Point-by-point Response to Reviewer's Comments

We appreciate the reviewers for taking time to carefully review the manuscript resubmission.

Below are point-by-point responses to Referee #1 and Referee #3.

Report #1 by Anonymous Referee #1

The reviewer thanks the authors for carefully addressing the comments. Also, the reviewer would like to clarify that there is no intention to undermine the importance of the XO2 measurements. The authors' efforts to make this important and challenging measurement are well appreciated.

Since the initial submission of this manuscript, the following two studies on radical chemistry in wildfire ozone have been published. Given their relevance, the reviewer recommends them to be cited in this manuscript.

1. Robinson et al., Variability and Time of Day Dependence of Ozone Photochemistry in Western Wildfire Plumes. Environ Sci Technol 55, 10280-10290 (2021).

2. Xu et al., Ozone chemistry in western U.S. wildfire plumes. Science Advances 7, eabl3648 (2021).

Response: These recent papers are quite relevant, and so we have cited them.

Robinson et al., was cited in line 104:

BB emissions also include unique VOCs that are typically unaccounted for by chemical mechanisms employed by models. For instance, the importance of furanoids for model predictions of secondary pollution formation has only recently been studied (Müller et al., 2016;Coggon et al., 2019;Decker et al., 2019;Salvador et al., 2021;Robinson et al., 2021).

and in line 296:

Our calculated values for P(ROx) are limited by the lack of measurements for HONO, which is the dominant HOx source in freshly emitted BB smoke (Peng et al., 2020;Robinson et al., 2021).

Xu et al., was cited in line 97:

Ozone formation in young BB plumes is, in almost all cases, initially NOx-saturated (VOC-limited) but transitions to being NOx-limited as the NOx is photochemically processed to nitric acid and organic nitrates (Xu et al., 2021;Alvarado et al., 2015;Müller et al., 2016;Folkins et al., 1997).

and in line 375:

Based on literature trends where $\Delta O_3/\Delta CO$ values increase with smoke age until an eventual plateau (Jaffe and Wigder, 2012;Baker et al., 2016;Xu et al., 2021), …

Report #3 by Anonymous Referee #3

The authors did a good job of responding to most of my comments. However, I still find my second comment regarding the apparent correlation between O3 and HCN in Fig. 4 to be unresolved, and I have a few follow up thoughts about my first comment on the role of the non-fire-related diurnal O3 cycle.

Regarding my first comment on the effect of the normal daily O3 cycle on the data in Fig. S8, I just want to acknowledge that I think the authors' strategy of omitting the 22 and 23 August data from the Fig. S8 analysis is certainly a great improvement, as those two days were most clearly impacted by normal daily O3 production. The remaining trends from the 16, 17, and 24 Aug data are more likely to be driven by smoke-related influence. I am less confident than the authors state they are that it is actually smoke related, but the text has been updated with language regarding the daily O3 cycle so readers can form their own opinions. Hopefully future analyses will make an attempt to use modeling to differentiate the natural O3 production from the smoke-related O3 production (which would be too much additional effort for this manuscript). Thank you for considering my comment.

Regarding my second comment on the correlation between O3 and HCN, I find the authors' response to be missing the point of my comment. Perhaps my comment was not clear enough, so I will try again. I understand that my comment about the impact of a smoke plume arriving at nighttime is irrelevant to a plot showing only daytime data, but the point I was trying to make was that the trends in Fig 4 will be driven by the time of day that the smoke arrives. The main reason that Fig. 4 has a positive slope is because the smoke plumes arrived predominantly in the afternoons for the days shown. For instance, the data for 22 and 23 aug show positive slopes for each day because the data in the morning starting at 9:00 MDT had low O3 and low smoke and HCN. As the day progressed to afternoon, HCN increased due to smoke arriving and O3 increased due to a combination of the natural daily cycle and smoke influence. The O3 increase is likely dominated by the natural daily cycle, but by showing Fig. 4 you are implying that increased O3 is due to smoke influence. I don't believe this is the correct plot to show to draw that conclusion.

