# $^{13}C$ composition of atmospheric carbon dioxide in Nanjing

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# Outline

- 1. Background
- 2. Objective
- 3. Material and Method
- 4. Preliminary results
- 5. Conclusions
- 6. Next work

# 1. Background

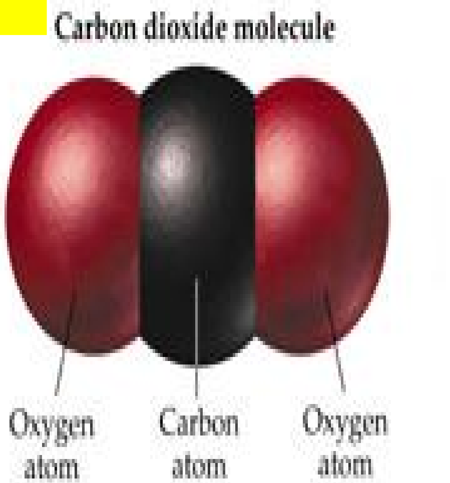
# Why do it?

- Anthropogenic C emission play a important role on land-atmosphere exchange of $CO_2$ in urban regions.

- It is in dire need of quality measurement to quantify anthropogenic $CO_2$ sources of the $^{13}C$ in an urban region by using $^{13}C$ tracer.

# How to do?

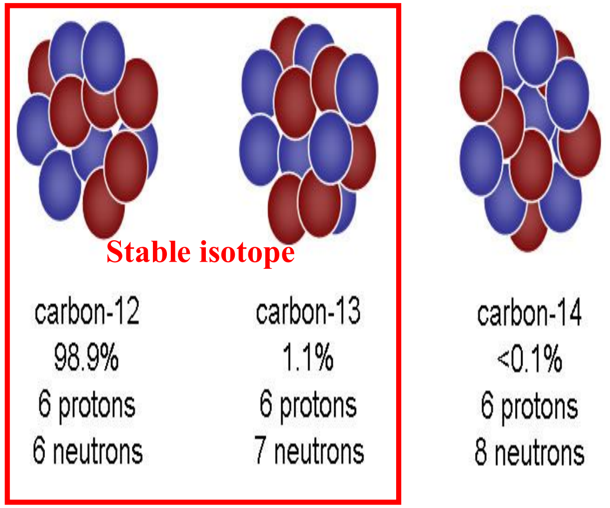
Step 1




$R_{\mathrm{VPDB}} = 11.2372 \times 10^{-3}$

$^{13}C/^{12}C$ standard molar ratio

(*Allison et al.*, 1995)



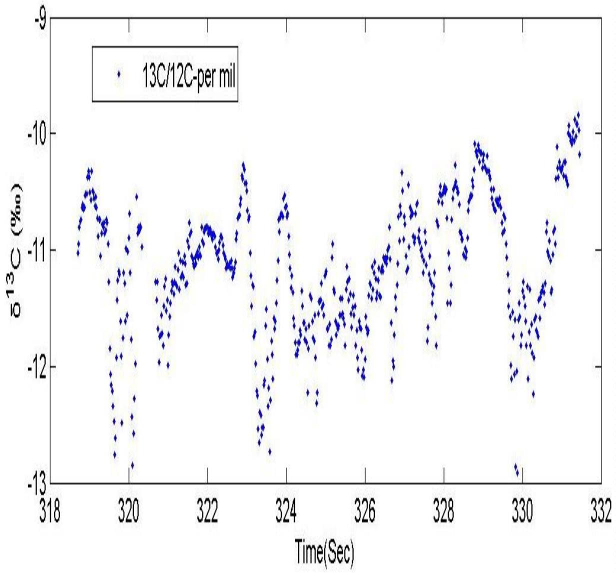

$$\delta = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \text{ , ‰}$$

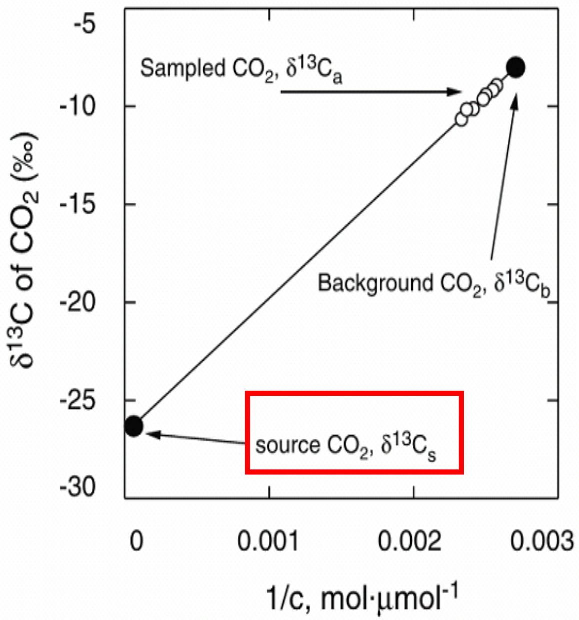
(MrReid.org, 2010)

| $CO_2$ sources | $\delta\,^{13}C$(‰) |
|---|---|
| Air | -8 |
| Plant respiration* | -9~--35 |
| Coal | -25-~-27 |
| Natural gas | -37~--42 |
| Gasoline | -28~-60 |

