From: Will Ollison
Sent: Thursday, March 27, 2014 3:26 PM
To: Hanlon, Edward
Subject: Comment to CASAC-AMMS teleconference

Dear Mr. Hanlon:

We talked late last week about providing some recent articles that might inform the AMMS consideration of a new O3 FRM.

Attached is a brief comment on the proposed development of an ozone FRM that will be discussed during the CASAC-AMMS April 3, 2014 teleconference (1) suggesting items that might be considered and (2) listing recent articles to inform the subcommittee in their response to the specific charge questions.

The Spicer et al., 2010 article is basically a review of earlier investigations into ozone monitor bias and precision; the Ollison et al., 2013 article a report of collocated comparisons of a candidate FRM (the NO-Chemiluminescence methodology) and an alternative NO-scrubbed UV photometric instrument (FEM application pending) to a conventional FEM UV photometer; the Johnson et al. 2014 article compares a conventional FEM UV photometer with the NO-scrubbed UV photometer during a series of public microenvironment measurements.

I've also attached a recent API consultant report that explores infirmities within the current ozone monitor performance and measurement network (CASTNet & SLAMS) protocols and offers recommendations that should be considered during the upcoming EPA revision of FRM & FEM performance specifications mentioned in Section 3.5.3 of the current O3 ISA.

Is there a docket where such comments should also be submitted?

Let me know if you have any questions.

All the best…

An Informational Response to the charge questions for EPA's "Request for Peer-Review/Advisory on the Proposed Promulgation of an Additional Federal Reference Method (FRM) for Ozone (O3)."

W.M. Ollison
American Petroleum Institute
Washington, DC
March 27, 2014

Suggested topics that the panel might consider and recent publications concerning such issues are provided below in the context of the Agency charge questions for AMMS convenience.

1. *What is the AMMS view on adding an additional O3 FRM for the purpose of establishing a new FRM that is implemented in analyzers currently in production status? This new O3 FRM will serve as an additional FRM to supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or supported.*

While it is necessary to supplement a current FRM which is no longer commercially available as an alternative to currently deployed FEM network photometers, given their demonstrated interferent bias[1] at locations where such interferences occur, why the current FRM has fallen out of favor should also be considered in choosing a new FRM. Several reasons encountered for this disfavor include the flammability of ethylene, the inconvenience of servicing expendable ethylene cylinders at remote monitoring locations, the ethylene cylinder-to-cylinder impurity variations requiring recalibrations, and the 3-4% positive bias in O3 measurement per 10,000 ppm increase in atmospheric humidity. Such considerations would include the necessity of expendables, their relative toxicity/flammability if necessary, and the ability to control for humidity effects.

2. *What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-CL) method (currently an FEM) as the new, additional O3 FRM?*

If the Agency envisions two FRMs, why should it not consider three? Individual candidate methodologies have their strengths and weaknesses for the different roles each may play in O3 NAAQS research and implementation. For example, a fast rise/fall time instrument might be optimal for aircraft or flux monitoring purposes while a lightweight/low-powered device might be better suited for self-contained, independent operation at remote locations. The NO-CL instrument is a strong candidate[2] and a large improvement over currently deployed network UV photometers as is an additional instrument with a pending FEM application discussed below.

3. *Do any other ozone measurement methods exist that the AMMS recommends for consideration of possible promulgation as new (additional) O3 FRM?*

An additional methodology that should be considered is NO-scrubbed UV photometry. FRM certification of such technology also provides a cost-effective opportunity for upgrading existing network photometers by replacing current solid phase metal oxide photometer O3 scrubbers with a gas phase NO scrubber - http://www.twobtech.com/model_GPT.htm. A commercial NO-scrubbed photometer has an FEM application pending and has also performed well both as a fixed site[2] and a portable battery-powered instrument[3] capable of sampling personal exposures in public indoor, outdoor, and vehicle microenvironments.

4. *What is the AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e., in rural areas)?*

A considered response to this question is difficult without more information than publically available at the EPA CASAC-AMMS website. The implications of "low-cost" in the question are unclear without some indication of the averaging times, accuracy, and precision expected from such technology and the anticipated regulatory use of such supplemental data. For example, remaining differences among sampling and quality assurance protocols used in the O3 FEM-based rural/remote CASTNet and the urban/suburban SLAMS compliance networks suggest that different results will be obtained and that anticipated Agency use of CASTNet sites to determine rural 2011-2013 O3 NAAQS compliance is premature[4]. However, the monitoring community will likely welcome any low cost sensor that meets FEM performance standards higher than those currently in effect.

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A Report on the Suitability of CASTNet and SLAMS Ozone Data for Use in Regulatory Decisions and Related Issues

March 26, 2014

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Executive Summary

EPA notes in Section 3.5.3 of the 2013 Ozone Integrated Science Assessment (600/R-10/076F) that current ozone monitor performance specifications need to be revised to more accurately reflect necessary ozone (O3) monitor performance requirements for the principally urban and suburban State and Local Air Monitoring Station (SLAMS) network to support the current NAAQS. Agency staff has also reported that recently upgraded O3 monitors in the Clean Air Status and Trends Network (CASTNet) will be used for the first time to determine rural and remote location NAAQS compliance beginning with the 2011-2013 period. Given the imminent technical changes in requisite monitor performance specifications, the report evaluates the current suitability of the CASTNet and SLAMS O3 data for use in regulatory decisions, identifying key parameters affecting field measurement bias and precision and including related categories of equipment alteration, siting/sampling configuration, procedural alternations, exceptional/natural event resolution, rounding error, federal reference and equivalent method performance specification, calibration and auditing procedures, and potential future sub-hourly measurement bias/precision. The report first considers the suitability of CASTNet data in comparison to SLAMS data collection and quality control procedures and concludes that in view of the imminent EPA revision of 40 CFR Part 58 quality assurance provisions and ongoing needed adjustments to the CASTNet instruments and protocols, it appears premature for the Agency to initiate design value and compliance determinations at rural and remote CASTNet locations for the 2011-2013 period. The report continues to evaluate needed adjustments in SLAMS instrument performance and clarifications in data treatment procedures that should be considered in 40 CRF Part 58 revisions, listing specific changes to selected parameters.

