Comments to the EPA CASAC Ozone Review Panel on Risk/Exposure and Policy Assessment Documents

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On Wednesday, January 29, 2014 the U. S. EPA published a Federal Register notice (FR/Vol. 79, No. 19 pp. 4693-4694) announcing a meeting of the Clean Air Scientific Advisory Committee's (CASAC) Ozone Review Panel. The stated purpose of this public meeting is

> *"… to conduct a peer review of three draft EPA documents: (1) Health Risk and Exposure Assessment for Ozone—Second External Review Draft (January 2014), (2) Welfare Risk and Exposure Assessment for Ozone—Second External Review Draft (January 2014) and (3) Policy Assessment for the Review of the Ozone National Ambient Air Quality Standards—Second External Review Draft (January 2014)…"*

The following comments are in response to the 1/29/14 FR notice in keeping with the FR notice "*Procedures for Providing Public Input*".

Comments

1. The "*Health Risk and Exposure Assessment for Ozone - Second External Review Draft*" (REA) notes (page 4-2, lines 10-12) that;

> "*…While CASTNET monitors did not begin reporting regulatory data to AQS until 2011, it is generally agreed that data collected from these monitors prior to 2011 is of comparable quality to the data reported to AQS…*"

While it is generally accepted that ozone (O3) *monitors* deployed by CASTNET prior to 2011 met Federal Equivalency Method (FEM) performance specifications and were generally sited in rural areas that avoided the impact of local sources; however, EPA acknowledged several, significant areas where the CASTNET O3 network *data* was deficient[1]. In view of the imminent EPA revision of 40 CFR Part 58 quality assurance provisions discussed in Section 3.5.3 of the O3 ISA and ongoing needed adjustments to the CASTNET instruments and protocols described below, it also appears premature for the Agency to initiate design value and compliance determinations at rural and remote CASTNET locations for the 2011-2013 period.

Table 1. QA/QC requirements of 40 CFR Part 58, Apdx A for ozone

QA requirement 40 CFR Part 58	Current EPA CASTNET	New procedures for compliance monitoring
O_3 calibration gas source (station transfer standard) 6x6 transfer standard initial verification (TAD)	Not performed	Convert to 6x6 transfer standard initial verification[1]
Zero air and O_3 calibration gas source (station transfer standard) [6/1 calibration check] (QA Handbook)	Not performed	Convert to once every 6 months schedule to calibrate field station transfer standard[1]
One-point quality control check (40 CFR 58)	Once every 2 days	Convert to daily[1]
Annual performance evaluation (40 CFR 58)	Once every 2 years	Convert to annually[2]
Multipoint verification/ calibration (QA Handbook)	Once every 6 months	Maintain current practice[1]
National Performance Audit Program (NPAP) (40 CFR 58) 20% of network per year	Not performed	Join NPAP[2]

[1] Performed by the EPA CASTNET contractor - MACTEC
[2] Performed by the third party CASTNET auditor - EEMS

In addition to these acknowledged shortcomings, the ambient sampling configuration, range of instrument models and other quality assurance (QA) and quality control (QC) activities utilized by CASTNET prior to 2011 were so varied and in some cases dissimilar to the O3 networks operated by State/Local/Tribal organizations (S/L/Ts) that CASTNET data prior to 2011 should not be considered to be "…*of comparable quality*…" to the O3 data compiled and submitted by S/L/Ts to the EPA AQS system.

To insure uniformity and report "comparable" air pollution data, discrete networks operated by a single entity should operate hardware and software from as few manufacturers as possible. Between the years 1990 and 2004, the National Park Service (NPS) at CASTNET sites has issued Standard Operating Procedures (SOPs) for operation and calibration of six different ozone monitor models in its Quality Management Plan[2]. Although a listing of O3 monitor models operated by the NPS each year could not be found, from the date of issue of the various SOPs it's plausible that two to four different models operated in the years beginning with 2003. Operating a variety of monitor types within a given network is difficult, due to the need for tracking maintenance, operation, and calibration activities from disparate monitor types, and often results in non-uniform and possibly biased data. Subsequent to 2010 and under EPA guidance, the NPS and the operators of all other CASTNET sites have standardized O3 measurement hardware, software and SOPs to meet the QA/QC requirements in 40 CFR, Part 58, Appendix A. However, despite the alterations and upgrades made to CASTNET infrastructure and operations, O3 data quality is still of concern.

