Mixing ratio and carbon isotopic composition investigation of atmospheric CO₂ in Beijing, China

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HIGHLIGHTS

- Continuous measurement of atmospheric CO₂ and $\delta^{13}\text{C}$ in Beijing.
- $\delta^{13}\text{C}$ depleted in heating season and enriched in vegetative season.
- Diurnal variation of $\delta^{13}\text{C}$ showed two peaks in heating season.
- Coal combustion was the main local CO₂ source.
- $\delta^{13}\text{C}$ showed significant liner relationship with air quality index (AQI).

GRAPHICAL ABSTRACT

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ABSTRACT

The stable isotope composition of atmospheric CO₂ can be used as a tracer in the study of urban carbon cycles, which are affected by anthropogenic and biogenic CO₂ components. Continuous measurements of the mixing ratio and $\delta^{13}\text{C}$ of atmospheric CO₂ were conducted in Beijing from Nov. 15, 2012 to Mar. 8, 2014 including two heating seasons and a vegetative season. Both $\delta^{13}\text{C}$ and the isotopic composition of source CO₂ ($\delta^{13}\text{C}_s$) were depleted in the heating seasons and enriched in the vegetative season. The diurnal variations in the CO₂ mixing ratio and $\delta^{13}\text{C}$ contained two peaks in the heating season, which are due to the effects of morning rush hour traffic. Seasonal and diurnal patterns of the CO₂ mixing ratio and $\delta^{13}\text{C}$ were affected by anthropogenic emissions and biogenic activity. Assuming that the primary CO₂ sources at night (22:00–04:00) were coal and natural gas combustion during heating seasons I and II, an isotopic mass balance analysis indicated that coal combustion had average contributions of $83.83 \pm 14.11\%$ and $86.84 \pm 12.27\%$ and that natural gas had average contributions of $16.17 \pm 14.11\%$ and $13.16 \pm 12.27\%$, respectively. The $\delta^{13}\text{C}$ of background CO₂ in air was the main error source in the isotopic mass balance model. Both the mixing ratio and $\delta^{13}\text{C}$ of atmospheric CO₂ had significant linear relationships with the air quality index (AQI) and can be used to indicate local air pollution conditions. Energy structure optimization, for example, reducing coal consumption, will improve the local air conditions in Beijing.

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1. Introduction

Stable carbon and oxygen isotopic compositions of atmospheric CO₂ can be used as tracers in the study of urban carbon cycles, which are affected by anthropogenic and biogenic CO₂ components. Plant photosynthesis, respiration and fossil fuel combustion (gasoline, coal and natural gas) lead to distinct isotopic signals in atmospheric CO₂, which can be used to identify and quantify the carbon sources and sinks and isotopic characteristics on various temporal and spatial scales (Gorka and Lewicka-Szczebak, 2013; Wada et al., 2011; Pataki et al., 2006; Sturm et al., 2006; Pataki et al., 2003a; Takahashi et al., 2002). High-resolution and long-term monitoring of atmospheric CO₂ mixing ratios and isotopic compositions can provide information about urban CO₂ sources and quantify the effects of plant photosynthesis, respiration and fossil fuel combustion on atmospheric CO₂ over various temporal scales from days to years (Wada et al., 2011; Pataki et al., 2006). These data can be used in high-resolution transport models, regional-scale ecosystem models and regional-scale flux inversions to improve our understanding of carbon cycle processes in urban ecosystems (Sturm et al., 2013) and also shed light on the effects of vegetation, soil and anthropogenic emissions on urban carbon cycles.

The development of isotope ratio infrared spectroscopy (IRIS) allows in situ, high frequency isotope measurements under ambient conditions (Griffis, 2013; Tanaka et al., 2013; Wen et al., 2013; McManus et al., 2010). This technology overcomes the limitations of traditional isotope ratio mass spectrometers (IRMS), which requires flask air sample collection and preparation and is relatively expensive (Bowling et al., 2003). High-temporal-resolution datasets give new insights into the spatial and temporal characteristics and underlying mechanisms of carbon cycle processes in urban ecosystems. To date, approximately 11 urban site studies have monitored atmospheric CO₂ and its isotopic composition for at least 1 month. A total of 8 of these sites used traditional IRMS methods, and the observed frequency ranged from 1 day to 2 month intervals. Sturm et al. (2006) used a semi-continuous method with an on-line CO₂ trap system coupled to an IRMS analyzer that could be sampled every 12 min, but it could only make measurements when the analyzer had no other measurements running. Measurements of $\delta^{13}\text{C}$ only have been performed at 4 sites: Dallas, Texas, USA (Clark-Thorne and Yapp, 2003); Paris, France (Lopez et al., 2013; Widory and Javoy, 2003); Bangalore City, Karnataka State, India (Guha and Ghosh, 2010); and Wrocław, Poland (Gorka and Lewicka-Szczebak, 2013). Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ observations have been conducted at another 4 sites: Kraków, Poland (Zimnoch et al., 2012; Zimnoch et al., 2004); Bern, Switzerland (Sturm et al., 2006); and Los Angeles Basin, California, USA (Djuricin et al., 2010; Newman et al., 2008). Only 3 urban sites have had long-term continuous observations of the mixing ratio and isotopic composition by IRIS technology. Measurements of $\delta^{13}\text{C}$ only was monitored in Salt Lake City, USA (Pataki et al., 2006), and both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ observations were conducted in Nagoya, Japan (Wada et al., 2011) and Boston, USA (McManus et al., 2010).

