Uncertainties in PM2.5 Gravimetric and Speciation Measurements and What Can We Learn from Them

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Non-urban and urban PM$_{2.5}$ networks

Interagency Monitoring of PROtected Visual Environments (IMPROVE) Network

Chemical Speciation Network (CSN)
Neighborhood- and Urban-Scale Monitoring Objectives

• Determine compliance with air quality standards
• Validation of regional scale models
• Assess source/receptor relationships
• Evaluate health, radiative, and ecological effects
IMPROVE Monitoring Objectives

- Tracking long term temporal changes in visibility (extinction)
- Assess source/receptor relationships
- Serve as a regional backdrop for special studies and understanding non urban background
- Used for regional modeling validation studies
OBJECTIVES

- Estimate average bias in gravimetric PM2.5 measurement
- Estimate average bias in reconstructed PM2.5 from measured aerosol species
- Estimate average bias in reconstructed extinction using standard IMPROVE algorithms
PM$_{2.5}$ Federal Reference Methods (FRMs)

Andersen RAAS
Thermo Fisher Scientific, formerly Andersen Instruments, Smyrna, GA

BGI PQ-200
BGI, Inc., Waltham, MA

Partisol Sampler
Thermo Fisher Scientific, formerly Rupprecht & Patashnick, Albany, NY

URG MASS
URG Corp., Raleigh, NC
Speciation Monitors (EPA Speciation Network)

Mass Aerosol Sampling System (MASS)
URG Corporation, Raleigh, NC

Reference Ambient Air Sampler (RAAS)
Andersen Instruments, Smyrna, GA

Spiral Aerosol Speciation Sampler (SASS)
Met One Instruments, Grants Pass, OR

Interagency Monitoring of Protected Visual Environments (IMPROVE) Sampler
Air Resource Specialists, Ft. Collins, CO
Other Speciation Monitors

Partisol 2300 Speciation Sampler
*Rupprecht & Patashnick, Albany, NY*

Dual Channel Sequential Filter Sampler
and Sequential Gas Sampler
*Desert Research Institute, Reno, NV*

Dichotomous Virtual Impactor
*Andersen Instruments, Smyrna, GA*

Paired Minivols
*Airmetrics, Inc., Springfield, OR*

URG 3000N Speciation Sampler
*URG Corporation, Raleigh, NC*

Dichotomous Partisol-Plus Sampler
*Rupprecht and Patashnick, Albany, NY*
## Sampler Design Characteristics

<table>
<thead>
<tr>
<th>Variable</th>
<th>IMPROVE</th>
<th>CSN</th>
<th>CSN</th>
<th>CSN</th>
<th>CSN</th>
<th>CSN</th>
<th>CSN</th>
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<tbody>
<tr>
<td>Network</td>
<td>IMPROVE</td>
<td>CSN</td>
<td>CSN</td>
<td>CSN</td>
<td>CSN</td>
<td>CSN</td>
<td>CSN</td>
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<tr>
<td>Sampler type</td>
<td>IMPROVE</td>
<td>Andersen</td>
<td>Met One SASS</td>
<td>URG MASS</td>
<td>R&amp;P2300</td>
<td>R&amp;P2025 sequential FRM</td>
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<tr>
<td>Number of Sites (2006)</td>
<td>181</td>
<td>18</td>
<td>179</td>
<td>6</td>
<td>14</td>
<td>22</td>
<td></td>
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<tr>
<td>Number of Channels</td>
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<td>4</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>2</td>
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<tr>
<td>Flow Rate</td>
<td>22.7l/min</td>
<td>7.3l/min</td>
<td>6.7l/min</td>
<td>16.7l/min</td>
<td>10.0l/min</td>
<td>16.7l/min</td>
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<tr>
<td>Filter Face Velocity</td>
<td>107.2cm/sec</td>
<td>10.3cm/sec</td>
<td>9.5cm/sec</td>
<td>23.7cm/sec</td>
<td>14.2cm/sec</td>
<td>23.6cm/sec</td>
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<tr>
<td>Sampling Frequency</td>
<td>3rd day</td>
<td>3rd day</td>
<td>3rd day</td>
<td>3rd day</td>
<td>3rd day/6th day</td>
<td>3rd day/6th day</td>
<td></td>
</tr>
<tr>
<td>Quartz Filter Pack Configuration</td>
<td>Q For QBQ</td>
<td>QF</td>
<td>QF</td>
<td>QF</td>
<td>QF</td>
<td>QF</td>
<td></td>
</tr>
<tr>
<td>Quartz Filter Type</td>
<td>25mm Pall</td>
<td>47mm Whatma</td>
<td>47mm Whatma</td>
<td>47mm Whatma</td>
<td>47mm Whatma</td>
<td>47mm Whatma</td>
<td></td>
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</tbody>
</table>
Sampler Intercomparison and Artifact Correction

• 1) Comparison of carbon across samplers
  – Warren H. White, 16 April 2008 EPA workshop

• 2) Converting the CSN carbon concentrations to match IMPROVE on the average
  – Accounting for positive additive and multiplicative negative artifacts
  – Accounting for different thermal optical methods.
Comparison of IMPROVE and CSN Carbon at Collocated Sites

urban collocations of CSN and IMPROVE carbon measurements
• The EC difference between CSN and IMPROVE shows little dependence on the CSN sampler, suggesting that it is mainly analytical.

