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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.

Anonymous Referee #2

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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.

My major concern in this paper is the use of the two different methods for determining

δ13C 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 $\sim$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.

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.

Please give uncertainties in measurements and values derived from them.

Specific comments: Throughout: use "mole fraction" not "molar fraction"

Line 29: insert "δ" before "13C"

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.

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

Line 51: insert “fuel” after “fossil”

Line 58: capitalize “Ternberg”

Line 77: “reveals” should be “reveal”

Line 82: “deployed” should be “employed”

Line 120: See Newman et al., 2016, ACP for 8 years of 13C data in a megacity

Line 125: “include” should be “includes”

Line 129: Reference?

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?

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

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

Line 159: Delete “at”

Line 175: Add “%” after “2.03” What are the uncertainties of your measurements, and how do the corrections for H2O to δ13C affect them?

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.

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.

Line 189: The first “Ca” should be “Ca – Cb”.

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.

Line 203: Where are the results of these calculations presented, in Table 1? “process” should be “processes”.

Line 204: Please explain what “the scope one procedure” is. This is not commonly known in this field.

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

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"

Line 231: Consider replacing “solved” with “determined”.

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

Line 260: Consider replacing “stronger” with “larger”. Do you mean that the relative seasonality is larger for δ13C than for CO2 mole fraction?

Line 269: Are times given as local time?

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.

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

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

Line 304: replace “fuel” with “fossil”

Line 311: Is “0.35‰ ” a statistically significant difference?

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

Line 401: Add “, respectively” after “Nanjing”.

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.

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

Line 448: How do you know that 0.38‰ is “too small”? How do you know what the correct value is?

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?

What are the 2 panels – different tanks? different time periods?

Figure 2. Move the year labels to the bottom – I didn’t notice them at first.

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!

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

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