Previous studies have shown that the variations in the atmospheric CO₂ and its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are modulated by biological processes and anthropogenic CO₂ emissions and contain distinct features over diurnal and seasonal time scales. The seasonal pattern is mainly affected by the variations in the contribution from biogenic photosynthesis, respiration and fossil fuel combustion (Guha and Ghosh, 2010; Pataki et al., 2007; Sturm et al., 2006). The CO₂ mixing ratios were highest in the winter and lowest in the summer (Pataki et al., 2007; Pataki et al., 2003a), and the values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were depleted in the winter and enriched in the spring and summer (Gorka and Lewicka-Szczebak, 2013; Sturm et al., 2006). The diurnal variabilities in the CO₂ mixing ratio and its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are driven by biogenic photosynthesis and respiration, fossil fuel combustion emissions, and the change in the atmospheric boundary layer (Guha and Ghosh, 2010; Sturm et al., 2006). The CO₂ mixing ratio has shown a diurnal variation with a minimum value in the afternoon and a maximum in the early morning;

the diurnal patterns of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ mirror the CO₂ variation, and the diurnal amplitude of $\delta^{13}\text{C}$ was ~2‰ (Guha and Ghosh, 2010; Sturm et al., 2006). The two peaks in the diurnal cycles of both the CO₂ mixing ratio and $\delta^{13}\text{C}$ were due to rush hour traffic (Lopez et al., 2013). The spatial distribution of the CO₂ mixing ratio showed an urban to rural gradient, with the highest value downtown and the lowest at the rural site (Pataki et al., 2007). Sampling sites near highways have also shown a significant increase in the CO₂ mixing ratio (Gorka and Lewicka-Szczebak, 2013).

The isotopic composition of source CO₂ ($\delta^{13}\text{C}_s$) is an integrated value of various urban CO₂ sources on different temporal and spatial scales. Because the contribution of biogenic photosynthesis, respiration and anthropogenic emissions are different during different times of the year, $\delta^{13}\text{C}_s$ shows a clear seasonal cycle, with depleted values in the winter and enriched values in the summer (Gorka and Lewicka-Szczebak, 2013; Sturm et al., 2006; Pataki et al., 2003a). The short-term $\delta^{13}\text{C}_s$ variability may be affected by air mass advection during different weather conditions and changes in the source CO₂ caused by changes in the wind direction (Wada et al., 2011; Sturm et al., 2006). $\delta^{13}\text{C}_s$ can be used to improve our understanding of potential urban CO₂ sources and underlying mechanisms. Many isotope mixing models based on atmospheric mass conservation have been used to evaluate the contribution of anthropogenic emission (including the combustion of fossil fuels, such as natural gas, gasoline and coal) and biogenic respiration (including plant and soil respiration) components to atmospheric CO₂ (Zimnoch et al., 2012; Djuricin et al., 2010; Pataki et al., 2007; Zimnoch et al., 2004). The development of IRIS technology allows for continuous in situ monitoring of the atmospheric CO₂ mixing ratio, and its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, which can provide additional mechanistic understanding of CO₂ source dynamics over diurnal or even shorter time scales (Wada et al., 2011; Pataki et al., 2006).

Beijing, one of the most crowded cities in the world, is the capital of the People's Republic of China and had more than 20 million inhabitants and more than 5.2 million motor vehicles at the end of 2011 (Liu et al., 2013; Zhai et al., 2013). The air quality in this region dramatically changed because of the emissions of air pollutants coupled with CO₂ from house heating, traffic and industrial activities (Zhao et al., 2012; Chan and Yao, 2008). Studies on the air quality in Beijing have focused on the physicochemical properties and sources of atmospheric pollutants (Gao et al., 2014; Guo et al., 2012; Zhang et al., 2013; Zhao et al., 2013), temporal and spatial distribution characteristics (Zhou et al., 2014; Schleicher et al., 2013; Zhao et al., 2009), and formation and evolution mechanisms (Wang et al., 2014; Liu et al., 2013; Zhao et al., 2013). Some studies have paid attention to the isotopic composition of water vapor and precipitation in Beijing (Wen et al., 2012, 2010, 2008) and the hydrochemical and isotopic characteristics of atmospheric precipitation (Zhai et al., 2013). Only a few studies have monitored both the mixing ratio and isotopic composition of atmospheric CO₂. Wen et al. (2013) reported the results of a short-term (7 days) study on in situ, high temporal resolution measurements of the mixing ratio and $\delta^{13}\text{C}$ measurements of atmospheric CO₂ in Beijing. Liu et al. (2014) analyzed the seasonal variations in background atmospheric CO₂ and $\delta^{13}\text{C}$ and their potential relationships with sources and sinks.

In this paper, we report the results of continuous in situ measurements of the mixing ratio and $\delta^{13}\text{C}$ of atmospheric CO₂ in Beijing using a Picarro stable isotope carbon dioxide analyzer based on cavity ring-down spectroscopy. The study began on Nov. 15, 2012 and ended on Mar. 8, 2014. We attempted to (1) elucidate the diurnal and seasonal patterns of the atmospheric CO₂ mixing ratio and $\delta^{13}\text{C}$, (2) evaluate the seasonal characteristics of the carbon isotope composition of CO₂ sources and the underlying mechanisms, (3) quantify the proportional contributions from coal combustion and natural gas combustion to atmospheric CO₂ during the heating season with a mass balance calculation, and (4) evaluate the relationships between the CO₂ mixing ratio and $\delta^{13}\text{C}$ and the air quality index (AQI).

2. Materials and methods

2.1. Analyzers, sampling, and calibration systems

In this study, the sampling and calibration system consisted of a Picarro G1101-i CO₂ δ¹³C analyzer (G1101-i, Picarro Inc., Sunnyvale, CA) and two three-way solenoid valves, which allowed for automated sampling of one ambient air sample and two calibration gases. The measurement sequence was controlled by the valve sequencer software provided by the analyzer. The cavity temperature and pressure in this instrument were tightly controlled and maintained at 45 °C and 140 Torr, respectively. The sample air and calibration gas were pumped continuously at a flow rate of 0.03 L min⁻¹ STP, and the mixing ratios of ¹²CO₂ and ¹³CO₂ were measured at 0.3 Hz.

The analyzer was upgraded in March of 2012 to correct the cross sensitivity caused by CH₄. A humid gas sample without drying was measured directly and only corrected for the water vapor dilution effect, the water vapor pressure broadening and the HDO spectral interference effects were not considered (Wen et al., 2013). According to Wen et al. (2013), the difference between the Picarro G1101-i and the Los Gatos DLT100 for atmospheric δ¹³C measurements was only 0.02 ± 0.18‰. In August 2014, the analyzer was upgraded to correct the spectral contamination caused by H₂O. According to Pang et al. (2015), before and after the upgrade, the atmospheric δ¹³C difference measurements by the Picarro G1101-i and the Picarro G2201-i were 0.07 ± 0.24‰ and 0.05 ± 0.30‰, respectively.

