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.

My main concerns are:

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?

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.

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 <u>need</u> 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.

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.

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 Nanjinh 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.

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 … -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.

Other comments

- page 3, line 42: plant uptake is not a source, consider reformulating
- page 3, lines 48 – 49: please give values or send to the information in the paper
- 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
- 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.
- page 7, Methods: I think a subsection on Nanjing and YRD (location, population, climate, plant types C3/ C4) etc is missing.
- page 7, Methods: please consider moving the information from page 8, lines 153 – 159 to line 141, after the phrase ending in “2015”.

- 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
- page 8, line 168: please give also the relative humidity values, for comparison with the values given later
- 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?
- pages7-9, Sect. 2.: Please discuss the precision and the accuracy of the measurements.
- page 9, line 181 and through the paper: “midnight” and “midday” are misleading. Consider using “nighttime” and “daytime”.
- page 9, line 182: what is the “geometric regression”?
- page 9, line 189: the Miller-Tans slope was obtained by linear regression of (δaCa-δbCb) against (Ca-Cb)
- page 9, line 191: please specify more precisely what data were used for MLO, and give a reference; also give coordinates
- 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?
- page 11, line 229: I think the cement source was separated from the other fossil fuel sources
- page 11, line 229: please give values for the source signatures, or send already to the tables containing them.
- 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)
- 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.
- 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.
- page 15, lines 304 and 309: “is “fuel-plus” the same “fossil-plus” used before?
- 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)
- page 16, line 324: the “annual mean plant flux” is in this case daytime flux, please specify.
- page 16, line 325: “the plant flux” is in this case the night-time flux, and it could only be positive.
- page 17, line 350: Fig. 2 does not show energy use seasonality
- page 17, line 356: what about the vegetation cover outside cities?
- page 18, line 374: can you exclude, as a reason for the high $\delta^{13}C$, any calibration issue?
- page 19, lines 394 – 395: does the cement production have a strong seasonality? Why would it have a seasonal effect?
- page 21, lines 435 – 437: I think such explanations should be included in the method
- page 39, Fig 7: please add error bars if possible
- page 40, Fig 8: please add error bars if possible
- 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.

Text / technical comments

- page 3, line 58: typo in Yakir and Sternberg

- page 4, line 66: I think “the fact the degree …” should be “ the fact that the degree”, please check
- page 4, line 68: typo, “to quantity” should be “to quantify”
- page 5, line 104: I think “strictly do not hold” should be “do not strictly hold” – please check
- page 9, line 175: typo H>2.03’
- page 11, line 222: “ we partitioned net …” should be “we partitioned the net” – please check
- page 11, line 236: I think “the cement isotopic composition” should be “the isotopic composition of CO_2 from cement production”
- page 17, line 355: “the overall he vegetation cover” – typo?
- pages 17 – 18, lines 365 – 366: “because much more” should be “because of much more” – please check
- page 31, line 767 – 768: “Mortgage Loan Origination” should be “Mauna Loa Observatory”; same for page 34, lines 800 – 801
- page 34, line 798: “monthly total” should be “monthly mean”?
- page 34, line 798: “the solid line with cycle” – something seems to be missing

References

Affek, H. P., and Eiler, J. M.: Abundance of mass 47 CO 2 in urban air, car exhaust, and human breath, Geochimica et Cosmochimica Acta, 70, 1-12, 2006.

Horváth, B., Hofmann, M., and Pack, A.: On the triple oxygen isotope composition of carbon dioxide from some combustion processes, Geochimica et Cosmochimica Acta, 95, 160-168, 2012.

Lopez, M., Schmidt, M., Delmotte, M., Colomb, A., Gros, V., Janssen, C., Lehman, S., Mondelain, D., Perrussel, O., and Ramonet, M.: CO, NOx and 13 CO2 as tracers for fossil fuel CO2: results from a pilot study in Paris during winter 2010, Atmos Chem Phys, 13, 7343-7358, 2013.

Prairie, Y. T., and Duarte, C. M.: Direct and indirect metabolic CO2 release by humanity, Biogeosciences, 4, 215-217, 2007.