Performance evaluation of an in-situ instrument for measuring ^{13}C-CO_2 in urban air

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Outline

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- 2. objective
- 3. The installment and setting of Picarro
- 4. The performance of Picarro with a 3-ways valve
- 5. Preliminary results
- 6. Conclusions
- 7. Next work
- 8. Problems

1. Background

Table 1. International reference. [Liu, 2009]

Medium	configuration	$\delta^{13}C$(‰)
Atmosphere	CO_2	-7
Lake		-8—16
River		-10
Sea		0±2
Terrestrial biology	C	-22
aquatic in lake	CO_2	-25
	C	-5
aquatic in river	CO_2	-25
	C	-12
aquatic in sea	CO_2	-24
	C	0
Coal		-24
Natural gas		-40
Fossil fuel		-20

Keeling plot

$$\delta_a = \delta_s + \frac{M}{C_a} \qquad (6)$$

$$M = C_b\left(\delta^{13}C_b - \delta^{13}C_S\right) \qquad (7)$$

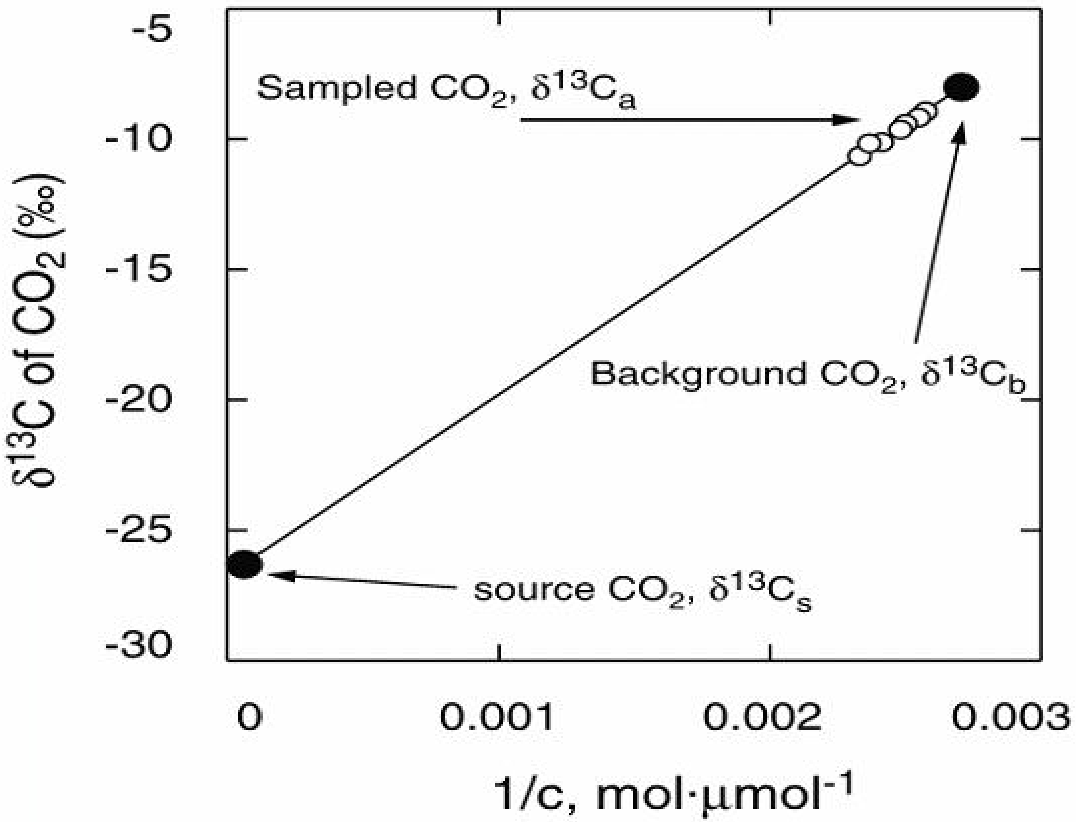


Fig 5. Keeling Plots. [Pataki,2003]

2. Objective

- Many factors can influence the working status of Picarro, such as H_2O concentration, switchover of pilots, calibration gas and so on.

- To ensure the data observed by Picarro is reliable, we should evaluate its performance carefully.

3. The installment and setting of Picarro

Fig 1 Full view of Picarro

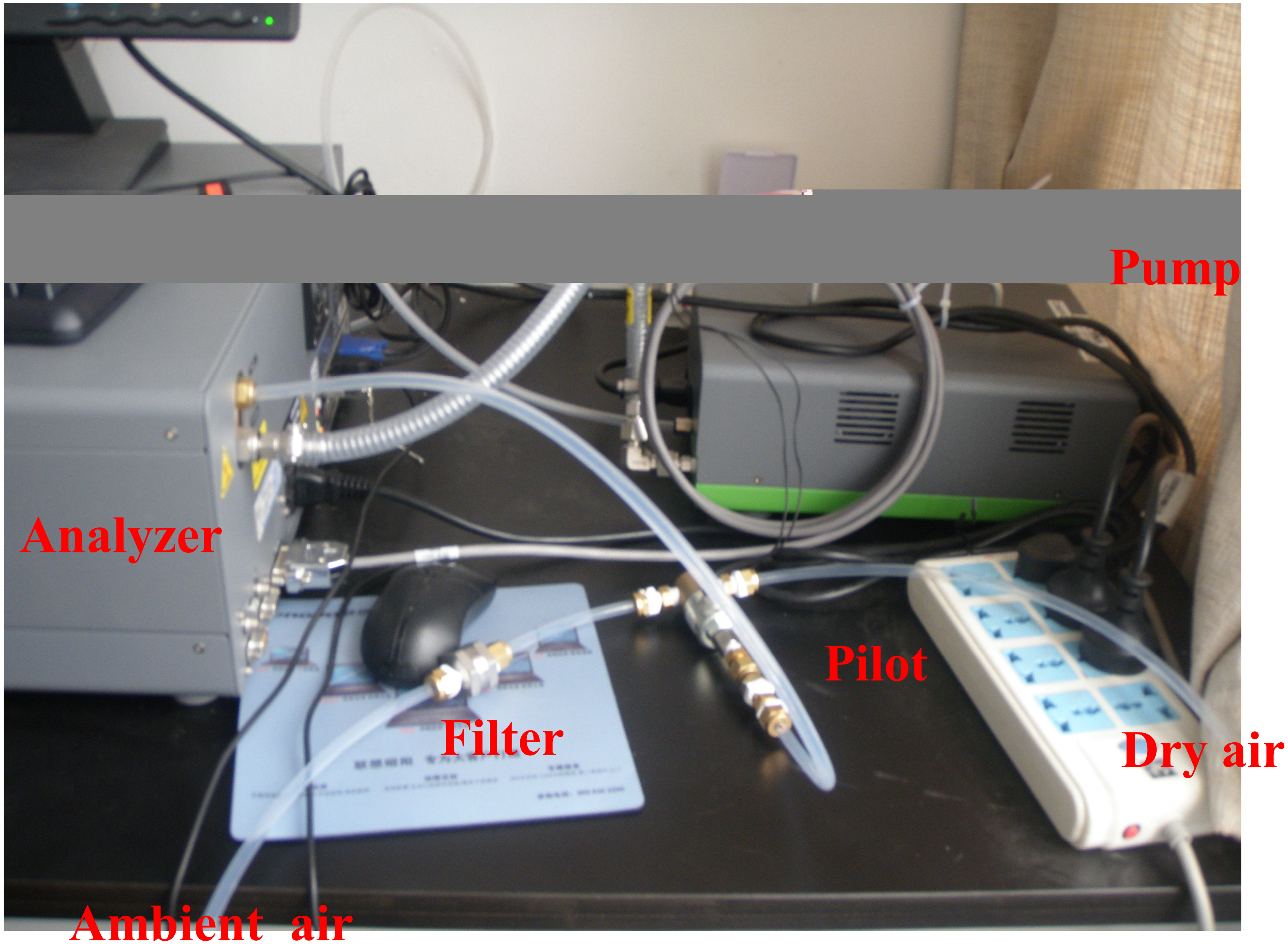


Fig 2 Design of gas path

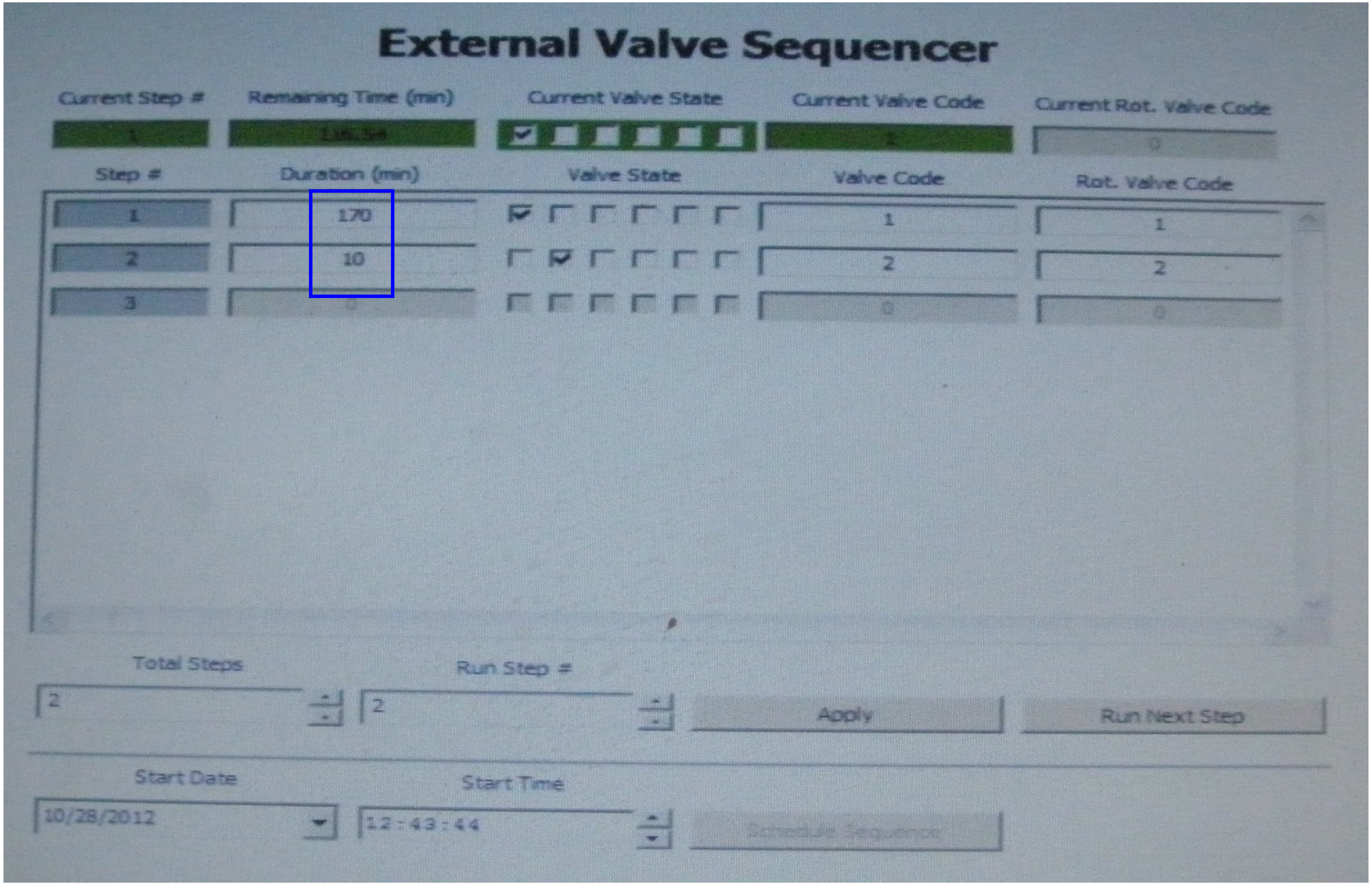


Fig 3 Design of switching cycle

4. The performance evaluation of Picarro

4.1 Standard deviation and Allan Variance

- Aim: To check the stability of the analyzer

- Data : Compressed dry air (300 ppm CO_2) was connected with analyzer from 3^{th} to 5^{th} Nov. (Beijing time)

- Method : Delete all repeated data to calculate delta ^{13}C.

