

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

### **Anonymous Referee #1**

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This manuscript examines the multi-year CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> time series as measured in Nanjing, China. Compared to other urban centers the seasonal <sup>13</sup>CO<sub>2</sub> amplitude is much smaller attributed to weak biological sink in the summer, reduced anthropogenic emissions in the winter, and <sup>13</sup>C signature from cement production. They infer the <sup>13</sup>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<sub>2</sub> emissions, partitioning, and <sup>13</sup>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:

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1) There seems to be a mis-understanding by the authors in the purpose of implementing the Keeling vs. Miller-Tans approaches to calculating the <sup>13</sup>C source. The authors suggest in line 105 ‘the intensity of traffic emission varies strongly through the diurnal cycle.. and therefore the effective source <sup>13</sup>C signature cannot be assumed constant.’ Both methods, whether they are Keeling or Miller Tans cannot account for a varying source <sup>13</sup>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 <sup>13</sup>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<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, 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 <sup>13</sup>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  $\delta^{13}\text{C}$ . It would have been instructive to perform both methods during the night, and then use the <sup>13</sup>C source inventory data to try to justify one approach over the other.

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<sub>2</sub>.

Why did the authors use a site that was so far removed from Nanjing as a background

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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.

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.

4) There was no explanation for how the CO<sub>2</sub> and  $\delta^{13}\text{C}$  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.

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

Line 31-32: "The highly enriched <sup>13</sup>C signal was attributed to the influence of cement production in the region." This is mis-leading because in the discussion you provide other reasons, and this was only one of them.

Line 90: Instead of "various" say something like "highly resolved" to emphasize the fine temporal nature of the measurements.

Line 129: Need a citation.

Line 134-135: You use the term 'plant' in this paper to describe both vegetation/biology,

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and a cement manufacturing 'plant'. This is confusing and suggest you use 'biological' flux instead of 'plant flux'.

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

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.

Lines 191-196: I assume you fitted the MLO data of both CO<sub>2</sub> and  $\delta^{13}\text{C}$  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.

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.

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

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  $\delta^{13}\text{C}$  requirement. A more relevant comparison of methods would be to perform full comparison of the Keeling and Miller-Tans method for determining  $\delta^{13}\text{C}$  source.

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?

Line 342-367: Very good discussion. Very informative.

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

Line 380: Of course MLO is going to have negligible shift in  $\delta^{13}\text{C}$  and CO<sub>2</sub>, 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.

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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  $\delta^{13}\text{C}$  response to strength of biological carbon sink, but still it seemed strange to me.

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 if the same enforcement exist in the summer (air conditioning)?

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

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

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

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  $^{13}\text{C}$  signature.

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.

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

Table 2: Remove 'plant' and put 'biological'. Plant can refer to a manufacturing facility.

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

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.

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

Figure 4: Unclear what 'valid' midday data was. Was there a data filter on your raw data?

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.

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

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