The data on 24 Aug in Fig. 4 is another good example. During the morning to midday hours, smoke arrived coincident with increasing daily O3, giving a positive slope to that portion of the data. However in this case, the smoke receded during the afternoon hours so HCN dropped dramatically but O3 remained roughly constant or perhaps dropped by only a few ppb (which may have been part of the natural evening decrease in O3). This portion of the data gives a slope near zero. If the smoke influence was the reason for increased O3, you would expect O3 to drop along with HCN as the smoke left the area. The data on 18 and 21 Aug give slopes that are nearly vertical, because O3 increased from the normal daily cycle while the smoke influence remained minimal.

Going back to my hypothetical example of a smoke plume arriving during nighttime, I will amend that to say it arrives instead at 9:00 MDT. HCN will start elevated, but O3 will not be elevated because daytime photochemistry has only just begun as the sun rose. Say the plume moved out of the area by midday, and HCN has decreased while O3 has increased to a daily maximum. The slope of the data for this day would be included in Fig 4 and would be negative.

Because of this reasoning, I believe the apparent positive correlation between O3 and HCN is a coincidence because the smoke tended to arrive in the mid afternoon at this site during this measurement period (and probably at most sites, because fires tend to burn most in the afternoon and into evening). By plotting all of the data from different days together in the same plot, the details I describe above are lost and the overall trend is driven mainly by the fact that 23 Aug happened to have both the highest O3 and the highest HCN during the afternoon hours. Was there more O3 because there was more smoke, or was it a particularly hot day that caused more natural O3 production as well as a larger fire with smoke? That is a question that cannot be answered with the analysis in Fig. 4. But by showing Fig. 4 and stating at line 419 (in the tracked changes doc) that "For the entire campaign, there is a positive correlation between daytime O3 (and Ox) concentrations and smoke tracer HCN", you are implying that smoke causes increased O3, or at least a reader is very likely to draw that improper conclusion from the plot when presented this way. It is definitely possible that smoke does lead to a relatively small amount of additional O3, but this analysis is not separating the natural photochemical cycle from the smoke-related increase, and thus Fig 4 and the paragraph at line 419 are misleading to the reader.

To address this comment, I have several suggestions. Figure 4 and the associated paragraph could probably just be removed, since they are not really critical to any of the other analyses in this paper. The authors could perform additional modeling to try to model O3 with and without the influence of smoke for the days of this study, but that is likely to be an entire manuscript on its own and too much additional work for this manuscript. Perhaps a middle ground would be to somehow alter Fig. 4 to try to remove/limit the impacts from the natural daily O3 cycle, as they did in response to my other main comment in the first review. E.g., they could restrict the plot to only show data for the hour or several hours during midafternoon when O3 typically peaks. This may show that peak daily O3 correlates positively with HCN, in a way that is more likely to be a true influence from smoke than the way Fig. 4 is currently shown. This method still could be misleading, because as I mentioned in the previous paragraph both O3 and increased smoke could just be the result of a hotter day or the specific photochemical conditions. So I would suggest the authors do some basic checks to see if that could be the case. I suggest they at least explicitly advise the reader in the text that there are external reasons why O3 and HCN could increase together due to external factors, rather than giving the reader the impression that the data is proving that smoke is the dominant cause for increased O3.

I'll thank the readers in advance for addressing this comment again.

Response:

We have considered the reviewer's concerns regarding the O_3-HCN correlation, and in response, we have updated Fig. 4 and the relevant text.

The updated Fig. 4 now includes further time restricted O_3-HCN comparisons (Fig. 4b and Fig. 4c). This follows the 'middle ground' approach suggested by the reviewer and was prepared for 2-hr periods that often had smoke influence. We have opted to keep the original figure (Fig. 4a using all daytime O_3 and HCN data). We still consider the overall O_3-HCN correlation to be apparent, though we make sure to include several caveats regarding this correlation. Following the reviewer's concerns, we state that the overall positive O_3-HCN correlation is partially coincidental due to smoke presence (high HCN) occurring at times that O_3 would be high in the absence of smoke. The updated Fig. 4 and its relevant text (new text is shown highlighted) are included below.

