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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Wildfire smoke in the lower stratosphere identified by in situ CO observations" *by* Joram J. D. Hooghiem et al.

Anonymous Referee #1

Received and published: 21 April 2020

General Comments:

The paper "Wildfire smoke in the lower stratosphere identified by in situ CO observations" presents new data collected in the stratosphere by two separate sampling systems. The scientific merit is high, and the analysis methods are sound. In particular, the authors have presented an algorithm for assessing the impact of OH on CO during transport to the stratosphere. The paper overall is well structured. However, at times the sentence structure and descriptions of the methods are confusing, and several key areas in the results and discussion sections lack needed clarity/explanations. Overall, the paper is excellent, and will make a great contribution to ACP after several minor revisions (see below).

Overview of Revisions Needed:

1. In section 2.2.2 and 2.2.3, the LISA sample transfer and CO isotopic measurements are described. Hooghiem et al. (2018) and Pathirana et al. (2015) are cited for reference on the LISA sampler and the CO isotopic analysis line, respectively. However, I was unable to find tests in either reference that show storage tests performed on the sampling containers used in this study. The authors make special note to point out the storage flasks are sealed with Viton O-rings, which is known to contaminate for CO mole fraction on the order of 1-2 ppb per day (e.g. Novelli et al., 1992). A reference or supplemental section should be included that describes laboratory tests which demonstrate that xCO, δ13CO, and δC18O are unaffected by a 7-month storage time in flasks with a Viton oring. This is especially important given the low mole fractions you have observed in the stratosphere as well as the few data points you present here. Any sampling bias could have a large impact on your source attribution.

2. The analysis of the enhancement CO:CO2 ratios presented in the results and discussion is confusing as it is presented currently. In the methods section, the authors describe a common method for obtaining enhancement ratios: assuming that an air parcel is a mixture of some sources plus a background. The authors further show that they have made good background measurements for the altitudes of interest in the stratosphere on Sept 6 and 7, at least for mole fraction.

However, in the analysis, particularly in Figure 4, it does not seem that any background values have been subtracted off. The enhancements presented in figure 4 appear to just be the mole fraction measurements from 4 and 5 September in figure 1. In figure 4, the authors appear to be attempting to find a slope to predict the overall CO:CO2 ratio in the plume. The x axis should range from 0 to 1 (or possibly 1.5) ppm, consistent with the 6th and 7th September xCO2 curves (background) being subtracted from the 4th and 5th September xCO2 curves. The xCO enhancement on the y-axis should similarly be adjusted. Given that the background curves are not constant through the altitude range considered, I think that the subtraction may alter the results of the slopes presented in figure 4. This is, of course, provided that the error

is not simply a typographical error in the labeling of the axis. If, on the other hand, the authors are attempting only to show the CO:CO2 ratios of the plume, and not subtract the background, then the methods should be clarified.

3. Lastly, the LISA flight from the 4th of September is mentioned in the methods section, but I have been unable to find this data in the results and discussion of the isotopic measurements. Why is this missing? It would further strengthen your source attribution section as you currently only have one plume and one background point. If it was discarded, the reasoning should be presented. I recommend that you add this point into your dataset if possible.

Specific Comments:

Pg 1, Ln 16: 1km? Into the stratosphere or you only sampled 1 km of the plume? Clarify.

Pg 2 Ln 24: Specify dates.

Pg 2 ln 47: You say that Mauzerall et al. 1998 also measured CO:CO2 just before stating that only Jost et al measured CO2 allowing for CO:CO2. Please reword/clarify this statement.

Pg 3 ln 69-71: These three sentences need to be reworded. They are awkward to read. Explain what you mean by the sample is limited. I.E. explain how the low pressure and high rate of descent in the stratosphere results in 0.3L air for xxx m of stratosphere, compared to 1.1L of air for xxx m of troposphere. The low resolution and small sample volume lead to the need for LISA, etc.. . .

Pg 3 ln 73: Larger amount relative to aircore? You specify the L STP for aircore, you should state the same here for LISA.

Pg 3 ln 75: Compare to Aircore here as well.

Pg 3 ln 80: “In addition to. . .” Combine these two sentences

Pg 3 ln 87: Explain why two different instruments and models for the two analyses?