*Including characteristic values of C3 and C4 plant

(Wen et al, 2013)




$$C_a = C_b + C_S$$ （Pataki, 2003b）

$$C_a\delta_a = C_b\delta_b + C_s\delta_s$$

$$\delta^{13}C_a = C_b\left(\delta^{13}C_b - \delta^{13}C_S\right)\left(1/C_a\right) + \delta^{13}C_S$$

**a: Ambient air**

**b: Background air**

**s : Sources**

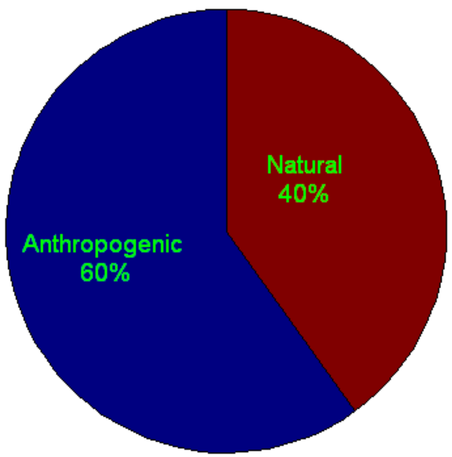
Step 2

Step 3

$$f_A + f_N = 1$$ （Pataki , 2003a）

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

**f: Fraction of contribution A: Anthropogenic sources**
**N: Natural sources**



# What had been done?

- We had testified the stability of isotopic analyzer (Allan Variance, Pilots test) and evaluated the dilution effect of $H_2O$ vapor.

- We had chosen reasonable method to calculate $CO_2$ concentration and its isotopic data.

- We thought that the performance of Picarro G1101-i was good and the analyzer is suitable to observe ambient air over a long period of time.

# 2. Objective

- 1. To measure $^{13}C$ composition of atmospheric carbon dioxide in Nanjing.

- 2. To show the temporal variability of $^{13}C$ composition of atmospheric carbon dioxide in Nanjing.

Now, what are we doing?

