuracy of  $\delta^{13}C$  measurement. This result was consistent with the 361 sensitivity of  $\delta^{13}$ C on water vapor concentration test. In addition, the second measurement was 362 conducted in winter when the atmospheric water vapor concentration was relatively low and the water 363 364 vapor interferences were small. 365 **5** Conclusion 366 In this study, the performance and comparability of Picarro G1101-i and G2201-i CO2 8<sup>13</sup>C analyzers

 $\delta^{13}C_8$  decreased from 1.24‰ to 0.36‰. The results confirm that we should pay attention to the

367 was evaluated. The main conclusions are as follows:

368 1) The Allan variation test indicate that the best precision of  $0.08 \sim 0.15\%$  and  $0.01 \sim 0.04\%$  measured

- 369 by G1101-i and G2201-i can be obtained with averaging time of  $1850 \sim 7400$  s and  $3700 \sim 7400$  s with
- 370 the  $CO_2$  ranged from 368.1 to 550.1 ppm.
- 371 2) With the gradient switching test lasted 48h, the dependence of  $\delta^{13}$ C on CO<sub>2</sub> concentration were





372	0.46% per 100 ppm	and 0.09% ner	100 nnm for G	G1101_i and G22	201_i in the range of	$f 368.1 \sim 550.1$
572	0.40/00 pci 100 ppin	and 0.09700 pcr	roo ppin ior d	J1101-1 and 022	201-1 in the range t	$1.508.1 \sim 550.1$

- 373 ppm, and the instruments drift ranged from 0.92‰ to 1.09‰ and 0.19‰ to 0.37‰. After calibrated by
- 374 the two-point mixing ratio gain and offset calibration method, the average  $\delta^{13}$ C values were -20.34 ±
- 375 0.07‰ and  $-20.45 \pm 0.09$ ‰, similar with actual value measured by IRMS (-20.38 ± 0.06‰).
- 376 3) With dew point temperature in the range 5 ~ 20 °C, the sensitivity of  $\delta^{13}$ C on water vapor mixing
- 377 ratio measured by G1101-i and G2201-i were 1.01 ‰/% H<sub>2</sub>O and 0.09‰/% H<sub>2</sub>O during the first test
- 378 and 0.15  $\frac{1}{20}$  and 0.13 $\frac{1}{20}$  during the second test. The standard deviation of  $\delta^{13}$ C measured
- 379 by G2201-i and upgraded G1101-i were  $\sim 0.08\%$  and  $\sim 0.10\%$ , which were smaller than instrument
- 380 precision(0.15%). These results indicate that the water corrections embedded in the instruments'
- 381 software work sufficiently within the dew point range of  $5 \sim 20$  °C.

4) Atmospheric  $\delta^{13}$ C measured by G1101-i and G2201-i captured the rapidly changing of atmospheric 382 383  $\delta^{13}$ C. Before G1101-i upgraded (DOY164 - 174), the difference of  $\delta^{13}$ C measured by G1101-i and 384 G2202-i analyzers ranged from -0.62‰ to 0.76‰, with average values of  $0.07 \pm 0.24$ ‰. After G1101-i upgraded (DOY348-356), the difference of  $\delta^{13}$ C measured by G1101-i and G2202-i analyzers ranged 385 386 from -0.57‰ to 0.85‰, with average value of  $0.05 \pm 0.30$ ‰. This difference exhibits a Gaussian 387 distribution. Before upgradation of G1101-i, a significant linear correlation was observed between the 388  $\delta^{13}$ C difference and water vapor concentration (P<0.01), but there is no significant correlation (P>0.05) 389 after upgradation of G1101-i. this is mainly due to the upgradation of G1101-i improved the 390 interference of water vapor on  $\delta^{13}C$  measurement. The difference of Keeling intercept value between 391 G1101-i and G2201-i decrease from 1.24‰ to 0.36‰, which indicate the importance of consistency 392 among different IRIS instruments.





