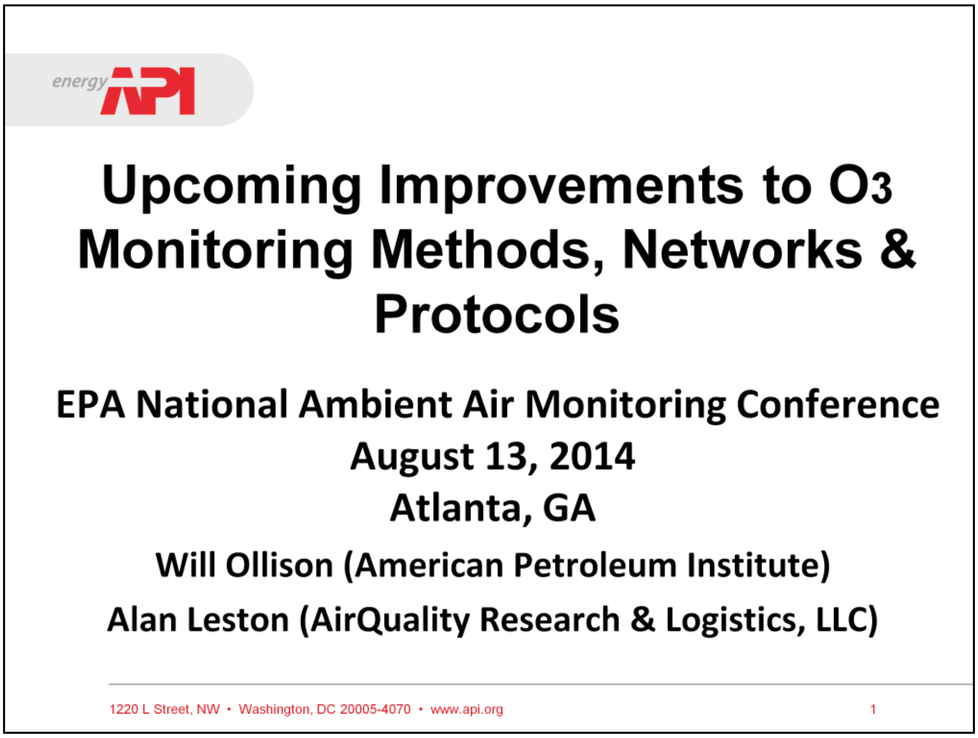
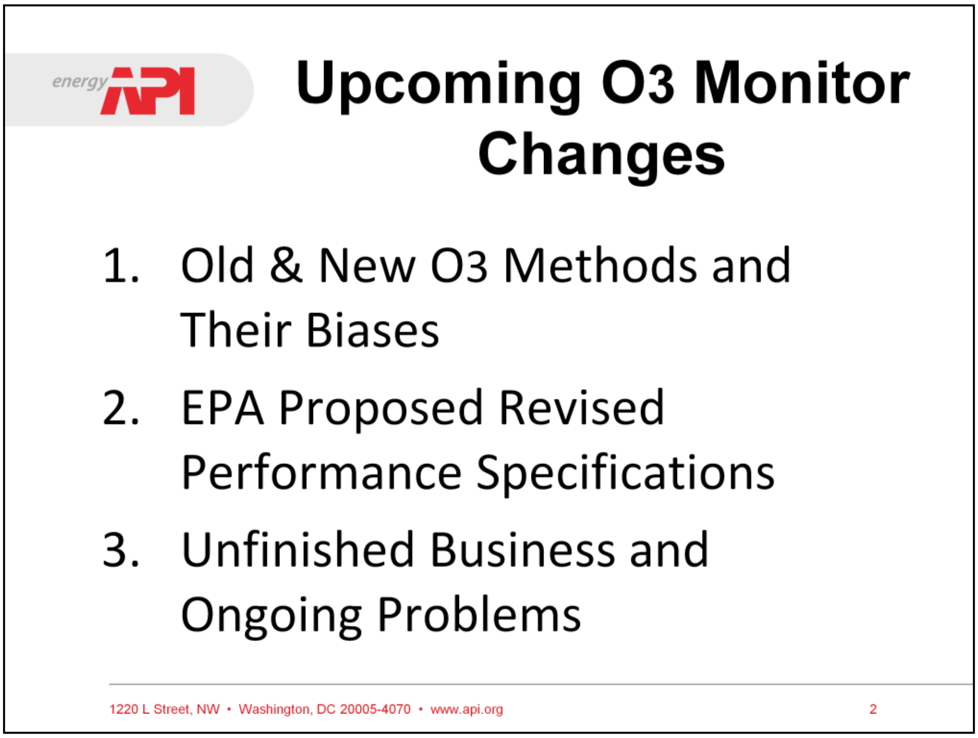
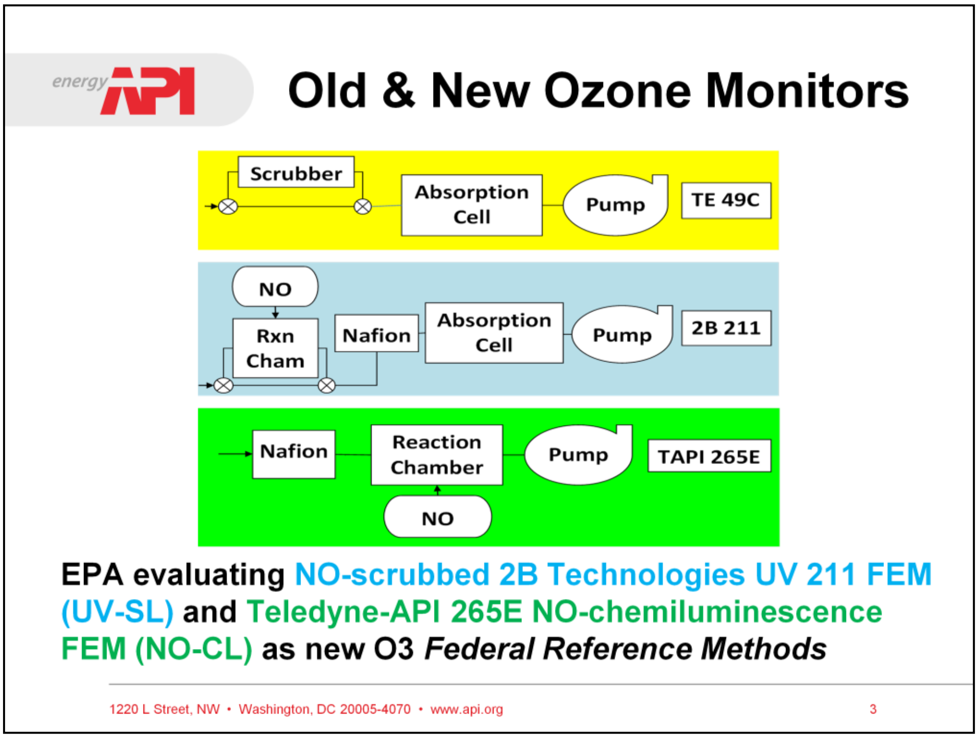