# 3. Material and Method

# 3.1 Analyzer and Material

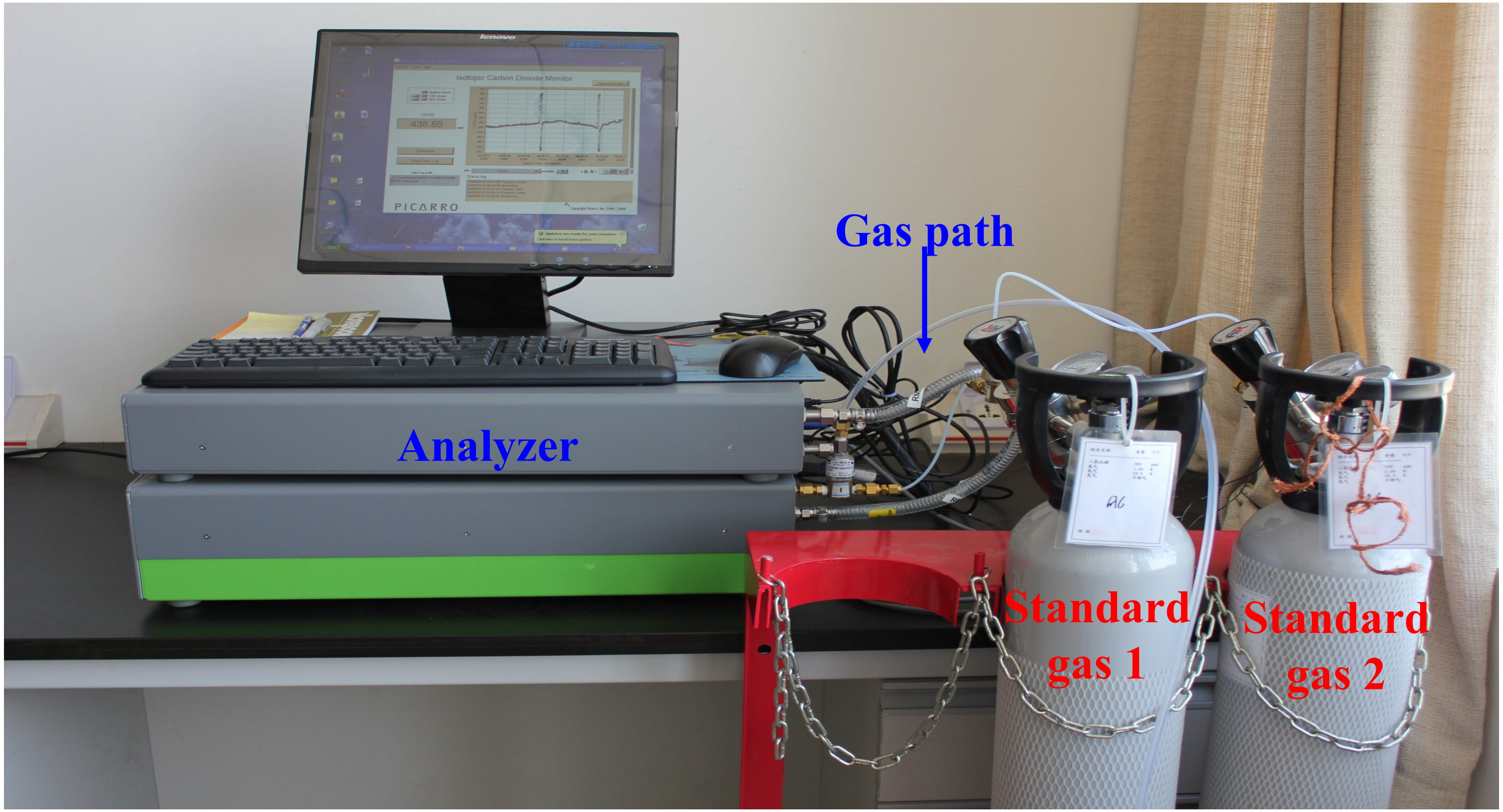



**Fig. 1. $^{13}CO_2$ analyzer (Picarro G1101-i)and calibration system.**


**Fig. 2. Gas Path.**

**Fig. 3. Inlet of ambient air.**

**Table 1. Information of standard gases.**

| Gases | $CO_2$ concentration (ppm) | $\delta^{13}C$* (‰) |
|---|---|---|
| Standard gas 1 | 380 | -29.75 ± 0.27 |
| Standard gas 2 | 500 | -30.01 ± 0.18 |

*** (n=41) Results from CAAS and CAFS**

**Table 2. Cycling of measurement.**

| Gases | Time (min) |
|---|---|
| Standard gas 1 | 5 |
| Standard gas 2 | 5 |
| Ambient air | 170 |

# 3.2 The method for calibrating measurement

Step 1

$$[CO_2] = [^{12}CO_2] + [^{13}CO_2] + f[CO_2] \quad (1)$$

$$f = 0.00474 \quad (2)$$

- To calculate total $CO_2$ concentration with f which stands for any other composition of $CO_2$ concentration in natural environment.

Step 2

$$R_a = [^{13}C]/[^{12}C] = [^{13}CO_2]/[^{12}CO_2] = R_{VPDB}(1+\delta_a/1000) \quad (3a)$$

$$R_{VPDB} = 0.0111797 \quad (3b)$$

$$[^{12}CO_2] = [CO_2](1-f)/(1+R_{VPDB}(1+\delta_a/1000)) \quad (3c)$$

$$[^{13}CO_2] = [CO_2](1-f) - [^{12}CO_2] \quad (3d)$$

- To calculate $CO_2$ concentration and $\delta^{13}C$ from raw data by using VPDB standard.

Step 3

$$X_{a,t}^{12} = \frac{X_{2,t}^{12} - X_{1,t}^{12}}{X_{2,m}^{12} - X_{1,m}^{12}}(X_{a,m}^{12} - X_{1,m}^{12}) + X_{1,t}^{12} \quad (4)$$

(Bowling et al , 2003)

$$X_{a,t}^{13} = \frac{X_{2,t}^{13} - X_{1,t}^{13}}{X_{2,m}^{13} - X_{1,m}^{13}}(X_{a,m}^{13} - X_{1,m}^{13}) + X_{1,t}^{13} \quad (5)$$

$$\delta^{13}C = (R_{sample} / R_{VPDB} - 1) \times 1000‰ \quad (6)$$

$$R_{sample} = X_{a,t}^{13} / X_{a,t}^{12} \quad (7a)$$

$$R_1 = X_{1,t}^{13} / X_{1,t}^{12} \quad (7b)$$

$$R_2 = X_{2,t}^{13} / X_{2,t}^{12} \quad (7c)$$

Subscript **i**=a,1,2 stand for ambient air, standard gas 1 and standard gas 2, respectively.

Subscript **t** and **m** mean true and raw data, respectively.

- A two-point linear interpolation was made to calibrate measured data to true data by using two standard gases.

# 3.3 Data set

- Two calibration gases which contains 380 ppm ( $\delta^{13}C$ =-29.75 ‰) and 500 ppm ( $\delta^{13}C$ =- 30.01 ‰) $CO_2$ were used to do this measurement.

