EPA Programs for NIST Traceability in NAAQS Gas Measurements

Status and Changes

Mark Shanis

Seattle, WA 2008

% of COMPLETED TTP PE OUT of 100% of Sites in 5 YRS

- In theory, looking for 60% counting from 2005 (20%/Yr); 2004 was a tryout year
- National Avg for all the Regions is 67%
- 5 Regions are higher by 21% or more
- 5 are lower by 12% or more
- Given impacts due to Katrina and funding cuts until 2007, this success on the 20%/yr
- Done with 6 Regionally based Mobile labs

Other Successes

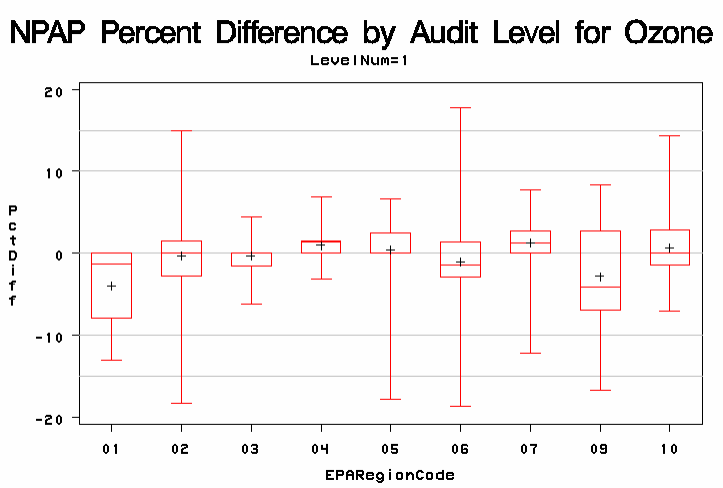
- Most of Data entered into AQS
- EPA Developed Data Entry and Report forms in EXCEL, DBase in ACCESS
- East and now West have Case-based Platforms; maybe Region 5 will have one by 2009
- Classroom Training now Remote
- TTP and Mailed System for Precursor Gases (PG) being tested in RTP for East
- Cert. PG Platform now in LV for West
- TTP Revision of QAPP posted on AMTIC; review competed

Initial Summary Analyses from Data in AQS

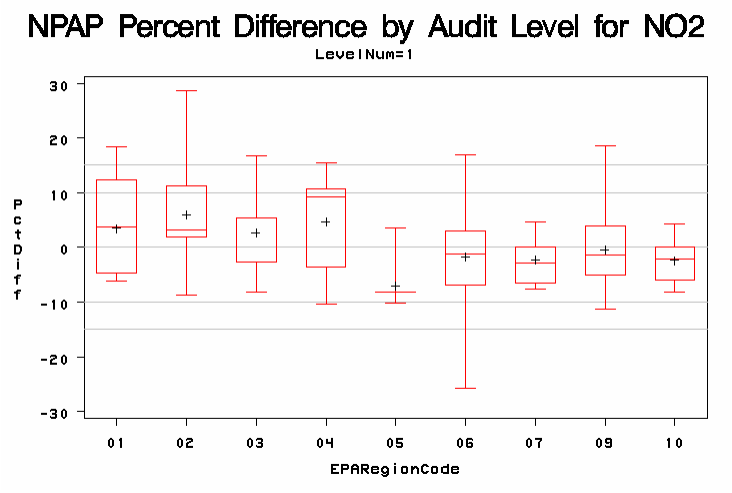
- Individual Values Compared to Range of Values-How to Show in an Accessible Way
  - Report Card Approach
  - Per Pollutant & Audit Level
- Analyses to address Changes in CFR: Acceptance Limit
  - Can we go to a lower Acceptance limit for O3
  - Can we go to a lower Limit for CO,SO2, NO2

Ozone APD by Region (%)

Region	n pairs	Mean	Max	95%tile	75th %tile	Median
1	12	2.5	13	13	3	0.6
2	77	2.8	18.3	18.3	2.9	1.5
3	200	1.8	6.2	5	3.1	1.5
4	109	1.5	7.8	3.5	1.7	1.3
5	228	2.2	17.7	6.1	3.1	1.8
6	221	2.5	18.6	8.6	2.9	1.6
7	318	2.3	15.6	6.5	3.1	1.7
8	*no data*					
9	267	5.5	21,7	17.7	7	3.9
10	78	2.5	14.3	8.5	.92	1.9



Level 1 audit range (O_3): 0.03 - 0.08 ppm



Level 1 audit range (NO_2): 0.03 – 0.08 ppm

QA Program Summary for TTP Audits of NAAQS Gases

- Personnel Certification
- Whole System Cert
  - All Now Compared to Reg 7 (Except Reg1)
- O3 Std Cert
- Blended Gas Std Cert