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- 397
- 398 Reference
- 399 Bowling, D. R., Burns, S. P., Conway, T. J., Monson, R. K., and White, J. W. C.: Extensive
- 400 observations of  $CO_2$  carbon isotope content in and above a high-elevation subalpine forest, Global
- 401 Biogeochem. Cy, 19, doi: 10.1029/2004gb002394, 2005.
- 402 Bowling, D. R., Sargent, S. D., Tanner, B. D., and Ehleringer, J. R.: Tunable diode laser absorption
- 403 spectroscopy for stable isotope studies of ecosystem-atmosphere CO<sub>2</sub> exchange, Agr Forest Meteorol,
- 404 118, 1-19, doi: 10.1016/s0168-1923(03)00074-1, 2003.
- 405 Chen, H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D.,
- 406 Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and
- 407 Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>)
- 408 using the cavity ring-down spectroscopy (CRDS) technique, Atmos Meas Tech, 3, 375-386, 2010.
- 409 Flowers, B. A., Powers, H. H., Dubey, M. K., and McDowell, N. G.: Inter-comparison of two
- 410 high-accuracy fast-response spectroscopic sensors of carbon dioxide: a case study, Atmos Meas Tech,
- 411 5, 991-997, doi: 10.5194/amt-5-991-2012, 2012.
- 412 Friedrichs, G., Bock, J., Temps, F., Fietzek, P., Kortzinger, A., and Wallace, D. W. R.: Toward
- 413 continuous monitoring of seawater <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> isotope ratio and pCO<sub>2</sub>: Performance of cavity
- 414 ringdown spectroscopy and gas matrix effects, Limnology and Oceanography-Methods, 8, 539-551, doi:
- 415 10.4319/lom.2010.8.539, 2010.
- 416 Griffis, T. J., Baker, J. M., Sargent, S. D., Tanner, B. D., and Zhang, J.: Measuring field-scale isotopic
- 417 CO<sub>2</sub> fluxes with tunable diode laser absorption spectroscopy and micrometeorological techniques, Agr
- 418 Forest Meteorol, 124, 15-29, doi: 10.1016/j.agrformet.2004.01.009, 2004.
- 419 Griffis, T. J.: Tracing the flow of carbon dioxide and water vapor between the biosphere and





- 420 atmosphere: A review of optical isotope techniques and their application, Agr Forest Meteorol, 174,
- 421 85-109, doi: 10.1016/j.agrformet.2013.02.009, 2013.
- 422 Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A
- 423 Fourier transform infrared trace gas and isotope analyser for atmospheric applications, Atmos Meas
- 424 Tech, 5, 2481-2498, doi: 10.5194/amt-5-2481-2012, 2012.
- 425 Guillon, S., Pili, E., and Agrinier, P.: Using a laser-based CO<sub>2</sub> carbon isotope analyser to investigate
- 426 gas transfer in geological media, Applied Physics B-Lasers and Optics, 107, 449-457, doi:
- **427** 10.1007/s00340-012-4942-8, 2012.
- 428 Hammer, S., Griffith, D. W. T., Konrad, G., Vardagl, S., Caldow, C., and Levin, I.: Assessment of a
- 429 multi-species in situ FTIR for precise atmospheric greenhouse gas observations, Atmos Meas Tech, 6,
- 430 1153-1170, doi: 10.5194/amt-6-1153-2013, 2013.
- 431 McManus, J. B., Nelson, D. D., Shorter, J. H., Jimenez, R., Herndon, S., Saleska, S., and Zahniser, M.:
- 432 A high precision pulsed quantum cascade laser spectrometer for measurements of stable isotopes of
- 433 carbon dioxide, JMOp, 52, 2309-2321, doi: 10.1080/09500340500303710, 2005.
- 434 Mohn, J., Werner, R. A., Buchmann, B., and Emmenegger, L.: High-precision  $\delta^{13}CO_2$  analysis by
- 435 FTIR spectroscopy using a novel calibration strategy, J. Mol. Struct., 834, 95-101, doi:
  436 10.1016/j.molstruc.2006.09.024, 2007.
- 437 Mohn, J., Zeeman, M. J., Werner, R. A., Eugster, W., and Emmenegger, L.: Continuous field
- 438 measurements of  $\delta^{13}$ CO<sub>2</sub> and trace gases by FTIR spectroscopy, Isotopes Environ. Health Stud., 44,
- 439 241-251, doi: 10.1080/10256010802309731, 2008.
- 440 Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of
- 441 air composition (N<sub>2</sub>, O<sub>2</sub>, Ar, and H<sub>2</sub>O) on CO<sub>2</sub> and CH<sub>4</sub> measurement by wavelength-scanned cavity
- 442 ring-down spectroscopy: calibration and measurement strategy, Atmos Meas Tech, 5, 2689-2701, doi:
- 443 10.5194/amt-5-2689-2012, 2012.
- Pang, J., Wen, X., and Sun, X.: Mixing ratio and carbon isotopic composition investigation of
  atmospheric CO<sub>2</sub> in Beijing, China, Sci. Total Environ., 539, 322-330, 2016.
- 446 Pataki, D. E., Bowling, D. R., Ehleringer, J. R., and Zobitz, J. M.: High resolution atmospheric