- The analyzer were running from 24th Feb to 6th Mar (DOY  54.9998–65.7361) in 2013. During this period, the intake kept the pressure at about 1300 hpa and the flow rate at about 2 psi.

# 3.4 Data processing

- 1. Remove methane data
- 2. Remove 4 min data after switchover
- 3. Filter $^{12}CO_2$ data that exceeded the mean $\pm$ 1 standard deviation (five data）
- 4. Calibrate raw data with standard gases according the method described in 3.2
- 5. Calibrated data in 30 min were averaged
- 6. Remove data of the beginning 12 hours and the last 12 hours
- 7. Adopt Fitting method as GMR (geometric mean regression).

# 4. Preliminary results

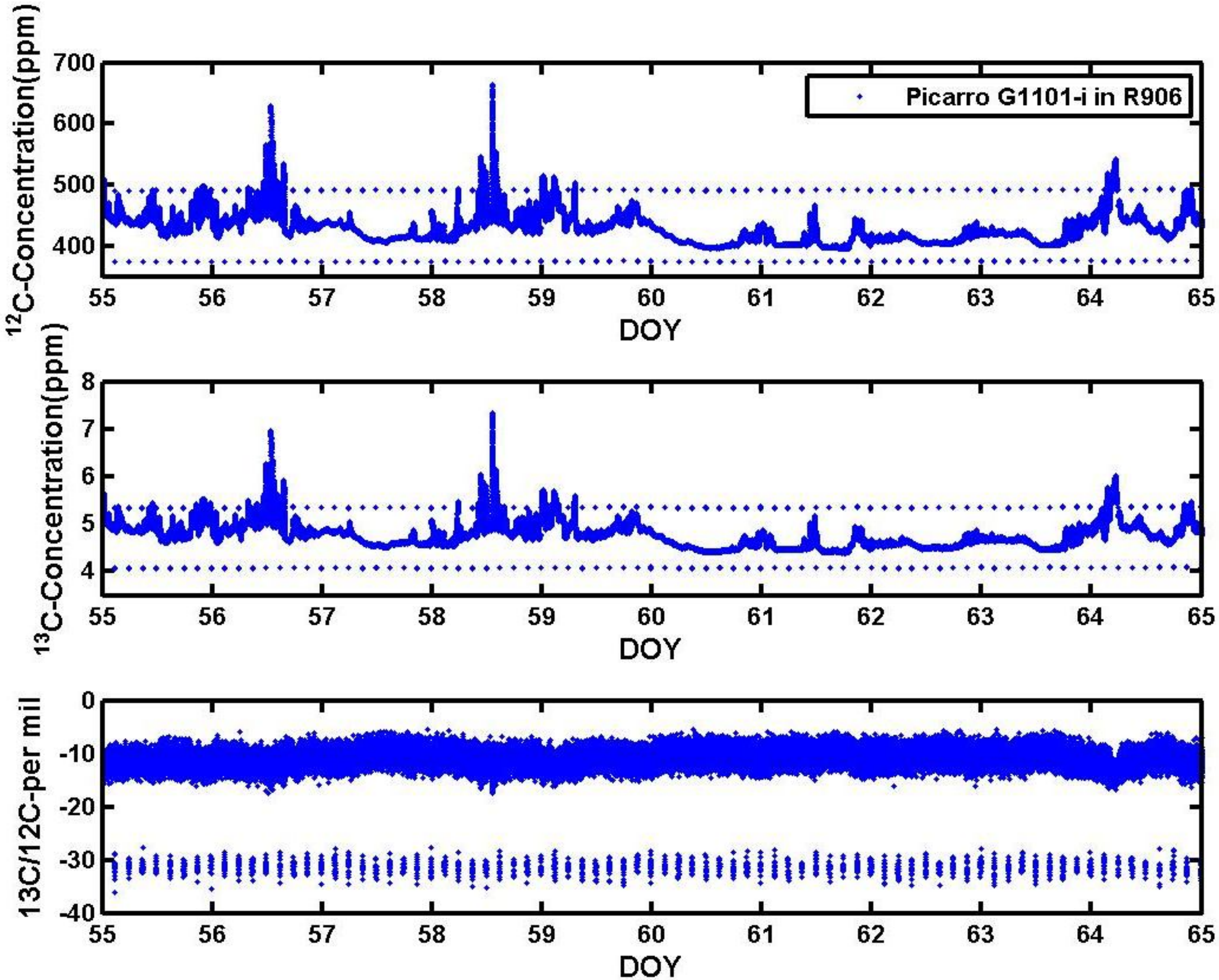



**Fig. 3. Time series of the $^{12}CO_2$ concentration, $^{13}CO_2$ concentration and $^{13}C/^{12}C$.**

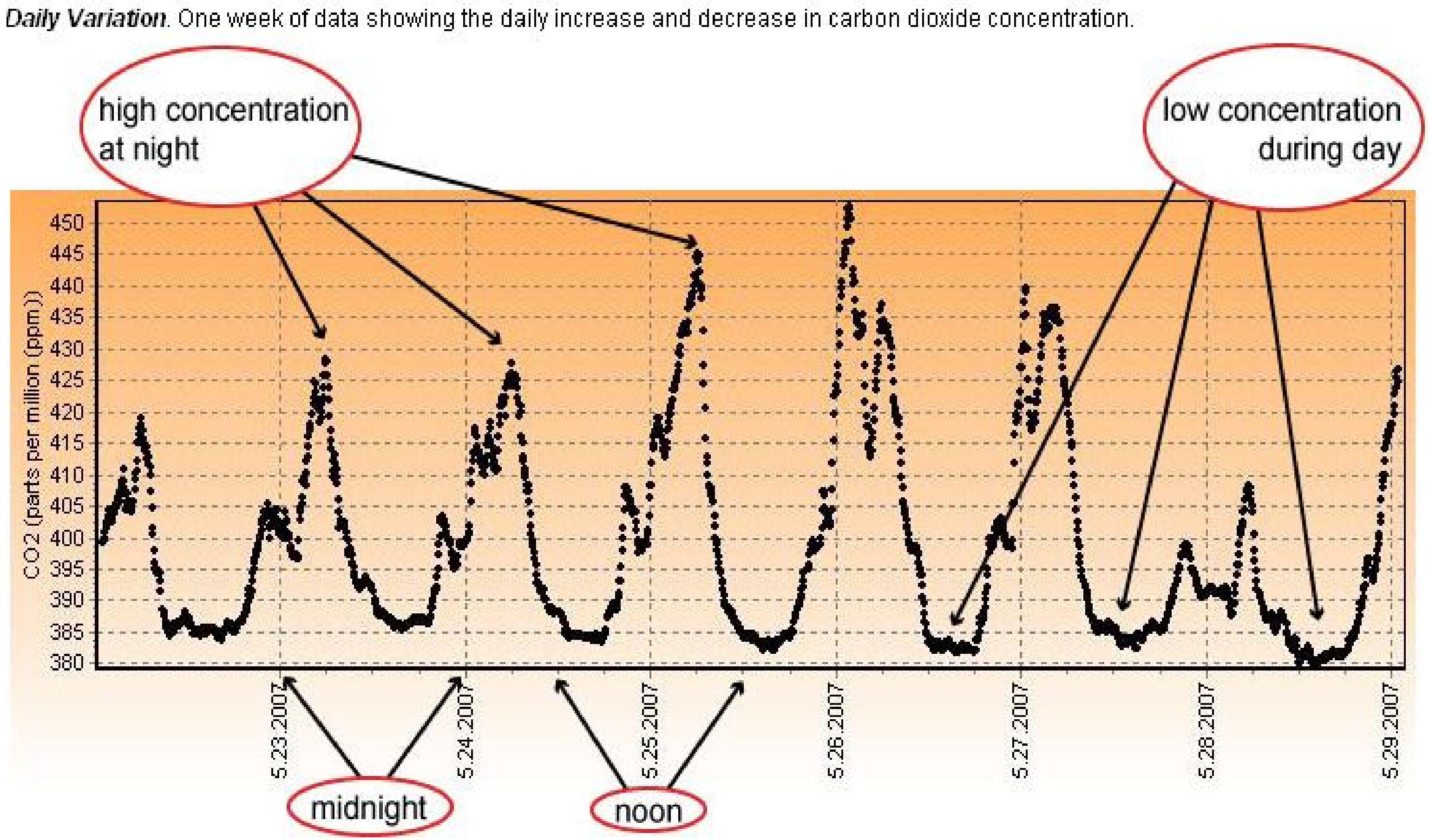



**Fig. 4. The classic daily variance of $CO_2$ concentration.(From UofU)**

**Table 3. The measurement of total $CO_2$ concentration in Standard gases.**

| Standard gases | True value (ppm) | Measurement value (ppm) |
|---|---|---|
| 1 | 380 | 380.83 |
| 2 | 500 | 499.42 |

- 2.99% data were out of range of 2 standard gases which need be calibrated by linear extrapolation .
- Except a high value at night, $CO_2$ concentration peaked at midday surprisingly.

