Comparison of ^{13}C composition of atmospheric CO_2 in Nanjing and Beijing

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Outline

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

1. Background

- The local CO_2 emission is highly dependent on the level of urbanization and regional climatic and geographical condition. It might be of great help for understanding the different roles of natural and anthropogenic CO_2 sources in urban areas by monitoring CO_2 concentration and its ^{13}C isotopic composition with a high frequency.

- The changes of land conversion and various local energy consumption structure can strongly influence terrestrial C cycle.

- Furthermore, meteorological and phenological factors, such as wind direction, heating demand and biological seasonality, can be the divers of the variation of atmospheric CO_2 in short (hourly) or long (seasonal) time scale.

2. Objective

- A comparison of ^{13}C composition of atmospheric CO_2 between Beijing and Nanjing can help us to find out the controlling factors of CO_2 emission in specific environment and to deeply comprehend the effects of human and urbanization on ecosystem processes, 'urban C cycle'.
- The relationship between the results of two cities might be useful to improve air quality and to reduce the effect of 'heat island'.
- The performance of analyzers are also evaluated in this experiment.

3. Material and Method

3.1 Analyzer and Material

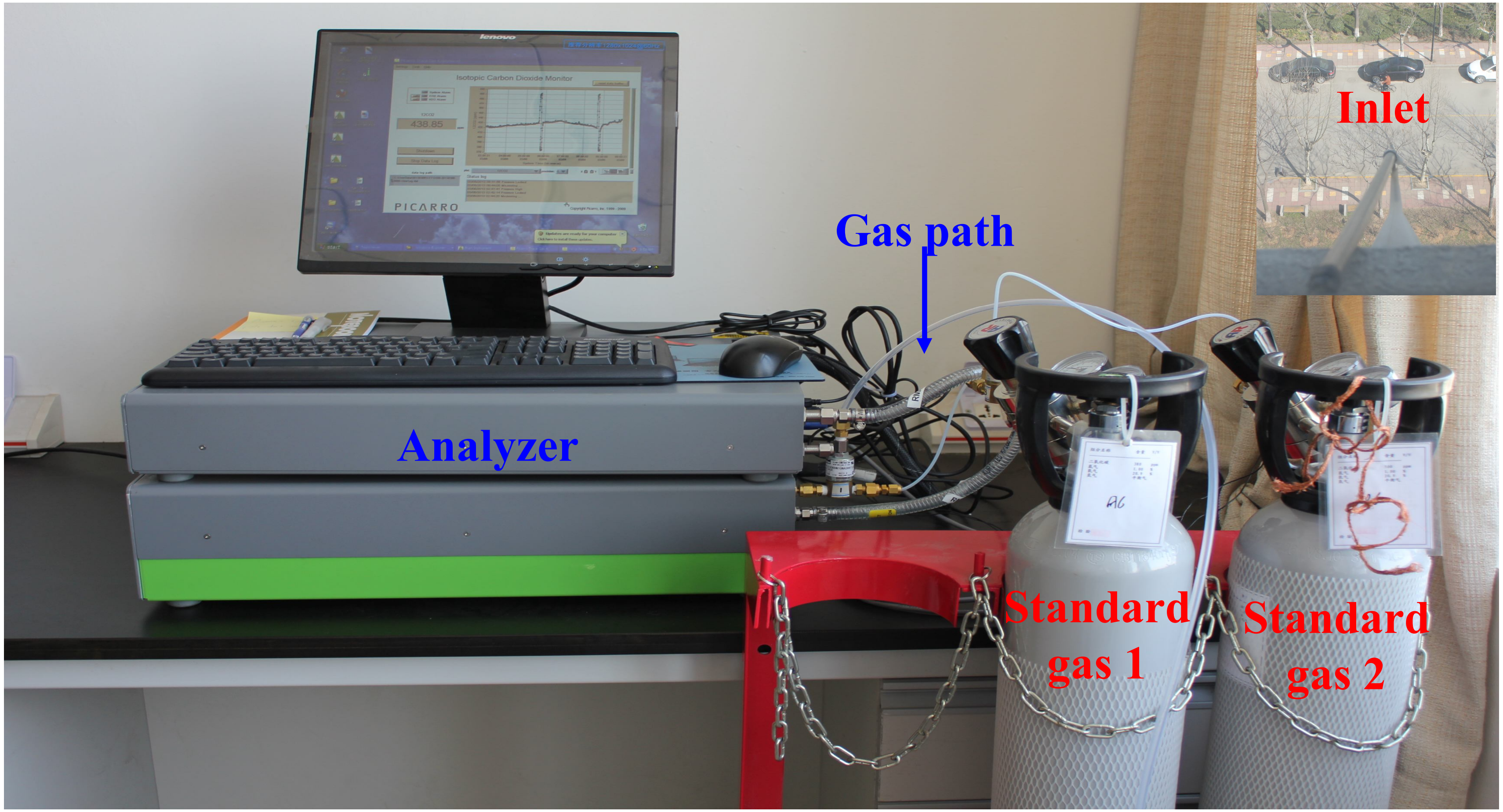


Fig. 1. $^{13}CO_2$ analyzer (Picarro G1101-i) and calibration system in Nanjing.

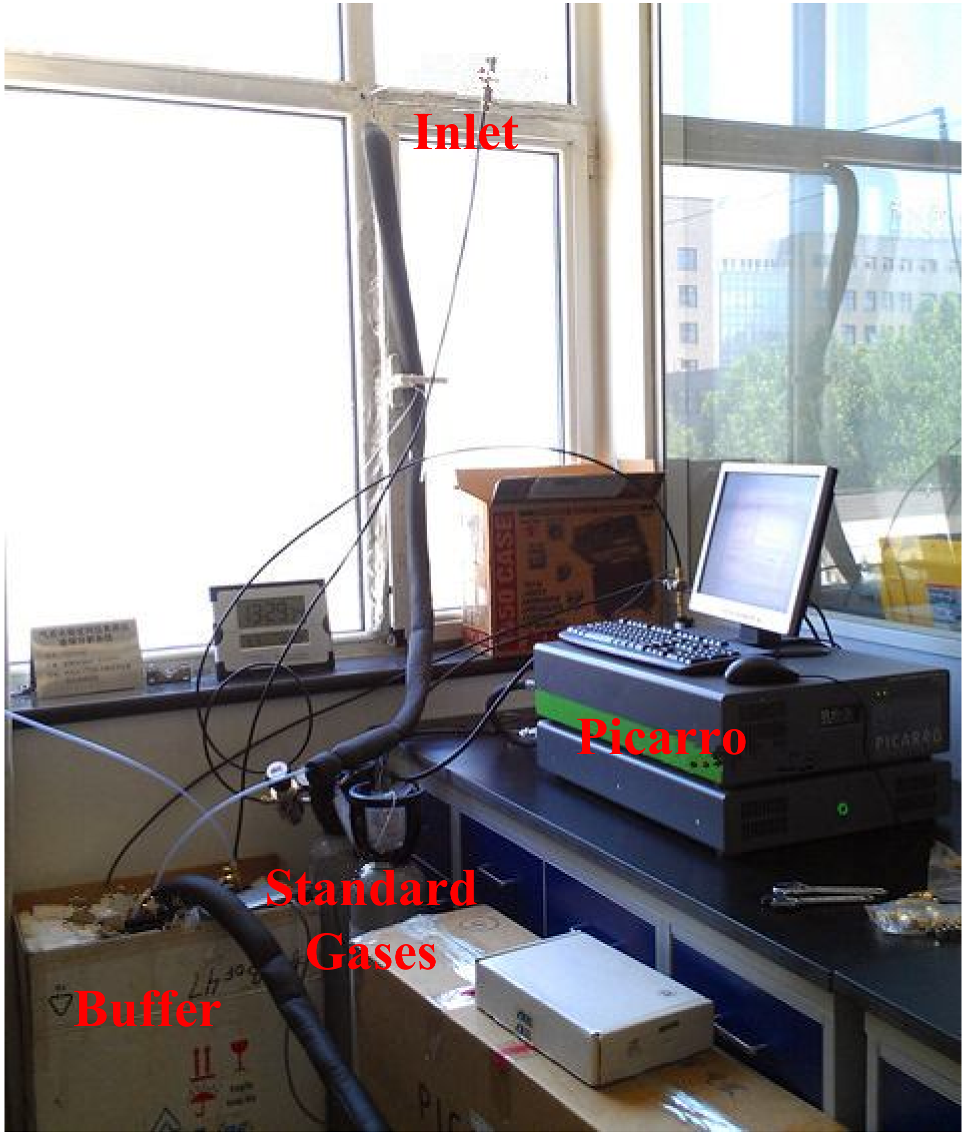


Fig. 2. $^{13}CO_2$ analyzer (Picarro G1101-i) and calibration system in Beijing.

Table 1. Dataset of Picarro.

Sites	Period of time
Beijing*	Nov.14,2012~Jun.30,2013
Nanjing	Feb.26,2013~Aug.26,2013

* Including meteorological data.

Table 2. Cycling of measurement.

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

Table 3. Information of standard gases.

Sites	Gases	CO_2 concentration (ppm)	$\delta^{13}C$* (‰)
Nanjing	Standard gas 1	380	-29.75± 0.27
	Standard gas 2	500	-30.01 ± 0.18
Beijing	Standard gas 1	379	-29.95
	Standard gas 2	499	-29.36

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

3.2 The method for correcting H_2O effect

$$\mathrm{RealH_2O} = f_{correction} * \mathrm{H_2O} \qquad \text{(Eq.1)}$$

$$\mathrm{w} = \mathrm{RealH_2O} / (100 - \mathrm{RealH_2O}) * 100 \qquad \text{(Eq.2)}$$

$$^{12}\mathrm{CO_2\_corrected} = {}^{12}\mathrm{CO_2\_wet} / (1 - \mathrm{w}/100) \qquad \text{(Eq.3)}$$

- **H_2O** means H_2O(V%) measured by analyzer.
- ***$f_{correction}$*** is the coefficient for correcting H_2O. 1.1875 for Beijing and 0.8576 for Nanjing.
- **RealH_2O** stands for the H_2O after correction according to the standard of dew generator.
- **w** means H_2O mixing ratio.
- **$^{12}CO_2$_wet** means the value of $^{12}CO_2$ with H_2O measured by analyzer.
- **$^{12}CO_2$_corrected** means dry $^{12}CO_2$ after removing H_2O dilution effect.

3.3 The method for calibrating measurement

Step 1

$$[CO_2] = [^{12}CO_2] + [^{13}CO_2] + f[CO_2] \quad \text{(Eq.4)}$$

$$f = 0.00474 \quad \text{(Eq.5)}$$

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

Step 2

$$R_a = [^{13}C]/[^{12}C] = [^{13}CO_2]/[^{12}CO_2] = R_{VPDB}(1+\delta_a/1000) \quad \text{(Eq.6a)}$$

$$R_{VPDB} = 0.0111797 \quad \text{(Eq.6b)}$$

$$[^{12}CO_2] = [CO_2](1-f)/(1+R_{VPDB}(1+\delta_a/1000)) \quad \text{(Eq.6c)}$$

$$[^{13}CO_2] = [CO_2](1-f) - [^{12}CO_2] \quad \text{(Eq.6d)}$$

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

Step 3

$$X_{a,t}^{12} = \frac{X_{2,t}^{12} - X_{1,t}^{12}}{X_{2,m}^{12} - X_{1,m}^{12}} (X_{a,m}^{12} - X_{1,m}^{12}) + X_{1,t}^{12} \quad \text{(Eq.7)}$$

(Bowling et al , 2003)

$$X_{a,t}^{13} = \frac{X_{2,t}^{13} - X_{1,t}^{13}}{X_{2,m}^{13} - X_{1,m}^{13}} (X_{a,m}^{13} - X_{1,m}^{13}) + X_{1,t}^{13} \quad \text{(Eq.8)}$$

$$\delta^{13}C = (R_{sample} / R_{VPDB} - 1) \times 1000‰ \quad \text{(Eq.9)}$$

$$R_{sample} = X_{a,t}^{13} / X_{a,t}^{12} \quad \text{(Eq.10a)}$$

$$R_1 = X_{1,t}^{13} / X_{1,t}^{12} \quad \text{(Eq.10b)}$$

$$R_2 = X_{2,t}^{13} / X_{2,t}^{12} \quad \text{(Eq.10c)}$$

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.

