Response to Review 1

This manuscript examines the multi-year CO_2 and $^{13}CO_2$ time series as measured in Nanjing, China. Compared to other urban centers the seasonal $^{13}CO_2$ amplitude is much smaller attributed to weak biological sink in the summer, reduced anthropogenic emissions in the winter, and ^{13}C signature from cement production. They infer the ^{13}C source within Nanjing and the Yangtze River Delta by performing a Keeling regression during the night-time hours, and a Miller-Tans regression during the daytime hours, and also compare this seasonal cycle to other urban centers around the globe.

In general, it is an important contribution to expand this type of analysis to industrialized areas of China in an effort to provide more complete global coverage of CO_2 emissions, partitioning, and ^{13}C signatures. It was especially interesting to see how this region behaved compared to other urban centers. My main concerns with the manuscript are as follows:

Main concern 1)
There seems to be a misunderstanding by the authors in the purpose of implementing the Keeling vs. Miller-Tans approaches to calculating the ^{13}C source. The authors suggest in line 105 'the intensity of traffic emission varies strongly through the diurnal cycle. And therefore the effective source ^{13}C signature cannot be assumed constant." Both methods, whether they are Keeling or Miller Tans cannot account for a varying source ^{13}C signature over the diurnal cycle because this manuscript grouped the data into monthly aggregates, therefore either method will calculate a mean diurnal and even monthly signature, UNLESS the data is aggregated into finer time increments, morning, afternoon etc, which the authors have not done. However, they do not necessarily have to do this if they are only looking for ^{13}C source changes across months.
The true benefit of the Miller-Tans approach, which the authors do not make clear, is that it accounts for varying BACKGROUND variation of both CO_2 and $^{13}CO_2$, thereby isolating only the local source contributions. Although this reviewer agrees with the authors that by performing a regression on the daytime readings it is representative of the greater YRD area, and that by performing a regression upon the night-time readings the footprint of the ^{13}C source is more localized (although not always because even at night there can be sufficient mixing of the boundary layer during windy, unstable conditions, -the authors do not address this), this reviewer fails to see why the Miller Tans approach was not applied to both night-time and day-time readings. It is likely the more complete method, because it will correct for background variation, which even under stable night-time conditions will play a role in the observed night-time $\delta^{13}C$. It would have been instructive to perform both methods during the night, and then use the ^{13}C source inventory data to try to justify one approach over the other.

*

In response to this comment and the comments made by the other two reviewers, we now apply the Miller-Tans method to both daytime and nighttime data. In the discussion section, we have added a short paragraph to compare this method with the Keeling plot method:

"We argue that Keeling plot method is not appropriate for daytime periods because the surface air is influenced by both the surface sources and by entrainment of the background air from above the boundary layer. If we applied the Keeling method to the daytime observations, the

linear correlation coefficient was on average -0.898 which is weaker than the correlation coefficient obtained with the Miller-Tans method (-0.956). The resulting mean $\delta^{13}C_S$ would be 0.61‰ lower than the mean value shown in Figure 6. The difference in $\delta^{13}C_S$ between the YRD (daytime observations, Keeling method) and Nanjing (nighttime observations, Miller-Tans method) would become too small (0.15‰).

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 was satisfied. If we applied Keeling plot method at monthly intervals to the nighttime data, the resulting $\delta^{13}C_S$ would decrease to -24.24‰ for Nanjing from -23.72‰, the value obtained with application of the Miller-Tans method to the nighttime observations."

We also acknowledge in the methods section that our method has omitted the influences of wind conditions:

"…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 CO_2 emissions ratio (Shen et al. 2014)."

Main concern 2)
The authors never truly justify the use of MLO (the Mauna Loa Observatory) as a background site for their study. I would have liked an explanation that MLO represents the marine boundary layer, and is relatively unaffected by landmass contributions of anthropogenic and biogenic CO_2. Why did the authors use a site that was so far removed from Nanjing as a background correction? Air from MLO has to pass through North America, Europe and much of Asia before it reaches the site of interest, therefore it is likely a poor background. A similar type of analysis was performed globally (Ballantyne 2010, 2011) which discussed the issue of a background site when performing Miller Tans regression. This manuscript could have benefitted by reviewing that work, and at least discuss the motivation for using MLO.

*
In response to this suggestion, we have replaced MLO with Mount Waliguan (WLG, 36°17'N, 100°54'E, 3816 m above the mean sea level) as the background site. WLG is located at the northeastern edge of the Tibetan Plateau, and is the closest upwind NOAA background site for our study region.

This switch changes the monthly mean source signature slightly, from the original -23.25‰ to -23.26‰ for the YRD and from -24.24‰ to -23.72‰ for Nanjing. The change for Nanjing is larger because we have also replaced the original Keeling method with the Miller-Tans method in the analysis of nighttime observations.

The papers by Ballantyne et al. (2010 and 2011) are now cited.

Main concern 3)
I would have liked a better explanation of the ecological system: vegetation type, climate conditions etc. It would have been instructive to understand the growing conditions in Nanjing to better understand the seasonal cycle in carbon flux, and how it influenced the overall carbon flux. It was also unclear to me why Park Falls, Wisconsin was used as biological example to explain some of the behavior in Nanjing. They seem to be from two entirely different ecosystems.

*

We have added the following text:

"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 main vegetation types are subtropical evergreen broad-leaved forest and shrubs, and the main crops are rice and winter wheat, all of which are C3 species."

We chose Park Falls because it is a well-documented site. Our main point is that even at a site with high photosynthetic activity (and hence high photosynthetic ^{13}C enrichment of atmospheric CO_2), the summer time $\delta^{13}C$ is lower than that of the background atmosphere. So we would expect $\delta^{13}C$ in the YRD which has low photosynthetic activity, to be even lower. But our observation shows the opposite.

Main concerns 4)
There was no explanation for how the CO_2 and $\delta^{13}CO_2$ data was evaluated for quality. Was all raw data assumed to be valid? If that is the case the regressions could have been subject to large errors. Some explanation is necessary regarding qa/qc procedure of data.

*

We have added the following text in the methods section:

"The typical 5-min measurement precision is 0.3‰ for $\delta^{13}C$ and 0.05 ppm for CO_2 mole fraction according to the instrument manufacturer. Our own Allan variance analysis revealed a precision of 0.05‰ for $\delta^{13}C$ and 0.07 ppm for CO_2 mole fraction at the hourly averaging interval. 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 40 3-minute data points during the transient periods after calibration gas changes. Additionally, data were removed if hourly CO_2 mole fraction was lower than 390 ppm or $\delta^{13}C$ were out of the range between -15‰ and -5.5‰.

Detailed Comments:
(1) Line 33: Do not use the term midnight and midday observations, because it makes it seem that only 12AM and 12PM readings were taken. Instead label this as night-time vs. day-time readings. Do this throughout the paper.

*We now use “daytime” and “nighttime” throughout the paper.

(2) Line 31-32: “The highly enriched ^{13}C signal was attributed to the influence of cement production in the region.” This is misleading because in the discussion you provide other reasons, and this was only one of them.

* We change the description to “The highly enriched ^{13}C signal was partly attributed to the influence of cement production in the region.”

(3) Line 90: Instead of “various” say something like “highly resolved” to emphasize the fine temporal nature of the measurements.

*Changed as recommended.

(4) Line 129: Need a citation.

*Citation added.

(5) Line 134-135: You use the term ‘plant’ in this paper to describe both vegetation/biology, and a cement manufacturing ‘plant’. This is confusing and suggest you use ‘biological’ flux instead of ‘plant flux’.

*Thank you. We have replaced “cement plant” with “cement factory” and used ‘biological’ flux instead of ‘plant flux’.

(6) Line 140: You never explain the delta notation of ^{13}C ($\delta^{13}C$). This requires a definition and an equation.

*We do not feel that there is a need for an equation because the delta notation is widely used. We did point out the notation is in reference to the VPDB standard.

(7) Line 146-147: “Table 1 lists the concentrations and their isotopic composition of the standard gases used in this study”. This is not true. Table 1 does not show this.

*Thank you for pointing out this omission. This table is now added.

(8) Lines 191-196: I assume you fitted the MLO data of both CO_2 and $\delta^{13}C$ with a harmonic fit, then used this as the background for your regressions for all years 2013-2015. This is not clear from the text.

*Yes. The text here has been improved:
“…we fitted the WLG data of both CO_2 and $\delta^{13}C$ with a four-harmonic quadratic function (Thoning et al. 1989) using the dataset from 2000 to 2014, and then used the function to estimate the monthly $\delta^{13}C_b$ and C_b values for 2015.”

(9) Lines 198-200: This is a key point, but is hidden deep in the text. Would suggest that wherever you use daytime or nighttime readings in the figures, also explain that they represent YRD and Yanjing respectively for this reason.

*Suggestion adopted.

(10) Line 204 and line 209: Terminology of 'scope one' is strange. Either capitalize it, or remove.

*We have replaced the term with "SCOPE 1", and have given a definition:
"The procedures consider only emissions from sources that lie within the geographic boundary of investigation."

(11) Line 279-280: It's unclear what you mean by 'data consistency check' and what purpose Figures 4 and 5 serve in the manuscript, if, as you suggest they violate the constant $\delta^{13}C$ requirement. A more relevant comparison of methods would be to perform full comparison of the Keeling and Miller-Tans method for determining $\delta^{13}C$ source.

*We have rephrased the text as: "So these data plots are meant more to show the range of variations of the hourly observations than for determining the true annual mean source signatures."

(12) Line 294-297: Not sure if this is necessary, it what this text is actually saying is statistically significant. Does this fall within the range of regression uncertainty?

*This short paragraph has been removed.

(13) Line 342-367: Very good discussion. Very informative.

*Thank you for your encouragement.

(14) Line 374: Get rid of negatives in front of o/oo.

*Removed.

(15) Line 380: Of course MLO is going to have negligible shift in $\delta^{13}C$ and CO_2, it is a marine boundary layer site in the middle of the Pacific Ocean. This should be discussed here, and also as to why it was chosen as the background.

*Please refer to our response to main point 2.

(16) Line 385: I found it peculiar that you chose Park Falls as a region in carbon-tracker as a comparison to Nanjing. Park Falls is at a far higher latitude, a forest, and no-where near an urban center. I understand that you are just making a comparison of $\delta^{13}C$ response to strength of biological carbon sink, but still it seemed strange to me.

*Please refer to our response to main point 3.

(17) Line 389-393: How do you suppose that emission in Nanjing during the summer season impacted the seasonal cycle? Earlier in the paper you mentioned that the government regulated limited heating in the winter (very low heating emissions). I wonder is the same enforcement exist in the summer (air conditioning)?

*No. The government does not restrict use of A/C in the summer. The inventory data available to us does not permit assessment of the emission seasonality, but according to a study for Shanghai, a city also in the YRD, the emission differs by less than 1% between the summer and the winter season (Liu et al. 2013, ACP, 13, 10873).

(18) Line 394: "cement production was factor responsible for high $\delta^{13}C$". I found this a bit strong. Maybe say a 'contributing factor'.

*Suggestion adopted.

(19) Line 416: instead of 'highly consistent' should use 'varied coherently' or 'highly correlated'

*Replaced with 'highly correlated'

(20) Line 438-440: What about the impact of methodology: Keeling vs. Miller-Tans approach at causing this difference?

*This cannot be explained by methodological difference (main point 1)

(21) Line 441-443: This is not a sufficient condition to violate the Keeling curve approach. You have to demonstrate that the background source is changing in flux magnitude for ^{13}C signature.

*We agree.

(22) Line 449-451: It is not clear to me why this condition will violate the Miller-Tans approach, or why the Keeling approach should be preferred under these conditions.

*Please refer to response to main point 1.

(23) Table 1: I don't like the use of 'fossil-plus' as a description of all non-cement anthropogenic emissions. It's not an intuitive description at all, and unless one reads deep into the text the reader cannot tell what it is. At least you should put it in quotations, or just get rid of that label. Also you should make it clear here in Table 1 and in all figures that: Also YRD: derived from daytime readings, Nanjing: derived from night-time readings

*We now put the term in quotations as "fossil-plus". In Table 3 and in the main text this term has been clearly explained:

“Here the “fossil-plus” category includes all non-cement anthropogenic emissions listed in Table 2.”

(24) Table 2: Remove ‘plant’ and put ‘biological’. Plant can refer to a manufacturing facility.