Suitability of 2011-2013 CASTNet Ozone Data for Regulatory Use

Introduction

The US Environmental Protection Agency (EPA) has determined that, beginning with calendar year 2011, hourly ozone (O3) data collected at the Clean Air Status and Trends Network (CASTNet) sites meets the quality assurance and quality control requirements set forth in 40 CFR Part 58 Appendix A which governs the collection of ambient air quality data for regulatory purposes. EPA therefore intends to include the CASTNet data in the calculations that determine O3 design values (DVs) for each State, Territory and Tribal Nation[1].

As of this date, the 80+ sites that comprise the CASTNet are all in rural or remote locations and are equipped with a range of monitoring and sampling instruments. The CASTNet was merged in large part with the National Dry Deposition Network (NADP) originally designed to collect data on the dry deposition of sulfur and nitrogen compounds[2]. CASTNet O3 data, unlike similar data from many State, Local and Tribal (S/L/T) agencies, is collected from inlets 10 meters (m) above ground level (AGL). The CASTNet is operated by a confederation of Federal, State, and Tribal agencies as well as University sponsors. The 78 sites collecting hourly ozone data in 2011 are a subset of the larger CASTNet program and are operated almost exclusively by EPA and the US National Park Service (NPS) contractors overseeing local site operators with the NPS operating 25 sites and EPA operating 57 sites[3].

Previous attempts by EPA to use CASTNet data for DV calculation were stymied by S/L/T monitoring organizations which pointed out that they were held to more strict operating and quality assurance procedures than were the operators of the CASTNet sites. EPA subsequently upgraded the O3 monitors at its CASTNet sites (Thermo Scientific Model 49i) and installed new calibration and data logging equipment. CASTNet site operators were instructed in the use of the new instruments and by January 1, 2011 the vast majority of sites were operating the new equipment. Relying on these equipment and operational changes EPA now intends to use the CASTNet O3 data for calculating 2011-2013 DVs in the S/L/T areas represented by the CASTNet sites.

This report examines the documented changes to O3 monitoring equipment and operating procedures in the new CASTNet with an eye toward determining the suitability of the reported data to meet regulatory needs. It also examines issues attendant to O3 monitoring at rural/remote sites. These include the scale-of-representation at rural/remote sites, O3 concentration gradients between 3 m and 10 m AGL, O3 monitor performance issues (i.e., measurement bias and/or interference) in the new CASTNet and the possible increased impact of exceptional events (e.g., biogenic emissions, wildfires, stratospheric intrusions). Finally, a review of reports on operations and data from the new CASTNet will be included.

Equipment Alterations

Ozone monitoring at EPA CASTNet sites is now performed with Thermo Scientific Model 49i ozone monitors. AMEC Environment & Infrastructure, Inc. (AMEC), the primary operator of EPA's CASTNet sites, does not describe the monitors in use at NPS/NFS (National Forest Service) sites but Model 202 monitors from 2B Technologies have been employed historically. Both the model 49i and the model 202 operate on the UV absorbance principal and both use a "scrubber" to cyclically remove ozone in order to perform baseline checks. Both models are subject to positive interferences due to a variety of volatile organic compounds, water vapor, and mercury vapor. These measurement interferences may unduly bias hourly O3 CASTNet measurements at some sites. See further discussion below under "Exceptional/Natural Events".

The on-site calibration standards now in place at CASTNet sites are variants on the Thermo Scientific Model 49 (i.e., 49, 49c and 49i). The ozone sources within the calibrator sections of those instruments are generally reliable but subject to drift. Any significant drift should be evident with the daily zero, span (400 ppb) and precision (90 ppb) checks[4] now performed at CASTNet sites. However, the Model 49i is known to become unstable[5] when presented with samples that vary significantly in moisture content. This instability may also be problematic when performing dry zero air O3 monitor "precision" checks. See further discussion below under "Procedural Alterations". Note however that the 2B Technologies Model 202 monitors possess sample and precision check Nafion humidity equilibration that greatly alleviates moisture-related instability.

Siting/Sampling Configuration

AMEC's Quality Assurance Project Plan (QAPP)[6] indicates that hourly O3 CASTNet measurements are representative of a roughly 10-kilometer radius circular area about 300 km^2 in size. Sites must be located at least 10 km away from large point sources, industrial complexes

and cities with population of 50,000 or more. Given the above siting criteria that area of representation appears to be appropriate but is 9-fold less than areas of influence used in current EPA exposure and risk assessments (e.g., Section 5.2.3, EPA-452/P-14-004a).

Many EPA compliance network O3 monitoring site inlets operated by S/L/T agencies sample at 3-4 meters AGL while CASTNet O3 is sampled at 10 meters AGL. This discrepancy in elevation could bias CASTNet data by the O3 concentration gradient that exists between 3 and 10 meters AGL. Data on such near-ground ozone gradients in rural/remote areas is sparse. However, the 2011 Annual CASTNet report prepared by AMEC[7] notes that CASTNet began collecting O3 data at the Howland Research Forest Ameriflux site (HOW191, Howland, ME) in September of 2011 at 2, 6, 10, 14, 17, 20.5, 23.5 and 28 meters AGL. Figure 4b in the AMEC report[7] graphed aggregated average data for each of the eight elevations for mornings (0600), afternoons (1400), and for all hours. All three time periods demonstrated an increasing O3 gradient of 3-4 ppb between 3 m and 10 m AGL. Although the measured gradient at Howland is not large it can be important. This becomes evident when examining the 2011 CASTNet Ozone Monitoring Review prepared by EPAs Clean Air Markets Division (CAMD)[8]. The CAMD report lists the four highest eight-hour O3 concentrations measured at the 78 CASTNet sites with complete data for 2011, the first year CASTNet data will be used for DV calculation. In 2011, there were 15 CASTNet sites reporting fourth-highest eight-hour O3 concentrations of 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 possibly exceeding the eight-hour O3 National Air Quality Standard, at 3 meters AGL, in 2011 should have been listed as seven instead of the reported 15 – a doubling of NAAQS exceedances.