2.2. Atmospheric measurements

This research was conducted at the Key Laboratory of Ecosystem Network Observation and Modeling located in Beijing, China. The sampling site was located 10 m above the ground on the outside of our laboratory. The ambient air inlet was equipped with a filter (2 μm pore size, Swagelok model B-4F-05, Connecticut Valves and Fittings, Norwalk, Connecticut) and drew continuously into the analyzer from November 15, 2012 to March 8, 2014. Two standard gases with different CO₂ mixing ratios and δ¹³C values (Std1: 379 ppm CO₂ mixing ratio and -29.36 ± 0.13‰ δ¹³C; Std2: 499 ppm CO₂ mixing ratio and -29.95 ± 0.12‰ δ¹³C) were used for calibration of the ambient air samples.

The measurement cycles ran every 320 min, including the first 20 min for Std1 and Std2, each lasting 10 min, and the remaining 300 min for the ambient air measurement. The first 3 min of each measurement after switching were discarded for cavity flushing and the transient response to the step change (Vogel et al., 2013; Flowers et al., 2012). The calibration was performed for each measuring cycle, and hourly mean values were produced from the calibrated ambient measurements.

2.3. Calibration procedures

According to Wen et al. (2013), the two-point mixing ratio gain and offset calibration method (Bowling et al., 2003) for the ¹²CO₂ and ¹³CO₂ mixing ratio calibrations was suitable for the IRIS analyzers. The ¹²CO₂ and ¹³CO₂ mixing ratios of standard gases can be measured by the CO₂ mixing ratio and δ¹³C values (Wen et al., 2013). The calibration equations for ¹²CO₂ and ¹³CO₂ are as follows:

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

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

where x^{12} and x^{13} are the mixing ratios of ¹²CO₂ and ¹³CO₂; the subscripts 1, 2 and a indicate the Std1, Std2 and ambient air; and the subscripts m and t represent the measured and true values of the ¹²CO₂ (¹³CO₂) mixing ratio, respectively.

The δ¹³C value can be derived using the calibrated ¹²CO₂ (¹³CO₂) mixing ratio data as

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{VPDB}} - 1) * 1000\text{‰} \quad (3)$$

where R is the molar ratio of ¹³CO₂ to ¹²CO₂, and the subscripts sample and VPDB indicate the sample and the international standard, respectively. δ¹³C is reported in parts per thousand (‰).

2.4. Precision of measurements

Only two standard gases (Std1 and Std2) were used in this study, no other gas can be used as the quality control gas calibrated by the two-point mixing ratio gain and offset calibration method (Bowling et al., 2003) for testing the long-term stability and accuracy of this system. Here, the single point mixing ratio and delta calibration method (Wen et al., 2013, 2008; Lee et al., 2005) was used to calibrate Std1 with Std2 and vice versa.

As expected, the raw data of Std1 and Std2 measured by the analyzer showed significant temporal drift (Fig. 1), the mean δ¹³C values of Std1 and Std2 were -31.6 ± 1.3‰ and -31.7 ± 1.1‰, respectively. After single point calibration, the δ¹³C values of Std1 and Std2 were -29.87 ± 0.36‰ and -29.44 ± 0.36‰, respectively. The differences between the calibrated δ¹³C values and the IRMS values (Std1: -29.36 ± 0.13‰; Std2: -29.95 ± 0.12‰) of Std1 and Std2 were 0.51‰ and -0.51‰, respectively, this bias may have been caused by the concentration dependence of the analyzer. The two-point mixing ratio gain and offset calibration method (Bowling et al., 2003) will eliminate the delta concentration dependence and provide more accurate results (Wen et al., 2013).

2.5. Keeling plot approach

The Keeling plot approach was used for the nighttime (22:00–04:00) CO₂ and δ¹³C data to estimate the carbon isotope composition of integrated atmospheric CO₂ sources. The basic assumption of the Keeling plot method is that the isotopic compositions of the background and source CO₂ do not change over the observation period (Pataki et al., 2003b).

$$\delta^{13}\text{C}_t = [\text{CO}_2]_b (\delta^{13}\text{C}_b - \delta^{13}\text{C}_s) \cdot (1/[\text{CO}_2]_t) + \delta^{13}\text{C}_s \quad (4)$$

Fig. 1. Time series of measured values of δ¹³C for two standard gases ((a) Std1 and (b) Std2). The gray triangles represent the actual values of δ¹³C (measured by the IRMS system). The black squares represent the Picarro raw data, and the black circles represent the calibrated data.

where $\delta^{13}\text{C}$ is the isotopic composition of CO_2 ; $[\text{CO}_2]$ represents the CO_2 mixing ratio; and the subscripts t, b and s indicate the total CO_2 , background CO_2 and additional CO_2 produced by the source, respectively. $\delta^{13}\text{C}_s$ is the y-intercept when $1/[\text{CO}_2]_t$ is zero.

Geometric mean regression was used for the Keeling plot intercept estimation (Pataki et al., 2003b; Bowling et al., 2002). The intercept values were removed based on the following quality criteria: (1) the range of CO_2 mixing during the measured period was less than 50 ppm and (2) the standard error of the intercept was greater than 1‰ (Schaeffer et al., 2008).

2.6. Dataset of the Air Quality Index

The Air Quality Index (AQI) is a dimensionless index that describes air quality and its effect on health. The air pollutants for the AQI evaluation include SO_2 , NO_2 , PM_{10} , $\text{PM}_{2.5}$, O_3 and CO , which come from power plants, domestic heating, vehicles and industrial sources (Chan and Yao, 2008). Pollutants such as CO , NO_2 and SO_2 have similar variation patterns, and their major sources are biofuel, coal and petroleum combustion (Liu et al., 2013). These pollutant emissions are coupled with CO_2 emissions. The AQI data were downloaded from the data center of the Ministry of Environmental Protection of China (<http://datacenter.mep.gov.cn/>) to evaluate the relationship between the CO_2 mixing ratio ($\delta^{13}\text{C}$) and the AQI. From Nov. 15, 2012 to Jan. 14, 2013, the air quality index was the API (Air Pollution Index), which included SO_2 , NO_2 and PM_{10} , and the measurement frequency was once per day. From Jan. 1, 2014 to Mar. 8, 2014, the air quality index was the AQI, which included SO_2 , NO_2 , PM_{10} , $\text{PM}_{2.5}$, O_3 and CO , and the measurement frequency was once per hour. There was no data from Jan. 14, 2013 and Jan. 1, 2014.

