The reviewers' comments are in black. Our responses to reviewers' comments are in blue and our modifications in the manuscript are in green.

Reviewer 2

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.

To address the reviewer's concern 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), Fig. 3a (originally Fig. 4a) is modified to show the colors upfront so that it is clear to see the dependence of nHCHO production rate on normalized OH-VOC reactivity. In addition, the scatter plots of nHCHO production rate vs. normalized VOC-OH reactivity and vs. normalized total OH reactivity are added in fig. S11a and fig. S11b.

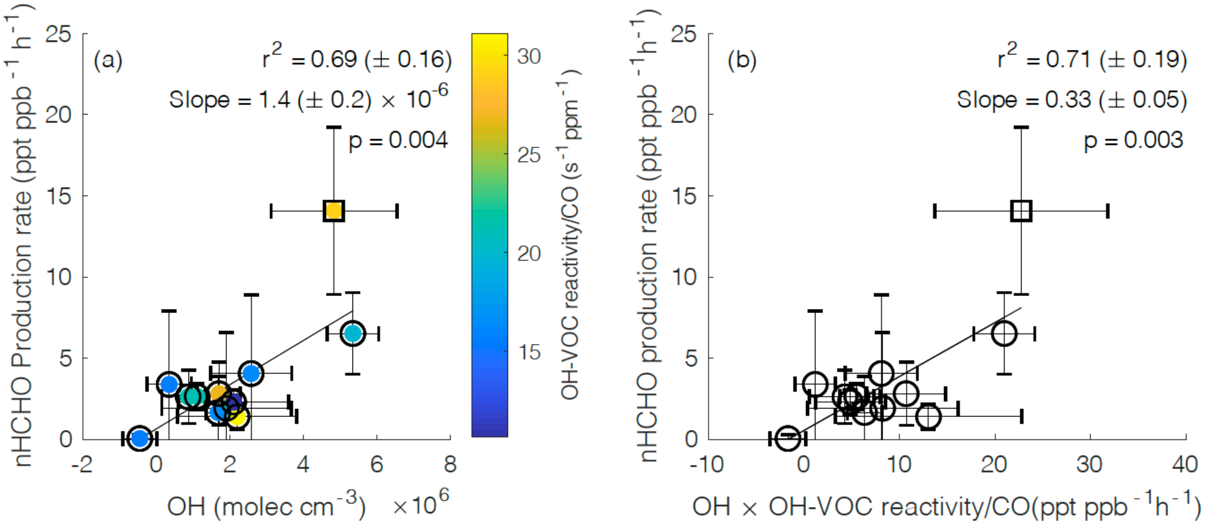

Figure 3. (a) Average secondary nHCHO production rate vs. average OH concentration, color-coded by normalized OH-VOC reactivity, for the 12 plumes including 11 western US wildfire plumes (circles) and 1 eastern US wildfire plume (square). An uncertainty weighted linear York regression (Derek, 1968) yields a slope = 1.4 (±0.2)× 10^{-6} and $r^2 = 0.69$ (±0.16) for the 12 wildfire plumes. (b) Average secondary nHCHO production rate vs. the average product of OH and OH-VOC reactivity normalized to CO (OH× OH-VOC reactivity/CO) for each plume. An uncertainty weighted linear York regression yields a slope = 0.33 (± 0.05) and $r^2 = 0.71$ (±0.19). The slope represents the estimated effective yield α_{eff} of HCHO per VOC molecule oxidized by OH for the US wildfires. The uncertainties in r^2 are from bootstrap analysis. P value in each panel is to evaluate if linear correlation is statistically significant ($p< 0.05$).

