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

Answers to reviewer 1:

The authors wish to thank the anonymous referee 1 for his/her helpful and constructive comments which improved the quality of our manuscript.

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 .

Answers to the general comments:
In order to improve the flow of section 3, we reorganized the results and discussion sections by moving calculation of CO2ff to part 2.2.2 (flasks sampling strategy). We also reduced the section 3.5 from not relevant information for this paper and clarify this section.
We added in Figure 5 the results of flasks measurements and all Tables and Figures have been revised.

Answers to the 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.
We changed the title to appear that CO and NOx are used as tracers:
"CO and NOx as tracers for fossil fuel CO2: results from a pilot study in Paris during winter 2010"

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?
R: We added the following sentence at the end of the abstract: "The estimation of the fossil fuel CO2 over the whole campaign shows a mean contribution of 20.6 ppm and 18.7 ppm using CO and NOx as tracer, respectively. By using both tracers we observed a diurnal cycle presenting the same shape with two maxima during the traffic rush hour."

Pg 2374 line 3. Please provide a full reference for AirParif.
R: The full reference is given in the address of co-authors:
"AIRPARIF, Association de Surveillance de la qualité de l'air, Paris, France"

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.
R: The radon tracer method has also been successfully applied in Asia or Australia, where ^{222}Rn emissions are well known. It is recognized that the ^{222}Rn emissions have to be known for applying the method and we kindly referred to van der Laan et al, 2009, Yver et al., 2009, Hammer and Levin, 2009 for more details about this method.

Pg 2377, section 2.1. A map showing the locations of the stations and the metropolitan area would be helpful.
R: We added a French map with Paris, Plateau of Saclay and Trainou. A zoom of this map permits to identify LHVP, Jussieu, Gif-sur-Yvette and SIRTA stations.

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?
R: As written in the manuscript, the inlet lines are located on the roof of the building but it is true that in urban area the micro meteorology is difficult to account for.
For all the stations, the inlet lines for the different species measurements are located at the same place and we are looking for the ratio between the different species.

Pg 2378, lines 13-16. A map of the local area would be helpful here too.
R: We added such a map.

Pg 2379, line 1-7. A figure showing the air masses would be helpful..
R: We added a figure showing the CO source contributions at LHVP for typical air masses from eastern Europe and from western Europe.

Pg 2381, lines 26-27. "At Jussieu, …" Please clarify what this sentence means.
R: We clarified the sentence: At Jussieu, we filled 35 flasks of 2.5L volume on a two hours frequency for two complete days (09-10 February and 14-15 February) and during one night (11-12 February). "

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?
R: we completed our sentence as follow: "in order to minimize the $14\Delta CO_2$ uncertainties. Compared to the whole campaign, the selected flasks represent well the typical diurnal gradients."
We modified also the figure 5 to let appear the flasks results.

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.
R: The large variability observed is typical for an urban station where we have large short-term variabilities of the signal. The absolute difference agrees well with the WMO recommendation showing the high quality of our data. As explain in the manuscript, the standard deviation is an artefact of the different temporal resolution of the in situ measurements and flask sampling.

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.

R: We added the reference of Atkinson et al., 2006 and the life-times are given for a mean annual OH value of 10^6 molecules cm^{-3}.
The life-time of CO is shorter in summer, but it is not relevant for our study as we do not discuss the summer case. The use of molecule's life-time is only qualitative in our study and we used the same OH value for calculating the life-time of CO, NOx, benzene and toluene. This choice does not influence our results.

Pg 2383, line 14. Is the NOx lifetime variable by time of year?
R: Please, see the answer before.

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.
R: We reduced this part by removing the details of the Student's t-test.

Pg 2384, lines 14-15. Please reference the CO2 and CO lifetimes, noting that CO2 lifetime depends on the interpretation and methodology.
R: We referred to Jacobson et al. (2005) who estimated a CO2ff lifetime between 30 to 95 years.

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.
R: We plotted the ratio NO/NO2 at Plateau of Saclay which suggests that the main pollution is not a local pollution (90% of the time, the ratio is lower than 1). It remains difficult to know if the NOx seen at Gif is long distance pollution or from Paris especially because it will depend on the wind regime. In our manuscript, we did not write that the pollution seen at Plateau de Saclay is from Paris, especially when the oceanic wind regime occurs.

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?
R: We added in the manuscript that benzene and toluene have been monitored during the whole campaign at LHVP. We showed that in oceanic regime, the ratio of toluene to benzene is higher than in continental regime. For NOx measurements, we do not see a significant difference between the two regimes because of its short lifetime. This indicates that NOx alone is not sufficient to be used as a tracer for air masses.

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.

R: Pg 2386, lines 16: there is a typographic error, we replaced 'while D14Cbio' with 'while D14Cbg'.