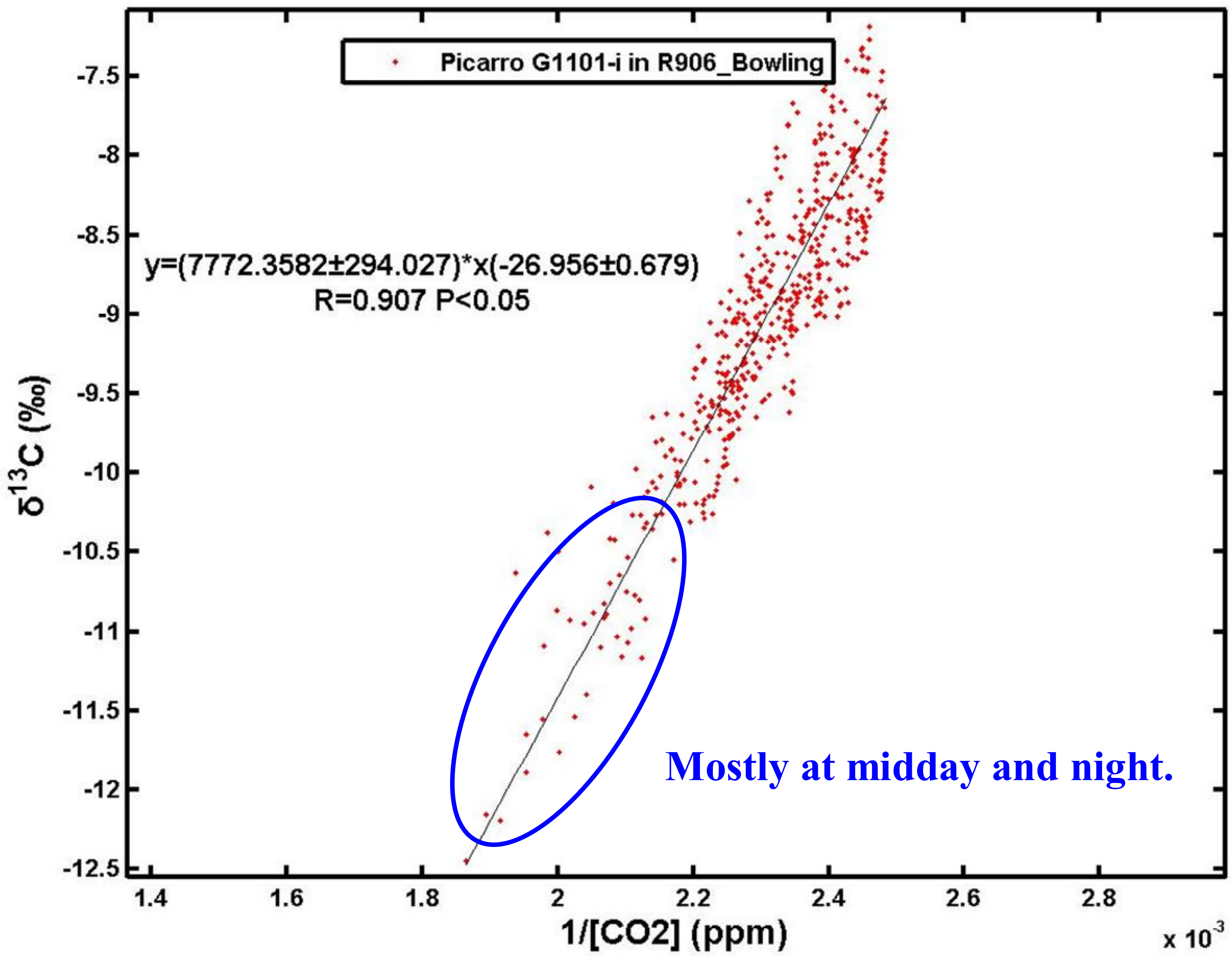



**Fig. 5. Keeling plot of the calibrated atmospheric $\delta^{13}C$ against the reciprocal of the calibrated $CO_2$ concentration.**

