Response to Reviewer 2 Comments

Comparison of Ozone Measurement Methods in Biomass Burning Smoke: An evaluation under field and laboratory conditions

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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-O3 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?

Response: The authors appreciate the time required to provide the review and feel that the suggestions provided by the reviewer will result in an improved manuscript for resubmission.

During both the prescribed and chamber burns, data were obtained for RH values and water vapor concentration and is included in the data associated with this paper that will be provided through the EPA Science Hub Web site (https://catalog.data.gov/dataset/epa-sciencehub) following the acceptance of this paper. . However the correlations between RH and the magnitude of the ozone artifact were not significant and therefore not included in the manuscript. In general, both the prescribed fire and chamber burns were conducted under dry conditions with RH≤50%. Past studies, which are now referenced in the updated manusript indicate that at those RH values humidity effects are expected to have little to no impact. It is the intention of the authors to add

an additonal section to this manuscript discussing implications of this research on real world ozone monitoring such as that that occurs at State and local moitoing sites. The authors intend to review data from sites downwind of wildfires that potentialy show the artifact in the UV-C O3 method and how it is correlated with markers of combustion processes. As stated in the text of the manuscript, the authors plan future studies to dig deeper into the hypothesized VOC caused artifact and which will include, as the reviewer suggest looking into interaction between VOCs and water vapor and the capabilities of Nafion in removing certain VOCs.

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.

Response: The authors did not look at the dependencies of the artifact magnitude on distance from the active fire line. However, the authors do agree that a more detailed look at data collected at sites being impacted by aged smoke (ex. State and local monitoring sites being impacted by nearby wildfires). This would aid in tying these measurments made in or near plume back to real world monitoring situations. Most likely this will be done by adding an implications section prior to the manuscript conclusion.

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?

Response: The calibrations did not reveal any systematic offsets or biases between the different analyzers and we will clarify this in the updated version of the manuscript. At present the authors have not investigated the relationship between fuel moisture content and VOC production. In order to simulate a range of natural burning conditions, the chamber burns manipulated the moisture content, fuel type (pine needles, pine needles + fine woody debris), and bulk density of the fuelbeds. These fuelbed properties influence the relative mix of flaming and smoldering combustion and the chamber burns covered a range of combustion efficiencies (modified combustion efficiencies of 0.85 – 0.97). The authors will investigate further and address these findings in a future manuscript.

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?

Response: The authors will work on this time series plot as well as others to make the figures more legible including looking into using a different scale on the y-axis. As suggested by the

reviewer, the authors will provide more insight into 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?

Response: In order for the scrubber to work correctly, it must remove O3 and only O3. Based upon the data, the damage most likely resulted in the scrubber also removing significant amounts of interfereing species during the reference measurement which would then be detected as ozone during the sample measurement resulting in the positive artifact. The data collected during the 2017 prescribed burns indicate that the scrubber was functioning properly in that there was excellent agreement between the UV-C and NO-CL methods when sampling out of the smoke plume.

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?

Response: Figure S9 includes data from the burn periods only. In the figure caption it describes it as "in-plume". The authors will add clarifying text similar to the following, "…and THC for all in-plume (burn period only) measurements…".

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

Response: Sampling rates and hence residence times are going to be similar for all instruments as they all operate with similar flow rates. The authors will address this comment by either adding analyzer flow rate to Table 1 or by inserting text in the Methods section under each corresponding analyzer type.

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.

Response: The authors agree with this comment and will work to include uncertainties (both in tables and in the text) of measurement methods and in fit parameters associated with regression statistics.

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 inthe immediate vicinity of the fire line?

Response: The authors focused on determining if significant ozone measurement artifacts do occur in near-field smoke events and did not look at the dependencies of the artifact magnitude as a function of distance from the active fire line. However the authors do agree that a more detailed look at data collected at sites being impacted by aged smoke (ex. State and local monitoring sites being impacted by nearby wildfires) and are currently collecting this data as part of the EPA MASIC study in Boise, ID; Missoula, MT; and Reno, NV. This additional data collection will aid in linking these research chamber and near field prescribed grassland burn measurements back to

real world regulatory monitoring situations. We will address these issues in a new "implications" section prior to the manuscript conclusion.

