Responses to Editor

1) Please re-attach the data supplement with the hourly measurement results. It seems to have gone missing during a previous iteration.

Upload.

2) In line 218, please replace "H2O < 2.03 %" by "C(H2O) < 2.03 %" (or "C(H2O) < 2.03 cmol mol⁻¹", for consistency with the rules of quantity algebra and the symbol for mole fraction adopted elsewhere.

Replaced.

3) Likewise, in line 219, please replace "H2O % - 2.03 %" with "C(H2O) - 2.03 %" or "C(H2O) - 2.03 cmol mol⁻¹").

Replaced.

4) Fig. S3 refers to the wrong dataset. According to the main text, it is supposed to show data from Los Angeles as published in the paper of Newman et al. (2016), but the caption refers to a site in Switzerland, as published by Sturm et al. (2016).

Figure S3 caption is actually accurate. Like a number of datasets shown in Table S1, this dataset requires a non-zero intercept (44.14 ± 8.48 ‰ μmol mol⁻¹).

We did not analyze the data published by Newman et al. (2016). According to their published result (their Figure A1), the original Miller-Tans method does not need an intercept.

We have modified the main text to avoid confusion:

“We tested the Miller-Tans method with other isotope data published for urban areas, and found that the intercept was nonzero for the data obtained by Sturm et al. (2006) at Bern, Switzerland (Supplementary Figure S3) and a number of other urban datasets (Supplementary Table S1).”

5) The numbering of figures in supplementary information should be made sequential (S4 is used twice). The references to supplementary figures in the main text also need to be updated.

Done.

6) Please add a sentence to reflect your response to the reviewer’s suggestion of post-calibrating the analyser (i.e. "We could not implement [an isotope delta calibration
using standards with delta values bracketing the sample values] because the detector of our analyzer failed at the end of the experiment." or similar).

We have added one sentence:

“...We could not implement this improved calibration procedure because our analyzer failed at the end of the experiment.”
Interpreting the $^{13}\text{C}/^{12}\text{C}$ ratio of carbon dioxide in an urban airshed in the Yangtze River Delta, China

Jiaping Xu1, Xuhui Lee1,2*, Wei Xiao1, Chang Cao1, Shoudong Liu1, Xuefa Wen3, Jingzheng Xu1, Zhen Zhang1, Jiayu Zhao1

1Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science & Technology, Nanjing, China

2School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut, USA

3Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China

* Corresponding author

Dr. Xuhui Lee
Sara Shallenberger Brown Professor
School of Forestry and Environmental Studies, Yale University,
21 Sachem Street, New Haven, Connecticut 06510, USA
Phone: (203)432-6271; Fax: (203)432-5023
E-mail: xuhui.lee@yale.edu
Abstract: Observations of atmospheric CO₂ mole fraction and the $^{13}$C/$^{12}$C ratio (expressed as $\delta^{13}$C) in urban airsheds provide constraints on the roles of anthropogenic and natural sources and sinks in local and regional carbon cycles. In this study, we report observations of these quantities in Nanjing at hourly intervals from March 2013 to August 2015 using a laser-based optical instrument. Nanjing is the second largest city located in the highly industrialized Yangtze River Delta (YRD), Eastern China. The mean CO₂ mole fraction and $\delta^{13}$C were $(439.7 \pm 7.5) \mu$mol mol$^{-1}$ and $(-8.48 \pm 0.56) \%_o$ over this observational period. The peak monthly mean $\delta^{13}$C $(-7.44 \%_o$, July 2013) was $0.74 \%_o$ higher than that observed at Mount Waliguan, a WMO baseline site on the Tibetan Plateau and upwind of the YRD region. The highly $^{13}$C-enriched signal was partly attributed to the influence of cement production in the region. By applying the Miller-Tans method to nighttime and daytime observations to represent signals from the city of Nanjing and the YRD, respectively, we showed that the $^{13}$C/$^{12}$C ratio of CO₂ sources in the Nanjing Municipality was $(0.21 \pm 0.53) \%_o$ lower than that in the YRD. Flux partitioning calculations revealed that natural ecosystems in the YRD were a negligibly small source of atmospheric CO₂.

Keywords: urban areas; CO₂ flux; Industrial process; Carbon isotope; In-situ observation
1 Introduction

Atmospheric CO₂ sources and sinks in urban areas consist mainly of plant uptake and release and fossil fuel combustion. These contributors have unique ¹³C/¹²C ratios. City clusters are human-dominated systems with high carbon emission intensity, contributing over 70% of the total anthropogenic CO₂ to the atmosphere (Satterthwaite 2008). Previous urban isotopic studies emphasize carbon emissions from fossil combustion (Zondervan and Meijer 1996, Pataki et al. 2003, Zimnoch et al. 2004, Affek and Eiler 2006, Newman et al. 2008). Relatively little attention is given to the δ¹³C of carbon dioxide released by cement production, which is much higher than that of fossil fuel origin (Andres et al. 1994). Likewise, the CO₂ emitted from burning of minerals in non-energy consumption industrial processes, such as iron and steel production, has higher δ¹³C than that of fossil fuel (Table 2, Widory 2006). In China, cement production and industrial processes contribute 13% of the total anthropogenic CO₂ emission (Mu et al. 2013). Many of these industrial activities occur in or near urban areas. So far, little is known about their roles in the atmospheric carbon stable isotope budget.

One scientific motivation for quantifying the δ¹³C of atmospheric CO₂ is that it provides constraints that allow partitioning of the net surface flux into component fluxes (Farquhar and Lloyd 1993, Yakir and Sternberg 2000, Pataki et al. 2003). The ¹³C-based partitioning method has been used primarily for vegetation ecosystems, such as forests (Lloyd et al. 1996, Lloyd et al. 2001, Ometto, et al. 2006, Zobitz et al. 2008), grasses (Ometto et al. 2002, Pataki et al. 2003), and crops (Leavitt et al. 1995, Griffis et al. 2005). The approach has also been used in a limited number of urban studies (Pataki et al. 2003, Zimnoch et al. 2004, Newman et al.
2008, Jasek et al. 2014). Compared with vegetation ecosystems, urban ecosystems have more complex CO₂ source configurations. We must consider both natural sources (plants and soils) and anthropogenic sources (fossil combustion and non-energy industrial processes) and the fact that the degree of mixing of urban air with the free troposphere and the air outside the urban boundary varies diurnally and seasonally. Anthropogenic emissions are hard to quantify because they depend on multiple factors including city size, population density, fossil mix, and climate.

One of the first measurements of the carbon isotope ratio of CO₂ in an urban atmosphere was made by Friedman and Irsa (1967). Since then, more experiments have been conducted in urban environments (Ehleringer et al. 2002, Koerner and Klopatek 2002, Takahashi et al. 2002, Clark-Thorne and Yapp 2003, Lichtfouse et al. 2003, Widory and Javoy 2003, Zimnoch et al. 2004, Bush et al. 2007, Guha and Ghosh 2010, Wang and Pataki 2012). The analytical technique employed in these studies is mainly based on isotope-ratio mass-spectrometry (IRMS). In recent years, the development of isotope ratio infrared spectroscopy (IRIS) and on-line calibration technology provides a new solution for long-term in-situ observation of the CO₂ mole fraction and δ¹³C at high frequencies (1 Hz to 1 hour; Pataki et al. 2006, Griffis 2013, Gorski et al. 2015). However, application of the IRIS technology in urban monitoring is still limited in terms of cities covered and measurement duration (McManus et al. 2002, Pataki et al. 2006, Wada et al. 2011, Moore and Jacobson 2015). Only a few published studies have presented data that span one full annual cycle (e.g., Pang et al. 2016).

