

Response to Reviewer 1 Comments

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

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General comments.

This paper uses measurements in highly concentrated fire plumes (within 100m of wildland grass fires, and in controlled burns at the Missoula Fire Lab) to assess interferences in UV absorption measurements of ozone at 254 nm.

This paper is motivated by the ozone measurements of UV absorption instruments, and the health impacts from that ozone. Large increases in ozone may be observed after precursor NO_x and VOC have had time to react. The time scale to produce that ozone is highly dependent on plume dilution, which itself is highly variable in time, but typically takes place over hours since emission. A fundamental question: for direct emissions, the interfering species will also be diluted, such that the lowest interferences may be expected at the highest levels of plume ozone. Secondary production of UV-active hydrocarbons, e.g., production of nitroaromatics following oxidation in the presence of NO₂, may dominate the ozone interference downwind. What balance of directly emitted vs. secondary species are conjectured to lead to interferences in ambient ozone measurements? Regardless of the source of the interference (primary vs. secondary), given the lack of consistency from fire to fire (or even between different implementations of the UV absorption technique) in the level of interferences measured, can the authors say what level of "fire impact" causes a non-negligible interference? Is 1 ppm of ozone acceptable? 10 ppm of ozone? Regardless, despite the experimental detail in this paper, it is not clear what ozone monitoring locations are expected to suffer from significant interferences as a result of wildfires or prescribed burns. Lacking these considerations, the paper's conclusions are qualitative at best, and by implication condemn a much larger portion of the U.S. ozone monitoring network during the fire season than I suspect is warranted. For a given UV absorption monitor, can they recommend what data to retain, and what data to eliminate because of fire impacts? Some additional clarity in the real-world effects of fire smoke on ozone monitoring is needed for this to make a novel and useful contribution to the literature.

The paper is overly long and can be shortened by removing extraneous details, repetitive text, and tables that do not provide any usefully generalizable data as suggested below. Earlier literature is not well cited, and additional references are also suggested below.

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.

The authors do agree that a more detailed look at data collected at sites being impacted by aged smoke (ex. State and local regulatory monitoring sites being impacted by nearby wildfires and long range transport of photochemically aged smoke plumes) 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.

The authors will, as suggested by the reviewer, attempt to shorten the length of the manuscript by removing text that is tangential to the scope of the paper. In addition, the authors will review earlier literature and cite as appropriate including those references suggested by the reviewer.

Specific comments.

line 14: "... large increases in ozone are also observed downwind ..." Is this always true?

Response: The authors did not imply that large increases in ozone are always observed down wind of wildfire events. To clarify this and prevent assumptions that these increases in ozone “always occur”, the text will be rewritten to include a statement like "... large increases in ozone have been observed downwind ..."

line 32 (and lines 38 and 182 and elsewhere): The NO-induced chemiluminescence measurement of ozone is repeatedly described as "interference-free", which is misleading - it has a known dependency on water vapor, which can lead to sensitivity variations of up to 8% if not accounted for. Please rephrase.

Response: The authors will rephrase these statements to emphasize that sample treatment steps, including the use of a drier, must be taken prior to analysis to remove the effects of water vapor.

line 52: for clarity, please change to "... generates nitrogen dioxide in an electronically excited state..." The original citation is Clough and Thrush, 1966, Chemical Communications, 728, pp. 783-784.

Response: The authors agree with this suggestion and will change the text accordingly.

line 93: please remove CO₂, as its absorption is negligible at 254 nm.

Response: The authors agree with this suggestion and will remove CO₂ from the text accordingly.

line 142: "...a supply of NO gas..." is not always needed - line 213 refers to one implementation of the "scrubberless" UV absorption method uses a supply of N₂O gas and produces NO by photolysis.

Response: The authors agree with this suggestion and to clarify will rewrite the sentence to read: “The SL-UV method requires a continuous supply of compressed NO or nitrous oxide (N₂O) (which the instrument converts to NO) to serve as the scrubber gas.

lines 230 - 237: Details of power, generator, charger, and batteries are tangential to the performance of the analyzers and could be eliminated to shorten the text.

Response: The authors agree with this suggestion and will review the manuscript and eliminate non-relevant text that will shorten the document.

lines 267-8: "...calibrations for THC were performed using... a methane/propane gas cylinder..." This work eventually concludes that VOCs are "likely to interfere with UV absorption measurements of O₃", no surprise there. What is surprising is the rudimentary approach to quantifying those VOCs in this manuscript. FID response factors vary with carbon number (for example, by up to a factor of 3 between methane and propane!), between aliphatic, aromatic, and cyclic structures, and with heteroatomic functionality. A sentence noting the uncertainty introduced in their measurement of VOCs (here called THC) by using only methane and propane to determine FID sensitivity would be appropriate here.