3. Results

3.1. Seasonal variations in the mixing ratio and $\delta^{13}\text{C}$ of atmospheric CO_2

The hourly mean air temperature was obtained for the period of November 15, 2012 through March 8, 2014 (Fig. 2a). It ranged from -14.1 to 37.6 °C and showed a clear seasonal variation with the maximum air temperature reached in July and the minimum in December; the mean air temperature during this study was 10.4 ± 11.7 °C. When the air temperature dropped below 5 °C, intensive residential heating is necessary and generally begins around the 15 of November. We defined the intensive heating period as the heating season and the other days as the vegetative season. Thus, our study was divided into 3 periods: heating season I (from November 15, 2012 to March 14, 2013), a vegetative season (from March 14, 2013 to November 14, 2013) and heating season II (from November 15, 2013 to March 8, 2014). The mean air temperatures of these 3 periods were -0.7 ± 5.4 °C, 19.9 ± 8.0 °C and 1.9 ± 4.2 °C.

The hourly mean CO_2 mixing ratio and $\delta^{13}\text{C}$ values showed the expected seasonal fluctuations (Fig. 2b and c). During the observation period, the CO_2 mixing ratio was highest during the heating seasons and lowest during the vegetative season, ranging from 372.2 ppm to 635.6 ppm with an average value of 440.9 ± 37.6 ppm. During heating season I, heating season II and the vegetative season, the CO_2 mixing ratios ranged from 401.8 ppm to 630.8 ppm, 402.0 ppm to 635.6 ppm and 372.2 ppm to 554.5 ppm, with average values of 456.0 ± 43.2 ppm, 452.8 ± 41.2 ppm and 427.3 ± 25.9 ppm, respectively. The seasonal CO_2 amplitudes were largest in the heating seasons and smallest in the vegetative season, with peak-to-peak values of 229.0 ppm, 233.6 ppm and 182.3 ppm for heating season I, heating season II and the vegetative season, respectively.

The $\delta^{13}\text{C}$ value mirrored the seasonal variation in the CO_2 mixing ratio. The most depleted value was during the heating seasons, and the most enriched value was during the vegetative season, ranging from -16.2 ‰ to -7.0 ‰ with an average value of -10.5 ± 1.3 ‰.

Fig. 2. One-hour aggregate time series of atmospheric (a) air temperature, (b) CO_2 mixing ratio and (c) $\delta^{13}\text{C}$ measured from November 15, 2012 to March 8, 2014 in Beijing. Shaded panels in this and subsequent figures denote heating season I (from November 15, 2012 to March 14, 2013) and heating season II (from November 15, 2013 to March 8, 2014).

During heating season I, heating season II and the vegetative season, $\delta^{13}\text{C}$ ranged from -16.2 ‰ to -8.4 ‰, -15.7 ‰ to -8.5 ‰ and -13.8 ‰ to -7.0 ‰, with average values of -11.2 ± 1.4 ‰, -11.0 ± 1.4 ‰ and -10.0 ± 0.9 ‰, respectively. The seasonal $\delta^{13}\text{C}$ amplitudes were largest in the heating seasons and smallest in the vegetative season, with peak-to-peak values of 7.8‰, 7.1‰ and 6.7‰ for heating season I, heating season II and the vegetative season, respectively.

The fast Fourier transform of the CO_2 mixing ratio and $\delta^{13}\text{C}$ data for Heating season I, vegetative season and heating season II are shown in Fig. 3. Prior to the transform, the missing data points were interpolated by a simple linear interpolation using the values from the hours before and after. Heating season I, vegetative season and heating season II showed clear diurnal (24 h) cycles of both CO_2 mixing ratio and $\delta^{13}\text{C}$, and the heating season signals showed larger magnitude of variation than vegetation season over longer periods.

3.2. Mean diurnal cycles of the CO_2 mixing ratio and $\delta^{13}\text{C}$

Based on the high temporal resolution measurements, we can observe the hourly and diurnal timescale variations in the CO_2 mixing ratio and $\delta^{13}\text{C}$ values. The mean diurnal variations in the CO_2 mixing ratio and $\delta^{13}\text{C}$ for heating season I, the vegetative season and heating season II are shown in Fig. 4. Heating seasons I and II had higher CO_2 mixing ratios and more depleted $\delta^{13}\text{C}$ values than the vegetative season. The peak-to-peak amplitudes of the mean diurnal variations were 20.1 ppm, 21.4 ppm and 35.2 ppm for the CO_2 mixing ratio and 0.6‰, 1.0‰ and 1.2‰ for $\delta^{13}\text{C}$ during heating season I, the vegetative season and heating season II, respectively. The difference in diurnal amplitudes of the CO_2 mixing ratio and $\delta^{13}\text{C}$ between heating seasons I and II primarily resulted from daytime peak values likely because increasing CO_2 emissions corresponded to a greater residential heating demand during the colder period in heating season I.

Heating seasons I and II showed similar diurnal cycles with two peaks. The CO_2 mixing ratio dropped slowly at night (0:00–07:00), which may have indicated inactivity of plant respiration and anthropogenic emissions. It then increased from 07:00 to a maximum value at $\sim 10:00$ likely due to anthropogenic emissions during morning rush hour. Then, the CO_2 mixing ratio started to drop and reached a minimum value at $\sim 15:00$ as strong atmosphere mixing conditions and photosynthetic activity developed. The CO_2 mixing ratio then increased with the onset of more stable atmospheric conditions and afternoon

Fig. 3. Comparison of fast Fourier transform results of (a) CO_2 mixing ratio and (b) $\delta^{13}\text{C}$ value for heating season I, vegetative season and heating season II.

rush hour and reached the second peak value at ~24:00. The $\delta^{13}\text{C}$ diurnal cycle showed a negative relationship with the CO_2 mixing ratio.