Slide 1 – Good afternoon, I appreciate the opportunity to share recent studies and regulatory developments with new ozone monitoring instruments, compliance networks, and proposed changes to regulatory monitor performance specifications. My coauthor, Alan Leston is also present and beginning his 43rd year in the Air Pollution field, after 31 years with the Connecticut Department of Environmental Protection and 11 years as an independent consultant.



Slide 2 – We'll briefly touch on the differences among current and new upcoming compliance network monitors, improved performance specifications, and some remaining issues with these proposed changes that are anticipated by the end of 2014.



Slide 3 – Conventional ozone photometers, such as the Thermo 49C, are illustrated in **yellow** schematic box and use a solid-state metal oxide ozone scrubber to determine ozone by UV absorption difference between scrubbed and unscrubbed sample streams. Interferences occur when such scrubbers remove additional 254 nm absorbing compounds which are then measured as ozone. The new 2B Technolgies (2B) 211 photometer in the **blue** schematic box uses a gas-phase nitric oxide scrubber that removes ozone without removing other UV absorbing compounds. The new Teledyne-API (TAPI) 265E nitric oxide chemiluminescence ozone monitor in the **green** schematic box is similar to the current U.S. ethylene-chemiluminescence Federal Reference Method (an instrument that is no longer manufactured or deployed in the compliance monitoring network), substituting nitric oxide for ethylene and sensing red rather than blue luminescence. Note that both new ozone instruments control sample humidity by Nafion treatment, the 2B 211 monitor by hydrating scrubbed & unscrubbed sample streams to local ambient humidity levels, and the TAPI 265 instrument by dehydrating the sample stream to near zero humidity. Both of these new ozone instruments are certified Federal Equivalent Methods (FEM) and are being considered by EPA for Federal Reference Method (FRM) designations. EPA-ORD staff has emphasized the need for humidity control in ozone monitors during the recent 2014 advisory committee FRM considerations.

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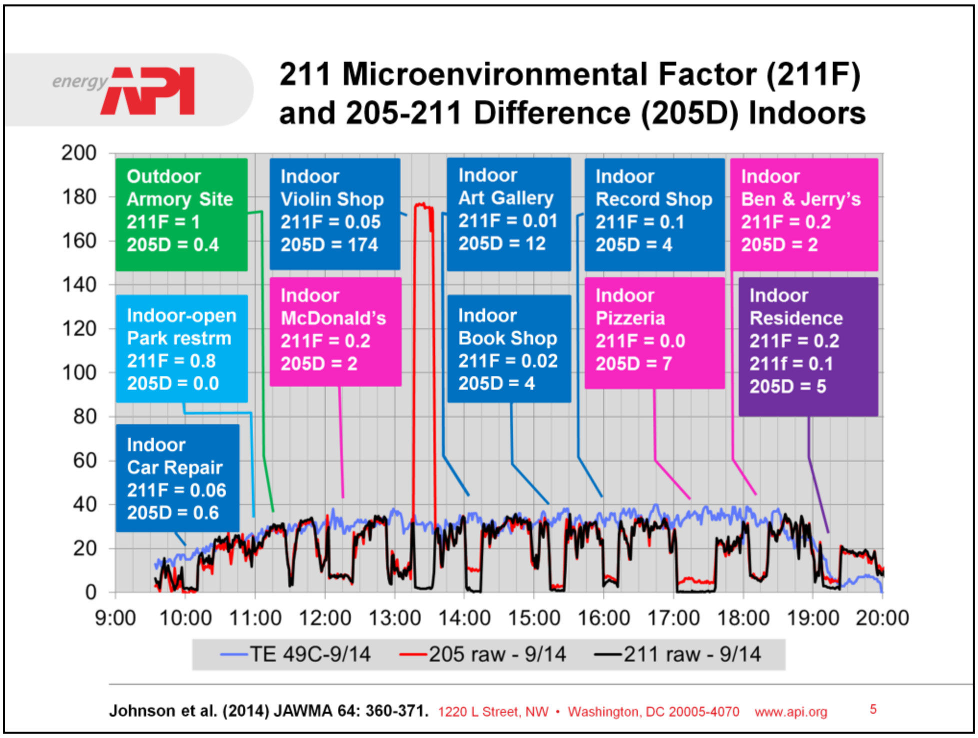
Current O3 Photometer Bias