Another difference between the CASTNet and S/L/T monitoring sites is site elevation. About 20% of CASTNet sites are at or above 5,000 feet altitude. The relatively large fraction of high elevation sites makes it likely that the CASTNet program will encounter more exceptional/natural events (EEs/NEs) which will in turn require more effort and resources by S/L/T organizations to meet EPA approval criteria (see additional comments under "Exceptional Events" below). To be sure, ozone monitors at high elevation/high latitude State and Local Air Monitoring Station (SLAMS) sites are and will continue to be impacted by EEs and NEs. Although the percentage of high elevation/high latitude SLAMS sites is much lower than CASTNet sites EEs/NEs can have a large impact. For example, the 4,600 foot Crestline site recorded the 2009-2011 design value for the Los Angeles South Coast Air Basin area.

A further altitude-related concern is the over-determination of individual O3 dose in EPA exposure and risk assessments. During earlier particulate matter (PM) rulemakings researchers noted that ignoring monitor altitude overestimated inhaled particle mass[9, 10]. EPA agreed and to address this problem currently allows measurement of the cubic meter (m^3) portion of the PM microgram/cubic meter (ug/m^3) standard metric at local barometric pressure. However, in contrast EPA currently specifies gas phase standards in parts per million (ppm) units which are barometric pressure invariant, thus penalizing areas with high elevation design value monitor locations such as Denver, CO with relatively more stringent O3 standards. For example, at a given breathing rate residents of mile-high cities like Denver exposed to 90 ppb O3 concentrations inhale about the same number of O3 molecules (mass) as those exposed to 75 ppb

at sea level. This bias could be removed if regulators would apply the PM approach to gases, stating the O3 standard in ug/m3 units and determining design values at local barometric pressure.

Also, EPA-sponsored CASTNet monitors employ "5 micron" Savillex Teflon particulate filters at the sample line inlet (atop the 10 meter tower) while NPS sites utilize "20 micron" filters at the tower inlet[11]. A second particulate filter is placed in the sample line close to the 'back plane' of the O3 monitor inside the shelter although the micron size of this filter is not stated. The use of different filters may create a bias between the EPA-sponsored and NPS-sponsored sites. NPS filters may allow more particles into the O3 monitor's inlet line and particles have been shown to positively bias O3 photometers of the type employed in CASTNet[12, 13]. Because the size of the second in-line particle filter is not stated the specific range of particles entering the CASTNet O3 instruments cannot be ascertained. Use of inlet line filters should be standardized.

Procedural Alterations

CASTNet has added an additional O3 monitor to each site which contains a 'certified' O3 calibrator that is NIST-traceable. This change allows an extra degree of "authority" for performing multi-point calibrations and for trouble shooting. The AMEC Standard Operating Procedures (SOPs) call for daily zero, span, and precision (ZSP) checks to ascertain analyzer performance. These ZSP checks are performed using the calibration source in the second monitor. Each of the three check points is sampled for 7 minutes beginning approximately 10 minutes before midnight. In this way no single hour loses more than 75% of its potential data and so no hours are invalidated due to the daily ZSP checks.

EPA requires "precision" point data from O3 monitors at a minimum of once every two weeks. The CASTNet daily ZSP checks easily fulfill this requirement but raise troubling issues. First, the checks are done at the same time every day, possibly missing biases due to ambient temperature, relative humidity, line voltage, O3 precursor interferences, or other variables with a diurnal cycle. Interferent absorption by the ozone scrubbers used in O3 photometers is generally the cause of the positive interference biases associated with those monitors. For example, interferents might accumulate in greater quantity on the scrubber surfaces during less humid or cooler periods. This bias, and other cyclical biases, in monitor performance cannot be observed by performing ZSP checks at the same time every day. True precision checks should be performed at random hours during the day to eliminate the potential for cyclical, diurnal biases.

Also, the ZSP checks at CASTNet sites are performed using scrubbed, desiccated "zero" air with dew points approaching minus 50 degrees Fahrenheit. It is well known that large changes in the sample air humidity entering O3 photometers such as the Thermo Scientific 49 series, can induce large, erratic changes in response[5]. The use of extremely dry calibration air should be reconsidered with an eye toward either using humidified zero air or installing Nafion treatment to minimize humidity differences in the sample and ozone-scrubbed air streams, as is currently present in 2B Technologies Model 202 units used at NPS CASTNet sites to alleviate this instability due to changing humidity and ultra-dry calibration air. For example, NIST staff[14] reports that use of dry calibration zero air will not reliably measure "…sample matrix effects arising from ambient humidity and interfering species…."

In any event, the current CASTNet procedure of checking the zero response followed by the upscale (span) response before checking the "precision" point should be altered. In order to provide unbiased precision data O3 monitor precision points must be introduced before the monitors' response has been altered in any way. The current CASTNet process for generating precision data alters the monitor performance by introducing instability (via dry air in the zero and span points) for approximately 14 minutes before introducing the precision point. This process does not gauge the monitor's unaltered performance and gives a false measure of precision. True precision assessment must be done with the monitor in an unaltered state (e.g., unperturbed by air flow or humidity changes) and with each quarterly precision assessment done randomly. Precision points should be taken from as many different days-of-the-week as possible and at different times of the day.