3.4 Data processing

- 1. Remove methane data
- 2. Remove 3 minutes data after switchover (about 44 data)
- 3. Filter outliers
- 4. Correct H_2O mixing ratio according to 3.2
- 5. Calibrate raw data according to 3.3
- 6. Average data in 30 min

4. Preliminary results

- 1. The dilution effect of H_2O mixing ratio
- 2. Temporal variation of CO_2 and its ^{13}C composition
- 3. The relationship between meteorological factors and ^{13}C composition

4.1 The dilution effect of H_2O mixing ratio

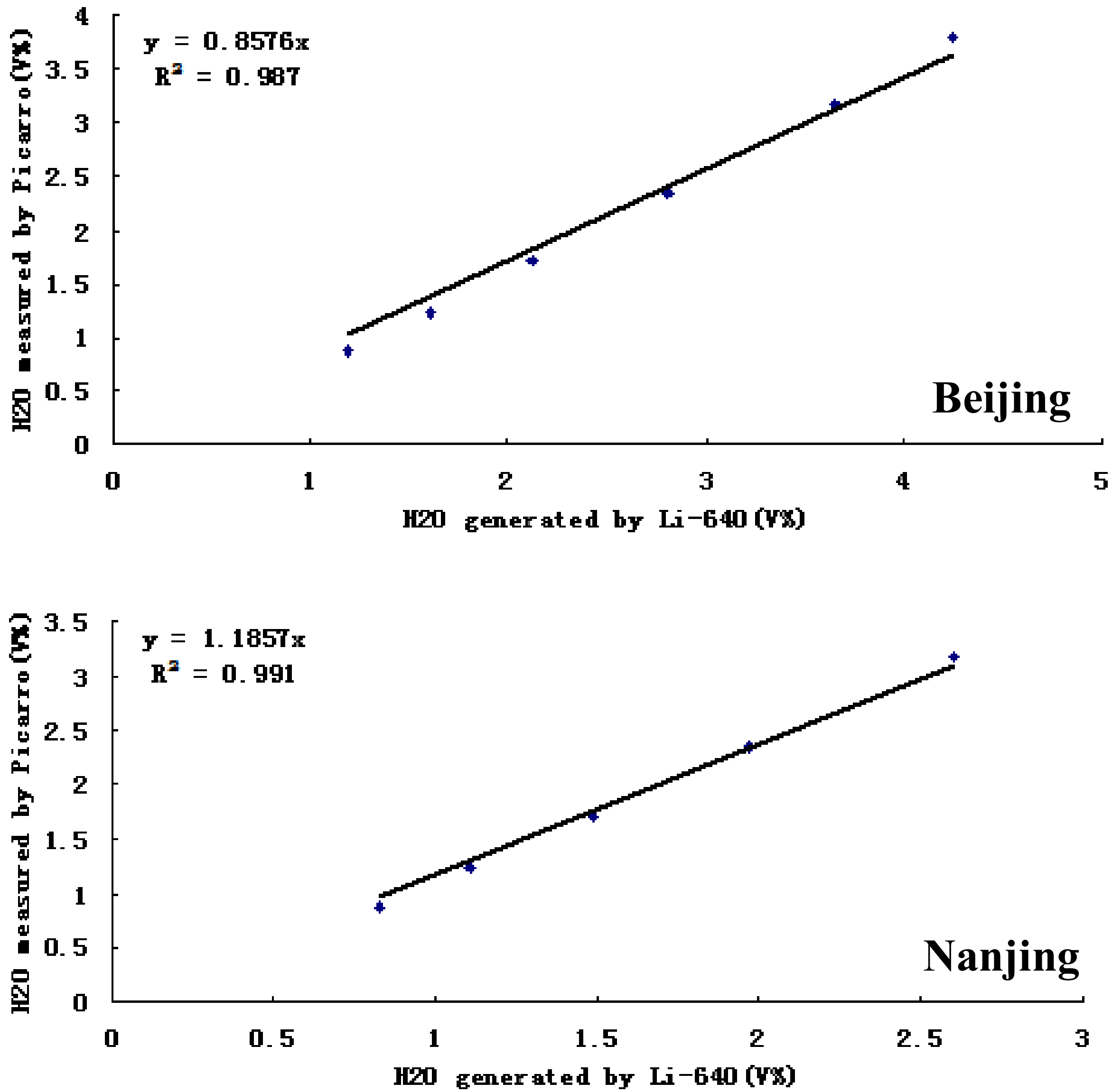


Fig. 3.The relationship between H_2O measured by Picarro and dew generator Li-640.

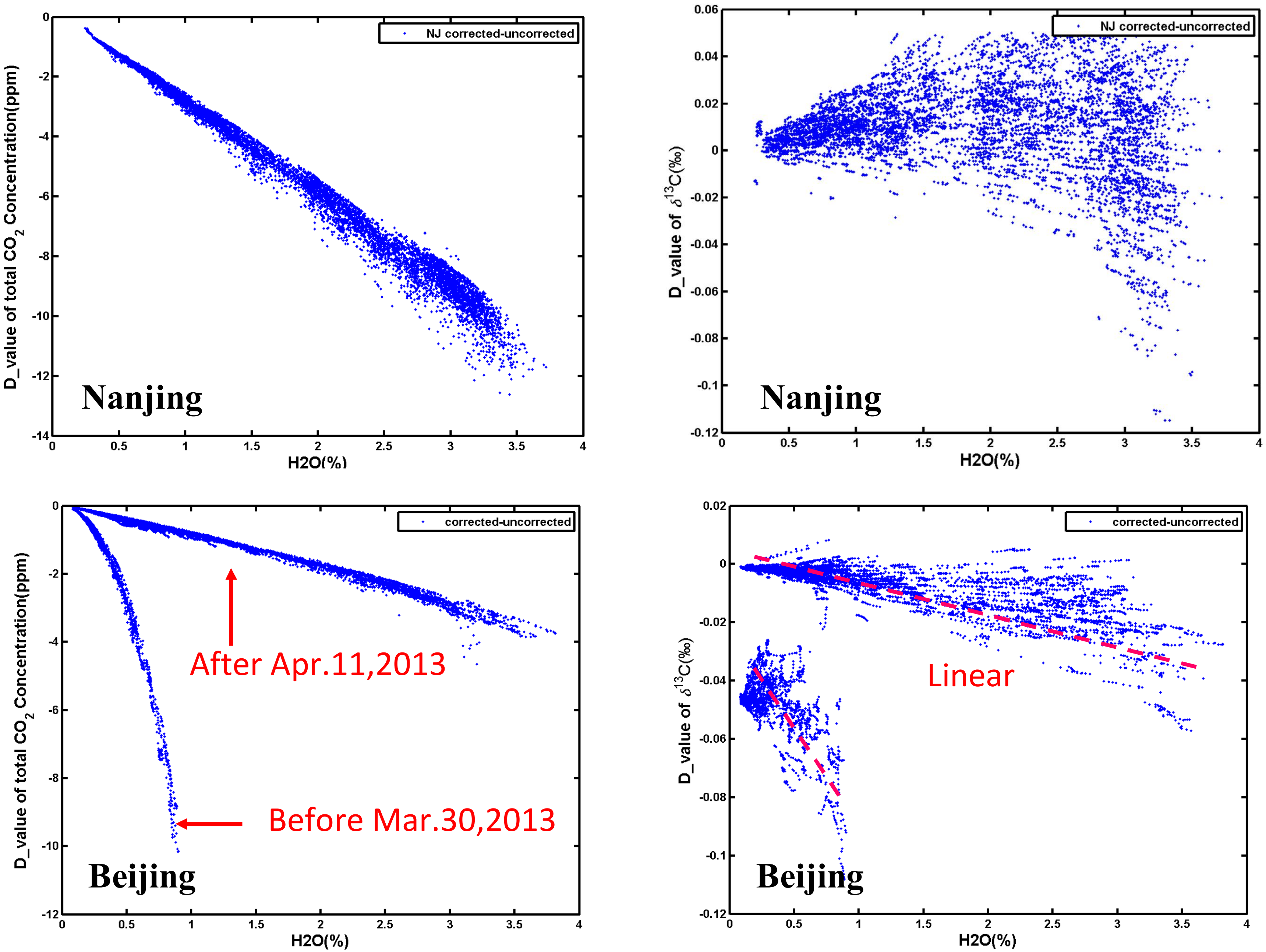


Fig. 4.The dilution effect of H_2O.

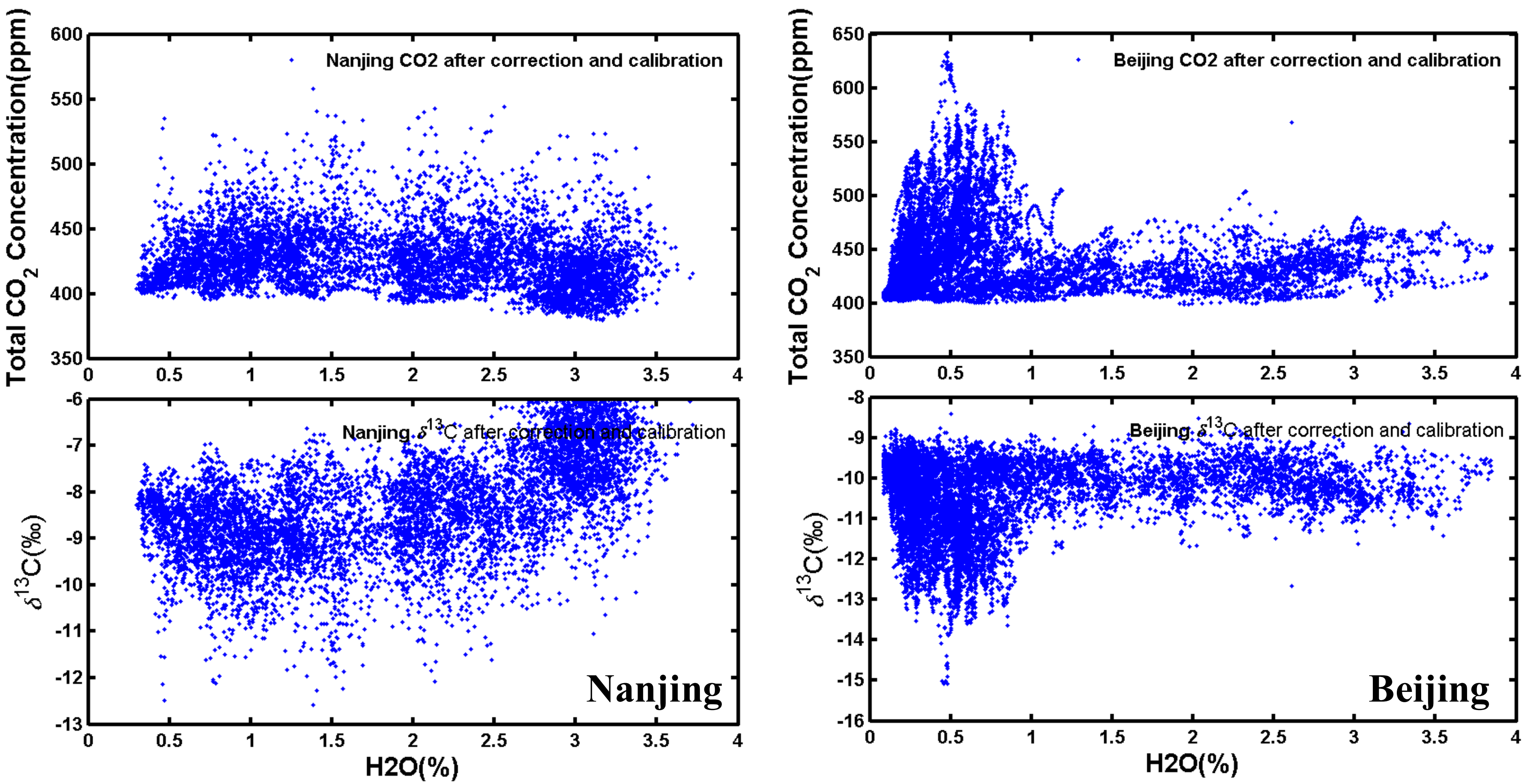
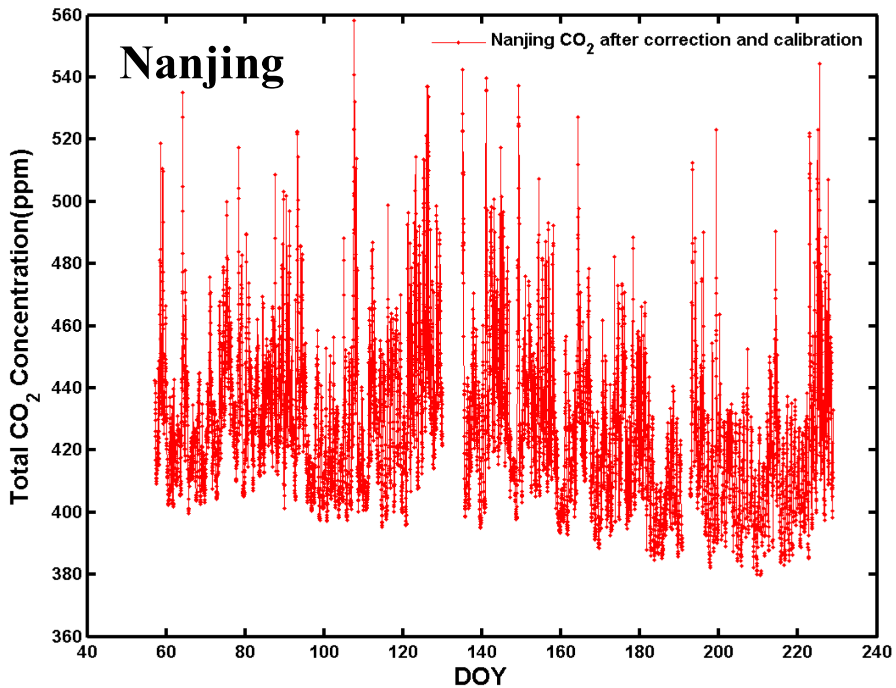


Fig. 5.H_2O(V%) against total CO_2 concentration and ^{13}C composition.

