QA 101: PM QA Requirements

Round Robins: Lab Bias & Accuracy

PM$_{2.5}$ PEP: Network BIAS
Intro/Overview

• **General Requirements**
  • Quality System: QMP & QAPP
  • Equipment
  • Network design and Siting

• **Operational Requirements**
  • Field
  • Lab

• **Data Management**

• QA Handbook Volume II, Appendix D is the “Rosetta Stone” for QA measurement requirements

General Requirements

• FRM requirements in Part 50 Appendices):

1. Appendix B ....... TSP (applies only to lead)
2. Appendix J ....... PM-10 (note refers to Appendix L for low-volume measurements)
3. Appendix L ...... PM$_{2.5}$

• FEMs performance specifications and testing requirements are listed in Part 53

• Lab climate and filter conditioning requirements: Part 50
But there is more! – The Part 58 appendices

1. Appendix A (and B in the future) – more later
2. Appendix C ARMs and Exceptions to Pb-TSP samplers
3. Appendix D Network Design:
   a. Geospatial scale
   b. Siting criteria
   c. Monitoring objectives

Established by Monitoring Plan and QAPP

You mean these are part of the QA program?
Yes, a site will either
- Meet established criteria
- Not meet established criteria, or
- Not meet established criteria, but has waiver
The FRMs specify, and SOPs and QAPPs should reflect key maintenance procedures.
General Requirements cont.

• And there is still more! --Part 58 appendices

3. Appendix E: Monitoring Path Siting Criteria for Ambient Air Quality Monitoring
   ▶ Horizontal and Vertical Placement.
   ▶ Spacing from Minor Sources.
   ▶ Spacing From Obstructions.
   ▶ Spacing From Trees
   ▶ Spacing From Roadways.
General Requirements cont.

BEFORE: Inlet height less than 1 meter from parapet

Courtesy of Laura Niles, CARB

Courtesy of Richard Guillot, EPA Region 4
General Requirements cont.

Courtesy of Thien Bui, EPA Region 8

Courtesy of Florida DEP
Reference: Appendix A Section 3.2 - 3.3

- **Field QA**
  1. Flow Verifications and Audits
  2. NIST-traceable Parametric measurement devices

- **Lab QA**
  1. Climate and Static controls
  2. Balance checks, blanks and Audits

- **Overall QA**
  1. Precision
  2. Bias
PM Flow Rate Verifications and Audits

You might ask “why are these important?”

- Designed to indicate sources of bias or relatively inaccuracy—
  - The cut point of the PM separators (size of the particles collected) are dependent on the flow rate
  - The final concentration value is directly influenced by the flow rate, i.e., 24-hour sample volume
## PM Flow Rate Verifications and Audits

### Effect of flow on cut point of particle size

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Kenny Data

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\[
d_{50} = 31.48Q^{-0.8963}
\]

Courtesy of MESA Labs. (BGI Inc)
Effect of flow on cut point of particle size

- At 14 Lpm the sampler will collect everything that is PM$_3$ or smaller

- A difference in real flow rate from 16.7 to 14 Lpm will permit particles to be collected that are 1.7 X larger than PM$_{2.5}$ ---remember volume ~ r$^3$!

- The effect on the Mass that is collected and therefore the apparent concentration will depend on the overall concentration of PM$_{3-2.5}$ relative to PM$_{2.5}$ and the density of that PM$_{3-2.5}$ fraction--maybe a little; maybe a lot!

Let’s see how dramatic it can be!
Effect of Flow on Concentration Value-a hypothetical case

\[ C_{\text{ind}} = \frac{221.8 \, \mu \text{g/filter} \times 1 \, \text{filter/event} \times 1000 \, \text{liters/m}^3}{16.7 \text{liters/min} \times 60 \, \text{min/hr} \times 24 \, \text{hr/event}} = 9.2 \, \mu \text{g/m}^3 \]

\[ C_{\text{act}} = \frac{221.8 \, \mu \text{g/filter} \times 1 \, \text{filter/event} \times 1000 \, \text{liters/m}^3}{14.0 \, \text{liters/min} \times 60 \, \text{min/hr} \times 24 \, \text{hr/event}} = 11.1 \, \mu \text{g/m}^3 \]

But what you probably don’t know is that the concentration of PM_{3-2.5} is 4 \mu g/m^3. So by having a real flow rate that is lower than what the sampler told you, your derived concentration was over 50% higher than the real PM_{2.5} Concentration of 7 \mu g/m^3!
PM Flow Rate Verifications and Audits