- 447 monitoring of urban carbon dioxide sources, Geophys. Res. Lett., 33, doi: 10.1029/2005gl024822,
- 448 2006.
- 449 Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L.,
- 450 Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy
- 451 measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos Meas Tech, 6,
- 452 837-860, doi: 10.5194/amt-6-837-2013, 2013.
- 453 Schaeffer, S. M., Miller, J. B., Vaughn, B. H., White, J. W. C., and Bowling, D. R.: Long-term field
- 454 performance of a tunable diode laser absorption spectrometer for analysis of carbon isotopes of CO<sub>2</sub> in
- 455 forest air, Atmos. Chem. Phys., 8, 5263-5277, 2008.
- 456 Sturm, P., Eugster, W., and Knohl, A.: Eddy covariance measurements of CO<sub>2</sub> isotopologues with a
- quantum cascade laser absorption spectrometer, Agr Forest Meteorol, 152, 73-82, doi:
  10.1016/j.agrformet.2011.09.007, 2012.
- 459 Tuzson, B., Zeeman, M. J., Zahniser, M. S., and Emmenegger, L.: Quantum cascade laser based
- 460 spectrometer for in situ stable carbon dioxide isotope measurements, Infrared Phys Techn, 51, 198-206,
- 461 doi: 10.1016/j.infrared.2007.05.006, 2008.
- 462 Vogel, F. R., Huang, L., Ernst, D., Giroux, L., Racki, S., and Worthy, D. E. J.: Evaluation of a cavity
- 463 ring-down spectrometer for in situ observations of <sup>13</sup>CO<sub>2</sub>, Atmos Meas Tech, 6, 301-308, 2013.
- 464 Wahl, E. H., Fidric, B., Rella, C. W., Koulikov, S., Kharlamov, B., Tan, S., Kachanov, A. A., Richman,
- 465 B. A., Crosson, E. R., Paldus, B. A., Kalaskar, S., and Bowling, D. R.: Applications of cavity
- 466 ring-down spectroscopy to high precision isotope ratio measurement of <sup>13</sup>C/<sup>12</sup>C in carbon dioxide,
- 467 Isotopes Environ. Health Stud., 42, 21-35, doi: 10.1080/10256010500502934, 2006.
- 468 Welp, L. R., Keeling, R. E., Weiss, R. F., Paplawsky, W., and Heckman, S.: Design and performance
- 469 of a Nafion dryer for continuous operation at  $CO_2$  and  $CH_4$  air monitoring sites, Atmos Meas Tech, 6,
- 470 1217-1226, doi: 10.5194/amt-6-1217-2013, 2013.
- 471 Wen, X. F., Meng, Y., Zhang, X. Y., Sun, X. M., and Lee, X.: Evaluating calibration strategies for
- 472 isotope ratio infrared spectroscopy for atmospheric  ${}^{13}CO_2/{}^{12}CO_2$  measurement, Atmos Meas Tech, 6,
- 473 1491-1501, doi: 10.5194/amt-6-1491-2013, 2013.