4.2 Temporal variation of CO_2 & its ^{13}C composition

4.2.1 All data in time series



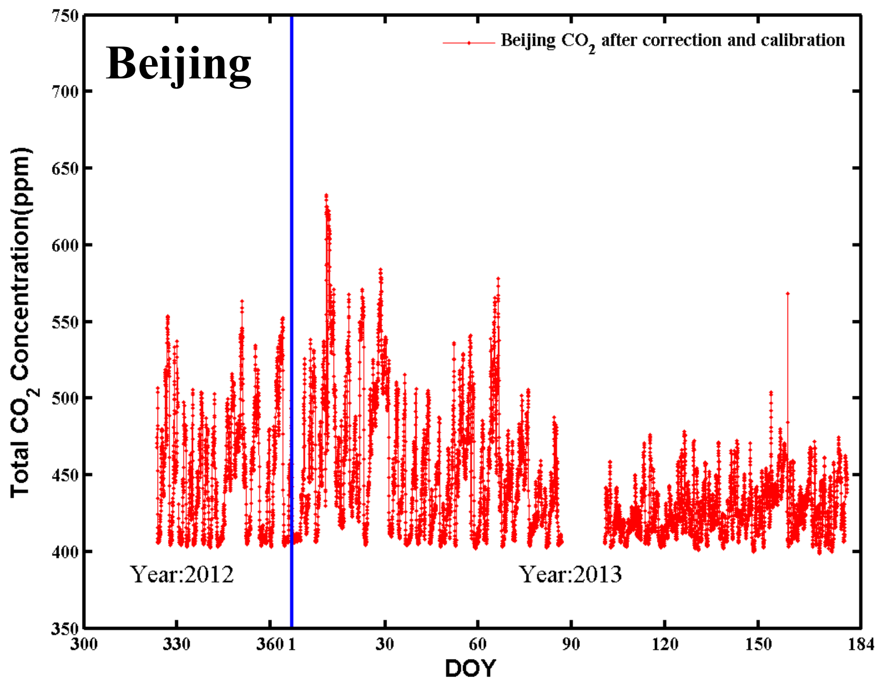


Fig. 6.The time series of total CO_2 concentration in Beijing and Nanjing.

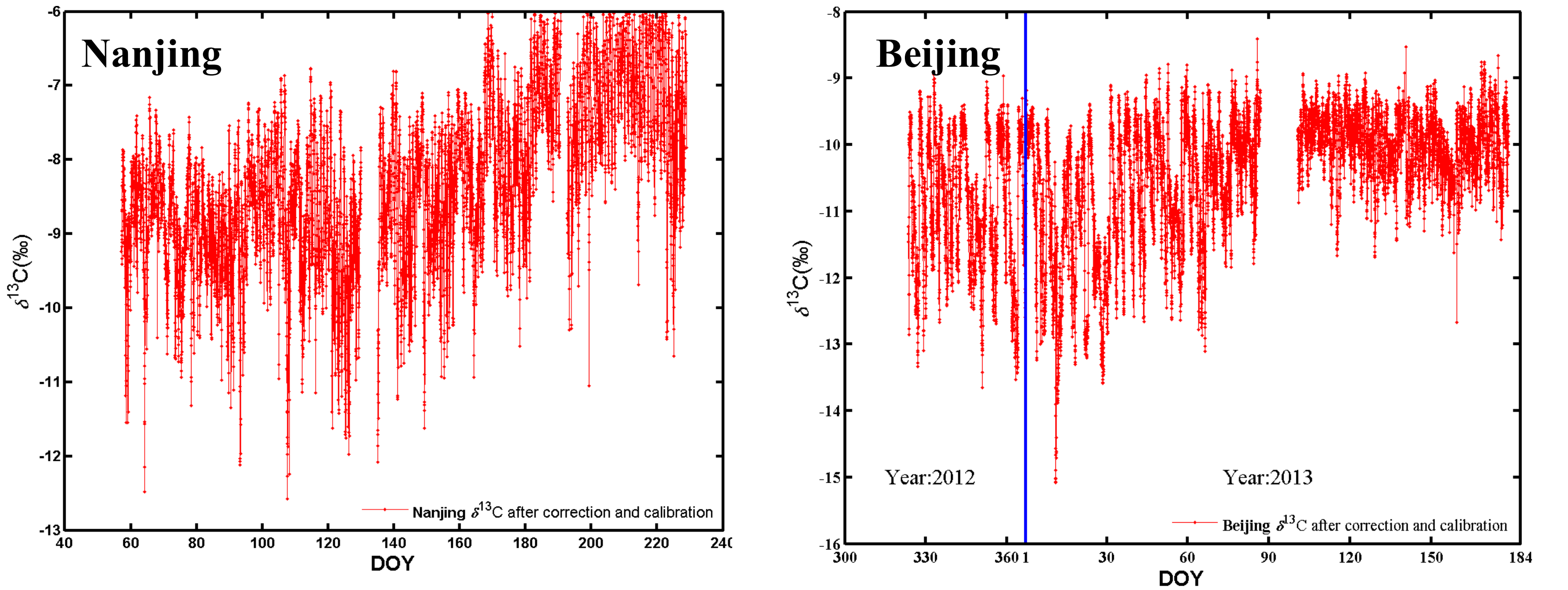


Fig. 7.The time series of $\delta^{13}C$ in Beijing and Nanjing.

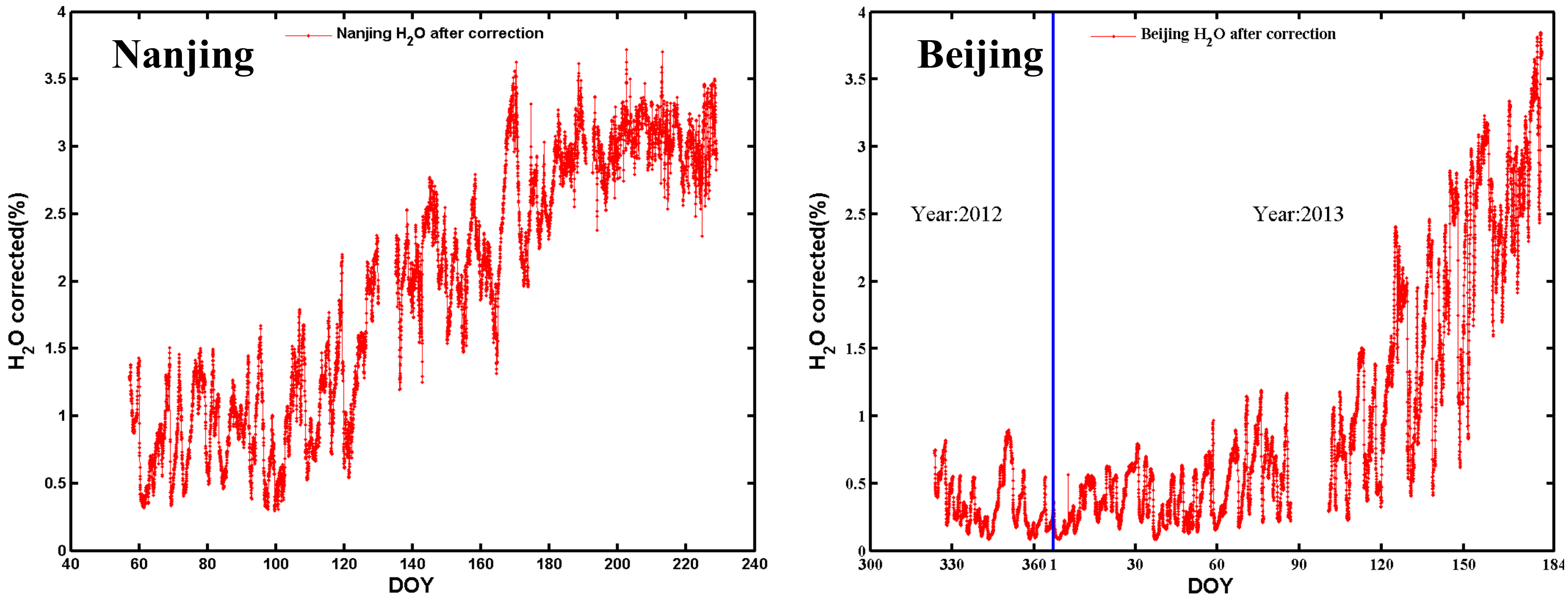


Fig. 8.The time series of H_2O in Beijing and Nanjing.

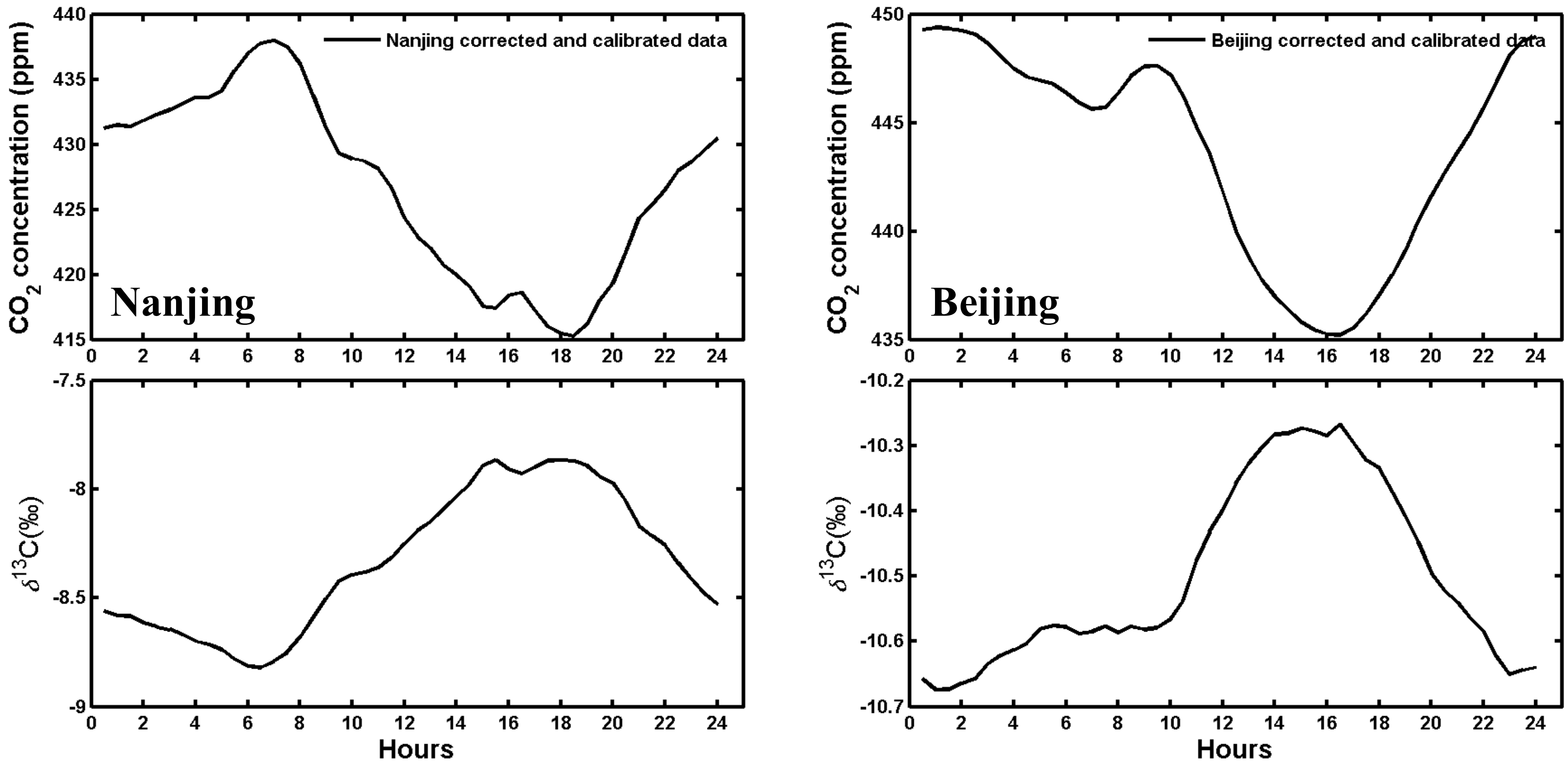


Fig. 9. Diurnal variation of CO_2 and δ 13C in Beijing and Nanjing.