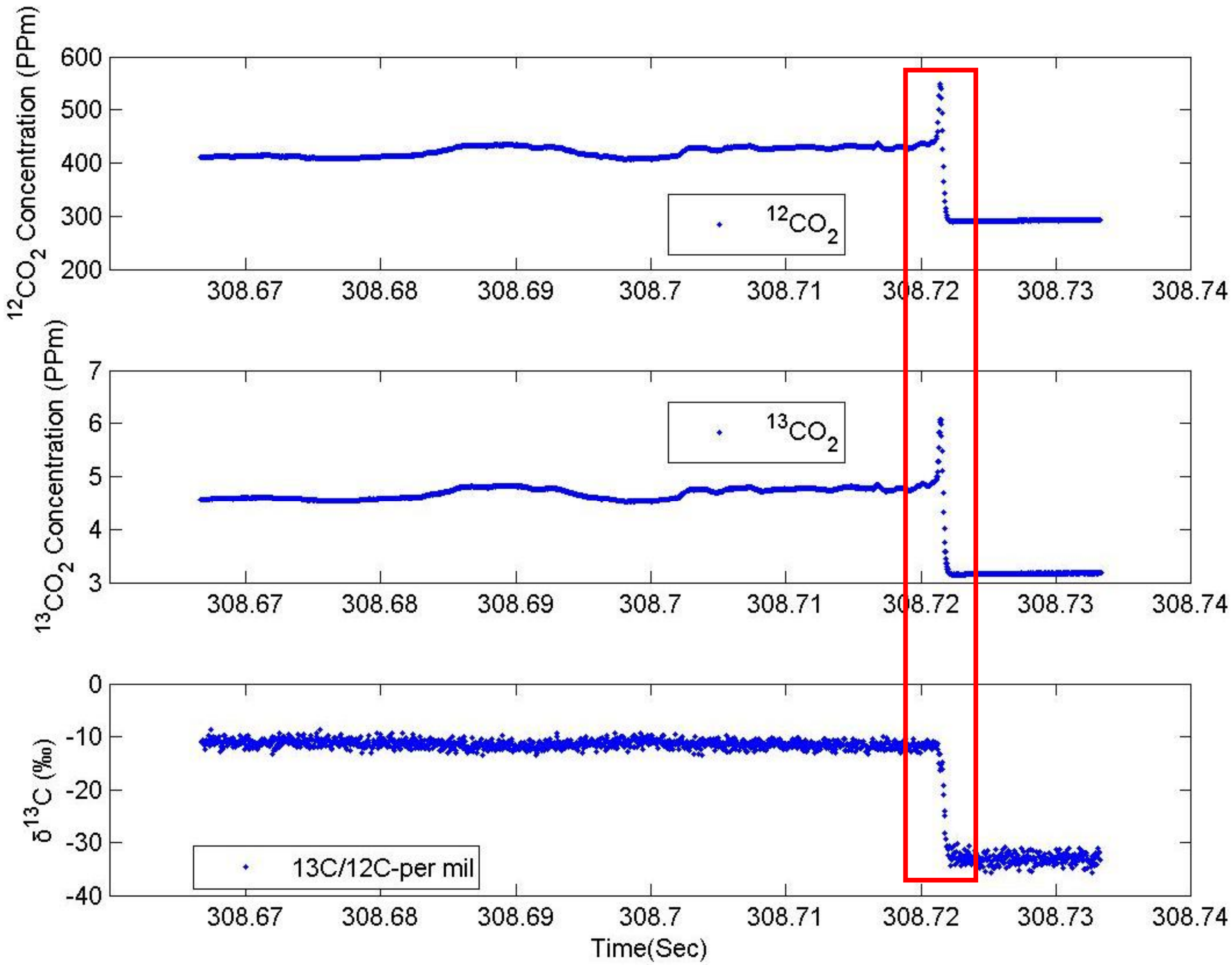


Fig 4 Beginning of the test

The effect of water vapor

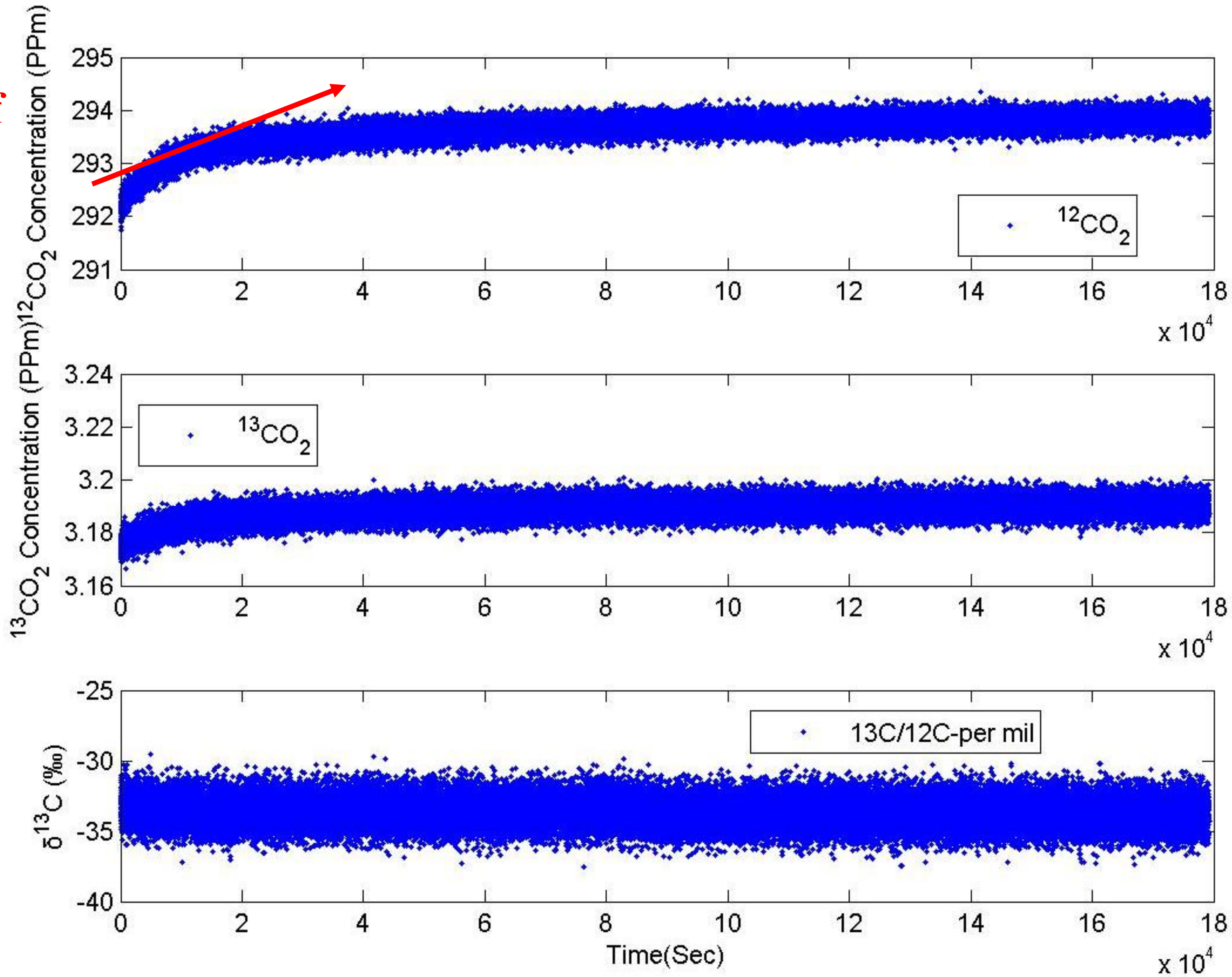


Fig 5 ^{12}CO2 concentration, ^{13}CO2 concentration, δ^{13}C measured from 3th to 5th Nov (Beijing time)

- So I chose the last 24 hours to calculate Allan variance. And I got a better result.

Time in Files: 2012-11-03 00:00:00.066 to 2012-11-05 03:17:08.598 (GMT)
Time of Measurement : 2012-11-03 01:30:00.013 to 2012-11-05 03:17:08.598
Time for Allan: **2012-11-04 00:00:00.230 to 2012-11-05 03:17:08.598**

Need Calibration?

Std	mean
0.1280	293.7932
0.0029	3.1900
0.9543	-33.7338

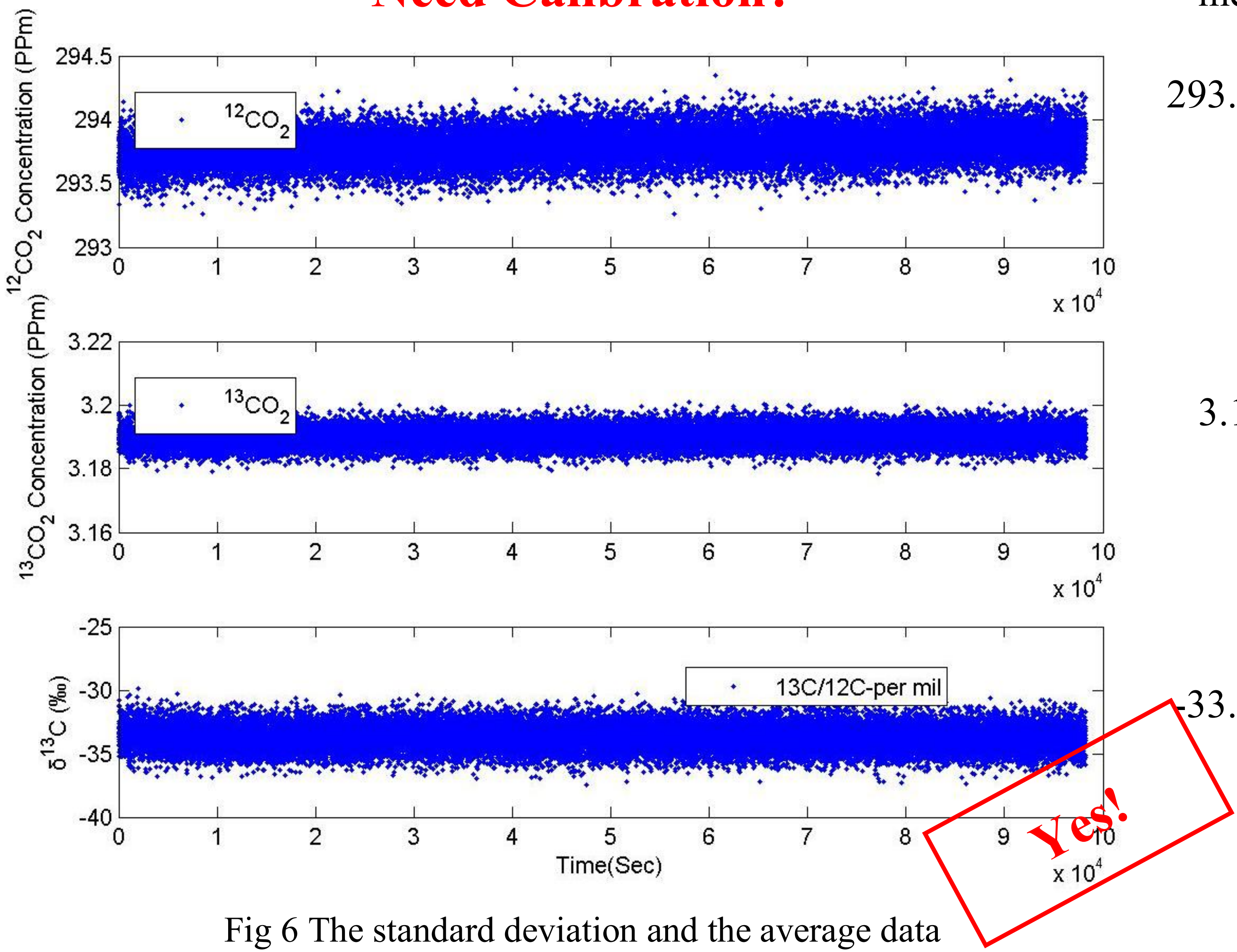


Fig 6 The standard deviation and the average data

What is the frequency?