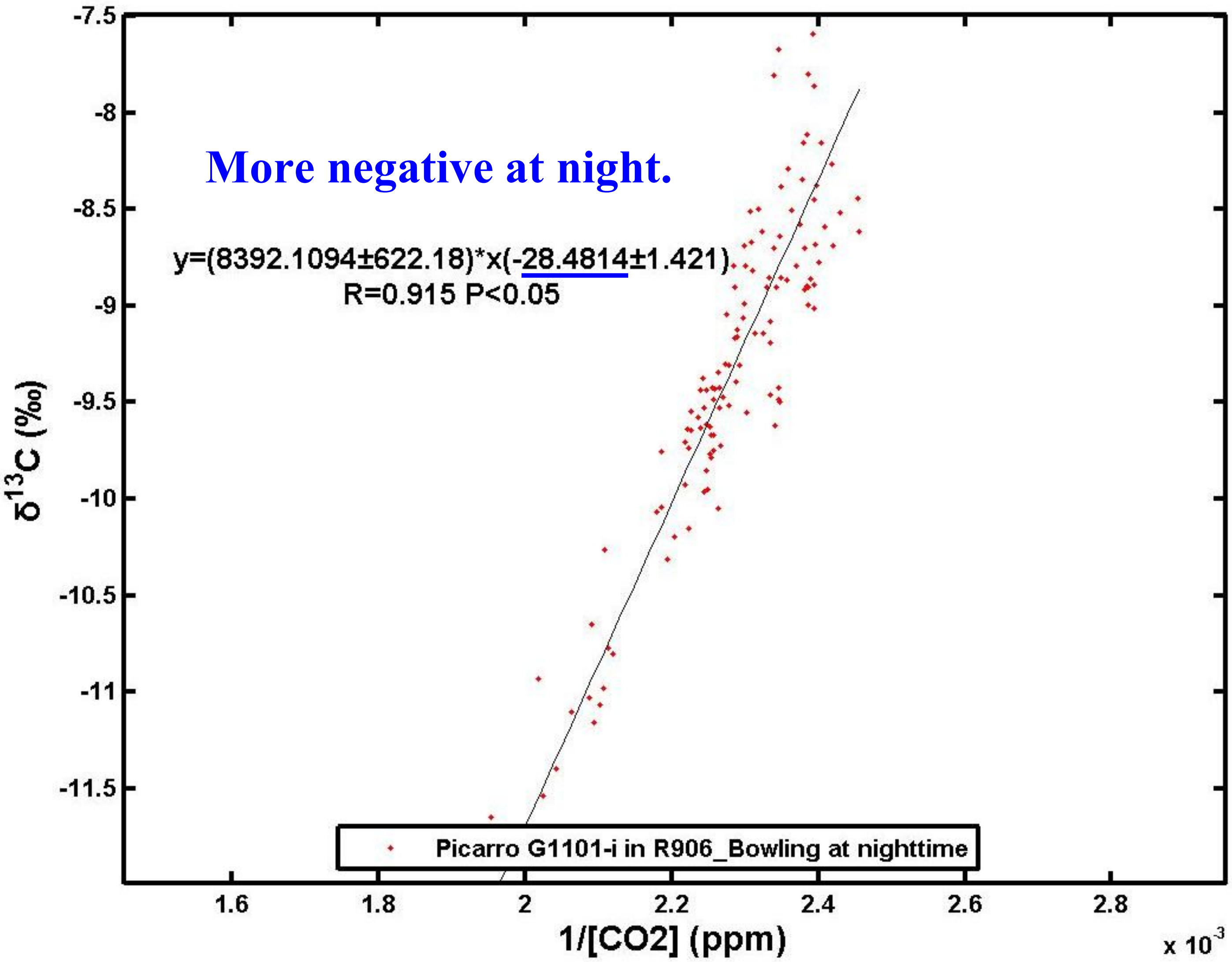



**Fig. 6. Keeling plot of the calibrated atmospheric $\delta^{13}C$ against the reciprocal of the calibrated $CO_2$ concentration at night (22:00 to 4:00 LT).**