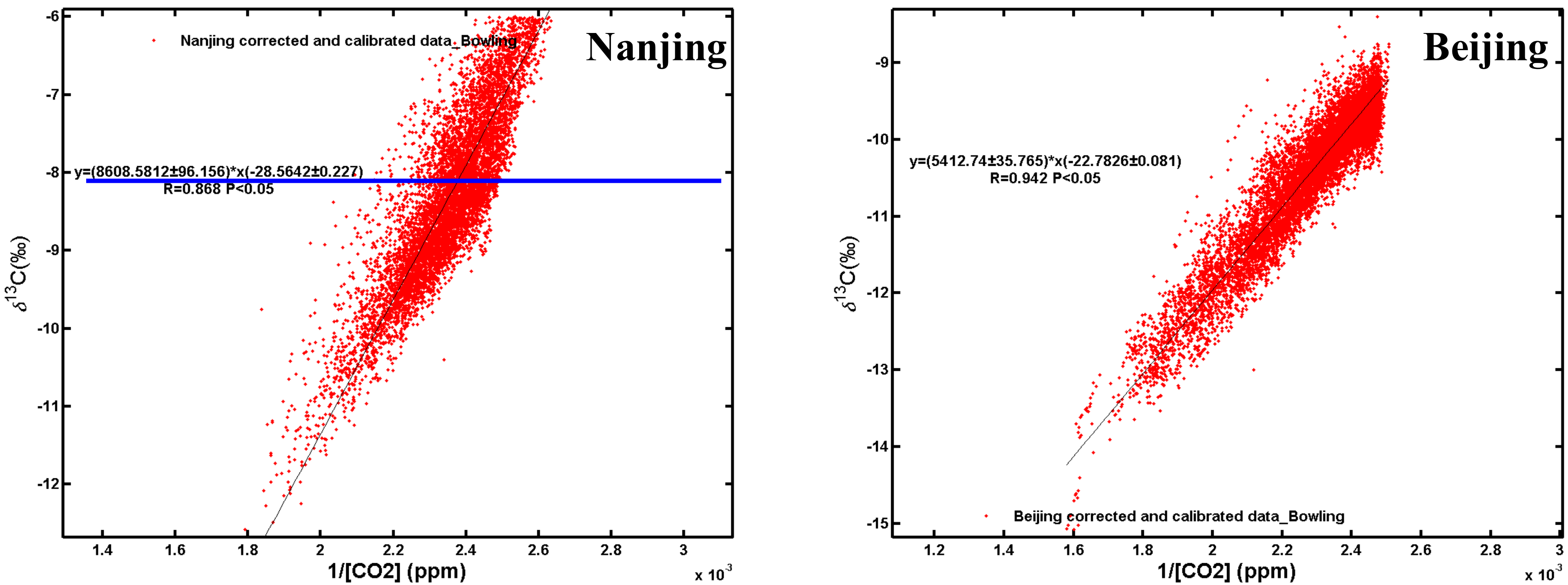


Fig. 9. Keeling plots in Beijing and Nanjing.

4.2.2 Seasonal variation

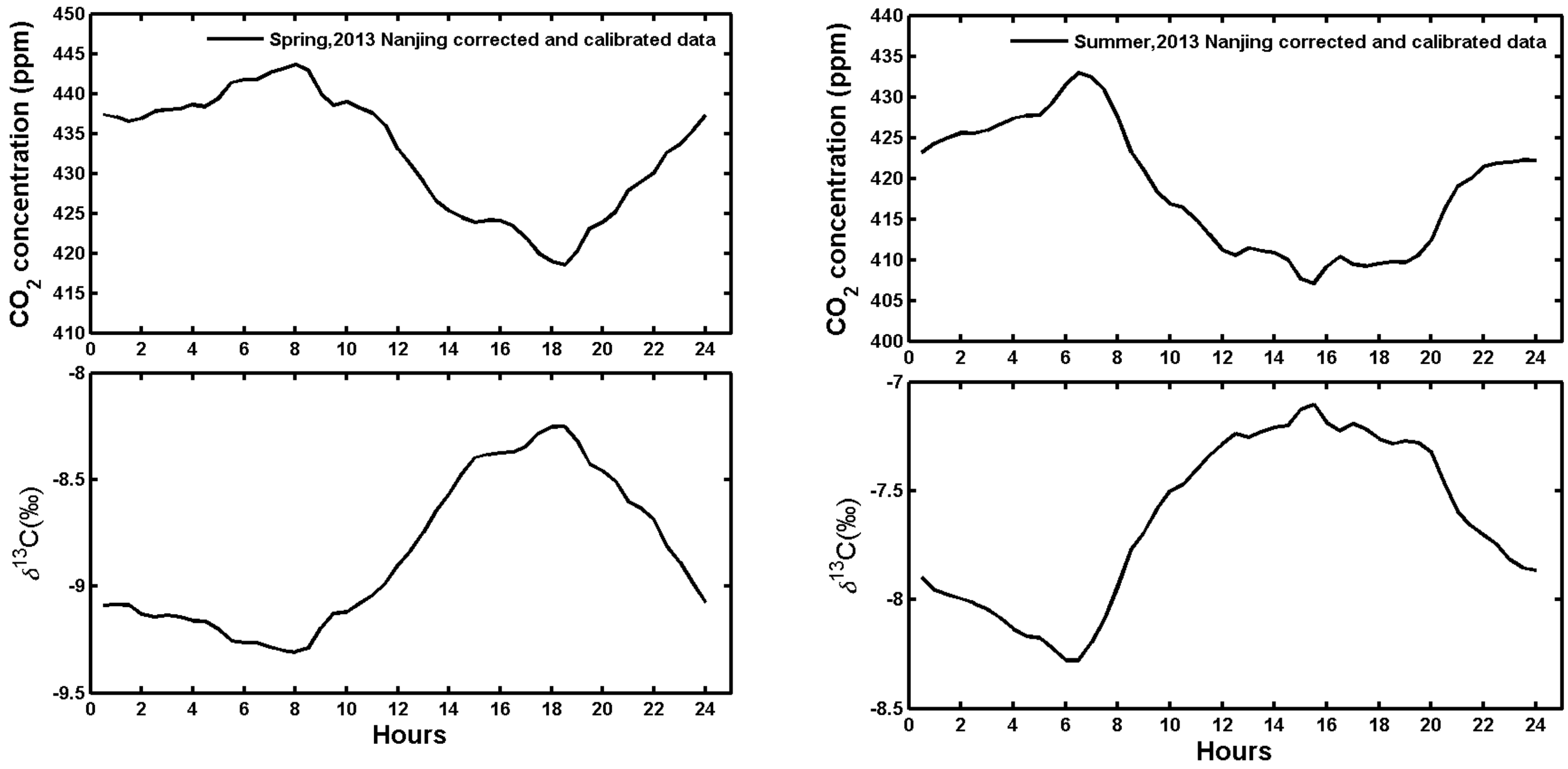


Fig. 10. Seasonal variation of CO_2 and $\delta^{13}C$ in Nanjing.

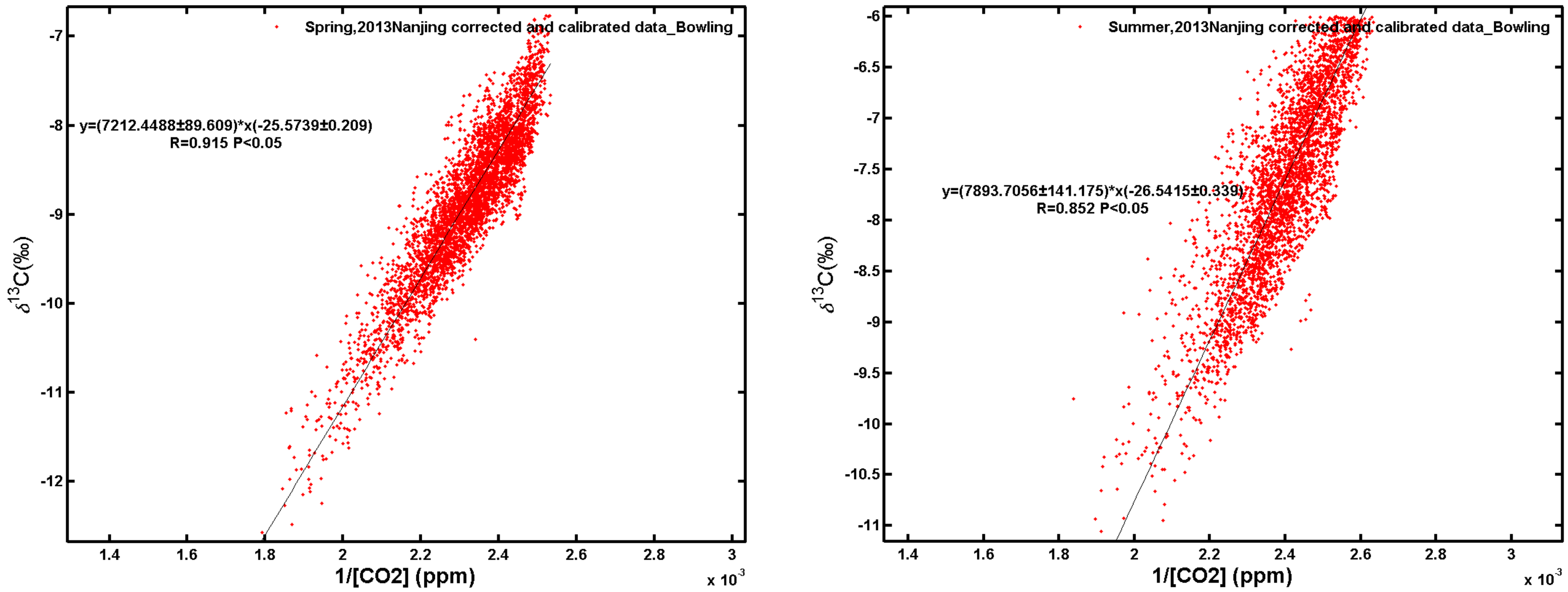


Fig. 11. Seasonal variation of Keeling plots in Nanjing.

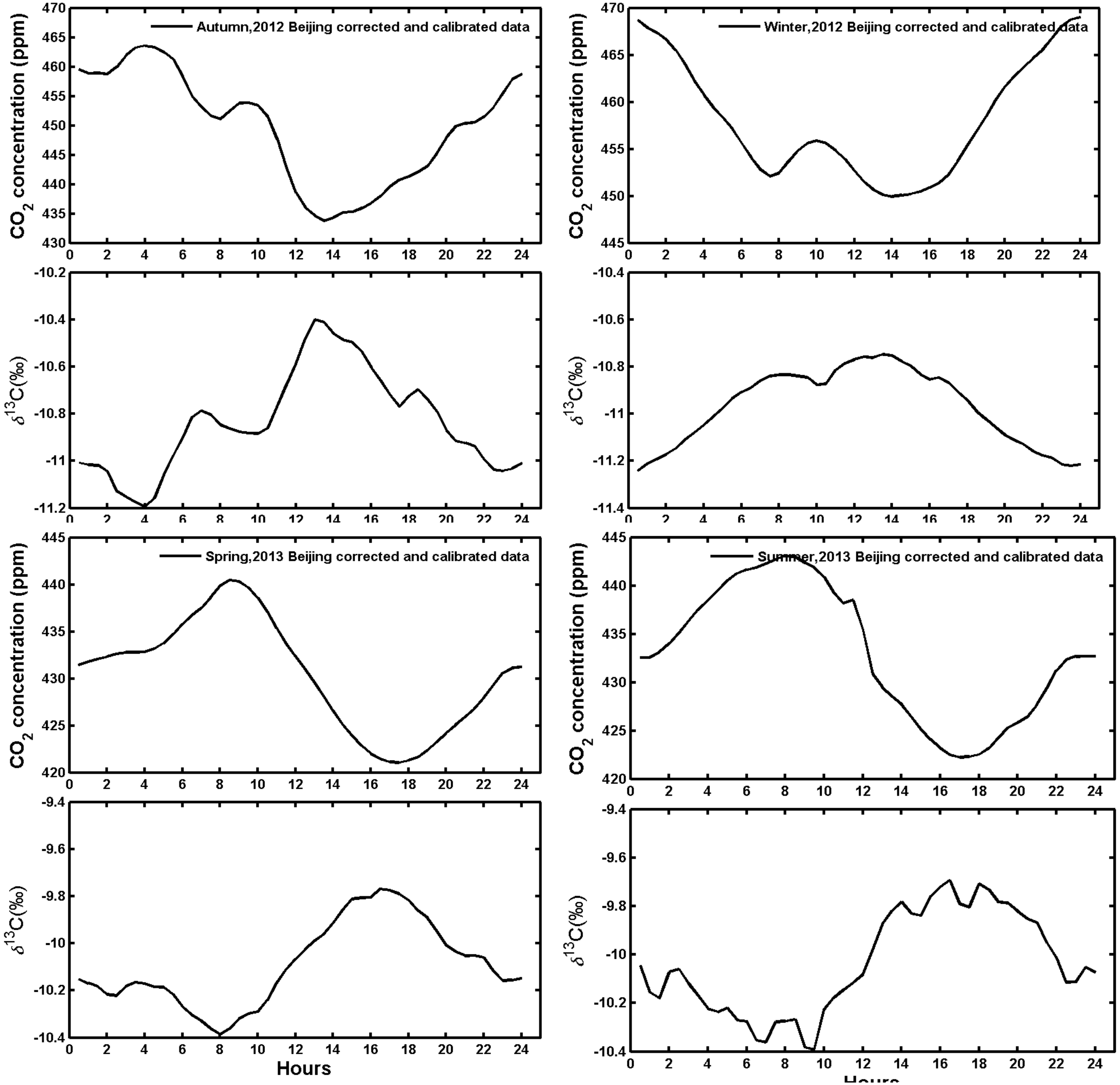


Fig. 12. Seasonal variation of CO_2 and δ 13C in Beijing.

