



Optimization of Ozone Compliance Photometer Network

Ollison, Will (American Petroleum Institute)

Leston, Alan (AirQuality Research & Logistics, LLC)

Recommendations

To optimize accuracy of ozone (O₃) NAAQS compliance determinations and design values (DV) site O₃ monitors, network operators could:

1. Compare current DV photometers with "interference free" FEM Teledyne-API (TAPI) NO-chemiluminescence T265 or NO-scrubbed 2B Technologies (2B) 211 photometers to evaluate suspected DV site monitor bias from H₂O, Hg, and polar aromatic VOCs - phenols, aldehydes, & nitroaromatics (1, 2);
2. Compare compliance site DVs to paired monitor sampling at a 2 meter (m) height above ground level to evaluate site inlet height bias (3) over typical outdoor ambient population nose height exposures at 0.5-2 m;
3. Convert compliance site ppm DVs to µg/m³ DVs, computing the m³ volume at local barometric pressure as allowed in deriving PM monitor DVs (4), to evaluate the altitude DV site bias (5, 6); e.g., Denver's (5300 feet) dFEV1 response bias is enlarged by 15% over coastal residents near sea level at the same ppm DV (7).

Methodology

Current distributions of compliance network inlet heights and monitors are presented in Figures 1 & 2 (8, 9). To evaluate near-ground O₃ gradient and measurement interference effects, we compared a TAPI T400 photometer upgraded with a 2B NO-scrubber (10) to the site's T400 MnO₂-scrubbed unit, sampling at 6.2 m on the 09-001-9003 Westport, CT site (41.11822, -73.33661) from 6/16-10/6/15, adjusting both for relative monitor drift. The upgraded T400 unit took 6-minute alternative sequential samples at 6.2 m and also at 2 m. Comparison of upgraded and conventional 6.2 m TAPI T400 time-series provides a measure of conventional monitor interference bias; a comparison of the upgraded monitor's 6.2 m and 2 m time-series provide a measure of the O₃ gradient between 6.2 m and 2 m. Figure 3 plots superimposed Westport, CT rolling 8-hour average O₃ values from a conventional T400 inlet at 6.2 m in blue, O₃ values from the upgraded NO gas phase titrated (GPTO3) T400 at 6.2 m in red, and alternating GPTO3 values sampled at 2 m in green with ppb O₃ differences between the two 6.2 m inlets and the GPTO3 inlets at 6.2 m and 2 m plotted in yellow and purple, respectively. The blue tips of the daily O₃ peaks indicate conventional monitor O₃ overestimation and the green valleys the degree of O₃ overestimation by the 6.2 m inlet height over the 2 m height.

References

1. Spicer et al. (2010) JAWMA 60: 1353-1384.
2. Wilson & Birks (2006) ES&T 40: 6361-6367.
3. 2006 O3 ISA (EPA/600/R-05/004aF-cF) § 3.3.1, pp. 3-15/-17
4. 40 CFR Part 50, Appendix L, Section 2.2
5. Wedding et al. (1987) JAPCA 37: 254-258.

Results

Fifteen daily maximum 8-hour averages ≥ 70 ppb appear at the daily peak values in Figure 3. The number of 70 ppb exceedances and 4th highest daily maximum 8-hour averages observed during the study period are distributed as follows: the conventional 6.2 m monitor's 4th highest daily maximum 8-hour value was 85.6 ppb with 13 values ≥ 70 ppb; the upgraded 6.2 m monitor's 4th highest was 84.8 ppb, a ppb less, with 15 values ≥ 70 ppb; and its 2 m inlet had a 4th highest of 81.9 ppb with 10 values ≥ 70 ppb. The O₃ conventional-upgraded units' 6.2 m differences range between 1-3 ppb while the upgraded monitor's 6.2-2 m differences range between 1-4 ppb. The average diurnal effect of O₃ interferences and 2 → 6.2 m O₃ gradients increase measured 6.2 m values by about 3 ppb over the 2 m values.

Unfinished Business

TAPI T265 This "interference free" O₃ FRM can be further corrected for effects of absolute humidity which may vary over the 0-4% H₂O range. Since this method dries the ambient air prior to O₃ reaction with NO, it concentrates ambient O₃ by up to 4% (about 3 ppb at 70 ppb levels) during humid periods.