*Corrected

(25) Figure 1: You should make clear that this is the ‘dependence of the observed STANDARD GASES of $\delta^{13}C$’. Also it would be nice what the ‘corrected’ values are after applying equation (2).

*Clarified.

(26) Figure 2: The line markers need to be larger so you can tell the difference. The descriptions of the markers need to be better too. Extremely disappointing that MLO was defined as Mortgage Loan Origination, instead of Mauna Loa Observatory. Shows a complete lack of understanding of the science by contributor who created plot, and should have been caught by co-authors.

*This embarrassing mistake has been corrected. Figure quality has been improved according to your suggestion.

(27) Figure 3: State that this is for years 2013-2015.

*Done.

(28) Figure 4: Unclear what ‘valid’ midday data was. Was there a data filter on your raw data?

*Please refer to our response to main point 4

(29) Figure 6: Do error bars represent the ‘regression’ error from the Miller-Tans and Keeling approaches? Also would be nice to show both the Miller-Tans and Keeling regressions for night and day.

*Yes, the error bars represent the regression error from the Miller-Tans regression.

Response to Review 2

The authors use bottom-up inventories of various sectors producing local anthropogenic emissions of CO_2 combined with expected values of the stable carbon isotopic signatures of these emissions and measurements of ambient air to solve for the biosphere's emissions from Nanjing and the Yangzte River Delta region, using mass balance calculations. The most important contribution of this paper is evidence of contributions to the emissions of an urban region by cement production, as indicated by values of $\delta^{13}C$ of the high CO_2 end member that are higher than background and than those expected from the biosphere. The authors use Keeling plot intercepts and Miller-Tans slopes to determine the isotopic compositions of the local anthropogenic emissions for the city of Nanjing and the Yangtze River Delta, using nighttime and daytime measurements, respectively.

Main concern 1)
My major concern in this paper is the use of the two different methods for determining ^{13}C for the high CO_2 end members. Why are two methods necessary? If concern is for varying background, then the Miller-Tans method is the method to use, since the Keeling plot method assumes that both end members remains constant during the time period of the data being examined. The authors mention that the Keeling plot method is appropriate at night because there is no mixing of free tropospheric air and boundary layer air when there is a stable shallow nocturnal boundary layer. However, most of the CO_2 in the nocturnal boundary layer is background, with mole fractions of 400-550 ppm, as seen in Figure 5, and the background used, from Mauna Loa Observatory (MLO), contains about 400 ppm. Therefore, there is mixing of background air and local emissions. The Miller-Tans method should probably be used for all of the data.

*We now use the Miller-Tans method for both time periods (Response to Review 1, main point 1).

Main concern 2)
Another important issue is whether the MLO data are the appropriate background to use. As shown by Turnbull et al. (2015) for Indianapolis, use of different backgrounds are appropriate for getting at the influence of emissions in different domains. Such a remote site as MLO may not be appropriate for looking at the sources of emissions in the region of Nanjing and the Yangtze River Delta. The background air there may be influenced by processes in the surrounding area, that may produce seasonal variations different from those observed at MLO.

*We have replaced MLO with Mount Waliguan (WLG) as the background site. The paper by Turnbull et al. (2015) is now cited (Response to Review 1, main point 2).

Main concern 3)
Please give uncertainties in measurements and values derived from them.

*We have provided information about measurement uncertainties (Response to Review 2, main point 4). We have also (1) performed Monte Carlo simulations to assess error propagation in the flux partitioning analysis, and (2) in response to review 3, have estimated errors arising from human metabolism. The following text has been added to the discussion section:

"We conducted Monte Carlo simulations to assess the sensitivity of the partitioned fluxes to uncertainties in $\delta^{13}C_P$ and $\delta^{13}C_F$. Errors in these parameters were assumed to follow a uniform distribution and varied in the range of ±1‰. The mean and standard deviation of F_S were 0.167 and 0.003 mg $m^{-2}s^{-1}$, and those of F_P were -0.005 and 0.003 mg $m^{-2}s^{-1}$, respectively for the YRD, based on an ensemble of 10,000 simulations. For Nanjing, the mean ± standard deviation of F_S and F_P was 0.209 ± 0.024 and 0.086 ± 0.022 mg m^{-2}s, respectively. These mean flux values are essentially the same as those obtained with the default $\delta^{13}C_P$ and $\delta^{13}C_F$ values giving in Table 3 and the standard deviations represent uncertainties of the partitioned fluxes.

Another 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 signature of human respiration is the same as $\delta^{13}C_P$ 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."

Specific comments:
(1) Throughout: use "mole fraction" not "mole fraction"

*Corrected

Detailed Comments:
(1) Line 29: insert "δ" before "^{13}C"

*Added

(2) Lines 32-35: Consider adding a sentence explaining that you distinguish between signals from the city of Nanjing and the YRD by looking at data collected at the same site at night and during the day, respectively, consistent with differing diurnal footprints. This is a very important part of your analysis.

*Added.

(3) Line 33: Replace "midnight" with "nighttime" and "midday" with "daytime". "Midnight" is a specific moment of the day.

*Corrected through whole paper.

(4) Line 51: insert "fuel" after "fossil"

*Added

(5) Line 58: capitalize "Ternberg"

*Corrected as "Sternberg".

(6) Line 77: "reveals" should be "reveal"

*Corrected.

(7) Line 82: "deployed" should be "employed"

*Corrected.

(8) Line 120: See Newman et al., 2016, ACP for 8 years of ^{13}C data in a megacity Line 125: "include" should be "includes"

*This paper is now cited. The typo is corrected.

(9) Line 129: Reference?

*A reference is added.

(10) Line 145: Is 5 minutes enough time to settle and measure for good statistics? Picarro specs are for 5-minute averages, but you have to run the standard for at least a few minutes first in order to stabilize on this instrument, especially if your standards are dry and your ambient air stream is not. What are the statistics for accuracy and precision of your standards?

*Because we used very small tube to deliver the standard gas, the transition to step change was fast enough so that 5 min sampling was adequate. (We did discard the data in the first 3 min after valve switching.) Humidity is not an issue because humidity was measured simultaneously and its effect was removed by firmware.

We have added a sentence here to clarify our calibration procedure:
"(To avoid transient effects, only the data collected in the last 2 minutes was used.)"

We have added the information on measurement precision (Response to Review 1, main point 4).

(11) Line 150: "NOAA-EASL" should be "NIST" (The NOAA group is NOAA-ESRL, but these standards are from NIST.)

*Corrected.

(12) Lines 156-157: There is no power plant on campus?

*There is no power plant on campus.

(13) Line 159: Delete "at"

*Removed.

(14) Line 175: Add "%" after "2.03" What are the uncertainties of your measurements, and how do the corrections for H_2O to $\delta^{13}C$ affect them?

*Since we defined H in the text as volume %, we choose not to include the unit in the equation.

The magnitude of the humidity correction is shown in Figure 1. Please also refer to Response to Review 3, detailed comment (9)

(15) Line 182: Zobitz et al. (2006, Agricultural and Forest Meteorology 136, 56-75) recommended ordinary least squares regression as introducing less bias to the results relative to geometric mean regression.

*We adopted the GMR for two reasons. First, there exists a self-correlation between the dependent and independent variables of the Miller-Tans scatter plot. The GMR can reduce the error caused by the self-correlation. Second, the OLS has a better performance only when the CO_2 range of variables is small (< than 20 ppm). But in the present study the range of variation was greater than 80 ppm on monthly intervals.

(16) Lines 181-187: See discussion above. Monthly intervals may be too long to consider that the background isotopic composition has remained constant. It would be more appropriate to use the Miller-Tans method.

*Done.

(17) Line 189: The first "Ca" should be "Ca–Cb".

*Corrected.

(18) Lines 198-200: The footprints during nighttime and daytime are critical to this study comparing the city and the region. Therefore it would be good to show back trajectories, at least in an appendix, indicating that the nighttime data emphasize the city and the daytime data include air coming in from a much broader region.

*The trajectory analysis was performed in an earlier study (Shen et al. 2014) showing that the daytime source area extends to the YRD. Our argument that nighttime observations had a smaller source area is based on the fact that CO_2 and pollution buildups in stable stratification is restricted mostly to the urban airshed, and is in agreement with the analysis of the CO_2 to methane emissions ratio for Nanjing (Shen et al. 2014).

(19) Line 203: Where are the results of these calculations presented, in Table 1? "process" should be "processes".

*Corrected.

(20) Line 204: Please explain what "the scope one procedure" is. This is not commonly known in this field.

*We have added this sentence:
"The procedure considers only emissions from sources that lie within the geographic boundary of investigation."

(21) Line 208: How are the emissions from electricity generation considered?

*Coal is the main fossil used to generate electricity. We only included the coal consumption in geographic boundary. Electricity imported from outside the YRD is not included in the SCOPE I emission.

(22) Line 219: This might be a good place to have a transition that explains how you are going to derive the important biospheric contribution. "biosphere" is probably a better term to use than "plant"

*Done.

(23) Line 231: Consider replacing "solved" with "determined".

*Replaced

(24) Lines 237-243: You only mention trees? What about grasses? C4 versus C3 plants?

*Please refer to Response to Review 1, main point 3.

(25) Line 260: Consider replacing "stronger" with "larger". Do you mean that the relative seasonality is larger for $\delta^{13}C$ than for CO_2 mole fraction?

*Replaced.

(26) Line 269: Are times given as local time?

*Yes. This is now noted.

(27) Lines 274-280: What is the conclusion of this paragraph – that the two methods give the same value over the same period? But then you say that the methods are not strictly valid over the entire period? Please see discussion of the Keeling plot and Miller-Tans methods above.

*We have rephrased the text here:

"…violating the condition of constant source signal under which the method can be used. So these data plots are meant more to show the range of variations of the hourly observations than for determining the true annual mean source signatures."

(28) Lines 294-297: Are the values being compared statistically distinct? Give uncertainties, including propagated errors where appropriate.

*Please see the response to main concern 3.

(29) Line 300: need a transition sentence here indicating how you got the values given below

*Done.

(30) Line 304: replace "fuel" with "fossil"

*Corrected

(31) Line 311: Is "0.35‰" a statistically significant difference?

*This difference was derived from the inventory estimates. We did not perform a statistical test.

(32) Line 341: See Newman et al. (2016, ACP) for a similar discussion for Los Angeles.

*This paper is now cited. Thank you.

(33) Line 401: Add ", respectively" after "Nanjing".

*Added

(34) Lines 435-438: Give more details explaining these pieces of evidence supporting your conclusion, so the reader does not have to go to this paper.

*Since the paper is already quite long, we chose to keep the conclusion section concise.

(35) Lines 444-445: Are these correlation coefficients statistically different?

*Yes. The p value is now indicated in the figure.

(36) Line 448: How do you know that 0.38‰ is "too small"? How do you know what the correct value is?

*We compared it with the bottom-up method: the difference between the overall $\delta^{13}C_S$ of the anthropogenic sources in the YRD and Nanjing is 1.76‰ (Table 3)

(37) Figure 1. The isotopic compositions of the tanks used are industrial CO_2, not ambient. The values are much lower than those measured in the study. Have you tested whether the H_2O correction is dependent on the value of $\delta^{13}C$?

*This is a good point. We did not evaluate the $\delta^{13}C$ dependence on both the CO_2 concentration and the ambient humidity. However, the dependence on the CO_2 concentration itself has already been corrected by our calibration procedure.

(38) What are the 2 panels – different tanks? different time periods?

*Yes. They are from two tests with different tanks. This is now noted in the figure caption.

(39) Figure 2. Move the year labels to the bottom – I didn't notice them at first.

*Edited

(40) Line 798: What does the phrase "The solid line with cycle" mean – "The solid lines with circles"? What does this represent? "Mortgage Loan Origination" must mean "Mauna Loa Observatory" but suggests some lack of care in proof reading!

*These errors have been corrected. Thank you for catching these embarrassing errors.

(41) Figure 3: Standard errors/standard deviations to show uncertainties and variability of the data?

*These are 95% confidence bound from the regression. (It is now noted in the figure caption.)

Response to Review 3

The study presents CO_2 and $\delta^{13}C$ data from a densely populated area in China. The diurnal and seasonal cycles in CO_2 mole fraction and ^{13}C composition are discussed in detail. The authors apply the Keeling and Miller – Tans methods for estimating the night and day-time emission signatures, and assume these represent the fluxes in Nanjing and YRD respectively. The plant and total fluxes are calculated using combined mole fractions and isotope mass balance. One interesting point is the significant contribution of CO_2 from cement production to the total CO_2 isotopic signature.