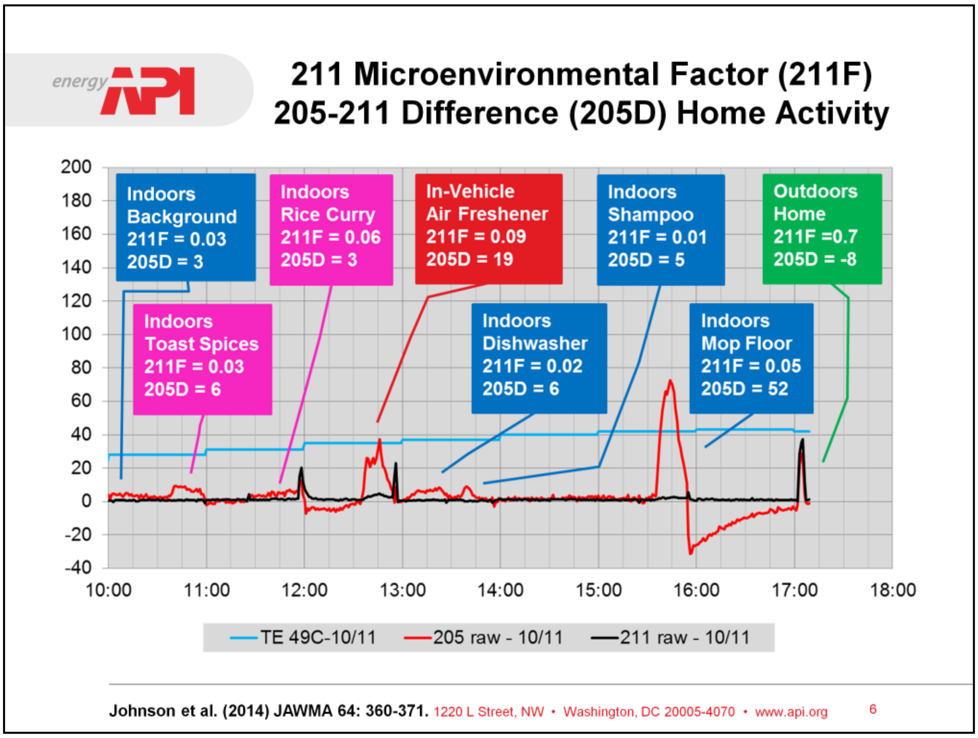
Interferents	O3 Equivalent Range
O3	1.0
Hg vapor	76 - 1400
Styrenes	0 – 1.5
Arene Aldehydes	0 – 0.8
Phenols	0 – 2.2
2-Nitrotoluene	0 – 0.8
Naphthalene	0 – 1.2

Spicer et al. (2010) JAWMA 60: 1353-1364.

Slide 4 – Conventional photometers are extremely sensitive to mercury vapor since they use mercury lamps to provide the 254 nm probe wavelength. However, they are also sensitive to UV-absorbing polar aromatic compounds with electron withdrawing ring substituents such hydroxyl, carbonyl, nitro, or vinyl groups. The range of the interference response depends on the specific compound isomer, the solid-phase scrubber design, the sample humidity, and scrubber history as noted by Spicer et al. 2010, JAWMA 60: 1353-1364.



<u>Slide 5</u> - In a recent microenvironmental (ME) study, a new 2B 211 O3 FEM photometer, which has a gas-phase nitric oxide scrubber, was compared to a conventional 2B 205 O3 FEM photometer sampling various indoor, in-vehicle, and outdoor microenvironments. The paired monitors were also collocated daily with a conventional Thermo 49C O3 FEM at a Durham, North Carolina, compliance monitoring site. Minute-resolution, multiple-monitor sequential ME measurements were taken each sampling day, that included daily monitor zero/spans and collocated comparisons with the Durham Armory site. Daily paired monitor drift was typically below 2 ppb and collocated ambient sampling tests agreed within a ppb or two with the Durham site. The three traces in the chart report 1-minute average ppb ozone levels, the **blue** trace is the Durham site Thermo 49C, the **red** trace is the conventional 2B Tech 205 FEM, and the **black** trace is the 2B 211 NO-scrubbed "interference-free" FEM monitor. The calculated 211 ME factor, reported as 211F, is the contemporaneous 10-15 minute average ratio of the **black** and **blue** curves and the 205-211 difference, reported as 205D, is a measure of the conventional monitor 10-15 minute average interference bias. As reported in the initial **green** chart box, all three monitors agreed this day when collocated at the Durham site. In the ME measurement reported in the first **blue** box, 205D is very large, the 174 ppb O3 level is over 5 times the ambient level, in a musical instrument sales and repair shop visited that day. Other ME 205-211 monitor differences reported on the chart were modest, ranging from 0-12 ppb O3. Johnson et al. (2014) JAWMA 64:360-371.



<u>Slide 6</u> – Sampled indoor activities that affected the 205-211 10-15 minute average monitor differences include cooking, cleaning, and personal care product usage. The 1-minute average **red** 205 trace illustrates how the conventional photometer metal oxide ozone scrubber absorbs and subsequently releases over time (or sometimes doesn't release) UV-absorbing interferences, giving both positive and negative O3 signals over differing time frames, depending on the type of interference. For example, the auto air freshener interference at 12:45 was not released (no negative following trace). However, the disinfectant floor cleaner interference at 15:45 was slowly released as a following negative signal over more than an hour. The **black** 211 trace shows little or no response to these corresponding interference challenges. The spikes in the 211 and 205 traces occur during brief excursions outdoors where ambient ozone is detected at the residential test site, which is about a mile away from the conventional monitor at the compliance site whose 1-hour average values are reported in the **blue** trace. The peak 205-211 outdoor difference reported in the green box is negative (-8 ppb) since the 205 instrument reading is still depressed by eluting scrubber-absorbed floor cleaner interferences at the time (17:05). Johnson et al. (2014) JAWMA 64:360-371.

O3 Monitor Certification

"The amount of allowable interference is 60 ppb at the current 75 ppb O3 NAAQS…These specifications *should be revised* to more accurately reflect the necessary performance requirements for O3 monitors used to support the current NAAQS."

2013 O3 Integrated Science Assessment EPA 600/R-10/076F

Slide 7 – EPA has recognized the difficulties that currently allowed interference bias presents for compliance determinations with the present and prospectively decreasing ozone standards (perhaps as low as 60 ppb) that are now under consideration. The Agency noted in the 2013 O3 Integrated Science Assessment (600/R-10/076F) that it plans to further tighten current FRM/FEM O3 monitor performance specifications, most likely in time for its December 2014 proposed revised O3 standards.

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Proposed Revised O3 FRM/FEM Performance Specifications

O3 Monitor Parameter	40CFR53 Table B-1	EPA-ORD Revised B-1*	Leston, 2014** Revised B-1	TAPI NO-CL	2B UV-SL
Range (ppb)	0-500	0-500	0-250	0-100, 0-2000	0-2000
Noise @ zero (ppb)	5	1	1	0.15	0.5
Noise @ 80% URL (ppb/%)	5	1?	1% at 100 ppb O3	0.5% at100 ppb O3	0.5%
LDL (ppb)	10	3	2	0.3	1
Zero Drift (ppb)	20	4	3	0.5	1
Span Drift @ 20% URL (%)	20	3?	5	0.5% at 100 ppb O3	0.5%
Span Drift @ 80% URL (%)	5	3	5	0.5% at 100 ppb O3	0.5%
Lag (minutes)	20	2	2	0.17	0.33
Rise (minutes)	15	2	2	0.33	0.33
Fall (minutes)	15	2	2	0.33	0.33
Precision @ 20% URL (ppb)	10	?	2	0.1 or 0.5% of value	0.5 or 1% of value
Precision @ 80% URL (ppb)	10	?	2	0.8 or 0.5% of value	0.5 or 1% of value