Response: The authors agree with this comment and will add a sentence to address the uncertainty associated with our use of the THC method and its calibration procedure to approximate VOC concentrations.

Figure 2: This is not a good graphic. There is absolutely no information conveyed by the third dimension of this graph; please turn this into a 2D bar graph and improve the legibility of the different hatches. The high level of interference from the UV-C and UVC- H techniques overwhelms any useful information on the other techniques - suggest plotting only to 50 ppb and annotating the UV-C maxima with text. These data are presented as O₃ in ppb - what is the correct, or expectation value? The NO-CL data are lost in this presentation and should be emphasized as the correct value.

Response: The authors agree 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 viewability. 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.

Figure 4: The NO-CL reference trace in the upper figure is the hardest to see; these figures could use some work for legibility. The text refers to positive artifacts for the UV methods during burning periods, ascribed to interferences from VOCs and PM_{2.5}. Another problematic feature is the negative artifact when the chamber is flushed with outside air, where the UV-C method falls below the NO-CL method (bottom panel). Why is that? Did I miss the explanation?

Response: The authors will work on this time series as well as others to make the figures more legible including looking into using a different scale on the y-axis. The authors assume that the negative artifact the reviewer mentions is visible in the bottom plot of Figure 4. There is no negative artifact where the UV-C method falls below the NO-CL method. This perceived artifact is due to the large differences in the two y-axis scales and will be eliminated by placing both the UV-V and NO-CL results on the same y-axis.

Lines 378-388: I could not follow the confusing thread discussing how and when the MnO₂ scrubber failed in these experiments - for clarity I'd recommend deleting this section and removing all data taken with an inoperative scrubber.

Response: The scope of this paper is a comparison/evaluation of ozone monitoring methods in smoke and the damage to the converter occurred while operating the UV-C analyzer in heavy smoke, the authors feel that this potential measurement issue is very important to those utilizing these instruments and should at a minimum be mentioned in this manuscript. The converter issue is important in that the effect continuous long after the smoke exposure is over and is not obvious when conducting typical QA/QC reviews (e.g., zero/span calibrations and checks). The authors will add/remove text to clarify when the damage occurred and the impact that the damaged converter had on the results obtained with the UV-C method.

Table 3: Since there appears to be very large fire-to-fire and technique-to-technique variability in the interferences, with no consistent dependence on any of the variables measured, quantifying their precise values in a table seems not very useful. I'm not sure what information this table provides; what quantitative use is it? Recommend deleting.

Response: The authors disagree with this comment. Regardless of the burning conditions or techniques used, artifacts in the UV photometric methods were observed and are presented in this table. The authors intend to include Table 3 in the manuscript.

line 498: This section recommends using Nafion dryers to minimize smoke interferences in UV absorption ozone measurements. This begs the question - under what range of conditions does the use of a Nafion dryer allow EPA to actually accept an ozone measurement by the UV absorption measurement? Please discuss.

Response: This comment goes beyond the scope of this paper which is primarily focused evaluation/comparison of ozone monitoring methods in smoke plumes. However, the authors intend to include an additional implication section that will discuss the potential impact of our findings on real world monitoring application at sites that might be impacted by nearby wildfire smoke plumes.

Table 4: Same comment as for Table 3, above: "Since there appears to be very large fire-to-fire and technique-to-technique variability in the interferences, with no consistent dependence on any of the variables measured, quantifying their precise values in a table seems not very useful. I'm not sure what information this table provides; what quantitative use is it? Recommend deleting."

Response: The authors disagree with this comment. Regardless of the burning conditions or techniques used, artifacts in the UV photometric method were observed and those artifacts are correlated with makers of combustion as illustrated in this table. The authors intend to include Table 4 in the manuscript.

line 581: I would suggest the authors review and cite the use of perfluorosulfonate membrane tubing to remove UV-active hydrocarbons, e.g., in SO₂ pulsed fluorescence instruments (Luke, W., 1997, JGR, 102, 16,255-16,265).

Response: The authors will review the suggested manuscript and if appropriate cite in the text as a possible solution in mitigating interferences by wildfire generated UV-active hydrocarbons as suggested by the reviewer.