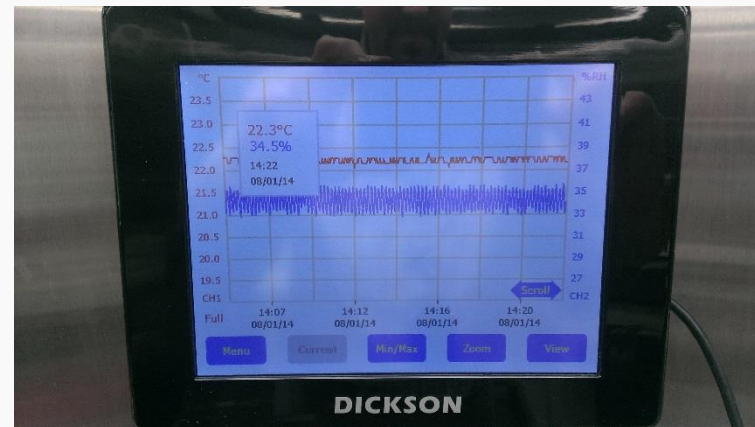


QA 101: PM QA Requirements





- ***ID important Regs and Guidance that pertain to QA***
 - ✓ ***Network***
 - ✓ ***Site & Sampler***
 - ✓ ***Lab***
 - ✓ ***Data Management***
 - ▣ ***Recent CFR Reg Changes will be marked like this***
- ***Spend some time looking at some of the QA elements that can help you assess and optimize network data quality***



What do I Need to “Get” from the PM QA 101 Session?

- 1. Understand Data Quality Objectives and Measurement Quality Objectives for $PM_{2.5}$ and PM_{10} monitoring***
- 2. Understand the measurements that are made to quantify or otherwise gauge our achievement of these objectives***
- 3. Understand what the results of the measurements or assessments tell me about my sites, my lab, my network and my monitoring data***

Reg Requirements



40 CFR Part 50 FRMs— samplers and labs

- a. Appendix B: Hi volume samplers
- b. Appendix J: PM_{10}
- c. Appendix L: $PM_{2.5}$ & PM_{10} (Low volume)

40 CFR Part 53 FEMs— samplers and labs

- a. FEM performance specifications;
- b. Testing requirements, and
- c. Approval designations

Reg Requirements Cont.



40 CFR Part 58

- ❑ ***Appendix A: QA for NAAQS pollutants***
- ❑ ***Appendix B (re-created): QA for PSD monitoring***
- **Appendix C: Monitoring Methodology; ARM alternatives to FRM/FEM; exceptions and waivers**

More Reg Requirements??



40 CFR Part 58

- **Appendix D Network Design:**
 - a. **Monitoring objectives**
 - b. **Network Scale Objectives (pollutant specific)**
 - i. **Microscale**
 - ii. **Middle Scale**
 - iii. **Neighborhood**
 - iv. **Urban**
 - v. **Regional**
 - c. **Site Classifications based on data usage, e.g., SLAMS, N CORE**

*Criteria
Established by
Monitoring Plan
and QAPP*

And More Reg Requirements!!!



40 CFR Part 58

Appendix E: Monitoring Path Siting Criteria for Ambient Air Quality Monitoring

- ▶ Horizontal and Vertical Placement of inlets
- ▶ Spacing from Minor Sources.
- ▶ Spacing From Obstructions.
- ▶ Spacing From Trees
- ▶ Spacing From Roadways.

Speaker Notes



Slide 7 All these are important Quality factors, which should be used whenever you are assessing site capability. Some are again very important to clean air demonstrations. For example, overgrown trees and construction of large buildings subsequent to the initial start-up of the samplers could end up invalidating entire years worth of data. TSAs are designed to identify these kinds of issues before they become critical. Horizontal and vertical placement of monitor inlets is very important in designing sites to enable QA assessments. Note the April 2016 provides opportunity for more flexibility with the advent of the FEMs. The Appendix A discussion will have more to say about inlet positions.

The next couple of slides illustrate some typical findings during TSAs at some sites. Slide 9 Inlet to close to Parapet, but new regs allow for a waiver. Even if the TSP sampler on the right is a Pb sampler. This source could create enough soot on the filter in some instances to dramatically affect the flow rate and created error in the calculated concentration

Slide 10 On the left there is much to much shrubbery and growth. It will continue to get worse unless it is cleared. The deck on the right takes near road sampling to a new level. It may still be ok if the vehicles per day count is below the threshold.

Part 58 Appx E Siting Requirements



BEFORE: Inlet height less than 1 meter from parapet

Courtesy of Laura Niles, CARB



Source too close to TSP Sampler

Courtesy of Richard Guillot, EPA Region 4

Part 58 Appx E Siting Requirements



Courtesy of Thien Bui, EPA Region 8



Courtesy of Florida DEP

Then there's Guidance!!



- Guidance Referenced by Regs
 1. QA Handbook Volume II, Appendix D is the “Rosetta Stone” for QA measurement requirements.
 - a. <https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf> and
 - b. <https://www3.epa.gov/ttn/amtic/pmqa.html>
 2. Quality Assurance Guidance Document 2.12: Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods
<https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212.pdf>
 3. Document 2.11 covers PM₁₀ (1990 !!)

Notes on Guidance



Slide 11 Ya gotta know how to get to these documents,--especially 1 & 2. Notice AMTIC is in the URL. The great thing about the templates is that they are 1-stop shopping for DQOs MQOs and other critical criteria. The current validation tables in the Vol II URL (1.a.) contains the PM 10 requirements. The second URL (1.b.) is a recent update to the PM2.5 validation template. Document 2.12 was revised earlier this year. Notice that the PM-10 guidance (document 2.11) is very dated. The entire Vol. II and the complete template are currently undergoing review and revision by the EPA Regional and SLT QA workgroup. It will incorporated the recent changes to PM2.5. A schedule has not been set to revise Document 2.11. By the way, this entire unabridged presentation will be in the national ambient air monitoring conference compendium---on AMTIC.



Assessing Your Network Performance

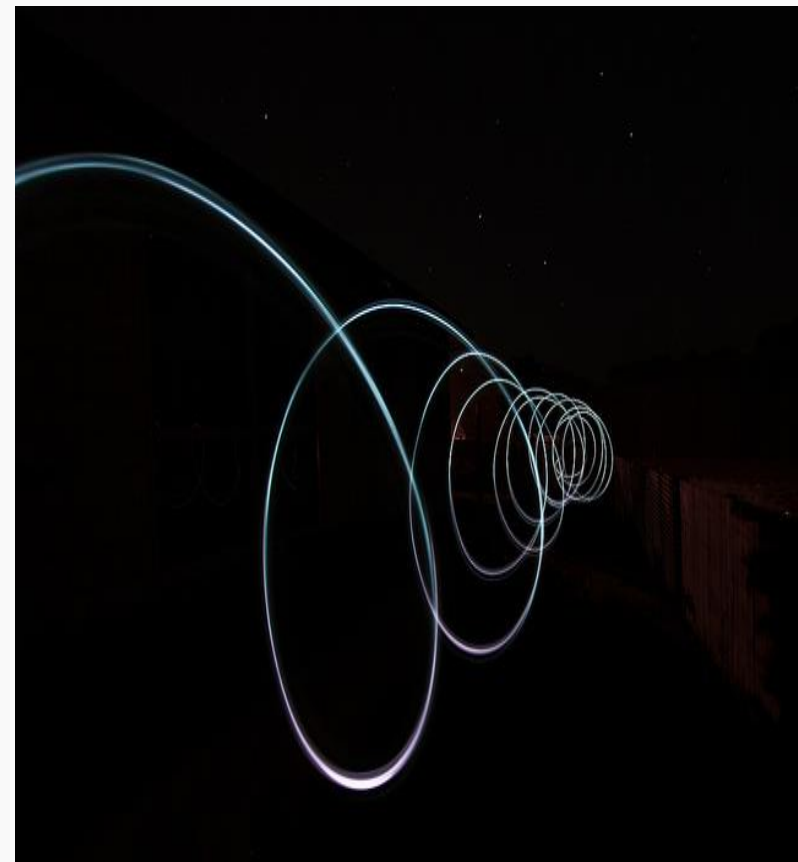
- 1. Assessing Monitor Performance**
 - a. NIST traceable Standards**
 - b. Flow rate verifications**
 - c. Flow rate audits**
- 2. Network: Data Quality Objectives:**
 - a. Collocation and Precision measurements, then**
 - b. Bias**
- 3. Laboratory QA/QC elements**
 - a. Environmental Conditions**
 - b. Analytical Equipment**
 - c. Routine QC Data Acquisition**

NIST-Traceable Reference Standards



❖ **40 CFR Part 58, Appendix A Sections 3.2.1, 3.2.2, 3.3.1 and 3.3.3: Flow rate standards must be NIST-traceable**

"Traceable" is defined in 40 CFR Parts 50 and 58 as meaning that "a local [field or transfer] standard has been compared and certified either directly [with] or via not more than one intermediate standard [one level from], [to] a primary standard such as a National Bureau of Standards Standard Reference Material (NBS SRM), or a USEPA/NBS-approved Certified Reference Material (CRM)."



NIST-Traceable Reference Standards



- ***40 CFR Part 50, Appendix L Sec 9.1 & 9.2***
- ***Verification, calibration and audit (“working”) standards should be “re-calibrated or re-verified at least annually”***
- ***Traceable to a NIST “Primary Standard”***

What if I cannot send my $6 \pm$ working standards to an independent Metrology Lab?

NIST-Traceable Reference Standards



At a minimum, the “certification procedure” for a working (or “transfer”) standard should:

- Find a NIST Traceable Primary standard—the Region, your own lab, a corporate lab
- Establish the parametric range of the working standard relative to the primary (Stationary Bench) standard;
- Certify that the primary standard (and hence the working standard) is traceable to a NIST primary standard; (It should have a certificate!)
- Include a test of the stability of the working standard over several days and test repetitions; and
- Specify a recertification interval (i.e. 365 days) for the working standard
- All this should be in an SOP and your QAPP!

Summary of Standard Certifications



Field Activities

Verification/Calibration Standards Recertifications – All standards should have multi-point certifications against [NIST Traceable](#) standards

Flow Rate Transfer Std.	every 365 days and once a calendar year	$< \pm 2.1\%$ of NIST Traceable Std.	1) 40 CFR Part 50, App.L Sec 9.1 & 9.2 2) Method 2-12 Section 4.2.2 & 6.4.3 3) 40 CFR Part 50, App.L Sec 9.1 & 9.2
Field Thermometer	every 365 days and once a calendar year	$\pm 0.1^\circ$ C resolution, $\pm 0.5^\circ$ C accuracy	1, 2 and 3) Method 2.12 Sec 4.2.2
Field Barometer	every 365 days and once a calendar year	± 1 mm Hg resolution, ± 5 mm Hg accuracy	1, 2 and 3) Method 2.12 Sec 4.2.2
Clock/timer Verification	Every 30 days	1 min/mo	1 and 2) Method 2.12 Sec 4.2.1 3) 40 CFR Part 50, App.L Sec 7.4.12

Laboratory Activities

Microbalance Readability	at purchase	1 μ g	1, 2 and 3) 40 CFR Part 50, App.L Sec 8.1
Microbalance Repeatability	every 365 days and once a calendar year	1 μ g	1) Method 2.12 Sec 4.3.6 2) Recommendation 3) Method 2.12 Sec 4.3.6
Primary Mass. Verification/Calibration Standards Recertifications Working Mass Standards	every 365 days and once a calendar year	0.025 mg	1, 2 and 3) Method 2.12 Sec 4.3.7

Comment #1

The associated leak test procedure shall require that for successful passage of this test, the difference between the two pressure measurements shall not be greater than the number of mm of Hg specified for the sampler by the manufacturer, based on the actual internal volume of the sampler, that indicates a leak of less than 80 mL/min.

For Hi Vol PM-10

Verification/Calibration Standards and Recertifications - All standards should have multi-point certifications against NIST Traceable standards			
Flow Rate Transfer Std.	1/yr	$\pm 2\%$ of NIST-traceable Std.	1,2 and 3) 40 CFR Part 50 App J sec 7.3
Field Thermometer	1/yr	$\pm 0.1^\circ$ C resolution, $\pm 0.1^\circ$ C accuracy	1,2 and 3) Method 2.10 section 1.1.2
Field Barometer	1/yr	± 1 mm Hg resolution, ± 5 mm Hg accuracy	1,2 and 3) Method 2.10 section 1.1.2
Clock/timer Verification	1/6 mo	15 min/day	1,2 and 3) Method 2.10 sec 9

PM Flow Rate Verification and Audit Frequency



- **Verifications**
 - i. **PM_{2.5} & LoVol PM₁₀-Monthly (◆ minimum 14 days apart)**
 - ii. **HiVol PM₁₀ -Quarterly**
 - iii. **Look at Avg Flow CV for each event**
- **◆ Report PM_{2.5} and PM₁₀ Verifications to AQS!!**
- **Flow Audits 2X+ per year**
 - ★ **By “Independent Auditors” or at least with independent, NIST-traceable standards**
 - ◆ **5 to 7 months apart**



A tribute to George Froelich

◆ **40 CFR Part 58 appendix A Sections 3.2.1, 3.2.2, 3.3.1 and 3.3.3**

PM Flow Rate Verification and Audit Criteria



1) Criteria (PM _{2.5} LC)	2) Frequency	3) Acceptable Range	Information /Action
CRITICAL CRITERIA- PM_{2.5} Filter Based Local Conditions			
Field Activities			
<i>Sampler/Monitor</i>	NA	<i>Meets requirements listed in FRM/FEM/ARM designation</i>	1) 40 CFR Part 58 App C Section 2.1 2) NA 3) 40 CFR Part 53 & FRM/FEM method list
<i>Pre-sampling</i>	<i>all filters</i>	<i>< 30 days before sampling</i>	1,2 and 3) 40 CFR Part 50, App L Sec 8.3.5
<i>Sample Recovery</i>	<i>all filters</i>	<i>≤ 7 days 9 hours from sample end date</i>	1,2 and 3) 40 CFR Part 50, App. L 10.10
<i>Sampling Period (including multiple power failures)</i>	<i>all filters</i>	<i>1380-1500 minutes, or if value < 1380 and exceedance of NAAQS ^{1/} midnight to midnight local standard time</i>	1, 2 and 3) 40 CFR Part 50 App L Sec 3.3 and 40 CFR Part 50 App N section 1 for the midnight to midnight local standard time requirement See details if less than 1380 min sampled
Sampling Instrument			
<i>Average Flow Rate</i>	<i>every 24 hours of op</i>	<i>average within 5% of 16.67 liters/minute</i>	1, 2 and 3) Part 50 App L Sec 7.4.3.1
<i>Variability in Flow Rate</i>	<i>every 24 hours of op</i>	<i>CV ≤ 2%</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 7.4.3.2
<i>One-point Flow Rate Verification</i>	<i>every 30 days</i>	<i>< ± 4.1% of transfer standard < ± 5.1% of flow rate design value</i>	1, 2 and 3) 40 CFR Part 50, App. L, Sec 9.2.5 and 7.4.3.1 and 40 CFR Part 58, Appendix A Sec 3.2.1
<i>Design Flow Rate Adjustment</i>	<i>After multi-point calibration or verification</i>	<i>< ± 2.1% of design flow rate</i>	1,2 and 3) 40 CFR Part 50, App. L, Sec 9.2.6
<i>Individual Flow Rates</i>	<i>every 24 hours of op</i>	<i>no flow rate excursions > +5% for > 5 min. ^{1/}</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 7.4.3.1
<i>Filter Temp Sensor</i>	<i>every 24 hours of op</i>	<i>no excursions of > 5° C lasting longer than 30 min ^{1/}</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 7.4.11.4
<i>External Leak Check</i>	<i>Before each flow rate verification/calibration and before and after PM_{2.5} separator maintenance</i>	<i>< 80.1 mL/min (see comment #1)</i>	1) 40 CFR Part 50 App L , Sec 7.4.6.1 2) 40 CFR Part 50 App L Sect 9.2.3 and Method 2-12 Section 7.4.3 3) 40 CFR Part 50, App. L, Sec 7.4.6.1
<i>Internal Leak Check</i>	<i>If failure of external leak check</i>	<i>< 80.1 mL/min</i>	1) 40 CFR Part 50, App. L, Sec 7.4.6.2 2) Method 2-12 7.4.4 3) 40 CFR Part 50, App. L, Sec 7.4.6.2

PM Flow Rate Verifications and Audits



You might ask “Why are these important?”