I think such a paper is in principle interesting and useful, especially for this high emission region, however I see some issues with the manuscript in its current form.

Main concern 1) Measurement quality (precision and accuracy)

I did not find sufficient information on the measurement precision and accuracy estimates. Through the paper, the isotope values are given with two decimals – does this reflect the real precision?

*This information is now added (Response to Review 1, main point 4).

Main concern 2) Use of Mauna Loa (MLO) as a background

The choice of the background site is important, since a significant part of the paper is related to the differences between the measurement site and the background. The choice of MLO as a background is not convincingly supported in the paper. I would think the air masses do not pass over MLO before arriving at Nanjing, but please state this in the paper if they do.

A second issue with this site is the unavailability of the data for the time interval of interest. The MLO background used here is extrapolated from the 2000 – 2013 dataset. This is an additional source of error, at both intra-annual and inter-annual scales.

I recommend (1) explaining the MLO choice or using a more suitable background, and (2) using actual data, if they became available in the meantime.

*We have replaced MLO with another more suitable site as the background (Response to Review 1, main point 2). The extrapolation was done only for 2015. But if we exclude the data for 2015, our conclusions would still stand.

Main concern 3) Use of Miller-Tans versus Keeling plots

The authors promise in the Introduction to evaluate the use of Miller-Tans and Keeling methods. However, I didn't find a real evaluation. The authors choose to apply Miller-Tans during day and Keeling during night, and the tentative argumentation on why these choice are correct

comes mostly afterwards in discussion (Sect. 4.4). Some of the arguments used are also not valid in my opinion, like the fact that the results would change if the other method was used, see e.g. line 448.

Another issue, that comes I think from a misunderstanding, is as follows. The Miller-Tans method had the advantage (over the Keeling method) that it can take into account a variable background. It does however not need a variable background. Thus Miller Tans method can in principle be used during night time as well. The fact that the surface inversion prevents vertical mixing during night (see lines 449 – 451) does not forbid the use of Miller-Tans method. In any case, the way it is applied here, the Miller-Tans method would not account for the variable background within one night, but only on monthly time scale.

The Miller-Tans method has also a potentially significant disadvantage, that is, the results are dependent on the choice of the background. An error in the background will produce an error in the isotopic signature calculate. In view of point 2 above, please estimate the error in $\delta^{13}C$ that is due to the MLO data processing (fitting and extrapolation).

As the authors show in Sect. 4.4, the differences between MLO, YRD and Nanjing would be quite different if the same method were used for both YRD and Nanjing. That means, for example, that part of the signal that is interpreted as cement influence could be in fact an artifact due to different data processing.

Please consider either using the same method, or demonstrate the use of the two methods for two sites better, including estimating and discussing the errors.

*Thank you for your suggestion. We now use the same method (Miller- Tans) for both daytime and nighttime period. The result is not very sensitive to choice of the background site. (Response to Review 1, main point 1).

Main concern 4) Photosynthesis (fractionation) not taken into account

The Miller-Tans (MT) method was used for estimating the day-time fluxes. This method assumes that we have a background and an emission, but no sink. In reality, however, both uptake and emission are present during day. The photosynthesis flux and its ^{13}C discrimination can affect the MT results, and this is not a simple linear effect that can be easily corrected for. I think this should be taken into account in calculations, or at least the potential error should be discussed.

*As pointed out by the reviewer, the exact ^{13}C signature of the photosynthesis flux is not known. (In our analysis, it was assumed to be the same as the ^{13}C of plant materials found in the region.) In response, we have conducted a Monte Carlo simulation to provide an error bound to the partitioned fluxes (Response to Review 2, main point 3).

Main concern 5) Day and night plant fluxes

The plant fluxes seem to be an important result of the paper, and are compared to other estimates, for example from Carbon Tracker. I think it should be stated very clearly that these are night (respiration) flux for Nanjing and day (mainly photosynthesis) flux for YRD. They should not be given as plant fluxes (e.g. lines 416, 425, 474…), but it should always be specified what they actually are. Since the day-night difference in plant fluxes can be large, none of these day or night fluxes can be assumed as representing the overall plant flux and should not be directly compared to overall fluxes from e.g. Carbon Tracker.

*Suggestion adopted.

Main concern 6) CO_2 from human breath

It has been shown that CO_2 from human respiration can account, in densely populated areas, for a significant proportion of the total CO_2 emitted (Lopez et al., 2013; Prairie and Duarte, 2007). For example in Paris, human respiration CO_2 can be 15% of the fossil fuel CO_2 (Lopez et al., 2013). Measurements of ^{13}C-CO_2 in human breath give $\delta^{13}C$ values of -24.5 to-22.3 (Affek and Eiler, 2006, Horvath et al., 2012), thus slightly enriched compared to the "fossil plus" category in this study.

Has this contribution been estimated? If yes, it should be mentioned; if not, I think this should be done, as the YRD region population is about 140 million.

*This is a very interesting point. In response, we have added a paragraph in the discussion section to address this issue (Response to Review 2, main point 3).

Detailed Comments:
(1) page 3, line 42: plant uptake is not a source, consider reformulating

*Edited

(2) page 3, lines 48 – 49: please give values or send to the information in the paper

*Reference added

(3) page 5, lines 104 – 106: "the intensity of traffic emissions varies … and therefore the effective source ^{13}C cannot be assumed constant" – I do not see the causality here, maybe something missing? – please check

*We have modified the text as:
"…the intensity of traffic emissions varies strongly through the diurnal cycle (McDonald et al. 2014), and therefore the composition of the surface source varies, and its ^{13}C signature cannot be assumed constant."

(4) page 6, lines 115 – 118: I do not understand this statement. Both Keeling and Miller-Tans methods make this assumption. The difference is that the Miller-Tans method can account for a

background that varies.

*We now state:
"We argue that because this approach takes into account the fact the background atmosphere varies, it is more suitable than the Keeling method for inferring $\delta^{13}C_S$ from the observations made in the urban area with complex emission sources"

(5) page 7, Methods: I think a subsection on Nanjing and YRD (location, population, climate, plant types C3/ C4) etc is missing.

*This information is added (Response to Review 1, main point 3).

(6) page 7, Methods: please consider moving the information from page 8, lines 153 – 159 to line 141, after the phrase ending in "2015".

*Moved

(7) page 7, line 146: I could not find this information on the standard gases in Table 1, or anywhere else; I think however it should be included.

*Added.

(8) page 8, line 168: please give also the relative humidity values, for comparison with the values given later

*Done.

(9) page 9, line 178: What was the humidity range in the real atmospheric measurements? How large was the correction? What is the potential error resulted from this correction?

*In response, we have added the following text:
"The ambient humidity varied from 0.16 to 3.64 V% during the measurement period. About 35% of the observations exceeded the threshold humidity of 2.03%V and required correction. The largest hourly correction was 0.74‰."

The potential error from this correction is not known. But the fact that the two dewpoint tests done at two different times yielded nearly identical correction factors indicated that this post-field correction method was reasonably robust.

(10) pages7-9, Sect. 2.: Please discuss the precision and the accuracy of the measurements.

*This information is now added (Response to Review 1, main point 4).

(11) page 9, line 181 and through the paper: "midnight" and "midday" are misleading. Consider using "nighttime" and "daytime".

*Changed

(12) page 9, line 182: what is the "geometric regression"?

*We meant to say "geometric mean regression".

(13) page 9, line 189: The Miller-Tans slope was obtained by linear regression of (δaCa-δbCb) against (Ca-Cb)

*Corrected.

(14) page 9, line 191: please specify more precisely what data were used for MLO, and give a reference; also give coordinates

*Done.

(15) pages 10–11, Sect 2.3: I could not understand most of this section, please consider re-writing. Is "scope one" a name? Line 209 "already considered in scope one" – is this not the discussion about the scope one? Lines 209 – 210: "CO_2 emission were estimated with IPCC methodology…" – were these not estimated following scope one (line 204)? Line 214: vehicle number, average annual driving distance …- are these not statistical data?

*Clarified and references added wherever appropriate.

(16) page 11, line 229: I think the cement source was separated from the other fossil fuel sources

*Yes. It is named "fossil-plus".

(17) page 11, line 229: please give values for the source signatures, or send already to the tables containing them.

*Added.

(18) page 12, line 257: "value observed at MLO for the same period" – this is misleading, the values used in this paper are not observed, but calculated based on previous years. (same for page 18, line 374)

*Edited.

(19) page 13, lines 274–276: Please state clearly (again) that the Miller-Tans was applied to daytime data and is considered to represent YRD, and Keeling was applied to night time data and represents Nanjing.

*Added.

(20) page 14, line 281: I suggest to state here that Fig 6 shows monthly ^{13}C signatures calculated

again with the Keeling method for the night and the Miller- Tans method for the day, and only afterwards comment on the results.

*Edited.

(21) page 15, lines 304 and 309: "is "fuel-plus" the same "fossil-plus" used before?

*Corrected. (Fuel-plus was a typo.)

(22) page 15, line 320: I suggest to first state that Fig. 7 shows the Fp and Fs calculated from the mass balance, and the Fc and Ff obtained …. (how), and only afterwards discuss the results. Also, from here the fluxes are given in mg/m2s – how were these obtained from the inventories mentioned before? (this info should be included in the Methods section)

* These suggestions are adopted. The flux density was computed as the ratio of the total emission to the geographic area. We have added this sentence:
"These fluxes are obtained by dividing the total emission by the surface area within the geographic boundary of Nanjing or YRD, having dimensions of mg CO_2 $m^{-2}s^{-1}$."

(23) page 16, line 324: the "annual mean plant flux" is in this case daytime flux, please specify.

*Edited

(24) page 16, line 325: "the plant flux" is in this case the night-time flux, and it could only be positive.

*Correct.

(25) page 17, line 350: Fig. 2 does not show energy use seasonality

*Figure 8 does not show seasonality, consistent with a previous study for a nearby city showing that winter-versus-summer change is less than 1% (Response to Review 1, point 17).

(26) page 17, line 356: what about the vegetation cover outside cities?

*This information is now added (Response to Review 1, main point 3).

(27) page 18, line 374: can you exclude, as a reason for the high $\delta^{13}C$, any calibration issue?

*Except for the high humidity interference—which we have corrected, we could not find any instrument related issues that can cause the high values.

(28) page 19, lines 394 – 395: does the cement production have a strong seasonality? Why would it have a seasonal effect?

*Yes. There is some seasonality (Figures 8 and 9) primarily related to the Chinese New Year

holidays.

(29) page 21, lines 435 – 437: I think such explanations should be included in the method

*Moved to method.

(30) page 39, Fig 7: please add error bars if possible

*We prefer to discuss the error in the text (Response to Review 2, main point 3).

(31) page 40, Fig 8: please add error bars if possible

*We prefer to discuss the error in the text (Response to Review 2, main point 3).

(32) general comment: the paper does not take advantage of the high frequency Picarro data, why? If it's a technical reason, it should be stated in the method section.

*The high frequency data was actually used in determining the source signature.

Text / technical comments
(1) page 3, line 58: typo in Yakir and Sternberg

*Corrected.

(2) page 4, line 66: I think "the fact the degree …" should be " the fact that the degree", please check

*Corrected.

(3) page 4, line 68: typo, "to quantity" should be "to quantify"

*Corrected.

(4) page 5, line 104: I think "strictly do not hold" should be "do not strictly hold" – please check

*Corrected.

(5) page 9, line 175: typo H>2.03'

*Corrected

(6) page 11, line 222: "we partitioned net …" should be "we partitioned the net" – please check

*Corrected.

(7) page 11, line 236: I think "the cement isotopic composition" should be "the isotopic composition of CO_2 from cement production"

*Corrected.

(8) page 17, line 355: "the overall he vegetation cover" – typo?

*Corrected as "the overall vegetation cover".

(9) pages 17 – 18, lines 365 – 366: "because much more" should be "because of much more" – please check

*Corrected.

(10) page 31, line 767 – 768: "Mortgage Loan Origination" should be "Mauna Loa Observatory"; same for page 34, lines 800 – 801

*Thank you for pointing out this embarrassing mistake.

(11) page 34, line 798: "monthly total" should be "monthly mean"?

*Corrected.

(12) page 34, line 798: "the solid line with cycle" – something seems to be missing

*Corrected.