Two reports from CASTNet on the topic of precision/bias are examples of such procedural differences. The 2010 CASTNet Annual Report[15] noted a consistent bias between a pair of collocated monitors in Suffolk County, NY. At this site a Thermo Scientific 49i monitor was collocated with a Dasibi Model 1008 and both were serviced by the same operator for the 2006-2009 period. Analysis of precision data from this site showed a consistent bias of 4-5 ppb between the two monitors. Similarly, an update delivered to the NACAA Monitoring Steering Committee by Timothy Sharac described an extensive investigation of collocated O3 monitors in Rocky Mountain National Park. In this case the ROM406 monitor was operated by the NPS and the ROM206 monitor was operated by EPA. Both monitors were identical (Model 49i) by Thermo Scientific. After replacing all monitors, transfer standards, laboratory standards, traveling standards, and reviewing procedures, site configurations, and data handling, it was determined that the bias (1-4 ppb), "…was due to the operating protocols of the two organizations…."[16]

These two cases illustrate the need for improved uniformity across the CASTNet in order to eliminate as much bias as possible. Although known biases between instrument models can be eliminated by standardizing instruments, it is also crucial to minimize biases in operating and quality assurance protocols such as performing precision checks at the same hour every day and using ultra-dry zero air for operational checks in monitors known to suffer instability due to changing humidity.

Previously, EPA has specified that multi-point calibrations (MPCs) be performed at least quarterly. The MPC consists of challenging a monitor with zero air and four upscale concentrations from a NIST-traceable calibrator. According to EPAs "Redbook" on quality assurance[17], MPCs are to be performed;

> *"…upon initial installation, following physical relocation, after any repairs or service that might affect its calibration, following an interruption in operation of more than a few days, upon any indication of analyzer malfunction or change in calibration, and at some routine interval (multi-point verification, see below)…."*

However, contrary to the bracketed text in the above "interval" specification, there is no routine interval specified here or anywhere else in the chapter and review of other EPA requirements/guidance found no indication of a required interval. Therefore, it appears that EPA

has dropped a mandated interval for MPCs. CASTNet currently performs MPCs at six month intervals and given the daily zero and span checks now available from many calibration systems (including those in CASTNet) the lack of regular MPCs may be acceptable. However, EPA should not assume that all monitoring agencies have access to modern equipment on-site at each O3 monitor and should therefore reinstate a minimum interval for performing MPCs.

Exceptional/Natural Events

The rural/remote CASTNet monitoring sites increase the likelihood of encountering more unusual events as does the use of conventional O3 UV photometers. In the Northern Hemisphere breakup of the circumpolar vortex often occurs during the months of February and March. During this breakup, the stratospheric ozone that has pooled around the North Pole during the winter months begins to fragment due to changing wind patterns. This ozone leaving the polar region can be extracted from the stratosphere during active weather events associated with frontal passages. These events are known as "stratospheric intrusions" (SI) and can raise ground level ozone concentrations by dozens of parts per billion[18, 19]. SIs that occur in the vicinity of rural/remote monitoring sites, especially high elevation/high latitude sites may produce significantly higher ground-level O3 concentrations that last longer than similar SIs near urban areas. This is so because of the higher urban prevalence of both stationary and mobile NOx emitting sources. The O3 from SIs in rural areas will linger due to low local NOx concentrations while in more urbanized areas the NOx will react and reduce the O3 concentrations, especially during the nighttime hours. Note too that ozone plumes from Asia are known to have a measurable impact at Western U.S. monitoring sites[20] on 8-hour O3 concentrations. Although Asian plume impact may be smaller than that of SIs[21], it is still important.

EPA clarified and extended its Exceptional Event classification in the March 10, 2006 Federal Register[22]. The concept of a "Natural Event" was added to EPAs list of data flags. Data flagged under the "Natural" or "Exceptional" event category is excluded from use in calculating design values which, in turn, determine the attainment status of the area around a given monitor. In the 2006 FR both SIs and forest fires were determined to be natural events.

Smoke from wildfires is prevalent in rural/remote areas especially in the Western U.S. Although some wildfires are due to human activity most are of natural lightning origin and can produce copious quantities of O3. For example, Nikolov[23] has estimated that wildfires can increase the natural background O3 concentration by 24-100%. Nikolov further notes that attempts to model such increases in O3 are hampered by the coarse scale of most models which do not allow for resolution of individual smoke plumes.

In addition to direct production of O3 that is beyond human control, wildfires may bias the O3 measurement process due to creation of high concentrations of wildfire smoke[12] which can positively bias O3 photometer readings by 5-7 ppb per 100 ug/m3 of smoke particulate matter – even when using inlet particle filters.

Another positive wildfire bias in UV O3 photometers is the presence of mercury in the smoke plume. Ozone photometers models can be exquisitely sensitive to mercury with responses up to 1,800 times that of O3, depending on scrubber design[24], and mercury is a well-known component of wildfire smoke[25]. The presence of both mercury and wildfire smoke components indicate that

such plumes are potentially the most highly biased atmosphere in which O3 is measured. Therefore, O3 data during smoke plume events should be critically evaluated for monitor bias.

Conclusions

1. The equipment and procedural modifications made during 2009-2010 have resulted in improvements in the quality of CASTNet O3 data to the point where it may meet the current quality assurance provisions of 40 CFR, Part 58. However, the Agency has acknowledged that such 1975-era O3 monitor performance criteria are outdated and that "These specifications should be revised to more accurately reflect the necessary performance requirements for O3 monitors used to support the current NAAQS."[26].

2. The O3 photometers at CASTNet sites are subject to over-reporting O3 concentrations due to bias from organic compounds, fine particles and mercury. Conventional solid-state O3 scrubbers used in these instruments should be upgraded with commercially available gas-phase nitric oxide scrubbers to eliminate such interferences - http://www.twobtech.com/model_GPT.htm.