- **In addition to detecting failures, indicates sources of bias or relatively inaccuracy—**

- ❑ ***Might actually save some data!!***
- ❑ ***The cut point of the PM separators (size of the particles collected) are dependent on the flow rate***
- ❑ ***The final concentration value derived from filter based measurement is mass gained on the filter divided by the sample volume, i.e., = mass / (24 hours X flow rate)***

Notes for Example on Slides 22 & 23



- **Keeping your flow rates within acceptance limits is crucial**, especially if ambient concentrations at the site in question might occasionally approach the standard. The reason is that the relationship between flow rate, cut-point of the PM separator are not linear. Outside of the flow rate acceptance limits of the FRM, the effects of PMcoarse (PM_{10-2.5}) can be counterintuitive.
- Let's use example the depicted on the VSCC Cyclone curve. Suppose your sampler is telling you the flow is 16.7 lpm but it is really 14.0 lpm. Under ordinary circumstances you would invalidate the data if you discovered this operational anomaly. Without an awareness of the anomalous flow rate an agency can be accepting data that is pretty far from reality and they could be drawing erroneous conclusions about the design value for the affected area. This particular cut point curve, happens to be for the MESA Lab's BGI PQ200 FRM Sampler with a VSCCB, but the principle would be true for all the VSCCs. Notice that at 14.0 lpm you are collecting some PM-3 and smaller. Suppose the lab measures 221.8 µg of PM mass collected on the filter. To actually estimate the real PM_{2.5} you would need to independently assess the mass of the PMcoarse fraction PM_{3-2.5} that is also collected by the sampler, i.e., fraction of the 221.8 µg PM mass that was collected. This would take some rather sophisticated and expensive non-FRM measurements.
- For illustration lets assume the concentration of PM_{3-2.5} is 4 µ/m³.
- If you do not account for the PM_{3-2.5}, you might simply correct for the flow rate with the second equation, which would push your apparent PM_{2.5} toward the annual NAAQS. However, if you know the real concentration of PM_{3-2.5}, which as assumed in this case, was 4 µ/m³, the last equation shows that the apparent PM_{2.5} concentration is significantly higher than the real concentration. In other words in this example, we significantly over estimated the PM_{2.5}.by nearly a factor of 2!!

PM Flow Rate Verifications and Audits

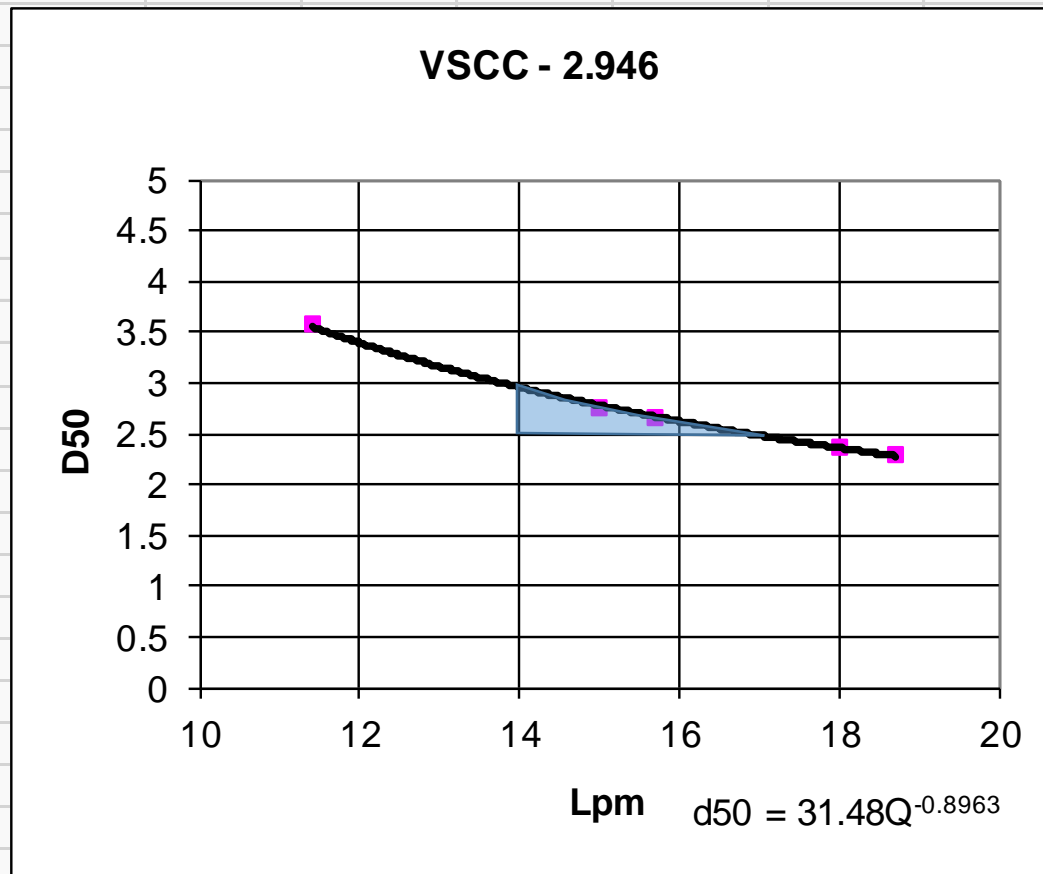


Effect of flow on cut point of particle size

Lpm	D50
2	19.768
4	10.057
6	6.773
8	5.116
10	4.116
12	3.446
14	2.965
16	2.603
18	2.32
20	2.094

Kenny Data	
18	2.36
15	2.758
11.4	3.57
15.7	2.66
18.7	2.295

Work Area	
Q	D50
45	1.04



D50= 2.50
Lpm= 16.67

PM Flow Rate Verifications and Audits



Effect of Flow on Concentration Value-a hypothetical case

Lab measures

$$C_{\text{ind}} = \frac{221.8 \mu/\text{filter} \times 1 \text{ filter/event} \times 1000 \text{ liters/m}^3}{\text{Sampler Reports} \rightarrow 16.7 \text{ liters/min} \times 60 \text{ min/hr} \times 24 \text{ hr/event}} = 9.2 \mu\text{g/m}^3$$

Flow standard Reports

$$C_{\text{app}} = \frac{221.8 \mu/\text{filter} \times 1 \text{ filter/event} \times 1000 \text{ liters/m}^3}{14.0 \text{ liters/min} \times 60 \text{ min/hr} \times 24 \text{ hr/event}} = 11.0 \mu\text{g/m}^3$$

But what if the concentration of $PM_{3-2.5}$ is $4 \mu\text{g/m}^3$ or $96.0 \mu\text{g}/\text{filter}$, as independently measured!! By having a real flow rate that is lower than what the sampler told you, your apparent concentration was nearly twice the real $PM_{2.5}$ Concentration!

$$C_{\text{real}} = \frac{C_{\text{app}} \times (221.8 - 96.0)}{221.8} = 6.3 \mu\text{g/m}^3$$

A couple more notes on flowrate verifications



Within flow rate acceptance limits of the ($FRM \pm 4\%$ of the design flow rate) the contribution of PM_{coarse} will be less dramatic, and in fact, maybe not distinguishable. In this case, as was also shown in the WINS study below. The loss of flow below the design value vs gain in extra mass above $PM_{2.5}$; or the loss of $PM_{2.5}$ when flow rate is above the design value vs increased flow volume times the $PM_{2.5}$ that is collected are considered to be offsetting factors

The Example in this presentation was based on a $PM_{2.5}$ sampler fitted with VSCC but the same principles is true for the WINS. In fact, there has been some research performed, early in the life of the network, on bias introduced by flow rates outside the design acceptance limits. The publication citation for this report is below.:

Robert W. Vanderpool, Thomas M. Peters, Sanjay Natarajan, Michael P. Tolocka , David B. Gemmill & Russell W. Wiener (2001) Sensitivity Analysis of the USEPA WINS $PM_{2.5}$ Separator, Aerosol Science and Technology, 34:5, 465-476, DOI: [10.1080/02786820120868](https://doi.org/10.1080/02786820120868)

The Bottom Line: Conduct your flow verifications and audits and report them AQS!!

Notes for PM Flow Rate Verifications and Audits



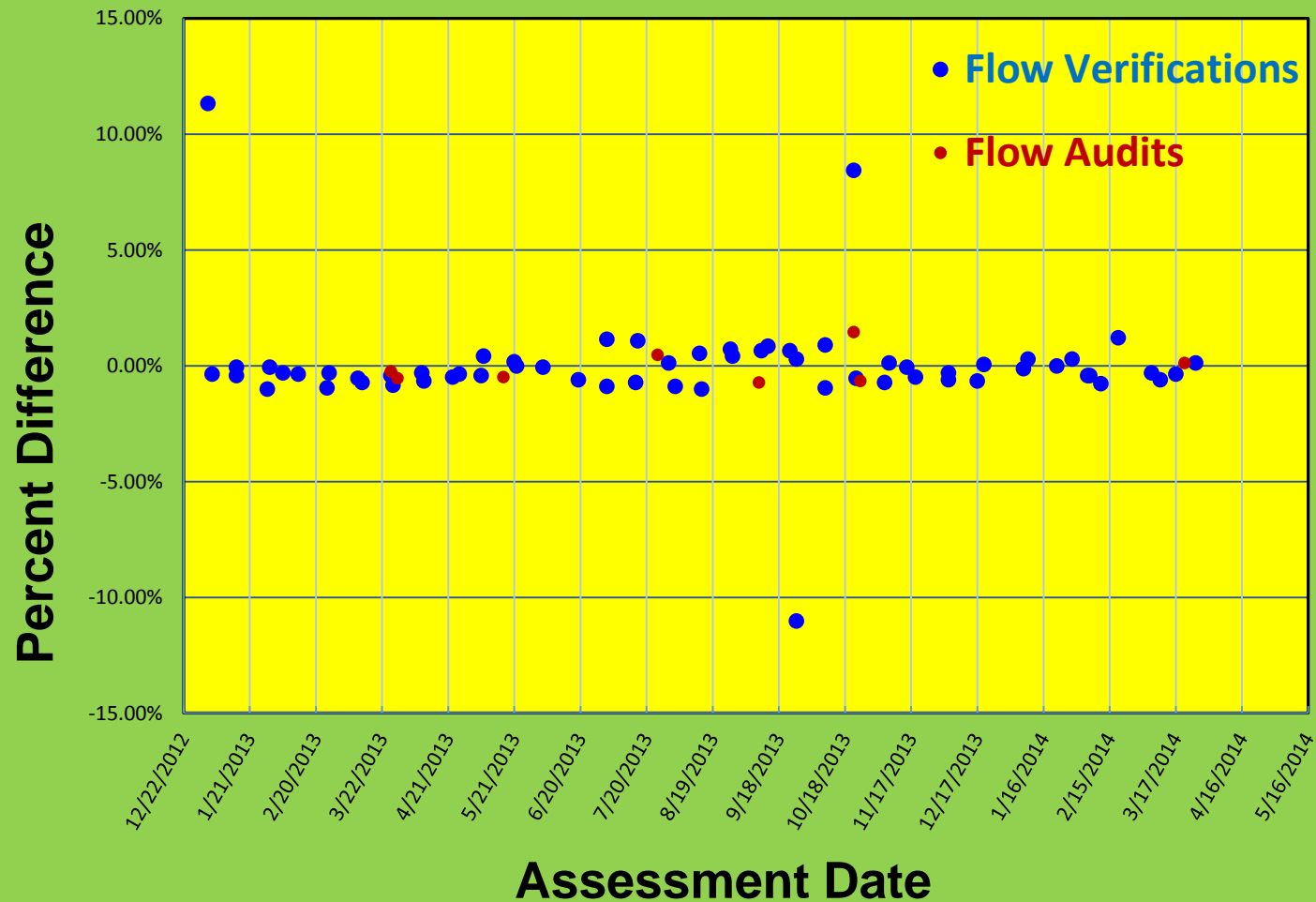
What are some cool and useful things you can do with verification data? What about a rather simple method of tracking sampler performance shown in the next slide(#26). Since audits occur only every 6 months if an audit reveals a malfunction, verifications can reveal how far the back the data must be rejected. In this example you can see it looks like corrections were made on the spot after verifications suggested the samplers went out of spec.

You can also use the event flow CVs (in the second slide #27) that are reported by the sampler to spot trouble and check out conditions before a crisis emerges. In this case the erratic behavior in several sampling events during September and October 2013 suggested someone should do a little trouble shooting—maybe the pump; maybe the power supply to the sampler.