So,

• Do your Verifications
  • Monthly basis
  • Look at Avg Flow CV for each event

• Do your Audits
  • By Independent auditors or
    at least with independent, NIST-traceable standards

• Report results to AQS for data certification and AMP 256 Report

• Graph your results for identification of trends

A tribute to George Froelich
PM Flow Rate Verifications and Audits

Charting Sampler Performance

Percent Difference

Assessment Date

12/21/2012
12/21/2013
2/20/2013
3/22/2013
4/21/2013
5/21/2013
6/20/2013
7/20/2013
8/19/2013
9/18/2013
10/18/2013
11/17/2013
12/17/2013
1/16/2014
2/15/2014
3/17/2014
4/16/2014
5/16/2014

-15.00%
-10.00%
-5.00%
0.00%
5.00%
10.00%
15.00%

Flow Verifications
Flow Audits
PM Flow Rate Verifications and Audits

Daily Avg Flow CV

Sample Run Date

- Sample Run Dates from 12/21/2012 to 11/17/2013
- Daily Avg Flow CV values from 0% to 3.5%
- Data points scattered across the range with some concentrations at specific dates.
"Traceable" is defined in 40 CFR Parts 50 and 58 as meaning that a local or working standard has been compared and certified, either directly to, or to an intermediate standard that is no lower than one level from, a primary standard such as a National Institute of Standards and Technology Standard Reference Material (NIST SRM) or a USEPA/NIST-approved Certified Reference Material (CRM)"
Frequencies

- Verification, calibration and audit ("working") standards should be certified "at least annually"
- Traceable to a NIST "Primary Standard"
- 40 CFR Part 50, Appendix L Sec 9.1 & 9.2

What if I cannot send my 6 working standards to an independent Metrology Lab?
At a minimum, the “certification procedure” for a working standard should:

- 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;
- Include a test of the stability of the working standard over several days; and
- Specify a recertification interval for the working standard
What’s Happening…
in the LAB?

**Four Areas of Control**

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

Lab: Environment Control

Lab Temperature Control

Upper Temperature limit

Lower Temperature limit

Degrees °C

Date

7-Dec-12 27-Dec-12 16-Jan-13 5-Feb-13 25-Feb-13 17-Mar-13 6-Apr-13 26-Apr-13

Upper limit Standard Deviation Temperature

Standard Deviation °C

Date

7-Dec-12 27-Dec-12 16-Jan-13 5-Feb-13 25-Feb-13 17-Mar-13 6-Apr-13 26-Apr-13
Relative Humidity Control

% Relative Humidity

Weighing Date

Daily RH Standard Deviation

Daily % RH Std.Dev

Weighing Date


% Relative Humidity

Daily % RH Std.Dev

Weighing Date

Redundant monitoring devices can prevent pain!!
• 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 and faraday cages 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 venders.
LAB: Analytical Equipment

- 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

• Lab Blanks and Trip blanks, Batch and Inter-batch duplicates
  ➢ Indicate 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

- Internal and independent performance testing
  - Technician accuracy and precision
  - Bias between/among several Technicians

Captured PM2.5 Determined by Each Test Lab and NAREL

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Post Mass - Tare Mass (mg)

- 0.340
- 0.290
- 0.240
- 0.190
- 0.140
- 0.090
- 0.040
- 0.010
Lab: QC Practices
Lab Blanks

Filter Weight Difference (µg)

Post-Weigh Date

QC Limit: ± 15µg

Weight Difference
Chart Outliers
Linear Regression Trendline

1/1/08 4/1/08 7/1/08 9/30/08 12/31/08 4/1/09 7/1/09 9/30/09 12/31/09 4/1/10 7/1/10 9/30/10 12/31/10
Found procedural screen-cleaning error by back-up lab tech

Changed screen cleaning method; Began using MTL filters and increased Polonium 210 Exposure

Lost data due to RH Monitor
“Did you get the Drift?”
So How is Your Network Performing?

Data Quality Objectives

- **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 years at the PQAO level!
Where does the data come from?

- **Precision derived from Agency owned and operated collocated samplers**
  - Appendix A, Section 3.2.5

- **Bias provided by “independent” FRM samplers collocated with Primary samplers**
  - Appendix A, Section 3.2.7 Performance Evaluation Program
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
- Picture shows precision and PEP (Bias)
Why do we want to collocate samplers?

- There is no single physical “reference” standard, material or measuring device for (most aggregated forms of) PM.
- Therefore the only way to gain some level of confidence in a measurement is to:
  a. Insure the sampler or monitor is performing within design specifications and
  b. Independently check on its ability to reproduce the results that it achieves
  c. Establish that other instruments designed to measure the same values achieve the same or at least consistently-different results
About Collocated Samplers?