During the vegetative season, the CO_2 mixing ratio and $\delta^{13}\text{C}$ showed different mean diurnal variations compared to the heating seasons, and only one peak was observed. During the night and early morning (0:00–09:00), the CO_2 mixing ratio increased slowly, which indicates strong plant and soil respiration at night and anthropogenic emissions during morning rush hour, it reached a maximum value at ~09:00 and then dropped to a minimum value at ~17:00. Compared with the heating seasons, the minimum value appeared later, which is likely due to the significant photosynthetic uptake of CO_2 during the vegetative season. Then, the CO_2 mixing ratio increased because of persistent biogenic respiration, anthropogenic emissions and stable atmospheric conditions. The $\delta^{13}\text{C}$ diurnal cycle also showed a negative relationship with the CO_2 mixing ratio.

Fig. 4. Mean diurnal cycles of the (a) CO_2 mixing ratio and (b) $\delta^{13}\text{C}$ values during heating season I, the vegetative season and heating season II. Error bars indicate standard error of the means ($n = 121, 245, \text{ and } 113$, for heating season I, the vegetative season and heating season II, respectively).

3.3. Seasonal variations in the isotope compositions of atmospheric CO_2 sources

$\delta^{13}\text{C}_s$ was calculated weekly using the nighttime (22:00–04:00) CO_2 mixing ratio and $\delta^{13}\text{C}$ value by the Keeling plot intercept method, the result showed an apparent seasonal variation (Fig. 5). $\delta^{13}\text{C}_s$ is an integrated isotopic composition of potential local CO_2 sources including the combustion of fossil fuels, such as coal, gasoline and natural gas, and plant and soil respiration during the measurement period. $\delta^{13}\text{C}_s$ was most enriched in the vegetative season and most depleted in the heating seasons, ranging from -32.1% to -21.9% with a seasonal amplitude of 10.2% . The seasonal cycle of $\delta^{13}\text{C}_s$ indicates changes in the contribution of CO_2 emissions from fossil fuel consumption and plant and soil respiration. During heating seasons I and II, $\delta^{13}\text{C}_s$ ranged from -30.7% to -24.1% and -32.1% to -25.7% with average values of $-27.1 \pm 1.5\%$ and $-27.4 \pm 1.5\%$, respectively. During the vegetative season, $\delta^{13}\text{C}_s$ was more enriched and ranged from -27.7% to -21.9% with an average value of $-25.3 \pm 1.8\%$. The nighttime CO_2 mixing ratio and $\delta^{13}\text{C}$ values during heating season I, the vegetative season and heating season II were used to calculate the seasonal $\delta^{13}\text{C}_s$ value by the Keeling plot intercept method, the $\delta^{13}\text{C}_s$ were $27.0 \pm 0.1\%$, $-25.1 \pm 0.1\%$ and $-27.1 \pm 0.1\%$, respectively. The differences between this method and the seasonal average value based on weekly derived $\delta^{13}\text{C}_s$ values were 0.1% , 0.2% and 0.3% , respectively.

According to the inter-comparison study of Pang et al. (2015), the difference in the Keeling plot intercept between G1101-i and G2201-i was 0.82% before G1101-i was upgraded, which decreased to 0.07% after the upgrade. This difference is likely due to the anomalous increase in $\delta^{13}\text{C}$ under high concentrations of H_2O . According to a sensitivity analysis of the error propagation in the concentration dependence method (Wen et al., 2013, Eq. 18), the error caused by the G1101-i analyzer would propagate through the Keeling plot method, resulting in enriched values of 1.0% , 0.9% and 0.8% for $\delta^{13}\text{C}_s$ during heating season I, heating season II and the vegetative season, respectively.

4. Discussion

4.1. Comparison of temporal variations in atmospheric CO_2 and $\delta^{13}\text{C}$ with other cities

The seasonal variabilities in the atmospheric CO_2 mixing ratio and $\delta^{13}\text{C}$ are controlled by the changes in local sources and sinks, such as photosynthetic activity, plant and soil respiration and anthropogenic emissions, and atmospheric mixing conditions (Wada et al., 2011; Pataki et al., 2007; Sturm et al., 2006). The seasonal patterns of the atmospheric CO_2 mixing ratio and $\delta^{13}\text{C}$ in Beijing were very similar to other study sites. The CO_2 mixing ratio in Beijing ranged from 372.2 ppm to 635.6 ppm with an average value of $440.9 \pm 37.6 \text{ ppm}$.

Fig. 5. The seasonal variations in carbon isotope composition of CO_2 sources ($\delta^{13}\text{C}_s$) calculated using the Keeling plot method.

The CO₂ mixing ratio was higher in the heating seasons, ranging from 401.8–630.8 ppm in heating season I and 402.0–635.6 ppm in heating season II, and lower in the vegetative season, ranging from 372.1 ppm to 554.5 ppm. The CO₂ mixing ratio in Dallas, USA ranged from 369–475 ppm over the period from August 1998 to December 1999 (Clark-Thorne and Yapp, 2003). In Salt Lake City, USA, the nighttime average CO₂ mixing ratio ranged from 390–480 ppm in winter and 375–400 ppm in summer throughout 2002 (Pataki et al., 2003a). In Bern, Switzerland, CO₂ mixing ratios were highest in the winter during atmospheric inversion events and lowest (close to background values) in the afternoon during summer from October 2003 to February 2005 (Sturm et al., 2006). In Los Angeles, USA, the CO₂ mixing ratio ranged from 380–600 ppm from October 22, 2007 to February 10, 2008 (Djuricin et al., 2010). In Nagoya, Japan, the CO₂ mixing ratio ranged from 385–470 ppm in May and 385–495 ppm in December from 2008 to 2009 (Wada et al., 2011). In Krakow, Poland, the monthly average value of the CO₂ mixing ratio ranged from 405–425 ppm over the period of January 2005 to December 2009 (Zimnoch et al., 2012).