2B 211 This second FEM "interference free" FRM candidate produces NO for its gas phase scrubber from photolysis of a 2% N₂O flow that's eventually added to the UV photometer reference flow; however, the vendor chooses not to add N₂O to the unscrubbed sampling flow to reduce N₂O consumption. Since this approach dilutes the reference flow only, about 2% of any interference signal remains as a positive bias.

Inlet Height Uncertainty Compliance network inlet heights are limited to a 2-15 m range above ground level but inlets are only required to be 1 m distant from shelter supporting structures, including the monitor shelter roof (11). Some network operators interpret these instructions as requiring inlets 2 m above the shelter roof but others adhere to a 1 m roof clearance height. To the extent that shelter roof wind turbulence mixes elevated O₃ down to a reactive roof surface (e.g., reactive from deposition/accumulation of windblown debris), a 1 m spacing may be equivalent to a 1 m inlet height above a shelter roof "ground".

Heated Graphite Scrubbers A new O₃ photometer scrubber may soon be available which substantially reduces conventional scrubber interferences as noted in reference 12 and Figure 4. This accuracy upgrade may relieve the operational burden of gas handling logistics for most non-DV monitors.

6. Liliquist et al. (1996) JAWMA 46: 172-173.
7. 2014 O3 HREA (EPA-452/R-14-004) p.6-8.
8. O3 NAAQS Docket EPA-HQ-OAR-2008-0699-0184.
9. Wayland, R. 8/20/15 memo to Ollison, W.
10. http://www.twobtech.com/model_GRP.htm.
11. 2013 QA Handbook (EPA-454/B-13-003) Table 7.3
12. http://www.twobtech.com/linked_files/Birks_Model_211_Scrubberless_Ozone_Monitor.pdf.

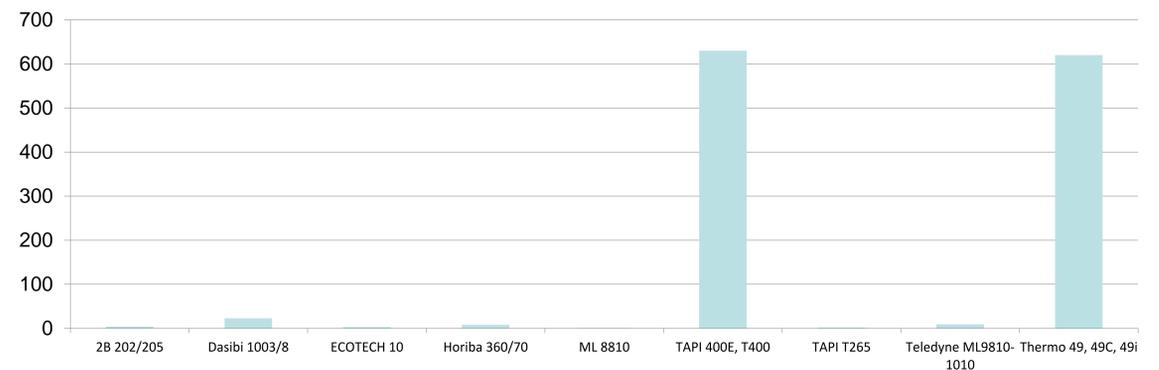


Figure 1. Distribution of Compliance Network Monitor types.