Interpreting the $^{13}C/^{12}C$ ratio of carbon dioxide in an urban airshed in the Yangtze River Delta, China

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Abstract: Observations of atmospheric CO_2 ~~molar fraction~~mole fraction and its ^{13}C isotope composition ($\delta^{13}C$) in urban airsheds provide constraints on the roles of anthropogenic and natural sources in local and regional C 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 CO_2 ~~molar fraction~~mole fraction and $\delta^{13}C$ were 439.7 ppm and -8.48‰ over this observational period. The peak monthly mean $\delta^{13}C$ (-7.44‰, July 2013) was 0~~1~~.7403‰ higher than that observed at the ~~Mauna Loa Observatory~~Mount Waliguan. The highly enriched ^{13}C signal was partly attributed to the influence of cement production in the region. By applying ~~the Keeling plot and~~ the Miller-Tans method to ~~midnight~~ nighttime and ~~midday~~daytime observations~~, respectively,~~ to~~for~~ represent~~ing~~ signals from the city of Nanjing and the YRD, respectively, ~~compared with the results of applying the Keeling plot line method.~~ ~~–~~we showed that the ^{13}C signal of C sources in the Nanjing Municipality was 0.48‰ lower than that in the YRD. Flux partitioning calculations revealed that natural ecosystems in the YRD were a negligibly small sink of atmospheric CO_2, consistent with the Carbon Tracker inverse modeling result.

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Keywords: urban areas; CO_2 flux; Industrial process; Carbon isotope; In-situ observation

1 Introduction

Atmospheric CO_2 sources and sinks in urban areas consist mainly of plant uptake and release and fossil fuel combustion. These ~~sources~~contributors have ~~their~~ unique ^{13}C isotopic signatures. City clusters are human-dominated systems with high carbon emission intensity, contributing over 70% of the total anthropogenic CO_2 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 isotopic signature of carbon dioxide released by cement production, which is much heavier than that of fossil fuel origin (Andres et al. 1994). Likewise, the CO_2 emitted from burning of minerals in non-energy consumption industrial processes, such as iron and steel production, has higher ^{13}C composition than that of fossil fuel (Table 1, Widory 2006). In China, cement production and industrial processes contribute 13% of the total anthropogenic CO_2 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 $\delta^{13}C$ budget.

One scientific motivation for quantifying the ^{13}C signature of atmospheric CO_2 is that it provides constraints that allow partitioning of the net surface flux into component fluxes (Farquhar and Lloyd 1993, Yakir and ~~ternberg~~ Sternberg 2000, Pataki et al. 2003). The ^{13}C-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,

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Zimnoch et al. 2004, Newman et al. 2008, Jasek et al. 2014). Compared with vegetation ecosystems, urban ecosystems have more complex CO_2 source configuration. 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 composition of CO_2 in an urban atmosphere was made by Friedman and Irsa (1967). Since then, a few more experiments have been conducted in urban environments. The data collected have been used to partition CO_2 contributors (Koerner and Klopatek 2002, Clark-Thorne and Yapp 2003), to quantify diurnal variations in the CO_2 ~~molar fraction~~mole fraction and its $\delta^{13}C$ in urban air (Zimnoch et al. 2004, Guha and Ghosh 2010) and across urban to rural gradients (Lichtfouse et al. 2003, Pataki et al. 2007), and variations among different land uses in urban areas (Clark-Thorne and Yapp 2003, Widory and Javoy 2003). The isotopic data reveal~~s~~ insights into energy consumption patterns (Widory and Javoy 2003, Bush et al. 2007), impacts of meteorology including temperature (Clark-Thorne and Yapp 2003, Zimnoch et al. 2004), atmospheric stability (Pataki et al. 2005) and wind (Clark-Thorne and Yapp 2003) on urban carbon cycling, and the role of vegetation phenology (Ehleringer et al. 2002, Takahashi et al. 2002, Wang and Pataki 2012). The analytical technique em~~de~~ployed in these studies is mainly based on mass-spectrometry (MS). Because sample collection, preparation and analysis are

labor intensive, the majority of these studies are limited to short campaigns (less than 60 days).

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 CO_2 ~~molar fraction~~mole fraction and its $\delta^{13}C$ at high frequencies (1 Hz to 1 hour; Pataki et al. 2006, Griffis. 2013, ~~–~~Gorski et al. 2015). Compared with the MS method, IRIS can capture diurnal or even shorter temporal variations with relatively high accuracy, enabling us to understand how anthropogenic emissions change atmopheric CO_2 at highly resolved~~various~~ temporal and spatial scales. Nevertheless, application of the IRIS technology in urban monitoring is still limited in terms of cities covered and measurement duration: ~~(~~less than 35 days in~~;~~ McManus et al. (2002), Pataki et al. 2006 and~~;~~ Wada et al. (2011) and~~;~~ 3 seasons in ~~;~~Moore and Jacobson (2015). O~~and o~~nly one published study has presented data that spans one full annual cycle (Pang et al. 2016).

Simultaneous measurement of atmospheric CO_2 concentration and its isotopic composition is used to determine the overall isotopic signature of local surface sources $\delta^{13}C_S$. All published urban studies to date have deployed the Keeling plot method (Keeling 1958, Keeling 1961) for the determination of $\delta^{13}C_S$. In this approach, a linear relationship is established between $\delta^{13}C$ and the reciprocal of the CO_2 ~~molar fraction~~mole fraction from the observed time series, and the intercept of the linear regression is taken as the isotopic composition of the local CO_2 emissions. The method assumes that the isotopic signature of the sources is invariant with time. It also assumes that changes in the CO_2 ~~molar fraction~~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 ~~do not~~ hold in an urban environment because the intensity of traffic emissions varies strongly through the diurnal cycle (McDonald et al. 2014), and therefore the composition of the surface~~effective~~ source varies, and its ^{13}C signature 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 $\delta^{13}C_S$ be determined as the slope of the linear relationship

$$\delta_a C_a - \delta_b C_b = \delta^{13} C_s (C_a - C_b) \quad (1)$$

where C_a is CO_2 ~~molar fraction~~mole fraction in urban air, C_b is CO_2 ~~molar fraction~~mole fraction in a background site ~~[taken in this study as that observed at the Mauna Loa Observatory~~Mount Waliguan ~~(MLOWLG)]~~, δ_a is ^{13}C isotopic composition of C_a, and δ_b is ^{13}C isotopic composition of C_b. We argue that because this approach ~~t~~takes into account ~~mixing of CO_2 generated locally with CO_2 in the~~the fact the background atmosphere varies, ~~, thereby isolating only the local source contribution. So this method~~ it is more suitable than the Keeling method for inferring $\delta^{13}C_S$ from the observations made in the urban area with complex emission sources~~the daytime when such mixing occurs~~. ~~–~~The method has been applied to local and regional carbon budget studies in nonurban settings (Miller et al. 2003). Here we~~We are not aware of studies that~~ extend the method to an urban environment.

In this study, we report the results of long-term (30 months) continuous measurement of atmospheric CO_2 ~~molar fraction~~mole fraction and its $\delta^{13}C$ at a suburban site in Nanjing using

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an IRIS instrument. Nanjing is the second largest city in the Yangtze River Delta (YRD), Eastern China, with a build-up area of 753 km^2 and a population of 8.2 million. Geographically, the YRD includes the provinces of Jiangsu, Zhejiang and Anhui and the Shanghai municipality (29.04°-33.41°N, 118.33°-122.95°E) with a population of 1.9 hundred million. The YRD is influenced by subtropical moist monsoon climate. The mean annual temperature is about 15ºC and the annual precipitation is between 1000 mm and 1800 mm. The main vegetation types, all of which are 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~~Our~~ objectives of this study are (1) to characterize the atmospheric $\delta^{13}C$ diurnal, 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 $\delta^{13}C$, (3) to evaluate the performance of the Keeling plot and the Miller-Tans method for determining $\delta^{13}C_S$, and (4) to explore the utility of the isotopic constraints for inferring the net surface flux and the plant CO_2 flux in Nanjing and in the YRD.

2 Methods

2.1 Atmospheric observation

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An IRIS analyzer (model G1101-i, Picarro Inc., Sunnyvale, CA) was used to measure atmospheric CO_2 ~~molar fraction~~mole fraction and its ^{13}C isotope composition ($\delta^{13}C$) 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 anthropogenic 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 ~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 was used.) Table ~~1~~ 12 lists the concentrations and their isotopic compositions of the standard gases used in this study. The CO_2 ~~molar fraction~~mole fraction of the standard gases was traceable to the WMO 2007 scale reported by the Central Calibration Laboratory of the World Meteorological Organization and their $\delta^{13}C$ was based on the NBS-19 and the NBS20 standards of NIST~~NOAA-EASL~~. The ambient measurement was averaged to hourly intervals. The isotopic composition was expressed in the delta notation ($\delta^{13}C$) in reference to the VPDB scale.

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~~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 anthropogenic 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. Lt and the Nanjing Chemical Industry Group, was located at ~ 5 km to the south of the site.~~

The typical 5-min measurement precision is ~~±~~0.3‰ for $\delta^{13}C$ and 0.05 ppm for ~~12~~CO_2 mole fraction according to the instrument manufacturer. Our own Allan variance analysis revealed a precision of 0.05‰ for $\delta^{13}C$ and 0.07 ppm for CO_2 mole fraction at the hourly averaging interval. W~~,~~ ~~w~~e did not adopt the strict filtering technique used for~~as~~ background sites ~~used~~ (Thoning et al. 1989)~~,~~ because of high natural variations in urban airsheds. We removed 40 3-minute data points during the transient periods after calibration gas changes. Additionally, data were removed if hourly CO_2 mole fraction was lower than 390 ppm or $\delta^{13}C$ were out of the range between -15‰ and -5.5‰.

The $\delta^{13}C$ measured by the analyzer in high humidity conditions suffers a high bias error 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 CO_2 standard gas (secondary standard gas, 439 ppm in test one and 488 ppm 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

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out of the dew point generator was regulated at eight levels in a dew-point temperature range of 1 and 30°C, giving a humidity ranging from 0.66 V% to 4.26 V%. Because the ^{13}C composition 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 humidity was below 2.03%. Above this humidity level, the measurement was biased high by 0.46‰ for every 1% increase in the water vapor volume, or ~~molar fraction~~mole fraction (Figure 1). The two tests, taken eight months apart, yielded essentially the same result. The correction equation is

$$\delta^{13}C = \delta^{13}C_{true} \quad H \le 2.03\% \quad \text{(2a)}$$

$$\delta^{13}C = \delta^{13}C_{true} + 0.46(H - 2.03) \quad H > 2.03\% \quad \text{(2b)}$$

where H is water vapor volume ~~molar fraction~~mole fraction in percent, $\delta^{13}C$ is the measured isotopic composition (after the two-point calibration), and $\delta^{13}C_{true}$ is the true isotopic composition. The ambient humidity varied from 0.16 to 3.64 V% during the measurement period. About 35% of the observations exceeded the threshold humidity of 2.03%V and required correction. The largest hourly correction was 0.74‰. In the following, all the data has been corrected for the humidity interference.

2.2 The isotopic composition ($\delta^{13}C_S$) of surface sources

~~We applied the Keeling plot method to the data collected during midnight hours (22:00-6:00 local time). We used the geometric regression to establish a linear relationship between the~~

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~~hourly $\delta^{13}C$ and the reciprocal of the hourly CO_2 molar fraction over monthly intervals. The intercept of the regression gives the effective isotopic composition of net surface CO_2 emissions. The buildup of CO_2 at night is primarily the result of sources in the city (Shen et al. 2014), so we considered the $\delta^{13}C_S$ determined from the nighttime observations to represent the signal of the sources located in the city.~~

We applied the Miller-Tans method to the data collected in ~~midday~~daytime hours (10:00 to 16:00 local time; Equation 1) to represent YRD and to the data collected during nighttime hours (22:00-6:00 local time) to represent Nanjing. The slope was obtained by linear regression of (C_a-C_b) against ($\delta_a C_a$-$\delta_b C_b$)~~, again~~ over monthly intervals. The monthly mean CO_2 ~~molar fraction~~mole fraction and the isotopic composition of the background air were those observed at ~~MLO~~~~WLG~~Mount Waliguan (WLG, 36°17'N, 100°54'E, 3816 m above the mean sea level; Zhou et al., 2005) located at the northeastern edge of the Tibetan Plateau, the closest upwind background station for Nanjing. Because the ~~MLO~~WLG data were not available for 2015 at the time of this analysis, we fitted the WLG data of both CO_2 and $\delta^{13}C$ with a four-harmonic quadratic function (Thoning et al. 1989) using the dataset from 2000 to 2014, and then used the function to estimate the monthly $\delta^{13}C_b$ and C_b values for 2015. ~~we first established a four-harmonic quadratic function (Thoning et al. 1989) using the dataset from 2000 to 2013, and then used the function to estimate the monthly $\delta^{13}C_b$ and C_b values for 2015.~~

The selection of a background site is a critical issue when applying the Miller-Tans method (Ballantyne et al., 2011 & 2010, Turnbull et al., 2015). Ideally, the background site should not be affected by local and regional emission and should lie~~s~~ in the upwind direction

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of the observation site. Based on these criteria, we chose WLG as the background site for our analysis.