Simultaneous measurement of atmospheric CO₂ concentration and δ¹³C is used to determine the overall ¹³C/¹²C ratio of local surface sources δₛ. The majority of published
Urban studies to date have deployed the Keeling plot method (Keeling 1958, Keeling 1961) for the determination of $\delta S$. In this approach, a linear relationship is established between $\delta^{13}C$ and the reciprocal of the CO$_2$ mole fraction from the observed time series, and the intercept of the linear regression is taken as the isotopic ratio of the local CO$_2$ emissions. The method assumes that the isotopic ratio of the sources is invariant with time. It also assumes that changes in the CO$_2$ mole fraction and in $\delta^{13}C$ are attributed only to the surface sources and are unaffected by regional carbon sources (Pataki et al. 2003). However, these assumptions do not strictly hold in an urban environment because the intensity of traffic emissions varies strongly through the diel cycle (McDonald et al. 2014), and therefore the composition of the surface source varies, and its $^{13}C/^{12}C$ ratio cannot be assumed constant. In addition, because of strong atmospheric mixing in the daytime convective boundary layer, the background air in the upper troposphere can be easily entrained to the surface layer, mixing the CO$_2$ that originates from regional sources with that emitted locally in the urban airshed.

Miller and Tans (2003) propose that $\delta S$ be determined as the slope of the linear relationship

$$\delta S = \frac{\delta \Delta C_a - \delta \Delta C_b}{\Delta C_a - \Delta C_b}$$ (1)

where $C_a$ is CO$_2$ mole fraction in urban air, $C_b$ is CO$_2$ mole fraction at a background site, $\delta \Delta C_a$ is the $\delta^{13}C$ value of $C_a$, and $\delta \Delta C_b$ is the $\delta^{13}C$ value of $C_b$. All the variables are time dependent. Because this approach takes into account the fact the background atmosphere varies, it may be more suitable than the Keeling method for inferring $\delta S$ from the observations made in the urban area with complex emission sources. The method has been applied to local and regional carbon budget studies in nonurban settings (Miller et al. 2003) and in an urban
environment by Newman et al. (2016). Here we extend the method to continuous
measurements in an urban environment.

In this study, we report the results of long-term (30 months) continuous measurement of
atmospheric CO₂ mole fraction and δ¹³C at a suburban site in Nanjing using an IRIS
instrument. Nanjing is the second largest city in the Yangtze River Delta (YRD), Eastern
China, with a built-up area of 753 km² and a population of 8.2 million. Geographically, the
YRD includes the provinces of Jiangsu, Zhejiang and Anhui and the Shanghai municipality
(29.04° to 33.41° N, 118.33° to 122.95° E) with a population of 190 million. The YRD is
influenced by subtropical moist monsoon climate. The mean annual temperature is about 15
°C and the annual precipitation is between 1000 mm and 1800 mm. The vegetation types are
all C₃ species. The YRD is the most industrialized region in China and had a higher urban
land fraction of 10.8 % as of 2014 than the global mean (2.4 %, Akbari et al. 2009). In 2014,
more than 220 large cement production factories (daily output exceeding 1000 tons) were
located in the YRD (China Cement, 2016), contributing about 20 % of the national cement
output.

The objectives of this study are (1) to characterize the atmospheric δ¹³C diel, seasonal and
annual variations in this urban environment, in a region where such measurement is
nonexistent, (2) to investigate the influence of cement production on atmospheric δ¹³C, (3) to
evaluate the performance of the Keeling plot and the Miller-Tans methods for determining δₛ,
and (4) to explore the utility of the isotopic constraints for inferring the net surface flux and
the plant CO₂ flux in Nanjing and in the YRD.
2 Methods

2.1 Atmospheric observation

An IRIS analyzer (model G1101-i, Picarro Inc., Sunnyvale, CA) was used to measure atmospheric CO$_2$ mole fraction and $^{13}$C/$^{12}$C ratio ($\delta^{13}$C) continuously from February 2013 to August 2015. The analyzer was housed on the 9th floor of our laboratory building on the campus of Nanjing University of Information, Science and Technology (NUIST, 32°12’ N, 118°43’ E), in the northern suburb of Nanjing, at a linear distance of 20 km to the city center. The instrument inlet was at a height of 34 m above the ground. There was no large industrial CO$_2$ source in the 3 km radius except for a commuting road located about 300 m east of the observation site. The nearest industrial complex, the Nanjing Iron & Steel Group Co. Ltd. and the Nanjing Chemical Industry Group, was located about 5 km to the south of the site.

The measurement was made at 0.3 Hz and at an air flow rate of 30 mL min$^{-1}$ at standard temperature and pressure. One three-way solenoid valve was combined with two two-way solenoid valves, so the analyzer could be switched for atmospheric sampling and for sampling of two standard gases. Calibration was carried out every 3 h by sampling each standard gas for 5 minutes following the procedure of Bowling et al. (2003) and Wen et al. (2013). [To avoid transient effects, only the data collected in the last 2 minutes of the 5-min calibration periods was used (Supplementary Figure S1).] Table 1 lists the concentrations and their isotopic ratios of the standard gases used in this study. These gases were balanced in air, and their concentration values bracketed the range of ambient concentration variability (Figure 3 below). Their CO$_2$ mole fractions were measured with a gas analyzer (model G1301, Picarro) and calibrated against three primary standards obtained from NOAA-
ESRL which were traceable to the WMO 2007 scale reported by the Central Calibration Laboratory of the World Meteorological Organization, and their δ¹³C values were measured with a mass spectrometer (MAT-253, Finnigan) using IAEA reference materials IAEA-CO-8 (-5.76 ‰ VPDB) and IAEA-CO-9 (-47.32 ‰ VPDB). The mass spectrometer measurements of these reference materials were (-5.81 ± 0.04) ‰ and (-46.64 ± 0.08) ‰. The ambient measurement was averaged to hourly intervals. The isotopic ratio was expressed in the delta notation (δ¹³C) in reference to the VPDB scale.

The typical 5-min measurement precision is 0.3 ‰ for δ¹³C and 0.05 μmol mol⁻¹ for CO₂ mole fraction according to the instrument manufacturer. Our own Allan variance analysis revealed a precision of 0.05 ‰ for δ¹³C and 0.07 μmol mol⁻¹ for CO₂ mole fraction at the hourly averaging interval. These improvements were simply statistical, due to the increase in the number of samples being used for averaging. The precision of the ambient measurement was lower than this due to errors propagated through the calibration procedure.

According to a laboratory test on an analyzer of the same model and using the same calibration procedure as ours, the hourly δ¹³C precision is about 0.4 ‰ (Wen et al., 2013).