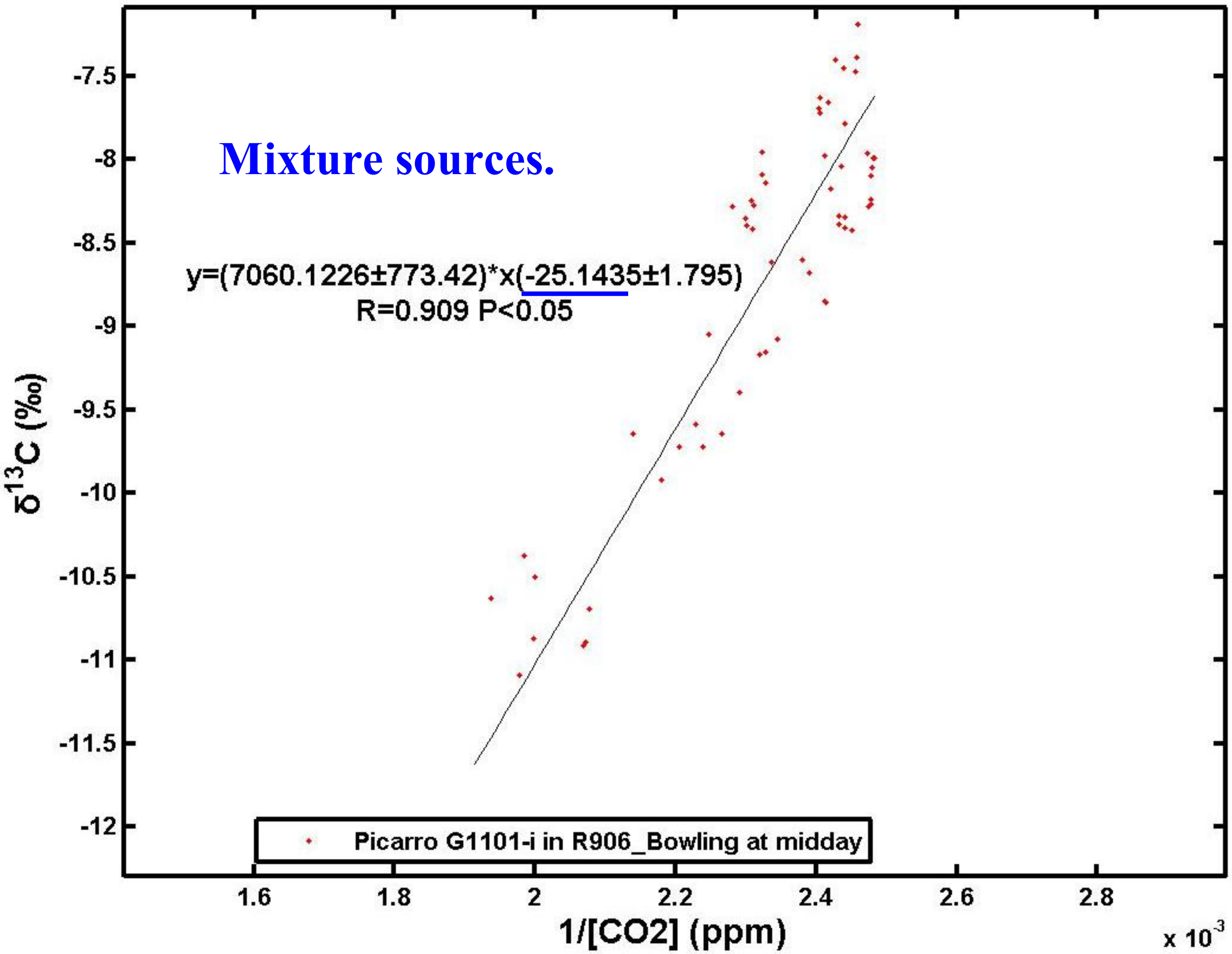



**Fig. 7. Keeling plot of the calibrated atmospheric $\delta^{13}C$ against the reciprocal of the calibrated $CO_2$ concentration at midday (11:00 to 14:00 LT).**

**Table 4. $\delta^{13}C$ in different weather situations in 2013.**

| Date | $\delta^{13}C$ (‰) | Error (‰) | $R^2$ | Tmax (℃) | Tmin (℃) | Weather | Wind direction | Wind force (level) |
|---|---|---|---|---|---|---|---|---|
| 02-24 | -28.5408 | 1.783 | 0.910 | 15 | 7 | Cloudy | ES~E | 3-4 |
| 02-25 | -23.6507 | 2.361 | 0.707 | 17 | 11 | Cloudy~ Light rain | E | 3-4 |
| 02-26 | -37.5551 | 3.962 | 0.814 | 15 | 7 | Overcast~ Cloudy | N~E | 3-4 |
| 02-27 | -27.0428 | 1.431 | 0.933 | 15 | 8 | Overcast | E~S | 3-4 |
| 02-28 | -29.0696 | 2.992 | 0.771 | 18 | 4 | Overcast~ Moderate rain | ES~EN | 3-4~4-5 |
| 03-01 | -29.593 | 4.261 | 0.591 | 7 | 0 | Light rain~ Overcast | EN | 5-6~4-5 |
| 03-02 | -32.6484 | 4.486 | 0.658 | 8 | -1 | Sunny | En | 3-4 |
| 03-03 | -29.473 | 4.307 | 0.575 | 12 | 5 | Sunny | S | 1-2 |
| 03-04 | -37.2514 | 6.51 | 0.482 | 17 | 6 | Sunny | N~E | 3-4 |
| 03-05 | -30.1337 | 2.328 | 0.874 | 20 | 8 | Overcast~ Sunny | S | 3-4 |


**Fig. 8. The map of NUIST.**

**(A for NUIST, B for Steel factory, C for chemistry factory )**

# 5. Conclusion

- 1. $\delta^{13}C$ was more negative at night which can represent the potential $CO_2$ sources in Nanjing's airshed which should be fuel combustion, factory emission and biogenic respiration.

- 2. More negative value of $\delta^{13}C$ occurred under overcast weather which indicated the strong biogenic respiration and anthropogenic emission.

- 3. $\delta^{13}C$ showed more negative when wind direction is S-E where located the factories and highways.

- 4. In some days $CO_2$ concentration were surprisingly high at noon. Maybe the reason is that the time is coincided with lunch-eating period and people were coming out in the campus but the reason is not very convincing.

# 6. Next work

- 1. Continue the experiment and ensure the quality of data.
- 2. To investigate potential CO2 sources in Nanjing, especially the regions around campus.
- 3. To analyze the data from different respectives.

# Thank You!