~~We also applied the Keeling plot method to calculate $\delta^{13}C$ in YRD and Nanjing by using data in daytime and nighttime. We used the geometric regression to establish a linear relationship between the hourly $\delta^{13}C$ and the reciprocal of the hourly CO_2 mole fraction over monthly intervals. The intercept of the regression gives the effective isotopic composition of net surface CO_2 emissions.~~

We interpreted the daytime results to represent the influence of surface sources in the YRD region and ~~interpreted~~ the nighttime results to represent the influence of surface sources in the Nanjing. ~~B~~T~~ecause t~~he vigorous turbulent exchange in the daytime boundary layer diminishes the role of local sources in the measured concentration and isotopic ratio, ~~or~~ I~~i~~n 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, ~~And~~ the buildup of CO_2 at night is primarily the result of sources in the city (Shen et al. 2014), so we considered the $\delta^{13}C_S$ 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 ~~This interpretation is also~~ supported by a trajectory analysis and by an analysis of the atmospheric methane to CO_2 emissions ratio (Shen et al. 2014).

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~~The vigorous turbulent exchange in the midday boundary layer diminishes the role of local sources in the measured concentration and isotopic ratio, or in other words, the midday measurement has a much larger source footprint than the size of the urban land itself or the footprint of the midnight measurement. Hence we interpreted the midday results to represent the influence of surface sources in the YRD region. This interpretation is supported by a trajectory analysis and by an analysis of the atmospheric methane to CO_2 emissions ratio (Shen et al. 2014).~~

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2.3 Inventory of anthropogenic sources

We calculated the anthropogenic CO_2 fluxes from energy consumption and industrial process following the SCOPE 1~~scope one~~ procedure~~, which only includes direct emissions from sources within the geographic boundary of investigation,~~ 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 consist~~sed~~ 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~~ SCOPE 1~~one~~. The amounts of CO_2 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 ~~both~~ the YRD region and for the Nanjing municipality. Because no statistical data were available for energy consumption in the transport sector in Nanjing, the CO_2

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 ~~net~~ the surface CO_2 flux (F_S) into three component fluxes according to the following mass conservation equations

$$F_S = F_F + F_C + F_P \quad (4\text{~~3~~}) \qquad \delta^{13}C_S F_S = \delta^{13}C_F F_F + \delta^{13}C_C F_C + \delta^{13}C_P F_P \quad (5\text{~~4~~})$$

where F_F 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_P is the biological~~plant~~ flux, and $\delta^{13}C_F$, $\delta^{13}C_C$, and $\delta^{13}C_p$ are the ^{13}C isotope composition of F_F, F_C and F_P, respectively. These fluxes are obtained by dividing the total emission by the surface area ~~And F_F and F_C are the unit CO_2 emission~~ within the geographic boundary of Nanjing or YRD, having dimensions of mg CO_2 $m^{-2}s^{-1}$. We separated the cement source from other non-energy consumption industrial processes because its isotopic signature is much higher. In these equations, the monthly net surface flux (F_S) and the biological~~plant~~ flux (F_P) are unknowns to be solved, and all other terms are either provided by the atmospheric measurement or by the inventory calculation. The partitioning analysis was done for both

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Nanjing and the YRD using the ~~midnight~~ nighttime and ~~midday~~daytime observations, respectively.

The $\delta^{13}C_F$ was weighted average of the $\delta^{13}C$ signal of individual fuel types and industrial processes (Widory 2006; Table 2~~1~~). The ~~cement~~ isotopic composition of CO_2 from cement production is provided by Tans (1981) and Anders (1994). We adapt a value of (-28.2‰) for $\delta^{13}C_P$ for the YRD and Nanjing, on account of a linear relationship between $\delta^{13}C_P$ and tree age (Fessenden and Ehleringer 2002), a typical tree age in this region (40 years) and an U-shaped relationship between $\delta^{13}C_P$ and annual precipitation (Pataki et al. 2007). Our $\delta^{13}C_P$ 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 compositions of the three source categories is given in Table ~~2~~3.

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 diurnal 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).

3. Results

3.1. Temporal variations in the CO_2 ~~molar fraction~~mole fraction and $\delta^{13}C$

The monthly CO_2 ~~molar fraction~~mole fraction during the summer was slightly lower than in the other seasons (Figure 2). The mean ~~molar fraction~~mole fraction was 446.7 ppm and 431.1 ppm for January and July, respectively, giving a seasonal amplitude of 15.6 ppm. The mean CO_2 ~~molar fraction~~mole fraction was 439.7 ppm during the whole experimental period (March 2013 to August 2015), which is 40.6~~7~~ ppm higher than value observed and estimated at ~~MLO~~WLG for the same period. In 2014, the calendar year with complete data coverage, the mean CO_2 ~~molar fraction~~mole fraction was 441.2 ppm, which is 42.5 ppm higher than the ~~MLO~~WLG value for the same year.

The ^{13}C composition of atmospheric CO_2 displayed a larger~~stronger~~ seasonal cycle than the ~~molar fraction~~mole fraction (Figure 2). The monthly mean value was -9.07‰ and -7.63‰ 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 ~~slightly more negative~~same as ~~than~~ the ~~MLO~~WLG value (-8.4~~8~~4‰). The summertime (June-August) $\delta^{13}C$ was 0.39~~55~~‰ more enriched than the ~~MLO~~WLG background value.

The strongest diurnal variation in the CO_2 ~~molar fraction~~mole fraction was observed in the autumn season and the weakest in the winter season, with a diurnal amplitude of 27.9 ppm and 13.4 ppm, respectively (Figure 3). In the summer season, the peak value was observed at 07:00 and the lowest value at 19:00. Contrary to the CO_2 ~~molar fraction~~mole fraction, $\delta^{13}C$ showed the lowest value in the early morning and the highest value in the afternoon in all the four seasons. The diurnal amplitude was 1.36‰ in the summer and 0.66‰ in the winter.

3.2 Isotopic composition of the surface sources ($\delta^{13}C_S$)

~~Again, Both Miller-Tans and Keeling plot method were applied to daytime data and nighttime data. Daytime data is considered to represent YRD and nighttime data is considered to represent Nanjing.~~ Applying ~~the Miller-Tans method and the Keeling plot~~the Miller-Tans~~is~~ approach to the whole experimental period yielded an apparent source signature of -24~~5~~.75~~51~~±0.26‰ (mean ± 95% confidence bound) for sources in the YRD (Figure 4) and -24~~5~~.24~~99~~±0.21‰ for sources in Nanjing (Figure 5). Strictly, this~~neither~~ method is not accurate when applied ~~valid~~ over such an extensive period because the source signature varies seasonally, violating the condition of constant source signal under which the method~~s~~ can be used. So these data plots are meant more ~~as a data consistency check~~to show the range of variations of the hourly observations than for determining the true annual mean source signatures.

Figure 6 shows the monthly ^{13}C signature~~s~~ calculated ~~again~~ with the Miller-Tans method for the daytime and nighttime. 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 $\delta^{13}C_S$ was lower in the winter and higher in the summer ~~(Figure 6)~~. The sources in the YRD had higher ^{13}C compositions than those in in Nanjing. The January mean value (mean of January 2014 and January 2015) was -24.13‰ and -24.78~~4.66~~‰, and the mean value of the three August months was -20.~~66~~67‰ and -2~~23~~.~~35~~76‰ for the YRD and Nanjing, respectively. The mean value of the whole observational period was -23.~~25~~26‰ and -~~24~~23.~~24~~72‰ for the YRD and Nanjing, respectively. These mean values based on the monthly analysis were 1~~2~~.49~~26~~‰ and

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0‰.5275‰ greater than the apparent source signatures derived from the application of the Miller-Tans method to ~~and the Keeling method to~~ the whole dataset (Figures 4 and 5)~~, respectively~~. The monthly $\delta^{13}C_S$ for the YRD (Figure 6) was highly correlated with the monthly atmospheric $\delta^{13}C$ (Figure 2; linear correlation = 0.63, n = 30, $p < 0.001$). The correlation between the monthly $\delta^{13}C_S$ for Nanjing and the monthly atmospheric $\delta^{13}C$ was not as strong (linear correlation = 0.2652, n = 30, $p = <0.2201$).

~~There appears to be some inter-annual variability in $\delta^{13}C_S$. In the YRD, the 12-month mean $\delta^{13}C_S$ was -23.321‰ from March 2013 to February 2014 and -23.276‰ from March 2014 to February 2015. The atmospheric $\delta^{13}C$ also showed an increasing trend, from -8.36‰ in the first period to -8.15‰ in the second period.~~

3.3 Inventory data for anthropogenic sources

The emission strength~~Inventory data of~~~~for~~ anthropogenic sources and their isotopic signature were calculated with~~based on~~ the inventory method 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~~1~~). Here the "fossil-plus"~~fossil-plus~~ emission includes contributions from ~~combustion of~~ all forms of fossil fuel and from non-cement industrial processes. The second and third largest source were ammonia synthesis and pig iron, with fractional contributions of about 9%. The ~~fuel~~"fossil-plus"~~-plus~~ source contribution to the total anthropogenic emission was 91%, with the remaining 9% contributed by cement production (Table 2).

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In the Nanjing municipality, the fractional contribution of coal to the "fossil-plus" ~~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~~1~~). The isotopic signature of the "fossil-plus" ~~fossil-plus~~ sources was 0.35‰ lower for Nanjing than for the YRD.

The overall effective isotopic signature of the anthropogenic sources weighted by the source contributions was also lower for Nanjing than for the YRD (Table 3~~2~~). 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 contribution 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_P and surface flux F_S calculated from the mass balance, and the cement flux F_C and "fossil-plus" F_F. The ~~plant flux~~ F_P flux obtained with the isotopic partitioning method for the YRD agreed with the seasonal phenology expected for plants in this region ~~(Figure 7)~~. It was slightly negative in the summer and positive in the winter, indicating ~~net~~ uptake and ~~net~~ release, respectively. The annual mean daytime biological~~plant~~ flux ~~in daytime (YRD) for the calendar year 2014~~ was -0.01 mg $m^{-2}s^{-1}$ i~~-~~n the YRD in the calendar year 2014. The net surface flux F_S ~~in daytime (YRD)~~ was 0.16 mg $m^{-2}s^{-1}$.

In Nanjing, the biological~~plant~~ flux was positive throughout the year. This is because the partitioning was done for the night hours when the natural ecosystems were a source of CO_2

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due to autotrophic and heterotrophic respiration. The flux was greater in the summer than in the winter (Figure 8). The annual mean nighttime biological~~plant~~ flux ~~in nighttime (Nanjing)~~ for the calendar year 2014 was 0.~~06~~ 03 mg $m^{-2}s^{-1}$. The ~~net~~ nighttime surface flux ~~in nighttime (Nanjing)~~ was 0.~~18~~ 16 mg $m^{-2}s^{-1}$.

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4 Discussion

4.1 CO_2 ~~molar fraction~~mole fraction and $\delta^{13}C$ seasonality

The atmospheric CO_2 ~~molar fraction~~mole fraction observed in Nanjing showed very small seasonal variation (summer versus winter difference of 7.9 ppm, July versus January difference of 15.6 ppm), in comparison with the data published for other cities. The CO_2 ~~molar fraction~~mole fraction difference between the cold and the warm season is about 66 ppm in Phoenix, USA (Idso et al. 2002). In Salt Lake City, USA, the CO_2 ~~molar fraction~~mole fraction in the summer is about 31 ppm lower than in the winter (Pataki et al., 2003). In Chicago, USA, the CO_2 ~~molar fraction~~mole fraction varied from 397 ppm in August 2011 to 427 ppm in January 2012, showing a seasonal amplitude of 30 ppm (Moore and Jacobson 2015). In Beijing, China, the seasonal variation of atmospheric CO_2 ~~molar fraction~~mole fraction is about 64.5 ppm (August versus January; Pang et al. 2016). However, a similar small seasonal amplitude of 5 ppm CO_2 was observed in Pasadena, USA during 2006 to 2013, which was consistence with the seasonal variation of background and emission from fossil fuel combustion (Miller et al. 2016).