The calibration gases had much lower δ¹³C than the ambient delta values. The mismatch in the delta value between the calibration standard and the ambient air is common in applications of the IRIS technique [¹³C(CH₄), Röckmann et al. 2016; ¹⁸O(H₂O), Lee et al. 2005; ¹³C(CO₂), Bowling et al. 2003]. For example, Bowling et al. (2003) used calibration standards with delta values of -29.55 ‰ and -40.58 ‰ to calibrate their optical ¹³C(CO₂) instrument. But because the system measures the concentrations of the major and the minor isotopologue independently, it is not critical that the calibration standards and the
measurement target have matching isotope ratios, so long as the standards bracket concentration variability of the target (Bowling et al. 2005). Nevertheless, the overall accuracy of the measurement may be further improved by using calibration standards that bracket variations in both the concentration and the delta values of ambient air samples. We could not implement this improved calibration procedure because our analyzer failed at the end of the experiment.

We did not adopt the strict filtering technique used for background sites (Thoning et al. 1989) because of high natural variations in urban airsheds. We removed the first 3 min of the data after switching to the ambient sampling mode from the calibration mode. Additionally, data were removed if the average hourly CO₂ mole fraction was lower than 390 μmol mol⁻¹ (or 30 μmol mol⁻¹ lower than the midafternoon value in the summer; Figure 3 below) or δ¹³C were out of the range between -15 ‰ and -5.5 ‰ (or about 3 standard deviations from the mean); A total of 217 hourly values were removed by these outlier criteria.

The δ¹³C value measured by the analyzer in high humidity conditions is biased high due to spectral broadening and direct spectral interference (Rella 2011). To correct for the humidity interference, we carried out two tests using a dew-point generator (model 610, LI-COR, Inc., Lincoln, NE). A CO₂ standard gas (secondary standard gas, 439 μmol mol⁻¹ in test one and 488 μmol mol⁻¹ in test two, balanced by dry air) was fed into the dew-point generator. The outlet of the dew-point generator was connected with a 3-way union with one end linked to the inlet of the analyzer and the other open to the room. The humidity level of the air coming out of the dew point generator was regulated at eight levels in a dew-point temperature range of 1 to 30 °C, giving a water vapor mole fraction ranging from 0.66 % to
4.26 % (0.66 to 4.26 cmol mol⁻¹). Measurement at each humidity level lasted 30 min, with the first 5 min excluded from the analysis. Because the ¹³C/¹²C ratio of the standard gas was constant, any observed variations were caused by the humidity artifact. We found that no correction was needed for our analyzer if the water vapor mole fraction was below 2.03 %.

Above this humidity level, the measurement was biased high by 0.46 ‰ for every 1 cmol mol⁻¹ increase in the water vapor mole fraction (Figure 1). This humidity effect is not negligible, but is an order of magnitude smaller than that reported by Rella (2011). The two tests, taken eight months apart, yielded essentially the same result. The correction equation is

\[
\delta^{13}C = \delta^{13}C_{\text{true}}
\]

\[C(\text{H}_2\text{O}) \leq 2.03 \%\] (2a)

\[
\delta^{13}C = \delta^{13}C_{\text{true}} + 0.46 \text{ ‰} (C(\text{H}_2\text{O}) \% - 2.03 \%) \quad C(\text{H}_2\text{O}) > 2.03 \%\] (2b)

where \(C(\text{H}_2\text{O})\) is water vapor mole fraction and was measured by the same isotope analyzer, \(\delta^{13}C\) is the measured isotope delta value (after the two-point calibration), and \(\delta^{13}C_{\text{true}}\) is the true isotope delta value. The ambient vapor mole fraction varied from 0.16 to 3.64 % during the measurement period. About 35 % of the observations exceeded the threshold mole fraction of 2.03 % and required correction. The largest hourly correction was 0.74 ‰. In the following, all the data have been corrected for the humidity interference.

2.2 The ¹³C/¹²C ratio of surface sources (\(\delta_S\))

We applied the Miller-Tans method to estimate the ¹³C/¹²C ratio of the surface source (\(\delta_S\)). Strictly, Equation 1 does not allow a non-zero intercept. When applied to the urban airshed in Los Angeles, Equation 1 does not require an intercept (Newman et al. 2016). But when applied to the data obtained at the monthly time scale in this study, the regression yielded a non-zero
To determine if a shorter time scale would improve the result, we applied the 5-h moving window technique described by Vardag et al. (2016) to the observations made in January and July 2014. Only 4% of the data, all obtained at nighttime, satisfies their data screening criteria. The mean regression equation of this subset is $y = (-26.41 \pm 4.03) x + (428.84 \pm 211.12)$ for January and $y = (-25.64 \pm 6.39) x + (687.83 \pm 264.67)$ for July, where $x$ is $(C_a - C_b)$ and $y$ is $(\delta_a C_a - \delta_b C_b)$. In these analyses, the background CO$_2$ mole fraction and the isotope ratio were those observed at Mount Waliguan (WLG, 36°17’ N, 100°54’ E, 3816 m above the mean sea level; https://www.esrl.noaa.gov/gmd/dv/data/index.php) located at the northeastern edge of the Tibetan Plateau (Zhou et al., 2005), the closest upwind WMO background station for Nanjing. Use of other WMO baseline sites as the background gave essentially the same results.

The selection of a background site is a critical issue when applying the Miller-Tans method (Ballantyne et al., 2011 & 2010). That the Miller-Tans intercept does not go to zero suggests that the baseline site WLG may not be a suitable background for this highly urbanized region. We tested the Miller-Tans method with other isotope data published for urban areas, and found that the intercept was nonzero for most of the urban datasets the data obtained by Sturm et al. (2006) at Bern, Switzerland (Supplementary Figure S3) and a number of other urban datasets (Supplementary Table S1).

In the following, we used the tropospheric CO$_2$ mole ratio calculated by CarbonTracker over the YRD region (altitude 3330 m; https://www.esrl.noaa.gov/gmd/dv/data/index.php) as the background concentration ($C_b$). The CarbonTracker mole ratio is on average 3.5 μmol
mol$^{-1}$ higher than that observed at WLG. To overcome the problem that CarbonTracker does not calculate tropospheric $\delta^{13}$C, we rearranged Equation 1 to a form that allows an intercept but without the need for a known background $\delta^{13}$C, as

$$\delta_{a}C_a = \delta_{S}(C_a - C_b) + \delta_{b}C_b$$ \hspace{1cm} (3)

The $^{13}$C/$^{12}$C ratio of the surface source was taken as the slope of the linear regression of $\delta_{a}C_a$ against $(C_a - C_b)$. A key difference between Equation 3 here and Equation 5 of Miller and Tans (2003) is that the $\delta_{S}$ appears only in the slope parameter in Equation 3 but in both the slope and the intercept parameter in Miller and Tans’ Equation 5. This modified Miller-Tans analysis requires knowledge of background CO$_2$ mole fraction but not $\delta_{b}$.

The Miller-Tans analysis was performed over monthly intervals, using the data collected in daytime hours (10:00 to 16:00 local time) to represent YRD and data collected during nighttime hours (22:00-6:00 local time) to represent Nanjing. Morning and evening transitional periods were omitted to avoid the confounding effects of sign change of the biological CO$_2$ flux and sudden changes in the atmospheric stability regime.

