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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.

Anonymous Referee #4

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This manuscript reports the comparison of O3 field measurements using three different methods: ultraviolet absorption, differential optical absorption spectroscopy, and open-path Fourier-transform infrared spectroscopy. The authors provide an excellent review of studies investigating potential issues with UV absorption O3 measurements, such as humidity and interferences from either particulates or gas phase species. Data obtained with the O3 UV absorption point monitors is then compared with two open path spectroscopic measurements, differential optical absorption spectroscopy and Fourier transform infrared spectroscopy. The reported discrepancies between the UV absorption measurements and the open-path measurements ranged from +13 % to -18 %. The authors suggest that majority of the discrepancies were due to incorrect calibra-

tions in the UV absorption monitors.

The complex results from this paper are challenging to interpret emphasize the difficulty of ambient measurements. Perhaps the most important result is that this comparison work essentially provides an indication of the precision that is currently realistically obtained for ambient O3 measurements using UV absorption monitors and standard practices. The discussion identifies many of the outstanding questions regarding UV absorption monitors. For the most part, the study is able to explain the relative impact of potential interferences for the specific measurements. It is clear, however, that more systematic and definitive studies are needed to truly resolve possible interferences from humidity, particulate, other VOC's, scrubbers, particulate filters, etc. in O3 measurements by commonly used UV absorption instruments. The study also suggests that the UV absorption O3 instruments require frequent and rigorous calibrations, especially those instruments which are exposed to environments that may contaminate the scrubber or particulate filter.

Several items that the authors should address are listed below. 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.

2) In section 3.2 the DOAS and FTIR measurements are introduced as "absolute measurements". While in theory, spectroscopic measurements are absolute, in practice this is challenging to actually realize. In principle, the UV O3 monitor should also be absolute as mentioned on page 3. Just as the UV O3 monitor is prone to measurement challenges which may impact quantitative measurements of O3, the DOAS and FTIR measurements are also susceptible to factors that may degrade the absolute nature of the measurement such as non-linearities, resolution issues, level of absorbance measured, interferences from other species which have spectral signatures overlapping with O3, etc. For example, the portion of the IR O3 band used for the analysis should

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be included. Also, a figure showing the IR spectrum, or at least a comment stating whether there were any spectral features other than O3, that had to be considered in the analysis. What was the apodization function used in the FTIR measurement and how was the FTIR spectrum modeled from the HITRAN database parameters. Similar details explaining the quantitative analysis of the DOAS measurements should be provided. 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. The uncertainties in these measurements should be evaluated and stated.

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 %).

4) The authors recognize the challenge of comparing point sampling methods and open-path methods. However, it is not convincing that there are minimal differences between point sampling and open-path measurements. Open-path data produce an average value of signal over the measured path length. Therefore, there could be portions of the path with significantly higher O3 concentrations and portions with significantly lower O3 concentrations. 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!

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