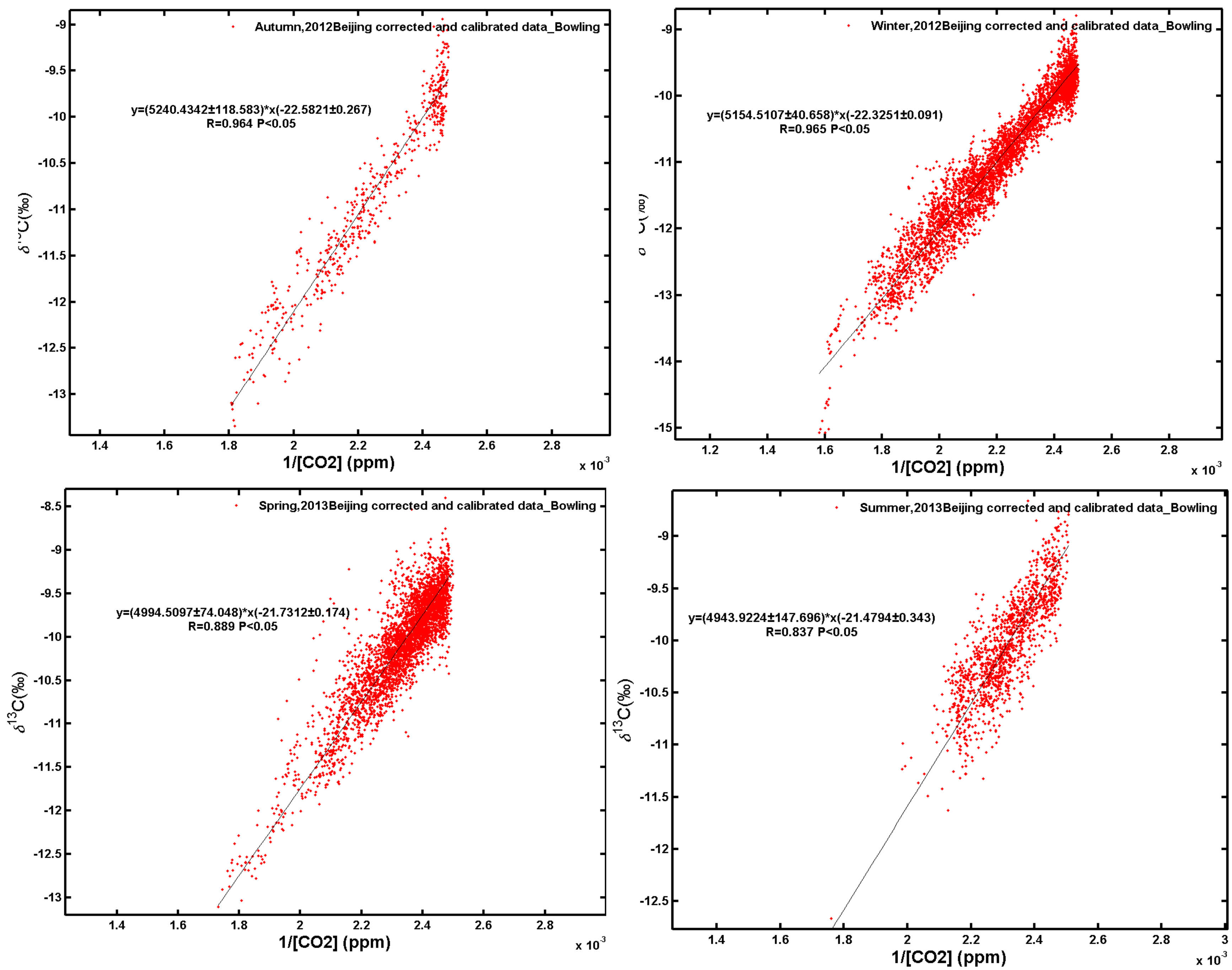


Fig. 13. Seasonal variation of Keeling plots in Beijing.

4.2.3 monthly variation

Table 4. Monthly Keeling plots.

Month	Beijing		Nanjing	
	Intercept of Keeling(‰)	R	Intercept of Keeling(‰)	R
Nov	-22.5638 ±0.255	0.99		
Dec	-22.8036 ±0.14	0.973		
Jan	-22.3356 ±0.132	0.837		
Feb	-22.3356 ±0.212	0.941	-26.0357 ±0.758	0.966
Mar	-21.2855 ±0.234	0.919	-25.65 ±0.352	0.912
Apr	-22.8417 ±0.434	0.855	-26.5785 ±0.358	0.922
May	-22.6419 ±0.426	0.76	-25.6818 ±0.339	0.931
Jun	-21.4794 ±0.343	0.837	0.26.2869 ±0.428	0.89
Jul			-24.6483 ±0.494	0.867
Aug			-22.9957 ±0.517	0.897

4.2.4 Comparison between Beijing and Nanjing

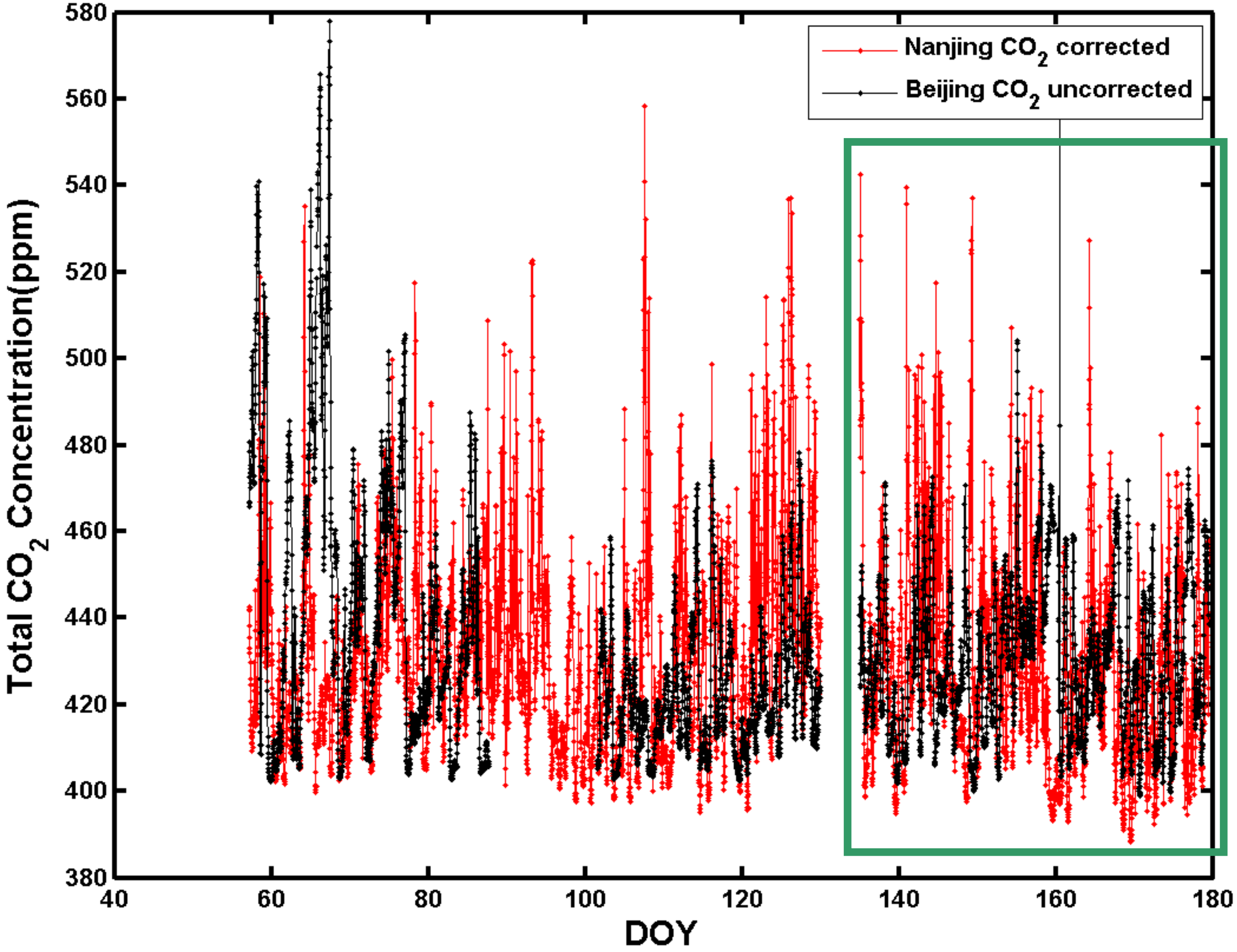


Fig. 14.The time series of total CO_2 concentration in Beijing and Nanjing.

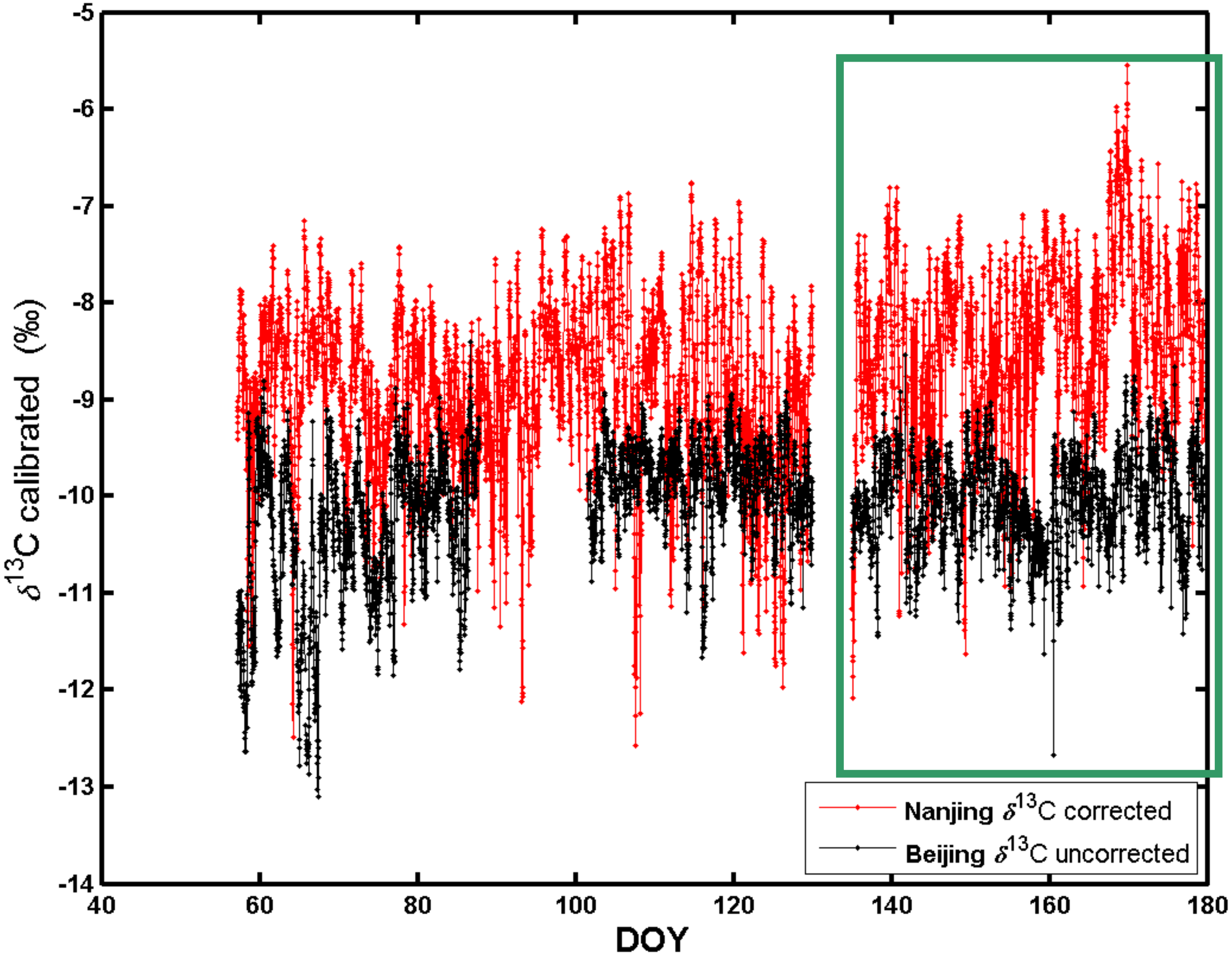


Fig. 15.The time series of δ^{13}C in Beijing and Nanjing.