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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

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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. In London, UK, natural gas usage in the winter heating season is 29% greater than in the non-heating autumn season (Helfter et al. 2011). In Salt Lake City, USA, energy consumption in the winter was 41% greater than in the summer (Bush et al, 2007). A similar seasonal trend of energy consumption has also been reported for Beijing (Pang et al, 2016). In Chicago, natural gas usage varied 70% to 80% in winter and about 50% in summer (Moore and Jacobson 2015). The weak energy use seasonality in the YRD ~~(Figure 2)~~ partially explains why the observed CO_2 ~~molar fraction~~mole fraction had a smaller seasonal amplitude (Figure 2) than reported for other northern cities.

The weak seasonality of the observed ~~molar fraction~~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 ~~he~~ 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 CO_2 in the summer season via photosynthetic uptake, amplifying the CO_2 seasonal amplitude.

Our $\delta^{13}C$ seasonal amplitude (January versus July difference 1.44‰) was ~~30~~ 4 times the amplitude observed or estimated at ~~MLO~~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 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 ~~midday~~daytime $\delta^{13}C$ reached -6.90‰ in July 2013 and -7.21‰ in August 2014, which were 1.28~~57~~‰ and 0~~1~~.95~~11~~‰ higher than the ~~MLO~~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~~1~~.74~~03~~‰, ~~-~~0.16~~44~~‰ and -0.77~~93~~‰ higher than the ~~MLO~~WLG value reported for the same months.

The high July values observed at our site cannot be fully explained by CO_2 removal by plant photosynthesis. Photosynthesis and respiration are the two processes that dominate the ^{13}C seasonality in plant-dominated landscapes, leading to higher $\delta^{13}C$ values in the summer and lower values in the winter. For example, i~~I~~n 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, $\delta^{13}C$ ~~at MLO~~was -8.24‰ and -8.38‰ at the Mauna Loa Observatory~~in these two months; And $\delta^{13}C$ at WLG~~ and~~was~~ -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~~t~~ 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 Carbon Tracker

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478 inversion analysis (Peters et al. 2007), the net ecosystem production at the grid point where
479 Parks Fall is located is -0.20122 mg $m^{-2}s^{-1}$ in July, 2014 but is only -0.13 059 mg $m^{-2}s^{-1}$ at
480 the grid point corresponding to the YRD region in 2014. We would expect from the
481 photosynthetic effect alone that the summertime ^{13}C enrichment at our site to be smaller, not
482 greater than that observed at Parks Fall.

483 Furthermore, in a human-dominated landscape, the plant photosynthetic enhancement of
484 ^{13}C is offset by the CO_2 from fossil fuel combustion which has low ^{13}C contents. In Chicago,
485 the monthly $\delta^{13}C$ peaked in August at -8.29‰ during the calendar year 2011, which is 0.05‰
486 lower than the MLOWLG for the same month. Similarly, in Beijing, the monthly $\delta^{13}C$ peaked
487 at -9.49‰ in August 2014, which is 1.2317‰ lower than the MLOWLG value for the same
488 month.

489 We suggest that cement production was the contributing factorfactor responsible for the
490 high $\delta^{13}C$ values in the summer. The evidence supporting this interpretation is provided by
491 data in Table 2 3 and Figure 7. The $\delta^{13}C$ signal of anthropogenic CO_2 in the YRD would be -
492 26.42‰ without cement production and increased to -23.71‰ after inclusion of the cement
493 source (Table 32). This $\delta^{13}C$ value is much higher than those reported for other urban lands,
494 such as -30.7‰ for Los Angeles, USA (Newman et al. 2008) and about -31‰ for Salt Lake
495 City, USA (Bush et al. 2007). The overall surface source signal derived from atmospheric
496 measurements (Figure 6, -23.265‰ and -234.2472‰ for the YRD and Nanjing, respectively)
497 was also more enriched than those obtained from atmospheric measurements in other cities,
498 such as -28.1±0.8‰ for Chicago in August and September (Moore and Jacobson, 2015), -
499 32.4‰ to -27.4‰ for Salt Lake City in the growing season (Pataki et al. 2003), -27.0‰ for

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

4.3 Net surface and biological~~plant~~ 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~~plant~~ flux F_P were highly correlated ~~consistent~~ with each other because the anthropogenic source strengths were almost constant. The mean F_S between March 2013 and February 2015 was 0.17 mg $m^{-2}s^{-1}$, which consisted of 0.16 mg $m^{-2}s^{-1}$ from fossil combustion and industrial processes, 0.02 mg $m^{-2}s^{-1}$ from cement production and -0.01 mg $m^{-2}s^{-1}$ from biological activities. The total anthropogenic CO_2 flux was 0.18 mg $m^{-2}s^{-1}$ in the YRD, a 67% 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 Carbon Tracker database for the ~~9~~ 6 by ~~*~~6 pixels that cover the YRD region. The results show that the mean daytime (11:00 to 17:00 local time) biological~~plant~~ flux ~~F_P (daytime 11:00 to 17:00 LT)~~ is slightly negative at -

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522 0.014 mg $m^{-2}s^{-1}$ for 20142 (Peter et al. 2007). Our estimate of F_P for 2014 also indicates that
523 the region was a negligibly small biological sink of CO_2 (-0.00909 mg $m^{-2}s^{-1}$).
524 We conducted Monte Carlo simulations to assess the sensitivity of the partitioned fluxes
525 to uncertainties in $\delta^{13}C_P$ and $\delta^{13}C_F$. Errors in these parameters were assumed to follow a
526 uniform distribution and varied in the range of ±1‰. The mean and standard deviation of
527 F_S were 0.167 and 0.003 mg $m^{-2}s^{-1}$, and those of F_P were -0.005 and 0.003 mg $m^{-2}s^{-1}$,
528 respectively for the YRD, based on an ensemble of 10,000 simulations. For Nanjing, the
529 mean ± standard deviation of F_S and F_P was 0.209 ± 0.024 and 0.086 ± 0.022 mg $m^{-2}s$,
530 respectively. These mean flux values are essentially the same as those obtained with the
531 default $\delta^{13}C_P$ and $\delta^{13}C_F$ values giving in Table 3 and the standard deviations represent
532 uncertainties of the partitioned fluxes.
533 Another source of uncertainty in our flux partitioning analysis is related to human breath
534 (Affek and Eiler 2006). Using the method of Prairie and Duarte (2007), we estimated that
535 human respiration flux was 0.006 and 0.013 mg $m^{-2}s^{-1}$, or 3.7% and 11.65% of anthropogenic
536 emission in the YRD and in Nanjing, respectively. The food diet in the region is
537 predominantly C3 grains. By including this additional source in Equations 3 and 4 and by
538 assuming that the isotopic signature of human respiration is the same as $\delta^{13}C_P$ shown in Table
539 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 $m^{-2}s^{-1}$
540 and 0.005 mg $m^{-2}s^{-1}$ in Nanjing, respectively.
541
542 **4.4 Comparison of the Miller-Tans and the Keeling method**

By applying the Miller-Tans ~~and the Keeling plot~~ method ~~separately~~ to ~~the both of~~ ~~midday~~daytime and ~~midnight~~ nighttime observation~~period~~s~~,~~ separately, we obtained the effective source signatures that are consistent with the inventory analysis for the YRD and for the Nanjing Municipality. The daytime ~~Miller-Tans method~~measurement revealed that the sources were on average ~~1.01~~0.46‰ more enriched in ^{13}C than the signature $\delta^{13}C_S$ obtained with the nighttime ~~Miller-Tans~~~~Keeling plot analysis~~measurement. For comparison, the overall $\delta^{13}C_S$ of the anthropogenic sources in the YRD was also higher than that in Nanjing, the difference being 1.76‰ (Table 2). The interpretation that the ~~midday~~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.

We argue that Keeling plot method is not appropriate for ~~midday~~daytime periods because the surface air is influenced by both the surface sources and by entrainment of the background air from above the boundary layer. If we applied the Keeling method to the ~~midday~~daytime observations, the linear correlation coefficient was on average -0.898 which is weaker than the correlation coefficient obtained with the Miller-Tans method (-0.956). The resulting mean $\delta^{13}C_S$ would be 0.61‰ lower than the mean value shown in Figure 6. The difference in $\delta^{13}C_S$ between the YRD (~~midday~~daytime observations, ~~–~~ Keeling method) and Nanjing (~~midnight~~ nighttime observations, ~~Keeling plot~~ Miller-Tans method) would become too small (0.15~~38~~‰).

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In comparison, ~~Conversely~~~~However,~~ the ~~Miller-Tans~~ Keeling plot method showed reasonably~~has~~ good performance when applied to ~~in~~the ~~–is not recommended for midnight~~ 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 was satisfied. If we applied Keeling plot ~~the Miller-Tans~~ method at monthly intervals to the ~~midnight~~ nighttime data, the resulting $\delta^{13}C_S$ ~~for Nanjing~~ would de~~in~~crease to -24.24~~3.72~~‰ for Nanjing from -23.72‰, the value obtained with application of the Miller-Tans method to the nighttime observations. ~~(Figures S4 and S6). For comparison, the $\delta^{13}C_S$ for the YRD, obtained by applying the Miller-Tans method to the middaynighttime data, was -23.2572‰.~~

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5. Conclusion

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 ~~at the Mauna Loa ObservatoryMount Waliguan~~of the background atmosphere in some of the summer months. The highest monthly ^{13}C was -7.44‰ observed in July 2013, which was ~~+~~0.7403‰ greater than the ~~MLO~~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 ^{13}C signal, the CO_2 ~~molar fraction~~mole fraction displayed very weak seasonality (July to January difference 15.6 ppm).

We hypothesized that the Miller-Tans method applied to the ~~midday~~daytime ~~observations~~ and ~~the Keeling plot method applied to the midnight~~ nighttime observations should yield the effective isotopic signature of surface sources at the regional (YRD) and the local (Nanjing) scale, respectively. According to the results of the~~monthly interval~~ Miller-Tans method, the effective source signal in the YRD was -23.25~~5.51~~‰, which was ~~0~~0.46~~.48~~‰ higher than that in the Nanjing Municipality ~~according to the Keeling plot method~~. These results were consistent with inventory estimates of anthropogenic source signatures at these two spatial scales.

By combining inventory data on anthropogenic C sources and the atmospheric measurement of CO_2 ~~molar fraction~~mole fraction and its ^{13}C composition in an isotopic partitioning framework, we inferred that natural ecosystems in the YRD were a negligibly small sink of atmospheric CO_2, with an average flux of -0.009 mg $m^{-2}s^{-1}$. The Carbon Tracker inverse analysis also reveals a small annual mean daytime biological flux (-0.014 mg $m^{-2}s^{-1}$) for this region.

Data availability:

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

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914 **List of Figure Captions**

915

916 Figure 1. Dependence of the observed $\delta^{13}C$ on the H_2O molar fractionmole fraction. The lines

917 represent Equation 32b. Error bars are ± one standard deviation. The first correction was on

918 1st Oct, 2014 using 439ppm standard gas. And the second correction was on 10th Jun, 2015

919 using 488ppm standard gas. When the H_2O is higher than 2.03%, the raw atmospheric $\delta^{13}C$

920 observed will be corrected.

921

922 Figure 2. Monthly total CO_2 (upper panel) and $\delta^{13}C$ (lower panel). The solid line with cycle, dash

923 line with up triangles: middaydaytime (10:00-16:00) means; dashed line with down triangles,

924 midnight nighttime (22:00-6:00) means; smooth solid line stands, monthly means observed at

925 the Mount WaliguanMortgage Loan Origination (MLOWLG). (YRD: derived from daytime

926 readings, Nanjing: derived from night-time readings)

927

928 Figure 3. Mean diurnal variation of the CO_2 molar fractionmole fraction (upper panels) and

929 the $\delta^{13}C$ value (bottom panels) between March, 2013 and August, 2015.