What is the primary sampler?

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

1. Make sure your primary sampler is designated correctly in AQS.
2. Know your order of data extraction for the purposes of precision and bias calculations
A couple more things to remember About Collocations!

1. In the FRM World a collocation sampler used for precision must be of identical design and operation (e.g., WINS to WINS; VSCC to VSCC)

2. With respect to deployment of the new FEMS, a collocation sampler will not be identical to the primary sampler. However it can provide a relative bias and a precision value if a sufficient number of collocated values are provided over an extended period of time.
   a. The average of the difference measurements provide the bias and
   b. The relative change in difference from one pair of measurements to the next provides the precision.
A few things regarding SLT Precision VS PEP Bias data

1. The monitoring agency (PQAO) has more control over how much precision data they generate and how fast the data becomes available.
   - At least 30 data points per year
   - Use their own site operators, gravimetric lab, or a contract gravimetric lab
   - Validation in-house

2. Less PEP Bias data is generated per PQAO and in general takes at least 60 days from the sampling event to posting in AQS
   - Usually not more than 9 data points per year
   - Always independent operators and gravimetric lab
Analyses you can get from your collocations

- Primary vs collocated scatter plot showing outliers
- Calculate and plot CV via the DASC tool
  - Overall CV
  - FRM-FRM
  - FEM-FRM
  - FEM-FEM, if you have FEM-FEM collocations
- 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.
  - trends in differences suggest trends in bias in one or both samplers.

**Ideal:** tight, slope \(\sim 0\), horizontal \(\sim 0\).

*Courtesy of Shelly Eberly*
Can Precision Data Give Insights into Bias?

- 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.

Bias: tight, slope ~ 0, horizontal at -4%.

Courtesy of Shelly Eberly
What do these indicate???

Noisy precision with possible upward trend in bias.

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

Courtesy of Shelly Eberly
What are the requirements and Process for Collocation

• 15% of the PQAO network monitors must be collocated (values of 0.5 and greater round up);
• At least 1 collocated monitor (if the number of network monitors is less than 3).
• The first collocated monitor must be a designated FRM monitor.
• In the case of PM10-2.5, Have at least 2 collocated monitors (if the total number of primary monitors is less than 10).
  • The second must be a monitor of the same method designation.
  • Both collocated FRM and FEM monitors can be located at the same site—based on each one’s purpose.
OK, How is it done for FEMs

1. The significant qualification is
   - The first collocation with an FEM that is proposed “primary sampler” must be with an FRM initially for a year prior to formal designation to verify that it is site/geo appropriate
   - A FEM that is a collocation monitor can only be placed with another FEM.

   **FEMs are not collocation monitors for FRMS**

2. Collocate 50% of the FEMs used by the PQAO, with identical FEMS and the other 50% of the monitors designated for collocation shall be accompanied by a audit FRM.
• **Collocates** an **independent** FRM audit sampler beside a FRM/FEM

• Applies **rigorous performance and QA/QC requirements** to field and laboratory operations

• Provides **independent assessment** of **network sampler bias**

• Might indicate if the monitoring agency’s FRM is experiencing performance issues, **BUT**
  - 60 days after the fact!
  - It is only 1 data point for one isolated sampling event
• PEP Requirements 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**
  • At least one of each “monitor type” audited each year, including “regulatory” FEMs and SPMS

\[ \text{Bias} = \frac{\text{SLTPrim} - \text{PEP}}{\text{PEP}} \]
USES for PEP Bias data

Alabama PEP vs Precision

8/11/2014

2014 National Air Monitoring Conference
• Collocated (precision) Requirements
  • 15% of sites in PQAO
  • Hi-vols TSP cannot be Surrogate Primary samplers for PM\textsubscript{10}
  • PM\textsubscript{10-2.5} Primary Samplers may constitute a Primary PM\textsubscript{10}
    Sampler provided same method designation
  • Low-vol Pb and PM\textsubscript{10} samplers may serve as collocations for each other, in which case
    • Total Mass of Pb filter must be measured before chemical analysis for Pb
• There are practical minimum limits on the DQOs for PM Methods
  • At certain Concentrations the Statistics do not provide data for Collocated Sampler or PEP measurements
    • (1) TSP: 20 μg/m3.
    • (2) Pb: 0.15 μg/m3.
    • (3) PM10 (Hi-Vol): 15 μg/m3.
    • (4) PM10 (Lo-Vol): 3 μg/m3.
    • (5) PM10–2.5 and PM2.5: 3 μg/m3.