Performance evaluation (PE) audits are an integral part of SLAMs and CASTNET systems. During PEs, independent auditors challenge O3 monitors with several gas concentrations (zero and at least three upscale O3 values) using clean air supplies and ozone generator calibration systems not involved in regular network performance checks or calibrations. EPA issued an overview of the CASTNET network status with respect to regulatory monitoring on May 16, 2013[3]. In that overview EPA stated that the PE audit concentrations chosen must bracket 85% of

a site's annual concentration range. Furthermore the acceptance criteria for O3 monitor response to audit concentrations was stated as ±15% (or ±1.5 ppb at concentrations below 20 ppb). No criteria for zero response was included in the Overview but PE reports for the 4th quarter of 2012 and the first two quarters of 2013[4] indicate that zero responses of ±5 ppb were acceptable during CASTNET audits. Those audit reports also specify that the regression slope of audit point data must be within 10% of a 1:1 best fit (i.e., a slope between 0.90 and 1.10). Note that these criteria also apply to O3 monitors operated by S/L/T organizations. Given these acceptance criteria, acceptable responses for an O3 monitor audited at 75 ppb could range from 64 ppb to 86 ppb.

Most S/L/T monitoring agencies scrutinize audit results closely and seek to minimize poor PE results by making frequent (sometimes daily) zero/span checks which trigger recalibrations when performance limits are exceeded. In general, agencies seek O3 monitor performance that is within 5-7% of ideal with zero offsets below 3 ppb. However, even with that level of performance errors of 4-5 ppb will be present at ozone concentrations equivalent to the current 75 ppb O3 NAAQS. Thus any additional "comparable" CASTNET O3 data variability is added to that of the State and Local Monitoring Station (SLAMS) data, which itself has considerable uncertainty.

Other major differences exist between CASTNET and SLAMs networks. For example, CASTNET O3 monitors draw sample air from inlets 10 meters above ground level (AGL) while the vast majority of S/L/T sites in the SLAMS network report data from O3 monitors with inlets placed 3-4 meters AGL. Measured gradients in O3 concentrations between 3 and 10 meters AGL at the Howland Maine site (HOW 191) indicate an inverse O3 gradient between 3 and 10 meters AGL of 3-4 ppb[5].

The importance of these small 3-4 ppb inlet height differences can be illustrated by examining the "2011 CASTNet Ozone Monitoring Review prepared by EPAs Clean Air Markets Division (CAMD)[6]. The CAMD report lists the four highest daily maximum eight-hour O3 concentrations measured at the 78 CASTNet sites with complete data for 2011 which is the first year EPA will use CASTNet data for Design Value (DV) calculations. In 2011, 15 CASTNET sites reported fourth-highest eight-hour O3 concentrations that exceeded 76 ppb or higher. The fourth-highest concentrations at eight of these sites were between 76 ppb and 79 ppb. If a 3-4 ppb O3 enhancement was indeed present due to sampling at the 10 meter elevation, the number of CASTNet sites exceeding the eight-hour O3 National Air Quality Standard, at 3 meters AGL, in 2011 should have been 7 instead of the reported 15 – a doubling of NAAQS exceedances. It is clear that hourly ozone data in both the CASTNET and SLAMS programs often deviate from ideal and it is also clear that such small deviations in O3 monitor performance can have a large impact on exceedances and ozone design values. EPA should expand the number of sites measuring ozone at both 3 and 10 meters AGL to insure that small differences in inlet elevation do not bias ground-based O3 data.

It should be noted that differential inlet height is only one of several potential or documented sources of O3 measurement bias. The collocated monitoring stations at Rocky Mountain National Park (RMNP) provide another example of how minor network differences can result in biased data. The primary O3 monitoring site at RMNP is designated ROM406 and is operated by Air Resource Specialists (ARS) under contract with the NPS. Data generated from the

ROM406 site is used to calculate the area's DV. The collocated site, ROM206, is operated by AMEC Environment & Infrastructure, Inc. (AMEC) under contract with EPA. Inlets for O3 monitors at both sites are at 10 m. AGL.

The report of a Technical Systems Review[7] (TSR) undertaken by EPA at the ROM sites indicates that the ROM406 monitor consistently over-reported O3 concentrations by 1-6 ppb and further states that;

> "*…periods of larger… (than 6 ppb)… differences have occurred intermittently…*"

but does not state the frequency, duration or magnitude of the "larger differences". Installation of "duplicate" O3 monitors at both ROM sites indicated a possible problem with the "primary" monitor at ROM406. The report notes that after replacing the primary ROM406 monitor;

> "*…there was better agreement between both… (ROM406)…analyzers and between ROM406 and ROM206….*"

Unfortunately, no indication was given as to the nature of the performance problem with the primary ROM406 monitor that caused it to over-report nor was it stated how long that monitor had been in-place at the ROM406 site. Both of those details would have been helpful in determining how to apportion the amount of bias due solely to the replaced monitor.

