Interactive comment on "Comparison of Ozone Measurement Methods in Biomass Burning Smoke: An evaluation under field and laboratory conditions" *by* Russell W. Long et al.

Anonymous Referee #2

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General Comments: This study compares O3 measurement techniques in fresh, concentrate smoke plumes. The authors sample smoke plumes from both prescribed prairie grass burns and controlled chamber burns using a NO chemiluminescence measurement as the interference-free standard with which to compare several iterations of UV absorption-based measurements. This study is motivated by the prevalence of UV-based O3 analyzers at EPA air quality monitoring stations and the increasing impact of fire emissions on local and regional air quality. Although these comparisons provide insight into the potential for UV-active VOCs in smoke plumes to generate positive artifacts in the UV-based O3 measurements, a more quantitative assessment is limited by the lack of detailed VOC measurements and the inability to quantitatively

disentangle the various CO-ΔO3 regimes. The authors also suggest the role of Nafion in mitigating potential artifacts, but do not provide enough information on the relative humidity conditions during the various sampling periods or the potential for interactions between water vapor and VOC. Further, the analysis emphasizes the effects of VOC interreferences in near-fire smoke plumes but does not provide much discussion on how the potential for interference diminishes with plume age and dispersion. For example, how quickly do VOC react/diffuse to the point where their levels are no longer of concern? How many ozone monitoring sites would be practically affected by these interferences?

Specific Comments: L243-244: Is there any dependence of the artifact magnitude on distance from the active fire line? How quickly do the VOC react/diffuse to the point where their levels are no longer detectable as a positive artifact? All the measurements presented are taken within ~100 m from the fires, but any data collected from aged smoke would be a useful counterpoint.

L262: The authors mention a +/- 10% performance objective between analyzers. Do the calibrations reveal any systematic offset between the CL and UV analyzers?

In describing the prescribed and chamber burns, the authors mention varying moisture content in the burn material. Did the authors observe whether the wetter grasses produced more VOC (lower combustion efficiency) in any systematic way?

Figure 4: In general, the scale mismatch on the O3 timeseries makes immediate comparison between methods difficult. The authors should perhaps switch to a log-scale on the y-axis that can effectively compare low and high concentrations and offsets in both smoke plumes and background air. The authors attempt to explain the positive offset of the UV-C method outside of the burning period, but there is also a significant negative offset in the UV-C-H method that is not discussed. Could the authors provide more insight on why the UV-C-H and NO-CL techniques disagree in background air?

L378+: If the damaged MnO2 scrubber ineffectively removed O3, I would expect the

UV-C measurement to be biased low in background air rather than high. Please elaborate on the mechanism of MnO2 damage resulting in a significant positive offset. Also, it's unclear when the scrubber damage became an issue. Did it affect data from the 2017 prescribed burns?

Figure S9 indicates there is potential artifact even <1-2 ppm CO. Do these plots just use data from the burn periods or include points when chamber is flushed with outside air?

L459-461: How does the residence time and sample rate vary for each instrument?

Table 4: The slope and intercept uncertainties should be included with the fit parameters. How different are the range of fitted slope values statistically? In general, there is lack of uncertainty treatment in the paper. How do the uncertainties compare for each measurement technique? This information should be included in the manuscript.

L550-552: See question 1 above. How close to the plume do you have to be for interferences to matter? Is this relevant for air quality monitoring stations not located in the immediate vicinity of the fire line?

L554: What is estimated CO-ΔO3 correlation for the chamber studies? It would still be worthwhile to include this information in the supplement.

Figures S9 and S10: Can you demonstrably separate CO-ΔO3 regimes based on "burn condition"? The authors allude to this in the text (L563) and show an individual burn in Fig S10, but a more in-depth analysis of the contributing burn condition factors would provide a more quantitative and perhaps predictive assessment of how CO links to O3 artifacts under the varied burn conditions. The authors also perform separate regressions for NO2 and THC, but a separate correlation with humidity might be illustrative (if the data exists).

L571: Is it possible that interactions between water vapor and VOC somehow compound the VOC effect? In other studies (e.g., Spicer et al. 2010, Turnipseed et al.

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2017), Nafion alone seems to play little role in mitigating VOC artifacts but does significantly reduce water vapor artifacts. In drier environments, does adding Nafion affect the positive artifact magnitude? This would be more conclusive evidence that Nafion does in fact remove certain permeable VOC species.

L605: Could this also be confounded by the faulty MnO2 scrubber?

Technical Corrections: Table 1: Add uncertainty associated with each measurement technique. Sample rate would also be useful.

Figure S1 and other timeseries in general: It's difficult to compare NO-CL and UV measurements of plumes and background air given the large mis-match in scale. Some other way of presenting this material (e.g., semi-log) might help the visual comparison. The lines are also not very easy to distinguish. Using different colors instead of just patterns would help.

Figure 2. Does not need to be in 3D and could use a color scheme instead of patterns.

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