• IMPROVE:TOR (DRI) – CSN: TOT(NIOSH)
For TC, unlike EC, different CSN samplers show different biases relative to IMPROVE.

Note that the CSN offset is not determined simply by flow rate.
The CSN offset shows no obvious seasonality. In that respect it behaves more like IMPROVE field blanks than IMPROVE backup filters.
Relating IMPROVE and CSN TC
Making CSN look like IMPROVE

• Recall
  - Measured TC has a positive OC artifact.
    - IMPROVE corrects for the artifact but CSN does not
  - IMPROVE TC has a negative multiplicative artifact due loss of OC from high face velocities (FV)
    - IMPROVE FV = 107.2 cm/s
    - CSM MetOne FV = 9.5 cm/s
  - Assume CSN negative artifact is 0

• Then

\[
[TC]^{\text{IMP}} = [TC] - B^{\text{IMP}}[\text{OC}] \\
[TC]^{\text{CSN}} = [TC] + A^{\text{CSN}}/V_{\text{MetOne}}
\]

- B - multiplicative artifact
- A/V – additive artifact

• Combine

\[
[TC]^{\text{CSN}} = [TC]^{\text{IMP}} + B^{\text{IMP}}[\text{OC}] + A^{\text{CSN}}/V_{\text{MetOne}}
\]
The multiplicative artifact \((1+b_{\text{OC}})\) and the monthly positive additive organic artifact \((a)\) used to relate CSN and IMPROVE carbon concentrations. The units for the positive artifacts are \(\mu\text{g/m}^3\) and \(1+b_{\text{OC}}\) is unitless.

<table>
<thead>
<tr>
<th>Month</th>
<th>MetOne</th>
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<tbody>
<tr>
<td>(1+b_{\text{OC}})</td>
<td>1.2</td>
</tr>
<tr>
<td>(a_{\text{Jan}})</td>
<td>1.1</td>
</tr>
<tr>
<td>(a_{\text{Feb}})</td>
<td>1.3</td>
</tr>
<tr>
<td>(a_{\text{Mar}})</td>
<td>1.2</td>
</tr>
<tr>
<td>(a_{\text{Apr}})</td>
<td>1.4</td>
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<tr>
<td>(a_{\text{May}})</td>
<td>1.6</td>
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<td>(a_{\text{Jun}})</td>
<td>1.7</td>
</tr>
<tr>
<td>(a_{\text{Jul}})</td>
<td>1.8</td>
</tr>
<tr>
<td>(a_{\text{Aug}})</td>
<td>1.9</td>
</tr>
<tr>
<td>(a_{\text{Sep}})</td>
<td>1.5</td>
</tr>
<tr>
<td>(a_{\text{Oct}})</td>
<td>1.2</td>
</tr>
<tr>
<td>(a_{\text{Nov}})</td>
<td>1.0</td>
</tr>
<tr>
<td>(a_{\text{Dec}})</td>
<td>1.1</td>
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</table>
Comparison of CSN and adjusted CSN to IMPROVE Carbon

![Graph showing the comparison of CSN and adjusted CSN to IMPROVE Carbon](image-url)
Governing equations

\[ PM_{2.5} = \left[ xSO_4 + NH_4 NO_3 \right] f'_{inorg}(RH_{lab}) + OCR_{oc} \left( \text{lots of stuff} \right) + LAC + Soil + SSf'_{ss}(RH_{lab}) \]

• \( x = \frac{(NH_4)_2SO_4/H_2SO_4}{ \leq 1.35 \) – lowest in summer – acidic aerosol

• \( f'(RH_{lab}) = \left( \frac{\rho_{\text{mix,species}}}{\rho_{\text{species}}} \right)^3 \left( \frac{D}{D_0} \right)^3 (RH_{lab}) \) highest in summer \( (D/Do)^3 \approx 1.3 \)