In addition to the problematic monitor the technical review also discovered a performance issue with the transfer standards used to calibrate the ROM406 monitor (and possibly other monitors at sites operated by the ROM406 Contractor. Transfer standards that require an external clean air supply (i.e., those that do NOT employ an internal scrubber) were found to have detection cell pressure variations which affected the concentration of ozone being reported while transfer standards equipped with internal scrubbers did not experience detection cell pressure differences. Furthermore, differences were discovered between the ROM sites' infrastructure that exacerbated the detection cell pressure differential and resulted in additional bias to transfer standard calibration results. Those differences were in analyzer inlet/exhaust line lengths as well as a difference in the internal diameter of the inlet/exhaust lines. It was also noted that "FEP" type Teflon was used at ROM406 for inlet lines while "PFA" type Teflon was used at ROM206.

Once these problem areas were identified and resolved the bias between ROM406 and ROM206 was greatly reduced. However, the report concludes:

> *"...Differences were identified and many have been resolved. Some inconsistencies still exist and future actions are recommended….*"

Areas cited in the TSR for additional study include; (1) comparison of PFA/TEF and tubing diameter, (2) evaluation of zero air scrubbing systems employing oxidizing agents versus systems using only charcoal and (3) ongoing intranetwork transfer standard comparison.

It should be noted that at no time did field-based calibrations, independent audits or regularly performed QA checks of any kind reveal the existing bias between data from ROM406 and ROM206. Once the bias in the data streams from these sites was noted it required a very large commitment of time and resources to discern the major causes of the bias.

To head off such data-related problems in the future, EPA should expand the number of collocated sites in both the CASTNET and SLAMS networks to include a wider variety of climate types. The collocated sites should be operated by different organizations in order to more fully discern the nature and extent of errors and biases inherent in different FRM/FEM O3 monitors and the infrastructure, operational and maintenance procedures used to support them.

2. Chapter 4 of the REA discusses the methods used in compiling and analyzing recent 2006-2010 ambient O3 data from both the EPA AQS system and the CASTNET database. Hourly O3 concentration data were employed in various risk and exposure assessments. The REA notes (p. 4-2) that "*…short gaps often occur at regular intervals in the ambient (O3) data….* " and states that linear interpolation was used to fill gaps of 1-2 hour duration. These gaps are ascribed to the EPA-mandated routine quality control checks that monitoring agencies perform on their O3 monitors.

The presence of these gaps raises two issues. First, the apparent "regularity" of gaps during overnight hours is troubling because it demonstrates the non-random timing of quality control checks designed to assess O3 analyzer precision. The REA notes (p. 4-2) that;

> "*…Quality control checks are typically performed between the hours of midnight and 6 AM when O_3 concentrations are low….*"

Checking O3 monitor performance only during late night periods creates a biased view of instrument precision.

Ambient temperature, humidity and O3 concentrations are diurnally cyclical as are line voltage and nearby traffic volumes. All these variables potentially impact ozone monitor performance. The O3 NAAQS is not concerned with average or low concentrations, but is based on the upper "tail" of concentrations. Design values (DV) on which an area's attainment of the O3 NAAQS is based are computed as the three-year average of the fourth highest daily maximum 8-hour average values. Quality control checks designed to estimate O3 monitor "precision" should *not* be performed at the same time every day, to avoid missing the impact of diurnal variable patterns. More importantly such checks should never be done solely "*…when O3 concentrations are low…*" due to the extreme value form of the O3 NAAQS and the need to assess O3 monitor precision across the range of data employed in DV calculations.

The second issue related to the O3 data gaps noted in the REA is the impact of ambient air matrix effects on O3 monitor performance. The vast majority of O3 monitors in use today are ultraviolet photometers using MnO2 scrubbers[8]. The scrubber has been identified as the source of unstable performance when switching between humid, ambient air and the very dry zero air gas stream used during O3 monitor calibrations[9, 10].

Routine quality control precision checks carried out with dedicated calibrator/air supply systems located at O3 monitoring sites should occur without sample alteration (e.g., prior zero air zero/span checks) to insure that the monitor's performance has not been perturbed by humidity changes. A valid precision check should take under 15 minutes (if a stable precision check concentration cannot be achieved within 15 minutes the monitor may be malfunctioning). Monitoring organizations typically arrange precision check schedules to begin 10-15 minutes

before the start of an hour and end them before 15 minutes after the hour to capture at least 45 minutes of each of the two hours spanning the precision check to meet the EPA-mandated 75% data capture requirement. Therefore, no data "gaps" should occur when performing O3 monitor precision checks. Other quality control procedures such as zero/spans are performed similarly to meet EPA data capture requirements so such checks should not result in data gaps.