*Long et al. *Review of Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence,* Briefing for CASAC-AMMS, *April 3, 2014 -* http://yosemite.epa.gov/sab/sabproduct.nsf/MeetingCalCASAC!OpenView&Grid=3&Date=2014-03-31

**Leston, March 26, 2014, *A Report on the Suitability of CASTNet and SLAMS Ozone Data for Use in Regulatory Decisions and Related Issues -* http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03

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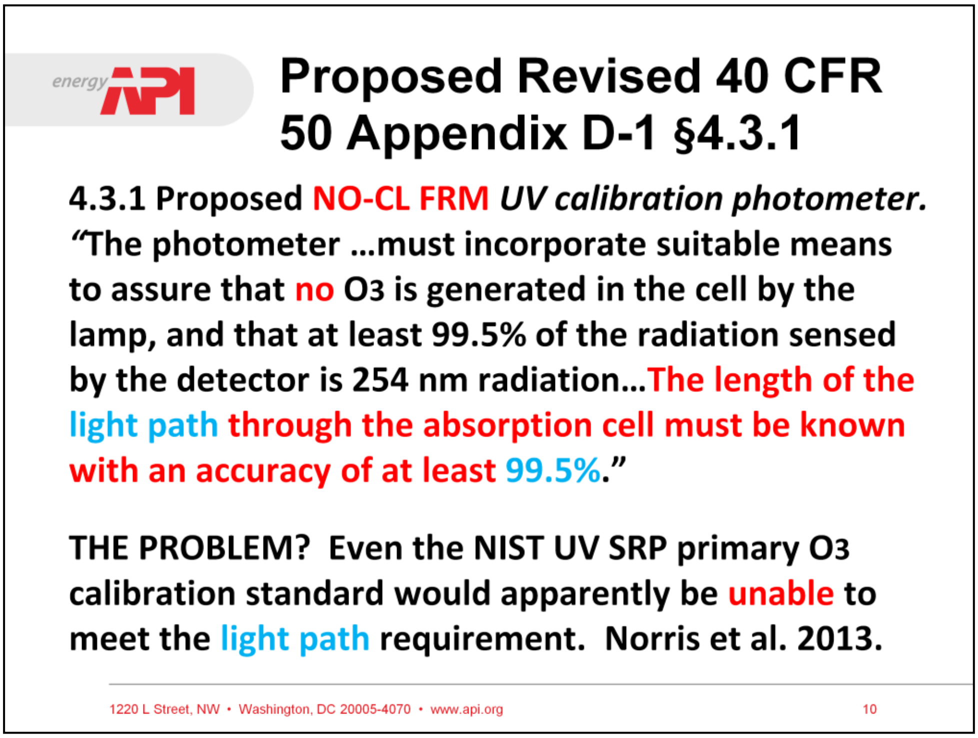
Slide 8 – This table compares the current 40 CFR 53 Table B-1 specifications to those proposed by EPA-ORD in presentations to Agency science advisors during their 2014 O3 FRM discussions - Long et al., *April 3, 2014 -* http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03. A monitor review by Alan Leston, *March 26, 2014 -* http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03 – and its recommendations are also tabulated along with vendor-posted performance specifications for the two new instruments. The two new monitors easily meet ORD's proposed revised specifications.

Proposed Revised O_3 FRM/FEM Performance Specifications

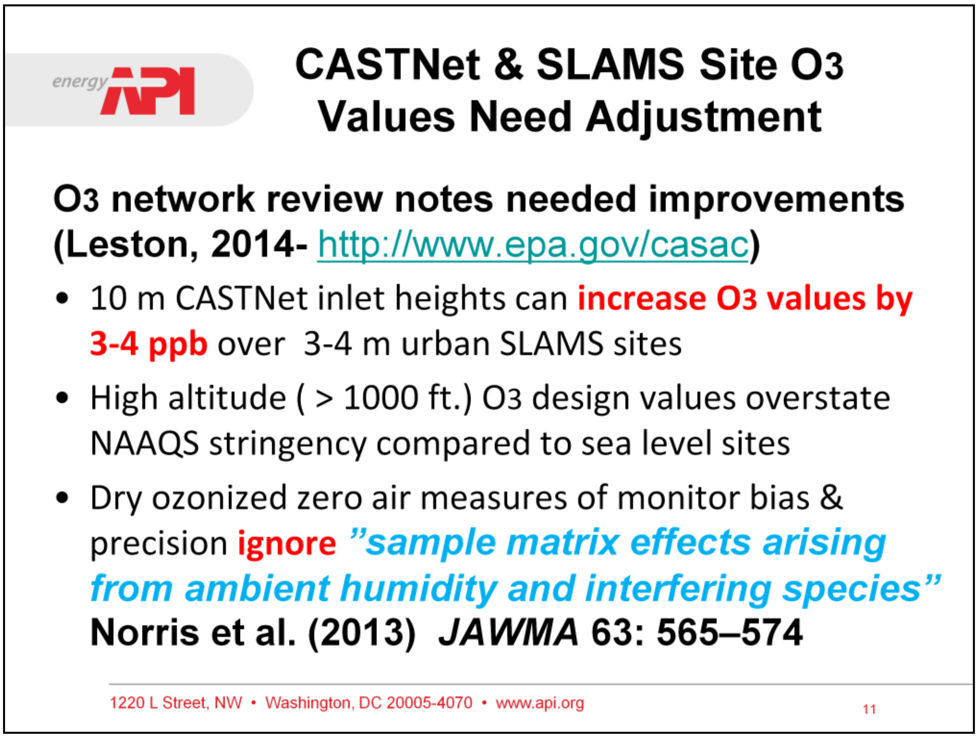
O_3 Monitor Interference Tests	40CFR53 Table B-3 ppb	EPA-ORD Revised B-3 ppb	Leston, 2014 Revised B-3	TAPI NO-CL ppb	2B UV-SL ppb
H_2O 20,000,000 ppb	20	5	H_2O 1,250,000 & 30,000,000	< 20	0* (-2) (selectivity > 10,000,000)
H_2S 100 ppb	20	5	Test reported interferents at 1x & 10x urban ambient levels in the presence of 60 ppb O_3	< 20	
CO_2 750,000 ppb	20	5		< 20	
SO_2 500 ppb	20	5?			0* (-1) (selectivity > 500)
NO 500 ppb	20	5?			0* (0) (selectivity > 1000)
NO_2 500 ppb	20	5?			0* (-2) (selectivity > 250)
m-Xylene 20 ppb	20	5?			0* (-1) (selectivity > 220)
Total allowed interference ppb	60	unlimited?	< 60		