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

Response: Regarding the correlation between ΔO3 and CO from the chamber based burns, the authors refer the reviewer to the original manuscript text:

"As indicated, ΔO3(UV-C) and CO appear to be correlated in time but when performing linear regression comparisons of ΔO3(UV-C) and CO during each years chamber burns as a whole, correlations tend to be poor. We suspect the positive O3 bias is driven by one or more VOCs (likely oxygenated VOCs). In fresh smoke the excess concentrations of individual VOCs (ΔX), and VOC sums (ΔVOC), tend to be highly correlated with ΔCO (Yokelson et al., 1999; Gilman et al. 2015). The emission ratios of individual VOCs to CO (ΔX/ΔCO) can vary considerably with combustion conditions such as fuel type and condition (e.g. moisture content and decay state), fuel bed properties, such as bulk density, and the relative mix of flaming and smoldering combustion (Gilman et al. 2015; Koss et al., 2017). Additionally, the response of ΔX/ΔCO to burn conditions varies among VOCs. When each burn is considered individually or in groups with similar conditions, the correlations between ΔO3, CO, and THC are enhanced. An example of this behavior is shown in Supplementary Fig. S10."

With that being stated, the authors will consider adding the CO-ΔO3 correlation (both for the entire chamber study period and also a subset of individual burns) either in Table 4 or in the body of the text give evidence to the above statement. Visual representations of the correlations are given in Figures S9 and S10.

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).

Response: The authors will consider elaborating further per the reviewers suggestion on CO-ΔO3 regimes based on burn conditions (i.e., individual burns or burns grouped by similar burn conditions). The authors previously attempted to establish a correlation between ΔO3 and humidity (water vapor concentration) but those correlation were extremely poor. As such the authors chose not to include this analysis.

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. 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.

Response: Both the 2017 prescribed fire and 2018-2019 chamber based burns were conducted under dry conditions (RH≤50%) and humidity interferences are expected to be minimal. As stated in the previous comment, the correlation between in plume water vapor concentration and ΔO3 was not significant. In addition, there is no signifcant correlation between the magnitude of the

artifact and RH. In both the prescribed grassland and chamber burns there was a UV instrument with a Nafion drier and a UV instrument without the drier and they were operated simultaneously. The magnitude of the artifact (both average and maximum) was greatly reduced in the method using the Nafion drier. In section 3.5 of the manuscript, the authors will attempt to clarify that in addition to our hypothesis of certain VOCs being removed by the Nafion, there may also be interactions between water vapor and VOCs that may be confounding the observed artifact.

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

Response: We do know that during the 2018 chamber studies the damaged scrubber did cause an approximate +10-15 ppb bias in the UV-C method which was present even in the absence of smoke. At the end of the 2018 chamber studies, the authors added a Nafion drier to the UV-C method as indicated in Figure 4. The addition of the Nafion to the UV-C method reduced the magnitude of the artifact by a factor of three making it compatible to the artifact observed for the UV C-U method. The addition of the nafion did result in a slight reduction in the bias that we attributed to damaged scrubber but not on the order of 3X. The authors will clarify this further in the body of the text. The reviewers comment would only apply to the 2018 chamber study as the MnO2 scrubber in the UV-C method was functioning properly during all other studies.

Technical Corrections:

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

Response: The authors will address this comment by either adding analyzer flow rate and uncertainties to table 1 or by inserting text in the Methods section under each corresponding analyzer type.

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.

Response: The authors agree with this comment and will take steps to improve the the time series plots, including looking into different scales (e.g. semi-log) and also using colored lines in the figures.

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

Response: The authors agree with the reviewers comment. The figure will be reformatted into 2D and assuming that AMT allows colored figures will include a color scheme to improve clarity and view ability. In addition, the y axis scale will be reduced to 50 ppb and the average values for all methods will be included in the figure as text. The figure caption will be revised to reflect these changes.