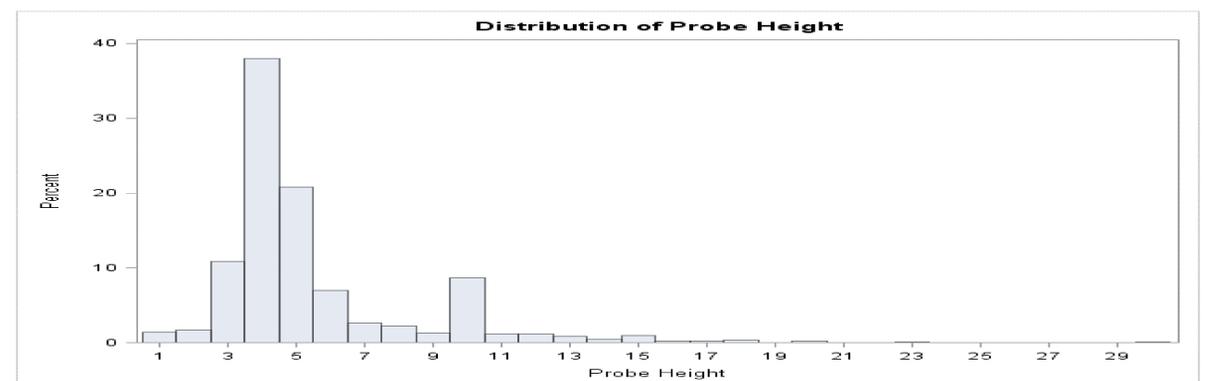


Figure 2. Distribution of Compliance Network Inlet Heights

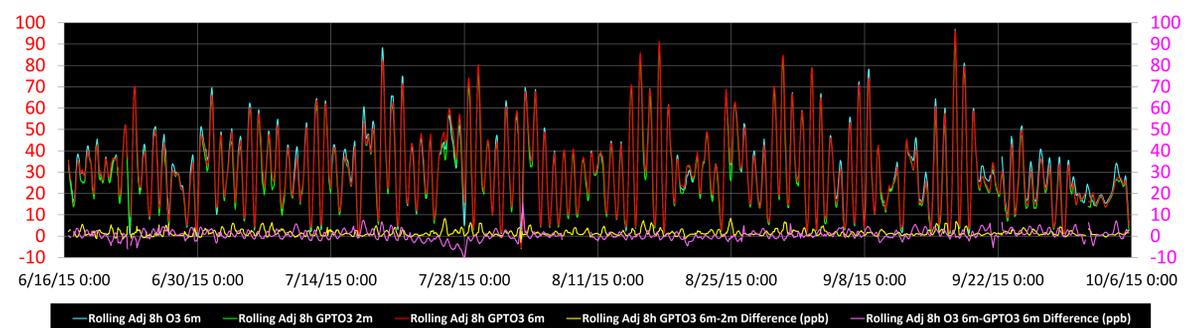


Figure 3. Superimposed rolling 2m & 6m 8h O₃ values for conventional and upgraded TAPI T400 monitors.

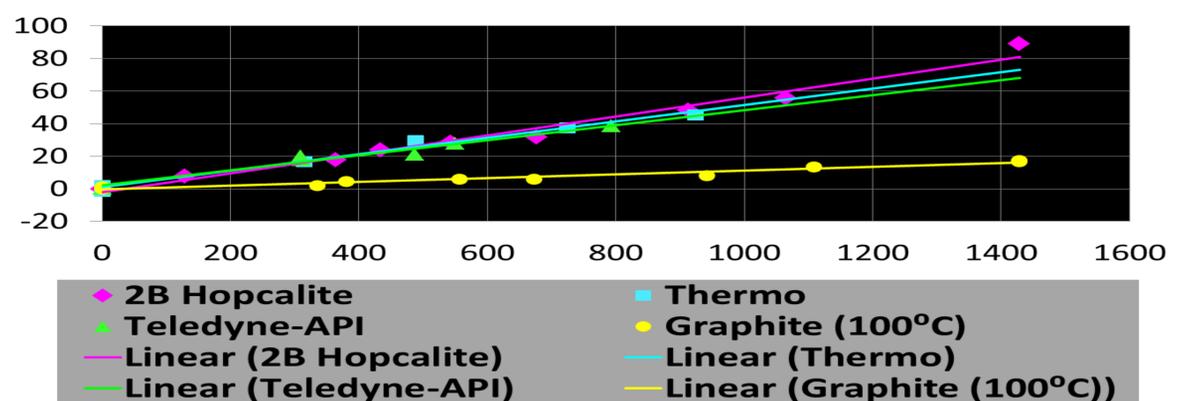


Figure 4. Comparison of p-Xylene (ppb) response of MnO₂ O₃ monitor scrubbers & heated graphite denuder.