NPAP TTP 2007 QUALITY ASSURANCE and QUALITY CONTROL ACTIVITIES					
PERSONNEL CERTIFICATION					
Date	**Remote Phone Sessions / Re-Certification**	**Personnel Training Certification & Recertification**	**WAMS Certification**	**Location**	**# Attending**
10/15&16/07 11/1/07	X (new certs) X (recerts)			RTP/Region	9 20
10/29&30/ 2007; 11/1/2007		Hands on Training/ Full Certs		EPA/RTP	9
3/2,5,9,12,13/ 2007	X			RTP/Region	8
3/20/2007		Hands on Training Recerts		Region 4 Athens, GA	14
3/21-23/2007		Hands on Training Full Certs		Region 4 Athens, GA	8
January & February 2008	X		X	RTP & Regions	4

Excedance/Corrective Action /Follow-up

- Excerpt from 2007 Table
  - For Audit on 2/9/07
  - **Corrective Action response for O3 audit point fail, 6/4/07 :**
  - The station calibrator for the site was repaired and PMA was conducted on the instrument in April 2007. Calibrator repaired and the ozone portion of this calibrator re-calibrated on 5/14/07 we calibrated the ozone monitor this same day. Corrective action for the NPEP-TTP audit for the above site has been completed. If you have any further questions call or email me.

CFR-Based, & Other Changes Coming

- More, lower audit levels, steps
- Lower Acceptance Limits, steps
- Reporting of all 3 NO/NOx/NO2 channels
- Changes in SOPs, Entry Forms, QAPP
- Note: Guidance Errors Corrected in QA Handbook, based on Audit Feedback
- 1st Air Toxics TTP Program in Region 5 State

SRP Actions Planned

- Proposed Changes in Ozone Regs to be Aided by additional SRP upgrade
- SRP Schedule Update Posted on AMTIC- 2nd year
- Assembly started and review planned of last 3yrs of Regional SRP certification data
- Traceability Terminology Review started

Protocol Gas Verification Program

- Resurrection attempt still in process
- EPA Completed Drafting and Revising Proposed Implementation Plan
- Distribution started
- Additional EPA –funded Audit Completed
- Regulation Changes in Parts 58 & 75
- Protocol Revision

NPAP Reports/Progress/New Directions 8:00-8:40 Session 4/23/2008

Design and Implementation of Through The Probe Audit Systems for Overseas Audits

By

Mustafa A. Mustafa and Avraham Teitz
US EPA Region 2

Edison, NJ

Ideal Overseas System

- Weightless/Self Propelled
- Perfectly Accurate
- One plug, one switch, one fitting, one tube
- Indestructable
- No customs/security clearance required
- Provides shade at the beach while it does all the work for you

TTP 1 Stock

Overseas System

Design Overseas System

- Reduction in equipment "packaging"
  - Vehicle
  - Equipment Racks
- Modify method for further size reduction
  - Flow Based vs. CO Based (NOx. SO2, CO)
- Demonstrate QA equivalency

TTP 1 Stock

TTP 1 Stock

TTP 1 Stock

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Reduction in Size – TTP 2

Method Modification – Flow based (TTP 3)

- Identical O_3 instrumentation to earlier TTP versions
- Identical Multi-blend gas generation as earlier TTP versions
- ***Audit Concentrations of NO_x, SO_2, and CO determined by flow measurement of GPT device at the time of the audit***

Method Modification – Flow based (TTP 3)

- Flow calibration of GPT device for Multi-blend gas audits
  - Eliminates need for CO analyzer
  - Eliminates need for 3 cylinders to calibrate CO device
  - Eliminates need for 3.5 hour CO analyzer warmup
  - Eliminates need for 2nd rack
  - Eliminates need for a big truck – cargo van is suitable
  - ***Requires supplemental QA for flow measurement***

Flow based (TTP 3)

Flow based (TTP 3)

Flow based (TTP 3)

Flow based (TTP 3)

Flow based (TTP 3)

Flow based (TTP 3)

Flow based (TTP 3)

Overseas System

- Split the TTP 3 system rack into separate Pelican 1660 cases.

Required Documentation for Overseas Transport

- Carrier Airbill (Fed EX, etc.)
- Commercial Invoice
- Shipper's Export Declaration
- Dangerous Goods Declaration (for cylinders)

Quality Assurance for Flow Based Systems

- Flow measurement on day of audit w/ flow transfer standard
- Flow transfer standard verified quarterly against primary standard
- Annual certification of system against OAQPS Reference system (TTP 2 – CO based system)