930

931 Figure 4. Application of the Miller-Tans method to all valid middaydaytime (10:00-16:00)

932 data obtained between March, 2013 and August, 2015. Each data point is one hourly mean.

933 The solid line is the geometric mean regression according to Equation 1. (YRD: derived from

934 daytime readings)

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Figure 5. Application of the Miller-TansKeeling mixing line method to all valid midnight nighttime (22:00-6:00) data obtained between March, 2013 and August, 2015. Each data point is one hourly mean. The solid line is the geometric mean regression according to Equation 1. The solid line is the geometric mean regression according to Keeling plot(Nanjing: derived from night-time readings)

Figure 6. Time series of monthly ^{13}C signature of surface sources in the YRD obtained with the Miller-Tans method (black line) and that in Nanjing obtained with the Miller-TansKeeling plot method (grey line). The error bars are ± one standard deviation. (YRD: derived from daytime readings, Nanjing: derived from night-time readings)

Figure 7. Time series of monthly net surface CO_2 flux (F_S), biologicalplant CO_2 flux (F_P), anthropogenic CO_2 flux excluded cement emission (F_F) and cement CO_2 flux (F_e) in the YRD. All the fluxes are in mg $m^{-2}s^{-1}$. (YRD: derived from daytime readings)

Figure 8. Time series of monthly net surface CO_2 flux (F_S), biologicalplant CO_2 flux (F_P), anthropogenic CO_2 flux excluded cement emission (F_F) and cement CO_2 flux (F_e) in the Nanjing. All the fluxes are in mg $m^{-2}s^{-1}$. (Nanjing: derived from night-time readings)

Figure 1. Dependence of the observed $\delta^{13}C$ on the H_2O ~~molar fraction~~mole fraction. The lines represent Equation 2. Error bars are ± one standard deviation. The data in the left panel ~~first correction~~ was obtained on ~~1~~st ~~-~~October 1, 2014 using a 439-ppm standard gas and the true $\delta^{13}C$ value of -32.8‰, ~~—~~ a~~A~~nd that in the right panel~~the second correction was~~ on ~~10~~th ~~-~~ June 10, 2015 using a 488-ppm standard gas and the true $\delta^{13}C$ value of -34.1‰.

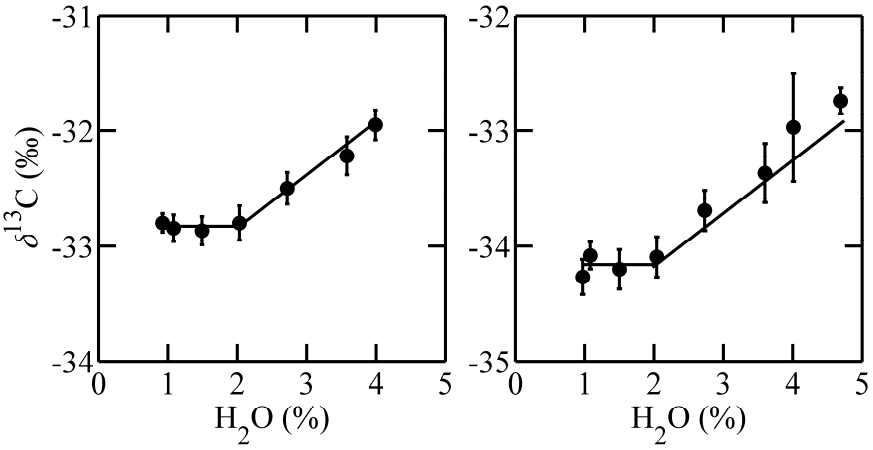
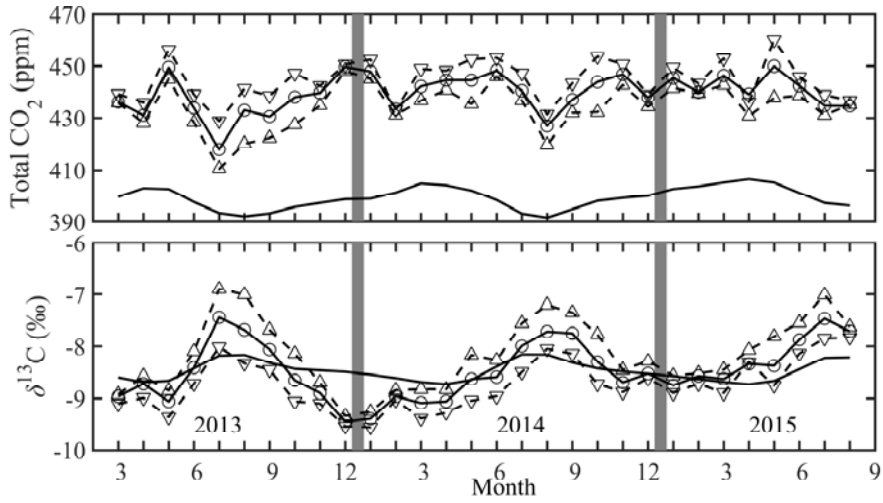


Figure 2. Monthly total CO_2 mole fraction (upper panel) and $\delta^{13}C$ (lower panel): ~~S~~The solid lines with c~~ycle~~ircles: whole ~~-~~day means; dashed lines with up triangles: ~~midday~~daytime (10:00-16:00) means; dashed line with down triangles~~, : midnight~~ –nighttime (22:00-6:00) means; smooth solid line~~s stands~~, monthly means observed at ~~the Mount Waliguan Mortgage Loan Origination (MLO~~WLG~~)~~.



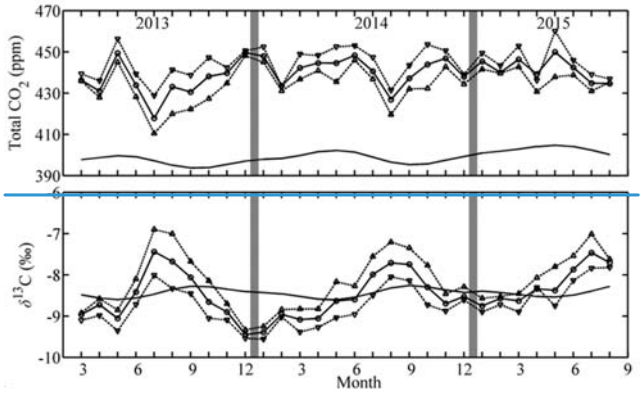


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Figure 3. Mean diurnal variation of the CO_2 ~~molar fraction~~mole fraction (upper panels) and the $\delta^{13}C$ value (bottom panels) between March, 2013 and August, 2015.

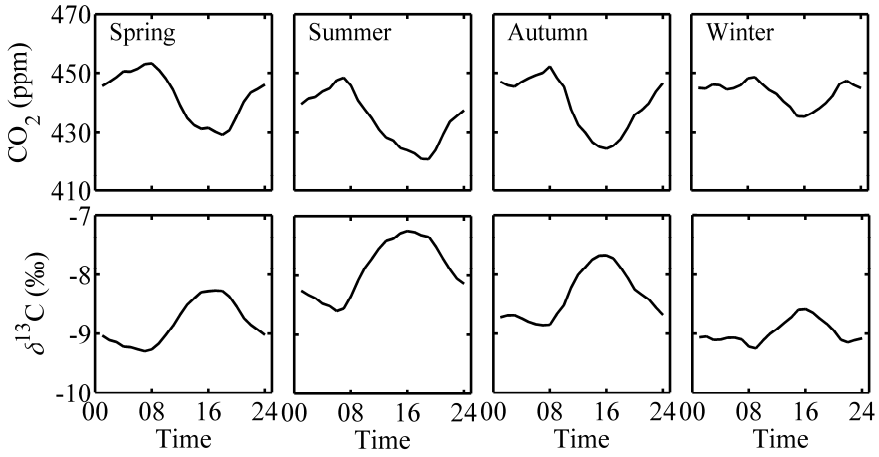
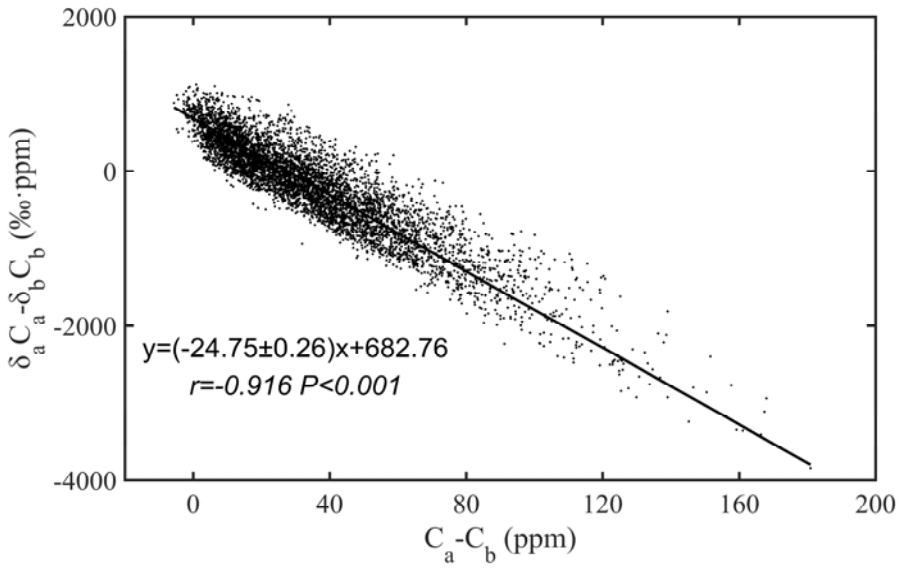


Figure 4. Application of the Miller-Tans method to all valid ~~midday~~daytime (10:00-16:00) data obtained between March, 2013 and August, 2015. Each data point is one hourly mean. The solid line is the geometric mean regression according to Equation 1. Errors bounds on the regression coefficient are 95% confidence interval.



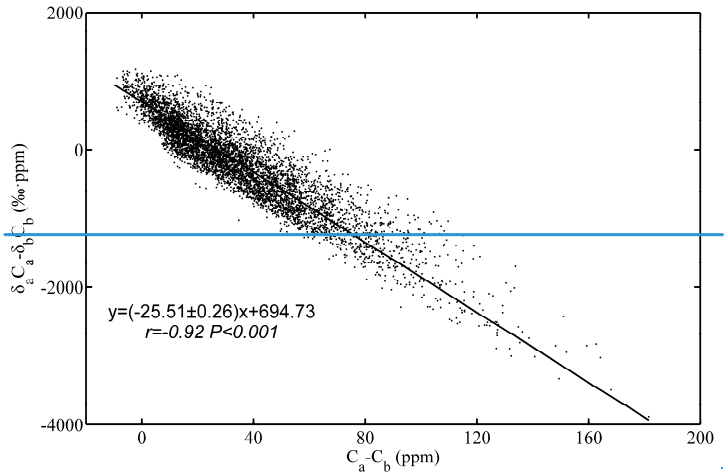
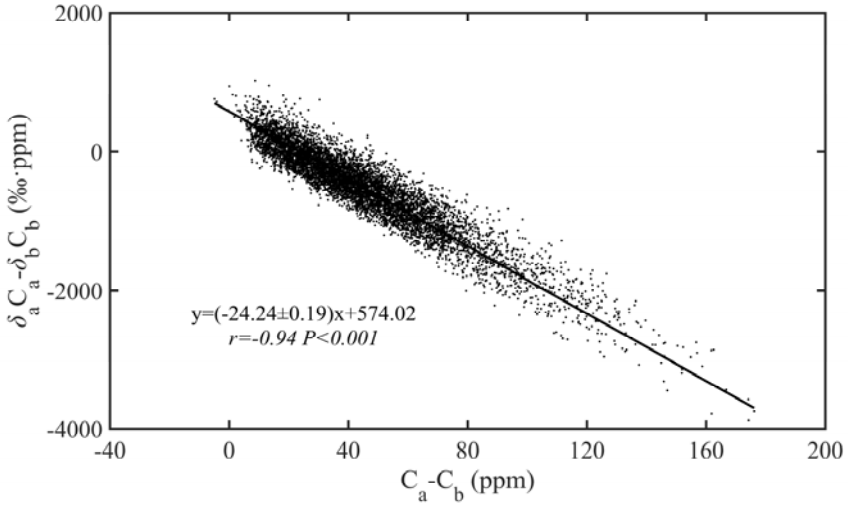


