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Comment

Interactive comment on “**Technical note:
Evaluation of standard ultraviolet absorption
ozone monitors in a polluted urban environment**”
by E. J. Dunlea et al.

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Response to reviewers' comments for: Manuscript # ACPD-2005-0431 Technical Note: Evaluation of Standard Ultraviolet Absorption Ozone Monitors in a Polluted Urban Environment E.J. Dunlea, S.C. Herndon, D. D. Nelson, R.M. Volkamer, B.K. Lamb, E.J. Allwine, M. Grutter, C.R. Ramos Villegas, C. Marquez, S. Blanco, B. Cardenas, C.E. Kolb, L.T. Molina and M.J. Molina

This response comment contains several general responses that are intended to address multiple referee comments. There is a separate response comment that contains responses to the individual referees' specific comments. Several supplemental figures (described, but not shown, in the text below) are available

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at <http://cires.colorado.edu/~dunlea/acpd-2005-0431-rp-supplementalFigures.pdf> if the reader wishes to view them. These figures will be incorporated into the new manuscript for submission to ACP.

General Response #1 - Further discussion of observed interference in UV O₃ monitor from diesel vehicles In response to the concerns raised by several referees here, we revisit the conclusion that particles are responsible for the O₃ spike events described in Section 3.1. There are several proposed explanations for the observed interferences: 1) Gas phase hydrocarbons emitted by diesel vehicles 2) Gas phase compounds (probably hydrocarbons) desorbed off of the particulate filter 3) Rapid fluctuations in ambient water vapor concentrations accompanying CO₂ spikes that interfere with absorption cell windows 4) Elemental mercury 5) Particles entering the absorption cell and absorbing and/or scattering UV radiation

1) The hydrocarbon levels typical of diesel exhaust are generally low. Typical hydrocarbon emission ratios are on the order of 0.05 ppb hydrocarbon / 1 ppm CO₂ (see Ref 1 listed below). If we use 350 ppm (750 ppm - 400 ppm background) as a typical CO₂ spike above background observed in the event displayed in Figure 2 and assume that a potentially interfering hydrocarbon has an emission ratio of 0.1 ppb / 1 ppm of CO₂, this leads to 35 ppb of hydrocarbon. It is the product of the concentration \times absorption cross section that matters in order to determine the resulting interference in the O₃ measurement. Because O₃ has such a large cross section at 253 nm (1.15×10^{-17} cm²), most compounds will have an absorption compound either roughly equivalent to O₃'s or lower, such that 35 ppb of a hydrocarbon would most likely translate to an O₃ interference of approximately 35 ppb or less, but not 300 ppb (see ASTM reference listed in manuscript). A figure has been added to the new manuscript to show that, indeed, measured hydrocarbon levels were low during the diesel event (this is Figure S1 in supplemental figures). None of the measured species (acetaldehyde, formaldehyde, acetone, methanol, benzene, C₂-benzenes, C₃-benzenes, toluene) show enough of an interference to account for observed O₃ spikes and almost all of them show a large

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event at 3:04:11pm that shows no corresponding interference in the O₃ measurement, indicating that these compounds are not responsible for the observed interference. It is possible that some unknown hydrocarbon is emitted from diesel vehicles with a much larger emission ratio, but this explanation does not seem likely.

2) The possibility of gas phase compounds desorbing off of the particulate filter to cause the observed interference cannot be completely ruled out with the available data. However, if the interference were due to this process, the interfering compound would have to be one that desorbs quickly off of the particulate filter. The O₃ instrument reported O₃ values every 10 seconds. The O₃ measurement recovered to normal levels within one reported data point in the midst of one of these diesel chase events (visible in Figure 2). Thus, the interfering compound(s) would have to completely desorb in less than 10 seconds in order not continue to affect the O₃ values for longer time periods. Again, although this is possible, it does not seem likely.

3) Water vapor - there were no measurements of ambient relative humidity on board the ARI mobile lab to help address the question of whether rapid changes in ambient water vapor content entering the UV O₃ monitor could be responsible for the observed O₃ interference. However, we reiterate that the interference was only observed in the exhaust plumes of diesel vehicles, and it seems unlikely that rapid fluctuations in water vapor are much greater in the exhaust of diesel vehicles as compared to that of gasoline vehicles. In fact, it is likely that there is more water vapor in the exhaust of gasoline vehicles than in diesels. We see the possibility of a water vapor based interference as an unlikely explanation for the observed O₃ interference.

4) If Hg levels on the roadway were indeed elevated, this would have been observed by the UV O₃ monitor on board the ARI Mobile Lab which spent much of the 5 week campaign driving on the roadways of Mexico City. Such an interference would have almost certainly appeared as spikes, similar to those observed in Section 3.1. However, Hg is not cited as a possible cause of these spike events because these spikes events were observed only when sampling diesel vehicles and the cultural practice of

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sprinkling elemental Hg within vehicles is not limited to diesel vehicles. A sentence has been added to Section 3.1 to address this.

5) Referee #1 asked that we provide details on the particulate filters used. None of filter types used during this campaign were specifically noted during the study, but information from the manufacturers^{2,3} indicates that these O₃ monitors most likely all employed 5 µm Teflon filters. According to a study on effectiveness of various filters⁴, this type of filter could allow transmission of as much as 15% of particles below 100 nm. There is sufficient particulate matter in the exhaust plume of a diesel vehicle that even a low percentage of transmission through the particle filter by small particles could potentially result in a large number of particles entering the UV instrument.