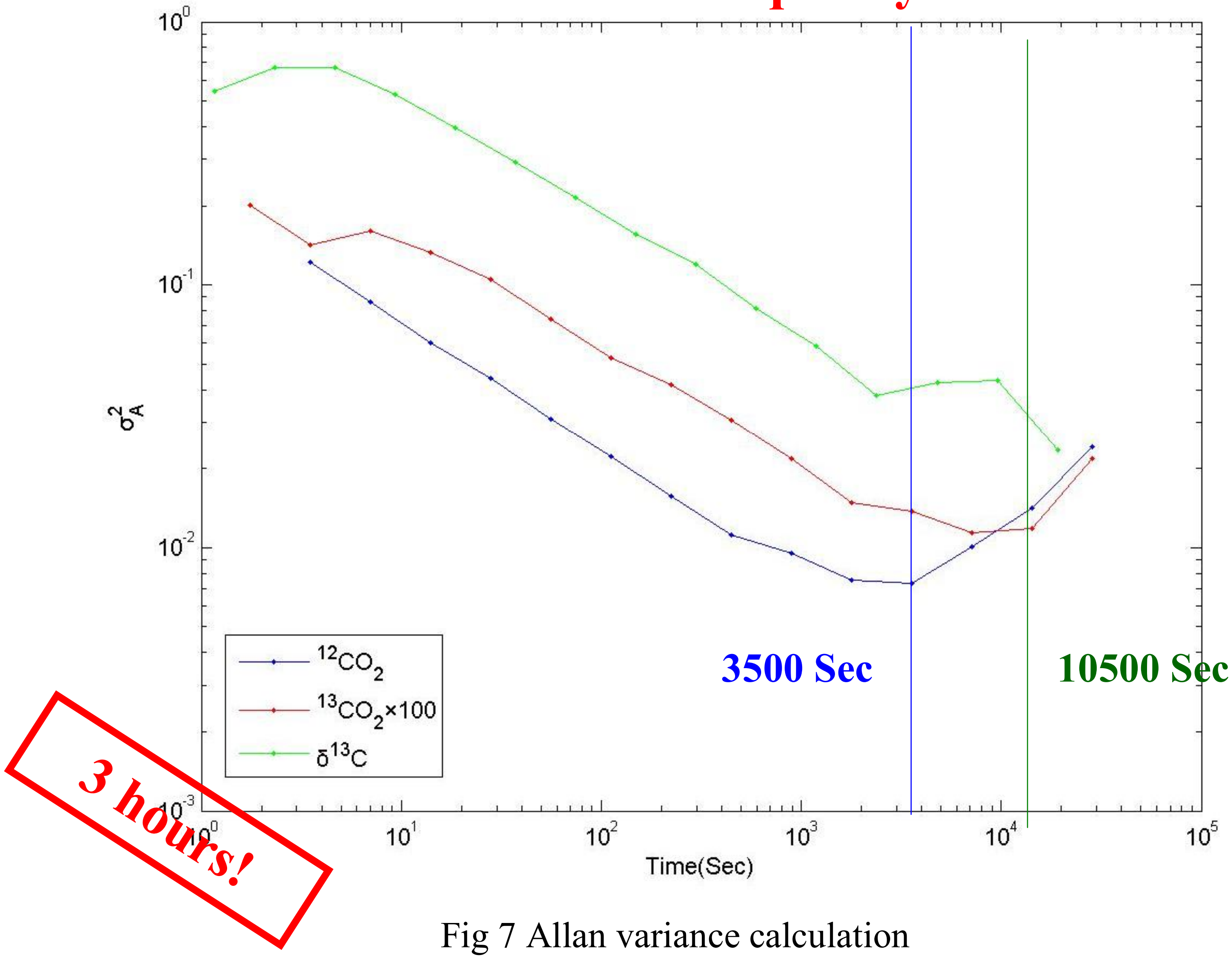


Fig 7 Allan variance calculation

Comparison with Wen's results

Table 2. Stability of analyzer

Analyzers		**Std**	**Inflexion**
Wen's Picarro	**^{12}C**	**0.2394**	**< 2000sec**
	^{13}C	**0.006**	**<2000sec**
	delta	**1.5222**	**< 2000sec**
My Picarro	**^{12}C**	**0.2266**	**< 3500sec**
	^{13}C	**0.0034**	**About 10000sec**
	delta	**0.9138**	**1500sec**

4.2 The effect of water vapor dilution

- Aim: To check the effect of water vapor on the measurement of [CO2] concentration.

- Test: Time: 2012-11-13 08:00:00.486 to 2012-11-26 07:59:58.927 (Beijing time). The cycling of measurement was 3 hours. Picarro drew air from the ambient for 170 min and from gas tank for 10 min.

- Method: Compare [$^{12}CO_2$ calibration] with [$^{12}CO_2$] and [$^{12}CO_2$ dry]

[$^{12}CO_2$] stands for wet [$^{12}CO_2$] measured by Picarro;
[$^{12}CO_2$ dry] means dry [$^{12}CO_2$] calculated by Picarro;
[$^{12}CO_2$ calibration] denotes dry [$^{12}CO_2$] calculated by oursleves.

- Data processing :

1. Moving 1 σ with 5 points after calculating 30-min-average valve.
2. Formation:

$[^{12}CO_2]$_corrected = $[^{12}CO_2]$_wet /(1 – w/100).

w=$[H_2O]$/(100-$[H_2O]$)*100

$[H_2O]$: H_2O concentration (%v) (The 35th column in data files) .

3. Using VPDB to calculate the ratio of ^{13}C isotope, but I did not calibrate $[CO_2]$ and its isotope with dry air in tank.

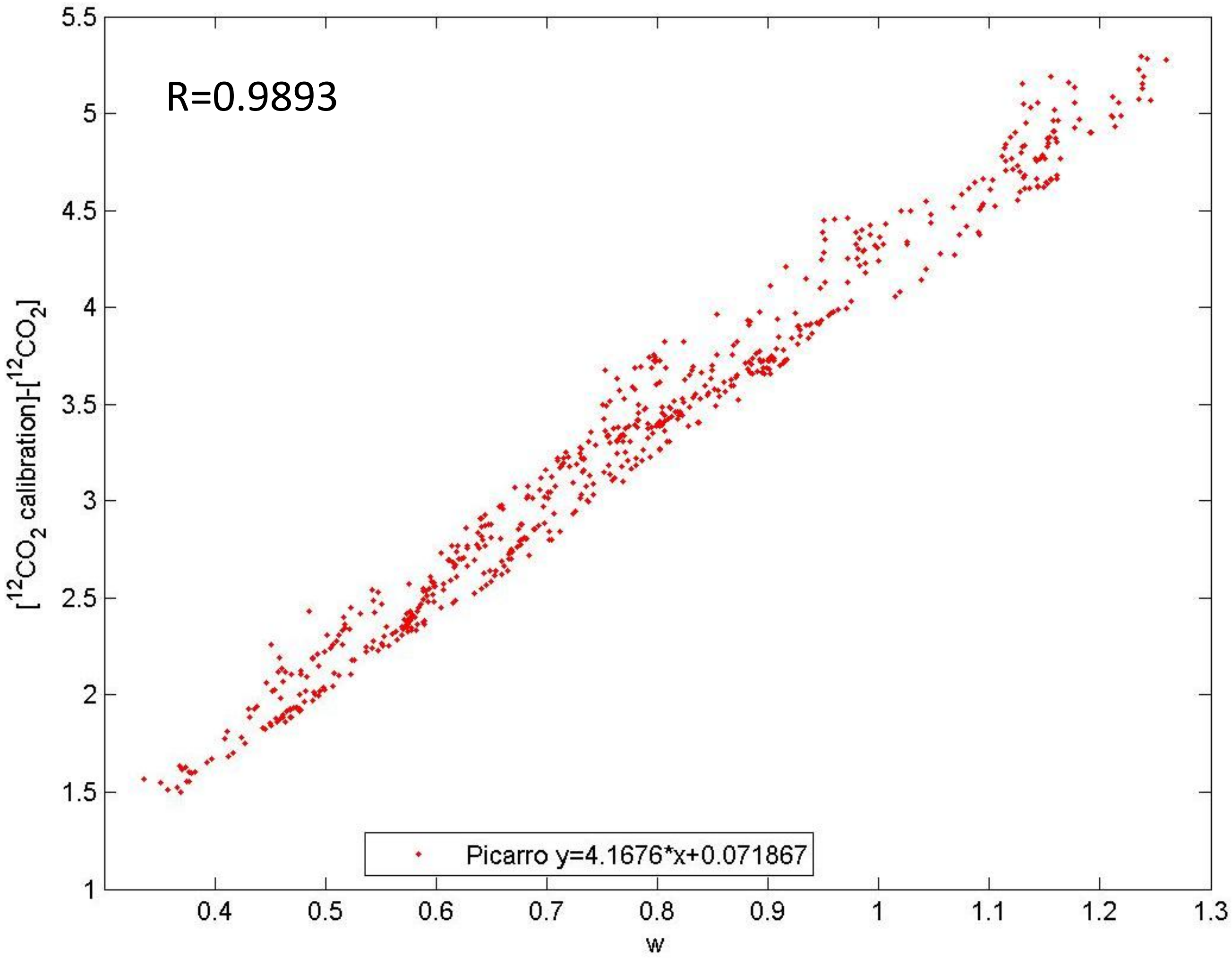


Fig 12 Comparison between [$^{12}CO_2$ calibration] and [$^{12}CO_2$]

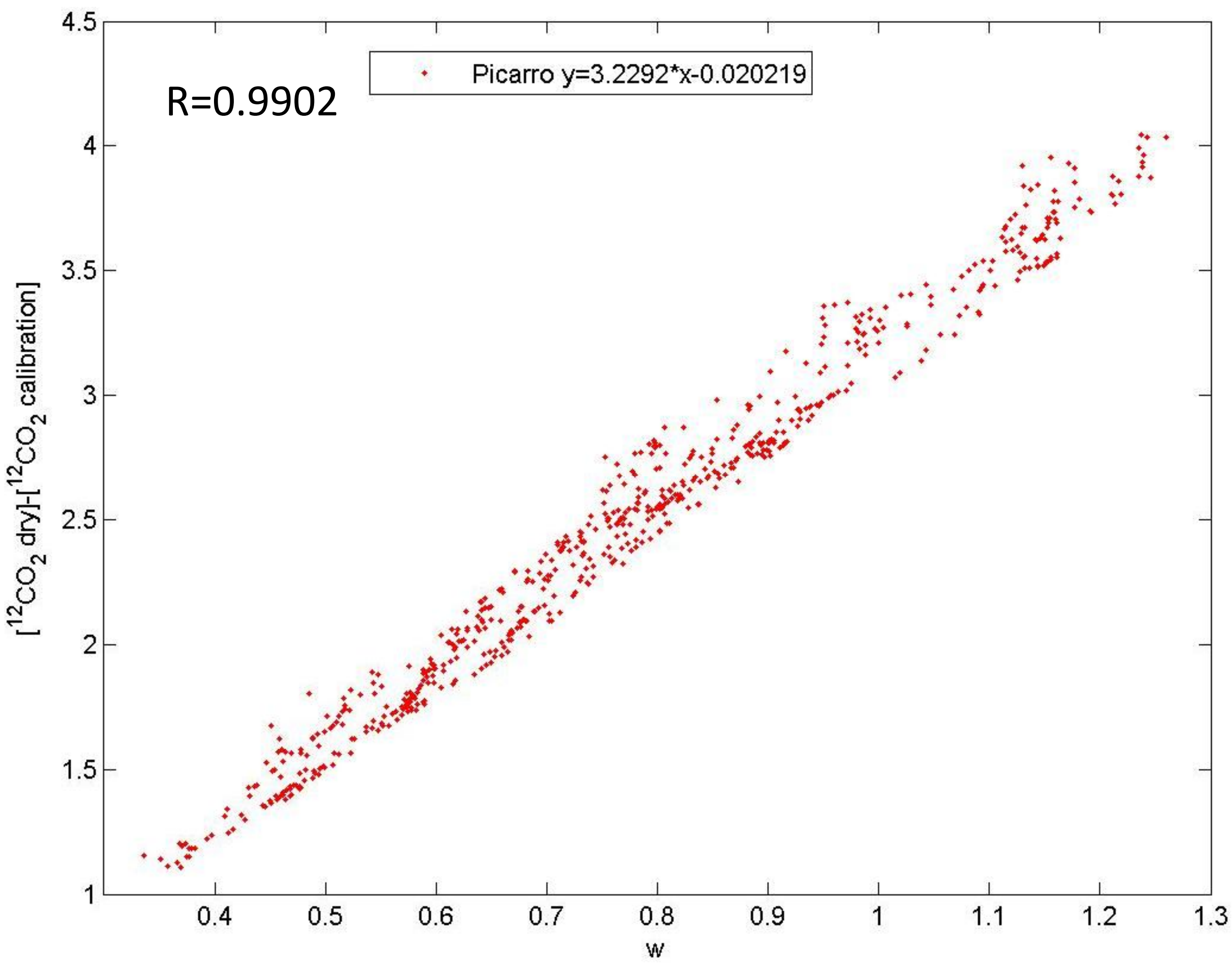


Fig 13 Comparison between [$^{12}CO_2$ dry] and [$^{12}CO_2$ calibration]

