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Atmospheric Chemistry and Physics Discussions

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 responses to the individual referees' specific comments. There is a separate response comment that contains several general responses that address multiple referee comments; references to these comments are described in the text below as "General Responses". To save space in this document,

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the comments from the referees have been abbreviated (with "..."), leaving enough text to remind the reader of the referee's main point in each comment. Again to save space, referee comments are designated by ">>>" with our subsequent response designated by ">". Several supplemental figures (described, but not shown, in the text below) are available 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.

Anonymous Referee #1

>>>... For example, point and open path measures might better correlate if categorized with respect to wind direction (e.g., parallel vs. perpendicular to open path direction) and air parcel shading (by highrise buildings, topography, or clouds) since point and open path monitors might then be sampling more similar air parcels. Authors should augment their highly averaged comparisons (e.g., monthly averages) with hourly time-series comparisons that are more relevant as regulatory measures of monitor reliability...

>To look at the influence of nearby roadways, we plotted the NOx concentrations as a function of wind direction (shown as supplemental Figure S2). The CENICA site shows very little variation, whereas the La Merced site shows a large variation of the average NOx levels with wind direction. This is consistent with the La Merced measurement site being in close proximity to a major roadway.

In order to address the referee's comments, further analysis was done on the La Merced data to look at the effects of wind direction. The La Merced data was categorized into three types based on the wind direction with respect to the open path light paths physical relation to the nearby major roadway (see Grutter and Flores, 2004): (A) wind perpendicular to open path measurements (and therefore parallel to roadway), (B) wind parallel to open path measurements and coming from roadway, and (C) wind parallel to open path measurements and blowing away from roadway. Category B shows

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enhanced NOx as compared to the other directions as expected (see Figure S3 in supplementary material). Although the absolute magnitude of the difference between the measurements varies, the percentage difference remained roughly constant for the majority of the daylight hours (as described in Section 3.2.2 of manuscript) and does not vary systematically as a function of wind direction. (This is shown in supplemental figures S4 and S5: Figure S4 shows the diurnally averaged profiles of O3 as a function of wind direction in a similar manner to Figure 3 in the manuscript; Figure S5 shows the diurnally averaged profiles for the differences between the UV O3 monitor and FTIR O3 measurements.) Thus, the conclusions presented in the manuscript are not influenced by categorizing the data by wind direction indicating that NO titration of O3 was not responsible for the observed differences in the O3 measurements, nor were potential interferences from other combustion products. This information has been added to the new manuscript.

There was no data on shading recorded during the MCMA-2003 campaign to potentially address the referee's point. Any shading of the open paths or the point sampling sites at both the CENICA and La Merced locations would have been due to clouds because there were no tall buildings in close proximity to shade either of these sites.

Concerning the "highly averaged comparisons", it is apparent that the nature of the comparisons has not been communicated effectively. The data presented in Table 1 (now Table 2), upon which the conclusions in the paper are primarily based, are indeed 1 hour averages. A side point is that there was a typo in the manuscript concerning the comparison of DOAS-1 to DOAS-2, which was described in the text as using 15 minute averaged data, when in fact, this data was also compared for hourly averages. This typo has been corrected and a sentence has been added to the caption for Table 1 to clarify that the data are comparisons of hourly averaged data.

The presentation of diurnally averaged profiles in Figure 3 was chosen for succinctness. The same patterns of behavior for the O3 measurements were revealed on a daily basis during this study, such that the average of a month's worth of diurnal pro-

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files allows for general conclusions on the instrument performance. As noted in the caption to Figure 3 “these are not the differences of the diurnal profiles, they are the diurnal profiles of the differences.” The idea was that averaging the discrepancy between the UV O3 monitors and the open-path measurements over the course of a month allows for a proper correction of the data from the UV O3 monitors. From there, the impact on the extreme-value standard compliance regulations is explored in Table 3. While time series graphs would indeed be useful to include, we have attempted to keep the manuscript as brief as possible to fit with the suggested format of a Technical Note.

>>> (2244: 15) Authors should make clear that the U.S. Federal Reference Method (FRM) is a gas-phase ethylene-chemiluminescence (CL) method ...