We interpreted the daytime results to represent the influence of surface sources in the YRD region and the nighttime results to represent the influence of surface sources in the Nanjing municipality. The vigorous turbulent exchange in the daytime boundary layer diminishes the role of local sources in the measured concentration and isotopic ratio. In other words, the daytime measurement has a much larger source footprint than the size of the urban land itself or the footprint of the nighttime measurement. In contrast, the buildup of CO$_2$ at night is primarily the result of sources in the city (Shen et al. 2014), so we considered the $\delta_{S}$ determined from the nighttime observations to represent the signal of the sources located in
the city. Admittedly, this interpretation of daytime versus nighttime source areas is a simplification because the actual source area also depends on thermal stratification and boundary layer wind. Nevertheless, it is supported by a trajectory analysis and by an analysis of the atmospheric methane to CO2 emissions ratio (Shen et al. 2014).

For the purpose of comparing with the Miller-Tans results, we also estimated the source $^{13}$C/$^{12}$C ratio using the Keeling mixing line method. According to Wehr and Saleska (2017), for the measurement uncertainties of our instrument system, the ordinary least squares procedure has much lower bias errors of parameter estimation than the geometric mean regression. In the following, the results of both the Miller-Tans method and the Keeling mixing line method were based on the ordinary least squares regression.

### 2.3 Inventory of anthropogenic sources

We calculated the anthropogenic CO2 fluxes from energy consumption and industrial process following the SCOPE 1 procedure issued by the International Council for Local Environmental Initiatives (ICLEI, 2008). The procedure considers only emissions from sources that lie within the geographic boundary of investigation. The energy consumption source consists of direct emissions from the three main energy consumption sectors (industry, transport, and household). We ignored the commerce sector here because the main energy consumption in this sector in Nanjing and in the YRD was electric power generated by coal and coal consumption which was already considered in SCOPE 1. The amounts of CO2 emission were estimated with the IPCC methodology adopting the emission factors for each fossil fuel type recommended by IPCC. The calculations were done separately for the YRD
region and for the Nanjing municipality. Because no statistical data were available for energy
consumption in the transport sector in Nanjing, the CO₂ emission from the transport sector
was deduced according to vehicle number, average annual driving distance and coefficients
of fuel economy (Bi et al. 2011). We obtained the data on energy consumption from official
sources (CESY 2013, CSY 2013, NSY, 2013).
The non-energy industrial processes included cement, raw iron, crude steel, and
ammonia synthesis processes. In the YRD, the data were available at monthly intervals. For
the city of Nanjing, only annual statistics were available.

2.4 Partitioning the net surface flux
We partitioned the surface CO₂ flux (Fₛ) into three component fluxes according to the
following mass conservation equations

\[ F_p = F_f + F_c + F_p \] (4)

\[ \delta_S F_S = \delta_F F_F + \delta_C F_C + \delta_P F_P \] (5)

where \( F_P \) is the flux from fossil fuel combustion and industrial emission except cement
production (termed “fossil plus”), \( F_C \) is the flux due to cement production, \( F_F \) is the biological
flux, and \( \delta_F, \delta_C, \) and \( \delta_P \) are the \( \delta^{13} \)C value of \( F_F, F_C \) and \( F_P \), respectively. These CO₂ mass
fluxes are obtained by dividing the total emission by the surface area within the geographic
boundary of Nanjing or the YRD, having dimensions of mg m\(^{-2}\) s\(^{-1}\). We separated the cement
source from other non-energy consumption industrial processes because its \( ^{13} \)C/\(^{12} \)C ratio is
much higher. In these equations, the monthly net surface flux (Fₛ) and the biological flux (F_P)
are unknowns to be solved for, and all other terms are either provided by the atmospheric
measurement or by the inventory calculation. The partitioning analysis was done for both Nanjing and the YRD using the nighttime and daytime observations, respectively.

The value for $\delta_F$ was the weighted average of the isotope ratio of individual fuel types and industrial processes (Table 2). The delta value of CO$_2$ from cement production is provided by Anders (1994). We adopt a value of (-28.2 ‰) for $\delta_F$ for the YRD and Nanjing, on account of a linear relationship between $\delta_F$ and tree age (Fessenden and Ehleringer 2002), a typical tree age in this region (40 years) and a U-shaped relationship between $\delta_F$ and annual precipitation (Pataki et al. 2007). Our $\delta_F$ is more negative than that reported for a boreal forest (-26.2 ‰; Pataki et al. 2007) but is in closer agreement with the value reported for a Ginkgo tree in Nanjing (-29.3 ‰; Sun et al. 2003). A summary of the isotopic ratios of the four source categories is given in Table 3.

Uncertainties in the delta values of the different fuel types and industrial processes were based on the data found in the references listed in Table 2. The uncertainty in $\delta_F$ was assumed to be ± 1.00 ‰ (Verdag et al. 2016). The mass flux terms $F_F$ and $F_C$ were assumed to have a 10% uncertainty, which is typical of fossil fuel consumption data (Vardag et al. 2016).

To partition the nighttime flux for Nanjing, we assumed that the nighttime $F_F$ was 20% of the daily value. The parameter 20% was determined by the diel variation of the CO$_2$ flux observed with an eddy covariance system in Nanjing (Bai 2011) and in several other cities (Coutts et al. 2007, Song and Wang 2011, Liu et al. 2012). At night, most of the factories in the city were closed and the traffic flow was reduced to about 80% of the daytime volume (Yang et al. 2011).
The partitioning equations are explicit expressions of the mass balance principle. But uncertainties in the isotope delta end members and the anthropogenic fluxes can propagate through these equations, causing uncertainties in the estimation of $F_S$ and $F_P$. Here we used a Monte Carlo analysis to quantify the error propagation. The same analysis has been applied to the partitioning of lake water budgets from isotope end members (Jasechko et al. 2014). The procedure employed a Gaussian distribution for errors in the input variables and an ensemble of 10,000 realizations for each month. Errors in $F_S$ and $F_P$ were computed as one standard deviation of these realizations after excluding the top and bottom 50 extreme ensemble members.

3. Results

3.1. Temporal variations in the CO$_2$ mole fraction and $\delta^{13}$C

The monthly CO$_2$ mole fraction during the summer was slightly lower than in the other seasons (Figure 2). The mean mole fraction was $446.7 \, \mu$mol mol$^{-1}$ and $431.1 \, \mu$mol mol$^{-1}$ for January and July, respectively, giving a seasonal amplitude of $15.6 \, \mu$mol mol$^{-1}$. The mean CO$_2$ mole fraction during the whole experimental period (March 2013 to August 2015) was $439.7 \, \mu$mol mol$^{-1}$, which is $40.6 \, \mu$mol mol$^{-1}$ higher than the value observed at WLG for the same period. In 2014, the calendar year with complete data coverage, the mean CO$_2$ mole fraction was $441.2 \, \mu$mol mol$^{-1}$, which is 42.5 ppm higher than the WLG value for the same year.