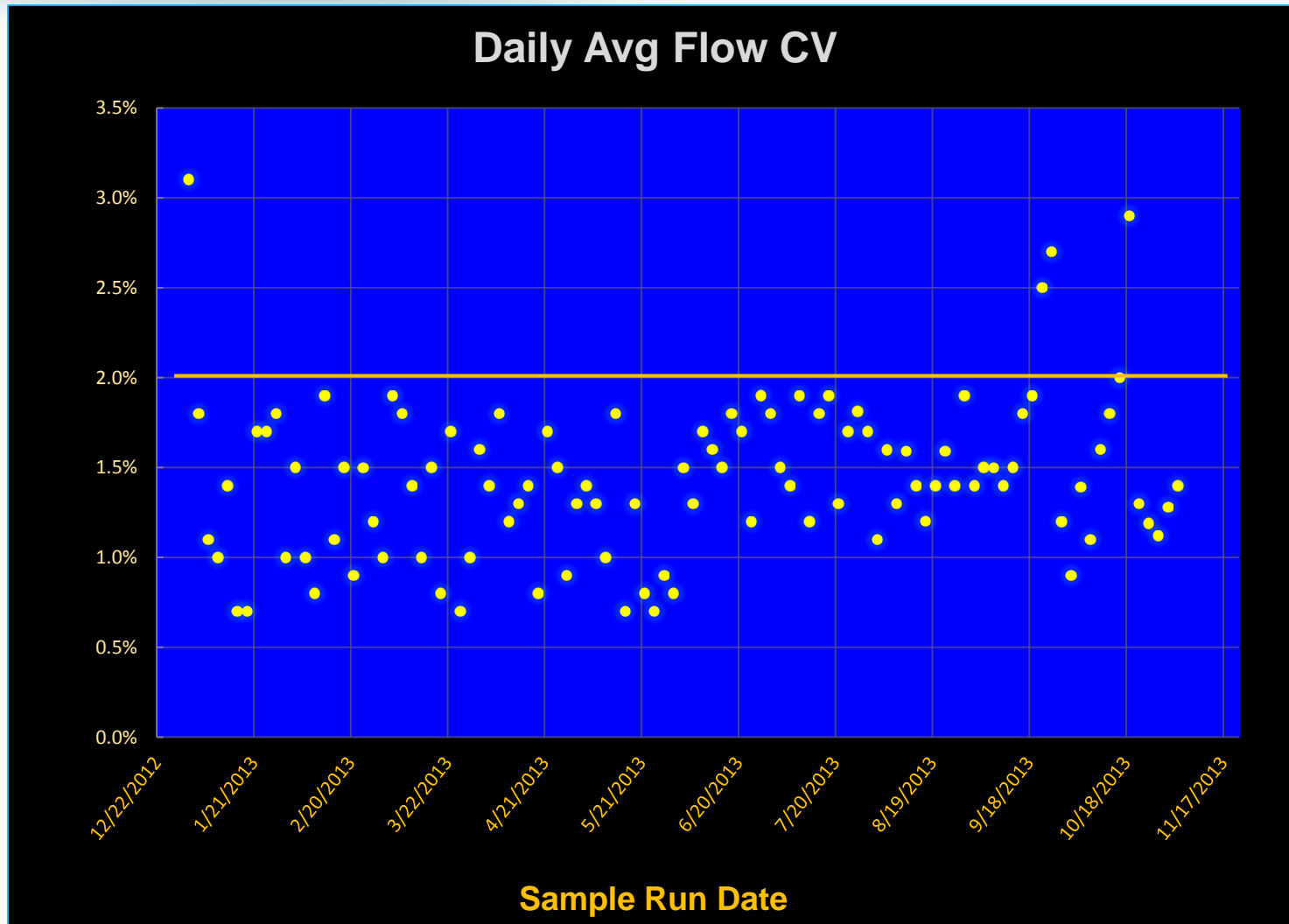
PM Flow Rate Verifications and Audits



Charting Sampler Performance



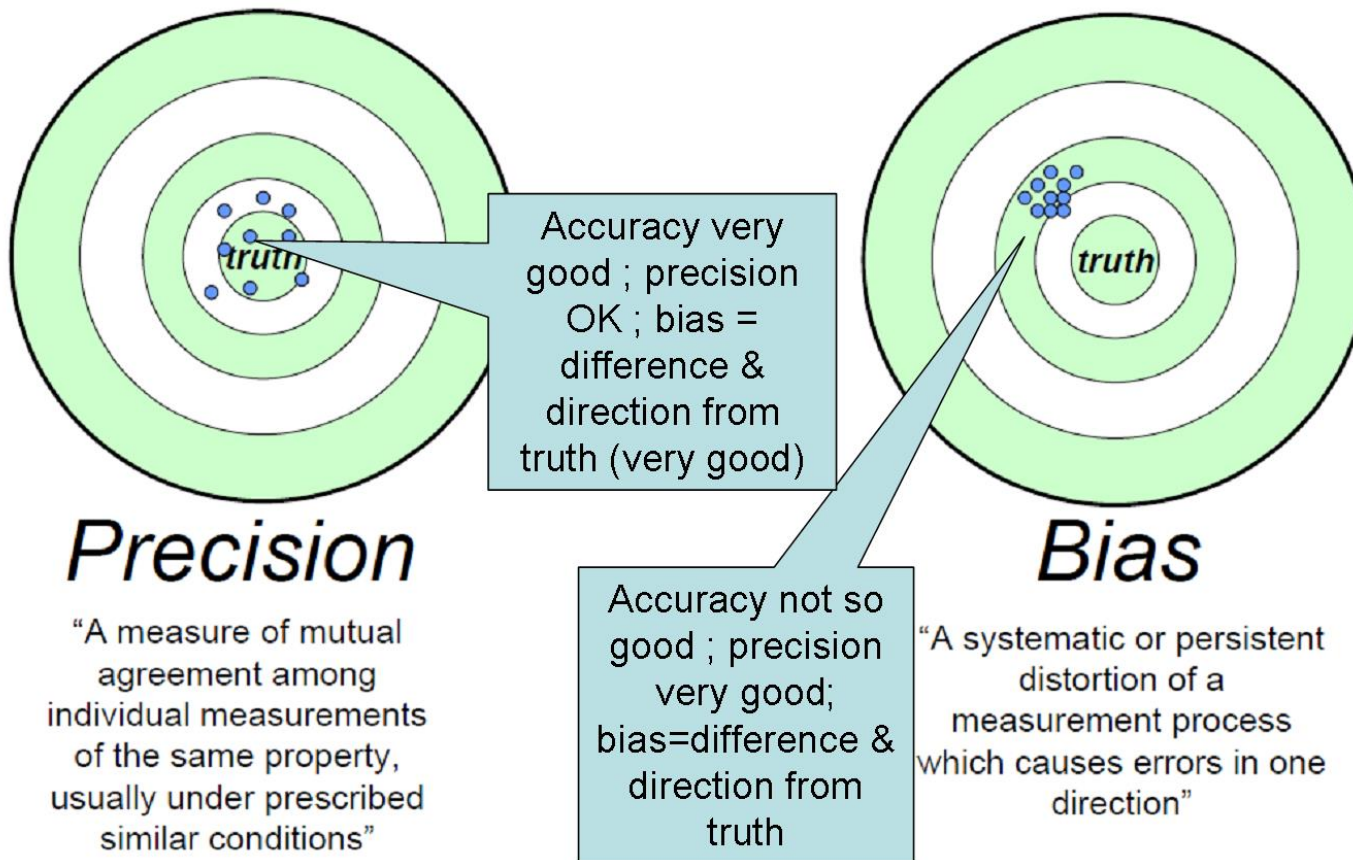
PM Flow Rate Verifications and Audits



Data Quality Objectives



What Are We Trying to Determine?



5

So How Should Your Network Perform?



Data Quality Objectives for $PM_{2.5}$

- ***40 CFR Part 58 Appendix A***

- 2.3.1.1 Measurement Uncertainty for Automated and Manual $PM_{2.5}$ Methods.

- ✓ 10 % CV for total precision, and

- ✓ ± 10 % difference for total bias.

➤ ***Aggregated over 3** year at the National level!***

So How Should Your Network Perform?



Wait a minute.....Data Quality Objectives for PM_{10} ... Are not in Appendix A !!



Ok; Where are they?

- Vol II Validation template
https://www3.epa.gov/ttn/amtic/files/ambien_t/pm25/qa/appd_validation_template_amtic.pdf, pages 33 and 39, respectively.
- <https://www3.epa.gov/ttnamti1/files/policy/pm10-low-vol.pdf>

So How Should Your Network Perform?



Data Quality Objectives for PM_{10} (per “Volume II” Validation template)

High volume

- ✓ Collocated Precision <10.1% CV for concentrations $\geq 15 \mu\text{g}/\text{m}^3$
- ✓ ***No independent Bias value for High-volume PM-10***

Low volume

- ✓ Same as $PM_{2.5}$ (per

➤ ***Aggregated over 3 years** at the National level!***

How do we get Precision and Bias data?



40 CFR Part 58 Appendix A

- **Precision is derived from Agency-owned and operated collocated samplers**
 - **$PM_{2.5}$: Section 3.2.3**
 - **PM_{10} : Section 3.3.4**
- **Bias provided by “independent” FRM samplers collocated with Primary samplers**
 - **$PM_{2.5}$: Section 3.2.4 Performance Evaluation Program (PEP), or**
- **Internal bias based on flow rate verifications for $PM_{2.5}$ and Low-vol PM_{10} : Sections 3.2.1 and 3.3.1**

What happens When the Ambient Concentration Gets Small



- Collocated precision measurements and PEP bias measurements are considered valid for the applicable statistical algorithm, if:
 - ❑ both the primary monitor and collocated sampler or PEP audit concentrations are otherwise valid, and
 - ❑ Each is above a prescribed threshold given at...
 - ❖ **40 CFR Part 58 Appendix A Section 4.(c).**
 - 1) PM₁₀ (Hi-Vol): 15 µg/m³.
 - 2) PM₁₀ (Lo-Vol): 3 µg/m³
 - 3) PM_{2.5} and PM_{10-2.5}: 3 µg/m³.
- AQS does not pair data from either event unless both concentrations are valid
- Also see ❖ **40 CFR Part 58 Appendix A Section 3.2.4**

Collocated Samplers Are Important !!!



What is a Collocated Sampler?

Any sampler placed beside a primary sampler for measurement or collection of data that can be related to the primary sampler



Begs an Important Question!!!



What is the primary sampler?

Sampler that produces ambient concentration data for determining compliance with NAAQS or other regulatory requirements



◆ **Appx A**
3.2.3 & 3.3.4.1
There can be only one primary PM_{25} or PM_{10} sampler per site for a specified period of time.

∴ Make sure your primary sampler is designated correctly in AQS!!

PM_{2.5} Collocation Requirements



Part 58 Appendix A Section "3.2.3"

3.2.3.1 General: For each distinct monitoring method designation (FRM or FEM) that a PQAQ is using for a primary monitor, the PQAQ must have 15 percent of the primary monitors of each method designation collocated. The First Collocated Monitor must be a FRM!!

 We took some of the "guess work" out of the FEM collocations:

<i>#Primary FEMS of each <u>unique</u> method designation</i>	<i>Collocations Required</i>	<i>#Collocated with an FRM</i>	<i>#Collocated with same method designation</i>
<i>1-9</i>	<i>1</i>	<i>1</i>	<i>0</i>
<i>10-16</i>	<i>2</i>	<i>1</i>	<i>1</i>
<i>17-23</i>	<i>3</i>	<i>2</i>	<i>1</i>
<i>24-29</i>	<i>4</i>	<i>2</i>	<i>2</i>



Part 58 Appendix A Section 3.2.3.4 Deployment

- ◇ 3.2.3.4 (a) and (b)--- 50% (of the 15%) locate at sites with ambient concentrations within $\pm 20\%$ NAAQS; If ambient concentrations $< 20\%$ NAAQS, 50% at sites with highest concentrations. Remaining 50% at SLT's discretion.**

- ◇ 3.2.3.4(c) Spatial requirements**
 - i. samplers 1-4 meters apart horizontally;**
 - ii. Rule clarification: EPA Waiver by Region can allow up to 10 meters horizontally and up to 3 meters vertically**

PM₁₀ Collocation Requirements



Part 58 Appendix A Section "3.3.4"

General: Applies to manual (filter based) samplers only

- **15 percent of the primary monitors collocated.**
- **Spatial deployment similar to PM_{2.5}**
- **Hi-vol TSP cannot be Surrogate Primary samplers for PM₁₀ Hi-vol samplers**
- **PM_{10-2.5} Primary Sampler may also be a Primary PM₁₀ Sampler; the method designation of the collocated sampler has to match**
- **Low-vol Pb and PM₁₀ samplers may share a collocated sampler, in which case**
 - ✓ **Total PM₁₀ Mass on the filter must be measured before chemical analysis for Pb**

The Appendix A Precision Equation



From 40 CFR Part 58 Sections 4.1.1 & 4.1.2

Equation 1

$$d_i = \frac{\text{meas} - \text{audit}}{\text{audit}} \times 100$$

Equation 2

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i \right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X_{0.1, n-1}^2}}$$

In Equation 1, “d” is the percent difference of the primary sampler’s measured concentration, “meas,” and the “audit” concentration of the collocated sampler. “i” is the single event in which a primary monitor and the collocated monitor have acquired valid samples.

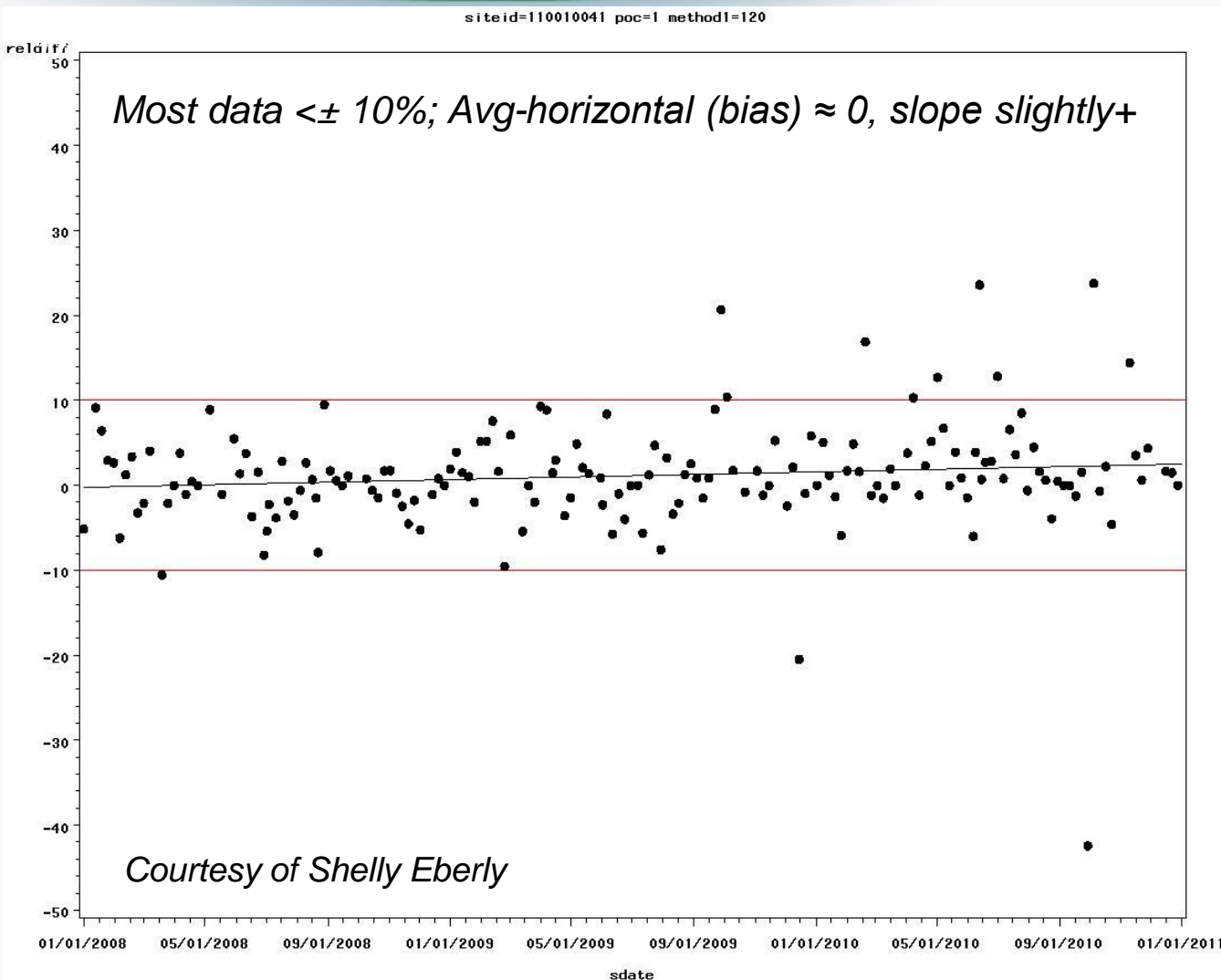
In Equation 2, “n” is the number of single point checks being aggregated; $X_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with n-1 degrees of freedom.