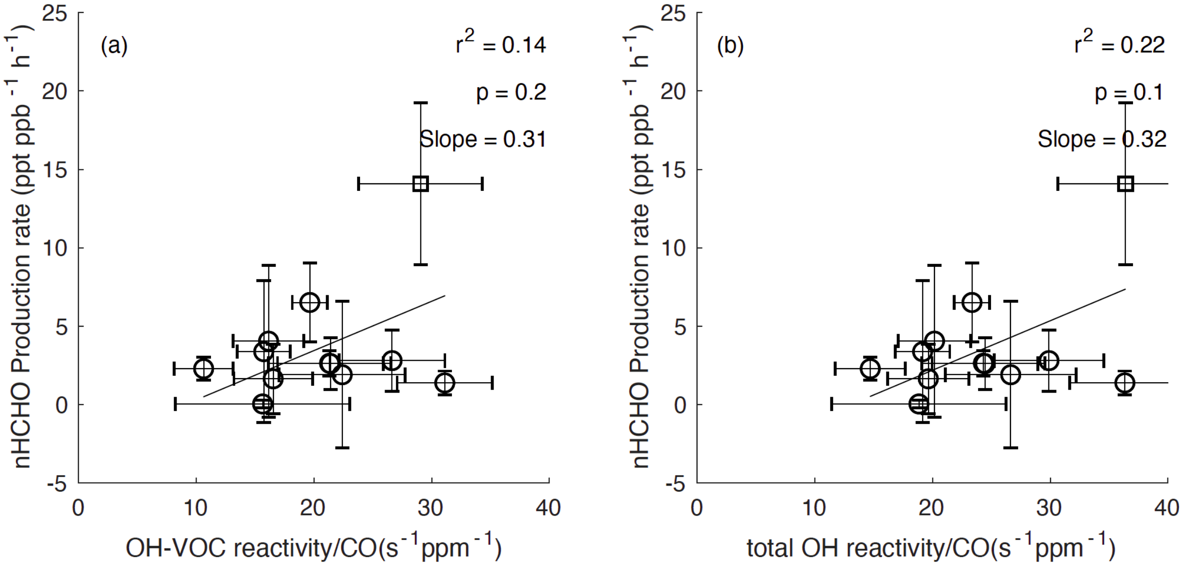

Figure S11 (a). Average nHCHO production rate vs. normalized OH-VOC reactivity (OH-VOC reactivity/CO) for the 12 plumes including 11 western US wildfire plumes (circles) and 1 eastern US wildfire plume (square). Unweighted bivariate linear regression was applied to fit the data because uncertainty weighted linear regression does not yield a reasonable fit. The unweighted (or equally weighted) bivariate linear regression yields a slope = 0.31, $r^2 = 0.14$, and $p = 0.2$ for the 12 wildfire plumes. (b) Average secondary nHCHO production rate vs. normalized total OH reactivity (total OH reactivity/CO) for the 12 plumes including 11 western US wildfire plumes (circles) and 1 eastern US wildfire plume (square). An unweighted (or equally weighted) bivariate linear regression yields a slope = 0.32, $r^2 = 0.22$, and $p = 0.1$ for the 12 wildfire plumes.

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?

Line 362 added “Although OH concentrations are used to calculate secondary nHCHO production rate, the nHCHO loss term (*k*[OH]nHCHO) due to OH only accounts for 2-35% of all the terms on the righthand side of eqn (6), which is used to calculate secondary nHCHO production rate for the plumes. This indicates that the good correlation between secondary nHCHO production rate and OH is not due to the inclusion of OH in nHCHO production rate calculation.”

- 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 R2 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.

As suggested by the reviewer, a panel about nHCHO production rate vs. OH-VOC reactivity/CO with coefficient of determination and *p* value is added to figure S11a.

Line 372 added “nHCHO production rates vs. normalized OH-VOC reactivity (Fig. S11a) shows a lower coefficient of determination (r^2) and a higher *p* value than Fig.3a. Because uncertainty weighted linear regression does not yield a meaningful fit for Fig. S11a, unweighted (or equally weighted) bivariate linear regression is used.”

- My last point on Fig. 4 is that R2 values tend to be driven up by outliers. In Fig. 4, I suspect that the R2 is being increased by one or both of the data points with [OH] > 4 $*10^6$ 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.

Bootstrap analysis is used to estimate the uncertainties in both the coefficients of determination r^2 provided in Fig. 3.

- 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.

Line 371 deleted ", and does not exhibit a clear relationship with OH"

--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 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.

Line 370-371 changed "total OH reactivity" to "normalized total OH reactivity".

We agreed that normalized OH-VOC reactivity is lower than normalized total OH reactivity by definition, but the differences can vary. We pointed out that the normalized OH-VOC reactivity is 20% lower, which can vary from cases to cases, than the normalized total OH reactivity for these plumes. This is reflected in line 370-371:

"Plume-average normalized OH-VOC reactivity ranges from 11 to 31 s^{-1} (ppm CO)$^{-1}$, which is about 20% lower than normalized total OH reactivity across the analyzed plumes."

In section 2.7, changed to "We calculate the OH-VOC reactivity ($\sum k_i VOC_i$) by excluding OH reactions with NO_2 and CO from the total OH reactivity and define normalized OH-VOC reactivity or normalized total OH reactivity as OH-VOC reactivity normalized by CO or total OH reactivity normalized by CO."

--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.

Line 371-274 deleted "This demonstrates that variability in OH, as well as secondary nHCHO production, likely depends principally on variability in OH sources (e.g., photolysis of HONO and conversion of HO_2 by NO) (Peng et al., 2020) rather than sinks."

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.

Changed the pink curves to gray curves in Fig. 2 (originally Fig. 1).