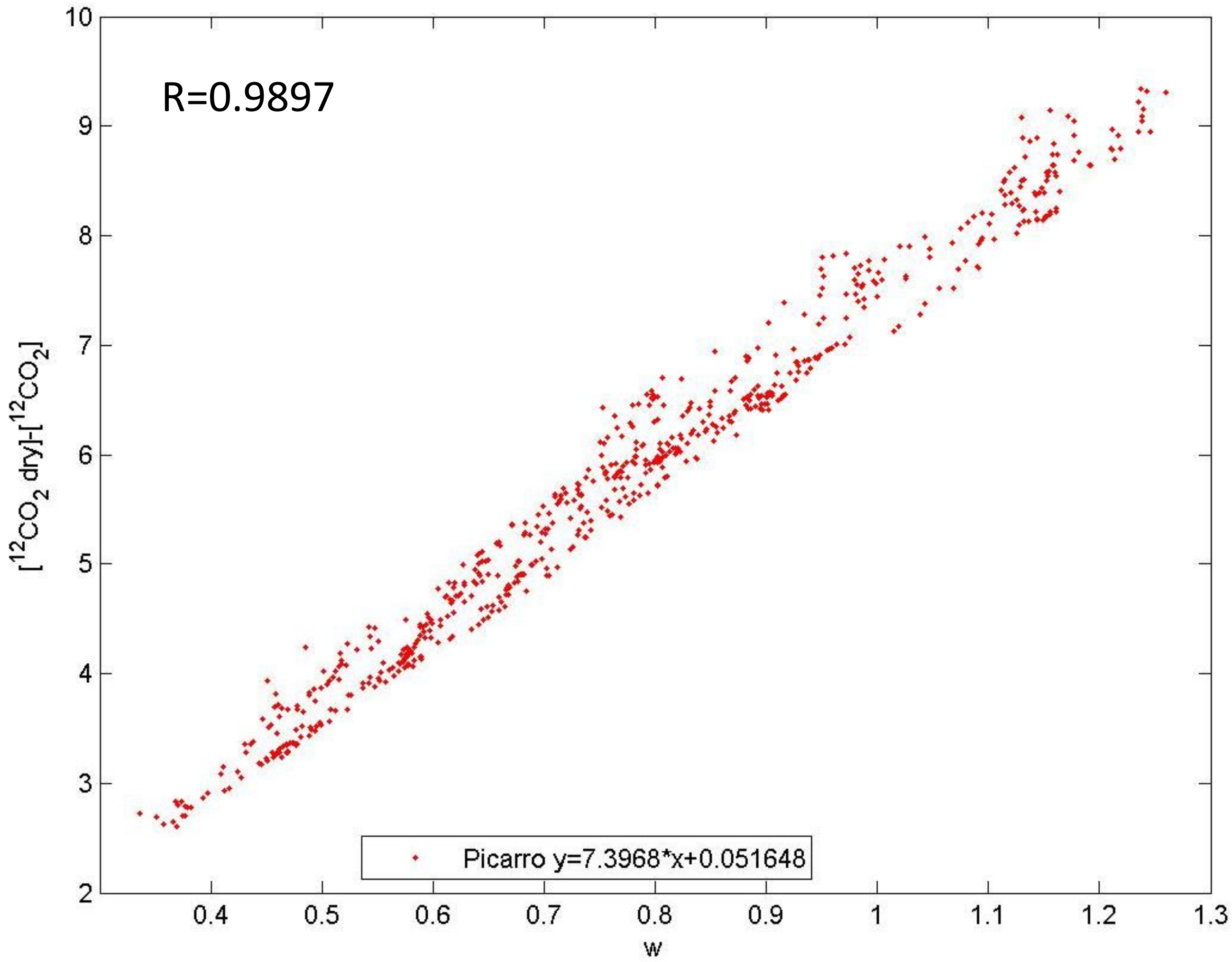


Fig 14 Comparison between [$^{12}CO_2$ dry] and [$^{12}CO_2$]