Quality Assurance for Flow Based Systems

Quality Assurance for Flow Based Systems

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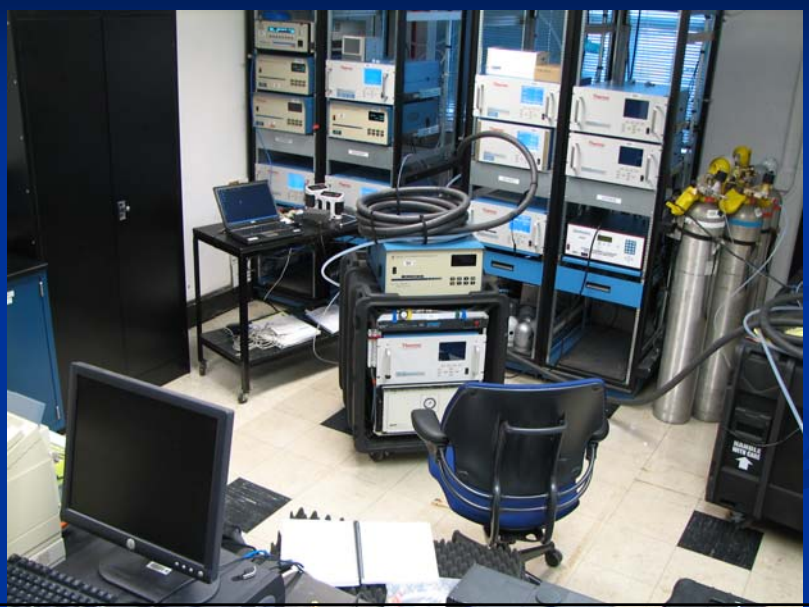
Quality Assurance for Flow Based Systems



EPA R2 TTP Systems

TTP 2

CO analyzer based

TTP 3

Flow based

Overseas

Flow based

TTP 2.0 RACK 2

NPAP Audits of Precursor Gas Analyzers

Mobile NPAP TTP Labs for Precursor Gas Audits Based in East(RTP,NC) and West(LV,NV)

Why NCORE

- Why- To help fill in the gaps of information that the current Networks do not provide to modelers and others, in space (rural, remote, urban upwind areas, etc)
- Why-To fill in gaps of knowledge due to the lower limits of the currently deployed analyzers, especially in rural, remote, or upwind urban areas

Relating NCore Monitoring System Objectives to other Ambient Networks

Objective	Monitor Types	Example Analyses/Rationale
Public reporting (continuous $PM_{2.5}$ and ozone)	Local sites (primary) NCore sites (secondary)	direct reporting through AIRNow and AIRNowTech
Emission strategy development (trace gases, $PM_{2.5}$ speciation, VOCs*)	NCore sites (primary)	model evaluation, source apportionment and other observational models
Assessing effectiveness of emission reductions and AQ trends (trace gases, $PM_{2.5}$ speciation, VOCs*)	NCore sites (primary) Local sites (secondary)	time series comparisons to emissions projections
Support health assessments and NAAQS reviews (trace gases, O_3, $PM_{2.5}$ and $PM_{10-2.5}$ (mass and species))	NCore sites (primary) Research and local sites (secondary)	ambient input to exposure models; direct association analyses
Compliance (NAAQS comparisons) ($PM_{2.5}$ and O_3)	Local sites (primary) NCore sites (secondary)	point and spatial field comparisons to NAAQS
Science support (all pollutants)	Research sites (primary) NCore sites (secondary)	methods evaluation, size distribution analyses, diagnostic analysis (model processes, particle formation)
Ecosystem assessment (NO_y, HNO_3*, NH_3*, O_3)	NCore sites	mass balance analysis, deposition calculations

* Not required in NCore regulation

Other Aspects of NCore Network Requirements

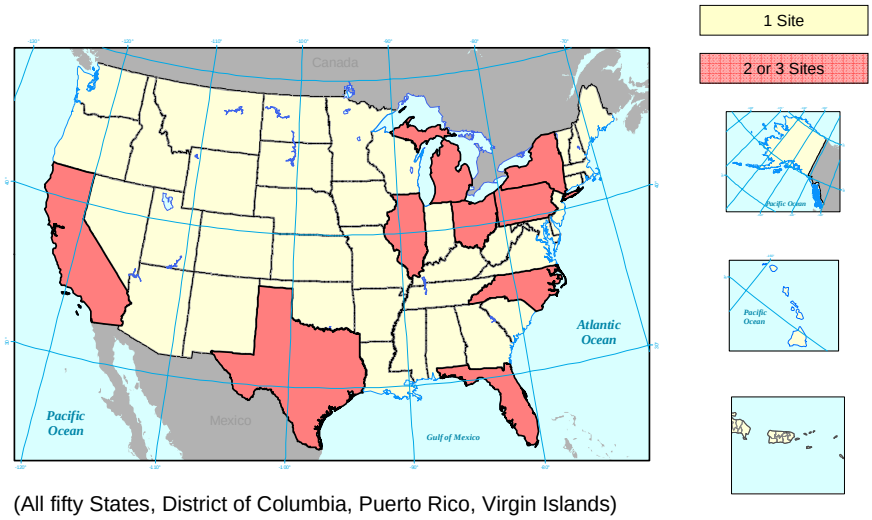
- Between 62 and 71 stations must be operational by **January 1, 2011**.
  - NCore monitoring plan due **July 1, 2009** as part of annual monitoring network plan. Items that can be negotiated:
    - Selection of two versus three stations in listed States.
    - Delegation of required sites between State and local agencies.
    - Operation of additional sites by States, local agencies, and/or Tribes.
    - Urban versus rural locations.
    - NOy and meteorological measurements (more later).
  - NCore sites are approved at Administrator level.
- Ultimate size of deployed network:~75 stations.