Pg 3 ln 84 and throughout text: Note: mole fractions to be represented by lower case x with subscript chemical formula per IUPAC standards. I personally do not have a problem with the nomenclature used in the text, but the authors may wish to make the change for technical correctness

Pg 4: Section 2.2.3: I am not seeing the number of samples you have measured. You state above that you flew LISA on 3 flights, with a total of 4 samples per flight. However, you only present 1 datapoint per day. Please explicitly state the number of flasks you analyzed for stable isotopes and if you averaged them for a given day. This is especially important below when you do not show the 4th Sept data (See further comments below and above on 4-Sept data).

Pg 5 ln 124: Replace “concentrations” with “mole fractions”.

Pg 5 Ln 135-138: It is unclear here what aspects of the CLaMS you used? This sentence seems to indicate that you used the advection scheme but not the mixing scheme, while at the same time implying that both the advection and mixing schemes are needed to resolve 2d filamentary structures. Please clarify.

Pg 5, ln 147: How accurately? This paragraph does not indicate the scale to which the smoke plume can be traced using this method. Suggest removing this word.

Pg 6 ln 153: “similar balance” should be “similar mass balance”.

Pg 6 ln 155: Suggest modifying equation (2) to include “approx. equal” since delta notation here is a good approximation for small changes in delta, but strictly speaking, there is loss of tracer (very small) in this approximation (see Tans 1980)

Pg 6, ln 170: Remove the sentence “The production. . .neglected”. This is confusing here and is not relevant to this section which is explaining the oxidation of CO by OH. This can be explained further in the Discussion section about how you determined the actual source.

Pg 8 Ln 200: “Volumetric Air Fraction”: this is a confusing term. Looking at your equations, f is the fraction of the total mole fraction. You have a measured mole fraction for your given air parcel that you are trying to partition with your model. Furthermore, you are looking at CO here, not air, and volumetric is additionally confusing as you have introduced no volumes in this equation that I can determine. Please clarify or restate.

Pg 8- Pg 9, Ln 216-219: This needs more explanation. Please expand or clarify. This currently leaves the reader with the impression that your signal to noise ratio is something like 1:1, which would mean that you could not differentiate between the measurement noise of your measurement system and real atmospheric signals. This is certainly not the case for the AirCore. Also, please explain/expand on why 2x the measurement uncertainty was chosen and why this is assumed to be valid. The current level of explanation makes this choice seem arbitrary.

Pg 10 ln 237: “This thus differs. . .” This sentence is not consistent with the values you list in tables 2 and 3. Table 2 lists a much larger range, but still contains the values for wildfire smoke that you list in table 3. Reword or delete.

Pg 10 Ln 245-247: As with my previous comment on this section, you need to clarify and explain more clearly how you are assigning uncertainty, how you are interpreting your results within the bounds of that uncertainty. Why are you limiting your results to live within the 1 sigma bounds, for example? I’m not suggesting this approach is wrong, but it certainly needs further explanation.

Figure 1: Why is 4- Sept LISA measurement missing from this plot?

Pg 13 Ln 276-279/throughout section 3.3/Figure 4: Figure 4 and the description presented here are confusing (see General comment 2 above). You refer to enhancements and enhancement ratios, and in Section 2 you describe the source attribution in terms of sources on top of a background, or wildfire plume injection on top of the background stratosphere. However, in this section, it is not clear where you have subtracted your

background or what you are using for a background. Are you using the profiles from the 6th and 7th averaged to assume a “typical” stratospheric background CO and CO2? Furthermore, figure 4 would be clearer if you displayed the enhancement CO vs the enhancement CO2 (e.g. the background subtracted off each parameter).

Pg 15 Ln 308: Given your stated measurement uncertainty, can you really say this is a significant change?

Page 15 Table 4: Include data from 4-Sept if possible

Pg 19, ln 376: Again, you are not presenting the enhancement ratios here. This is just the CO:CO2 ratio from your overall flight. To get the enhancement ratio, you would subtract your background profile from your plume profile to plot the enhancement CO:CO2 ratios.

References

Novelli, P. C., L. P. Steele and P. P. Tans (1992). "Mixing ratios of carbon-monoxide in the troposphere." Journal of Geophysical Research-Atmospheres 97(D18): 20731-20750.

Tans, P. P. (1980). "On calculating the transfer of carbon 13 in reservoir models of the carbon cycle." Tellus 32(5): 464-469.

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