The seasonal patterns of $\delta^{13}\text{C}$ showed a negative relationship with the CO₂ mixing ratio, ranging from -16.2 to -7.0% with an average value of $-10.5 \pm 1.3\%$. $\delta^{13}\text{C}$ showed more depleted values in the heating seasons, ranging from -16.2 to -8.4% in heating season I and -15.7 to -8.54% in heating season II, and more enriched values in the vegetative season, ranging from -13.8 to -7.04% . For comparison, $\delta^{13}\text{C}$ ranged from -12.0 to -8.1% in Dallas, USA (Clark-Thorne and Yapp, 2003), and -14 to -8% in Bern, Switzerland (Sturm et al., 2006). In Los Angeles, USA, the $\delta^{13}\text{C}$ value varied from -9.3 to -7.5% , -12.5 to -8.8% , -12.2 to -9.2% and -12.5 to -10.2% in October, December, February and April samples, respectively (Djuricin et al., 2010). In Krakow, Poland, the $\delta^{13}\text{C}$ value ranged from -11% to -9.5% (Zimnoch et al., 2012). In Nagoya, Japan, the $\delta^{13}\text{C}$ value ranged from -13.4 to -8.5% in May and -15.0 to -8.5% in December from 2008 to 2009 (Wada et al., 2011). The $\delta^{13}\text{C}$ value in Salt Lake City, USA ranged from -18 to -8% over the period from December 2004 to January 2005 (Pataki et al., 2006).

The diurnal patterns of the atmospheric CO₂ mixing ratio and $\delta^{13}\text{C}$ were likely caused by the diurnal changes in local CO₂ source and sink fluxes and the development of atmospheric boundary layers (Newman et al., 2013; Guha and Ghosh, 2010; Sturm et al., 2006; Zimnoch et al., 2004). The diurnal patterns of CO₂ mixing and $\delta^{13}\text{C}$ contained two peaks in heating seasons I and II, but only one peak in the vegetative season. The minimum value of the CO₂ mixing ratio and the most enriched $\delta^{13}\text{C}$ value commonly appeared in the afternoon. Higher CO₂ mixing ratios and more depleted $\delta^{13}\text{C}$ values in the heating seasons were observed compared to the vegetative season. The average daily amplitudes were 20.1 ppm, 21.4 ppm and 35.2 ppm for the CO₂ mixing ratios and 0.6%, 1.0% and 1.2% for $\delta^{13}\text{C}$ during heating season I, the vegetative season and heating season II, respectively. For comparison, in Bern, Switzerland, the daily amplitude of the CO₂ mixing ratio varied between 55 to 60 ppm in the summer and 15 to 25 ppm in the winter (Sturm et al., 2006). In Los Angeles, USA, the daily amplitudes of the CO₂ mixing ratio and $\delta^{13}\text{C}$ were ~ 40 ppm and 1.8 to 3.7% (Djuricin et al., 2010). The daily amplitudes of the CO₂ mixing ratio and $\delta^{13}\text{C}$ were 30 ppm and $\sim 2\%$ in Bangalore city, India (Guha and Ghosh, 2010). In Krakow, Poland, the diurnal variation of the CO₂ mixing ratio and $\delta^{13}\text{C}$ reached up to 100 ppm and 4% in summer and were more stable in winter during the period from March to December, 1992 (Zimnoch et al., 2004). The diurnal cycles of the CO₂ mixing ratio and $\delta^{13}\text{C}$ contained two peaks, which reflects the effect of traffic rush hour emissions (Lopez et al. 2013).

4.2. Comparing the characteristics of $\delta^{13}\text{C}_s$ with other cities

In urban ecosystems, $\delta^{13}\text{C}_s$ represents a flux-weighted average of the potential local sources, which include anthropogenic (coal, gasoline and natural gas combustion) and biogenic (plant and soil respiration

and organic matter decomposition) CO₂ components (Tanaka et al., 2013; Wen et al., 2013; Wada et al., 2011; Pataki et al., 2003a). The spatial and temporal patterns of $\delta^{13}\text{C}_s$ can be used to discriminate anthropogenic and biogenic emissions in urban processes at different spatial and temporal scales and to infer atmospheric CO₂ sources and energy usage patterns. In this study, $\delta^{13}\text{C}_s$ was enriched in the vegetative season with an average value of $-25.4 \pm 0.1\%$ and depleted in the heating seasons with average values of $-26.8 \pm 0.1\%$ and $-27.1 \pm 0.1\%$ in heating seasons I and II, respectively. In similar studies carried out in other cities, $\delta^{13}\text{C}_s$ ranged from -27.6 to -25.7% in Wroclaw, Poland during the heating season (Gorka and Lewicka-Szczepak, 2013), and the annual mean value was -27% in Dallas, USA (Clark-Thorne and Yapp, 2003). These values are close to the $\delta^{13}\text{C}_s$ values in our study, whereas other studies found more depleted $\delta^{13}\text{C}_s$ values. In Bern, Switzerland, $\delta^{13}\text{C}_s$ ranged from -33 to -25% (Sturm et al., 2006). In Salt Lake City, USA, $\delta^{13}\text{C}_s$ ranged from -37.2 to -30.0% in winter and -32.4 to -27.4% in summer (Pataki et al., 2003a). In Tokyo, Japan, the most depleted $\delta^{13}\text{C}_s$ value of -40.1% was observed during stable atmospheric conditions with drastic changes in atmosphere CO₂ and $\delta^{13}\text{C}$ (Tanaka et al., 2013).

The $\delta^{13}\text{C}_s$ differences in different cities are related to local energy usage patterns and plant photosynthetic pathways. In general, the stable carbon isotope composition of ecosystem respiration within C₃ ecosystems ranged from -19.0% to -32.6% with an average value of $-26.2 \pm 0.2\%$ (Pataki et al., 2003b), and a mean value of -12% has been observed in C₄ ecosystems (Fassbinder et al., 2012). The $\delta^{13}\text{C}$ values of coal, gasoline and natural gas combustion ranged between -27 to -25% , -32 to -28% and -43.8 to -37% , respectively (Wada et al., 2011; Bush et al., 2007; Clark-Thorne and Yapp, 2003; Takahashi et al., 2002). In this study, the $\delta^{13}\text{C}_s$ values of heating seasons I and II were close to the $\delta^{13}\text{C}$ value of coal combustion, which indicates that the main source of atmospheric CO₂ during intensive residential heating periods was coal combustion. The $\delta^{13}\text{C}_s$ value of the vegetative season was more enriched than most fossil fuel combustion values, which indicates that the respiration of C₃ and C₄ plants was an important component of atmospheric CO₂. The larger variation in the $\delta^{13}\text{C}_s$ values in the vegetative season was mainly caused by local source and sink changes under various meteorological conditions (Sturm et al., 2006). On the diurnal time scale, $\delta^{13}\text{C}_s$ variability can be affected by the atmospheric mixing condition variation and the distribution of CO₂ sources (Wada et al., 2011; Sturm et al., 2006). In Wroclaw, Poland and the Los Angeles basin, USA, the $\delta^{13}\text{C}_s$ differences over different time periods indicate changes in energy usage patterns (Gorka and Lewicka-Szczepak, 2013; Newman et al., 2008). In this study, the consistent $\delta^{13}\text{C}_s$ values of heating seasons I and II indicate that local energy consumption did not change during this period. The $\delta^{13}\text{C}_s$ signal is a qualitative indicator of the main CO₂ sources in urban atmospheres, but it cannot be used to quantify the proportion of each source.