NCore Parameter Requirements

Measurements	Comments
$PM_{2.5}$ FRM mass	typically 24 hr. average every 3rd day
$PM_{2.5}$ speciation	Organic and elemental carbon, major ions and trace metals (24 hour average; every 3rd day)
$PM_{10-2.5}$ FRM mass	typically 24 hr. average every 3rd day
$PM_{10-2.5}$ speciation	typically 24 hr. average every 3rd day Species and analyses to be determined
continuous $PM_{2.5}$ mass	1 hour reporting interval
ozone (O_3)	all gases through continuous monitors
carbon monoxide (CO)	capable of trace levels (low ppb and below) where needed
sulfur dioxide (SO_2)	capable of trace levels (low ppb and below) where needed
nitrogen oxide (NO)	capable of trace levels (low ppb and below) where needed
total reactive nitrogen (NO_y)[1]	capable of trace levels (low ppb and below) where needed
surface meteorology[2]	wind speed and direction, temperature, relative humidity Not required but desirable: precipitation, solar radiation

[1] In areas with negligible expected difference between NOy and NOx measured concentrations, the Administrator may allow for waivers that permit NOx monitoring to be substituted for the required NOy monitoring at applicable NCore sites.
[2] The requirement for meteorological monitoring can be waived by the Administrator if the NCore site is not suitable for representative meteorological measurements due to the site's physical surroundings and it is possible for nearby meteorological measurements to fulfill this data requirement.

Minimum NCore Network Requirements



(All fifty States, District of Columbia, Puerto Rico, Virgin Islands)

Location Of Candidate Precursor Gas Sites-Where They May Be

Home Bases & Shared Locations of 2007 NPAP TTP Systems

- Region 1: Was From Region 2: Will be from Region 1;
- Region 2:Case-Based; Edison, NJ
- Region 3: Region 2's
- Region 4:Truck-Mounted; Athens, GA
- Region 5:Trailer-Mounted; Chicago, IL
- Region 6: Trailer Mounted; Houston,TX
- Region 7: Truck – Mounted; Kansas City
- Region 8:Region 7's
- Region 9: Trailer Mounted; Adding Case-Mounted; Richmond, CA
- Region 10: Region 9's

2008 Additions

- 2 Trailers have been equipped with Precursor (Trace Level) Gas(PG) Analyzers (trace level for CO and SO2; & NOy) and standards calibration gas Cylinders
- They also have the standard NPAP TTP mobile lab equipment and features for generation, analysis, & delivery to a sample station inlet; and data handling collection, processing and reporting
- One is in RTP, NC; one is in Las Vegas, NV

Exterior Views(Note Sampling Station);Interior Views

Hose Reel(L); Instrument Racks Showing 2 Manifolds & Flow Path Controls

Status of NPAP TTP PG System

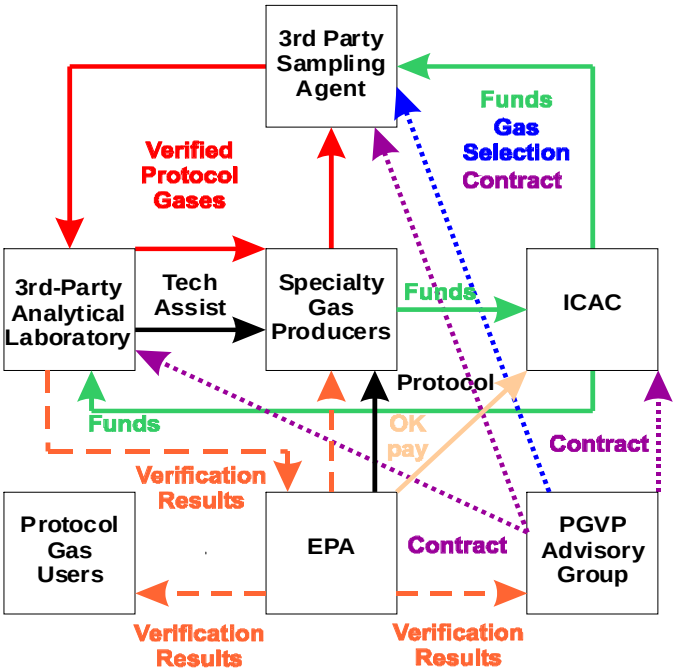
- Being Tested now in RTP
- Tested 1st in Lab E462A in 2007, now at Trailer at Burden's Creek; then Audit PG monitors at Burden's Creek Station(05/08)
- Just received Climatronix Sonic WS/WD in RTP; ozone will be added in May to both
- SOP additions to NPAP TTP SOP for PG
- Transport to Regions with Established PG Sites