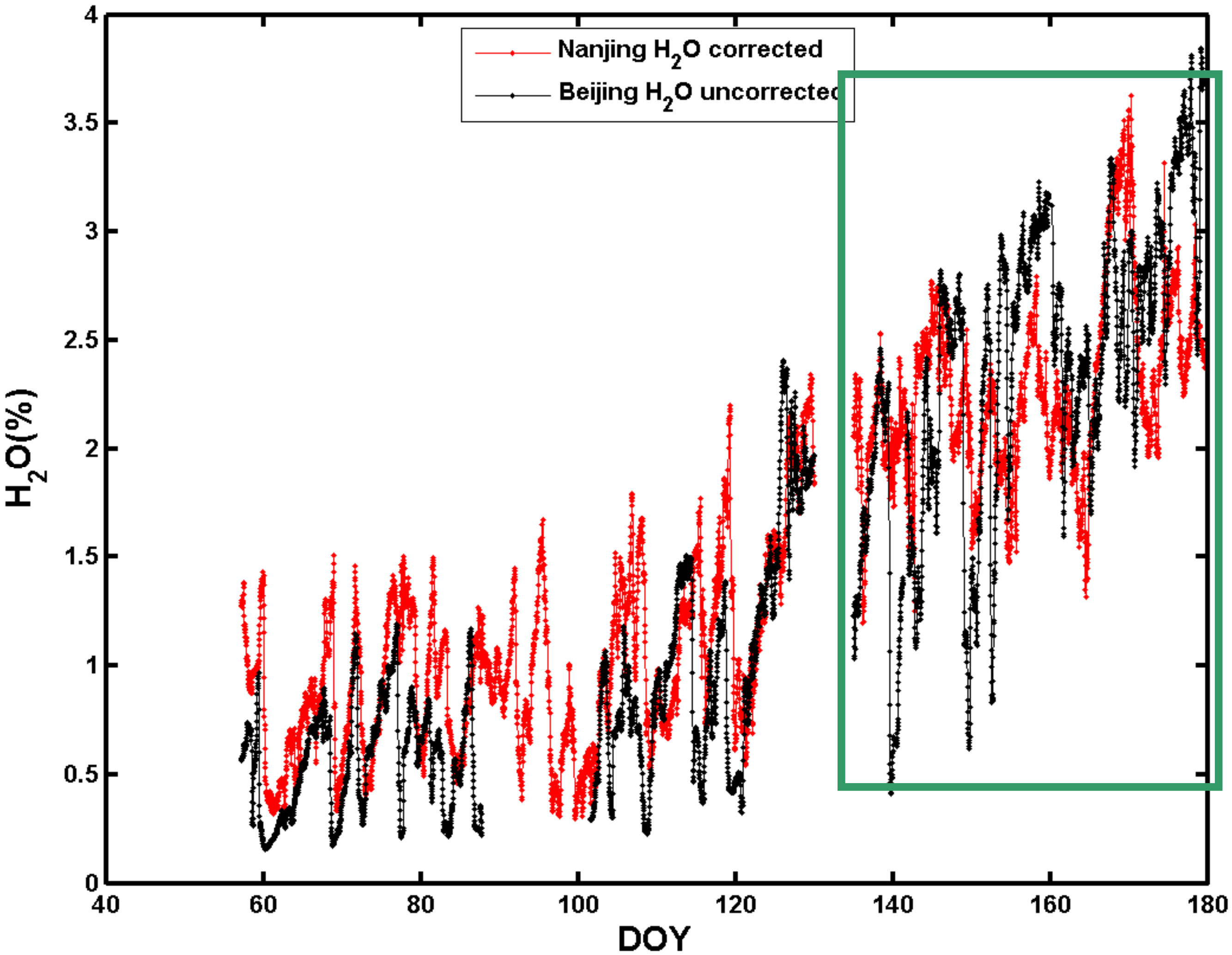


Fig. 16.The time series of H_2O in Beijing and Nanjing.

4.3 The relationship between meteorological factors and ^{13}C composition

4.3.1 Wind

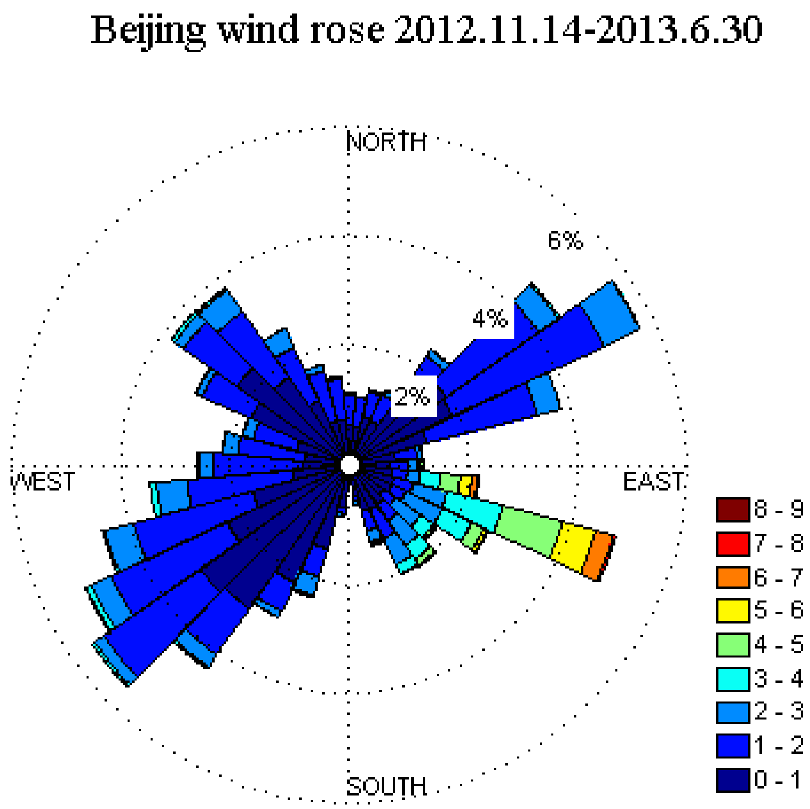


Fig. 17.The wind rose in Beijing.

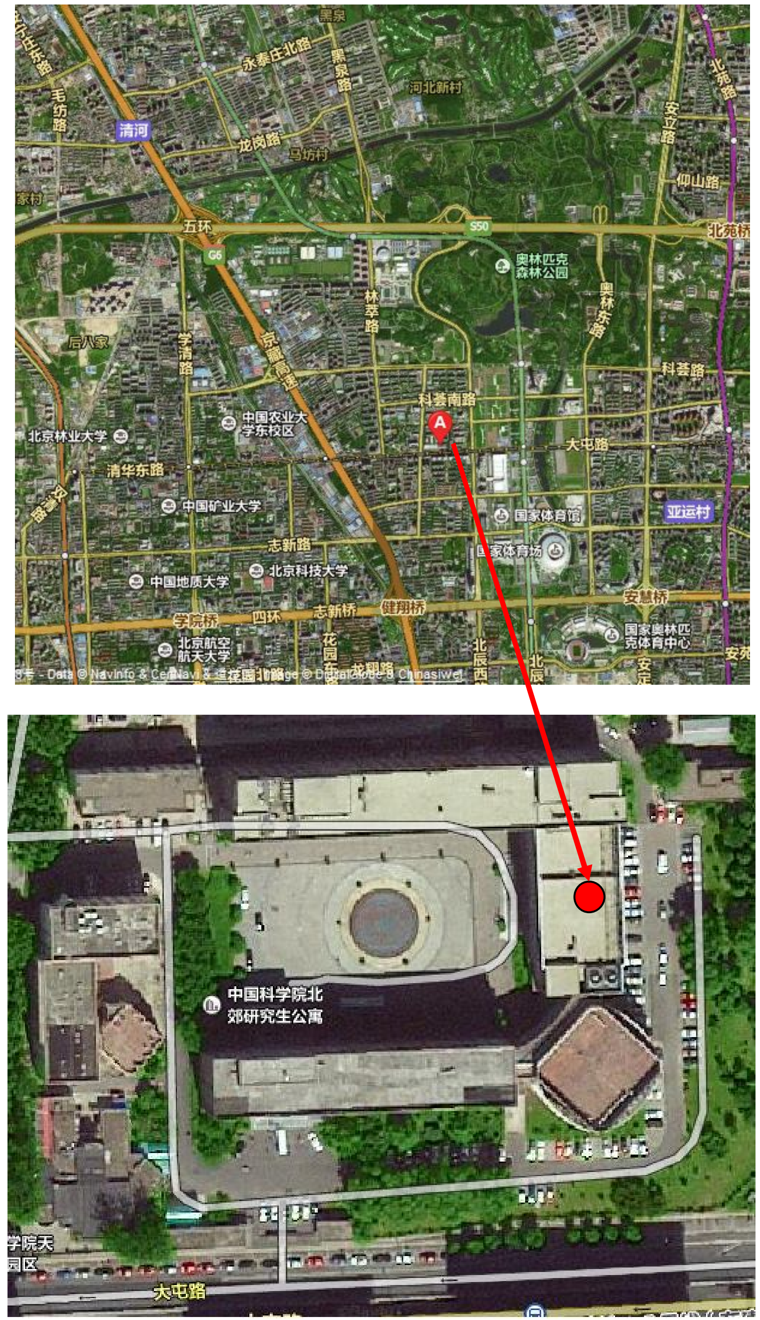


Fig. 18.The map of observation site.

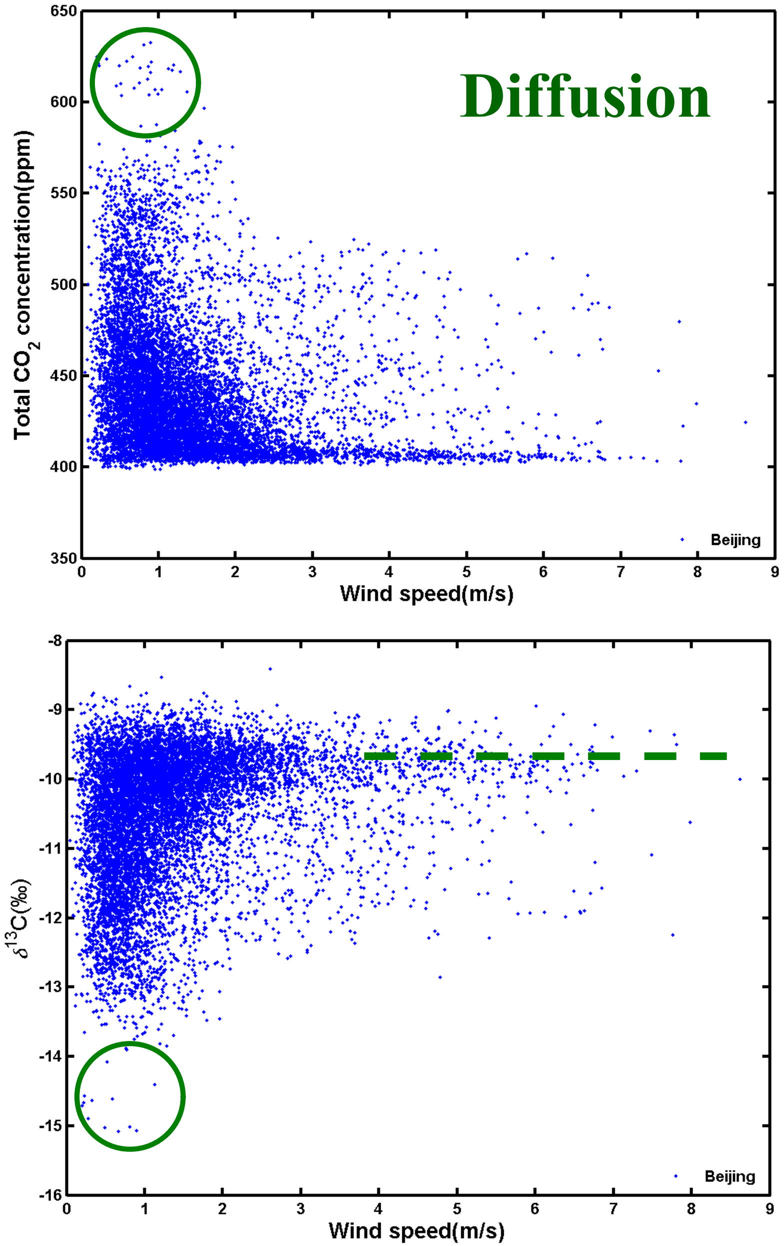


Fig. 19.Wind speed against CO_2 and $\delta^{13}C$.

