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Interactive Comment

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

Anonymous Referee #3

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General:

The manuscript provides helpful information regarding the current debate over the accuracy of ozone measurement techniques in urbanized areas. The authors identify many of the issues relevant to the difficulties encountered when comparing fixed point and long-path techniques and they correctly note that significant challenges still remain with regard to the calibration and operation of ozone monitors. The large measurement differences (-18% to +13%) between state-of-the-art instruments operated by highly trained personnel indicate the need for better, or certainly for different, operating procedures and for more robust measurement techniques. Key results include precision

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estimates of collocated open path and fixed point monitors, details of a diesel emission interference in the widely used UV photometric ozone technique and recommendations for improving the quality assurance procedures associated with ozone measurement.

Specific:

The abstract (p. 2244, lines 7-8) notes that an “average” discrepancy between fixed UV photometry-based instruments and open path monitors of “13% to -10%” was found. It is presumed that “average” refers to results of the five-week study shown in Tables 1a-1d but the results from the La Merced “UV” monitor versus the open path “UNAM DOAS” at that site show a -18% difference. The authors subsequently (p. 2256) acknowledge this large discrepancy and state that the FTIR open path monitor at La Merced was “probably a better indicator of the actual difference” based on a previous study (Grutter and Flores, 2004). However, 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%.

The large errors between fixed point and open path monitors at La Merced and CENICA are attributed to incorrect resetting of the calibration factors in the UV-based monitors (p. 2258, lines 15-17). Although this is a likely scenario the authors should note that the fixed point monitors at these sites use different scrubbers. Scrubbers have been identified by many of the cited references (Leston et al, 2005, Maddy, 1999, Hudgens et al, 1994, Huntzicker et al, 1979) as the source of measurement interference and the ramifications of using different scrubbers should be explored.

Furthermore, in discussing the UV monitor calibration factors as the source of the large errors at La Merced and CENICA the authors note (p. 2258, line 12) that weekly instrument checks were performed in the RAMA network and that span adjustments of up to 10% were made as a result. It is not likely that the proposed mis-adjustments were made at one point in time but rather resulted from serial adjustments. This being the case, the instrument log books kept by the site technicians should be examined.

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It is to be expected that any changes in zero or span settings are logged as part of the quality assurance process for the express purpose of tracing the origin of problems such as the calibration errors suspected at La Merced and CENICA.

The "spike events" (discussion starts p. 2251, line11) during which diesel vehicles caused short-term "apparent" ozone concentrations of over 300 ppb in a UV-based monitor are quite interesting. The author's note that the spikes were "Ědue to interferences in the O3 measurementĚ" (p. 2252, line 21-22) and postulate that fine particles which pass through the inlet filter scatter or absorb light causing spurious ozone concentrations. However, 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. For this reason, the alternative scenario proposed by the authors (off gassing of a gaseous interferant from material captured by the O3 monitor's particulate filter) is more likely.

The interference noted in the O3 monitor on ARI's mobile platform occurred under extreme conditions and the authors note that the influence of fine particles on typical O3 monitors would be small "owing to a more suitable placement of most UV O3 monitors" (p. 2254, line 1). However, the revised national monitoring strategy under development by the U.S. EPA (http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/naamstrat2005.pdf) would place key ozone monitors at highly urbanized locations and also seek to expand "roadside" monitoring. Implementing that strategy will place more O3 monitors in locations where fresh diesel emissions are more likely to cause interference. Therefore, it is of the utmost importance to determine the actual cause the spike events and to develop a strategy to eliminate the interference(s).

The authors were able to demonstrate good agreement between fixed point and open path monitors by correcting the UV-based monitor data from two sites for apparent mis-calibration (p. 2257, line 19) and suggest (but do not rule out) that no interference was present in the UV monitors (p. 2265, line 2). However, 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. One reference cited by the authors (Leston et al, 2005) notes that the likelihood of interference in UV-based monitors increases on days when ozone concentrations are high. The authors should consider an analysis of high ozone days (perhaps the highest 20 percent) wherein they compare the corrected UV monitor data to the open path data (La Merced and CENICA) during non-rush hour periods (10AM to 5PM local time). Any interference pattern noted during high ozone days could then be compared to a similar population of low ozone days. This approach would overcome the difficulties in detecting concentration-dependent effects in data sets that have significant zero and span biases such as those from the La Merced and CENICA sites.

In their Conclusions, the authors make four excellent recommendations for improving fixed point ozone measurements which one can only hope will be implemented. If there is any weakness in the recommendations it is the second one calling for finer filters (pore size of 0.2 microns or less) in order to eliminate the interferences due to diesel particles in urban areas. In discussing the "spike events" the authors note three possible scenarios but focus on the inability of the inlet filter to capture sub-micron particles. Although the passage on fine particles into the photometer might cause the effect noted, it is not the most likely culprit (see comments above). Since other scenarios are also likely it would be best to call for additional studies on the impact of fresh diesel emissions instead of assuming a finer filter would solve the problem.

Technical:

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)?

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 since the text does not mention the significance of, or need for, such forcing. Also, when a regression is forced through zero the R2 value changes and becomes fundamentally different since the regression line does not go through the mean of the data and the residuals may not sum to zero.

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