Planned Usage

- Plans are to use these Mobile labs for training, auditing, and, if need be, sampling.
- The east and western systems will be used to audit SL&Ts nearby and then further in each area of the country, as Regional & national priorities and logistics dictate

Protocol Gas Verification Program

Progress or lack there of

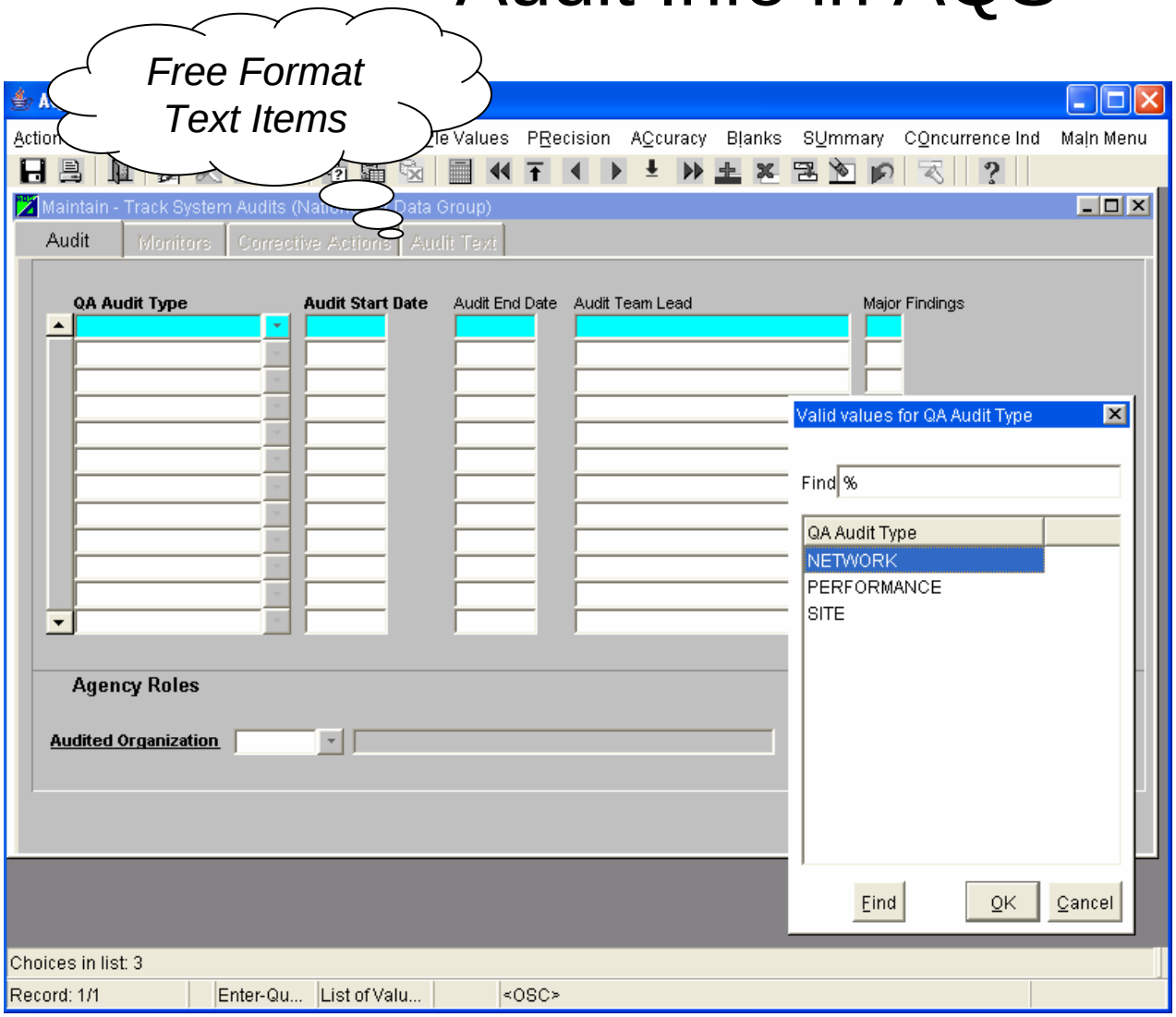


Another Option ?

