(10-220412-A) **Bias in O_3 Measurements in Smoky Air When using some UV Instruments**

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With the recent increase in wildfires in the western U.S. there are now many days with $PM_{2.5}$ and O_3 concentrations above the health and air quality standards (Kalishnikov et al 2022). It is known that smoke increases the concentration of O_3, both in isolated plumes and when mixed into urban areas (Buysse et al 2019; Jaffe et al 2020; McClure and Jaffe 2018; Ninneman and Jaffe 2021; Pollack et al 2021). However because of the large quantities of VOCs in smoke plumes, we felt it important to evaluate possible biases in the UV measurement of O_3. The UV instruments operate by measuring the absorbance with and without O_3 in the sample stream. A bias could occur if UV absorbing compounds are removed, along with O_3, in the scrubber.

Our first evaluations on this were done in the summer of 2015 by comparing two UV O_3 instruments (a Dasibi and an Ecotech) to a chemiluminescent measurement of O_3 using nitric oxide (NO) during strong smoke episodes. The results showed no significant difference using these two UV instruments, compared to the chemiluminescent method at CO concentrations up to 700 ppb (Gao and Jaffe 2015). More recently, an analysis by Long et al (2021) report strong positive biases in fresh and heavy smoke plumes, compared to chemiluminescent measurements. However we have some questions about the conclusions, which depend on the type of O_3 scrubber. Our recent analysis indicates that large O_3 biases are present in some UV instruments, but not others, due to the nature of the O_3 scrubber used (Bernays et al 2022). In particular the Thermo 49 series of UV instruments seems to be most strongly impacted, compared to other UV models.

Figure 1 shows a recent example of observations at the Mt. Bachelor Observatory in in fall of 2020, when heavy smoke reached the observatory. At that time we were running two UV instruments, one an Ecotech (used previously by Gao and Jaffe 2017) and the second a Thermo 49c. As seen in the figure, concentrations measured by the Thermo were substantially higher and correlated with the amount of smoke, as measured by CO. The slope indicates a bias of approximately 11 ppb per ppm of CO. We note that during non-smoke periods (CO<200 ppb), we find excellent agreement between the two O_3 measurements with an R^2 of 0.98 and a root mean squared error (difference) of 0.9 ppb. As noted by Bernays et al (2022), the most likely cause of the bias in the Thermo 49 series UV instruments appears to be the type of scrubber used in the Thermo instruments, which is quite different from those more commonly employed. The bias in the Thermo UV O_3 measurements in smoky conditions is substantial, and users of this instrument should be aware of it and may want to take corrective actions.

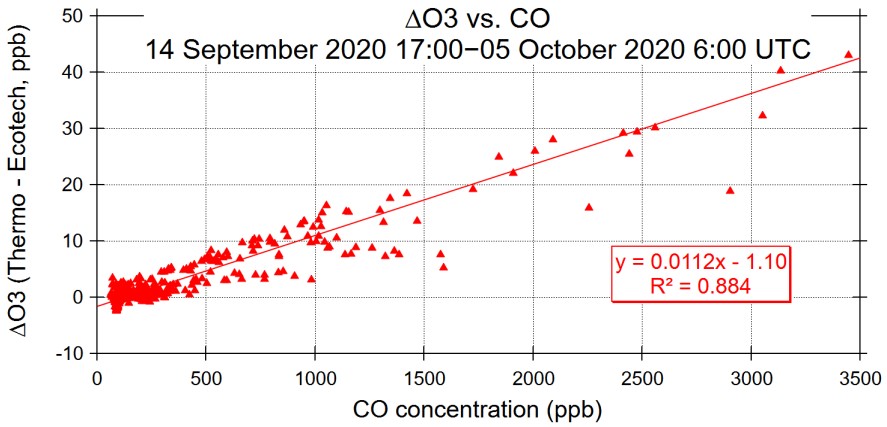

Figure 1. Difference (Thermo minus Ecotech) in O_3 concentrations measured at the Mt. Bachelor Observatory vs. CO (carbon monoxide) for a 3-week period with strong wildfire smoke (9/14/202-10/15/2020). During this period, the difference was as high as 45 ppb and was well correlated with CO, an indicator of the amount of smoke. Values are hourly averages.