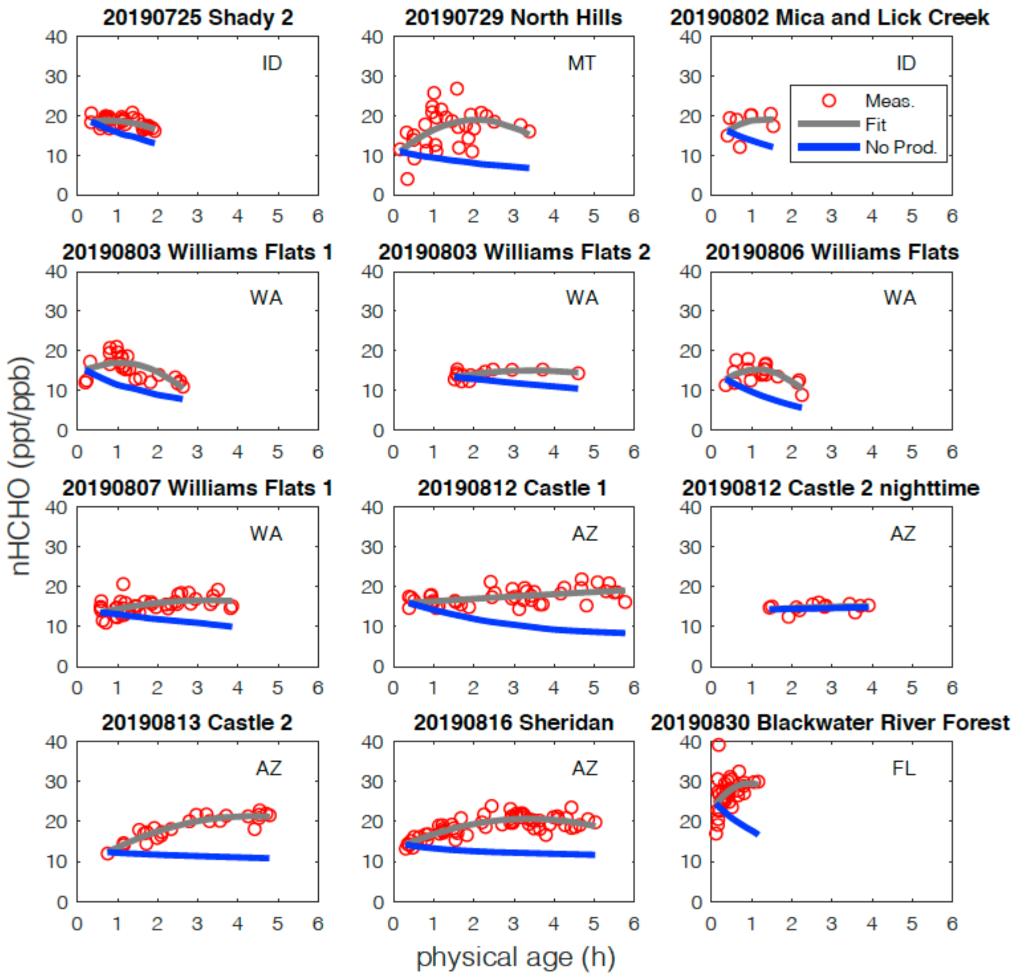

Figure 2. Observed nHCHO (HCHO to CO NEMR) trends (red circle), quadratic polynomial fit (pink curve), and calculated decay of nHCHO trend without secondary production (blue curve) using measured photolysis rates along plume physical age for the 12 wildfire plumes. The state of fire location for each fire plume is listed.

- 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.

Line 215 added "The nighttime plume on 12 August was after 8:00 pm local time with average O_3 photolysis rate of essentially zero."

- Sect. 2.2 does not include justification for using CO 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 CO is a reasonably accurate metric for dilution (ideally in biomass burning plumes) or (b) demonstrate using FIREX-AQ data that normalizing by CO 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 (Muller 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 → 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.

Line 166 added "Because photochemical production of CO is very small compared to the high CO concentrations in the biomass burning plumes (e.g., CO production from HCHO photolysis and OH oxidation for 1 hr is < 1% of CO concentrations in the plumes), trace gases concentrations are normalized to CO in the biomass burning plumes to account for dilution, as in many previous biomass burning studies (e.g., Müller et al., 2016; Selimovic et al., 2018)."

- 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:

$$\text{slope}_{\text{butene}} = (k_{\text{butene+OH}} - k_{\text{propene+OH}})[\text{OH}] + (k_{\text{butene+O}_3} - k_{\text{propene+O}_3})[\text{O}_3]$$

⇨ $$\text{slope}_{\text{butene}} - (k_{\text{butene+O}_3} - k_{\text{propene+O}_3})[\text{O}_3] = (k_{\text{butene+OH}} - k_{\text{propene+OH}})[\text{OH}]$$

⇨ $$\frac{Slope\ butene - (k_{butene+O3} - k_{propene+O3})[O3]}{k_{butene+OH} - k_{propene+OH}} = [\text{OH}]$$

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.

$$\text{Slope}_{\text{butene}} = -\{(k_{\text{butene+OH}} - k_{\text{propene+OH}})[\text{OH}] + (k_{\text{butene+}O_3} - k_{\text{propene+}O_3})[\text{O}_3]\}.$$

The slope in your calculation is missing a minus sign.

$$\text{Slope}_{\text{butene}} + (k_{\text{butene+}O_3} - k_{\text{propene+}O_3})[\text{O}_3] = -(k_{\text{butene+OH}} - k_{\text{propene+OH}})[\text{OH}]$$

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

References

Muller, 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.