- Make the program an appropriate parallel to the SRP program for ozone traceability to NIST
- Goal
  - Try to test cylinders from as many vendors as possible each year or
  - Use process as a trouble shooting process
- EPA buys SRMs, or equivalent and runs check to ensure/establish concentration.
- Base the cylinder sets in the 10 Regions.
- NAACA polls monitoring organizations to identify those planning on purchasing standards in the year.
  - Info collected- vendor/ concentration
- EPA takes list and solicits monitoring organizations for participation in verification
- EPA sends SRMs (or equivalent) to monitoring organizations. Monitoring orgs run verification, provide results to EPA and return SRM cylinder
- EPA checks SRM (as appropriate) before shipping to next monitoring org.
- EPA collects and posts test results each year.
- Funding options ????:

AQS Audit Tracking 9:20-9:40 Session 4/23/2008

Audit Info in AQS



QA Handbook Review 2:45- 3:30 Session 4/23/2008

QA Handbook Evaluations
Comments

- Thanks QA Strategy Workgroup
- I'll be reviewing Notes one more time
- Heavy into URL through footnotes
  - It's a PDF issue
- Hopefully updated with current jargon
- Removed high volume PVC laminar inlets
- Removed zero/span calibration 1 and 2
  - Calibration section needs work
- New Attachments
  - Monitoring Program Fact Sheets –loaded with URL
  - QA Info attachment (copies available)
  - Color validation templates
- Initial Draft Review by May 30, 2008

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QA Handbook - So

- What need to be addressed?
  - Something not right
  - Gaps
- Let's get validation template done
- Calibration section
  - Who wants to help?

SRP and Traceability Nomenclature 3:30 – 4:00 Session 4/23/2008

EPA O3/Flow standard Requirment Terms & Associated Equipment Issues

Primary, Traceable, or Comparable: Is It a Political Election or a Reliable, Accurate Comparison?

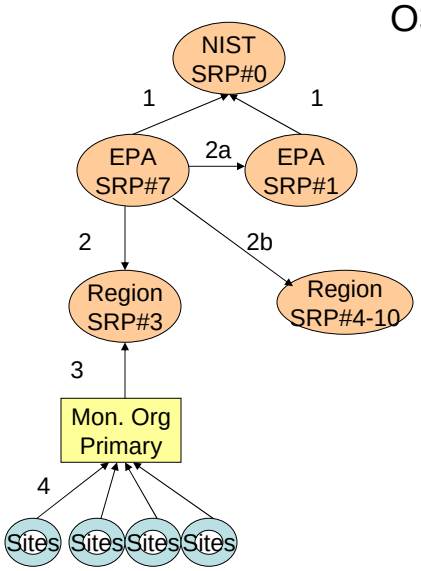
Air QA Workgroup, April 24 2008

New Equipment, Old Terms

- BIOS is selling their ML-800 as NIST-Traceable Primary Standard
- My info about cost is as much as ~$30K up front, and $3-4K a year for the NIST-Traceable recertification
- EPA definitions for primary and transfer standard come from 1979 Ozone standard certification guidance

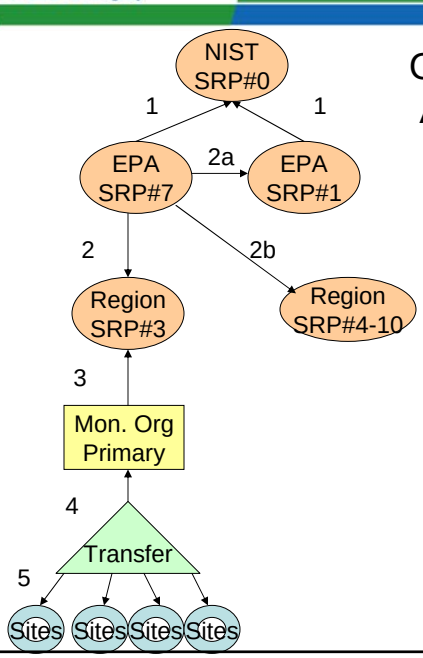
4

O3 Traceability Scenario #1 Preferred

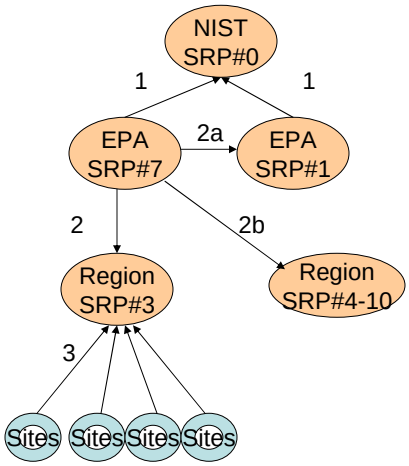


1. EPA SRP 7(& 1?) certified at NIST each year
   - SRP #7 travels to Regions
   - SRP # 1 stays home
2. SRP # 7 certifies Regional SRPs
   - a- Upon completion of one audit SRP #7 gets verified by SRP #1
   - B- before going to next Region
3. Mon. Org. bring it's **local primary standard (LPS)** to Region SRP
   - LPS stays at lab
4. Mon. Org. brings **working standard** to lab to verify against **LPS**