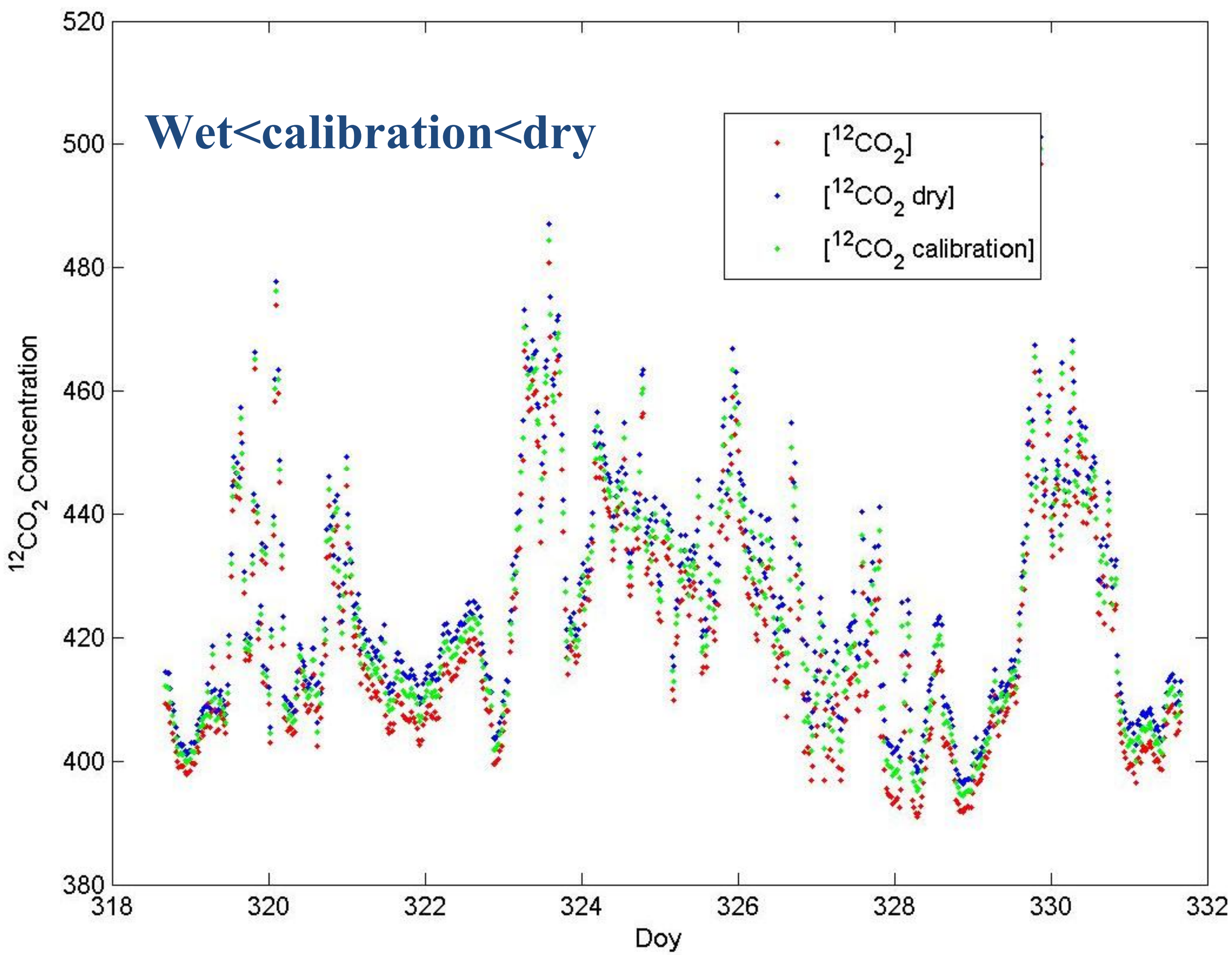


Fig 15 30-min average $^{12}CO_2$ concentration

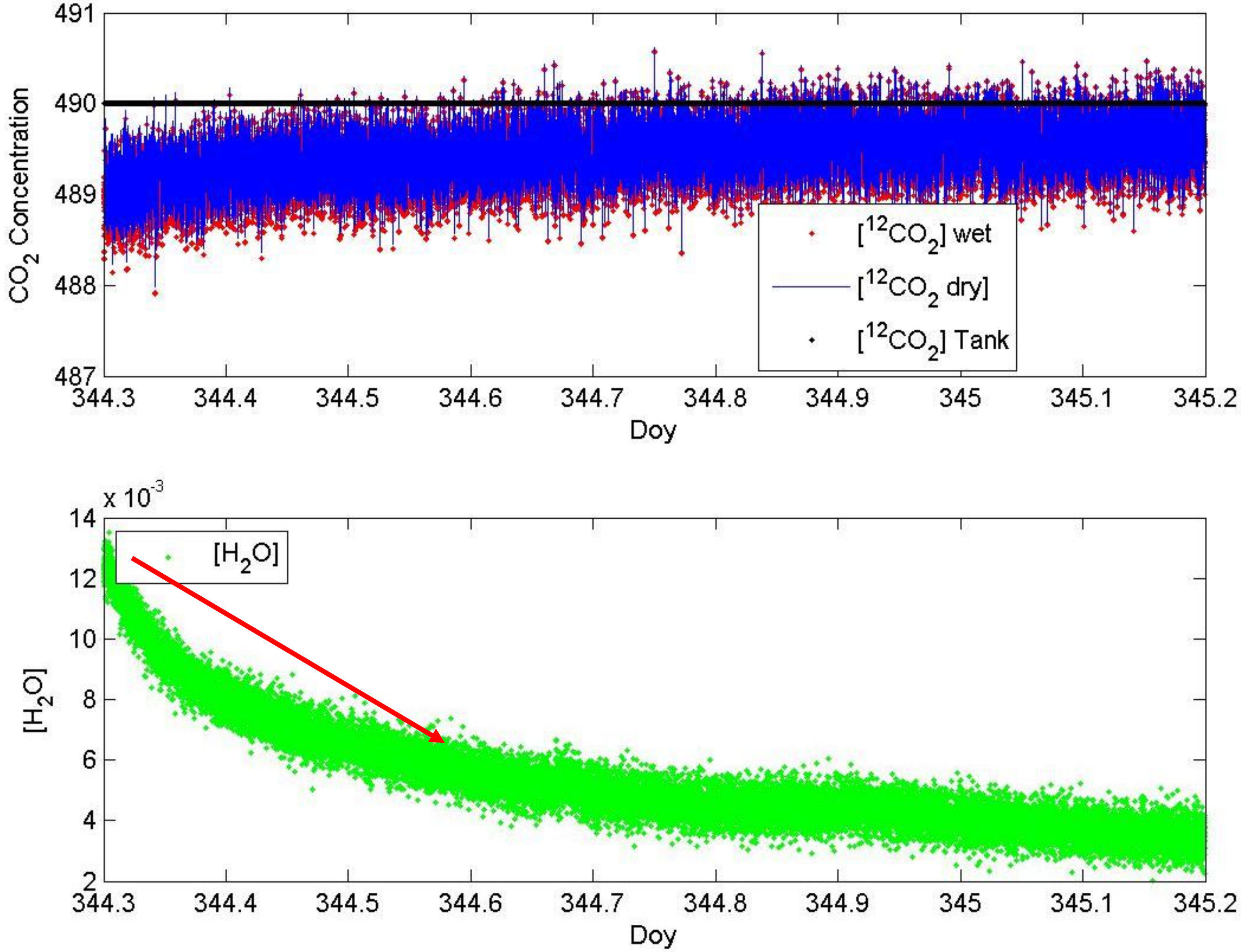


Fig 16 The measurement of $[H_2O]$ concentration

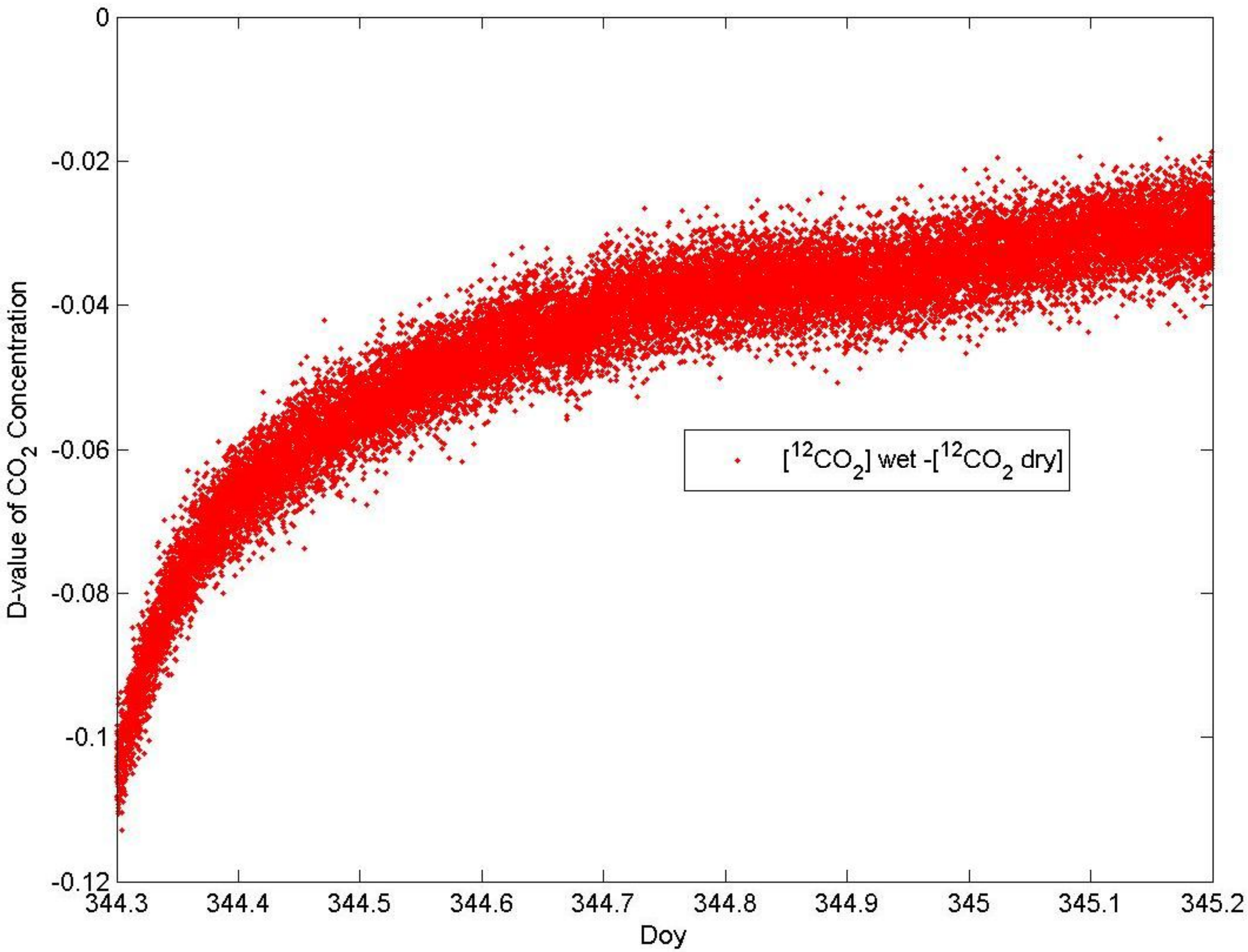


Fig 17 D-value of CO_2 concentration

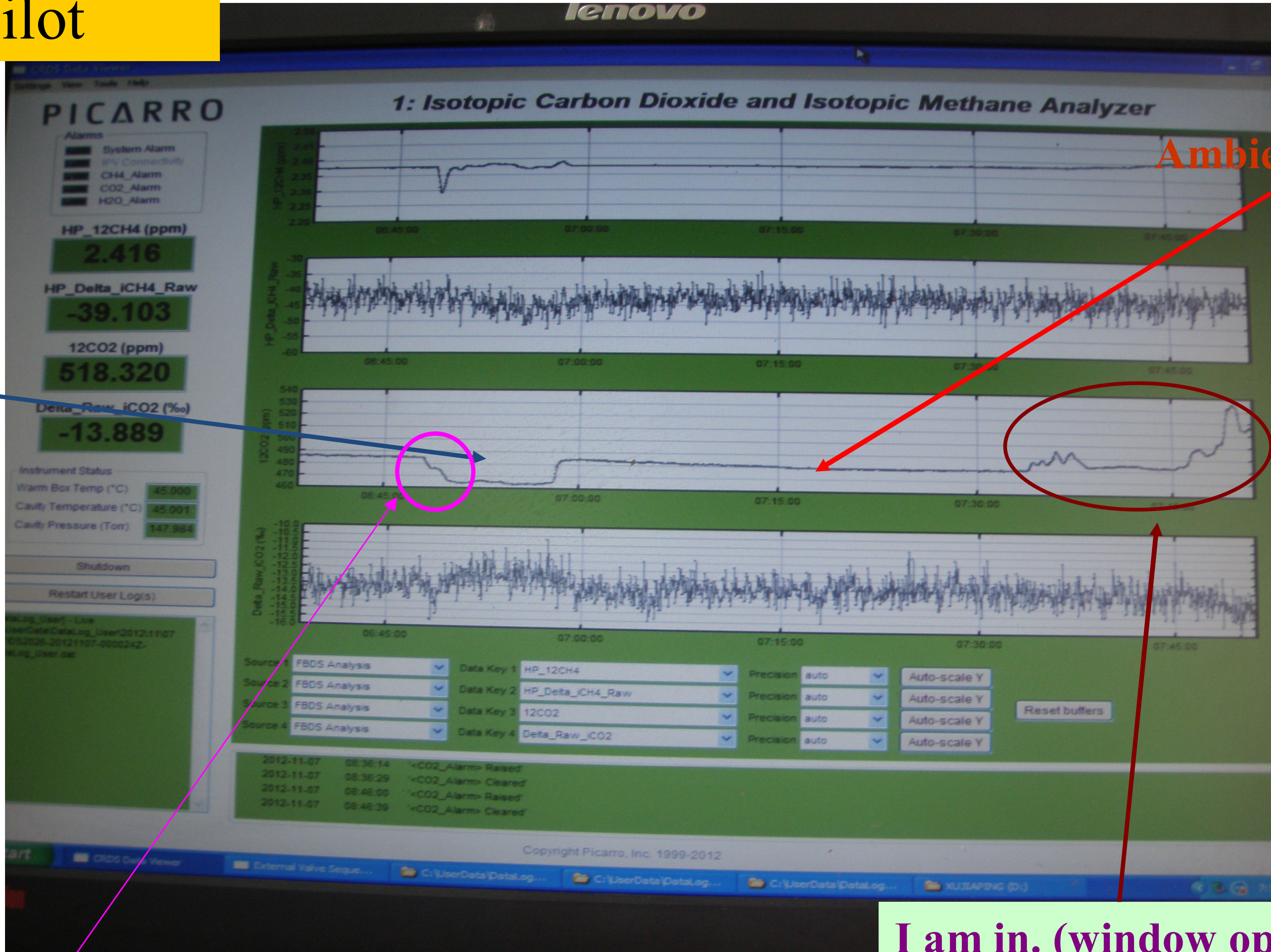
4.3 Pilot test

- Aim: To check the performance of pilots and to estimate response time of Picarro after switchover

- Data : Compressed dry air and ambient air were connected with the analyzer from 13th to 25th Nov and from 17th to 19th Dec. (Beijing time)

- Method : (1) 1 σ with 5-point-mowing.
  (2) Data of ambient air calibrated with data of compressed dry air .

One pilot



Ambient air

Dry air

I am in. (window opened)

90 sec for switchover.

Fig 18 A screenshot on 8:00am 8th NOV

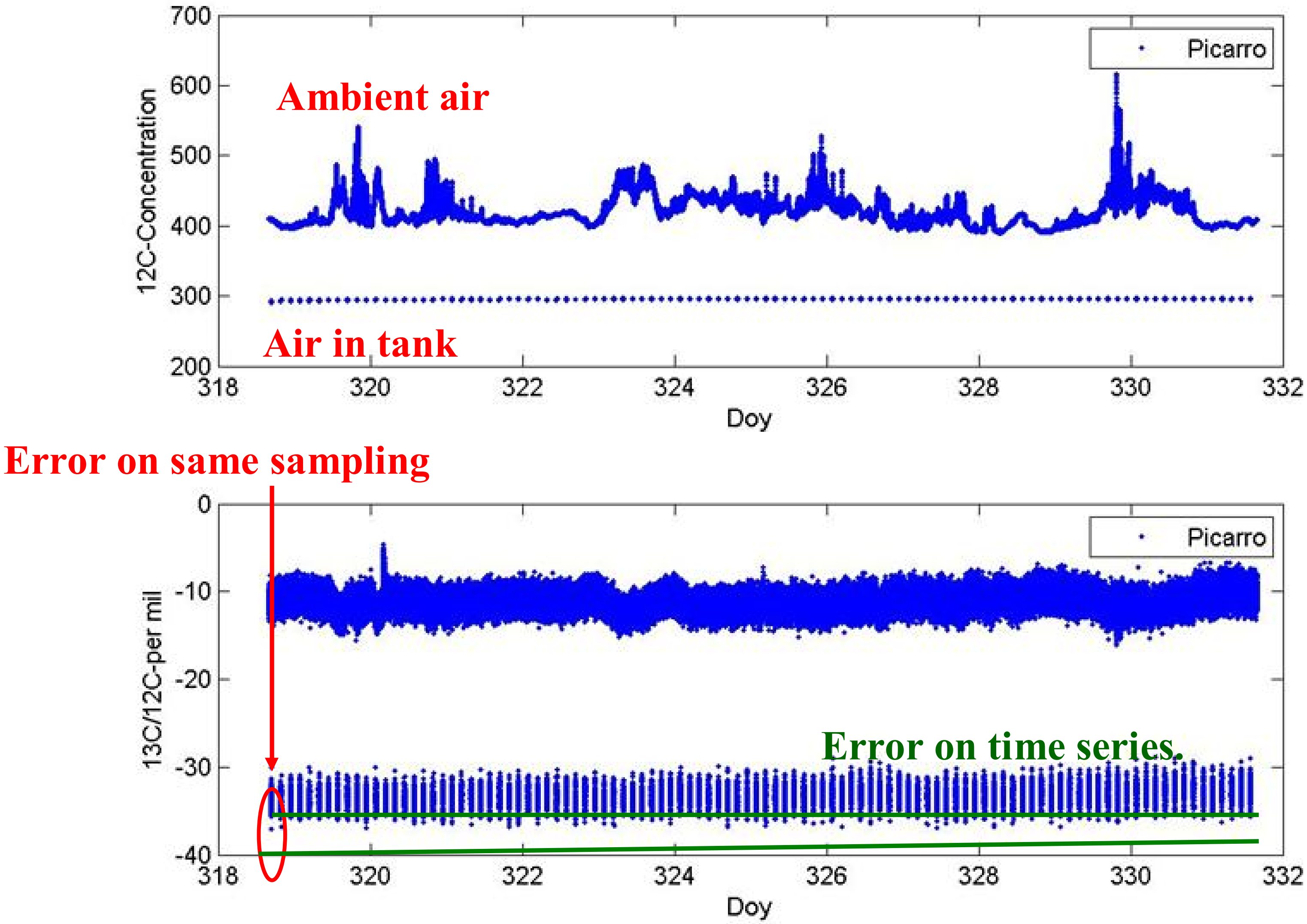


Fig 19 ^{12}C-concentration and ^{13}C/^{12}C measured from 13th to 25th Nov ,2012