* Note that the small negative values for the interference measurements are due to 1-3% dilution of the 81-86 ppb O3 level by the added interference flow; actual interference level is zero within experimental error for all measurements

Slide 9 – The EPA-ORD proposed revised 40 CFR 53 Table B-3 monitor tests substantially tighten allowed FEM interference bias. The new gas-phase, nitric oxide scrubbed photometer, noted as the 2B UV-SL, easily meets the current and newly proposed interference limits, as noted from the vendor-posted 2B UV-SL FEM certification report - http://www.twobtech.com/model_211.htm. The TAPI NO-CL chemiluminescence monitor report also likely does so as well; however, only the current 40 CFR 53 B-3 requirements are tabulated since its FEM certification report is not publically available to quantitatively document this presumption. EPA-ORD has presented lab results for their NO-CL H2O, H2S, and CO2 interference testing as 0.0005, 0.001, and -0.1 ppb, respectively - http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03. However, their H2O value is questionable since it is carried out in the absence of O3 and so does not measure water vapor effects on an actual O3 chemiluminescence signal (40 CFR 53 Table B-3, footnote 3).



Slide 10 – In its proposed revised 40 CFR 50 Appendix D-1, designating the NO-CL monitor as an FRM, EPA appears to over-specify performance aspects of the UV reference photometer required to calibrate the NO-CL FRM. For example, even the NIST standard reference photometer (SRP), used as the primary O_3 standard for the current compliance network, would not meet the proposed Appendix D-1 light path accuracy test, due to inadequate SRP lamp beam collimation and the resulting multiple light path reflections remaining within the photometer cell. Norris et al. (2013), JAWMA 63: 565–574.



Slide 11 – Our network review suggests that several additional improvements are needed in the CASTNet-expanded compliance network. These include downward O3 design value adjustments (1) to correct a rural 10 meter CASTNet inlet height O3 bias of about +15% (3-4 ppb) compared to typical urban population-based compliance network inlet heights of 2-3 meters above grade (Wisbith et al., 96-RA111.02, *in* Proceedings, 89th Annual AWMA Meeting, June 23-28, 1996, Nashville, TN; 2011 CASTNet Report, page 56, Figure 4b – http://www.epa.gov/castnet/javaweb/does/annual_report_2011.pdf, (2) to account for the reduced inhaled O3 mass, at a given breathing rate and parts per million (ppm) O3 exposure level, that occur at high altitudes (>1000 feet) since O3 mixing ratio measurements are altitude invariant and in effect require elevated sites to meet more stringent standards than sea level locations (Wedding, et al. 1987, JAPCA 37: 254-258; Lillquist et al. 1996, JAWMA 46: 172-173), and (3) to account for overly optimistic dry zero air characterizations of conventional monitor bias & precision, which ignore local humidity and interference effects (Norris et al. 2013, JAWMA 63: 565-574).

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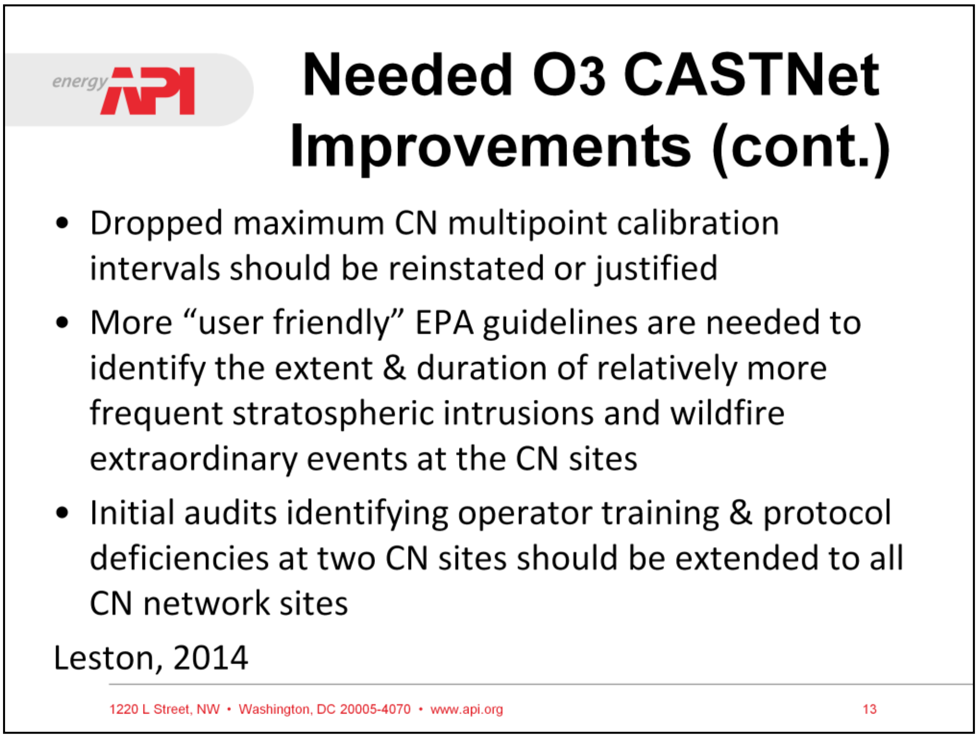
Needed O3 CASTNet (CN) Improvements

- Current CN photometers need upgrades to include humidity controls and NO scrubbers
- EPA should adjust CN data for 3-4 ppb 10 m inlet height bias compared to SLAMS 3-4 m inlet height
- Daily zero/span/precision data should be taken at different hours of the day to capture diurnal changes in T, RH, line voltage, and interferences

Leston, 2014

Slide 12 – EPA has recently decided to use 2011-2013 CASTNet ozone monitors to determine O3 standard compliance in rural and remote areas. Our review of the current state of this network suggests the decision is premature for a number of reasons listed here and on next slide – Leston, 2014, http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03.