Figure 5. Same as Figure 4 but for ~~Application of the Miller-Tans~~Keeling mixing line ~~method to all valid midnight~~ nighttime (22:00-6:00) data. ~~obtained between March, 2013 and August, 2015. Each data point is one hourly mean. The solid line is the geometric mean regression according to Equation 1.The solid line is the geometric mean regression according to Keeling plot. (Nanjing: derived from night-time readings)~~



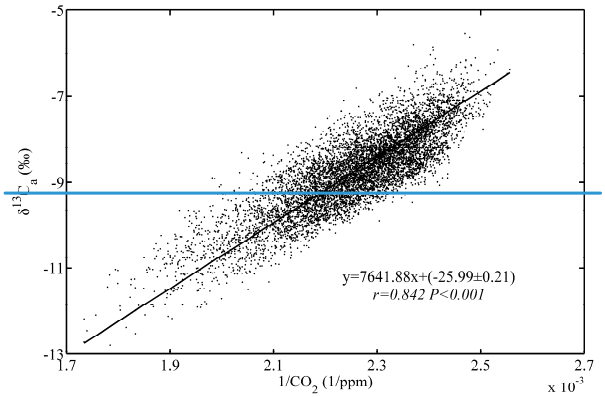
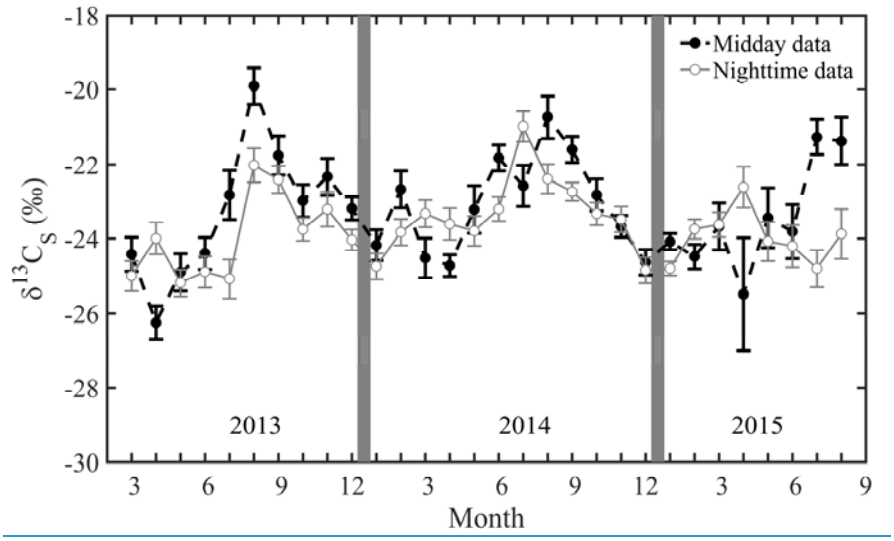


Figure 6. Time series of monthly ^{13}C signature of surface sources in the YRD ~~obtained with the Miller-Tans method~~ (black line) and ~~that~~ in Nanjing ~~obtained with the Miller-Tans Keeling plot method~~ (grey line), obtained from daytime and nighttime measurement, respectively. ~~-~~ The error bars are ± one standard deviation of the Miller-Tans regression.



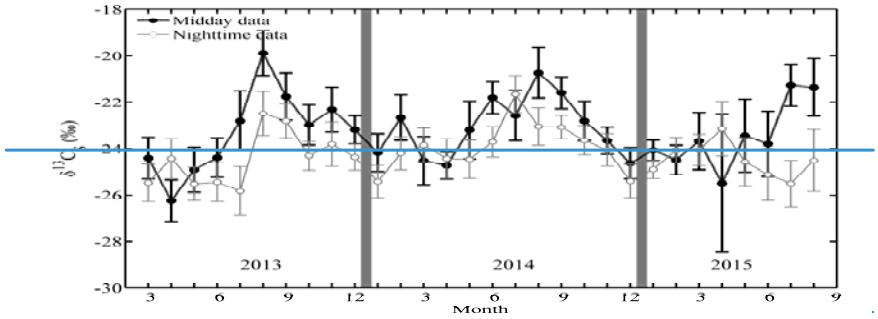


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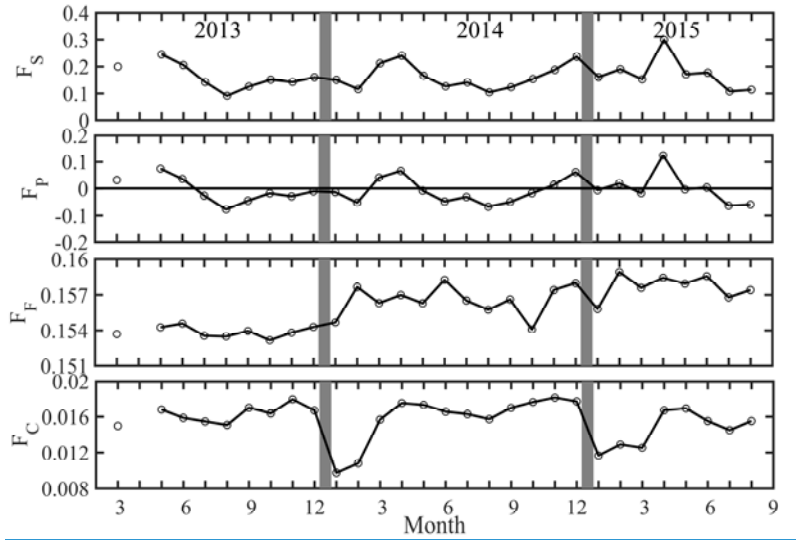
Figure 7. Time series of monthly net surface CO_2 flux (F_S), biological~~plant~~ CO_2 flux (F_P), anthropogenic CO_2 flux excluding~~ed~~ cement emission (F_F) and cement CO_2 flux (F_c) in the YRD. All the fluxes are in mg $m^{-2}s^{-1}$. The results are based on the source signature derived from daytime atmospheric measurements.



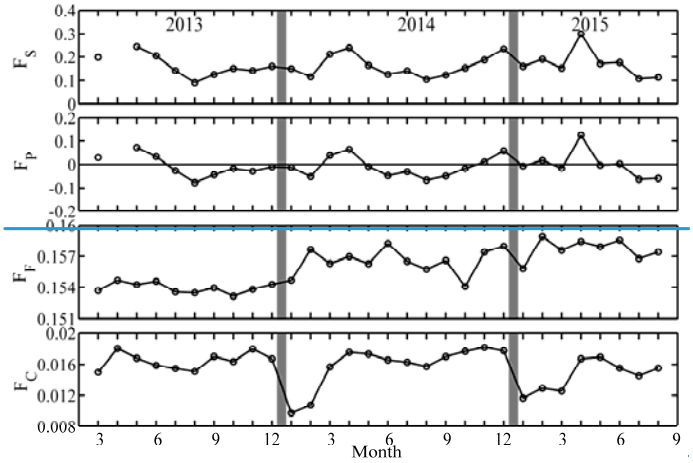


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Figure 8. Time series of monthly net surface CO_2 flux (F_S), biological~~plant~~ CO_2 flux (F_P), anthropogenic CO_2 flux excluding~~ed~~ cement emission (F_F) and cement CO_2 flux (F_c) in the Nanjing. All the fluxes are in mg $m^{-2}s^{-1}$. The results are based on the source signature derived from nighttime atmospheric measurements.

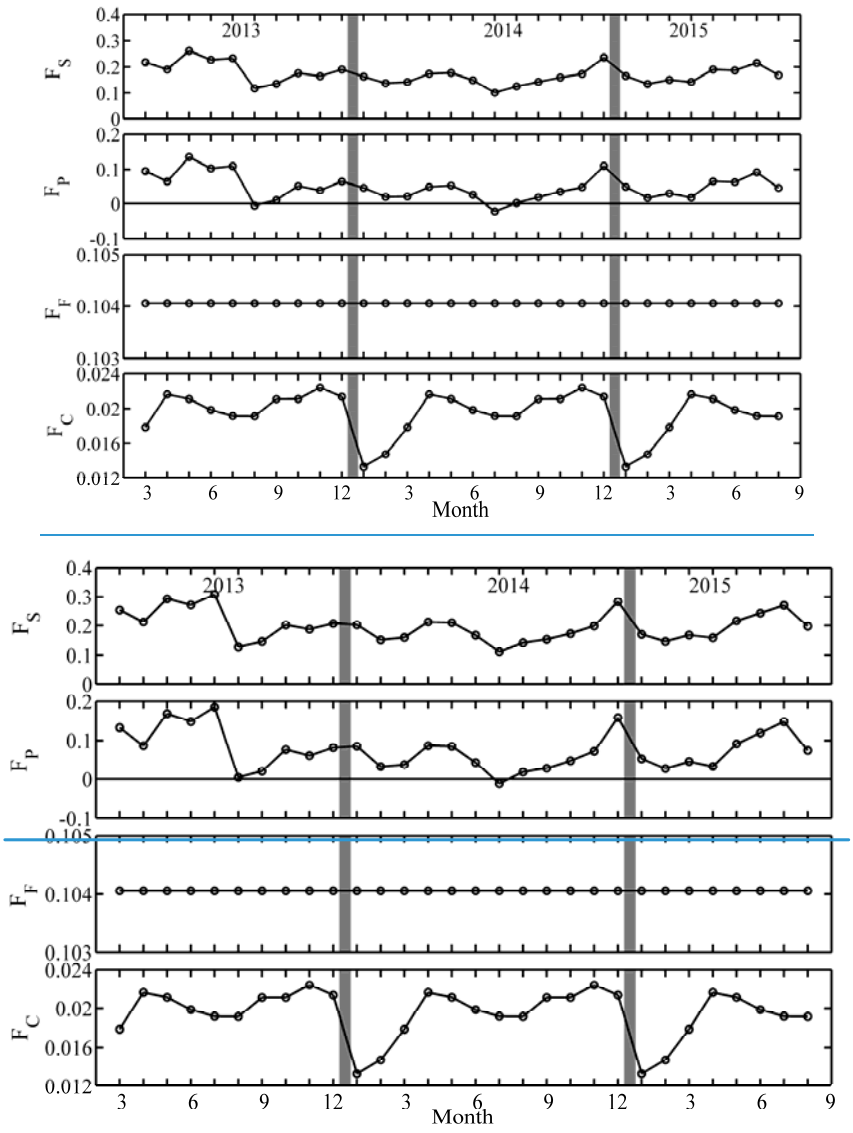

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Table 1 Standard gases used for instrument calibration.

ID	CO_2 (ppm)	$\delta^{13}C$ (‰)	Period
1 Low	381.89	-29.75	Mar, 2013 - Aug, 2014
1 High	502.35	-30.01	Mar, 2013 - Aug, 2014
2 Low	380.92	-29.75	Sep, 2014 - Aug, 2015
2 High	501.05	-30.01	Sep, 2014 - Aug, 2015

Table ~~1~~ 2 Percentage of "fossil-plus" sources and their $\delta^{13}C$ values for the YRD and Nanjing.

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	Percentage (%)		$\delta^{13}C$ (‰)		
Sources	YRD	Nanjing	YRD	Nanjing	References
Coal	70.0	52.3	-25.46	-25.46	Duan 1995, Widory 2006
Gasoline	2.1	11.4	-28.80	-28.80	Widory and Javoy 2003
Diesel	3.2	1.6	-29.80	-29.80	Widory 2006
Fuel oil	2.1	0.3	-28.93	-28.93	Widory and Javoy 2003
Natural gas	2.7	5.0	-39.50	-39.50	Pang et al. 2016
LPG	0.7	0.2	-31.70	-31.70	Widory 2006
Pig iron	8.7	12.7	-24.58	-24.58	this study
Crude steel	1.5	0.7	-24.82	-24.82	this study
Ammonia synthesis	9.0	15.9	-28.50	-28.50	this study
Total	100	100	-26.07	-26.42	

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Table ~~2~~3. Inventory data for t~~T~~he 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.

Sources	YRD		Nanjing	
	$\delta^{13}C$ (‰)	Percentage (%)	$\delta^{13}C$ (‰)	Percentage (%)
"Fossil--plus"	-26.07	91.0	-26.42	96.4
Cement	0.20	9.0	0.20	3.6
Anthropogenic	-23.71	100	-25.47	100
B~~b~~iologicalP~~lant~~	-28.2	——	-28.2	——

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