- 474 Wen, X. F., Sun, X. M., Zhang, S. C., Yu, G. R., Sargent, S. D., and Lee, X.: Continuous measurement
- 475 of water vapor D/H and <sup>18</sup>O/<sup>16</sup>O isotope ratios in the atmosphere, J Hydrol, 349, 489-500, doi:
- 476 10.1016/j.jhydrol.2007.11.021, 2008.
- 477 Wen, X. F., Zhang, S. C., Sun, X. M., Yu, G. R., and Lee, X.: Water vapor and precipitation isotope
- 478 ratios in Beijing, China, J Geophys Res Atoms, 115, doi: 10.1029/2009jd012408, 2010.
- 479 Werle, P., Mucke, R., and Slemr, F.: The limits of signal averaging in atmospheric trace-gas
- 480 monitoring by tunable diode-laser absorption-spectroscopy (TDLAS), Applied Physics B-Photophysics
- 481 and Laser Chemistry, 57, 131-139, doi: 10.1007/bf00425997, 1993.
- 482 Werner, C., Schnyder, H., Cuntz, M., Keitel, C., Zeeman, M. J., Dawson, T. E., Badeck, F. W.,
- 483 Brugnoli, E., Ghashghaie, J., Grams, T. E. E., Kayler, Z. E., Lakatos, M., Lee, X., Maguas, C., Ogee, J.,
- 484 Rascher, K. G., Siegwolf, R. T. W., Unger, S., Welker, J., Wingate, L., and Gessler, A.: Progress and
- challenges in using stable isotopes to trace plant carbon and water relations across scales,
  Biogeosciences, 9, 3083-3111, doi: 10.5194/bg-9-3083-2012, 2012.
- 487 Wingate, L., Ogee, J., Burlett, R., Bosc, A., Devaux, M., Grace, J., Loustau, D., and Gessler, A.:
- 488 Photosynthetic carbon isotope discrimination and its relationship to the carbon isotope signals of stem,
- soil and ecosystem respiration, New Phytol., 188, 576-589, doi: 10.1111/j.1469-8137.2010.03384.x,
  2010.
- 491 Yakir, D., and Sternberg, L. D. L.: The use of stable isotopes to study ecosystem gas exchange,
- 492 Oecologia, 123, 297-311, doi: 10.1007/s004420051016, 2000.
- 493







# 494 **Tables and Figures:**

495

496 Figure 1: Allan deviation of the  $\delta^{13}$ C for the (a) G1101-i and (b) G2201-i analyzers with 3 different CO<sub>2</sub>

497 concentration with same  $\delta^{13}$ C standard gases.

498







501



503 concentration with 3 different  $\rm CO_2$  concentration with same  $\delta^{13}\rm C$  standard gases.







505

506 Figure 3: Time variations of  $\delta^{13}$ C of the 3 different CO<sub>2</sub> concentration with same  $\delta^{13}$ C standard gases

507 (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)

508 and (d) are data from Std2, and (e) and (f) are data from Std3.







510

511 Figure 4: Sensitivity of the measured  $\delta^{13}C$  by G1101-i and G2201-i on water vapor mixing ratio. (a)

512 measured before G1101-i upgraded and (b) measured after G1101-i upgraded.







514

515 Figure 5: Time variations of (a) and (d) hourly atmospheric  $\delta^{13}$ C, (b) and (e) difference between the

516 Picarro G1101-i and G2201-i analyzers and (c) and (f) histogram of the differences. The left panels (a, b, and

517 c) were measured before G1101-i upgraded (DOY 164 - 174) and the right panels (d, e, and f) were measured

518 after G1101-i upgraded (DOY348 - 356).







520

521 Figure 6: Time series of the 10 min averaged  $\delta^{13}$ C of quality control gas (std2) monitored by (a) G1101-i

522 analyzer and (b) G2201-i analyzer.









526 Figure 7: Keeling plot of the calibrated atmospheric  $\delta^{13}$ C against the reciprocal of the calibrated CO<sub>2</sub>

527 concentration for the Picarro (a, b) G2201-i and (c, d) G1101-i analyzers. (a) and (c) was measured before

528 G1101-i upgraded (DOY 164 - 174), and (b) and (d) was measured after G1101-i upgraded (DOY348 - 356).

- 529 Both daytime and nighttime data were used.
- 530
- 531







532

533 Figure 8: Dependence of the atmospheric δ13C difference between the Picarro G1101-i and G2201-i

534 analyzers on the CO2 and H2O concentration. (a) and (c) was measured before G1101-i upgraded (DOY 164

535 - 174), and (b) and (d) was measured after G1101-i upgraded (DOY348 - 356).