5. Preliminary results

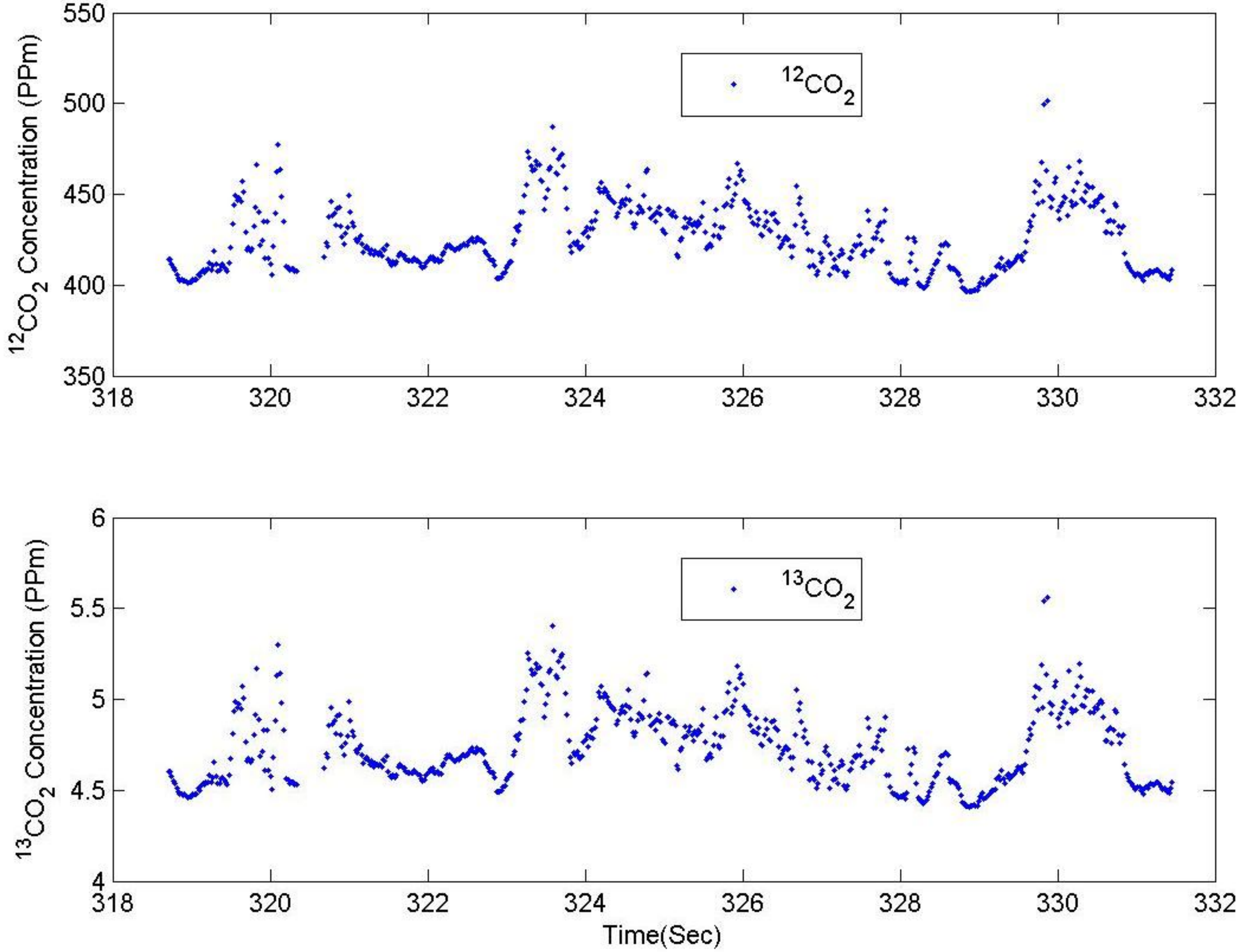
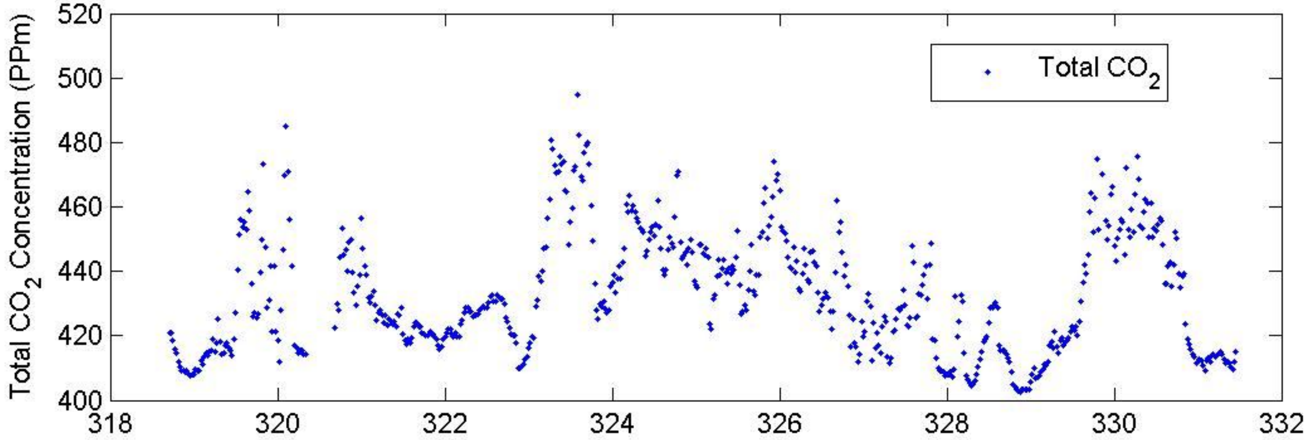


Fig 20 $^{12}CO_2$ concentration and $^{13}CO_2$ concentration measured from 13th to 25th Nov ,2012



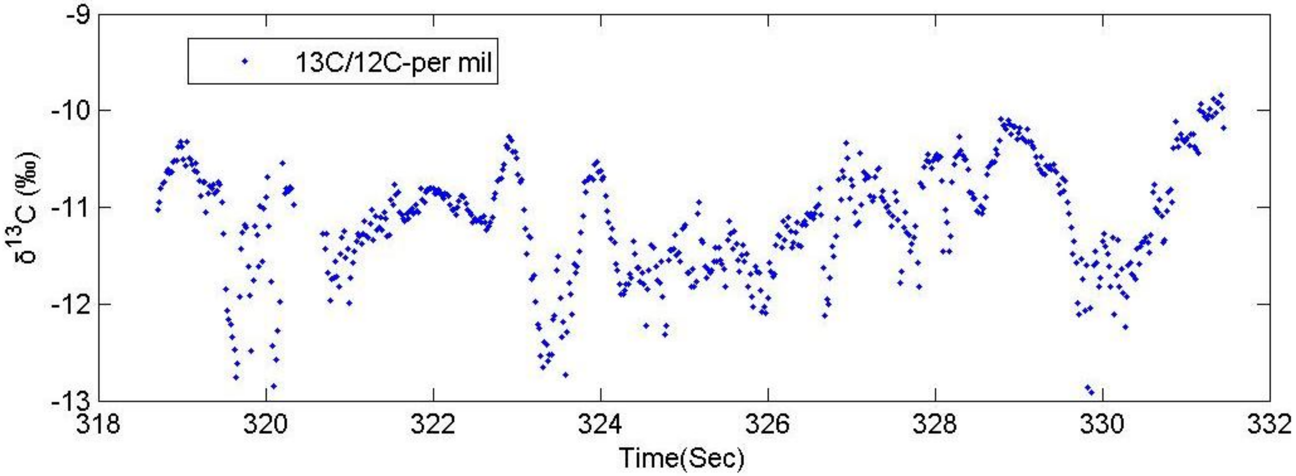


Fig 21 Total CO_2 concentration and $\delta^{13}C$ measured from 13th to 25th Nov ,2012

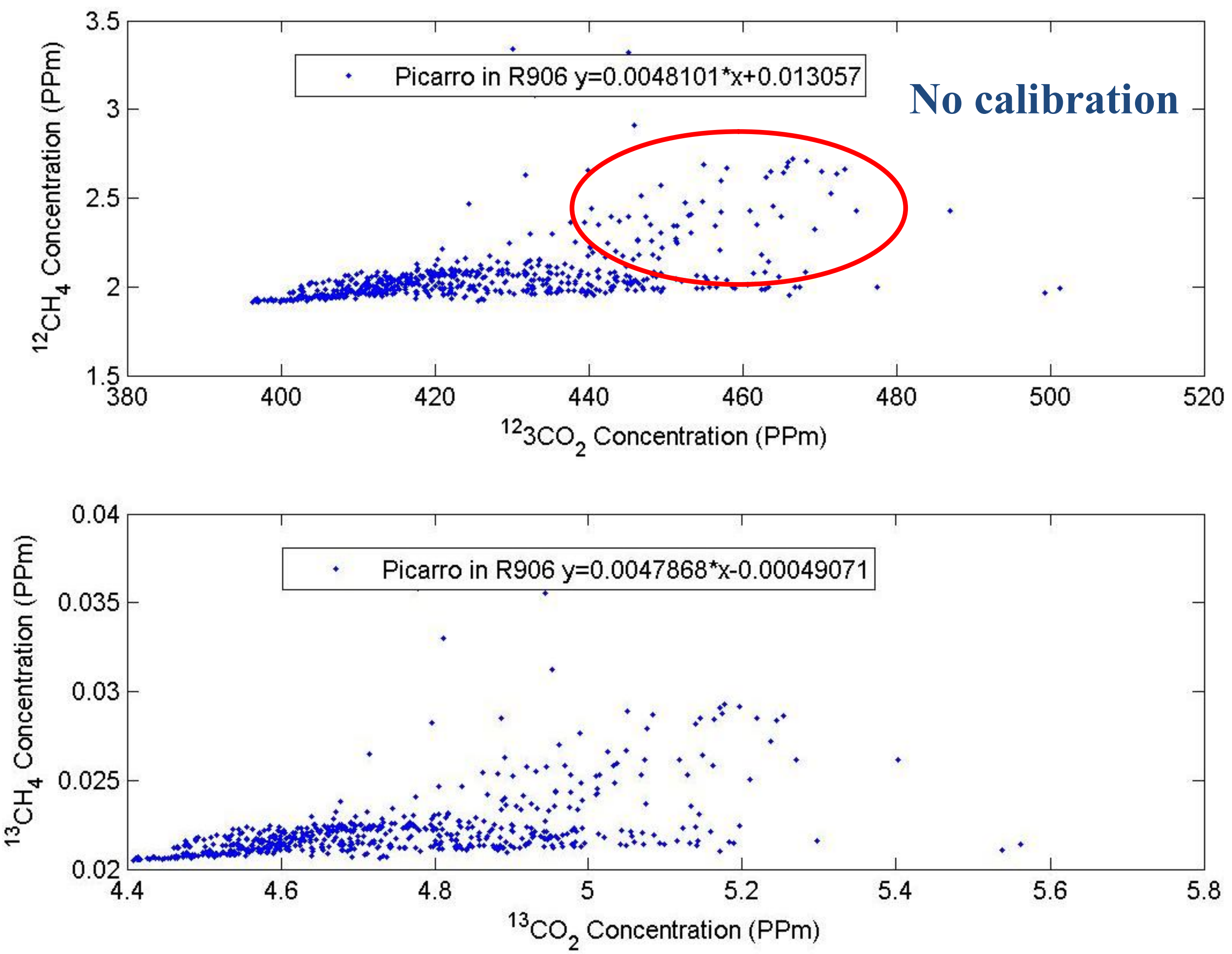


Fig 22 $^{12}CH_4$ concentration and $^{13}CH_4$ concentration measured from 13th to 25th Nov ,2012

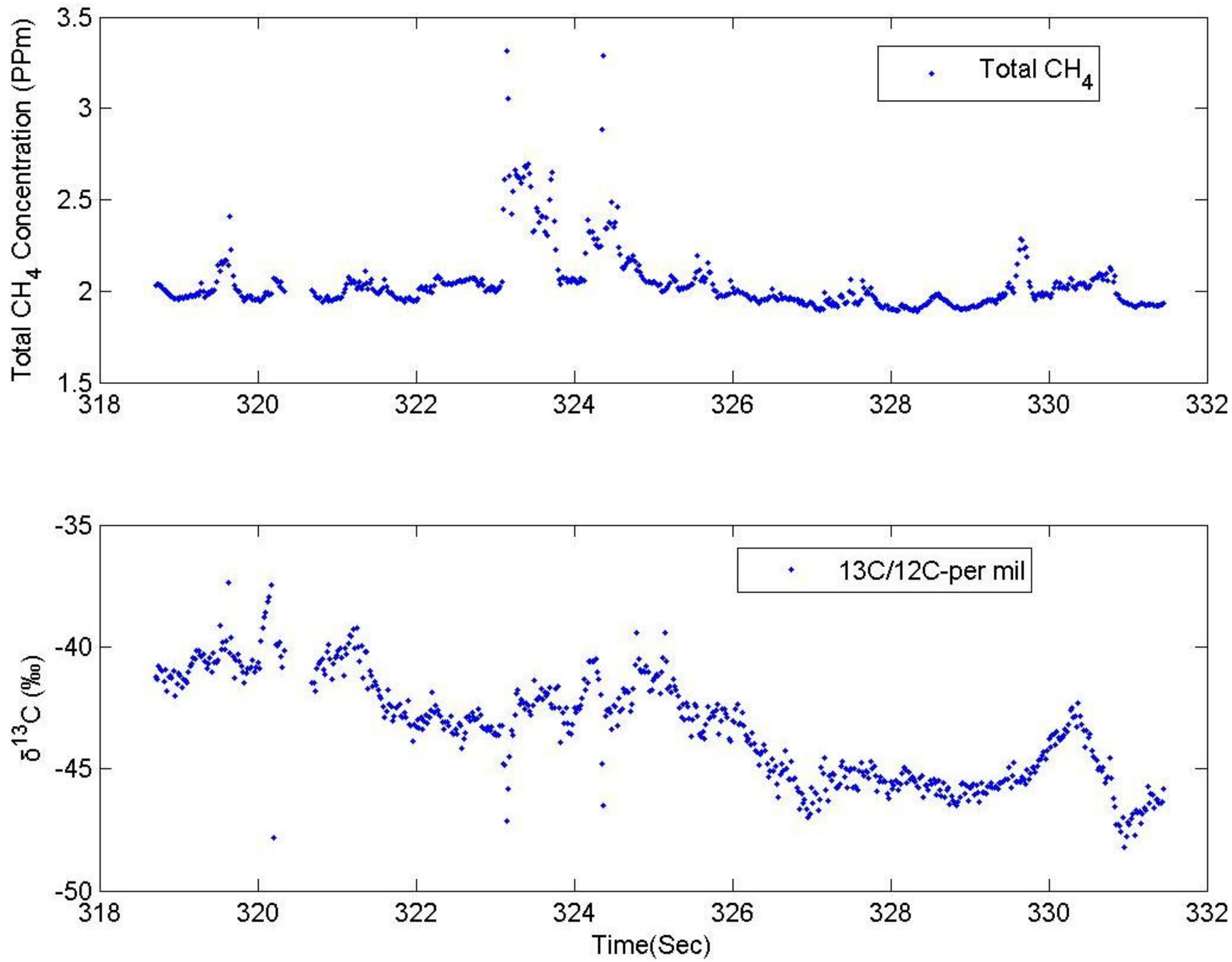


Fig 23 Total CH_4 concentration and $\delta^{13}C$ concentration measured from 13th to 25th Nov ,2012