3. The monitors at EPA-sponsored sites are also subject to instability when ultra-dry calibration gas is introduced and this instability can alter estimates of monitor precision. Commercially available humidity controls should be added at CASTNet sites to remedy this condition - http://www.twobtech.com/dewline.htm.

4. A small O3 gradient between 3 and 10 meters AGL can exist that biases CASTNet data upward. Although small the gradient can increase a site's design value and noncompliance frequency. EPA should account for such differences in its DV calculations.

5. EPA and NPS CASTNet sites employ inlet particle filters with different characteristics; this should be standardized to minimize previously proven biases at CASTNet sites caused by minor differences in equipment and procedures.

6. Precision point data at CASTNet sites is potentially biased by testing at the same time every day. A more random process should be devised to evaluate O3 monitor precision during all hours of the day to address diurnal patterns of monitoring variables (e.g., shelter temperature, relative humidity, line voltage, O3 precursor interferences). As part of this randomization process precision data from different days of the week should also be included in quarterly precision calculations.

7. EPA has dropped requirements for maximum intervals between multi-point calibrations and should reinstate the previous quarterly interval or provide a rationale for dropping the requirement.

8. Stratospheric intrusions are more likely to occur at high latitude and high elevation sites. Recent model improvements show that SIs play an important role in surface O3 concentrations. EPA should prepare more detailed guidance on identifying SIs and determining their extent and duration. For example, although the Agency has included such SI events in 2006 revised exceptional event guidance[22], EPA acknowledges that "No EPA Region has concurred on a

flagged ozone SI event [although] historically some Regions do not act if the flagged data does not affect attainment status"[27].

9. EPA should also prepare more detailed guidance on operator identification of wildfire natural events that impact CASTNet O3 data, helping to determine the areal extent of the event and its duration.

10. Given the operator training and protocol updating deficiencies discovered in the recent EPA AMEC Technical Systems Audit of two CASTNet sites, such audits should be extended to the full EPA and NPS Network - http://epa.gov/castnet/javaweb/ozone/FINAL_TSA_OZONE_REPORT.pdf; http://epa.gov/castnet/javaweb/ozone/Response_FINAL_TSA_OZONE_REPORT_Final.pdf.

EPA notes[1] that "in 2011 EPA upgraded all ozone monitoring equipment at CASTNet sites to comply with the requirements in 40 Code or Federal Regulations (CFR) Part 58", in contrast to the February 2014 O3 REA (EPA-452/P-14-004a) Section 4.2 assertion 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". In view of the imminent EPA revision of 40 CFR Part 58 quality assurance provisions and the above listed and ongoing needed adjustments to the CASTNet instruments and protocols, it appears premature for the Agency to initiate design value and compliance determinations at rural and remote CASTNet locations for the 2011-2013 period.

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Suitability of SLAMS Network Ozone Data for Regulatory Use

Introduction

As noted above, the U.S. Environmental Protection Agency (EPA) has determined that beginning with calendar year 2011, hourly ozone (O3) data collected at the Clean Air Status and Trends Network (CASTNet) sites meet the quality assurance and quality control requirements set forth in 40 CFR Part 58 Appendix A, which governs the collection of ambient air quality data for regulatory purposes. EPA therefore intends to include the CASTNET data in calculations that determine O3 design values (DVs) for each State, Territory and Tribal Nation[1].

As discussed earlier, although network operators have made extensive upgrades to ozone measurement and data-logging instrumentation, questions remain regarding the use of CASTNET data for regulatory purposes. Moreover several additional aspects of ozone measurement at the nationwide State/Local Air Monitoring Stations (SLAMS) network are also in need of clarification and adjustment. These include EPA's data rounding convention, performance specifications for Federal Equivalent/Federal Reference Methods (FEMs/FRMs), audits and calibrations using dry zero air, and requisite monitor performance specifications for NAAQS with multiple averaging times (e.g., annual, 3-month, 24-hour, 8-hour, 3-hour, 1-hour (and potentially sub-hourly).

Rounding

EPA rounding conventions for 1-hour and 8-hour average ozone concentrations[2] specify that reported hourly concentrations and the 8-hour averages calculated from them,

> "*…shall be reported in parts per million (ppm) to the third decimal place with additional digits to the right of the decimal place truncated….*"

Given that the vendor-stated lower detection limit (LDL) of the current generation of O3 analyzers is now less than 0.60 ppb (0.0006 ppm)[3], this rounding convention might seem reasonable. However, the overall uncertainty in the O3 measurement process greatly exceeds the vendor LDL, making the data reporting policy to the nearest part-per-billion unsupportable. The ambient O3 data uncertainty arises from two main sources; (1) field monitor traceability to the calibration standards and (2) analyzer drift.

The authority of the Standard Reference Photometers (SRPs) maintained by the National Institute of Standards and Technology (NIST) is imparted to State, Local and Tribal (SLT) monitoring organizations through a series of "transfer" standards[4] and at each level of transfer measurement uncertainty increases. EPA defines "measurement uncertainty" as;

> "*…a region about an observed value of a physical quantity which is likely to enclose the true value of that quantity. Measurement uncertainty is related with both the systematic and random error of a measurement, and depends on both the bias and precision of the measurement instrument. At each measurement phase… errors can occur, that in most cases, are additive….*"

All valid ozone data contained in EPAs database is ultimately traceable to the standard (SRP #27) maintained by the International Bureau of Weights and Measures (BIPM)[4]. Every two years NIST compares one of its SRPs to SRP #27 at BIPM, returns that standard to its facilities and transfers the BIPM "authority" to another SRP which is then compared annually with two SRPs maintained by EPAs Office of Research and Development (ORD). During comparison of the BIPM/NIST SRPs and NIST/ORD SRPs a slope of 1.00 ($\pm$0.01) and intercept of 0.0 ($\pm$1 ppb) must be achieved in order to "verify" the transfer of authority.