Revised Figure 4:

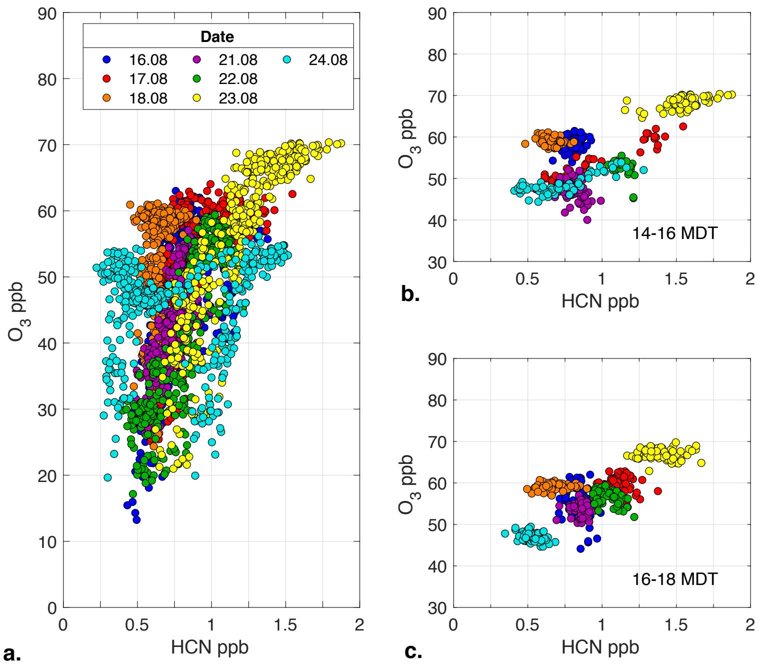

Figure 1 Correlation between O_3 and smoke tracer HCN for all observations between 9:00 and 22:00 MDT (panel a), 14:00 and 16:00 MDT (panel b), and 16:00 and 18:00 MDT (panel c). Data points are colored by date collected.

Revised Text (line 369):

For the entire campaign, there is a positive correlation between daytime O_3 (and Ox) concentrations and smoke tracer HCN (Fig. 4a) with the highest values for both observed on 23 August. Most periods of elevated HCN occurred during the times of day when [O_3] was usually high even in the absence of smoke (afternoon or early evening), so the overall positive correlation between O_3 and HCN may be partially coincidental. The positive correlation remains, however, when the analysis is restricted to 2-hour periods of afternoon and early evening data to limit the time-of-day dependence (Fig. 4b and Fig. 4c). These more specific O_3-HCN comparisons remain impacted by day-to-day variability in O_3 from changes in background O_3 values, meteorology, and BB emissions of HCN and O_3 precursors. Smoke age also plays a role in this correlation plot. Based on literature trends where $\Delta O_3/\Delta CO$ values increase with smoke age until an eventual plateau (Jaffe and Wigder, 2012;Baker et al., 2016;Xu et al., 2021), young smoke plumes are likely to have smaller O_3 enhancements relative to smoke tracers like HCN compared to aged plumes. Clusters of data points at HCN concentrations below 0.75 ppbv are observed for the 18 August and 24 August data sets. For 18 August, there was no distinct BB influenced period and a minimal range in [HCN]. This led to the cluster of 18 August data points with [O_3] near 60 ppbv. The 24 August data cluster near 50 pbbv [O_3] captures the stable period after [O_3] is depleted by ~7 ppbv upon smoke departure followed by a slow build in concentration.A similar figure with O_3 plotted against CO but for times specific to the arrival or departure of smoke is shown in the SI (Fig. S8).