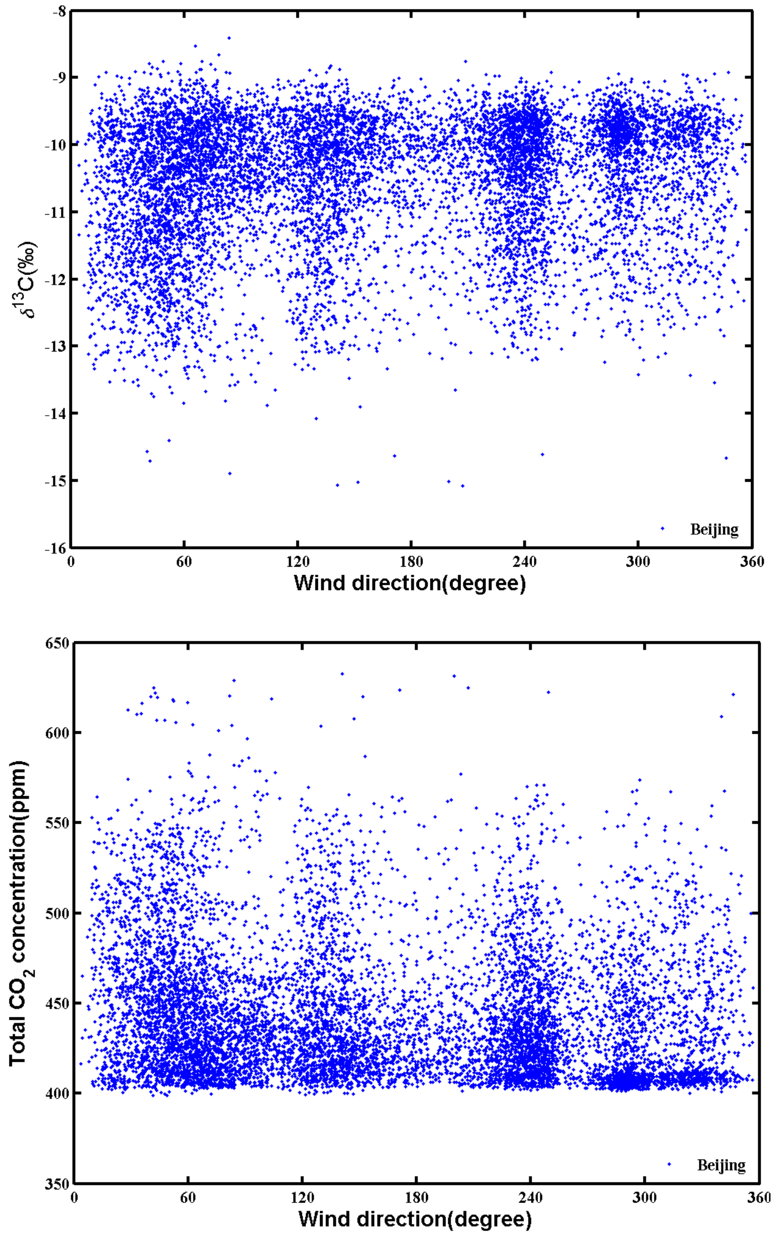


Fig. 20.Wind direction against CO_2 and $\delta^{13}C$.

4.3.2 Air temperature

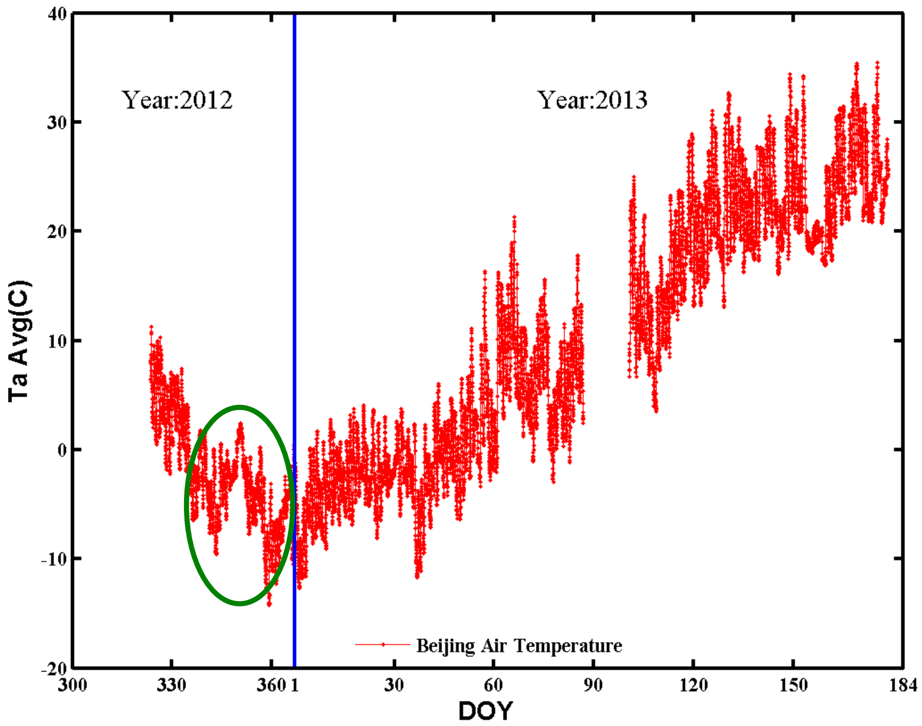


Fig. 21.Time series of air temperature.

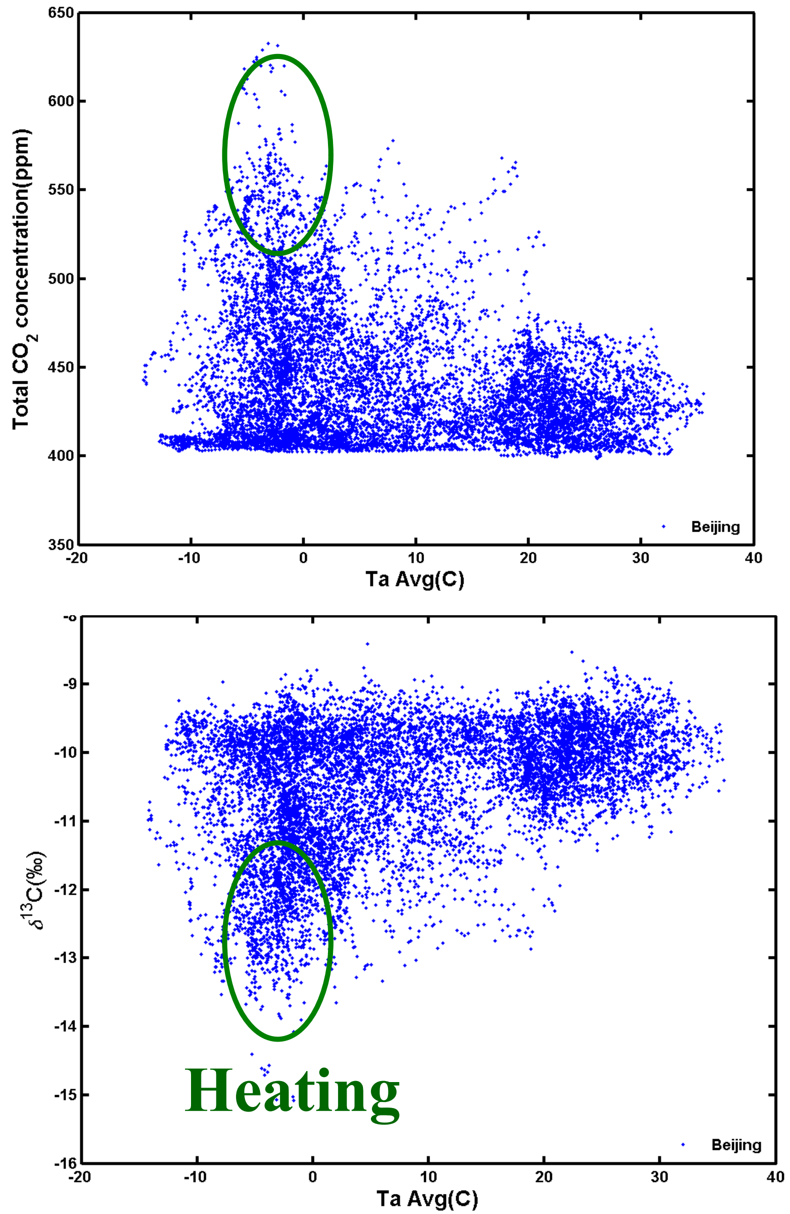


Fig. 22.Air temperature against CO_2 and $\delta^{13}C$.

4.3.3 Precipitation

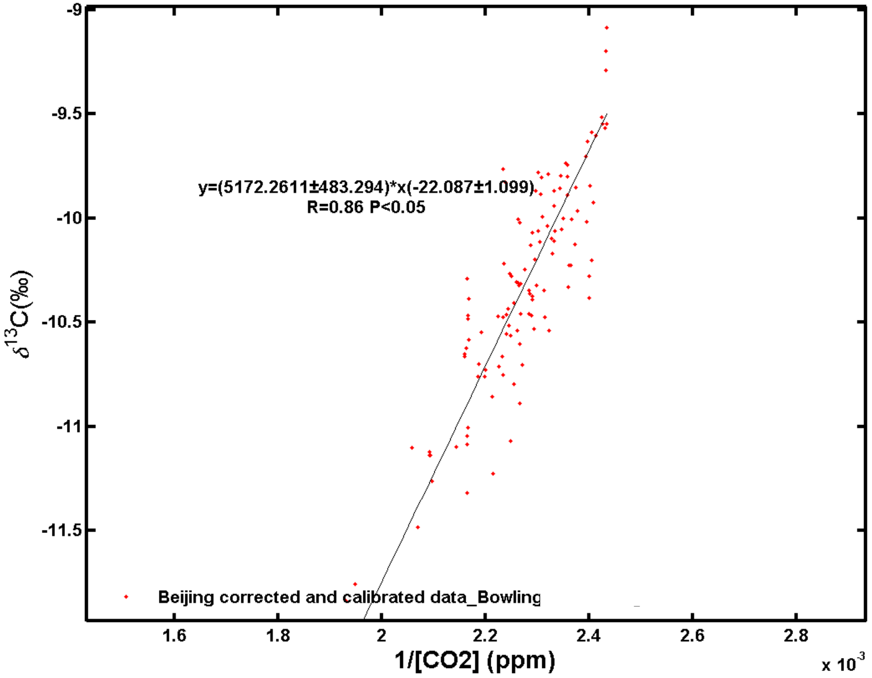


Fig. 23.Keeling plot in raining time.