Analyses you can get from your collocations



- Calculate and plot CV via the DASC tool
 - Overall CV
 - FRM-FRM
 - FEM-FRM
 - FEM-FEM, if you have FEM-FEM collocations
- Primary vs collocated scatter plot showing outliers
- Plot of % difference FEM(s) vs FRM (the $PM_{2.5}$ Bias equation gives an in-house bias
 - Plot of Daily Bias over time using 1 point QC check equation provides precision

Can Precision Data Give Insights into Bias?

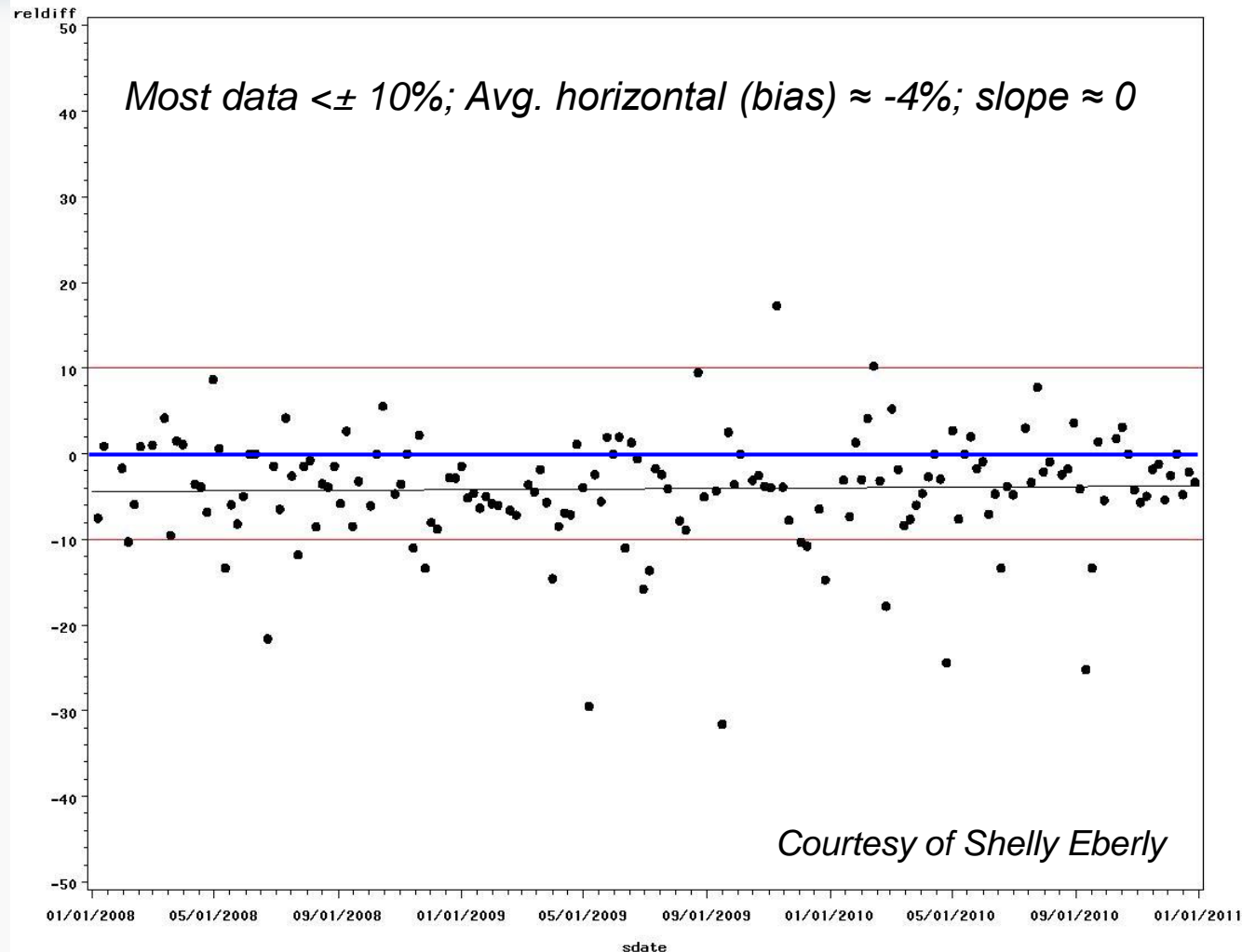


- Using 2008-2010 precision data,
 - consistent differences suggest bias in one or both samplers.
 - A trend in differences suggest a progressive bias in one sampler.

Can Precision Data Give Insights into Bias?



siteid=390933002 poc=1 method=120

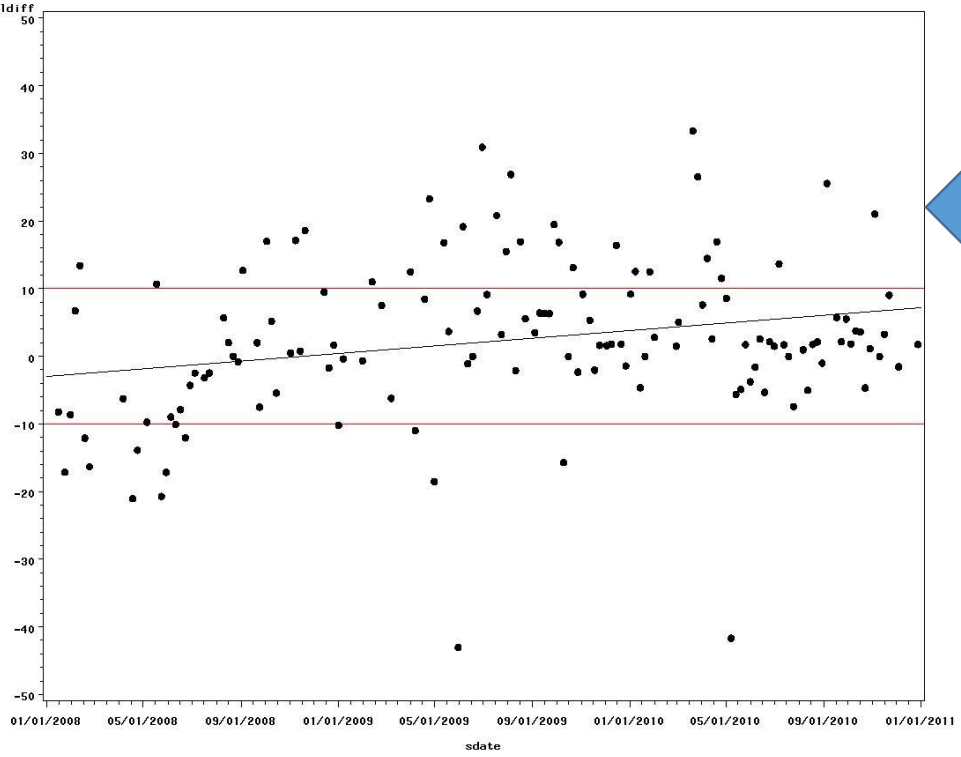


- Using 2008-2010 precision data,
 - consistent differences suggest bias in one or both samplers.
 - trends in differences suggest trends in bias in one or both samplers.



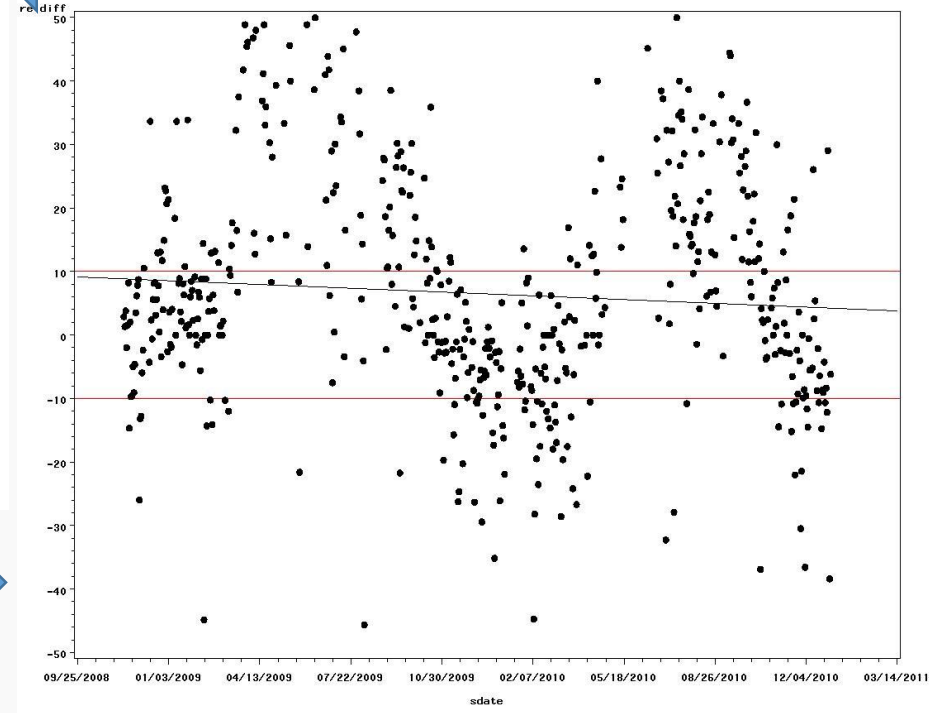
What do these indicate????

siteid=170313301 poc=1 method=120



Noisy precision with possible upward trend in bias.

siteid=300630024 poc=3 method=170



Noisy precision with oscillations. Larger positive relative differences in summer, larger negative relative differences in winter (Method Code 170).

Courtesy of Shelly Eberly

Section 3.2.4: PM_{2.5} Performance Evaluation Program



- Collocates an independent FRM audit sampler beside a FRM/FEM
- Provides independent assessment of network sampler bias
- Applies rigorous performance and QA/QC requirements to field and laboratory operations
- Might indicate if the monitoring agency's FRM is experiencing performance issues, **BUT**
 - **60 days after the fact!**
 - **Each measurement is only 1 data point for one isolated sampling event.....**

PM_{2.5} FRM/FEM Performance Evaluation Program



• PEP Event Count for Each PQAO:

- 15% of all sites audited per year; all sites in 6 years
- If **5 sites or less**: 5 audits per year
- If **>5 sites**: 8 sites per year unless > 48 sites
- At least one of each “monitor type” audited each year
- FEMs and SPMS are included in the site count, unless classified as “excluded from design value determinations”

Speaker notes: We now perform about 600 Bias measurements per year The take away messages is that every PQAO is not going to get very many data points in any given year. I even wonder about annual aggregation. You will see why this may be an growing issue in the following slides.

The PEP Bias Equation



From 40 CFR Part 58 Appendix A Sections 4.1.1 & 4.1.2

$$\text{Bias} = \frac{1}{n_j} \sum_{j=1}^{n_j} \left(\frac{\text{SLT} - \text{PEP}}{\text{PEP}} \right)_j \times 100\%$$

where n_j is the number of bias pairs to be averaged. Note that this term $\left(\frac{\text{SLT} - \text{PEP}}{\text{PEP}} \right)_j$ is “ d_i ” in Equation 1 of Appendix A.

See the DASC tool at <https://www3.epa.gov/ttn/amtic/files/ambient/qaqc/dascv3.xls>

Uses for PEP Bias data

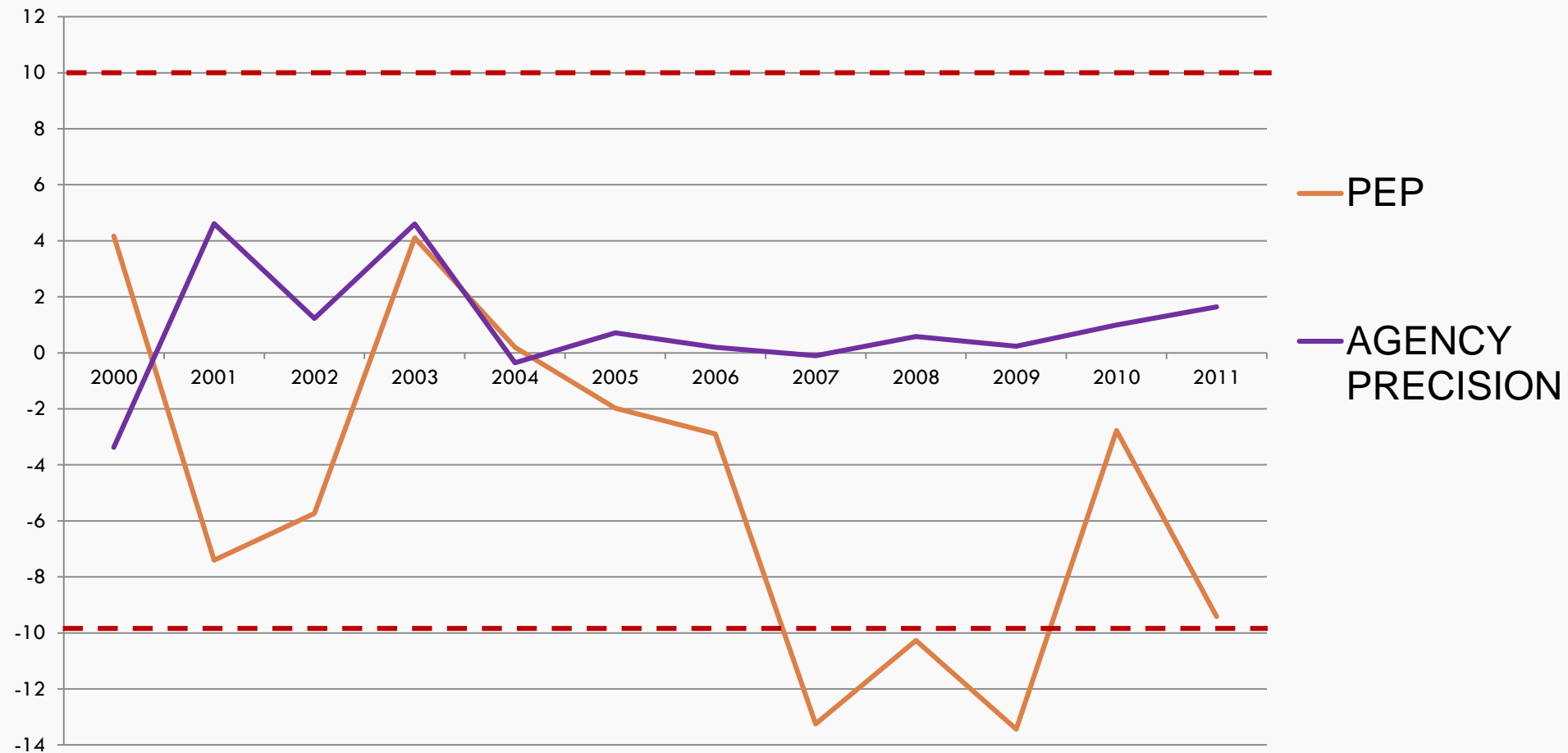
Speaker notes



What does the PM_{2.5} data look like? Exactly what can it tell us. Slide 48 is a plot of one agency's annual bias data over several years and some precision data superimposed. We used the bias equation for the precision data in this analysis to keep everything scaled similarly. We have reported in past conferences the dramatic shift in bias during 2007-2009. Notice while the difference between the bias and the precision seem dramatic the annual averages rise and fall in the same direction from 2007 through 2010. And again note that the precision average is based on about 30 data points 1 in 6 day sampling and the bias no more than 9 events annually, at least after 2006. There are several factors that we have concluded contribute to this disparity but also keep in mind that the math itself can over emphasize the difference. As the ambient concentration measurements get smaller less than 10 $\mu\text{g}/\text{m}^3$, the probability of creating a bias value $> \pm 10\%$ increases.