The $^{13}$C/$^{12}$C ratio of atmospheric CO$_2$ displayed a more clear seasonal cycle than the mole fraction (Figure 2). The monthly mean value was (-9.07 ± 0.17) ‰ (mean ± standard
error) and (-7.63 ± 0.18) ‰ for January and July, respectively, with a seasonal amplitude of 1.44 ‰. The mean value for the whole experimental period was -8.48 ‰, which is the same as the WLG value (-8.48 ‰). The summertime (June to August) δ¹³C was 0.39 ‰ higher than the WLG background value. The seasonality of the δ¹³C/δ¹²C ratio at Nanjing was greater than that at WLG.

The strongest diel variation in the CO₂ mole fraction was observed in the autumn season (September to November) and the weakest in the winter season (December to February), with a diel amplitude of 27.9 μmol mol⁻¹ and 13.4 μmol mol⁻¹, respectively (Figure 3). In the summer season, the peak value was observed at 07:00 and the lowest value at 19:00. In contrast to the CO₂ mole fraction, δ¹³C showed the lowest value in the early morning and the highest value in the afternoon in all the four seasons. The diel amplitude was 1.36 ‰ in the summer and 0.66 ‰ in the winter.

3.2 δ¹³C/δ¹²C ratio of the surface sources (δₛ)

Figures 4 and 5 show an example of the modified Miller-Tans approach applied to the month of January 2014. According to the slope parameter estimation, the δ¹³C/δ¹²C ratio of the surface sources was (-25.01 ± 0.90) ‰ (mean ± 95 % confidence limit) for the YRD (Figure 4) and (-25.23 ± 0.74) ‰ for Nanjing (Figure 5).

Figure 6 shows the monthly isotopic ratio calculated with the Miller-Tans method for the whole observation period. The reader is reminded here that the results obtained for the daytime and the nighttime period represent sources in the YRD and in Nanjing, respectively. During the two and a half years of observation, the monthly δₛ for the YRD was lower in the...
winter ([-24.37 ± 0.71] ‰) and higher in the summer (-23.42 ± 1.79 ‰). The seasonal difference for Nanjing was smaller than for the YRD ([-24.87 ± 0.51] ‰ in the winter (December to February) and -24.80 ± 1.79) ‰ in the summer months (June to August)]. The sources in the YRD had slightly higher $\delta_S$ than those in in Nanjing. The mean $\delta_S$ value of the whole observational period was (-24.37 ± 0.61) ‰ and (-24.58 ± 0.44) ‰ for the YRD and Nanjing, respectively. The monthly $\delta_S$ for the YRD (Figure 6a) was highly correlated with the monthly atmospheric $\delta^{13}C$ [Figure 2; $\delta_S = (2.29 ± 0.78) \delta^{13}C + (-5.71±6.37)$, linear correlation coefficient = 0.47, n = 30, p <0.01]. The correlation between the monthly $\delta_S$ for Nanjing (Figure 6b) and the monthly atmospheric $\delta^{13}C$ was weak [$\delta_S = (2.39 ± 0.92) \delta^{13}C + (-3.71 ± 8.07)$, linear correlation coefficient = 0.03, n = 30, p = 0.87]. These correlation patterns suggest that atmospheric $\delta^{13}C$ was influenced more by surface sources at the regional scale than at the local (city) scale.

3.3 Inventory data for anthropogenic sources

The emission strength of anthropogenic sources and their $^{13}C/^{12}C$ ratios were calculated with the inventory method and the data found in the literature, as described in section 2.3. In the YRD, coal combustion was by far the largest source of anthropogenic CO$_2$, contributing 70 % of the overall “fossil-plus” emission (Table 2). Here the “fossil-plus” emission includes contributions from all forms of fossil fuel combustion and from non-cement industrial processes. The second and third largest source were ammonia synthesis and pig iron manufacturing, with fractional contributions of about 9 %. The “fossil-plus” source
contribution to the total anthropogenic emission was 91 %, with the remaining 9 %
contributed by cement production (Table 2).

In the Nanjing municipality, the fractional contribution of coal to the “fossil-plus” total
was 52 %, lower than that for the YRD, and the other three major sources were ammonia
synthesis (16 %), pig iron (13 %), and gasoline (11 %). The fractional contribution of fuel-
plus sources to the total anthropogenic emission was 96.4 % and the fractional contribution of
cement production was 3.6 % (Table 2). The isotopic ratio of the “fossil-plus” sources was
0.35 ‰ lower for Nanjing than for the YRD.

The overall effective isotopic ratio of the anthropogenic sources weighted by the source
contributions was also lower for Nanjing than for the YRD (Table 3). The difference was
1.76 ‰ and was a result of lower fractional contributions in Nanjing of coal combustion and
cement production, which have relatively high $^{13}$C contents, and a higher fractional
collection of natural gas, which is the fuel type with the lowest $^{13}$C content.

### 3.4. CO$_2$ fluxes in YRD and Nanjing

Figure 7 shows the biological flux $F_B$ and surface flux $F_S$ calculated from the mass balance,
and the cement flux $F_C$ and “fossil-plus” $F_F$. The $F_B$ flux obtained with the isotopic
partitioning method for the YRD agreed with the seasonal phenology expected for plants in
this region. It was near zero or slightly negative in the summer and generally positive in the
winter, indicating uptake and release, respectively. The annual mean daytime biological flux
was $(0.03 \pm 0.64) \text{ mg m}^{-2}\text{ s}^{-1}$ in the YRD in the calendar year 2014. The net surface flux $F_S$
was $(0.17 \pm 2.02) \text{ mg m}^{-2}\text{ s}^{-1}$ in 2014. The standard deviations of these estimates are quite
large. If the extreme standard deviations of $F_P$ (5.16 mg m$^{-2}$ s$^{-1}$) and $F_S$ (22.00 mg m$^{-2}$ s$^{-1}$) in March 2014 were excluded, the mean standard deviation of $F_P$ would decrease to 0.23 mg m$^{-2}$ s$^{-1}$ for and that of $F_S$ to 0.20 mg m$^{-2}$ s$^{-1}$.

In Nanjing, the biological flux was positive throughout the year (Figure 8). This is because the partitioning was done for the night hours when the natural ecosystems were a source of CO$_2$ due to autotrophic and heterotrophic respiration. The annual mean nighttime biological flux for the calendar year 2014 was $(0.06 \pm 0.26)$ mg m$^{-2}$ s$^{-1}$. The nighttime surface flux was $(0.18 \pm 0.22)$ mg m$^{-2}$ s$^{-1}$ in 2014.