The SRPs maintained by NIST and EPA are classified as "Level 1" while the highest level transfer standards maintained by S/L/Ts are classified as "Level 2". Level 1 and 2 standards remain in a fixed laboratory environment and isolated from exposures to ambient air. S/L/Ts

typically maintain additional Level 3 transfer standards for calibration of field-based O3 analyzers and Level 4 instruments for daily/weekly zero/span/precision (0/400/90 ppb) performance checks of field-based ozone analyzers.

Level 1 standards are allotted a slope uncertainty of ±1% (intercept ± 1 ppb) while Level 2 standards are allowed a slope uncertainty of ± 3% (intercept ± 3 ppb) To *qualify* as a Level 3 transfer standard, a device is allowed a slope uncertainty of ± 4% and an intercept of ± 4 ppb. Level 4 standards are not typically used for calibration but only for quality control purposes, e.g., checking to see if zero/span/precision drifts sufficiently to require monitor recalibration. Thus an imprecision of up to ± 8% (sum of 1, 3 and 4%) is inherent in the transfer of authority from BIPM SRP #27 to the Level 3 transfer standards used to calibrate field-based O3 analyzers. However, field-based analyzers are subject to drift due to a variety of causes and also to changes in ambient air sample humidity and interferences that calibration standards (Levels 1-3) never experience due to the use of desiccated zero air ozone calibration mixtures. The span drift of field-based O3 analyzers is acceptable up to ± 7%[5].

Therefore, it is possible for an O3 analyzer to pass all semiweekly quality control checks as well as longer interval calibration/audit verifications and report valid data that is in error by up to ±15% (sum of 8% calibration and 7% drift uncertainties). At the 0.075 ppm level of the current 8-hour ozone National Ambient Air Quality Standard (NAAQS) a 15% error amounts to 0.011 ppm. This degree of uncertainty (11 ppb) does not support the use of three decimal places when reporting O3 ppm data unless the 1 ppb rounding convention is considered a policy wholly disconnected from actual field-monitor precision.

FRM/FEM Performance Specifications

EPAs 2013 Integrated Science Assessment for Ozone and Related Photochemical Oxidants[3] notes the inadequacy of current ozone monitor performance specifications used to certify O3 monitors as either Federal Reference Method (FRM) or Federal Equivalent Method (FEM) instruments and calls for revisions to those specifications in order to

> "*…more accurately reflect the necessary performance requirements for O_3 monitors used to support the current NAAQS…*"

Detailed instructions are provided in 40 CFR, Part 53, Subpart B[6] for those wishing to qualify an O3 monitor as an FRM or FEM. As a clarification EPA should define what is meant by a "stable measurement reading", a phrase used extensively throughout Subpart B. Table 3-4 in Subpart B contains a summary of the performance specifications for O3 monitors and includes definitions for "Lag Time" and "Rise Time". Any definition of "stability" should include both these terms and additional descriptors regarding minimum elapsed time and output signal variation over time (e.g., *Sample the test atmosphere until the analyzer output varies by no more than ± X ppb over a period of at least Y minutes where "Y" is the lag time plus twice the rise time.*).

Noise

EPA's current definition of noise is based on the standard deviation of 25 readings taken at two minute intervals. Noise is specified at both the "zero" level (S_0) and 80% of full scale (S_{80}). The test procedures refer to "Table B-1" as containing the noise specifications for S_0 and S_{80} but there

is only a single specification for ozone analyzer noise (0.005 ppm). EPA should also clarify whether both S_0 and S_{80} have different specifications or not.

Of the nine manufacturers granted FEM status since 2000[7] only four listed S_0 performance figures in on-line specifications and only one listed an S_{80}. From this survey a 1 ppb S_0 appears plausible. The only manufacturer reporting an S_{80} value listed it as "(< 0.5% *of reading (RMS) above 100 ppb*" and since the full-scale values of the monitor spanned the "0 – 100 ppb" to "0 – 10 ppm" range, EPA might adopt a similar approach, specifying an S_{80} of "< 1.0% of RMS reading above 100 ppb".

Lower Detectable Limit

The Subpart B technical definition of "Lower Detectable Limit" is

> "*The minimum pollutant concentration that produces a measurement or measurement output signal of at least twice the noise level.*"

Candidate analyzers must be challenged with the 0.01 ppm lower detectable limit ozone concentration currently listed in Table B-1. The response is then compared to the previously determined noise level and the analyzer passes the detection limit specification if that response is greater than twice the noise limit. If EPA adopts the noise specification suggested above the Lower Detectable Limit would be 0.002 ppm (2 ppb).

Interference Equivalent

Table B-3 of Subpart B lists three compounds known to likely interfere with the FRM "Ethylene/chemiluminescent" method (NH_3, CO_2, and water vapor) and five compounds for the ozone "UV Photometric" FEM (SO_2, NO_2, NO, m-xylene, and water vapor). In addition to testing candidate analyzers for these "likely" interferents, Subpart B also specifies that

> "*In the event that there are substances likely to cause a significant interference* ***which has not been specified in table B-3*** *to subpart B of part 53,* ***these substances shall*** *also be tested, in a manner similar to that for the specified interferents,* ***at a concentration substantially higher than that likely to be found in the ambient air***." (***emphasis added***).

EPA has acknowledged at least since May 1, 1997[8] that many aromatic organic species positively bias FEM UV Photometers. Therein EPA also acknowledged that localized sources of interferents such as mercury spills (e.g., broken thermometers) and pesticide/herbicide applications around monitoring shelters <u>significantly</u> bias UV-based ozone analyzer responses. A recent review of ozone monitor interferences[9] identifies specific compounds and their reported photometer sensitivities that EPA could also list in Table B-3. As per previous admonitions[8], EPA should also evaluate the interfering compounds that are emitted from "asphalt plants", "asphalt paving operations", "large asphalt parking lots" and "herbicide/pesticide formulations" that significantly bias the UV-Photometric technique.