O3 Traceability Scenario #2 Acceptable – not preferred



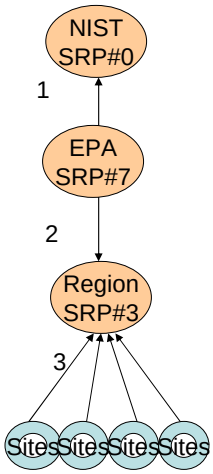
1. EPA SRP 7 (& 1?) certified at NIST each year
   - SRP #7 travels to Regions
   - SRP #1 stays home
2. SRP # 7 certifies Regional SRPs
   - a- Upon completion of 1-? Audits, SRP #7 gets verified by SRP #1
   - B- before going to next Region
3. Mon. Org. bring it's **local primary standard (LPS)** to Region SRP
   - LPS stays at lab
4. Mon. Org. brings **transfer standard (TS)** in to certify against LPS and then takes TS to site
5. TS certifies sites **working standard**



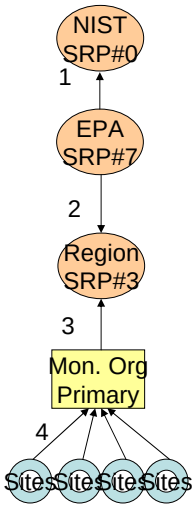
O3 Traceability Scenario #3
Best but usually not feasible
Small Organizations ?

1. EPA SRP 7 (& 1?) certified at NIST each year
   - SRP #7 travels to Regions
   - SRP # 1 stays home
2. SRP # 7 certifies Regional SRPs
   - a- Upon completion of one audit SRP #7 gets verified by SRP #1
   - b - before going to next Region
3. Mon. Org. bring it's standards at site to Region SRP
   - Each site has a **local primary standard (LPS)**

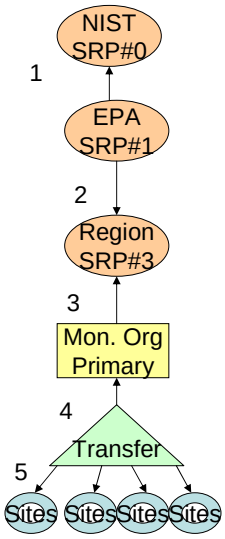
Best
(may not be practicable)



Good



Acceptable
(the limit)



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Buy High or Clarify Requirements?

- Terminology Issue: primary-no calibration needed to determine value; or, compared directly to NIST; transfer-need to calibrate; not compared directly to NIST- 1 +? steps
- Should Cert. include adjustment (Region 5?)
- Cost Issues: Are there are reliable, accurate flow standards devices that are cheaper; c*ert of SRP#1 would cost $3k more/yr; verification of SRP #7 would cost more time /fewer Regional Certs/yr*
- Technology Issue: piston (ML-800) vs orifice (Dry CAL, TriCal, MolBloc, etc)

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Changes to Consider

- Cert SRP#1vs NIST, not SRP#7;verify SRP#7 vs SRP#1, 1-?x/yr (use data of Regions to choose)
- Procedures: NIST certifies flow stds. using a tandem comparison design that controls for effects due to test level order and power status(on\off).
- Per Test-Do more than once, varying flow levels (Lo, med, hi), and turning on and off and on, and preferably over more than one day.
- Who-All agencies
- What- Performing flow standard certification
- A Region 5 state wants to make physical adjustments at the end of the SRP certification of their O3 standards

10

Proposal for Discussion on Frequency

- 1. Primary "Bench" flow, temperature, pressure standard certified NIST traceable annually.
- 2. Compare Field (Travel) standards against primary "bench" standard annually. [We could pose this as one option among other frequencies such as semiannual or quarterly given the biweekly calibration of ozone span/zeros as a basis]
- 3. Submit Field standards to manufacturer every three years for refurbishment and NIST certification.

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Technology Tradeoffs

- Piston type std.
  - Pros: values are based on “first principles”- linear dimension measurement, no calibration needed
  - Cons: erratic hang-ups in cold or dry &sandy conditions

Technology Tradeoffs (cont'd)

- Orifice–type Stds
  - Pros: not prone to erratic values, due to physical conditions; easier top spot & correct any problems
  - Cons: values are not based on "first principles"- calibration needed, based on a better, Primary std., for which values are based on direct, 1st principle parameters

QA Issues with Precursor Gas Sites 4:00- 4:20 Session 4/23/2008

DQO for Precursor Gas Parameters

•AAMG staff began the DQO process in 2006

•Wanted to ascertain the day to day and annual variability using Simulation Models

•Compare those results against 1-pt QC checks from different stations with Trace Level Instruments

Precision and Bias for PG Instruments

Carbon Monoxide

Site	Instrument Type	Coefficient of Variance	Bias
Burden's Creek	API 300 EU	6.9	+9.4
Burden's Creek	TEI 48C-TLE	5.8	+/-5.4
Garinger HS	API 300 EU	5.3	+5.8
Cheeka Peak	API 300 EU	17.5	+/- 11.3
Hamilton Co.	Ecotech 9830 T	14.1	+/- 10.1
Cumulative (n = 1223)		**12.6**	**+/-8.6**