Slide 13 – Suspect CASTNet practices and protocols include (1) quality assurance (QA) tests that are taken only at a single time of day, which miss possible effects from diurnal changes in site parameters such as temperature, humidity, line voltage, or local interference source strength, (2) continuing operator training deficiencies, and (3) insufficient EPA regional guidance in identifying relatively more frequent network "exceptional events" such as impacts of stratospheric O3 intrusions and wildfire smoke plumes, in particular their extents and durations, that will occur at these rural and remote CASTNet locations - Leston, 2014, http://yosemite.epa.gov/sab/sabproduct.nsf/bf498bd32a1c7fdf85257242006dd6cb/cf242b410033450885257c5b004f008d!OpenDocument&Date=2014-04-03.

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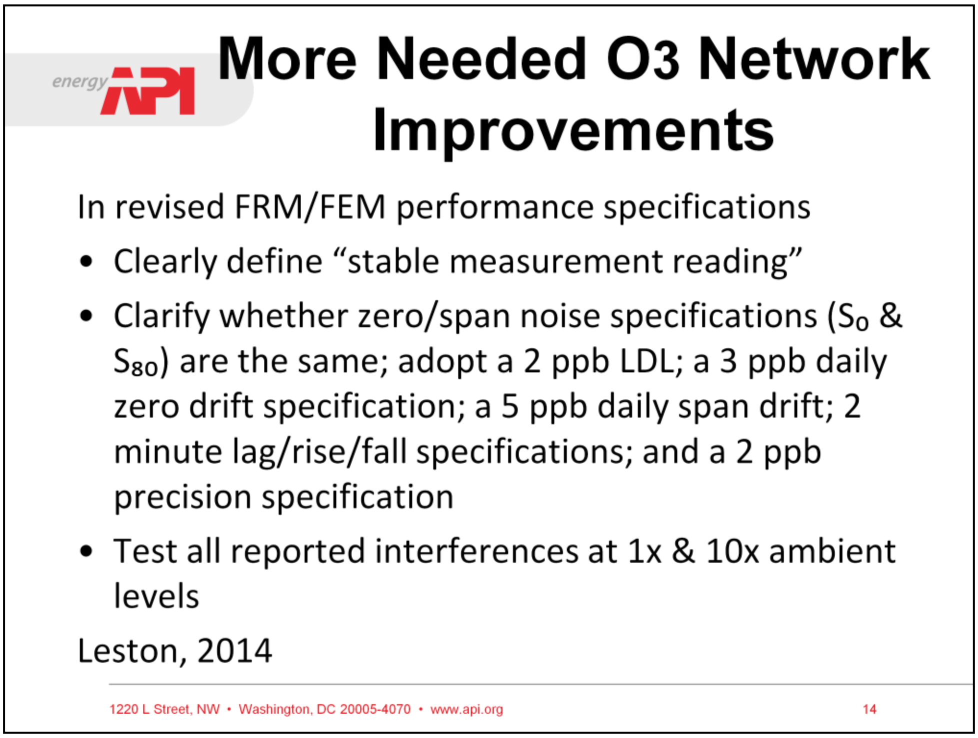


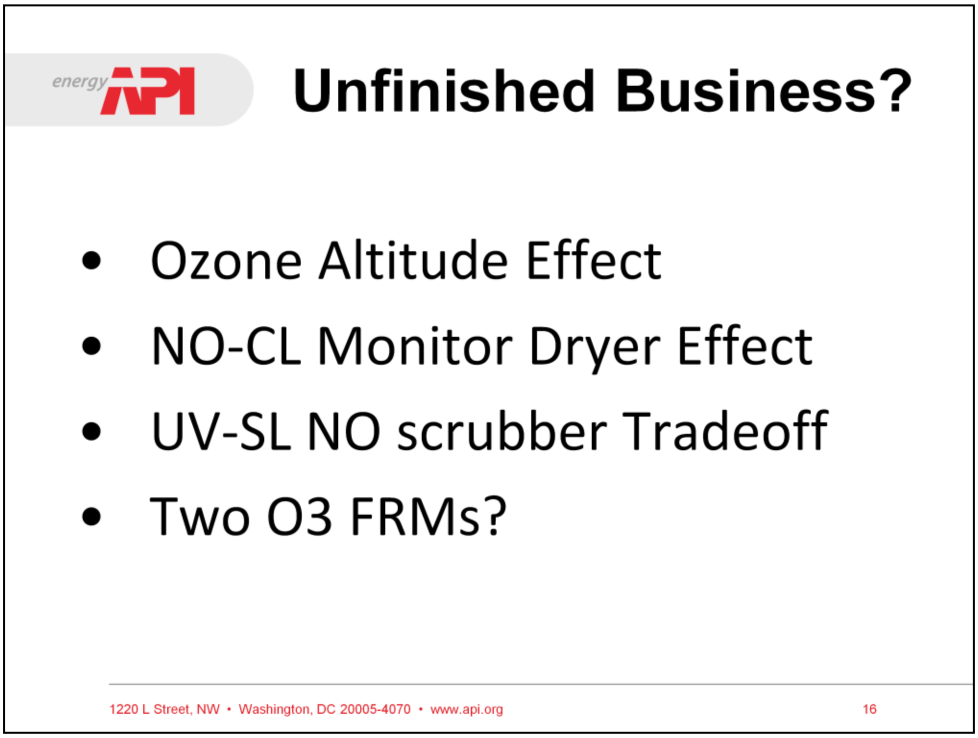
Slide 14 – As noted in this list, proposed revised FRM/FEM performance specifications at all network sites should also include additional EPA clarifications of prescribed tests, for example, how to determine when instruments have reached a "stable measurement reading" and how vendors should test for known and subsequently reported monitor responses to additional interferences not currently included in 40 CFR 53 Tables B-1 and B-3.

More Needed O3 Network Improvements (cont.)