4 Discussion

4.1 CO$_2$ mole fraction and $\delta^{13}$C seasonality

The atmospheric CO$_2$ mole fraction observed in Nanjing showed very small seasonal variation (summer versus winter difference of 7.9 $\mu$mol mol$^{-1}$, July versus January difference of 15.6 $\mu$mol mol$^{-1}$), in comparison with the data published for other cities. For example, in Salt Lake City, USA, the CO$_2$ mole fraction in the summer is about 31 $\mu$mol mol$^{-1}$ lower than in the winter (Pataki et al., 2003). Several factors contributed to the weak seasonality in Nanjing. The climate in the YRD is relatively mild. The governmental energy policy prohibits winter heating in public buildings. Most residential buildings also lack space heating in the winter. This is in contrast to energy use patterns in northern cities in China and elsewhere. The weak seasonality of the observed mole fraction was also related to the low vegetation cover in the YRD and in Nanjing. The forest cover ratio is about 35 % in Nanjing and in the YRD, and the overall vegetation cover (forest plus other vegetation types) ratio in the major
cities in the YRD is lower than 45 % (CESY, 2013; CSY, 2013). For comparison, the vegetation cover ratio is 56 % in Salt Lake City (Pataki et al. 2009) and 44 % in Chicago (Rose et al. 2003). Dense vegetation is known to deplete atmospheric CO2 in the summer season via photosynthetic uptake, amplifying the CO2 seasonal amplitude.

Our $\delta^{13}C$ seasonal amplitude (January versus July difference of 1.44 ‰) was 4 times the amplitude observed or estimated at WLG (Figure 2) but agreed with those reported by most urban studies. For comparison, the seasonal amplitude of $\delta^{13}C_a$ in Bangalore, India, was 0.89 to 1.32 ‰ (Guha and Ghosh 2015). Similar amplitudes have also been reported for Chicago (January versus August difference of 1.25 ‰; Moore and Jacobson, 2015) and Beijing (2.13 ‰; Pang et al. 2016). In Salt Lake City, the seasonal amplitude of $\delta^{13}C$ was approximately 1.6 ‰ because of much more natural gas consumption for heating in the winter than in the summer (Pataki et al. 2006).

4.2 Influences of cement production on atmospheric $\delta^{13}C$

The high summer $\delta^{13}C$ was one of the most unique characteristics at our site. The daytime $\delta^{13}C$ reached -6.90 ‰ in July 2013 and -7.21 ‰ in August 2014, which were 1.28 ‰ and 0.95 ‰ higher than the WLG values. The highest monthly mean $\delta^{13}C$ occurred in July: -7.44 ‰ in July 2013, -7.99 ‰ in July 2014 and -7.46 ‰ in July 2015. These values were 0.74 ‰, 0.16 ‰ and 0.77 ‰ higher than the WLG value reported for the same months.

The high July values observed at our site cannot be fully explained by CO2 removal by plant photosynthesis. Photosynthesis and respiration are the two processes that dominate the $^{13}C/^{12}C$ seasonality in plant-dominated landscapes, leading to higher $\delta^{13}C$ values in the
summer and lower values in the winter. For example, in Park Falls, Wisconsin, USA, a site in a heavily-forested landscape, $\delta^{13}C$ was -7.75 ‰ in August 2011 and -8.77 ‰ in February 2012 (Moore and Jacobson, 2015). For comparison, $\delta^{13}C$ was -8.24‰ and -8.38 ‰ at the Mauna Loa Observatory and -8.02 ‰ and -8.66 ‰ at WLG in these two months, respectively.

In other words, the photosynthetic effect raised the August $\delta^{13}C$ by 0.5 ‰ above the background value, a smaller enrichment than observed at our site. Because of the low vegetation fraction, the summer photosynthetic CO$_2$ uptake in the YRD and in Nanjing should be lower than at Park Falls. According to the CarbonTracker inversion analysis (Peters et al. 2007), the net ecosystem production at the grid point where Park Falls is located is -0.201 mg m$^{-2}$ s$^{-1}$ in July, 2014 but is only -0.059 mg m$^{-2}$ s$^{-1}$ at the grid point corresponding to the YRD region. We would expect from the photosynthetic effect alone that the summertime $^{13}C$ enrichment at our site to be smaller, not greater than that observed at Park Falls.

Furthermore, in a human-dominated landscape, the plant photosynthetic enhancement of $^{13}C$ is offset by the CO$_2$ from fossil fuel combustion which has lower $^{13}C/^{12}C$ ratios than the atmosphere. In Chicago, the monthly mean $\delta^{13}C$ peaked in August at -8.29 ‰ during the calendar year 2011, which is 0.05 ‰ lower than the WLG value for the same month. Similarly, in Beijing, the monthly mean $\delta^{13}C$ peaked at -9.49 ‰ in August 2014, which is 1.23 ‰ lower than the WLG value for the same month.

We suggest that cement production was the contributing factor responsible for the high $\delta^{13}C$ values in the summer. The evidence supporting this interpretation is provided by data in Table 3 and Figure 7. The delta value of anthropogenic CO$_2$ in the YRD would be (-26.36 ± 0.42) ‰ without cement production and increased to (-23.95 ± 0.41) ‰ after inclusion of the
cement source (Table 3). This value is much higher than those reported for other urban lands, such as -30.7 ‰ for Los Angeles, USA (Newman et al. 2008) and about -31 ‰ for Salt Lake City, USA (Bush et al. 2007). The overall surface source $^{13}\text{C}/^{12}\text{C}$ ratio derived from atmospheric measurements (Figure 6; -24.37 ‰ and -24.58 ‰ for the YRD and Nanjing, respectively) was also more enriched than those obtained from atmospheric measurements in other cities, such as (-28.1 ± 0.8) ‰ for Chicago in August and September (Moore and Jacobson, 2015), -32.4 ‰ to -27.4 ‰ for Salt Lake City in the growing season (Pataki et al. 2003), -27.0 ‰ for Beijing in the winter heating season (Pang et al. 2016), and -29.3 ‰ for Los Angeles, USA (Newman et al. 2008).

The influence of cement production on atmospheric $\delta^{13}\text{C}$ has also been suggested for at least two other urban sites. In Bangalore, India, $\delta^{13}\text{C}$ is 0.05 ‰ higher than that observed at an island station in the Indian Ocean, and cement production in southern India is offered as a reason to explain the enrichment of urban $\delta^{13}\text{C}$ (Guha and Ghosh 2015). The other urban site is Beijing, China, where the $\delta^{13}\text{C}$ measurement may have been influenced by cement factories outside the city (Ren et al. 2015, Pang et al. 2016).

**4.3 Net surface and biological fluxes in the YRD**

As a human-dominated landscape, the YRD was a net source of CO$_2$ on the monthly scale even in the growing season ($F_s$, Figure 7). The seasonal trends of the net surface flux $F_s$ and the biological flux $F_p$ were highly correlated with each other ($R^2 = 0.88$ after exclusion of three extreme outliers) because the anthropogenic source strengths were almost constant. The mean $F_s$ between March 2013 and February 2015 was $(0.19 \pm 1.16)$ mg m$^{-2}$ s$^{-1}$, which
consisted of (0.15 ± 0.02) mg m⁻² s⁻¹ from fossil combustion and industrial processes, (0.02 ± 0.002) mg m⁻² s⁻¹ from cement production and (0.05 ± 1.31) mg m⁻² s⁻¹ from biological activities. The total anthropogenic CO₂ flux was (0.17± 0.02) mg m⁻² s⁻¹ in the YRD, a 70 % increase from the value of 0.10 mg m⁻² s⁻¹ reported for 2009 (Shen et al. 2014). From 2009 to 2012, the GDP increased by 56 % according to the National Statistic Yearbook.