4.3. CO₂ source partitioning

The distinct carbon isotope signals of coal, gasoline and natural gas combustion and background air can be used to partition urban CO₂ sources into their component parts. During the heating seasons, nighttime biological activity and gasoline combustion are negligible, and we assumed that the primary CO₂ source at night (22:00–04:00) was derived from coal and natural gas combustion in heating seasons I and II, the following mass balance equations were constructed to partition the urban sources of CO₂ into coal combustion ([CO₂]_C) and natural gas combustion ([CO₂]_N):

$$[\text{CO}_2]_T = [\text{CO}_2]_B + [\text{CO}_2]_C + [\text{CO}_2]_N \quad (5)$$

$$\delta^{13}\text{C}_T[\text{CO}_2]_T = \delta^{13}\text{C}_B[\text{CO}_2]_B + \delta^{13}\text{C}_C[\text{CO}_2]_C + \delta^{13}\text{C}_N[\text{CO}_2]_N \quad (6)$$

where $[CO_2]$ is the mixing ratio; $\delta^{13}C$ is the isotopic composition of CO_2 ; and the subscripts T, B, C, and N refer to the total ambient air CO_2 , background CO_2 , coal combustion and natural gas combustion, respectively. In this study, $\delta^{13}C_T$ and $[CO_2]_T$ were measured by the G1101-i analyzer (Fig. 2), and $\delta^{13}C_C$ and $\delta^{13}C_N$ were adopted from the relevant literature with average values of -26‰ and -39.5‰ , respectively; $\delta^{13}C_B$ and $[CO_2]_B$ were estimated from annual smoothed data from a background site in Shangdianzi, Beijing measured from 2008 to 2011 (Liu et al., 2014).

Nighttime (22:00–04:00) contributions of coal and natural gas combustion were obtained hourly, and average nighttime data were used here. The nighttime mean contributions of local CO_2 from coal and natural gas combustion are shown in Fig. 6. Coal combustion had a larger contribution with average values of $83.83 \pm 14.11\%$ and $86.84 \pm 12.27\%$, and natural gas combustion had a smaller contribution with average values of $16.17 \pm 14.11\%$ and $13.16 \pm 12.27\%$ in heating seasons I and II, respectively. The similar proportions of coal and natural gas combustion indicate that the energy usage patterns did not change during this period, which is consistent with Section 4.2.

A series of sensitivity analyses was conducted with respect to the average values of $\delta^{13}C_C$ and $\delta^{13}C_N$ from the relevant literature used in the mass balance equations, the contributions of coal and natural gas combustion to the ambient air CO_2 were not strictly assessed. Here, $\delta^{13}C_C$, $\delta^{13}C_N$ and $\delta^{13}C_B$ decreased by 1‰, and the CO_2 contributions from coal and natural gas combustion were recalculated. The result showed that a 1‰ decrease in $\delta^{13}C_C$ and $\delta^{13}C_N$ resulted in 1.30% and 1.11% increases in the coal combustion contribution for heating season I and 0.43% and 0.73% increases for heating season II (Table 1). However, a constant mean $\delta^{13}C_B$ value of -8.29‰ (Liu et al., 2014) caused 10.39% and 9.20% decreases in coal combustion emissions for heating seasons I and II, which indicates that the $\delta^{13}C$ of background air CO_2 was the main error source in the isotopic mass balance model.

The contribution of each CO_2 source to the urban atmosphere of different cities could improve our understanding of energy usage patterns and underlying mechanisms. Based on the mass balance equations and the $\delta^{13}C$ and $\delta^{18}O$ signals, the proportional contributions of natural gas and gasoline combustion and plant respiration were quantified in Salt Lake City, USA. The contribution of natural gas combustion was ~60% in winter and negligible in summer, and the contribution of biogenic respiration was up to 60% in summer but lower in winter; the contribution from gasoline combustion remained higher all year (Pataki et al., 2003a). On the diurnal time scale, the contribution of natural gas combustion was 30 ~ 40% during evening rush hour and 60 ~ 70% during pre-dawn in winter (Pataki et al., 2006). A three-component mixing model was used in Krakow, Poland, and results showed that ~90% of the atmospheric CO_2 sources was due to biogenic respiration in summer

and that ~85% of the atmospheric CO_2 sources was due to anthropogenic emissions in winter (Zimnoch et al., 2004). At Kasprowy Wierch, Poland, anthropogenic emission was approximately 1/5 of that derived for Krakow (Zimnoch et al., 2012). In Paris, France, ^{14}C and ^{13}C were used to identify the proportion of fossil fuel combustion and biogenic respiration sources, which were 77% and 23%, respectively, and the contributions from gas and liquid fuel to the fossil fuel combustions were 70% and 30%, respectively (Lopez et al., 2013). In Nagoya, Japan, a mass balance analysis indicated that natural gas combustion, gasoline combustion and biogenic respiration contributed 42%, 33% and 25% of the local CO_2 sources in the spring, respectively. The short-term variations in the contribution of each component depended on the wind direction, and the long-term variations were likely due to seasonal changes in biological activity and residential heating demand (Wada et al., 2011). In Los Angeles, USA, $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{14}C$ measurements and a mass balance analysis were used to quantify the proportion of each CO_2 source; the relative contributions of natural gas combustion, gasoline combustion, belowground respiration and aboveground respiration were $9.2 \pm 1.9\%$, $20.4 \pm 3.1\%$, $26.8 \pm 3.3\%$ and $43.6 \pm 3.8\%$ in October and $18.9 \pm 8.9\%$, $29.1 \pm 13.0\%$, $24.2 \pm 10.9\%$ and $27.9 \pm 12.0\%$ in December, respectively (Djuricin et al., 2010).