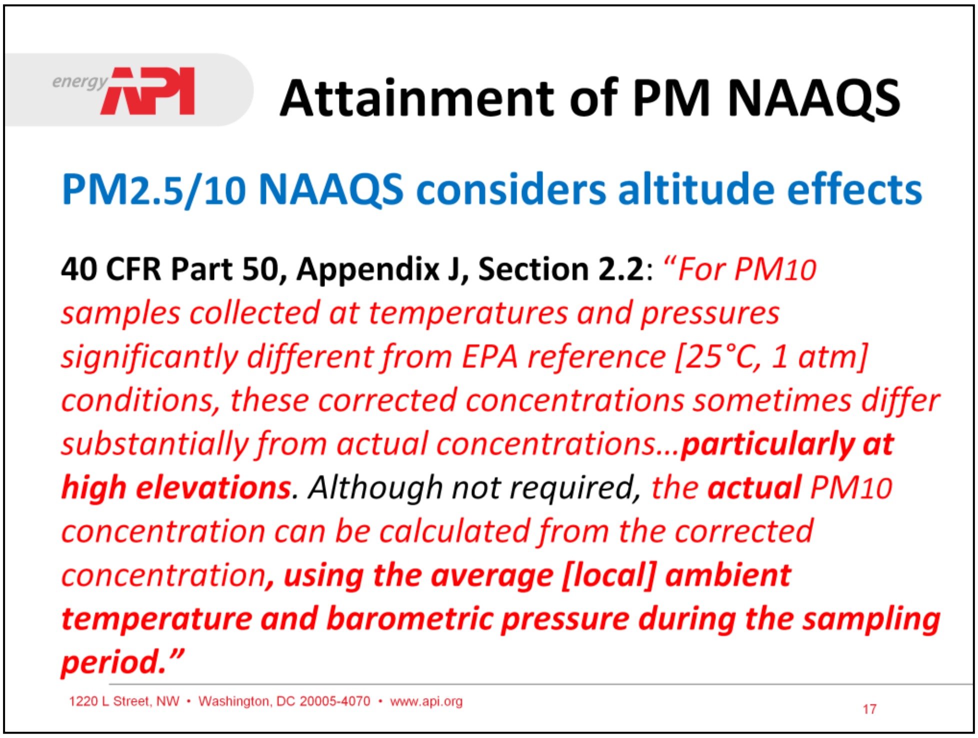
- Network O3 value uncertainty does not support reporting ppm data to 3 decimal places, reinstate a rounding convention
- Develop separate performance specifications for sub-hourly (e.g., 5 minute) monitoring data, adopting initial zero noise levels of 2 ppb, an LDL of 4 ppb, and precision (P_{20}) of 4 ppb.
- Promote methods which minimize sample matrix effects
- Require vendors to list interferences in instrument literature and EPA to track, verify, & report method interferences in their List of Designated Reference and Equivalent Methods

Leston, 2014

<u>Slide 15</u> – EPA should also consider additional urban network changes such as (1) reinstating the prior 5 ppb O3 rounding convention, given the level of current network photometer interference bias, (2) encouraging network operators to upgrade their current conventional O3 photometers with humidity controls and nitric oxide gas-phase scrubbers, and (3) requiring that both vendor and Agency literature include additional EPA-verified published interferences so that network operators can deploy instruments appropriate to their local monitor locations.



Slide 16 – We highlight several remaining O3 network issues needing further EPA attention and evaluation: (1) the altitude effect, mentioned earlier; (2) the effect of NO-CL humidity controls that dehydrate monitor sample streams on reported O3 design values, (3) suggested improvements to new UV-SL photometers, and (4) the EPA-ORD proposed designations of multiple O3 FRMs.



Slide 17 – In determining compliance with the PM NAAQS, network operators are presently allowed by 40 CFR 50 regulations to account for altitude inhalation effects. This is accomplished by calculating μg/m3 PM design value concentrations from cubic meter flow measurements taken at local barometric pressure for reasons discussed by Wedding and Lillquist. Wedding, et al. 1987, JAPCA 37: 254-258 and Lillquist et al. 1996, JAWMA 46: 172-173.

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Attainment of O3 NAAQS

O3 NAAQS does **not** consider altitude effects

40 CFR Part 50 Appendix P, Section 2.2: *"The standard-related summary statistic is the annual fourth-highest daily maximum 8-hour O3 concentration, **expressed in parts per million**, averaged over three years."*

At a given O3 ppm level and breathing rate, less O3 is inhaled at higher altitudes. However, *mixing ratios* are pressure invariant.