Apparent wintertime ozone concentrations may be enhanced in part from enhanced gas phase photolysis of snowpack precursor NOx and VOC emissions[10] and likewise also from directly emitted O3 photometer interferences (e.g., oxidized aromatic VOCs) produced by singlet molecular oxygen photochemistry occurring at the irradiated snow surface[11]. Such newly recognized heterogeneous photochemical mechanisms have yet to be included in winter ozone

models. Elevated gaseous elemental mercury (GEM)[12] and Hg (II) compounds deposited with snowpack can also be re-emitted photochemically as GEM[13].

In Table 3-4 of Subpart B, EPA allows ozone measurement methods to have a bias of 0.02 ppm for each interfering species up to a total interference of 0.06 ppm. Results from FRM/FEM certification application testing are not generally available to the public. However, it is clear that the current list of species interfering with the photometric method in Table B-3 is inadequate and that the acknowledged allowed interference levels are unacceptable[3] for the current 8-hour O3 standard of 0.075 ppm.

EPA should drop current performance "specifications" for both interfering species and total interferents. In their place EPA should require testing of candidate analyzers for known interferents at concentrations ranging from typical ambient levels to 10-fold enhancements in certification test atmospheres containing background O3 concentrations (e.g., 60 ppb) at 1,250 and 30,000 ppm H_2O humidity to simulate dry wintertime and hot summertime conditions. This approach would better quantify the impact of "sample matrix" effects on O3 monitor performance.

Finally, EPA should establish a formal procedure for tracking, verifying and reporting performance issues and interferents discovered subsequent to FRM/FEM designations. As part of the reporting procedure EPA should require that sample matrix interference test results (available at the time of manufacture) be included in vendor advertisements and instrument manuals for each designated FRM/FEM model. This information will assist monitoring organizations in optimizing analyzer choices best minimizing the known/expected interferents at specific monitoring locations. Interferents or performance issues (e.g., imprecision, bias or instability) discovered subsequent to FRM/FEM designation should be published as addenda updates to EPAs "List of Designated Reference and Equivalent Methods".

Analyzer Drift

Current monitor "zero drift" specifications are defined as

> "*The change in measurement response to zero pollutant concentration over 12- and 24-hour periods of continuous unadjusted operation.*"

and are limited to "± 0.02 ppm (20 ppb) for both 12- and 24-hour periods.

Current monitor "span drift" specifications are defined as;

> "*The percent change in measurement response to an up-scale pollutant concentration over a 24-hour period of continuous unadjusted operation.*"

and are limited to ± 0.02 ppm (20 ppb) for a 24-hour period.

EPA may be able to drop a 12-hour drift requirement if current generation O3 analyzers are certified as possessing little short-term drift. EPA should retain daily zero/span checks with zero drift ≤ ± 3 ppb/day and span drift ≤ ±5 ppb/day measured at the existing standard concentration.

Lag Time, Rise Time, Fall Time
Current EPA Table 3-4 specifications call for analyzer lag times ≤ 20 minutes and rise/fall times ≤ 15 minutes. Current generation O3 monitors have analyzer cycles ≤ 30 seconds or less so a reduced lag time of 2 minutes seems appropriate. Current generation analyzer rise/fall times needed to reach 95% of final value are ≤ 1 minute so reasonable rise/fall times could also be 2 minutes.

Precision
Current precision specifications for ozone analyzers are "± 0.01 ppm" (10 ppb) at both "20% of upper range limit (100 ppb)" (P_{20}) and at "80% of upper range limit (400 ppb)" (P_{80}). Precision is calculated as the standard deviation of six checks of P_{20} and P_{80} each day for a minimum of seven days. The candidate analyzer achieves the precision specification if each day's P_{20} and P_{80} standard deviations are ≤ ± 0.01 ppm.

As mentioned earlier, recently certified ozone analyzers claim precisions ranging from "< 0.5% of reading" to "The greater of 1.0 ppb or 2% of reading for a 10 second average". At the level of the current NAAQS the precision of these most recently approved analyzers would range from ± 0.4 ppb to ± 1.5 ppb, justifying a new dry zero air audit precision specification of 0.002 ppm (2 ppb).

Calibration/Auditing

Norris et al note [14] that:

> "*Ambient ozone measurements in the United States are traceable to a National Institute of Standards and Technology Standard Reference Photometer (NIST SRP)…that serves as the highest level ozone reference standard to state, local, and tribal regulatory agencies for calibration of network photometers used for compliance purposes. Such regular audits currently provide reliable measures of field monitor precision and bias in response to challenges of* <u>*ozone in zero air*</u>*, although not of sample matrix effects arising from ambient humidity and interfering species* (citations omitted and emphasis added)."

The article then describes a rigorous investigation and correction of small irregularities in the sample cell path length and temperature control of Standard Reference Photometers operated by BIPM and NIST.

The authors' recognition of the zero air audit mischaracterization of field monitor precision and bias due to sample matrix effects is of perhaps greater importance. A recent study of O3 monitor interferents[9] reported dynamic water vapor-interferent bias effects on ozone UV-photometers with changing humidity.

A classic approach to removing sample matrix effects in analytical chemistry is the method of "standard addition" in which a calibration standard is added directly to the aliquots of analyzed sample. Although feasible, an alternative simpler approach to the difficulty of generating precise concentrations of reactive ozone at elevated sampling inlets in the field may be use of new generation humidity-controlled NO-chemiluminescence and NO-scrubbed UV-absorption O3 monitors that eliminate interferences due to aromatic compounds, mercury, and water vapor.

Being humidity controlled, both approaches also allow continued use of current dry zero air calibration/audit procedures.

Monitor Performance for Sub-hourly Short-Duration Measurements

Ozone

The updated O3 monitor performance specifications proposed above are sufficient for one-hour and greater averaging times. However, should EPA determine that an O3 NAAQS with a sub-hourly averaging period (i.e., 1-10 minutes) be required a more stringent (or certainly different) performance specification is in order.