Slide 49 is a good example We know historically that the PEP values are a little higher than the SLT values, so if the PEP sampler is off by no more than 1 $\mu\text{g}/\text{m}^3$ (half of the method LDL) from an SLT's primary sampler on a given day, the bias can be easily skewed to unacceptable values by the regulations. One or two PEP results like this can easily put the DQO out of reach in a given year even though the actual difference between the PEP and SLT measurements are 1 $\mu\text{g}/\text{m}^3$. keep in mind that the FRM LDL is 2 $\mu\text{g}/\text{m}^3$.

Uses for PEP Bias data



Example: One Sampling Event



The SLT sampler has produced a concentration measurement of 5 $\mu\text{g}/\text{m}^3$ and the PEP sampler 6 $\mu\text{g}/\text{m}^3$. According to Equation 1:

$$\text{Bias} = \left(\frac{5 \mu\text{g}/\text{m}^3 - 6 \mu\text{g}/\text{m}^3}{6 \mu\text{g}/\text{m}^3} \right) \times 100\%$$

A "1 $\mu\text{g}/\text{m}^3$ " difference yields a Bias = -17%

SLT and PEP values of 4 and 5 $\mu\text{g}/\text{m}^3$, respectively, would yield a bias of -20%, etc.

Uses for PEP Bias data

Speaker Notes



Slide 51 Here's what has been happening the last 3 and a half years across the nation. Thankfully the average has stabilized around – 7ug/m³. But there is still a lot of variability. You cannot tell from this plot that the data set includes about 190 events in which either the PEP or the SLT value was 3ug/m³ or less. When I extracted all of those values, the bias, SD and UCL/LCL changed to the next graph.

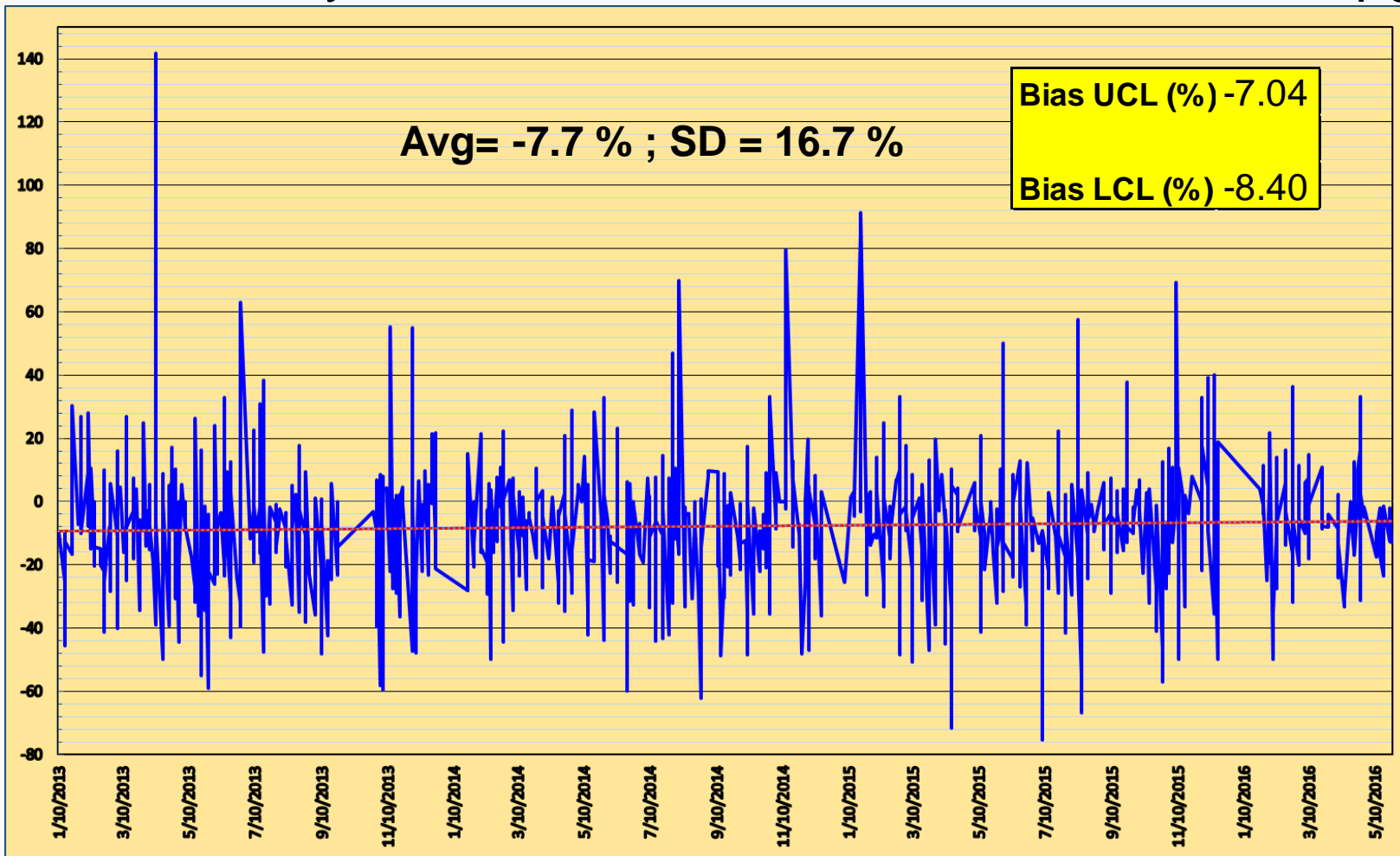
Slide 52 Notice that there are still a lot of data points that fall considerably outside of the $\pm 10\%$ (SD = 15.2 %) even though the UCL/LCL values for the nation look pretty good. Do we know why there are so many excursions? Its speculation at the moment, but I believe it is the higher variability exhibited by the FEMs overlaid by the influence of lower concentrations. Why did I take out the events at 3 $\mu\text{g}/\text{m}^3$? Because the reg says so, and the AQS AMP 256 and AMP 600 reports, which use the same statistical metric, also exclude them. Look at the following slide.

Slide 53 We have already seen what can happen to bias at values between 3 and 6 ug/m³. The 3 ug/m³ cut-off for data exclusion in the bias statistic poses a second dilemma. We have essentially lost about 200 data pairs thus far since Jan 2013 due to the cut off, and the rate is increasing rapidly. Since we only collect 5 or 8 PEP samples annually anyway, it is conceivable that the confidence level utilized for development of the DQO may no longer adequately represent the bias of an individual PQAQO's data set each year.

Uses for PEP Bias data



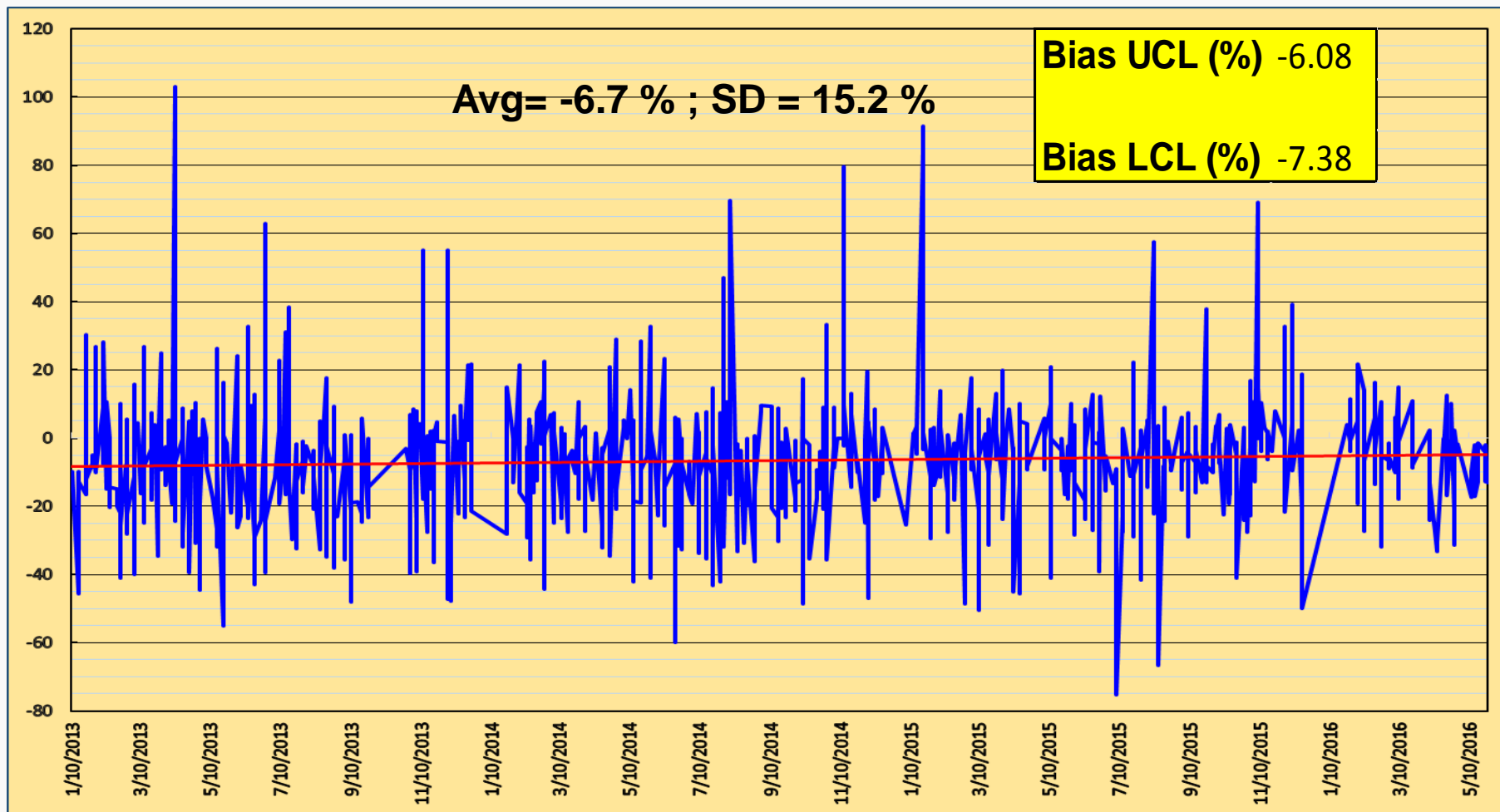
Jan 2013 - May 2016 National PM 2.5 Bias with data $< 3 \mu\text{g}/\text{m}^3$



