The Role of QA in Determination of Effects of Shipping Procedures for PM2.5 Speciation Filters

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Overview

- The Evolution of the shipping study
- The Data Quality Objectives
- The Measurement Quality Objectives
- The Data Starts to Speak
- The Lessons Learned
Why is the Shipping Study Important?

- The current PM2.5 speciation trends and supplemental network annual shipping bill: $1,600,000
- EPA Budget shrinking
- National Monitoring Strategy evolving
- Speciation QA program beefing up
Whoa!!!! Speciation? What are We Talking About?

- PM2.5 Chemical composition
- 24 - hr. integrated filter samples-3 media
- Multiple analyses
  - Gravimetric
  - Chromatographic
  - X-ray fluorescence and Thermo optical
- Results used for pollutant source attribution in SIP development
What Makes Speciation Shipping Expensive?

- ~250 sites collecting filter samples
  - 1 in 3 day or 1 in 6 day sampling -50/50
- Cold shipping requirement
  - Coolers with ice packs - 35 lbs (16 kg)
  - Overnight delivery
  - Both Ways
  - Average $40 per cooler one way
Why ship cold?

Prevent losses of semi-volatiles?
How to Attack the Question

Devise a study where we can limit variables to just the procedure by which the sample filters are shipped.

Seems simple enough............

Doesn’t it ???
What are the Challenges

- Three different filter media: Teflon, Nylon, Quartz
- Which Sites do we pick
  - Lab vs reality?
  - Dominant Semi-volatiles: nitrates and organics
- Time!! – limited windows for optimum effect
- Money!! – adequate number of events $$$
- Quality!! – Instrument variability; operators’ experience and expertise
## The Study

| Sites: dominant pollutants | Atlanta: sulfates, organic carbon  
|                           | Riverside, CA: nitrates  
|                           | Tacoma, WA: woodsmoke carbon  
| Instruments               | 2 Collocated Metone™ SASS  
| Channels per filter media | 1-2, 2-1 Teflon alternating days  
|                           | 2-1, 1-2 Nylon alternating days  
|                           | 2- Quartz  
| Target no. sampling events | 30 24-hr periods  

Data Quality Objectives

First approximation – reliance on network data for collocated instruments

<table>
<thead>
<tr>
<th>Species</th>
<th>Collocated Average (Abs Rel Diff)</th>
<th>Lab Average (Abs Rel Diff)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>9.3%</td>
<td>4.6%</td>
</tr>
<tr>
<td>Organic C</td>
<td>14.2%</td>
<td>5.5%</td>
</tr>
<tr>
<td>Sulfate (IC)</td>
<td>8.2%</td>
<td>3.9%</td>
</tr>
</tbody>
</table>

Courtesy of James Flanagan, et.al., Ref 1.
Decision Points

Differences in measured pollutant concentrations would constitute a discernable and significant impact by ambient shipping if the values were at the 95% confidence limit:

- >10% for mass,
- >15% for nitrate and ammonium,
- >20% organic carbon, and
- >7% for sulfate.

Ref [2], [3], [4]
The Lynch-pin of the Study: Measurement Quality Objectives

- Flowrates 6.7 l/min
- Paired Channel Concentrations within network collocated values
Measurement Quality Control

- Careful Instrument installation and calibration
- Operator Training
- Weekly Flowchecks and recalibration
- Trip and Field Blanks
- Skipped rainy days
Gravimetric Mass: Cold vs Ambient Shipping

Using Averages of paired channels against a single

\[ y = 0.9995x + 1.2087 \]

\[ R^2 = 0.9434 \]
Comparison of Channels 2 & 3 Collecting Total Mass Shipped Cold and Ambient

Compared Channels 2 & 3 on each instrument when loaded with Teflon Filters

Cold-Shipped
Slope = 0.926
Intercept = 0.417
$r^2 = 0.977$
RSD = 0.044

Ambient-Shipped
Slope = 1.044
Intercept = -1.51
$r^2 = 0.983$
RSD = 0.048 ug/m³
Comparison of Sulfates on Channels 1 & 2
Nylon Filters

Channel 1 (ug/m³)

Channel 2 (ug/m³)

Cold shipped
\[ y = 0.9977x + 0.2183 \]
\[ R^2 = 0.9971 \]
Sulfate from Cold- vs Ambient-Shipped Nylon Filters

\[ y = 0.9737x - 0.0017 \]

\[ R^2 = 0.9897 \]
Lessons Learned

- The DQO process helps design the study
- Setting and diligently pursuing MQO’s is crucial to getting believable results
  - Make sure the instrumentation is completely serviced
  - The Data Quality Assessment can reveal things about the network
  - Weather can be a huge determinant factor
- Scope of this kind of study is a challenge logistically
  - Labor, materials and hardware (boxes), scheduling
Conclusions

- Appears Instruments sampled consistently on Nylon and Teflon Channels (#1-3)
- Some loss of mass does seem noticeable, but the difference appears to be within network variability DQOs.
- Sulfates do not appear to affect loss of mass
- More analysis of the Nitrate and carbon losses and variability should be conducted
References


