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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isotope- and tracer-based measurements of fossil fuel and biospheric carbon dioxide in Paris during winter 2010" *by* M. Lopez et al.

Anonymous Referee #1

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Review of Lopez et al., Isotope- and tracer-based measurements of fossil fuel and biospheric carbon dioxide in Paris during winter 2010

General comments: This paper presents measurements of Parisian CO2 and related trace gas and isotope measurements. They use radiocarbon and stable isotopes to separate the fossil fuel CO2 components from total CO2. They also measure CO and NOx, and use these to determine emission ratios of fossil fuel CO2 to these gases, therefore obtain higher resolution fossil fuel CO2 estimates. They also examine diurnal variability. This paper presents an excellent new dataset, and this is one of the few urban fossil fuel CO2 measurement studies yet performed. This is the first study to

relate fossil fuel CO2 and NOx, and it makes some interesting new observations. The research is an important contribution to the field.

Yet I find that significant improvement in the presentation of the results is needed to make the paper more compelling and readable. Results and discussion does not flow well, so that the reader finishes a section or paragraph with a lot of questions, which are not answered until much later in the text. The figures and tables should be revised and added to, to more adequately present the full results. The hourly CO2, CO and NOx measurements could be much better related to the CO2ff and CO2bio results from the isotope measurements. The sections describing the calculation of fossil fuel CO2 from radiocarbon, and the separation of the fossil fuel components using 13C could perhaps be moved into the methods section, leaving only the results and discussion of these in section 3.

Specific comments:

Title: This title doesn't quite capture the content of the paper, since a significant part of the paper is devoted to CO and NOx measurements and examining their diurnal cycles and emission ratios.

Abstract, Lines 10-12. Can you say something about the conclusions to be drawn from the continuous fossil fuel CO2 record here in the abstract?

Pg 2374 line 3. Please provide a full reference for AirParif.

Pg 2375 lines 2-5. 222Rn only works if 222Rn emissions are sufficiently known. They are probably only well-constrained for Europe at the moment.

Pg 2377, section 2.1. A map showing the locations of the stations and the metropolitan area would be helpful.

Pg 2377, line 20. Where on the building is the inlet located, and how are local eddies from the building and surrounding buildings accounted for?

Pg 2378, lines 13-16. A map of the local area would be helpful here too.

Pg 2379, line 1-7. A figure showing the air masses would be helpful.

Pg 2381, lines 26-27. “At Jussieu,. . .” Please clarify what this sentence means.

Pg 2382, lines 4-5. How does the flask selection criteria influence the results, since this is not regular or random sampling, it is biased by the selection. Do samples with high CO2 gradients also have emission ratios that are biased relative to a fuller dataset?

Pg 2382, lines 14-19. Is the large variability in the flask – in situ comparison important? Does it matter for the interpretations made later? Is the difference an artifact of matching the timing of the flask and in situ measurements? Or does it indicate something about the full uncertainty in the measurements? Please expand to explain this.

Pg 2383, line 12. Please reference the CO lifetime. The lifetime is much shorter in summer, which may be important for the interpretations given later.

Pg 2383, line 14. Is the NOx lifetime variable by time of year?

Pg 2384, lines 10-14. There is a lot of detail on the statistical differences between the different regimes and the different sites, which could be reduced, perhaps adding the details to the table rather than including in the text.

Pg 2384, lines 14-15. Please reference the CO2 and CO lifetimes, noting that CO2 lifetime depends on the interpretation and methodology.

Pg 2384, lines 22-30. The NOx values could and should be used to give a sense of where the pollution is coming from – local or more distant. It suggests that the pollution seen at Gif is long distance pollution, and not from Paris.

Pg 2385, lines 22-30. Were the benzene and toluene measurements made only during certain periods? How do these results and the interpretation that they indicate older air masses compare with the NOx data?

Pg 2386, lines 16-24. The D14Cbio correction is hard to follow as written. I think I understand that D14Cbio is assumed to be equal to D14Cbg. Other authors have made different assumptions for the terrestrial disequilibrium isoflux and for the nuclear power industry flux. What is the impact of neglecting these? The biospheric CO2 contribution is calculated (on the following page) to be quite significant, so one might expect that the D14Cbio value needs to be accounted for. Graven and Gruber (2011) showed nuclear power plant emissions in Western Europe may bias the fossil fuel CO2 determination by up to several ppm. This is likely particularly important when Mace Head is used as background. On page 2387 and figure 4, one questions whether the CO2bio signal may be an artifact of neglecting the biosphere/nuclear correction to the calculation of CO2ff, since CO2bio seems to scale to CO2ff.

Pg 2387 lines 12-13 and lines 16-17. These sentences repeat the figure caption and are not necessary in the text.

Pg 2388, lines 3-6. Some explanation of why the comparison with the Turnbull et al (2011) results is done is needed. Clearly comparison with results from other cities and studies is useful, but the current phrasing in the text makes it seem spurious.

Pg 2388, line 10. This is confusing. The 77% CO2ff is obtained from the measurements reported in this paper, but the specific sources mentioned in this sentence were obtained from an AirParif report. Please rephrase to clarify what is new information from this paper, and what is reported from elsewhere.

Pg 2388 -2389. If bioethanol from gasoline and diesel explains only 15% of CO2bio, then why would one expect such strong co-variance of the CO2ff and CO2bio diurnal cycles? See also Wang, Y., J. W. Munger, S. Xu, M. B. McElroy, J. Hao, C. P. Nielsen and H. Ma (2010). ("CO2 and its correlation with CO at a rural site near Beijing: implications for combustion efficiency in China." Atmospheric Chemistry and Physics 10(18): 8881-8897) for another calculation of the human respiration contribution.

Pg 2390. Bioethanol is often derived from corn, which would change the delta13C

signal of CO2bio to a more positive value and alter the calculated partitioning.

Pg 2391, line 10. Earlier, it was CO2ff, now it is FFCO2. Please choose one or other and be consistent. Please reference previous work on proxy tracers CO and NOx.

Pg 2392, lines 0-5 and table 4. How many data points were included in the calculation of each emission ratio? Are the slopes and coefficients of determination strongly influenced by a few data points with high values? A figure showing the data would be very helpful. See also Miller et al., 2012 who used median ratios rather than slopes to determine emission ratios, and avoid the influence of low values where the error bars are proportionally larger.

Pg 2392, lines 10-11. The ratios are determined from only a few points – is it reasonable to assume a constant emission ratio, especially for points that are outside the range of values measured in the flasks?

Pg 2392, lines 19-24. Please explain why you did not consider the diurnal patterns in emission ratios, since they may be quite important.

Pg 2392, lines 25-26. What are "implied emission ratios"?

Pg 2392-2393, section 3.5, paragraph 1. The spatial extent of the inventory data needs to match with the spatial extent of the catchment that you are sampling. What is the spatial extent of the catchment area you are sampling? Presumably you are sampling a different catchment in different wind regimes. Paragraph 2 – the inventory estimates need to be related back to the results of this study.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2371, 2013.