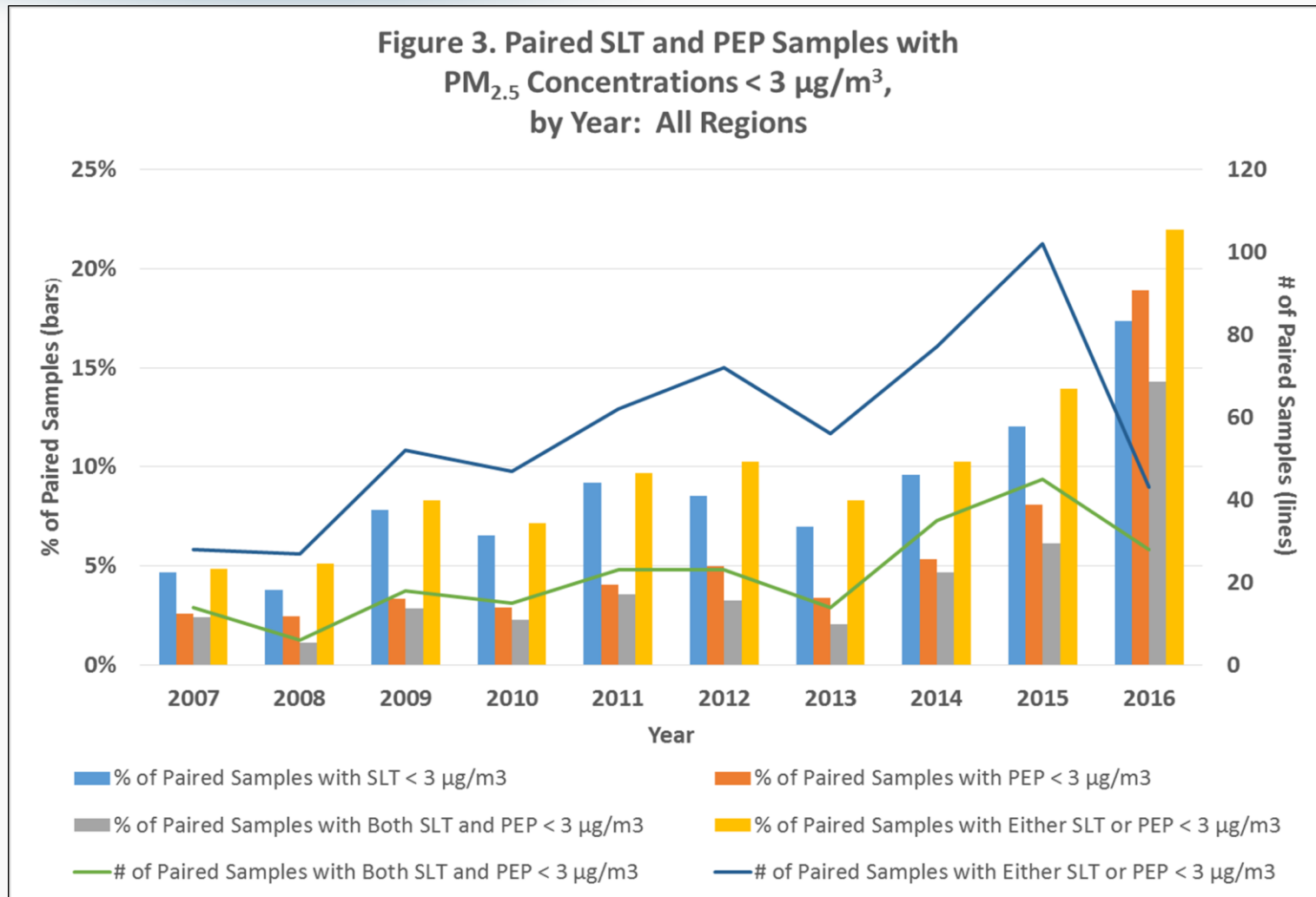
Uses for PEP Bias data



Jan 2013 - May 2016 National PM 2.5 Bias with data $>3 \mu\text{g}/\text{m}^3$



Falling PM_{2.5} Concentrations' Effect on BIAS



Falling PM2.5 Concentrations

Speaker Notes

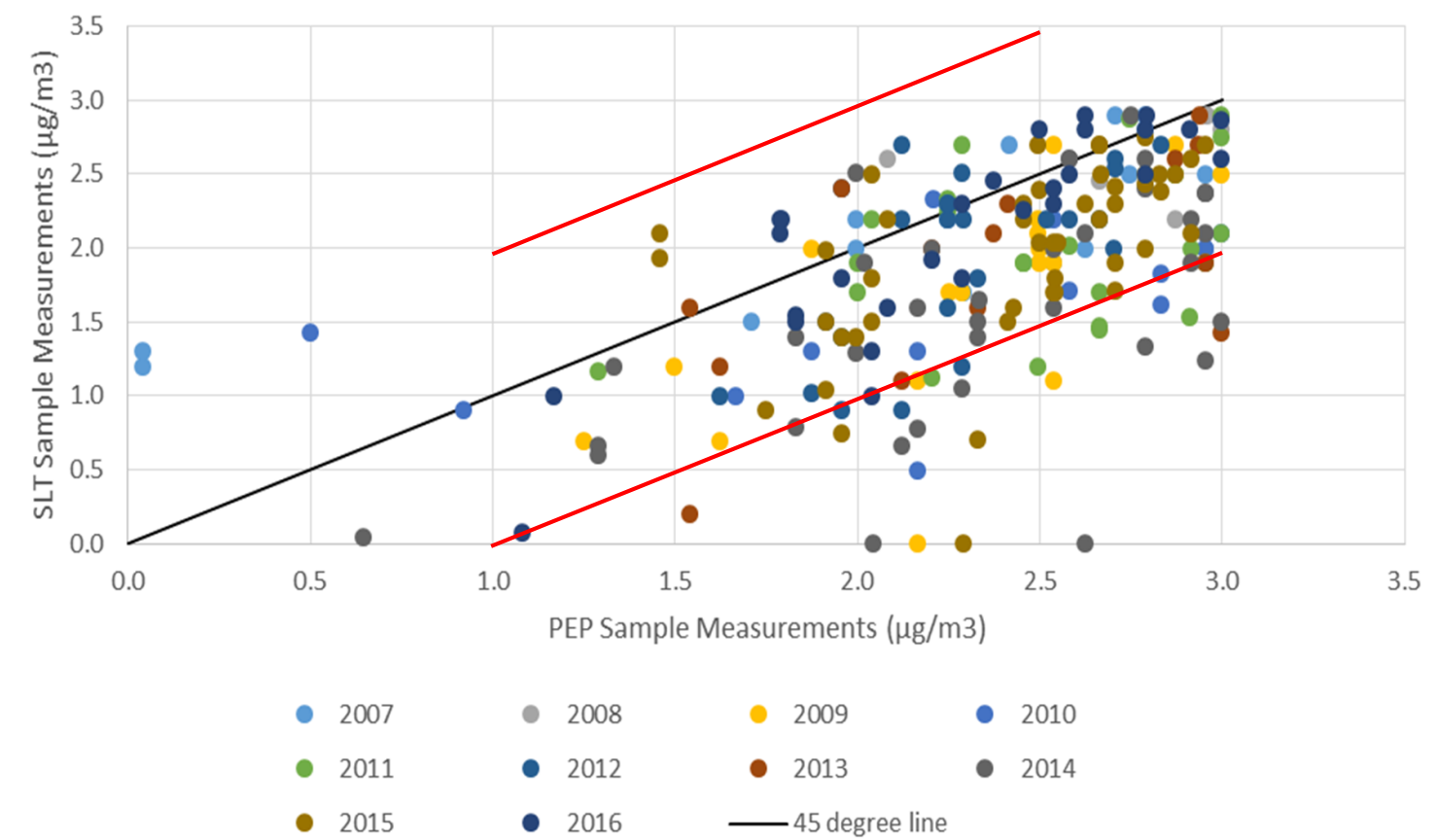


Slide 55 We have noticed an interesting characteristic of the data below the 3 ug/m³ threshold. In all but a few instances the absolute difference between the PEP and SLT's measured concentration is 1 ug/m³ or less. This is half the FRM's LDL. As a result we are now considering a change to the Bias statistic. You will see in our PEP field blanks slide (#69) below that 1 ug/m³ is not an unrealistic practical LDL for the PEP program at least. You may be able to establish a similar LDL in which case a practical rationale for annually certifying your data may be apparent.

Falling PM_{2.5} Concentrations Effect on BIAS



Figure 5. Paired SLT and PEP Samples with Both PM_{2.5} Measurements Below 3.0 µg/m³



What's Happening... in the LAB?



Four Areas of Control

- Lab Environment
- Analytical Equipment
- Analytical and QA/QC procedures
- Data Management



https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/PM2.5_Val_Template_4_27_16.pdf

What's Happening... in the LAB?



https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/PM2.5_Val_Template_4_27_16.pdf

Laboratory Activities			
<i>Post-sampling Weighing</i>	<i>all filters</i>	<i><10 days from sample end date if shipped at ambient temp, or ≤30 days if shipped below avg ambient (or 4° C or below for avg sampling temps < 4° C) from sample end date</i>	1, 2 and 3) 40 CFR Part 50 App L Sec 8.3.6 Sampled filters must be protected from exposure to temperatures above 25C from sample retrieval to conditioning 40 CFR part 50 Appendix L Sec 10.13. See technical note on holding time requirements at : https://www3.epa.gov/ttn/amtic/pmpolguid.html
1) Criteria (PM2.5 LC)	2) Frequency	3) Acceptable Range	Information /Action
<i>Filter Visual Defect Check (unexposed)</i>	<i>all filters</i>	<i>Correct type & size and for pinholes, particles or imperfections</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 10.2
Filter Conditioning Environment			
<i>Equilibration</i>	<i>all filters</i>	<i>24 hours minimum</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.2.5
<i>Temp. Range</i>	<i>all filters</i>	<i>24-hr mean 20.0-23.0° C</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.2.1
<i>Temp. Control</i>	<i>all filters</i>	<i>< 2.1° C SD* over 24 hr</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.2.2
<i>Humidity Range</i>	<i>all filters</i>	<i>24-hr mean 30.0% - 40.0% RH or Within ±5.0 % sampling RH but ≥ 20.0%RH</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.2.3
<i>Humidity Control</i>	<i>all filters</i>	<i>< 5.1 % SD* over 24 hr.</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.2.4
<i>Pre/post Sampling RH</i>	<i>all filters</i>	<i>difference in 24-hr means < ± 5.1% RH</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.3.3
<i>Balance</i>	<i>all filters</i>	<i>located in filter conditioning environment</i>	1, 2 and 3) 40 CFR Part 50, App. L Sec 8.3.2
<i>Microbalance Auto-Calibration</i>	<i>Prior to each weighing session</i>	<i>Manufacturer's specification</i>	1) 40 CFR Part 50, App. L, Sec 8.1 2) 40 CFR Part 50, App. L, Sec 8.1 and Method 2.12 Sec. 10.6 3) NA

More Validation Template



Laboratory Activities			
Filter Checks			
Lot Blanks	9 filters per lot	< ±15.1 µg change between weighings	1, 2, 3) Recommendation and used to determine filter stability of the lot of filters received from EPA or vendor. Method 2.12 Sec. 10.5
Exposure Lot Blanks	3 filters per lot	< ±15.1 µg change between weighings	1,2 and 3) Method 2.12 Sec. 10.5 Used for preparing a subset of filters for equilibration
Filter Integrity (exposed)	each filter	no visual defects	1,2 and 3) Method 2.12 Sec. 10.7 and 10.3
Lab QC Checks			
Field Filter Blank	10% or 1 per weighing session	<± 30.1 µg change between weighings	1) 40 CFR Part 50, App. L Sec 8.3.7.1 2 and 3) Method 2.12 Table 7-1 & Sec.10.5
Lab Filter Blank	10% or 1 per weighing session	<± 15.1 µg change between weighings	1) 40 CFR Part 50, App. L Sec 8.3.7.2 2 and 3) Method 2.12 Sec. 10.5
Balance Check (working standards)	beginning, 10th sample, end	<±3.1 µg from certified value	1,2 and 3) Method 2.12 Sec. 10.6 Standards used should meet specifications in Method 2.12, Section 4.3.7
Routine Filter re-weighing	1 per weighing session	<± 15.1 µg change between weighings	1,2 and 3) Method 2.12 Sec 10.8
Microbalance Audit	every 365 days and once a calendar year	<± 0.003 mg or manufacturers specs, whichever is tighter	1,2 and 3) Method 2.12 Sec. 11.2.7
Lab Temp Check	Every 90 days	< + 2.1°C	1,2 and 3) Method 2.12 Sec. 10.10
Lab Humidity Check	Every 90 days	< + 2.1%	1,2 and 3) Method 2.12 Sec. 10.10
Verification/Calibration			
1) Criteria (PM2.5 LC)	2) Frequency	3) Acceptable Range	Information /Action
<i>Microbalance Calibration</i>	<i>At installation every 365 days and once a calendar year</i>	Manufacturer's specification	1) 40 CFR Part 50, App. L, Sec 8.1 2) 40 CFR Part 50, App. L, Sec 8.1 and Method 2.12 Sec. 10.11 3) NA
Lab Temperature Certification	every 365 days and once a year	<± 2.1°C	1-3) Method 2.12 Sections 4.3.8 and 9.4
Lab Humidity Certification	every 365 days and once a year	<± 2.1%	1-3) Method 2.12 4.3.8 and 9.4
Calibration & Check Standards -			
<i>Working Mass Stds. Certification</i>	<i>Every 365 days and once a calendar year</i>	0.025 mg tolerance (Class 2)	
Compared to primary standards	Every 90 days	0.025 mg tolerance (Class 2)	1, 2 and 3) Method 2.12 Sec 4.3.7 & 9.7
Primary standards certification	every 365 days and once a calendar year	0.025 mg tolerance (Class 2)	1, 2 and 3) Method 2.12 Sec 4.3.7 & 9.7

More Validation Template Specs



Laboratory Activities			
<i>Microbalance Readability</i>	<i>at purchase</i>	<i>1 µg</i>	1, 2 and 3) 40 CFR Part 50, App.L Sec 8.1
Microbalance Repeatability	every 365 days and once a calendar year	1 µg	1) Method 2.12 Sec 4.3.6 2) Recommendation 3) Method 2.12 Sec 4.3.6
Primary Mass. Verification/Calibration Standards Recertifications Working Mass Standards	every 365 days and once a calendar year	0.025 mg	1, 2 and 3) Method 2.12 Sec 4.3.7
Comment #1 The associated leak test procedure shall require that for successful passage of this test, the difference between the two pressure measurements shall not be greater than the number of mm of Hg specified for the sampler by the manufacturer, based on the actual internal volume of the sampler, that indicates a leak of less than 80 mL/min.			

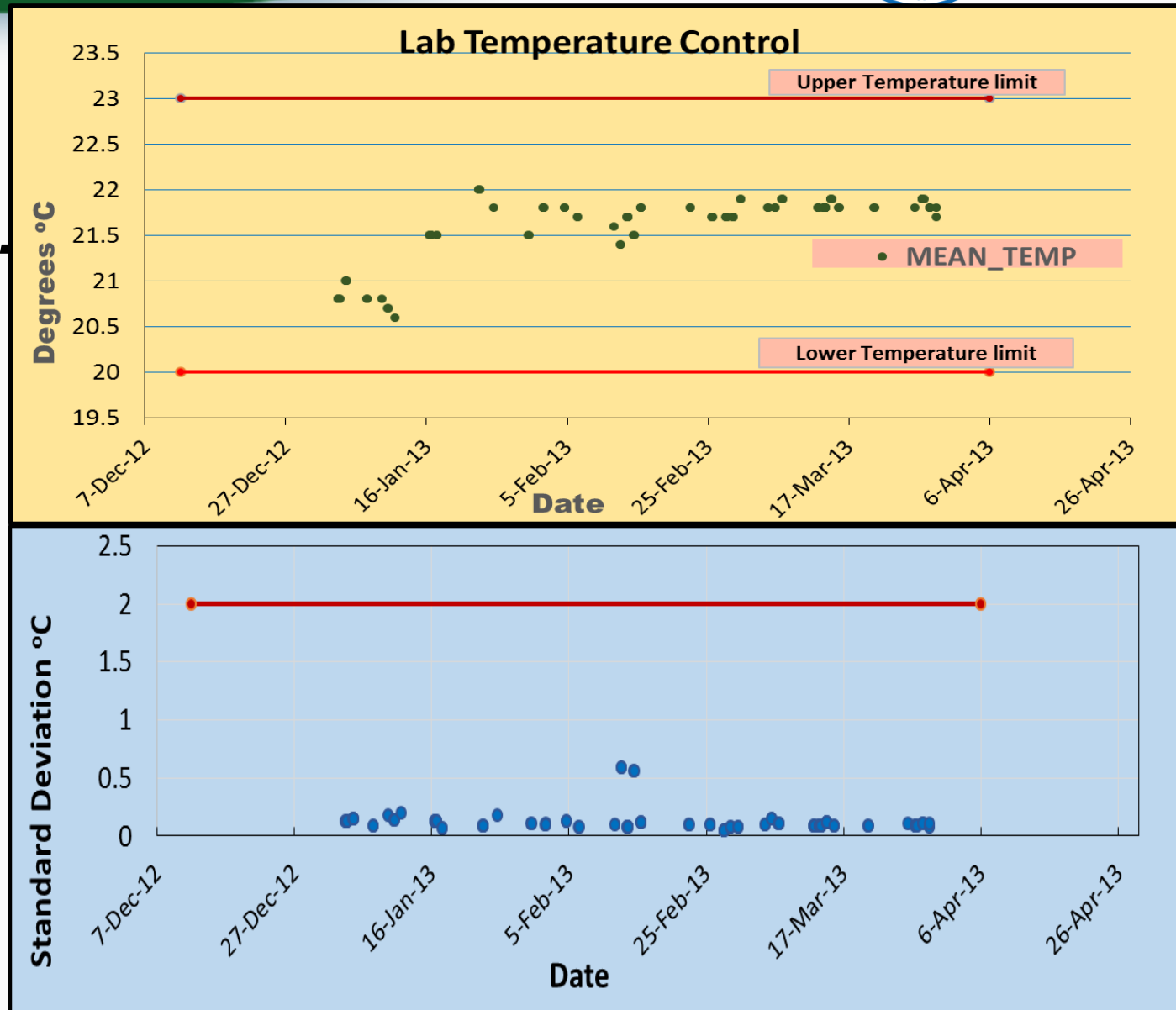
How Does one verify and document conformance?