Two preventable problems might be responsible for the existence of the regular gaps in O3 data noted in the REA. The first problem is procedural, involving the performance of precision, and zero/span checks in a single session which lead to "off line" monitor times exceeding 30 minutes and result in loss of at least one hour of data. Monitoring organizations can certainly accept a daily data loss of one hour if they choose this operational approach. However, as noted above, true "precision" checks must be done without prior alteration to the monitors operational state (i.e., precision checks must be the first check in any multi-check procedure) and "true" precision checks must also be performed on a random basis to capture diurnal variable effects mentioned earlier. While zero/span checks may be performed at the same time every day because they provide information to the monitoring agency regarding the state of monitor performance, precision checks provide information on the quality (i.e., the repeatability) of collected data. Precision checks should not be performed in conjunction with other operational checks and should not be performed at the same time every day.

A second problem might be excessively long stabilization times for control checks involving zero/span concentrations. As noted above, MnO2 scrubbers in most current O3 monitors (and virtually all monitors in use between 2006 and 2010) can result in excessively long stabilization periods following a rapid change in sample humidity. This problem can be addressed by addition of appropriately placed Nafion tubing in the monitor plumbing that will mitigate humidity effect differences among ambient scrubbed/unscrubbed sample and calibration gas streams, such a configuration is currently available in a 2B Technologies Federal Equivalent Method monitors. A drop-in nitric oxide gas phase replacement scrubber for most current O3 SLAMS network monitors is available from 2B Technologies that also eliminates non-humidity MnO2 scrubber-related interferences (e.g., Hg vapor and aromatic volatile organic compounds[11]). Recent remeasurements[12] of APEX-type ambient-microenvironment relationships using such nitric oxide gas phase scrubbed interference-free O3 monitors indicate that current APEX microenvironmental factor bias likely leads to O3 REA exposure overestimates of an additional 40-100% in the closed indoor/in-vehicle locations where individuals spend most of their time.

3. The REA states (p. 4-2) that;

> *"…In general, O3 design values were lower in 2008-2010 than in 2006-2008, especially in the Eastern U.S…."*

However the PA, using a more recent data set, indicates that (p. 2-3);

"… the design value maps … show an increase in the number of monitors violating the existing O3 standard in 2010-2012 relative to 2009-2011…."

EPA should emphasize that the REA and the PA use different data sets to avoid reader confusion concerning whether ozone trends are up or down.

The PA notes that meteorology plays an important role in the magnitude and distribution of 4th high daily maximum annual 8-hour O3 concentrations (and by extension – design values). The cooler, wetter average summer weather in 2009 is cited as contributing to the lower average of 4th high 8-hour concentrations recorded that year (Fig. 2-2) and this is a reasonable assertion; however, the extremely low value for 2004 in Fig. 2-2 is attributed solely to implementation of the EPA-mandated

"*…NOx SIP Call… a program designed to reduce summertime emissions of NOx in the eastern U.S.*"

which spanned the 2002-2004 period. According to the National Oceanic and Atmospheric Administration's web site the summer of 2002 was "much warmer" in the Eastern US, which might account for the spike in 4th high values shown in Fig. 2-2 while the summers of 2003 and 2004 in the Eastern US were wetter than average with near normal temperatures. Taken together these departures from mean meteorological values might account for the large decline in design values between 2002 and 2004. To be fair EPA should also highlight the impact of meteorology on the 2002-2004 period in addition to the implementation of a regional control program.

Also, the second and third paragraphs of section 2.1.2 in the PA mix references to both the terms "4th high annual 8-hour average" and "design value". Although it is stated in subsection 2.1.2 that design values are derived from 4th high 8-hour averages, for clarity those terms should not be comingled in paragraphs discussing figures dedicated to each term (e.g., Fig. 2-2 demonstrates annual 4th high 8-hour concentrations while Figs. 2-3 and 2-4 show design value data).

References

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4. See sidebar labeled "Quarterly Audit Results" at http://epa.gov/castnet/javaweb/ozone.html.

5. 2011 Clean Air Status and Trends (CASTNet) Annual Report, EPA Contract No. EP-W-09-028, Feb., 2013. http://epa.gov/castnet/javaweb/docs/annual_report_2011.pdf.

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