Reducing the average O3 measurement period from one-hour to several minutes results in less short-term signal drift but increases the amount of noise in the signal. Because noise and drift can impact an instrument's LDL and precision, it follows that O3 monitor performance specifications for noise and drift should be given extra scrutiny for monitors making sub-hourly measurements.

Because analyzer manufacturers have not been required to submit performance data on short-term sub-hourly average performance, such information is relatively scarce. However, empirical data is available from a long-term study of an API 400A O3 analyzer making short-term average measurements[15]. A sub-report from this study by Hyslop et al[16] describes a 13 month study in which 1-minute ozone measurements from the API 400A UV-photometric analyzer were aggregated into 5-minute averages. Data completeness for the 5-minute averages was 87%. The Lower Quantifiable Limit (comparable to the LDL) was derived from 5-minute samples of zero air while precision was derived from 5-minute samples of calibration span gas (80 ppb) introduced on a nightly basis.

Hyslop et al calculated the 5-minute LDL as two times the standard deviation of the 5-minute zero calibration measurements (n = 205) and found it to be 1.9 ppb. This is substantially higher than the vendor's stated LDL of "< 0.6 ppb". However, given the short equilibration period associated with such real-world calibration atmospheres (i.e., 5-10 minutes) and the subsequent increase in noise during such short-term measurements, an increased LDL is to be expected.

The precision for 5-minute data was computed by Hyslop et al as the absolute value of the 95% confidence interval (CI) of the nightly calibration precision checks at 80 ppb and found to be 0.26 ppb (n = 199). Reverse calculations show the standard deviation to be 1.87 ppb (n = 199). The EPA currently calculates precision as the standard deviation of six precision-level concentrations over at least seven days. Therefore the 1.87 ppb precision for short-term measurements arrived at by Hyslop et al is essentially equal to the proposed revised 1-hour precision values of 2 ppb noted above. Although the Hyslop et al data is enlightening, similar tests by others may yield different results, therefore revised performance specifications for O3 analyzers making sub-hourly measurements should be more lenient than those for one-hour measurements.

In light of such empirical data EPA should consider adopting a separate set of performance criteria for O3 analyzers measuring sub-hourly O3 averages. These short-term performance

specifications should include a zero noise (S_0) level of 2 ppb, an LDL of 4 ppb, and a precision (P_{20}) of 4 ppb.

In addition to assessing O3 data quality Hyslop et al also evaluated the quality of short duration SO_2[17] and NO/NOy[18] data during the long-term study. For SO_2 and NO/NOy the LDL was not derived from response to zero air but was determined from 12 consecutive 5-minute periods

> "*…during relatively stable periods with concentrations close to zero…*".

Although dissimilar to the EPA method for computing LDLs this approach is conservative in that it measures both instrument noise and atmospheric variations.

Sulfur Dioxide

For SO_2 the LDL (calculated as two times the standard deviation of twelve 5-minute averages) was found to be 0.14 ppb. Recently approved SO_2 analyzers have LDLs of approximately 0.050 ppb[7] (50 parts per trillion) or about one third of the conservatively calculated real-world value determined by Hyslop et al.

Precision for short duration SO_2 concentrations was calculated in the same manner as O3 precision with the exception that the target concentration was 40 ppb (versus the 80 ppb target for ozone). The 5-minute precision (n = 65) at 40 ppb was determined to be 0.2 ppb.

Nitrogen Oxides

The LDL for NO (using 5-minute data from a time period different than for SO_2) was 0.02 ppb and 0.11 ppb for NOy. Recently marketed NO/NOy analyzers have LDLs of about 0.050 ppb[7] which are somewhat lower than the conservatively derived real-world LQLs for NO and NOy. Precision for NO was calculated identically as for ozone except that the NO target concentration was 90 ppb. At 90 ppb the NO precision was determined to be 0.5 ppb (n = 320) and 0.4 ppb for NOy (n = 320).

The performance of recently marketed SO_2 and NO/NOy analyzers exceeds that determined by Hyslop et al. However given the conservative nature of methodology employed by Hyslop et al and the paucity of information available regarding the quality of sub-hourly ambient air measurements, performance specifications of 0.002 ppm (2 ppb) for both LDL and precision (P_{20}) should be adequate for modern SO2 and NO/NOy analyzers making sub-hourly measurements.

Conclusions

1. The large uncertainty associated with current O3 measurements does not support the use of reporting hourly O3 data to three decimal places.

2. With respect to FRM/FEM instrument performance testing specifications for O3 monitoring methods EPA should

> a) clearly define the term "stable measurement reading",

b) clarify whether zero and span noise specifications (S_0 & S_{80}) have different values and adopt a span noise (S_{80}) specification based on a "percent of scale" basis,
c) adopt an LDL of 0.002 ppm (2ppb),
d) drop current interference specifications in favor of testing all known interferents at both expected ambient concentrations and at ten times those concentrations,
e) require FRM/FEM instrument manufacturers to include information on matrix effects and interfering species in their sales literature,
f) track, verify and report (in the List of Designated Reference and Equivalent Methods) all existing and subsequently reported method issues and interferents,
g) adopt a daily (24 hour) zero drift specification of $\leq$0.003ppm (3 ppb) and span drift of $\leq$ 0.005 ppm (5 ppb),
h) adopt Lag/Rise/Fall specifications of 2 minutes each,
i) adopt a Precision specification of $\pm$2 ppb and,
j) promote FRM/FEM methods (especially for O3) which minimize "sample matrix effects".

3. For the emerging field of short-duration monitoring EPA should consider a separate set of performance specifications for O3 (and other pollutant) measurement techniques. Initially EPA should consider adopting a zero noise (S_0) level of 2 ppb, an LDL of 4 ppb, and a precision (P_{20}) of 4 ppb.

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