Background air

≈-8.5‰, 385-390ppm

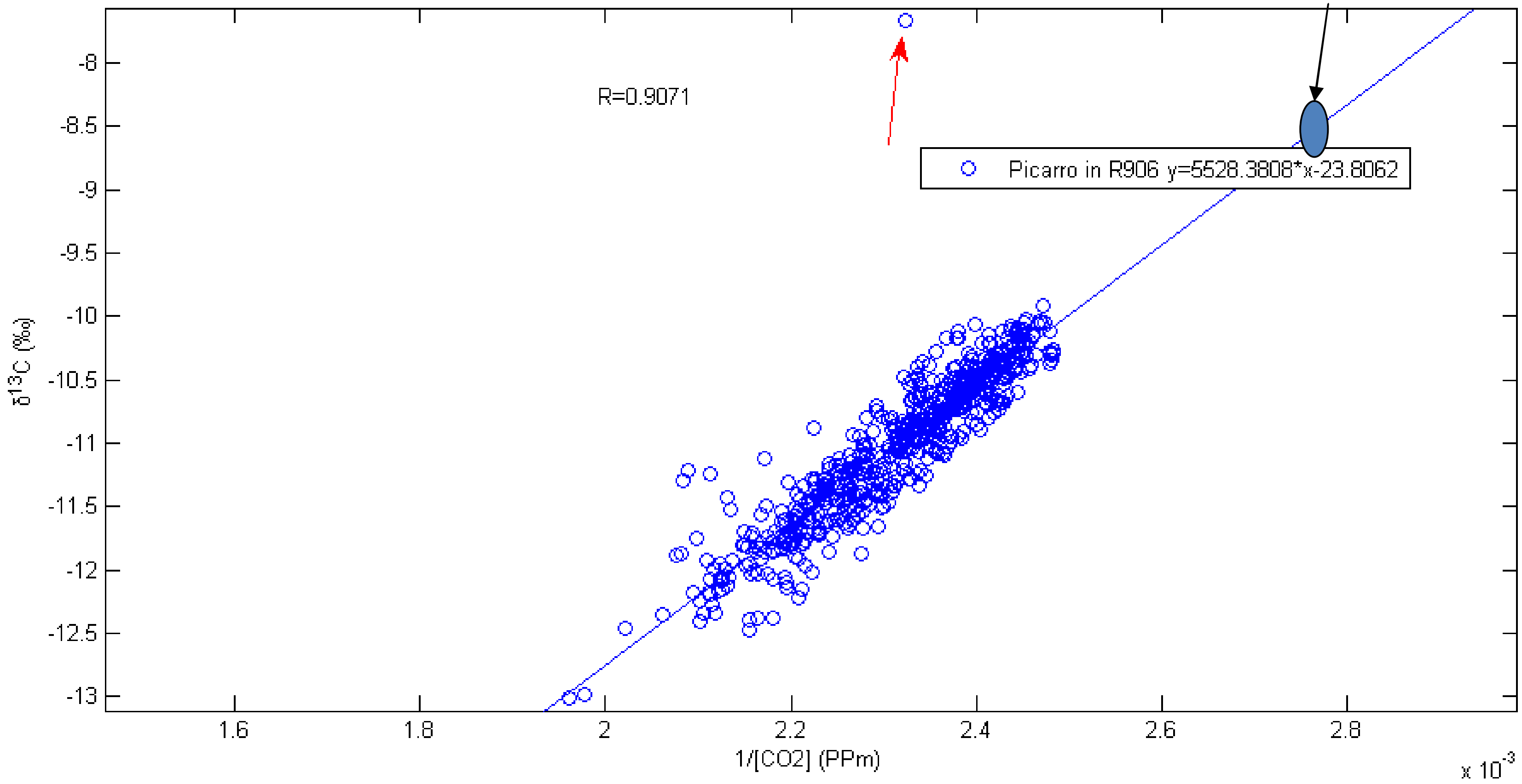


Fig 24 The Keeling plot of CO_2

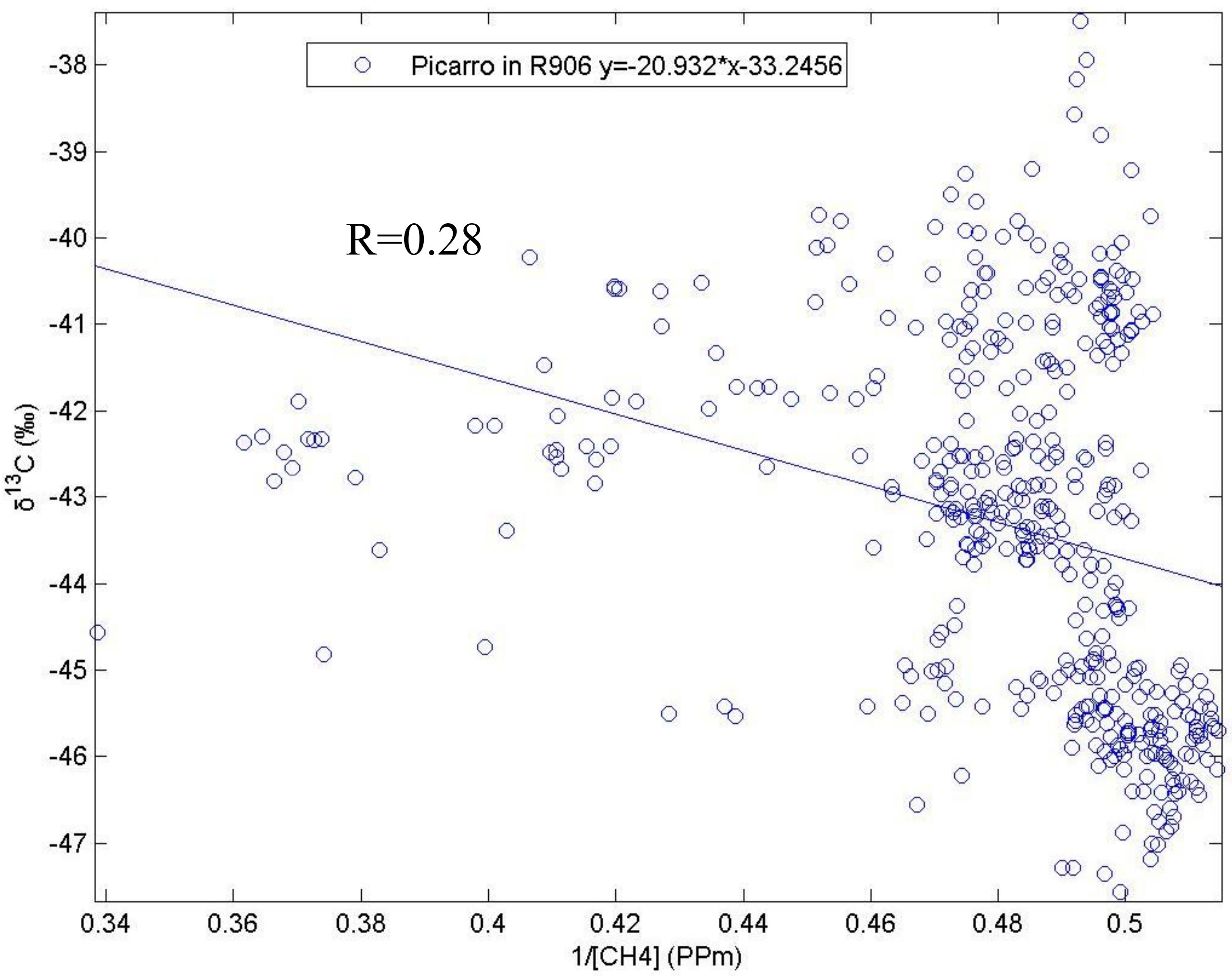


Fig 25 The Keeling plot of CH_4

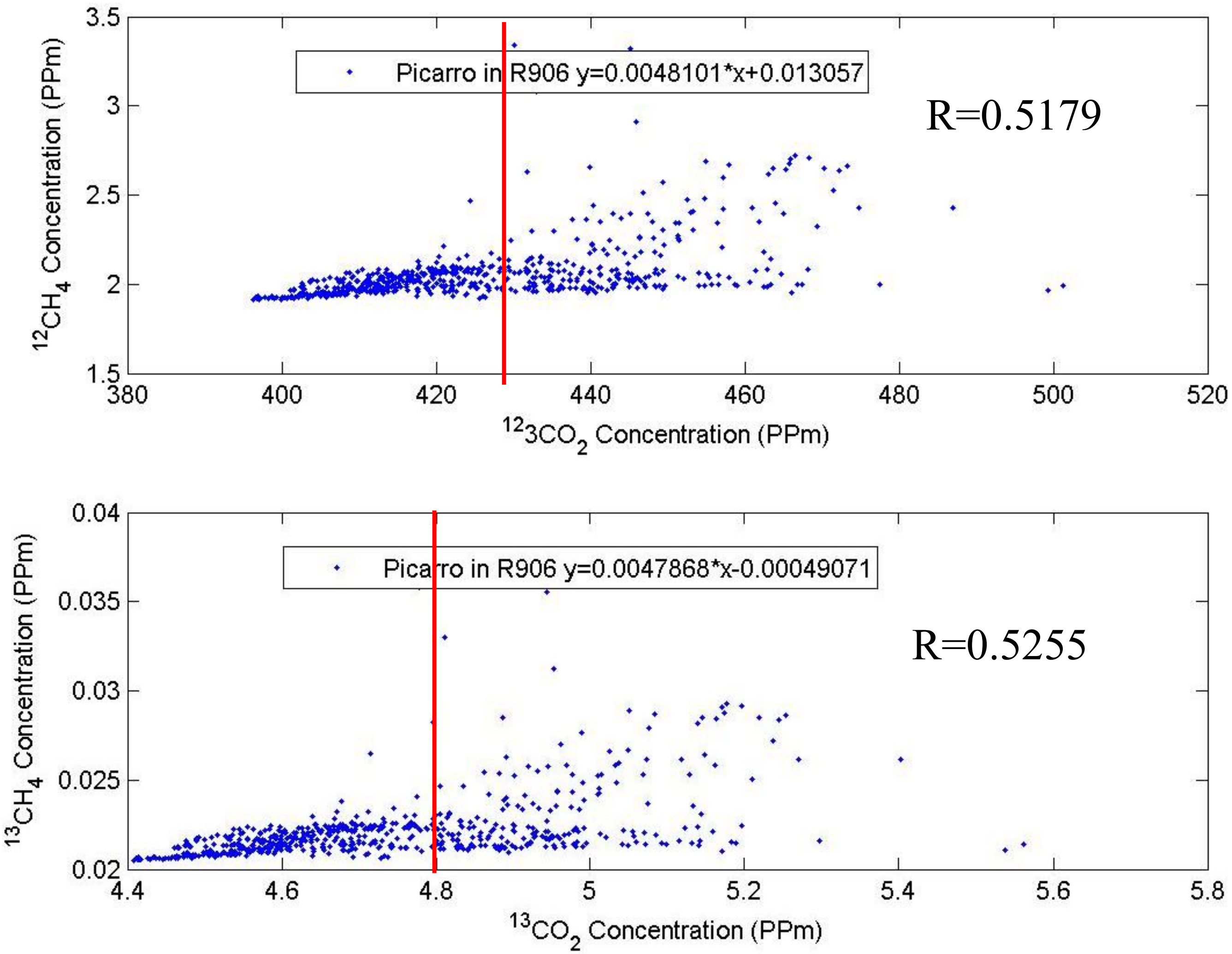


Fig 26 The comparison between CO_2 and CH_4 (1)