> Clarifications on the types of chemiluminescence monitors have been added.

>>> (2245:4)Author references to ‘absolute measurement techniques’ should be deleted...

>See General Response #2.

>>> (2245:19) Authors should qualify their citation of Ryerson et al. 1998 ...

> A note has been added to clarify that the Ryerson et al. NO-CL instrument is not an EPA FEM.

>>> (2246:15) Authors may wish to tabulate method characteristics...

> A table has been added as Table 1 in new draft with the following columns: Site, Instrument, Type, Sampling Height, Distance from Roadway, Scrubber Type and Absorption Cell Material

>>> (2251:13 & 2252:9) Authors should explain why the mobile source UV ozone monitor spikes correlated well with CO2, PM, and NO spikes but correlated poorly with CO, NO2, HCHO, SO2 and VOC, species also likely to be elevated in diesel bus

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exhaust plumes.

> No claim was made that the spikes correlated well with CO2 or NO, and a sentence has been added to call the reader's attention to the fact that Fig. 2 shows that similar concentrations of CO2 and NO from a gasoline vehicle do not cause an interference in the O3 monitor, so it is concluded that CO2 and NO are not responsible for the interference. The explanation for why the spikes correlate well with PM is indeed given as the main point of this section - that the spikes are due to the particles. The validity of this conclusion is discussed in General Response #1.

>>> (2252:23ff) ...1. Since UV monitors measure ozone by difference, spikes should be encountered only if particles penetrating the inlet filter are efficiently removed by the ozone scrubber, a device designed to denude ozone but transmit everything else...

> See General Response #1.

>>> 2. Authors also invoke gaseous species desorbing from particles retained on the inlet filter as an alternative explanation...

> See General Response #1.

>>> 3. Another possibility is that water vapor spikes that accompany CO2 spikes in the diesel combustion plume might also affect ozone monitor response...

> See General Response #1.

>>> (2253:9) Authors should note that the 'suitable filter' cited from Arshinov et al., 2002 is likely the zero-air filter from his ozone calibrator...

> The authors thank the reviewer for pointing out the details of the filter used in the Arshinov et al. study. The idea of determining what constitutes a "suitable filter" has been removed; instead further research to confirm that particles are indeed the cause of this interference has been included in the recommendations for future research.

>>> (2255:1) Authors rightly discuss the difficulties of comparing point and open path

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sampling measurements but their case for comparability remains unpersuasive...

> This has been addressed above in the response to the first comment by this referee.

>>> (2256:7) ... do authors conclude that daily 10-20% operator adjustments of monitor span calibration are in effect chasing temporal zero and span test drift (e.g., water vapor effects and elution of UV-active species from the scrubber)?...

> The situation appears to be that proper calibration procedures were being followed, yet large discrepancies between UV O3 monitors and open path measurements were found. The explanation has been altered in an attempt to make it clearer without changing the content; see response to comment #5 by referee #2 below and in General Response #3 above.

>>> (2259:25) Authors should discuss the role that different ozone scrubbers (heated metal wool/CENICA; unheated MnO2/La Merced) might play in the positive and negative biases observed at CENICA and La Merced...

> See General Response #3.

>>> (2261:14) Mercury interferences may be more important than authors conclude...

> See General Response #1.

>>> (2263:12) Authors should discuss the roles that different scrubbers (heated metal; unheated MnO2), absorption cells (quartz; aluminum-poly vinylidene fluoride), and inlet heights (16 m; 5 m) play in their Figure 4 comparison ...

> See General Response #3. Further discussion of the comparison of the UV monitor on the ARI mobile lab versus the point sampling monitor seems excessive; the purpose of Figure 4 is to provide an example of how the UV monitor on ARI mobile lab compared poorly with all other O3 measurements, which is summarized in Table 1d (now Table 2d). Because the ARI mobile lab UV monitor compared poorly with not only the co-located open path instruments, but also other UV monitors (including both those with

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different scrubbers and those with the same type of scrubber). The general conclusion is that the problem was with the monitor on board the ARI mobile lab.

