Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-349-AC1, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Interpreting the ^{13}C/^{12}C ratio of carbon dioxide in an urban airshed in the Yangtze River Delta, China" *by* J. Xu et al.

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Received and published: 31 July 2016

** Response to Review 1 **

This manuscript examines the multi-year CO2 and 13CO2 time series as measured in Nanjing, China. Compared to other urban centers the seasonal 13CO2 amplitude is much smaller attributed to weak biological sink in the summer, reduced anthropogenic emissions in the winter, and 13C signature from cement production. They infer the 13C 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 CO2 emissions,

partitioning, and 13C 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 13C source. The authors suggest in line 105 'the intensity of traffic emission varies strongly through the diurnal cycle. And therefore the effective source 13C signature cannot be assumed constant." Both methods, whether they are Keeling or Miller Tans cannot account for a varying source 13C 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 13C 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 CO2 and 13CO2, 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 13C 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 δ13C. It would have been instructive to perform both methods during the night, and then use the 13C 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 δ13CS would be 0.61‰ lower than the mean value shown in Figure 6. The difference in δ13CS 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 δ13CS 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 CO2 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 CO2. 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 13C enrichment of atmospheric CO2), the summer time δ13C is lower than that of the background atmosphere. So we would expect δ13C 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 CO2 and δ13CO2 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 δ13C and 0.05 ppm for CO2 mole fraction according to the instrument manufacturer. Our own Allan variance analysis revealed a precision of 0.05‰ for δ13C and 0.07 ppm for CO2 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 CO2 mole fraction was lower than 390 ppm or δ13C 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 13C signal was attributed to the influence of cement production in the region." This is misleading because in the discussion you pro-

vide other reasons, and this was only one of them.

* We change the description to "The highly enriched 13C 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 13C (δ13C). 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 CO2 and δ13C 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 CO2 and

δ13C 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 δ13Cb and Cb 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 δ13C requirement. A more relevant comparison of methods would be to perform full comparison of the Keeling and Miller-Tans method for determining δ13C 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 δ13C and CO2, 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 carbontracker 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 δ13C 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 δ13C". 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 13C 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 δ13C’. 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. âĂČ

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** Response to Review 2 **

The authors use bottom-up inventories of various sectors producing local anthropogenic emissions of CO2 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 δ13C of the high CO2 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 13C for the high CO2 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 CO2 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 δ13CP and δ13CF. Errors in these parameters were assumed to follow a uniform distribution and varied in the range of $\pm$1‰.The mean and standard deviation of FS were 0.167 and 0.003 mg m-2s-1, and those of FP were -0.005 and 0.003 mg m-2s-1, respectively for the YRD, based on an ensemble of 10,000 simulations. For Nanjing, the mean $\pm$ standard deviation of FS and FP was 0.209 $\pm$ 0.024 and 0.086 $\pm$ 0.022 mg m-2s, respectively. These mean flux values are essentially the same as those obtained with the default δ13CP and δ13CF 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-2s-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 δ13CP shown in Table 3, FS and FP would increase by 0.008 and 0.001 mg m-2s-1 in the YRD and by 0.018 mg m-2s-1 and 0.005 mg m-2s-1 in Nanjing, respectively."

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

*Corrected

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

*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 13C 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 δ13C 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 δ13C than for CO2 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 δ13CS 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 CO2, not ambient. The values are much lower than those measured in the study. Have you tested whether the H2O correction is dependent on the value of δ13C?

*This is a good point. We did not evaluate the δ13C dependence on both the CO2 concentration and the ambient humidity. However, the dependence on the CO2 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.) âĂČ

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** Response to Review 3 **

The study presents CO2 and δ13C data from a densely populated area in China. The diurnal and seasonal cycles in CO2 mole fraction and 13C 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 CO2 from cement production to the total CO2 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 δ13C 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 13C 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 13C signature of the photosynthesis flux is not known. (In our analysis, it was assumed to be the same as the 13C of plant mate-

rials 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) CO2 from human breath It has been shown that CO2 from human respiration can account, in densely populated areas, for a significant proportion of the total CO2 emitted (Lopez et al., 2013; Prairie and Duarte, 2007). For example in Paris, human respiration CO2 can be 15% of the fossil fuel CO2 (Lopez et al., 2013). Measurements of 13C-CO2 in human breath give δ13C 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 13C 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 13C 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 δ13CS 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: "CO2 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 13C 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 CO2 m-2s-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 δ13C, any calibration issue?

*Except for the high humidity interferenceâĂŤwhich 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 CO2 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.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-349/acp-2016-349-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-349, 2016.