Turnbull et al. (2006) showed that the effect of the terrestrial disequilibrium isoflux is a positive 0.2 ppm in winter, which is within our measurement uncertainties. We added the following sentence: "Turnbull et al. (2006) showed that in winter, the terrestrial disequilibrium isoflux has a contribution of 0.2ppm"

Graven and Gruber (2011) derived potential biases in fossil fuel CO2 because of nuclear power plant. They provided a global map of the annual average of these biases. For Paris, potential annual bias is between 0.5 and 1.0 ppm. The grid cells used are 1.8*1.8 degree and we are afraid that the numerical diffusion in their model was too large which induce an overestimation of the nuclear power plants effect for each grid cell containing a nuclear power plant. In France, the main bias is from La Hague (a nuclear waste treatment plant, located approximately 300 km west from Paris) which emits an amount of 14C about 100 times higher than the nuclear power plants. Using a diffusion model, we did not see an influence of air masses from La Hague at Paris during the four days of flasks sampling. We expect only a small influence of nuclear power plant in our study (smaller than 0.5 ppm) and we did not want to introduce a wrong bias. We preferred neglect the influence of the nuclear power plants due to the large observed CO2 gradient in Paris.

D14C is also monitored at Trainou station at 180m above ground level in France and it could be used as a background site. There are two nuclear power plants less than 100 km from Trainou. We have done a sensibility test relative to the background value by using the D14Cbg from Trainou. We found a CO2ff signal lower than 0.5 ppm in average in Paris using Trainou for D14Cbg instead of Mace-Head. We did not see significant differences and we preferred to use the European background site of Mace-Head.

Pg 2387 lines 12-13 and lines 16-17. These sentences repeat the figure caption and are not necessary in the text.
R: We deleted the following sentence: "Fossil fuel CO2 (in grey) and biogenic CO2 (in green) are plotted in Fig.4 using the right axis, which has the same amplitude as the left axis"

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.
R: Following the referee 2, we replaced the Turbull et al., 2011 comparison with Pataki et al., 2006 for Salt Lake City, Newman et al., 2008 for Pasadena.

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.
R: We deleted "(AirParif)" in order to avoid the confusing.

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.

R: We observe the same shape for CH4 and SF6 flask measurements. For these two species we don't expect that the diurnal cycle is driven by emissions from road transport. This co-variance of the different species can be explained by the boundary layer dynamics.
We deleted the following sentence from the manuscript:
"This could explain the covariance of CO2ff and CO2bio as observed in Fig.4"

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.
R: Since the measurements by Widory and Javoy (2003), the use of biofuel increases from 1% to 7%. In France, 70% of cars are diesels and 30% of cars are gasoline. The biofuel added to diesel is mostly produced from rape and sunflower while the biofuel added to gasoline is partly produced from sugar-beet, wheat, corn and potatoes. Among all listed plants, only corn has is a C4 plant with a d13C signature of around -14‰ but the contribution is less than 7.5% in biofuel and 0.5% in total fuel. Therefore, we can neglect the influence of the isotopic signature from corn.
We added a sentence in the manuscript to explain this.

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.
R: CO2ff notation is used as fossil fuel CO2 contribution directly derived from Δ14C flasks measurements while FFCO2 is used as notation for the fossil fuel CO2 contribution derived from the proxies CO and NOx.
We referred to Gamnitzer et al., 2006 and Levin and Karsten, 2006 for proxy CO study. We also added a sentence to note that to our knowledge, this is the first time that NOx are used as proxy for determiing the CO2 fossil fuel contribution.

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.
R: We added in table4 the number of points used.
As already answered, compared to the whole campaign, the selected flasks represent well the typical diurnal gradients. We included in figure 5 the flasks measurements.

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?
R: The selected flasks represent well the typical diurnal gradients.

Pg 2392, lines 19-24. Please explain why you did not consider the diurnal patterns in emission ratios, since they may be quite important.
R: We do not have enough measurements to characterize the diurnal patterns in emission ratios in Paris. Our study was a pilot study and further study should have more measurements to characterize these diurnal patterns.

Pg 2392, lines 25-26. What are "implied emission ratios"?
R: We deleted the word "implied" to avoid the confusion.

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.

R: We totally agree with this comment. We could only determine the different wind regimes and it is hard to relate them with the catchment area. We performed the flasks sampling between 7am to 12am early February. During this period, and especially in winter, the planetary boundary layer is low and not completely developed, which limits our catchment area most probably to Paris. Therefore we chose to compare our results with emission inventories grid cell corresponding to Paris.

We added at the end of the section the following sentence: “The ratios derived with our atmospheric approach for the different regimes agree well with the emission inventories given the uncertainties of the different approaches.”