Anonymous Referee #2

>>> ...1. In practice neither DOAS nor FTIR can be "considered absolute" ...

> See General Response #2.

>>> 2. The authors mention that the ozone monitors are being regularly "calibrated". I find this statement very misleadingĚ

> See General Response #4 concerning the history of adjustments made during the 2003 campaign. Despite the referee's point, the term "calibration" is used commonly to refer to this procedure of comparing a UV O3 monitor with a reference O3 monitor. Regular adjustments of zero and span are commonly performed, whether or not they should be done in theory, that is the practice. However, the referee's point is duly noted and a recommendation along these lines has been added to the conclusions section.

>>> 3. The interferences might be different for ozone monitors employing different types of scrubbers. Was this investigated?

> See General Response #3.

>>> 4. I would like to see more scatter plots like then one in Fig. 4...

> Originally, the manuscript included such figures, but including 13 scatter plots became a bit overwhelming, as well as confusing. The authors respectfully disagree and decline to include more scatter plots.

>>> 5. ...It is stated that average mixing ratios of aromatic VOCs were around 15 ppb in the morning and 30 ppb in the afternoon. This leads me to the following argument...

> The referee appears to be confused here. It is stated in the paper that: "These measurements provide a consistent picture that within Mexico City overall loadings of

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gas phase aromatics were higher during the morning hours (on order of ˜ 30 ppbv) and lower during the afternoons (on order of ˜15 ppbv). This was inconsistent with the overall pattern of the observed differences between the UV O3 monitors and the open path instruments, which showed a maximum in the afternoon."

The concluding sentence mentioned ("Thus, measured hydrocarbon levels during MCMA-2003 provided no evidence for interferences in the UV O3 monitors from oxidized and/or nitrated aromatic compounds, but did not definitively rule out the possibility.") attempts to summarize what has been argued up to that point: that there is no evidence of VOC compounds contributing to this interference in the UV O3 monitors, but that a contribution of VOC compounds to this interference (specifically photochemically oxidized and/or nitrated products of directly emitted VOCs) cannot be definitively ruled out by the available data.

In order to make things clearer, a paragraph from Section 3.2.3 has been broken out and made into its own section (3.2.4) to clearly state what the conclusions are concerning the overall comparisons of the UV O3 monitors. No new information has been added here, just a rearrangement of the material to hopefully make things clearer. Additionally, Section 3.2.3 has been rearranged in an effort to improve clarity.

Anonymous Referee #3

>>> ... since all monitors in the study were presumably functioning correctly and properly calibrated the authors should use the actual error range of +13% to -18%.

> This has been adjusted in text.

>> ...the authors should note that the fixed point monitors at these sites use different scrubbers...

> See General Response #3.

>>> ... the instrument log books kept by the site technicians should be examined...

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> See General Response #4 above.

>>> ...in order to produce the positive interference noted, the particle must both scatter/absorb at the wavelength of interest (254 nm) and be removed by the instrument's scrubber. Although no information on the filtration efficiency of the manganese dioxide scrubber employed in the monitor could be found, it is hard to imagine a scrubber (typically MnO2-cooated copper screens) that could effectively remove the fine aerosols (<0.2 microns) implicated in the spike events...

> See General Response #1. To reiterate, the authors do not consider the scenario of MnO2-coated copper screens removing fine aerosols to be out of the question, nor do the technical support personnel at the monitor manufacturer. The key may be that the scrubber may not have to effectively remove fine particles to cause a large interference, given the large number density of particles within a diesel exhaust plume.

>>> ...the revised national monitoring strategy under development by the U.S. EPAĚ would place key ozone monitors at highly urbanized locations and also seek to expand "roadside" monitoring...

> The authors thank the referee for pointing out this reference, which is now included in the new manuscript. As previously mentioned, further research on this topic is clearly warranted and is included as part of the recommended research in the conclusions.

>>> ...a more conclusive approach might be to "correct" the UV-based monitor data to the extent possible (for both span and zero error) and to then assess the difference between fixed and open path monitors on days when interference(s) might be expected...