NOy

Site	Instrument Type	Coefficient of Variance	Bias
Burden's Creek	API 200 AU/501Y	3.3	-5.7
Cheeka Peak	TEI 42 CY	10.1	+/- 7.7
Hamilton Co.	Ecotech 9841 NOy	10.0	+/-5.4
Cumulative (n = 828)		**8.5**	**-6.2**

SO2

Site	Instrument Type	Coefficient of Variance	Bias
Burden's Creek	TEI 43C TLE	3.6	+/-3.0
Garinger HS	TEI 43C TLE	3.4	+/-2.3
Cheeka Peak	TEI 43C TLE	3.6	+/- 2.8
Hamilton Co.	Ecotech 9850 T	12.3	+/-6.7
Cumulative (n = 1023)		**6.5**	**+/-3.6**

DQO for Precursor Gas Parameters

From the modeling and Precision and Bias information we propose these Measurement Quality Objectives:

In order to detect annual trends of 5 percent or greater across the 75 station NCore network, the SO2 and NOY instruments should maintain the coefficient of variance (CV) at < 10%, bias at +/- 10% and annual data completeness of > 90%.

In order to detect annual trends of 5 percent or greater across the 75 station NCore network, the CO instruments should maintain a CV at < 15%, bias at +/- 10% and annual data completeness of > 90%.

<u>However, we realize 90% data capture is difficult, and we have set a minimum requirement of 75% data completeness</u>.

QA for Pb NAAQS 4:30-4:45 Session 4/23/2008

Pb NAAQS
Lots of Maybes

- Sampling Method
  - PM10- Lo- Vol
  - TSP – Hi-Vol
  - PM10-Lo-Vol "TSP-Like" (TSP-Factor)
- Sampling Frequency
  - If monthly NAAQS: 1-in-3 day sampling
  - If quarterly NAAQS: 1-in-6 day sampling
- Analytical Method (if Pb in PM10 only)
  - XRF
  - GFAA, ICP-MS that meet performance

Pb QA

- Flowrate (no change)
  - Verifications
    - TSP- Quarterly
    - PM10- Monthly
  - Audits both semiannual
- Pb Strips (no change in frequency)
  - Range 1 30-100% of Pb NAAQS
  - Range 2 200-300 of Pb NAAQS
- Collocation (no change)
  - Same 15% of each method designation 1-in-12 day
- PEP (new)
  - I PEP/ PQAO and
  - 1 collocated sample sent to independent lab
  - Total of 5 values per PQAO per year

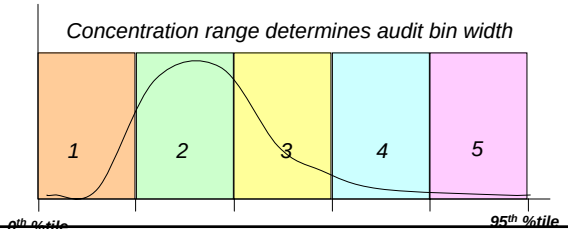
Summary and Status of Pb NAAQS Review

- Final Criteria Document - 10/06
- Final Staff Paper – 11/07
- Final Risk Assessment – 11/07
- ANPR signed – 12/07
- CASAC Review – 12/07
- Court ordered deadline for proposed rule – 5/1/08
- Court ordered deadline for final rule – 9/1/08

Gaseous Audit Levels- guidance and new proposal 4:45-5:00 Session 4/23/2008

Another Way of Choosing an Audit Limit

- Each year (or appropriate period of time) assess concentrations for either
  - each site within a PQAO (Primary Quality Assurance Organization)
  - all sites within a PQAO (urban/rural split ??)
- Find 0-95% concentration range (95th %tile – 0th %tile)
  - Removes potential outliers
- Divide the range by 5 to create 5 evenly spaced concentration bins within this range
- At minimum, select the 3 bins which contain the highest amount of data (generally will be bins 1-3 or 2-4).
- AMP 255 report could be modified to determine whether these audit concentrations were selected correctly.
- CFR would not have to post ranges.



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PAMS P & A Reporting 5:00-5:15 Session 4/23/2008

PAMS P&A Reporting

- Started from 2006 data certification memo
  - Required certification of PAMS
  - Including 240 Report (P&A) ???
- Well….
  - No P&A data has been required to be reported for PAMS
  - Region 1 looking into some consistent reporting requirements
  - CT proposal
    - Precision- subset of GC autocals (every 6th day autocal)
    - Accuracy- “High calibrations” (1/month)

The Workgroup did not get to this discussion

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SO…PAMS P&A

- Do monitoring organizations support some consistent reporting of PAMS QA data to AQS?
  - We are talking about 100 sites and ~10 States
- How do we enforce?
  - Regulation
  - In the grant
  - Guidance
  - Other?

Wish List and Priorities 5:15 - end Session 4/23/2008

Wish list Review and this years QA Priorities

- We can only do so much (little)
- What is most needed