

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 #1

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Review of Long et al., manuscript ID amt-2020-383, “Comparison of ozone measurement methods in biomass burning smoke: an evaluation under field and laboratory conditions”

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

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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.

Specific comments.

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

C2

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.

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.

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

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.

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.

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.

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 UV-C-H techniques overwhelms any useful information on the other techniques - suggest

C3

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.

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?

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.

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.

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.

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."

C4

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).

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