Lab: Environment Control Temperature



Limit =
 $21^{\circ}\text{C} \pm 2.^{\circ}\text{C}$
for the 24 hrs.
preceding
weighing
Session

SD (UL) =
 2°C
over that
period

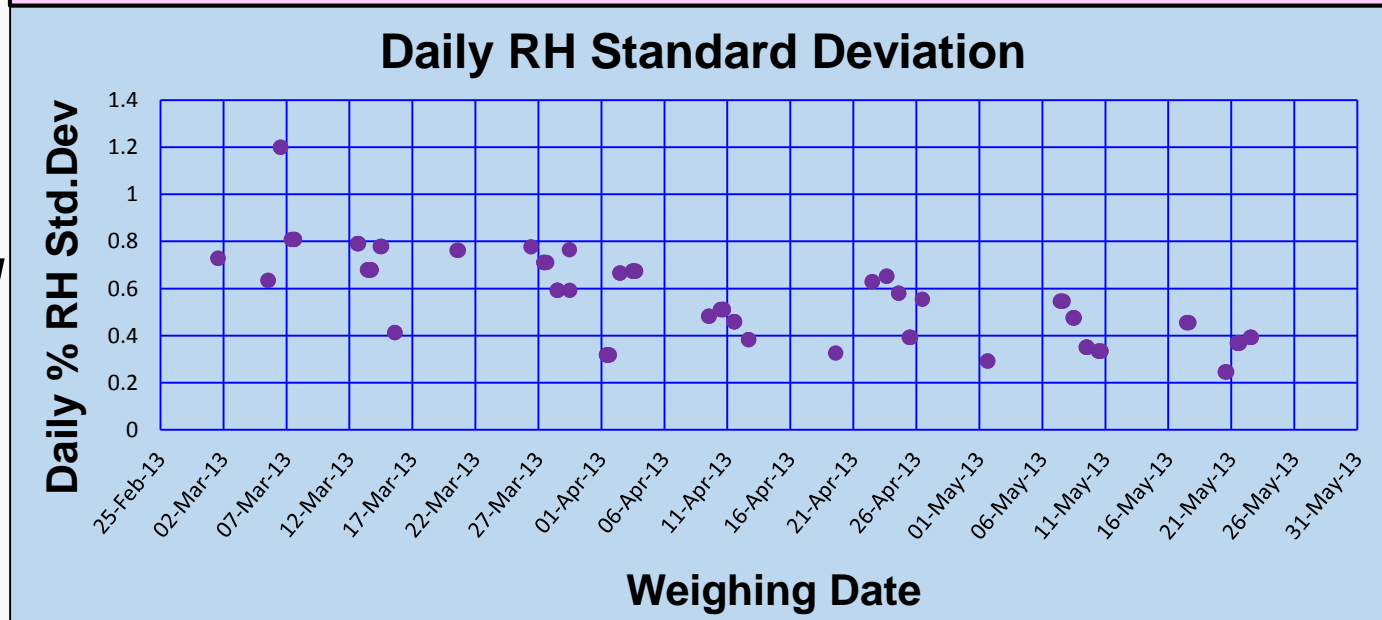
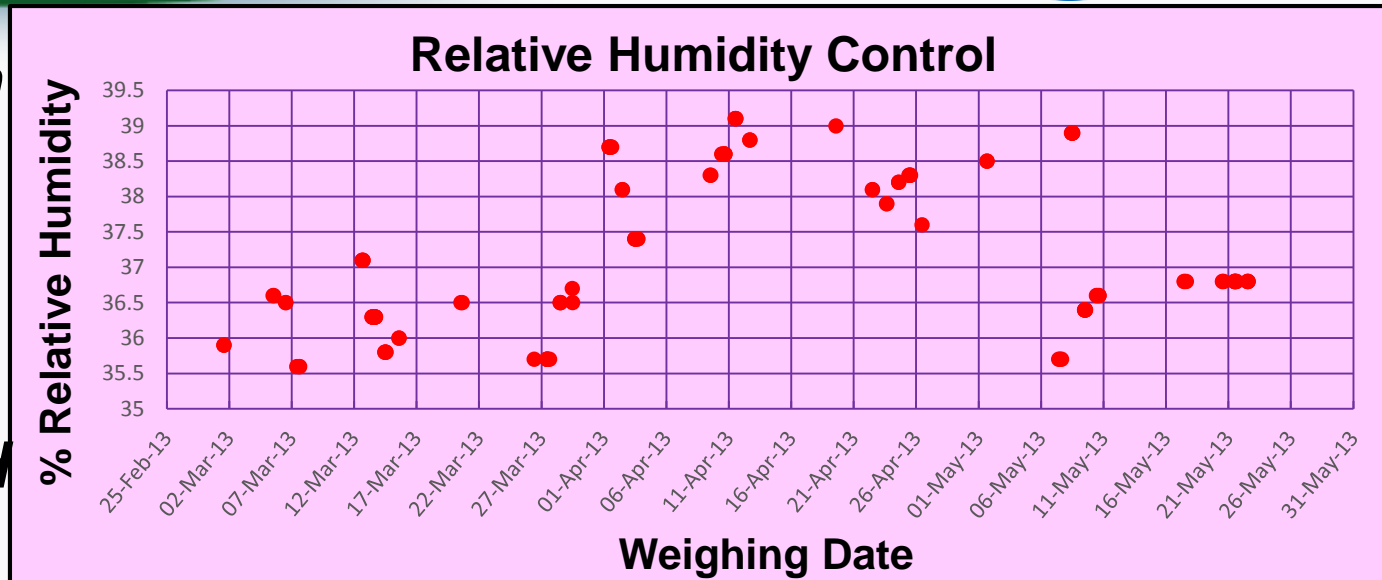


Lab: Environmental Control Relative Humidity



Avg RH between 30-40% for the 24 hrs. preceding weighing Session. (in arid region <5% of RH during sampling event). Variability = ± 5 RH % of Avg over that period but >30% (arid >20%)

8/8/2016

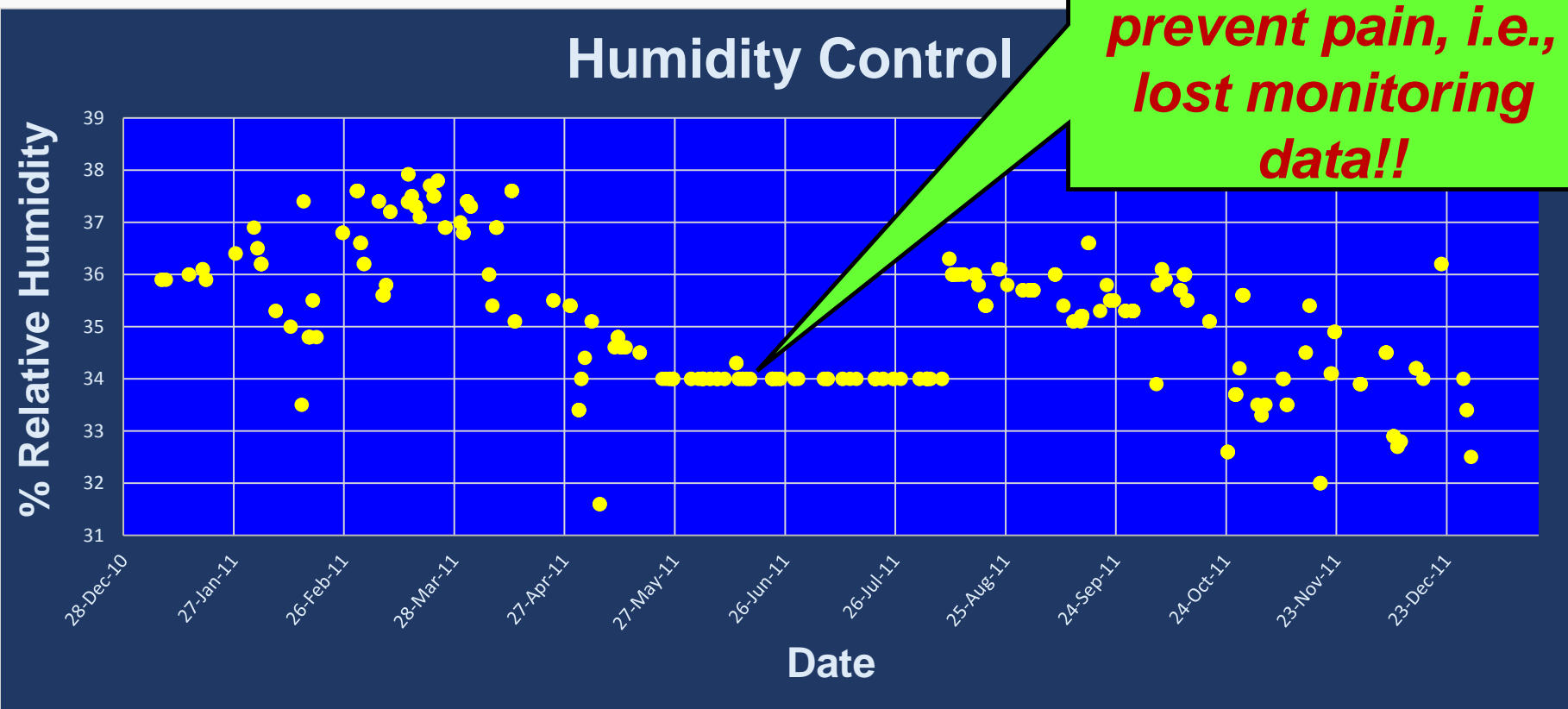


Lab: Environmental Control Charting and



In 2011 we lost a significant amount of PEP data because the deployed logger was stuck on a single value and we were not watching the control chart.

Redundant monitoring devices can prevent pain, i.e., lost monitoring data!!



Lab: Analytical Equipment-- Static Control



- Grounded Equipment
- Fresh Polonium 210 (more efficient)
 - Center filters between strips positioned 2 inches apart
 - Give it time! Waving a filter between 2 strips for a half a second probably will not be adequate
- Additional equipment such as U-bars also improve the dissipation of electrons
- Test your procedure by charging, weighing and then reweighing filters. (hint: slide them in a petri across a counter top)
- Consult with the filter and balance vendors.

LAB: Analytical Equipment Verifications & Audits



- Gravimetric balance: Vender maintenance and calibration—1/year
- ASTM Calibration Weights: NIST Certification—1/year
- ASTM Check Weights compare against Calibration weights—1/quarter
- Remember to Bracket the combined mass of the filter and expected PM filtrate 1-500 mg and 1-300 mg

LAB: Analytical QA/QC Procedures

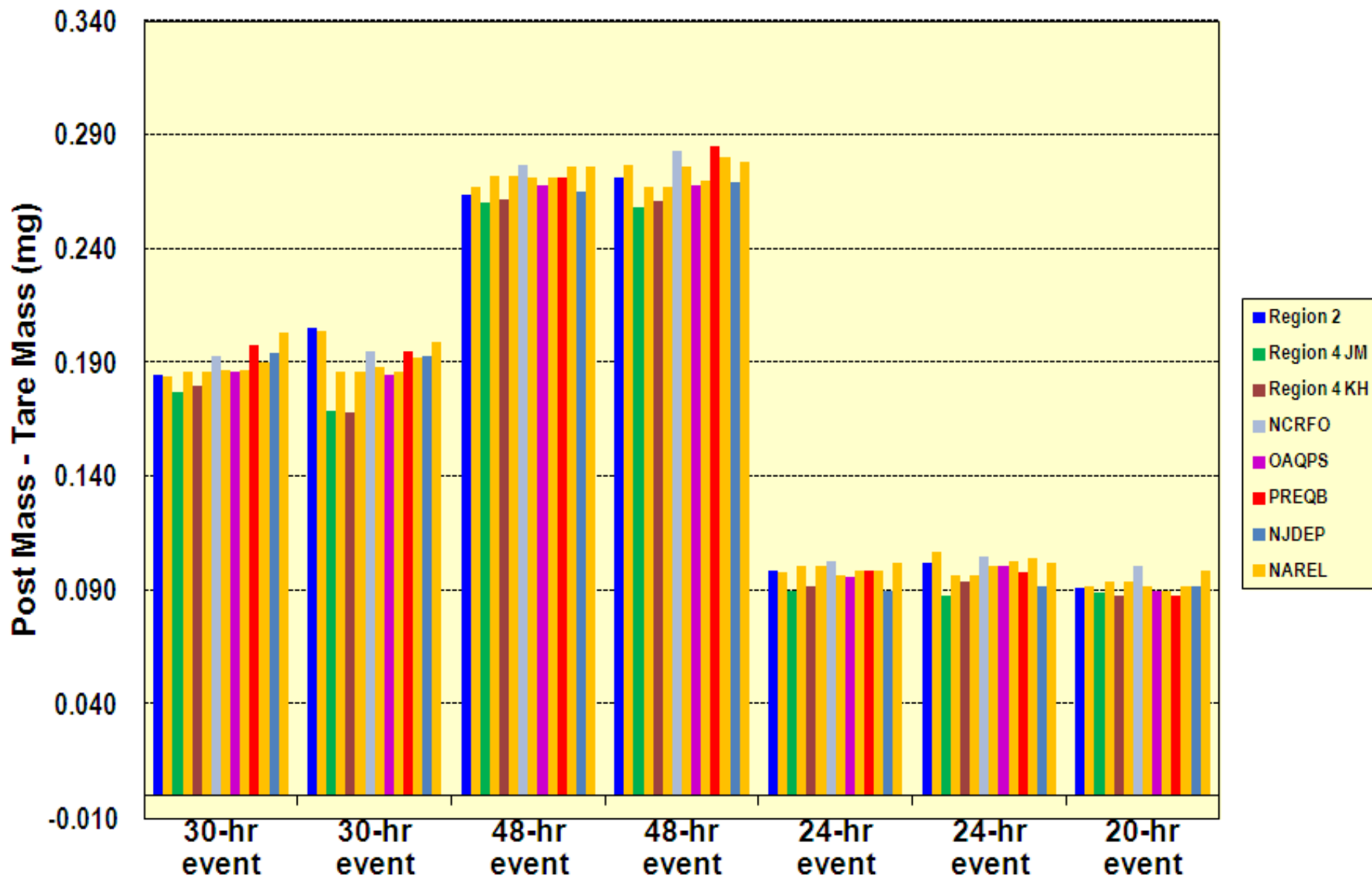


- Internal and independent performance testing
 - Technician accuracy and precision
 - Bias between/among several Technicians
- ASTM/NIST-traceable Check and calibration weights
 - Monitor the condition and performance of the balance **and the weights**
- Lab Blanks and Trip blanks, Batch and Inter-batch duplicates
 - Indicates what is going on in the lab environment and the filter handling process
- Field Blanks
 - Indicate level of contamination in lab and the field