For comparison, we extracted the flux data from the CarbonTracker database for the 6 by 6 pixels that cover the YRD region. The results show that the mean daytime (11:00 to 17:00 local time) biological flux is slightly negative at -0.01 mg m⁻² s⁻¹ for 2014 (Peter et al. 2007). Our estimate of F_p for 2014 was (0.03 ± 0.64) mg m⁻² s⁻¹. As pointed out earlier, the F_p value for March 2014 was highly uncertain [(0.21± 5.16) mg m⁻² s⁻¹]; If we replace this value by the mean value of February and April 2014, the 2014 mean F_p would be reduced to (0.02 ± 0.22) mg m⁻² s⁻¹.

A source of uncertainty in our flux partitioning analysis is related to human breath (Affek and Eiler 2006). Using the method of Prairie and Duarte (2007), we estimated that human respiration flux was 0.006 and 0.013 mg m⁻² s⁻¹, or 3.7 % and 11.65 % of anthropogenic emission in the YRD and in Nanjing, respectively. The food diet in the region is predominantly C3 grains. By including this additional source in Equations 3 and 4 and by assuming that the isotopic ratio of digestion is the same as δP shown in Table 3, F_S and F_P would increase by 0.008 and 0.001 mg m⁻² s⁻¹ in the YRD and by 0.018 mg m⁻² s⁻¹ and 0.005 mg m⁻² s⁻¹ in Nanjing, respectively.

4.4 Comparison of the Miller-Tans and the Keeling methods
By applying the Miller-Tans method to daytime and nighttime observations separately, we obtained the effective source ratios that are consistent with the inventory analysis for the YRD and for the Nanjing Municipality. The daytime measurement (Figure 6a, solid circles) revealed that the $^{13}$C/$^{12}$C ratio of the all sources (anthropogenic and biological) was on average 0.21 ‰ higher than that obtained with the nighttime measurement (Figure 6b, solid circles), although the difference is not statistically significant ($p = 0.38$). For comparison, the overall $\delta_S$ of the anthropogenic sources in the YRD was also higher than that in Nanjing, the difference being 2.01 ‰ (Table 3). The interpretation that the daytime observations capture the influence of surface sources in the YRD region is supported by a trajectory analysis and by an analysis of the atmospheric methane to CO$_2$ emissions ratio observed at the same site (Shen et al. 2014). We note that the atmospheric measurements gave a smaller difference between the YRD and Nanjing than that obtained by the inventory data, likely because of different biological contributions between the two spatial scales.

One open question with regard to the modified Miller-Tans method is what constitutes the true background air for the YRD. In this study, the background was assumed to be the tropospheric air above the YRD. The background delta value ($\delta_b$) backed out from the intercepts shown in Figures 4 and 5 is -7.6 ‰, which is higher than expected, suggesting that the true background concentration $C_b$ may be higher than the tropospheric value. One noteworthy feature about Equation 3 is that its slope parameter is not sensitive to $C_b$, but its intercept parameter is. By increasing $C_b$ by 15 μmol mol$^{-1}$, the slope of the regression in Figure 5 would remain unchanged, but the $\delta_b$ backed out from the new intercept value would become more reasonable (-8.23 ‰). In Newman et al. (2016), the background air was
measured at a coastal location upwind of the Los Angeles airshed. It is recommended that a
similar strategy should be used in future experiments, where simultaneous measurement is
made at the coast of East China Sea and only data collected in easterly winds are selected for
the Miller-Tans analysis.

We also calculated the $^{13}$C/$^{12}$C ratio of the surface sources with the Keeling plot method.
Using the daytime data, the Keeling result was lower and more variable than that inferred
from the Miller-Tans method using the daytime data (Figure 6a). The two methods differed
by an average of -1.51 ‰ (Supplementary Table S2).

In comparison, the Keeling plot method showed reasonably good performance when
applied to the nighttime observations. This is because surface inversion conditions effectively
prevented mixing of the free atmospheric air with the surface air, so that the single-source
assumption implicit in the Keeling plot method could be satisfied. When we applied Keeling
plot method at monthly intervals to the nighttime data, the resulting $\delta_S$ showed very similar
month-to-month variations with the value obtained with application of the Miller-Tans
method to the nighttime observations (Figure 6b). The two method differed by an average of
1.21 ‰ (Supplementary Table S2).

When the $\delta_S$ derived from the Keeling plot method was used for flux-partitioning, the
results were much more erratic than shown in Figures 7 and 8 (Supplementary Figures S43
and S44). The uncertainty ranges of the monthly $F_P$ and $F_S$ were two to three times larger. The
biological flux $F_P$ for the YRD was out of range for 4 months, and did not display an obvious
seasonal pattern (Supplementary Figure S43). These results support our choice of the
modified Miller-Tans method as the preferred approach for inferring the overall $^{13}$C/$^{12}$C ratio of the surface sources in this study.

5. Conclusions

We showed that the temporal changes of $\delta^{13}$C followed the seasonal patterns of anthropogenic and biologic CO$_2$ emissions, with lower values in the winter than in the summer. An unusual feature that has not been seen in other urban environments is that the $\delta^{13}$C exceeded that of the background atmosphere in some of the summer months. The highest monthly $\delta^{13}$C was -7.44‰ observed in July 2013, which was 0.74‰ greater than the WLG value for the same month. Evidence points to cement production as the key reason for why the atmospheric $\delta^{13}$C was higher than at the background site. In contrast to the isotope ratio, the CO$_2$ mole fraction displayed very weak seasonality (July to January difference 15.6 µmol mol$^{-1}$).

We hypothesized that the Miller-Tans method applied to the daytime and nighttime observations should yield the effective $^{13}$C/$^{12}$C ratio of surface sources at the regional (YRD) and the local (Nanjing) scale, respectively. According to the results of the modified Miller-Tans method, the effective source $^{13}$C/$^{12}$C ratio in the YRD was -24.37‰, which was 0.21‰ higher than that in the Nanjing Municipality. These results were consistent with inventory estimates of anthropogenic source ratios at these two spatial scales.

By combining inventory data on anthropogenic carbon sources and the atmospheric measurement of CO$_2$ mole fraction and $^{13}$C/$^{12}$C ratio in an isotopic partitioning framework, we inferred that natural ecosystems in the YRD were a negligibly small source of
atmospheric CO₂, with an average flux of \( (0.02 \pm 0.22) \text{ mg m}^{-2} \text{ s}^{-1} \) for 2014. For comparison, the CarbonTracker inverse analysis reveals a small annual mean daytime biological flux (-0.01 mg m\(^{-2}\) s\(^{-1}\)) for this region for 2014.

**Data availability:**

The atmospheric data are available upon request and from the Yale-NUIST Center website http://yncenter.sites.yale.edu/publications.