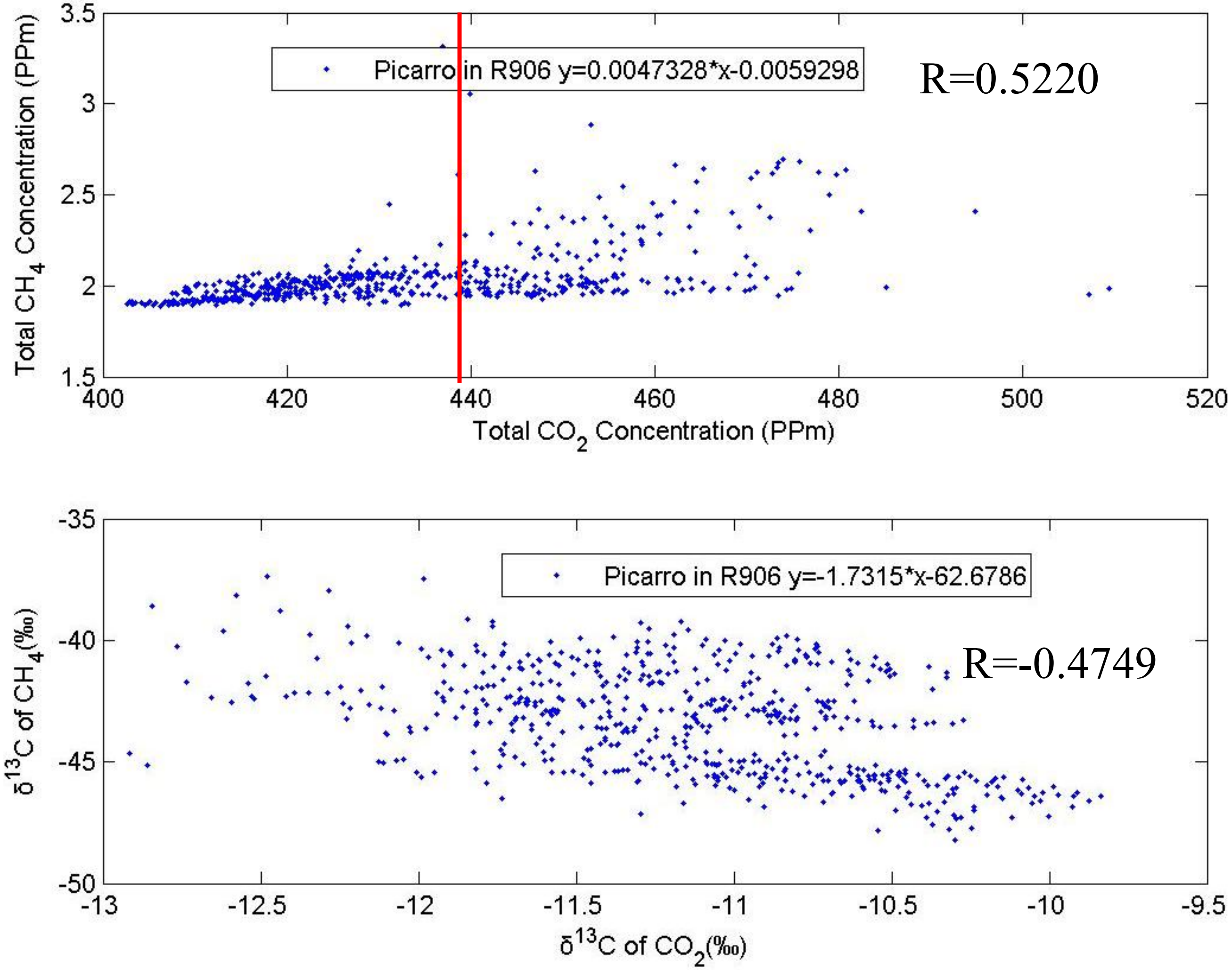


Fig 27 The comparison between CO_2 and CH_4 (2)

The Contribution of CO_2 sources

- Data : 13th - 25th Nov
- Method:

$$f_A + f_N = 1$$

$$f_A \cdot \delta^{13} C_A + f_N \cdot \delta^{13} C_N = \delta^{13} C_S$$

(Pataki,2003)

I assumed $\delta^{13}C_A$ (Anthropogenic sources)=-22‰ and $\delta 13C_N$ (Natural sources)=-25 ‰. f stands for the proportion of different sources in total CO_2 sources.

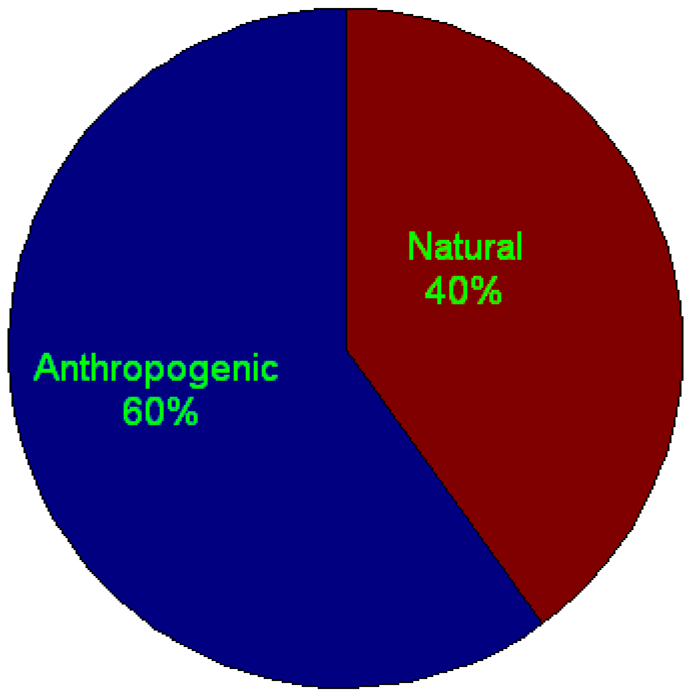


Fig 27 The Contribution of CO_2 sources in Nanjing from 13th to 25th Nov

6. Conclusion

- Picarro has high stability and accuracy.

- [H_2O] concentration can influence the accuracy of observation and measurement.

- Anthropogenic CO_2 sources are strong contributor in local region.

7. Next work

1. The performance of Picarro with 3 pilots (air inlets).

2. To testify the accuracy of [H_2O] measurement with dew generator.

Three pilots

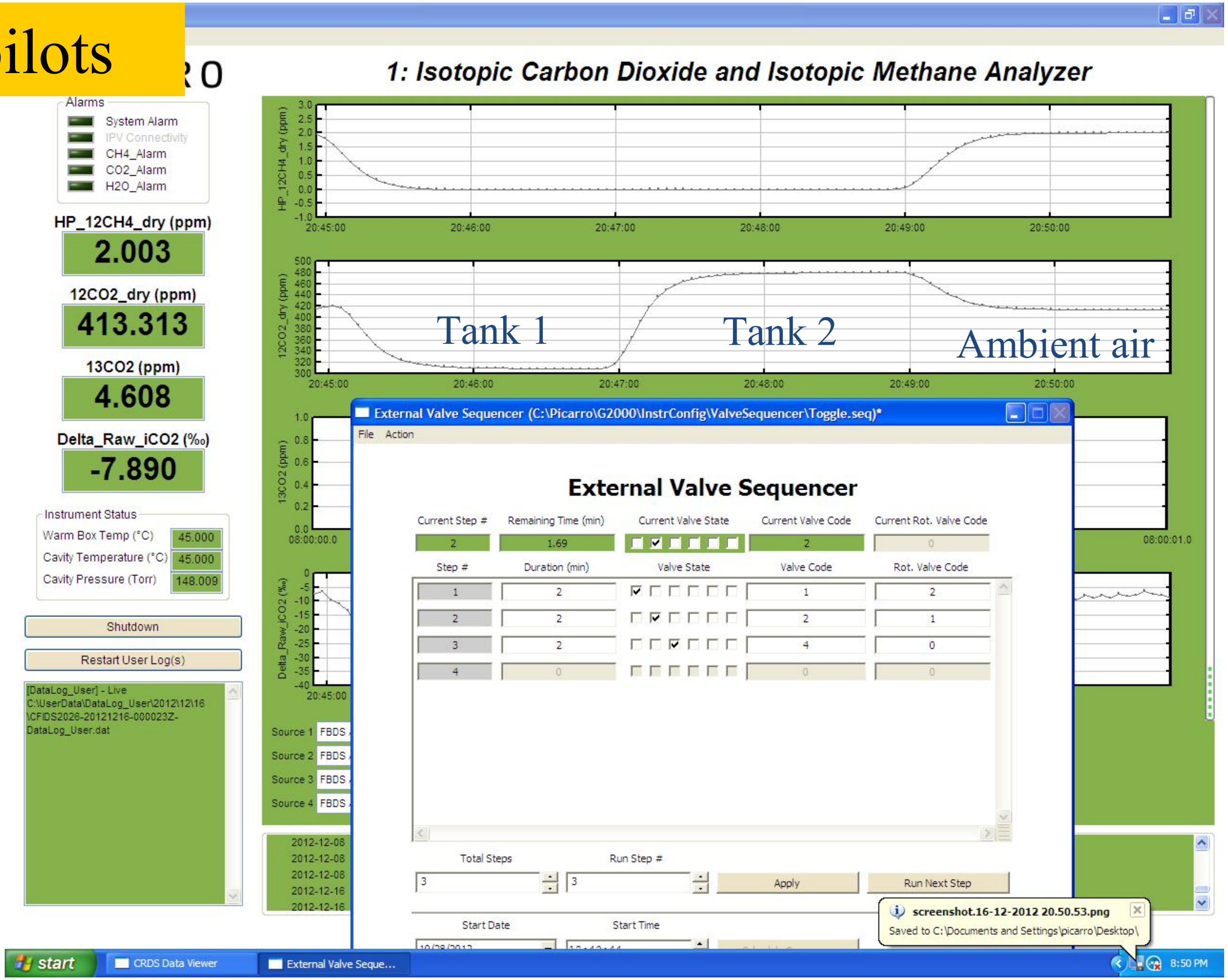


Fig 21 A screenshot on 16th Dec

8. Problems

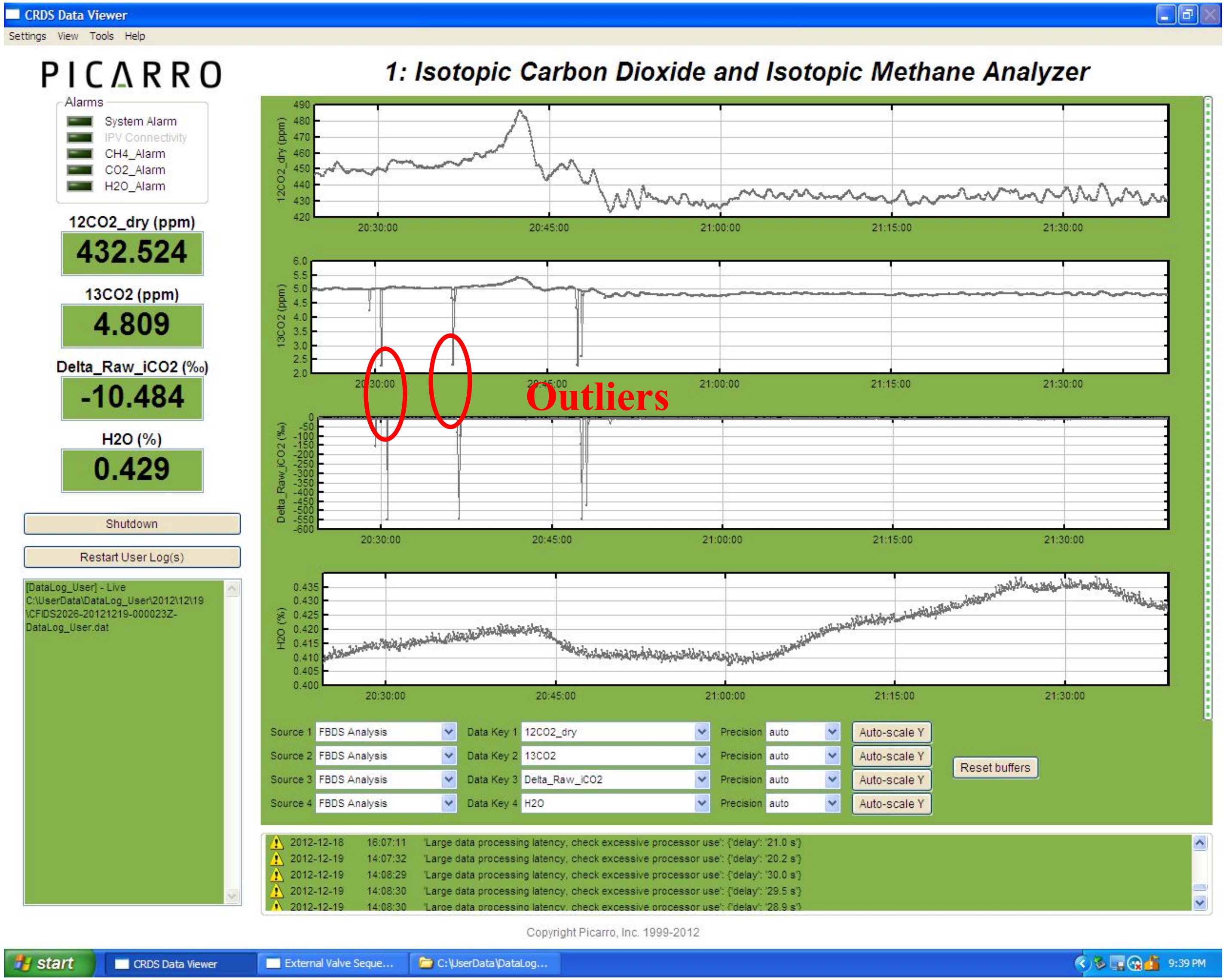


Fig 22 A screenshot on 16th Dec, 2012

Thank You!