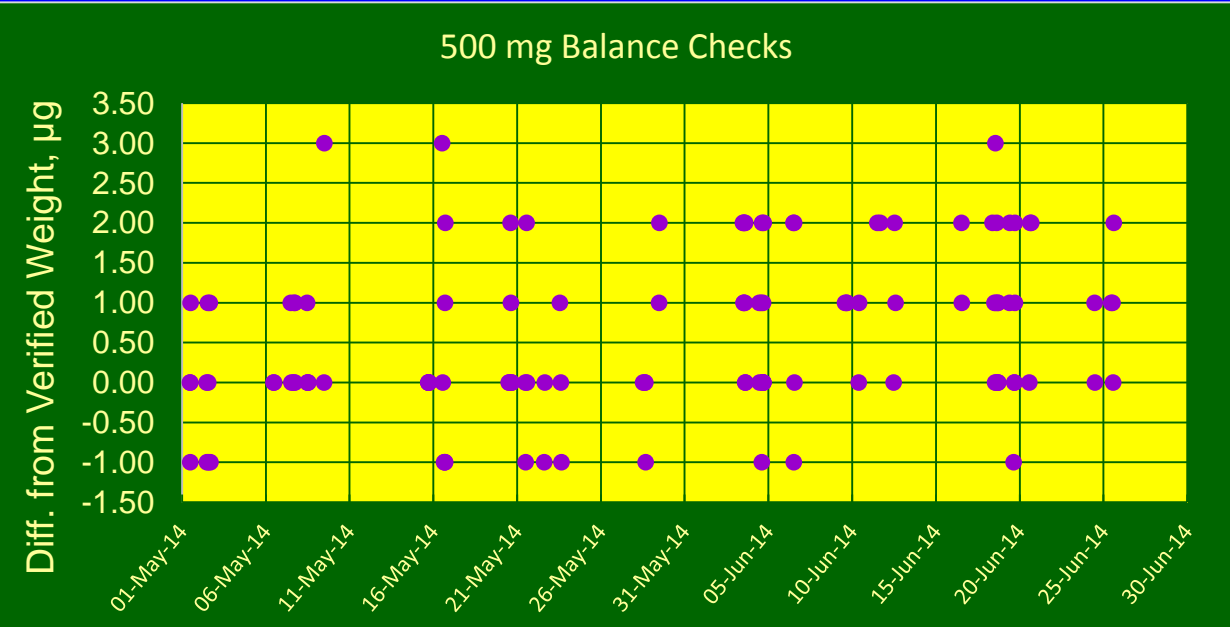
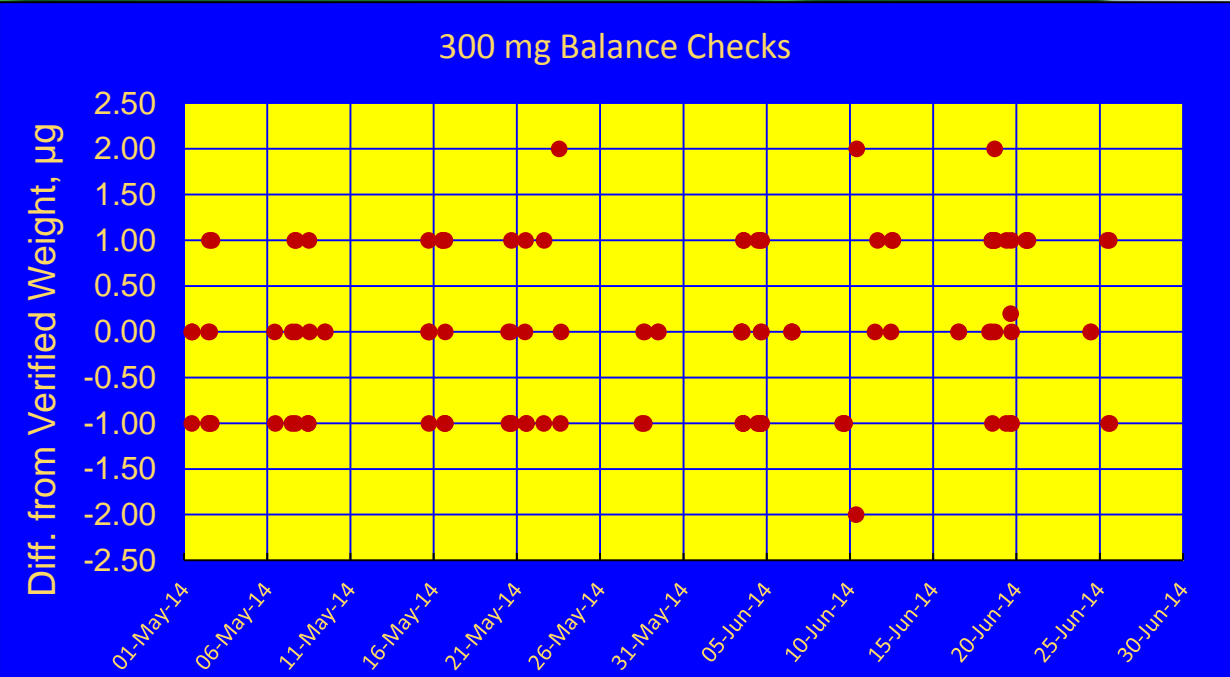
LAB: Analytical QA/QC Procedures



Captured PM2.5 Determined by Each Test Lab and NAREL

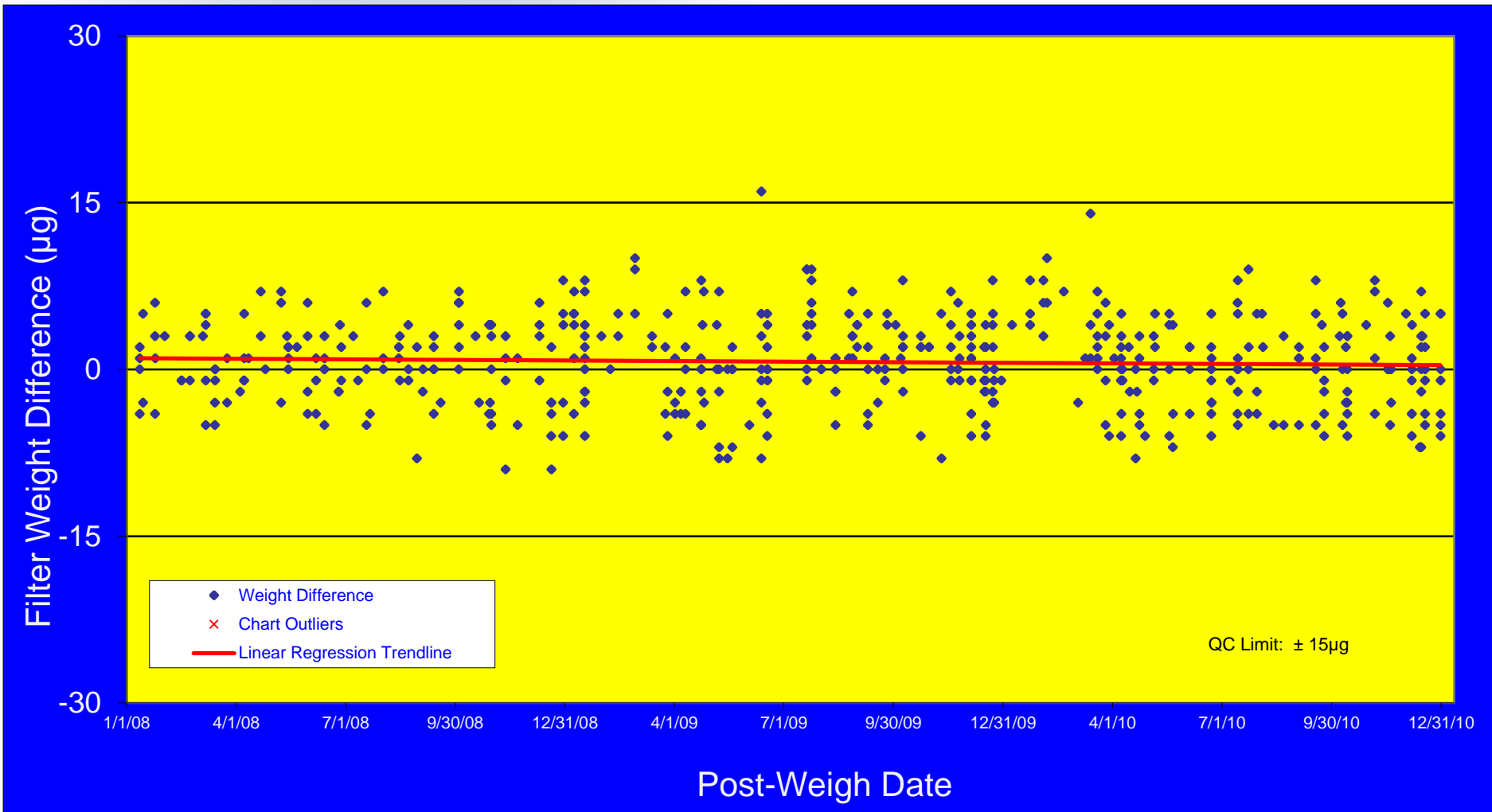


Lab: QC Balance Checks

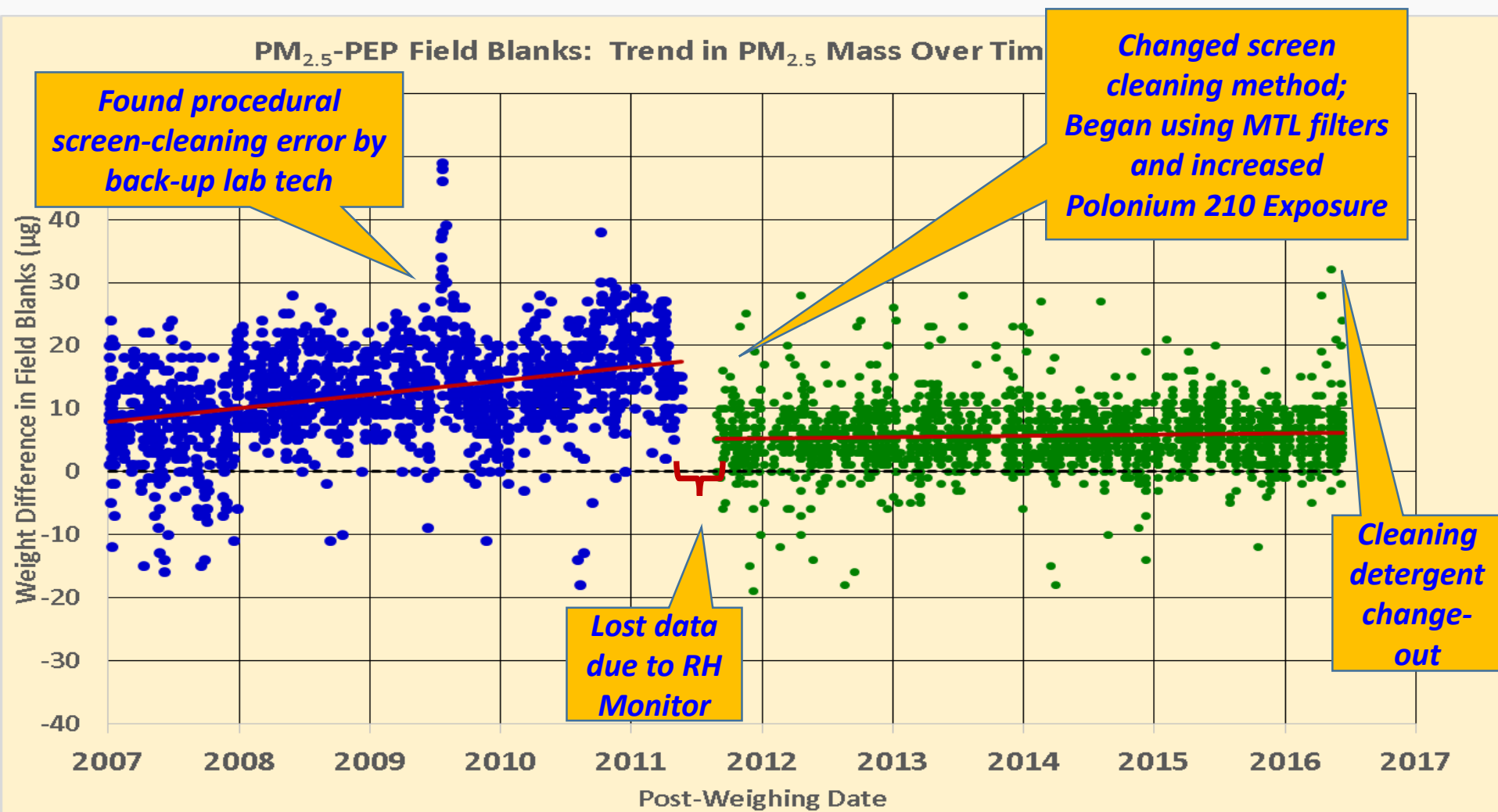


Lab: QC Practices

Lab Blanks



Lab: QC Practices Field Blanks

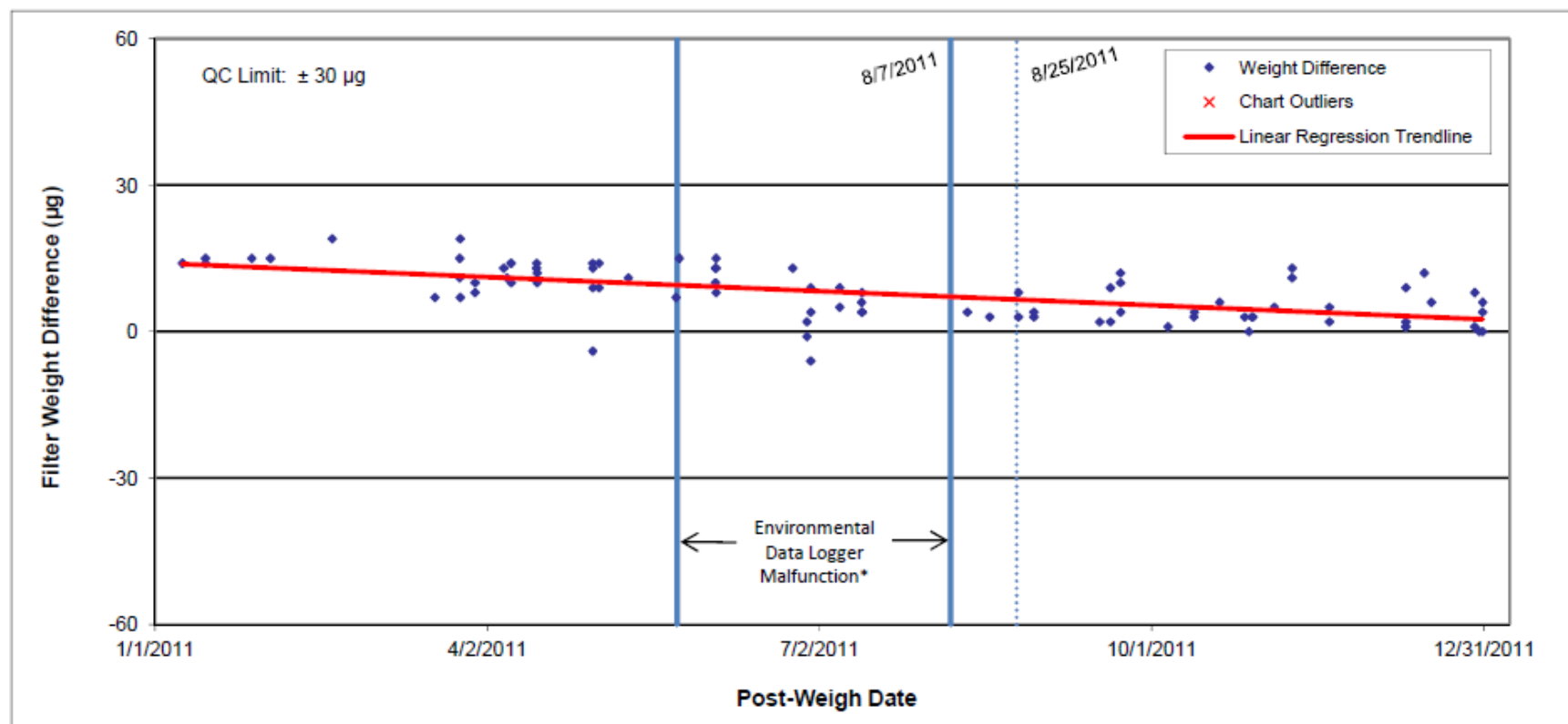


Lab: QC Practices

Trip Blanks



2011 Trip Blanks - Region 4





"Did you get the Drift?"

- ❖ *If you would like more coverage of any PM QA topics not covered or covered in this session,*
- ❖ *Send an e-mail to crumpler.dennis@epa.gov*
- ❖ *If enough interest is expressed we will put on a series of Webinars with more depth and discussion*