**Acknowledgments:**

This research was supported by the National Natural Science Foundation of China (Grant 41475141, 41505005), the U. S. National Science Foundation (Grant 1520684), the Ministry of Education of China (Grant PCSIRT), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (Grant PAPD). The first author also acknowledged a visiting scholarship from China Scholarship Council and a Graduate Student Innovation Grant from Jiangsu Provincial Government (Grant KYLX_0848). We thank the handling editor Dr. Jan Kaiser and four anonymous reviewers whose constructive comments have greatly improved this paper.
References


Andres, R. J., Marland, G., Boden, T., Bischof, S. (1994). Carbon dioxide emissions from fossil fuel consumption and cement manufacture, 1751-1991; and an estimate of their isotopic composition and latitudinal distribution, Oak Ridge National Lab., TN (United States);


Figure 1. Dependence of the observed $\delta^{13}C$ on the $H_2O$ mole fraction. The lines represent Equation 2. Error bars are ± one standard deviation of 1-min averages. The data in the left panel was obtained on October 1, 2014 using a 439 $\mu$mol mol$^{-1}$ standard gas and the true $\delta^{13}C$ value of -32.8 ‰, and that in the right panel on June 10, 2015 using a 488 $\mu$mol mol$^{-1}$ standard gas and the true $\delta^{13}C$ value of -34.1 ‰.
Figure 2. Monthly total CO₂ mole fraction (upper panel) and δ¹³C (lower panel): Solid lines with circles: whole-day means; dashed lines with up triangles: daytime (10:00-16:00) means; dashed line with down triangles: nighttime (22:00-6:00) means; smooth solid lines, monthly means observed at WLG.
Figure 3. Mean diel variation of the CO$_2$ mole fraction (upper panels) and the $\delta^{13}$C value (bottom panels) between March, 2013 and August, 2015.
Figure 4. Application of the Miller-Tans method to the daytime (10:00-16:00) data obtained in January 2014. Each data point is one hourly mean. The solid line is the least squares regression according to Equation 3. Errors bounds on the regression coefficients are 95% confidence intervals.
Figure 5. Same as Figure 4 but for nighttime (22:00-6:00) data obtained in January 2014.
Figure 6. Time series of monthly $^{13}$C/$^{12}$C ratio of surface sources in the YRD (a) and in Nanjing (b), obtained from daytime and nighttime measurement, respectively. The error bars are ± one standard deviation of the regression coefficient.
Figure 7. Time series of monthly net surface CO$_2$ flux ($F_S$), biological CO$_2$ flux ($F_P$), anthropogenic CO$_2$ flux excluding cement emission ($F_F$) and cement CO$_2$ flux ($F_C$) in the YRD. All the CO$_2$ mass fluxes are in mg m$^{-2}$ s$^{-1}$. The flux terms $F_F$ and $F_C$ are assumed to have a 10% uncertainty typical of fossil fuel consumption data. The partitioning results ($F_P$ and $F_S$) are based on the source $^{13}$C/$^{12}$C ratio derived from daytime atmospheric measurements.
**Figure 8.** Time series of monthly net surface CO$_2$ flux ($F_S$), biological CO$_2$ flux ($F_P$), anthropogenic CO$_2$ flux excluding cement emission ($F_A$) and cement CO$_2$ flux ($F_C$) in Nanjing. All the CO$_2$ mass fluxes are in mg m$^{-2}$ s$^{-1}$. The flux terms $F_P$ and $F_C$ are assumed to have a 10% uncertainty typical of fossil fuel consumption data. The partitioning results ($F_P$ and $F_S$) are based on the source $^{13}$C/$^{12}$C ratio derived from nighttime atmospheric measurements.
Table 1 Standard gases used for instrument calibration. The mean and standard deviation of the CO₂ mole fraction and Δ²⁹C were based on 6 and 5 repeated measurements, respectively.

<table>
<thead>
<tr>
<th>ID</th>
<th>CO₂ (μmol mol⁻¹)</th>
<th>δ²⁹C (%)</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Low</td>
<td>381.89 ± 0.99</td>
<td>-29.75 ± 0.27</td>
<td>Mar, 2013 - Aug, 2014</td>
</tr>
<tr>
<td>1 High</td>
<td>502.35 ± 0.28</td>
<td>-30.01 ± 0.18</td>
<td>Mar, 2013 - Aug, 2014</td>
</tr>
<tr>
<td>2 Low</td>
<td>380.92 ± 0.95</td>
<td>-29.75 ± 0.27</td>
<td>Sep, 2014 - Aug, 2015</td>
</tr>
<tr>
<td>2 High</td>
<td>501.05 ± 0.33</td>
<td>-30.01 ± 0.18</td>
<td>Sep, 2014 - Aug, 2015</td>
</tr>
</tbody>
</table>
Table 2 Percentage of “fossil-plus” sources and their $\delta^{13}C$ values for the YRD and Nanjing.

The uncertainty in the total “fossil-plus” source is a weighted mean of the individual uncertainties.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Percentage (%)</th>
<th>$\delta^{13}C$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YRD</td>
<td>Nanjing</td>
<td>YRD</td>
</tr>
<tr>
<td>Coal</td>
<td>70.0</td>
<td>52.3</td>
<td>-25.46 ± 0.39</td>
</tr>
<tr>
<td>Gasoline</td>
<td>2.1</td>
<td>11.4</td>
<td>-28.69 ± 0.50</td>
</tr>
<tr>
<td>Diesel</td>
<td>3.2</td>
<td>1.6</td>
<td>-28.93 ± 0.26</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>2.1</td>
<td>0.3</td>
<td>-29.32 ± 0.15</td>
</tr>
<tr>
<td>Natural gas</td>
<td>2.7</td>
<td>5.0</td>
<td>-39.06 ± 1.07</td>
</tr>
<tr>
<td>LPG</td>
<td>0.7</td>
<td>0.2</td>
<td>-31.70 ± 0.40</td>
</tr>
<tr>
<td>Pig iron</td>
<td>8.7</td>
<td>12.7</td>
<td>-24.90 ± 0.40</td>
</tr>
<tr>
<td>Crude steel</td>
<td>1.5</td>
<td>0.7</td>
<td>-25.28 ± 0.40</td>
</tr>
<tr>
<td>Ammonia synthesis</td>
<td>9.0</td>
<td>15.9</td>
<td>-28.18 ± 0.55</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>-26.36 ± 0.42</td>
</tr>
</tbody>
</table>
Table 3. Inventory data for the isotopic composition of surface CO$_2$ sources and their percentage of contribution in the YRD and in Nanjing. Here the “fossil-plus” category includes all non-cement anthropogenic emissions listed in Table 2. The cement isotopic ratio is based on Andres et al. (1994). The uncertain range in the biological isotope ratio is based on Vardag et al. (2016).

<table>
<thead>
<tr>
<th>Sources</th>
<th>YRD $\delta^{13}$C (‰)</th>
<th>Percentage (%)</th>
<th>Nanjing $\delta^{13}$C (‰)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fossil-plus”</td>
<td>-26.36 ± 0.42</td>
<td>91.0</td>
<td>-26.97 ± 0.46</td>
<td>96.4</td>
</tr>
<tr>
<td>Cement</td>
<td>0 ± 0.30</td>
<td>9.0</td>
<td>0 ± 0.30</td>
<td>3.6</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>-23.99 ± 0.41</td>
<td>100</td>
<td>-26.00 ± 0.45</td>
<td>100</td>
</tr>
<tr>
<td>Biological</td>
<td>-28.20 ± 1.00</td>
<td>——</td>
<td>-28.20 ± 1.00</td>
<td>——</td>
</tr>
</tbody>
</table>