Review of "Formaldehyde evolution in U.S. wildfire plumes during FIREX-AQ"

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Liao et al. "Formaldehyde evolution in U.S. wildfire plumes during FIREX-AQ" uses data from ~ 12 fire plumes to study the relative importance of primary vs. secondary HCHO production in fire plumes along with the dominant factor controlling the magnitude of secondary HCHO production. The main conclusion is that OH concentrations, rather than total VOC reactivity with OH, is the main factor setting the magnitude of secondary HCHO production. The topic is appropriate for publication in ACP.

While the general methodology is sound as far as I can tell, I agree with the other reviewer that a more detailed explanation of how the authors arrived at their conclusions would strengthen this paper. In particular, I find that Fig. 4 in the main paper is not sufficient support of the primary conclusion (that OH concentrations rather than VOC reactivity are the primary control on HCHO production). There are also issues with definitions or concepts being introduced out of order that make the manuscript difficult to follow.

Thus, I recommend that revision be required to address these issues before final publication in ACP.

Major comments

- In Fig. 4a, as I understand it, the y-axis values of nHCHO production depend on plume OH concentration (in order to determine the loss rate of primary nHCHO to subtract primary from total nHCHO) and is plotted against OH concentration. This makes me concerned that the correlation might be driven in part by the relationship encoded in that calculation, rather than the physical relationship between OH and secondary HCHO production. Could you describe any tests you have done to determine whether that is the case?

- Also for Fig. 4 and the related text, I do not find it convincing to show secondary nHCHO production vs. OH concentrations colored by the VOC reactivity as evidence

that the former controls the nHCHO production rate. It is very difficult to evaluate the correlation between the y-axis and the colors. It would be a stronger argument, in my opinion, to have a panel that shows nHCHO production vs. OH-VOC reactivity (perhaps colored by OH concentration) to directly compare with the current panel (a). Further, I did not see anywhere that the R^2 value, slope, or slope uncertainty for the regression of nHCHO production vs. OH-VOC reactivity were reported. To claim that the correlation of nHCHO production with OH concentration is greater than the correlation of nHCHO production with OH-VOC reactivity without providing the latter value is rather unconvincing. Please provide this comparison.

- My last point on Fig. 4 is that R^2 values tend to be driven up by outliers. In Fig. 4, I suspect that the R^2 is being increased by one or both of the data points with [OH] $> 4 \times 10^6$ molec. cm^{-3}. I recommend the authors apply a bootstrap analysis to test the effect of these two points and calculate the uncertainty on the R^2 and confirm the uncertainty on the slope.

- In Sect. 3.3, lines 369 to 371, I am confused by the statement "Plume-average normalized OH-VOC reactivity...is lower than total OH reactivity across the analyzed plumes, and does not establish a clear relationship with OH."

  - It is not clear from the writing why there would be any expectation that OH-VOC reactivity would correlate with OH; one depends on VOC concentrations and rate constants, the other on OH itself. If the assumption is that increased OH would tend to decrease OH-VOC reactivity because the OH will react with the most reactive VOCs first, that is not explained in this section—and would also likely be a very non-linear relationship, so I would not naively expect this to have a clear correlation.

  - Please be clear about the difference between "(normalized) OH-VOC reactivity" and "total OH reactivity." The latter is not defined explicitly anywhere in the paper, and it should also be made clear whether both quantities are being normalized to Δ CO or not. Further, if the "total OH reactivity" is the OH-VOC reactivity plus OH reactivity with CO and NO$_2$, then the statement in lines 369 to 371 that OH-VOC reactivity is lower than total reactivity is true by definition, and not particularly useful.

  - Given that it is not clear what the difference between these quantities is, it is impossible to understand how this difference tells anything about the relative importance of sources vs. sinks of OH. In addition to clearly defining both quantities, please provide more detail on the logic for how this difference informs the relative OH source/sink importance.

Minor/technical comments

- The pink curve in Fig. 1 is really hard to see, a color with more contrast to the red would be more visible.

- How late are the nighttime plumes? I wouldn't expect there to be much OH chemistry after sunset with no photolysis, unless there is some longer-lived HO_x reservoir in these plumes.

- Sect. 2.2 does not include justification for using ΔCO as a method to normalize for dilution. While I recognize that CO is often used in this manner, this section should include either (a) a citation to previous work showing that ΔCO is a reasonably accurate metric for dilution (ideally in biomass burning plumes) or (b) demonstrate using FIREX-AQ data that normalizing by ΔCO does account for dilution.

  - Since using CO as a tracer generally requires that production or loss of CO be minor relative to the concentration of CO in the plume (Müller et al. 2016), it would be helpful to show that this is true in these plumes. For example, while I assume that the amount of CO produced from $HCHO + OH \rightarrow HO_2 + CO$ (~ 3 ppb/hr at 298 K) is small enough to not impact this analysis, without knowing the CO mixing ratios in the plumes, I cannot be sure.

- Please confirm that Eq. (3) is provided and used correctly. Following on from Eq. (2), I assume that the whole term multiplied by t is set equal to the slope, thus:

$$slope_{butene} = (k_{butene+OH} - k_{propene+OH})[\text{OH}] + (k_{butene+O_3} - k_{propene+O_3})[\text{O}_3]$$
$$\Rightarrow slope_{butene} - (k_{butene+O_3} - k_{propene+O_3})[\text{O}_3] = (k_{butene+OH} - k_{propene+OH})[\text{OH}]$$
$$\Rightarrow \frac{slope_{butene} - (k_{butene+O_3} - k_{propene+O_3})[\text{O}_3]}{(k_{butene+OH} - k_{propene+OH})} = [\text{OH}]$$

Specifically, in Eq. (3) it looks like the sign of the O_3 term is wrong and the order of terms in the denominator is reversed.

References

Müller, Markus et al. (2016) "In situ measurements and modeling of reactive trace gases in a small biomass burning plume." *Atmos. Chem. Phys.*, 16, 3813–3824. doi: 10.5194/acp-16-3813-2016