4.4. The relationship between atmospheric CO_2 isotope composition and the AQI

The anthropogenic CO_2 emission process was coupled with other gaseous and particulate pollutant emissions, including CO, SO_2 , NO_2 , PM_{10} , $PM_{2.5}$ and O_3 , that were used for the air quality index (AQI) evaluation. The local sources of these pollutants include power plants, residential heating, industrial production and vehicle emissions (Chan and Yao, 2008). In this study, a positive linear correlation ($R^2 = 0.84$, $p < 0.001$) was found between the AQI and the CO_2 mixing ratio, and a negative linear correlation ($R^2 = 0.77$, $p < 0.001$) was observed between the AQI and $\delta^{13}C$ in heating season II; the slopes were 0.34 ± 0.01 and -0.01 ± 0.00 , respectively (Fig. 7c, d). A similar relationship was found in heating season I, and the slopes were 0.35 ± 0.05 and -0.01 ± 0.00 , respectively (Fig. 7a, b). Covariance analysis was used to examine the differences in the regression slopes between AQI and CO_2 and between AQI and $\delta^{13}C$ in heating seasons I and II; no significant difference was found between these two seasons ($p = 0.092 > 0.05$; $p = 0.709 > 0.05$), which indicates consistent sources for the CO_2 mixing ratio and air pollutants in the heating seasons. According to a source analysis, the contributions of coal combustion, industrial pollution and secondary inorganic aerosols can reach 69% of local $PM_{2.5}$ in Beijing (Zhang et al., 2013). The CO_2 mixing ratio and $\delta^{13}C$ measurements can be used to indicate local air pollution events, but long-term data analysis is needed to test this relationship. The consistent linear relationship of AQI and CO_2 and of AQI and $\delta^{13}C$ between heating seasons I and II also indicates that the energy usage patterns did not change during this period. Energy structure optimization, for example, reducing coal consumption in Beijing, will improve the poor air condition and change the slope and intercept of the linear regression. The pollutants CO, SO_2 and NO_2 are excellent indicators of different CO_2 sources (Lopez et al., 2013; Newman et al., 2013; Djuricin et al., 2010; Li et al., 2007), and data on these pollutants combined with the atmospheric CO_2 mixing

Fig. 6. Nighttime contribution from coal and natural gas combustion to local CO_2 sources during heating season I (from Nov 15, 2012 to Mar 15, 2013) and heating season II (from Nov 15, 2013 to Mar 8, 2014).

Table 1

Sensitivity analysis of calculations of the mean contributions of coal and natural gas combustion to the total CO_2 source during heating season I and heating season II.

	Heating season I		Heating season II	
	% coal	% natural gas	% coal	% natural gas
Baseline	83.83 ± 14.11	16.17 ± 14.11	86.84 ± 12.27	13.16 ± 12.27
1‰ depletion $\delta^{13}C_N$	84.94 ± 13.14	15.06 ± 13.14	87.56 ± 12.09	12.44 ± 12.09
1‰ depletion $\delta^{13}C_C$	85.13 ± 14.94	14.87 ± 14.94	87.27 ± 13.13	12.73 ± 13.13
Constant mean $\delta^{13}C_B$	73.44 ± 20.09	26.56 ± 20.09	77.64 ± 16.85	22.36 ± 16.85

Fig. 7. The correlation of AQI with CO_2 and with $\delta^{13}\text{C}$. (a) and (b) are for heating season I (from Nov 15, 2012 to Jan 14, 2013), and (c) and (d) are for heating season II (from Jan 1, 2014 to Mar 8, 2014). The linear fit results with 1σ uncertainty (in parentheses) are also given.

ratio and $\delta^{13}\text{C}$ measurements will improve our understanding of carbon cycle processes in urban ecosystems.

5. Conclusions

On the seasonal time scale, the CO_2 mixing ratio was highest in the heating seasons and lowest in the vegetative season. The average values were 456.0 ± 43.2 ppm, 427.3 ± 25.9 ppm, and 452.8 ± 41.2 ppm in heating season I, the vegetative season, and heating season II, respectively. The $\delta^{13}\text{C}$ values mirrored the CO_2 variation with average values of $-11.2 \pm 1.4\text{‰}$, $-10.0 \pm 0.9\text{‰}$ and $-11.0 \pm 1.4\text{‰}$. On the diurnal time scale, the CO_2 mixing ratio and $\delta^{13}\text{C}$ presented two peaks in the heating seasons and one peak in the vegetative season. The diurnal amplitudes were 20.1 ppm, 21.4 ppm and 35.2 ppm for the CO_2 mixing ratio and 0.6‰, 1.0‰ and 1.2‰ for $\delta^{13}\text{C}$ in heating season I, the vegetative season and heating season II, respectively.

$\delta^{13}\text{C}_s$ was calculated by the Keeling plot intercept method, with the most enriched value in the vegetative season and the most depleted value in the heating season. The seasonal average $\delta^{13}\text{C}_s$ values were $-27.1 \pm 1.5\text{‰}$, $-27.4 \pm 1.5\text{‰}$ and $-25.3 \pm 1.8\text{‰}$ in heating season I, heating season II, and the vegetative season, respectively.

Assuming that the primary CO_2 source at night (22:00–04:00) was derived from coal and natural gas combustion during the heating seasons, the mass balance analysis can be used to quantify the proportional contributions of coal combustion and natural gas combustion to atmospheric CO_2 . Coal combustion had a relatively larger contribution with average values of $83.83 \pm 14.11\%$ and $86.84 \pm 12.27\%$, and natural gas had smaller contributions with average values of $16.17 \pm 14.11\%$ and $13.16 \pm 12.27\%$ in heating seasons I and II, respectively. Sensitivity analyses indicated that the $\delta^{13}\text{C}$ of background air CO_2 was the main error source in the isotopic mass balance model.

A positive linear correlation was found between the AQI and the CO_2 mixing ratio, and a negative linear correlation was observed between the AQI and $\delta^{13}\text{C}$ in the heating seasons, which indicates that the CO_2 mixing ratio and $\delta^{13}\text{C}$ can be used as indicators of local air pollution events. If the energy usage pattern can be optimized by, for example, reducing coal consumption in Beijing, the poor air conditions will be improved.

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