> The pattern of discrepancies between the UV monitors and open path instruments is the same on all days for both locations (CENICA and La Merced), i.e., on both high and low O3 days. As a result, correction factors derived from all of the data are appropriate. This has now been stated explicitly in the text in Section 3.2.2 of the new manuscript.

>>> ...If there is any weakness in the recommendations it is the second one calling

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for finer filters (pore size of 0.2 microns or less) in order to eliminate the interferences due to diesel particles in urban areas...

> This suggestion has been replaced by suggestion for further research on exact cause of observed interference as well as subsequent quantification of that interference.

>>> With respect to the measurement of fine particle (PM2.5) mass (p. 2251, line 24) was the “DustTrack” instrument actually a “DustTrak” (TSI, Minneapolis, MN)?

> Yes, the authors thank the referee for pointing out this typo.

>>> Tables 1a, 1b and 1c show regression results both with a y-intercept and with the equation forced through zero. Some explanation should be provided...

> The first two regressions where the linear fit was forced through zero were for two CENICA comparisons of O3 measurements where the regression intercept was relatively large. The larger intercepts are driven by discrepancies at low O3 values, which are generally night time values. Boundary layer mixing is less at night and allows for the formation of thin layers that can drive spatial differences, which can lead to differences in the concentrations measured by the open path and point sampling instruments. Forcing the linear fits through zero was a convenient way of addressing this. However, a more appropriate way to address this issue is to compare day time data. Therefore, we have removed these forced regression fits and replaced them with regressions for only daytime data. The slope does not change greatly in either case.

The other regression for which the linear fit was forced through zero was for the CO comparison at La Merced. Here, the forced fit was inappropriate and the authors thank the reviewer for inquiring about this. The linear fit that is not forced through zero shows that the RAMA station point sampling monitor, although expected to have higher measured CO values because of its proximity to a major roadway, actually shows lower values than the UNAM open path FTIR CO. This speaks to potential problems with the RAMA CO monitor that are beyond the scope of this paper. A note has been added to

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the new manuscript concerning this point. The larger R2 value for the O3 regression at the La Merced site compared to that for the CO regression makes the point that the O3 comparison is at least as good as the CO comparison. The possible influence of the nearby roadway on the O3 comparison has been addressed above in the response to Referee #1's first comment concerning the wind direction.

A new version of Table 1 (now Table #2) has been inserted into the new manuscript which removes these forced regressions and replaces them with day time only regressions.

Anonymous Referee #4

>>> ...1) The comparison of the three different O3 measurement techniques is a substantial undertaking. While the data from the ARI mobile laboratory is fascinating, especially with the huge 400 ppb spike in the O3 signal, it is a large distraction from the main discussion. Authors should consider significantly condensing this section.

> An attempt has been made to keep this section short (this section currently includes five paragraphs and one figure). However, it appears that other referees consider this subject to be of considerable interest, so no reduction of this section was done.

>>> 2) ...Great care should be taken when claiming that measurements are absolute and more details should be provided to demonstrate the quality of these quantitative measurements...

> See General Response #2.

>>> 3) It is not clear that the justification that the claims for spatial homogeneity are valid. It is claimed that the DOAS-1 and DOAS-2 are in "high-level" of agreement, but the 0.93 in regression slope is almost half of the disagreement between the UV O3 monitors and the DOAS & IR measurements (+13 % to -18 %).

> Much of the discrepancy between the two DOAS O3 measurements at CENICA occurred at low O3 levels during the night, driven by a lower mixing and vertical strat-

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ification leading to different air masses being sampled by the two DOAS light paths which were at two different sampling heights. Day time measurements show an improved agreement owing to the enhanced mixing (see response to last comment by referee #3 and the new version of Table 1, now Table 2, above).

>>> 4) ...The statement that “comparisons between the point sampling UV O3 monitor and either of the DOAS instruments should be able to achieve the same level of agreement” is not necessarily true!

> The main point is that thee comparison of the two DOAS instruments provides a way to frame the comparisons between the point sampling and open path instruments. The wording has been changed here to address the referee’s point here.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2241, 2006.