The major objection that has been raised to the explanation that particles entering the absorption cell are the cause of the observed interference was that particles would need to be lost on the scrubber in order to scatter more UV radiation in the measurement channel compared to the reference (scrubbed) channel, and thus appear as a positive interference. The scrubbers employed in these instruments are mesh screens coated with MnO₂ and the hypothesis that particles could be lost on this type of scrubber seems completely reasonable to the authors, even if referee #3 disagrees. Indeed, this idea was confirmed as probable by technicians at the manufacturer of the O₃ monitor². Additionally, anecdotal evidence from a technician at the manufacturer² described observed interferences from cigarette smoke, which was definitively linked to particles causing apparent spikes in the O₃ concentration.

To estimate if there would be enough particles to cause such a large O₃ interference, we can use the measured active surface area from a diffusion charger monitor (EcoChem, DC 2000 CE) that was also on board the ARI mobile lab. As an example, during the event shown in Figure 2, the active surface area was as much as 1600 µm² cm⁻³ at the same time that apparent O₃ rose by more than 300 ppb (see Figure S1). The path length of the absorption cell within the UV monitor is 35 cm, such that the calculated absorption from this particle surface area would be 6×10^{-4} , corre-

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sponding to an O₃ concentration of 70 ppb (where $1 \text{ ppb O}_3 \sim 8 \times 10^{-6}$ absorption)². The measured active surface area is generally a good approximation of the total scattering surface area⁶, such that this amount of absorption may not be enough to explain the potential interference. Additionally, this estimate assumes that all particles contribute to the interference, which means that all particles are lost on the scrubber in the reference channel. It seems more likely that some small percentage of the particles is lost on the scrubber and thus contributing to the interference, so fine particles may not fully explain the observed interference. We note that there is considerable uncertainty in this estimate, and as is discussed in Section 4, this topic warrants continued research and further study is recommended in the conclusions of the new manuscript.

General Response #2 - Further discussion of FTIR and DOAS data The term “absolute” has been replaced with “highly accurate” in referring to the spectroscopic measurement techniques. Additionally, the comments referring to UV monitors as being an absolute measurement in theory have been removed as well. References to other publications that discuss the DOAS and FTIR techniques are included and an extended discussion of these techniques has been deemed outside the scope of this paper by the authors. This is, after all, supposed to be a Technical Note, and is already much longer than the suggested length for such a paper. Further discussion of the DOAS measurements made during MCMA-2003 is planned for a future publication⁷.

General Response #3 - Further discussion of overall performance of UV O₃ monitors - role of different scrubber types The observed differences between the UV O₃ monitors and the co-located spectroscopic measurements have been attributed to the mis-calibration of the UV O₃ monitors. Several referees have asked about the possibility that different scrubber types on the UV monitors located at CENICA (heated silver wool) and La Merced (unheated MnO₂) could have contributed to the observed differences. If we look at the results of Leston et al. (2005), we see that UV monitors with heated silver wool scrubbers are shown to perform well compared with the Federal Reference Method (FRM) chemiluminescence instruments or measure slightly low

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if anything, whereas UV monitors with MnO₂ scrubbers show a positive interference from photochemical products in a smog chamber, presumably aromatic hydrocarbons or their derivatives. In our study however, we observed a positive bias in the UV monitor at the CENICA site, which employed a heated silver wool scrubber and should thus agree well or measure lower values. Additionally, we observed a negative bias in the UV monitor at the La Merced site, which employed a MnO₂ scrubber and would thus be prone to positive interferences according to the Leston et al. study. Given that the observed differences at both locations are opposite in sign to the previously reported differences expected from interferences, it is left as our conclusion that the most likely reason behind the observed discrepancies between the UV monitors and the co-located open path spectroscopic instruments is the mis-calibration of the UV monitors. Nonetheless, it is obvious that this issue is complex enough to warrant further research and comparing various UV O₃ monitors with different scrubber types has been added to the new manuscript as a suggested subject of future study.

General Response #4 - Further discussion of overall performance of UV O₃ monitors - changes made to calibration factors in UV monitors The CENICA UV O₃ monitor was calibrated at the beginning of the campaign, as noted in the manuscript. Further inquiry has revealed that, for this calibration, the measured values were within 7% of the introduced amounts from the calibrated O₃ monitor, such that the monitor was deemed to be working acceptably and no adjustment made during the campaign. This information has been added to the new manuscript. At this time, information on the zero and span adjustments made during the 2003 campaign are unavailable.

References for General Responses

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2) Personal communication with Technical Service Group at Thermo Electron Corporation

3) Personal communication with technical services at API

4) Liu BYH, Pui DYH, Rubow KL [1983]. Characteristics of air sampling filter media. In: Marple VA, Liu BYH, eds. Aerosols in the mining and industrial work environments. Ann Arbor, MI: Ann Arbor Science 3:989-1038

5) D. Imhof, E. Weingartner, A. S. H. Prévôt, C. Ordóñez, R. Kurtenbach, P. Wiesen, J. Rodler, P. Sturm, I. McCrae, M. Ekström, U. Baltensperger, Aerosol and NO_x emission factors and submicron particle number size distributions in two road tunnels with different traffic regimes, Atmos. Chem. Phys., 6, 2215-2230, 2006

6) K. Siegmann, L. Scherrer, H. C. Siegmann, Physical and chemical properties of airborne nanoscale particles and how to measure the impact on human health, J. Mol. Struct.: THEOCHEM, 458, 191-201, 1999.

7) Personal communication with Dr. Rainer Volkamer

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