Atmos. Chem. Phys. Discuss., 6, S950–S955, 2006
www.atmos-chem-phys-discuss.net/6/S950/2006/


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 #1**

Received and published: 22 May 2006

General Comments:

Although authors identify many of the difficulties in comparing point sampling to kilometer length open path ozone measurements, further subcategorization of their comparisons might improve the persuasiveness of their conclusions. 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 high-rise 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)



Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

with hourly time-series comparisons that are more relevant as regulatory measures of monitor reliability. Current extreme-value standard compliance regulations require that monitors be reliable each day on an hourly or 8-hour average basis rather than on average over longer time periods.

Specific Comment (page:line)

(2244: 15) Authors should make clear that the U.S. Federal Reference Method (FRM) is a gas-phase ethylene-chemiluminescence (CL) method in contrast to other NO-CL (Ryerson et al. 1998) and solid dye-CL (Arshinov et al., 2002) ozone monitoring methods discussed later in the article.

(2245:4) Author references to 'absolute measurement techniques' should be deleted since they may apply to none of their ozone study methods. For example, Beer-Lambert path lengths in point sampling devices are indeterminate since UV absorption cells operate as light pipes due to inadequate lamp collimation (Wilson, 2005); open path instruments may suffer interferences from incomplete trace-gas reference spectra in urban areas (Reisinger, 2000).

(2245:19) Authors should qualify their citation of Ryerson et al. 1998 by noting (1) that the reported agreement of UV and CL instruments stemmed from after-the-fact correction factors applied to account for a failing CL photo-detector and (2) that the custom-built NO-CL instrument used by Ryerson et al. is not certified for ozone standard compliance monitoring in the U.S. Nor is any commercially available NO-CL instrument currently designated as an EPA-certified Federal Equivalent Method (FEM).

(2246:15) Authors may wish to tabulate method characteristics to condense Section 2. Such a table might include location, method, open path height, length, direction, UV point monitor inlet height, distance from roadway, scrubber type, and absorption cell type (e.g., quartz or fluorocarbon coated aluminum).

(2251:13 & 2252:9) Authors should explain why the mobile source UV ozone monitor



ACPD
6, S950–S955, 2006





EGU

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 exhaust plumes.

(2252:23ff) Investigation of the trailing vehicle spiking effects is important because understanding this phenomenon may help determine UV ozone monitor reliability in other situations. Since authors conclude that particle penetration of inlet filters is the problem, they should also identify, characterize, and discuss the efficiency of the inlet filters used in their study to support this conclusion (Liu et al., 1983). However, alternative causes of the spiking phenomenon may be more likely.

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. This postulated filter-scrubber role-reversal seems an unlikely explanation for the spiking events.

2. Authors also invoke gaseous species desorbing from particles retained on the inlet filter as an alternative explanation. This explanation seems more likely given that bus exhaust plume emissions would be sampled within tenths of a second by a tail-gating mobile lab when 'fresh' particles might still be supersaturated with UV-active diesel combustion products (e.g., naphthalenes, aromatic nitrates/phenols). Such particle-bound species might promptly degas into the analyzer under reduced inlet filter pressures during the relatively clean-air periods between sporadic plume encounters.

3. Another possibility is that water vapor spikes that accompany CO2 spikes in the diesel combustion plume might also affect ozone monitor response. Wilson, 2005 reports similar UV ozone monitor spiking phenomena to occur with step changes in relative humidity.

(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, a charcoal-filter device that would also remove UV-active gaseous combustion species covariant with the fresh cigarette



ACPD
6, S950–S955, 2006

smoke aerosol used to test his solid dye-CL ozone monitor and so fails to distinguish between particle and gaseous interferences. Such a device would also remove ozone and thus not be suitable for ozone monitoring use.

(2255:1) Authors rightly discuss the difficulties of comparing point and open path sampling measurements but their case for comparability remains unpersuasive. For example, at line 23 they contrast ozone and carbon monoxide measures and suggest that O3 levels will not have comparable CO source proximity inhomogeneities; however, co-emitted NO should titrate ozone, producing similar O3 source proximity gradients. Authors might improve point-open path sampling comparisons if data were categorized by wind direction; monitors sampling during advection along the open path direction would measure more similar air parcels than during perpendicular air flow conditions.

(2256:7) Authors discussion of ozone monitor calibration error is difficult to follow. Is the bottom line (at 2258:17) really that correctly implemented, USEPA-approved calibration procedures result in the miscalibration of UV ozone monitors? A clearer explanation of how this is understood to occur should be provided, for example, 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)? If so, this is a substantial indictment of current ozone standard compliance monitoring network reliability.

(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. Large differences in measured ozone values have been reported between instruments using these two scrubber technologies (Leston et al., 2005).

(2261:14) Mercury interferences may be more important than authors conclude. Cultural practices among some Latino groups include sprinkling elemental mercury within their vehicles (Riley et al., 2001) so roadway levels might be elevated under some cir-



ACPD
6, S950–S955, 2006





EGU

cumstances. Short-duration Hg events have also been noted in Europe (Zdanevitch, 2002) and such occurrences could affect compliance with current extreme value ozone standards.

(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 of rooftop and ARI Mobile Lab UV point sampling monitors at CENICA. For example, Leston et al., 2005 report higher interference sensitivities in monitors with unheated MnO2 scrubbers than in monitors with heated metal scrubbers; Wilson, 2005 reports both different levels and directions of water vapor bias in instruments with quartz and metal (fluorocarbon coated) absorption cells.

Arshinov, M.Y., Belan, B.D., Drasnov, O.A., Kovalevskii, V.K., Pirogov, V.A., Plotnikov, A.P., Tolmachev, G.N., and Fofonov, A.V.: Comparison of ultraviolet and chemiluminescent ozonometers, Atmos Oceanic Opt., 15, 8, 656-658, 2002.

Leston, A.R., Ollison, W.M., Spicer, C.W., and Satola, J: Potential interference bias in ozone standard compliance monitoring, J. Air Waste Manage. Assoc., 55, 1464-1472, 2005.

Liu, B.Y.H., Pui, D.Y.H., and Rubow, K.L.: Characteristics of air sampling filter media, in Aerosols in the Mining and Industrial Work Environments, V.A. Marple & B.Y.H. Liu, eds., Ann Arbor Science, 1983.

Reisinger, A.R.: Unidentified interference in DOAS measurements of ozone, Appl Spec 54, 72-79, 2000.

Riley, D.M., Newby, C.A., Leal-Almeraz, T.O., and Thomas, V.M.: Assessing elemental mercury vapor exposure from cultural and religious practices, Environ Health Perspec 109, 779-

Ryerson, T.B., Buhr, M.P., Frost, G.J., Goldan, P.D., Holloway, J.S., Hubler, G., Jobson,



ACPD

6, S950–S955, 2006

B.T., Kuster, W.C., McKeen, S.A., Parrish, D.D., Roberts, J.M., Sueper, D.T., Trainer, M., and Fehsenfeld, F.C.: Emissions lifetimes and ozone formation in power plant plumes, J Geophys Research, 103, 22569-583, 1998.

Wilson, K.L.: Water vapor interference in the UV absorption measurement of atmospheric ozone, Univ of Colorado, http://www.twobtech.com/Wilson.Thesis.pdf, 2005.

Zdanevitch, I.: Etude des interferents sur la mesure de l'ozone, Institut National de L'Environnement Industriel et des Risques (INERIS), Rapport Final, December 2002.

---

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