• FM biased low because of volatilization (nitrate, SVOC, etc?)
• \( R_{oc} \) (lots of stuff) probably highest in summer months
• \( f'_{ss}(RH_{lab}) \approx 1.3 \)
• LAC may have a multiplier
• Soil may have some seasonal and spatial dependence
Bias Between Estimated Fine Mass and Gravimetric Fine Mass and
Bias as function of mass

$$\text{PM2.5} = 1.375 \times \text{SO}_4 + 1.29 \times \text{NO}_3 + 1.8 \times \text{OC} + \text{Other}$$
Temporal plot of PM2.5-PM2.5avg and the percent difference between reconstructed and gravimetric mass (Brigantine WR)

\[
\%DM = \left\{ \frac{(PM2.5 - RPM2.5)}{PM2.5} \right\} \times 100 = b_1 + b_2 \cos(f(T))
\]
Average percent seasonal variability between reconstructed and gravimetric mass for the IMPROVE monitoring network

\[%DM=\frac{(PM2.5-RPM2.5)}{PM2.5} \times 100 = b1+b2(\cos(f(T)))\]
Average percent bias between reconstructed and gravimetric mass for the IMPROVE monitoring network. The red or green color indicates that reconstructed mass is an over or underestimate of gravimetric mass respectively.
<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Std Dev</th>
<th>Min</th>
<th>Max</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Seasonal Variability (IMPROVE)</td>
<td>14.9</td>
<td>6.14</td>
<td>0.0</td>
<td>26.7</td>
<td>158</td>
</tr>
<tr>
<td>% Seasonal Variability (CSN)</td>
<td>7.6</td>
<td>4.51</td>
<td>0.0</td>
<td>19.0</td>
<td>168</td>
</tr>
<tr>
<td>AVG BIAS (IMPROVE)</td>
<td>-3.9</td>
<td>4.44</td>
<td>-17.9</td>
<td>9.4</td>
<td>158</td>
</tr>
<tr>
<td>AVG BIAS (CSN)</td>
<td>3.4</td>
<td>7.00</td>
<td>-17.7</td>
<td>22.7</td>
<td>168</td>
</tr>
</tbody>
</table>
Assumptions

• Do not account for volatilization of SVOC’s
• SVOC loss on Teflon and quartz substrates are the same
• Gravimetric mass of soil dust, seasalt, and non-volatilized POM are measured without bias
• Nitrate and sulfates are measured without loss on nylon substrate and nitrate and sulfates are fully ammoniated
Stacked bar charts showing average concentrations of each species for all and seasonal data for IMPROVE, CSN suburban, and CSN urban.
Inorganic water retention, nitrate loss and Roc factor

PM2.5 = a1*1.375*SO4 +a2*1.29*NO3+a3*OC+a4*Other
Comparison of regression and ratio method for estimating Roc

- Other = (NH₄)₂SO₄ + NH₄NO₃ + Soil + LAC + SS
- POM = FM - Other
- R_{oc} = (FM - Other) / OC
PM2.5-RPM2.5 = \sum_{i} (FM_{i} - RFM_{i})

= \left( PM2.5_{SO4} - 1.375 \times SO_{4} \right) + \left( PM2.5_{NO3} - 1.29 \times NO_{3} \right) + \left( PM2.5_{POM} - 1.8 \times OC \right) + \left( PM2.5_{other} - Other \right)

SUM of Bias IMPROVE

Average Winter Spring Summer Fall

Concentration (ug/m^3)

Bias (Center City)

Average Winter Spring Summer Fall

Concentration (ug/m^3)

Bias (Suburban)

Average Winter Spring Summer Fall

Concentration (ug/m^3)

SUM

FMNO3-1.29*NO3
FMPOM-1.8*OC
FMSO4-1.375*SO4
FMother-Other
SUM
Assumptions for estimating gravimetric and reconstructed mass bias sans accounting for SVOC loses

- Weighing of Teflon filter includes retained water on sulfate and nitrate aerosols
- Nitrate and sulfates are measured without loss on nylon substrate
- Organic volatilization from Teflon and quartz substrates are the same
- Gravimetric mass of total carbon, soil dust, and sea salt determined without bias

**Gravimetric:**

\[
PM2.5 \text{ Bias} = (a_1 - 1) \times 1.375 \times SO_4 + (a_2 - 1) \times 1.29 \times NO_3
\]

**Reconstructed:**

\[
RPM2.5 \text{ Bias} = (1.8 - a_3) \times OC + (1 - a_4) \times \text{Other}
\]
Average bias in gravimetric and reconstructed PM2.5 mass concentration for the IMPROVE and CSN datasets

**FM Bias on Teflon filter**

<table>
<thead>
<tr>
<th>Season</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Fall</th>
<th>AVG</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVG</td>
<td>1.20</td>
<td>0.80</td>
<td>1.00</td>
<td>1.00</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**Reconstructed Mass Bias**

<table>
<thead>
<tr>
<th>Season</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Fall</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPROVE</td>
<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>Suburban</td>
<td>1.00</td>
<td>1.00</td>
<td>1.50</td>
<td>1.50</td>
<td>1.20</td>
</tr>
<tr>
<td>City Center</td>
<td>1.50</td>
<td>1.50</td>
<td>2.00</td>
<td>2.00</td>
<td>1.80</td>
</tr>
</tbody>
</table>