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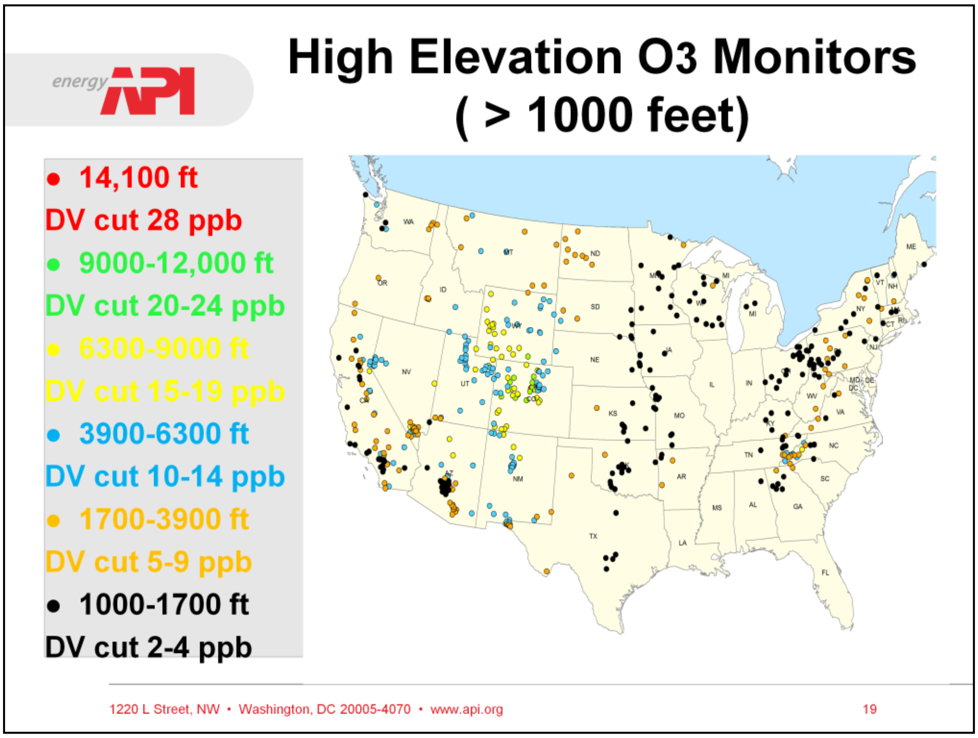
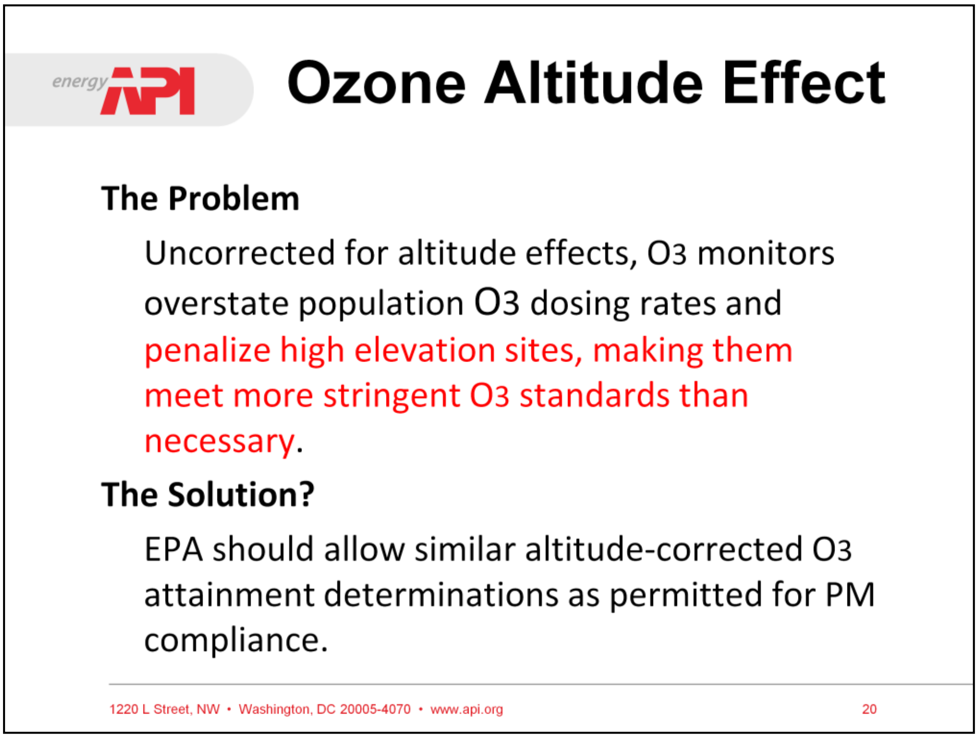
Slide 18 – The same altitude correction is not currently allowed for the gaseous standards such as ozone since their current ppm mixing ratio metrics do not vary with barometric pressure. This situation is a possible EPA oversight stemming from an earlier switch in gaseous standards from µg/m3 to mixing ratio ppm metrics. In effect, EPA now incorrectly presumes that high altitude populations inhale the same pollutant mass at a given breathing rate and pollutant ppm exposure level as do sea level residents under the same conditions (Wedding, et al. 1987, JAPCA 37: 254-258; Lillquist et al. 1996, JAWMA 46: 172-173) and consequently requires higher altitude locations to meet more stringent pollutant standards than are necessary. Unaddressed, this altitude inequity may result in gaseous standards that violate the Clean Air Act since courts require that National Ambient Air Quality Standard formulation stringency be uniformly "sufficient, but not more than necessary" in all cities. Whitman v. American Trucking, 531 U.S. 457, 473 (2001).



<u>Slide 19</u> - The map and legend denote the locations and amount that a 75 ppb O3 design value would need to be reduced to correct for the altitude effect. Such downward ozone adjustments would occur at about a third of the current compliance network sites and would generally range in magnitude from 2-20 ppb. The highest mapped O3 site (14,000 feet) is located in central Colorado.



Slide 20 – Simply stated, this altitude effect is an easily corrected problem, EPA should simply allow a similar altitude adjustment to ozone compliance values that it already allows for PM.

NO-CL Monitor Dryer Effect

The Problem

The nitric oxide-chemiluminescence monitor (NO-CL) dryer eliminates humidity interference but removes water vapor, thereby concentrating reported O_3 by up to 3-4% in humid locations.

The Solution?

EPA advisors recommend NO-CL vendors add a post-dryer humidity sensor to confirm dryer performance; sensing both pre- and post-dryer humidity would allow a correction for dryer effect.

Slide 21 – An additional technical problem with the FRM candidate NO-CL instrument, that should be considered by EPA and its scientific advisors is the O3 concentration effect of the Nafion dryer. The simple technical fix suggested is an extension of EPA scientific advisors' suggestion to add a humidity sensor to the NO-CL monitor.

UV-SL Monitor NO scrubber Tradeoff

The Problem

The "scrubberless" UV-CL photometer's nitric oxide O_3 scrubber currently adds NO flow only to the scrubbed sample stream, eliminating only 98-99% of the UV interferences in exchange for halving N_2O or NO/N_2 cylinder gas consumption.

The Solution?

The UV-SL monitor could be replumbed to allow a toggled operator option of adding NO flow to both scrubbed/unscrubbed sample streams when increased accuracy is required.

Slide 22 – An issue that remains with the FRM candidate UV-SL photometer is its design compromise that trades slightly reduced accuracy for reduced expendable NO gas consumption. Our suggested technical fix would provide network operators the flexability to reverse this tradeoff for site locations where higher monitor accuracy is desirable.

Two O3 FRMs?

The Problem

EPA proposes to designate both the ethylene- and nitric oxide-chemiluminescence monitors (ET-CL & NO-CL) as FRMs, to maintain FEM certifications of existing network UV photometers; however, the ET-CL fails to meet the proposed revised FRM/FEM 5 ppb water vapor interference specification.

The Solution?

EPA might maintain existing current network UV FEM certifications for photometers upgraded with humidity control and NO scrubbers as a cost-effective option to deploying new NO-CL or UV-SL network monitors.

Slide 23 – The EPA-ORD proposal to retain the ethylene-chemiluminescence FRM along with the prospective NO-CL and UV-SL FRMs is questionable. The current FRM is unable to meet ORD's newly proposed revised 5 ppb FRM/FEM 20,000 ppm water vapor interference sensitivity test (ASTM Method D5149-02 at Annex A2). We recommend EPA certify gas-phase NO-scrubber upgrades of existing network O3 photometers as a preferable, cost-effective remedy to any actual network photometer recertification issues.