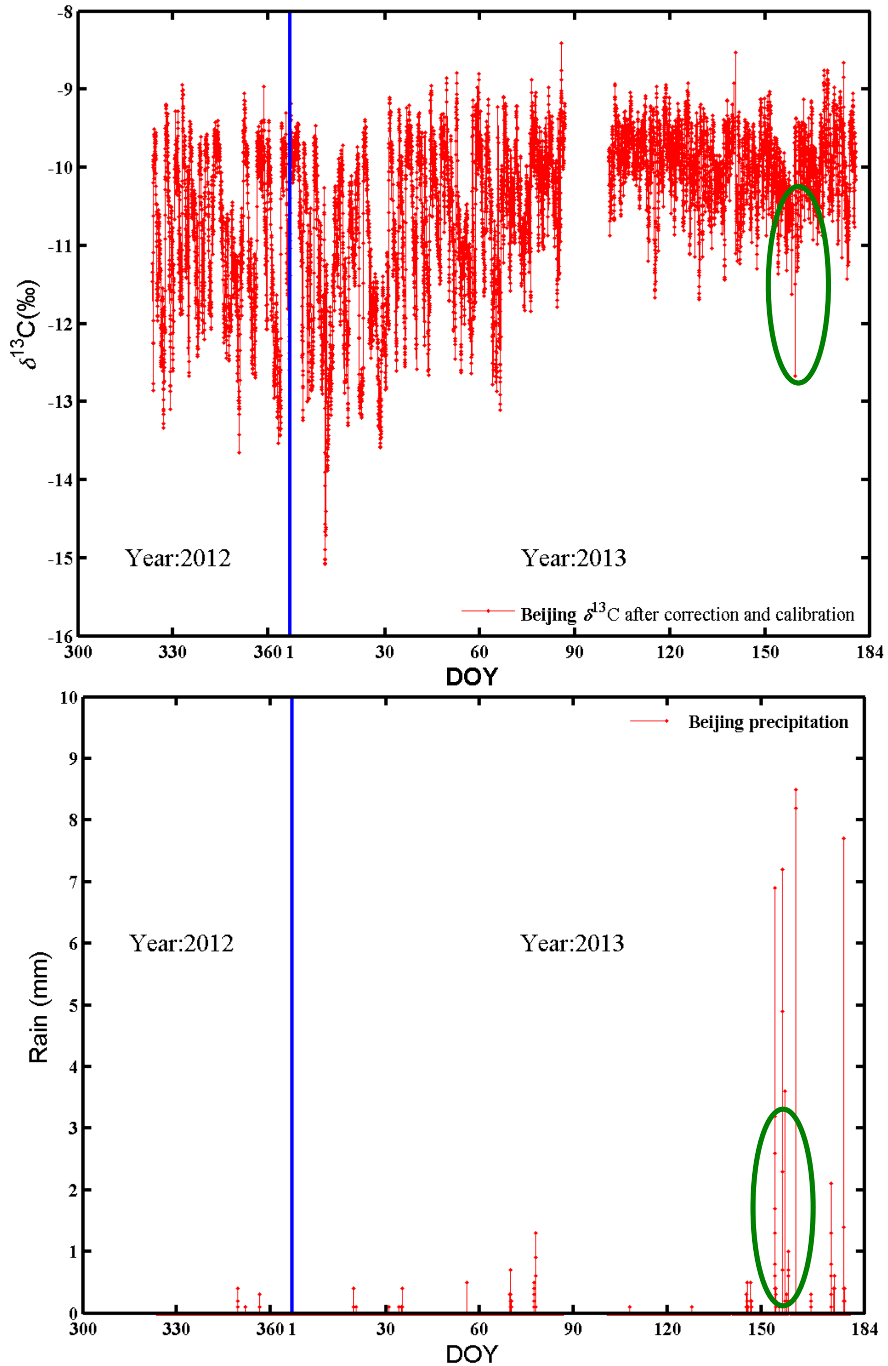


Fig. 24.Time series of $\delta^{13}C$ and rain.

4.3.4 Down Radiation

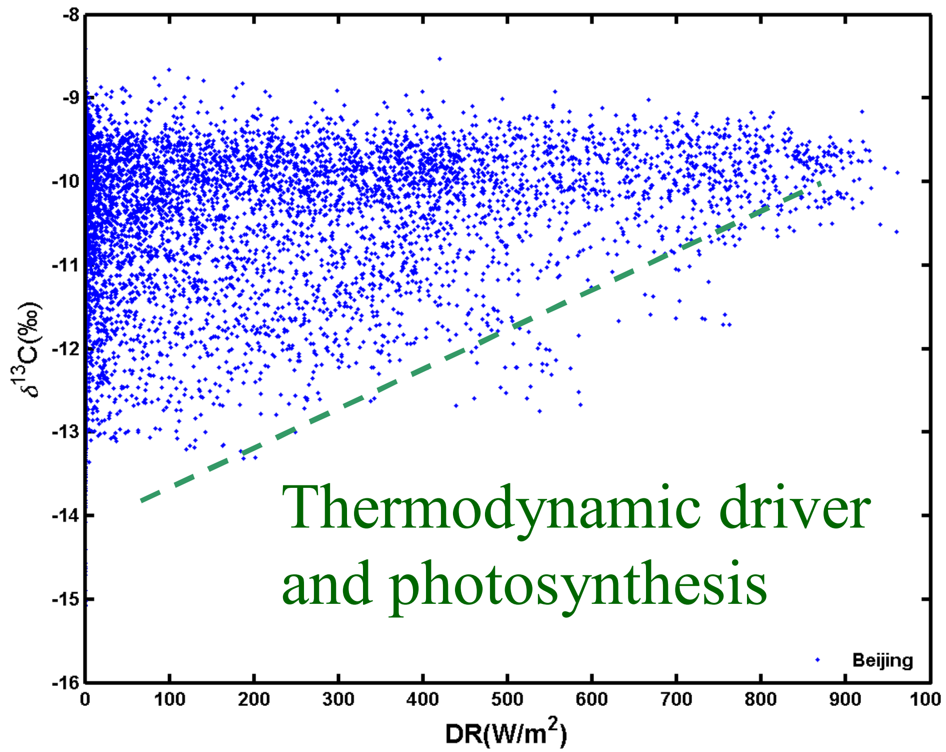


Fig. 25.DR against CO_2.

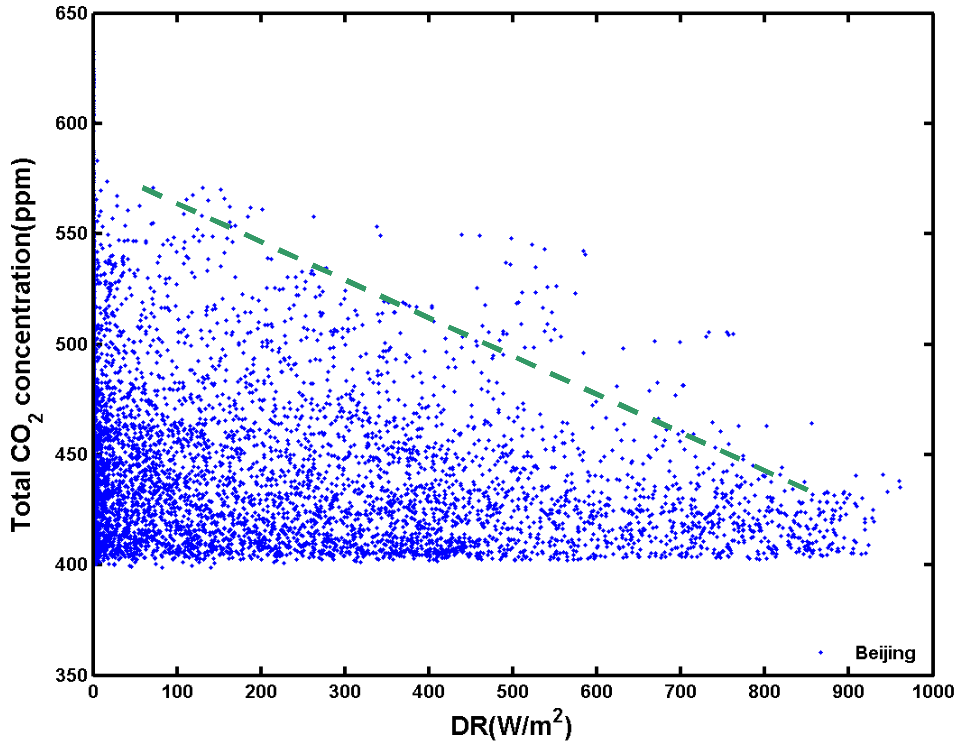


Fig. 26.DR against $\delta^{13}C$.

4.3.5 Relative humidity

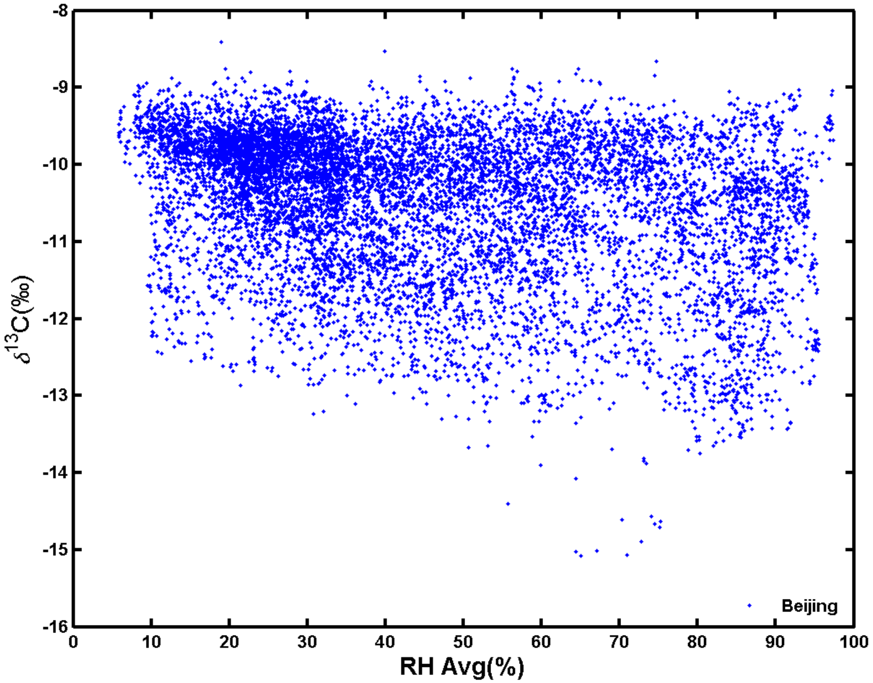


Fig. 27.RH against $\delta^{13}C$.

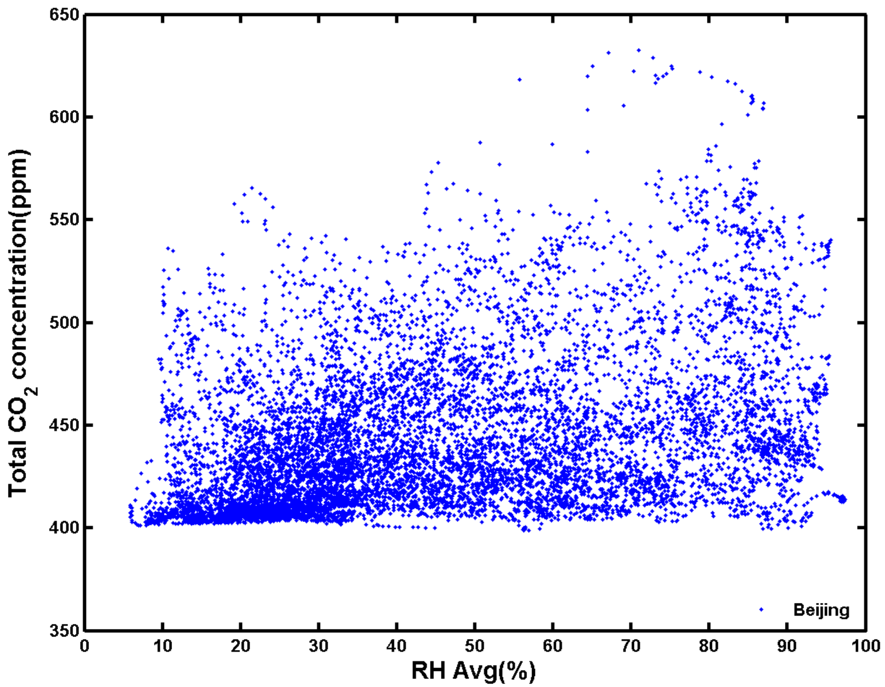


Fig. 28.RH against CO_2.

5. Conclusion

- 1. High H_2O mixing ratio in ambient air deeply influenced the measurement of ^{13}C composition. Therefore the correction of H_2O was needed.
- 2. More negative $\delta^{13}C_S$ (the intercept of Keeling plot) could be found in Nanjing and this maybe due to the huge amount of industrial emission around NIUST site. The obvious seasonal variation of CO_2 and $\delta^{13}C$ in Beijing show the complex natural and anthropogenic effect.
- 3. Thermodynamic factors, such as air temperature and DR, can affect plants' phenology and peoples' behavior and this could further influence CO_2 and its ^{13}C composition in a long time scale.
- 4. The wind fields can determine the sources and the mixing degree of atmospheric CO_2 in a short time scale, which were also affected by surrounding structures.

6. Next work

- 1. To keep the quality of data.
- 2. To analyze the Picarro's data combined with meteorological data in YF site.
- 3. To divide the CO_2 contributors in Beijing and Nanjing in a high frequency.

Thank You!