- AVG: Average
Seasonal and spatial variability in fine gravimetric mass bias for the CSN monitoring network.
Seasonal and spatial variability in fine gravimetric mass bias for the IMPROVE monitoring network
Seasonal and spatial variability in reconstructed mass bias for the CSN monitoring network.
Seasonal and spatial variability in reconstructed mass bias for the IMPROVE monitoring network

PM$_{2.5}^{\text{measured}}$ - PM$_{2.5}^{\text{reconstructed}}$
• Approximately 20% of OC is volatilized in the IMPROVE sampling system
• The Roc factor (POM/OC) has a seasonal dependence that varies from about 1.4 in the winter to 1.6-1.8 in the summer
• Urban/suburban Roc factors may be marginally higher than rural factors
• Nitrate volatilization from the Teflon substrates vary from about 10% in the winter to 35-40% in the summer
• There doesn’t appear to be a systematic difference in nitrate volatilization between CSN and IMPROVE monitoring sites
• About 20% of inorganics species mass is retained water
SUMMARY (Cont)

- Bias between PM2.5 gravimetric and reconstructed mass is lowest (negative) in winter and highest (positive) in summer.
- This bias is primarily driven by assuming a constant Roc factor and retained water by inorganic species.
- Gravimetric PM2.5 in CSN network is biased high by one to two ug/m3 in most the east and during the summer biased low by about two ug/m3 in southern California.
- IMPROVE reconstructed mass is biased high during all seasons but highest in winter. During summer it is biased low in the desert southwest.
END
IMPROVE TC, ug/m³

CSN-STN TC, ug/m³

MetOne
Anderson
R&P
URG

2005

CSN TC, ug/m³

IMPROVE TC+, ug/m³

MetOne
Anderson
R&P
URG

6.7 lpm
7.3 lpm
16.7 lpm
16.7 lpm
Considerably more scatter is observed in routine CSN measurements by collocated MetOne samplers, particularly in the earlier years.

Data are from Bakersfield, *Boston, *Cleveland, *New Brunswick* and Rubidoux.

* **Not** collocated with IMPROVE
EXPECTATION:

\[ [TC]^{CSN} = [EC]^{IMP} + (1 + B^{IMP} \times)[OC]^{IMP} + A^{CSN}/V_{\text{MetOne}} \]

OLS REGRESSION:

\[ [TC]^{CSN} = (1 + b_{EC})[EC]^{IMP} + (1 + b_{OC})[OC]^{IMP} + a_1 + \ldots + a_{12} + e \]

2005-6 observations at 7 MetOne sites (excluding Phoenix):

- \( b_{EC} = 0.008 (+/-0.05) \)
  - no sampling artifact for IMPROVE EC
- \( b_{OC} = 0.22 (+/-0.03) \)
  - ~20% sampling loss for IMPROVE OC
- \( \text{rms}(e) = 0.9 \, \text{ug/m}^3 \)  \( r^2 = 0.94, \, n = 728 \)

\( a_{mm} \rightarrow \) next slide
**EC** – the short story:

- $\varepsilon_{\text{IMP}} \equiv 0$, $\varepsilon_{\text{IMP}} = \text{artifact } \_ \text{adj}$

- $\text{IMP}_{\text{new}} \equiv \alpha CSN$, $\alpha > 1$

- $CSN_{\phi} \equiv CSN_{\varphi}$, $\phi \neq \varphi$ samplers

- EC has little to no positive artifact for both IMPROVE and CSN

- Multiplicative bias between CSN and IMPROVE that is sampler independent
TC – the short story:

\[ \varepsilon_{\text{IMP}} = \text{artifact } _{\text{adj}} \]

\[ \text{IMP}_{\text{new}} \equiv \lambda (\text{CSN} - \theta), \quad \lambda < 1, \theta > 0 \]

\[ \text{CSN}_\phi \neq \text{CSN}_\varphi, \quad \phi \neq \varphi \quad \text{samplers} \]
Relating IMPROVE and CSN EC
Making CSN look like IMPROVE

- Recall
  - EC has little to no positive artifact for both IMPROVE and CSN
  - CSN and IMPROVE have a multiplicative bias that is sampler independent

- $EC_{\text{IMP}} = \alpha \times EC_{\text{CSN}}$
- $\alpha \approx 1.3$
Non-urban and urban PM$_{2.5}$ networks

Interagency Monitoring of PROtected Visual Environments (IMPROVE) Network

Chemical Speciation Network (CSN)

Virgin Islands
Ammonium Nitrate
Fine Soil

[Map of the United States showing distribution of fine soil with color scale indicating ug/m3]