Comparison of the STN and IMPROVE Networks for Mass and Selected Chemical Components
(Preliminary Results)

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Regional Planning Organization Technical Meeting
St. Louis, MO
November 5, 2003
Credits

Taken from Presentation by Paul Solomon to State Air Monitoring Working Group
San Francisco, CA
October 16-18, 2003
STN - IMPROVE Networks Comparison Study

**Over Arching Questions**

- Is there a Difference Between the Two Networks and for Which Species?
- If Yes, How Large?
- Does Bias Matter Or is Consistency More Important?
  - Do We Need to Know Absolute Concentrations?
    - If Yes, Which Network Provides EPA the Least Bias Results for Implementation Needs???
  - Is Highly Correlated Data Sufficient?
- Can We Define the Bias and Uncertainty in Either Network, Between Networks?
- Can We Make Improvements to Existing Protocols in Either/Both Networks to Reduce Uncertainty in the Results
Cradle to Grave Comparative Protocol Analysis

- It is Not Just the Analysis Methods
- From Monitor Inlet* to Data Mgmt
  - Sample Collection
  - Handling, Shipping, and Storage (after collection)
  - Chemical Analysis
    - Extraction
    - Analysis Methods
  - Standards
    - Or Lack Thereof for Ambient Field PM Measurements
  - Data Manipulation
    - Blanks, Artifacts

* Begins w/ Filter Purchase, Acceptance Testing, Handling, & Storage
STN Sample Collection

Components - Affects

Inlet and Fractionators:
- Efficiency Curve (Slope & Cutpoint)
- Wall Losses

Manifold: Wall Losses

Transfer Lines:
- Wall Losses

Denuders:
- Efficiency
- Capacity
- Selectivity

Filter - Inert
- Loss of Volatiles
- Blank Levels
- Flow Rate/Face Velocity

Filter - Reactive
- Efficiency
- Capacity
- Selectivity
- Stability
- Blank Levels

Air Flow

Inlet

Cyclone Fractionator

Wins Impactor

Manifold

MgO Denuder

Quartz

Teflon

Nylon

Manifold

MgO Denuder

Teflon

Nylon

Quartz

Sampler Housing

Pump

* Initially MgO

OC, EC

Mass, Elements by XRF

SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, K$^+$, Na$^+$

Mass, Elements, Ions

OC, EC

AND

MET

URG
EPA EPA

Mass, Elements by XRF*, PESA

Size Selective Inlet

Size Selective Cyclone

Teflon Filter

Pump

Sampler Housing

* Enhanced Sensitivity

Air Flow 22.7 Lpm

SO_{4}^{2-}, NO_{3}^{-}, NH_{4}^{+}

Size Selective Inlet

Size Selective Cyclone

Nylon Filter

Pump

Sampler Housing

OC, EC

Size Selective Inlet

Size Selective Cyclone

Quartz Filter

Pump

Sampler Housing
Chemical Analysis Methods

- Filter Purchase, Acceptance, & Pretreatment
- Storage and Handling (Before & After Collection)
- Mass - Gravimetric using Teflon Filter
  - STN - FRM Protocol
  - IMPROVE - Similar
- Trace Elements - Teflon Filter
  - STN - XRF only
  - IMPROVE - XRF with Enhanced Sensitivity, PESA (H, other?)
Post Sample Analysis

**Data Manipulation**

- **Blank Correction**
  - How, When, Why
- **Artifact Correction**
  - How to Define
  - How to Correct?
- **STP?**
- **Others**
How Might Protocols Affect Results Between Networks*

- **Inlets**
  - Effect of Slope of Efficiency Curve
  - Cutpoint

- **Flow Rate Differences**
  - Effect of Pressure Drop/Face Velocity/Residence Time
    - Influences Collection of Semi-Volatiles
      - Negative vs Positive Artifacts
      - Blank Values Likely Different

- **Shipping and Storage**
  - STN at Reduced Temperatures
  - IMPROVE at Ambient Temperatures
    - Influences Collection of Semi-Volatiles

* Not an Exhaustive List
Use of IMPROVE in Urban Areas

- Higher Flow Rate, Smaller Filters
  - Filter Clogging Potential
  - Denuder Capacity and Efficiency
    - Na$_2$CO$_3$ vs MgO
    - Refurbishing Frequency of Na$_2$CO$_3$
  - Effect on Semi-volatiles
Given All these Differences, Do the Networks Provide Similar Results for Mass and the Components of Mass?
Methods Comparison Study: STN-IMPROVE

Operated According to Each Network’s Protocols

STN/IMPROVE Monitoring Intercomparison

- Mt. Rainier NPS
- Phoenix
- Tonto National Monument
- Haines Point, NPS
- Seattle
- Beacon Hill
- USDA FS Dolly Sods Wilderness
- Anderson RAAS 401 STN Samplers
- USDA FS Dolly Sods Wilderness
- Met One SASS STN Samplers
- USDA FS Dolly Sods Wilderness

- Official or designated STN site, host to IMPROVE sampler
- Official IMPROVE site, host to STN sampler
Urban – Rural Temporal Analysis Comparison: PM2.5 Mass

**Haines Point**

**Dolly Sods**

**Phoenix**

**Tonto**
Urban - Rural Comparison of Means: PM2.5 Mass

Annual Average Results

- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 50-100%
- There Is Better Agreement at Urban Sites, but Not Necessarily Due Just to Higher Pollution Levels
Frequency Distributions Analysis: Mass (Paired Values)

- Log Normal if Mean Is Greater Than Median
- If Notches Do Not Overlap – Distribution Median is Different at the 95% Confidence Limit
- Data As Supplied by Network
- Oct 01 – Sept 02
- Investigation of Outliers Continuing
Urban - Rural Comparison of Means: Sulfate

Comparison of Annual Average Sulfate During the 6 Site STN-IMPROVE Comparison Study

Annual Average Results
- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 35->200%
- There Is Better Agreement at Urban Sites, and May be Related to Higher Pollution Levels
Urban - Rural Temporal Analysis Comparison: Nitrate

Haines Point

Dolly Sods

Phoenix

Tonto
Urban - Rural Comparison of Means: Nitrate

Comparison of Annual Average Nitrate During the 6 Site STN-IMPROVE Comparison Study

- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 200-400%
- Rural Sites Tend to Agree Better Than Urban Sites, Which May Be Due to Difference in Denuder Protocols
Urban - Rural Temporal Analysis Comparison: OC

STN vs. IMPROVE Chemical Speciation for Organic Carbon at Haine’s Pt - Washington

Chemical Speciation for STN vs. IMPROVE for Organic Carbon at Dolly Sods from 10-01 to 9-02

Chemical Speciation for STN vs. IMPROVE for Organic Carbon at Puget Sound-Beacon Hill from 10-01 to 9-02

STN vs. IMPROVE Chemical Speciation for Organic Carbon at Mt. Rainier
Urban – Rural Comparison of Means: OC

Blank Values Are Based on Trip and Field Blanks for the Averaged Over the Time Period of the Study

Annual Average Results
- East and West Coast Sites Can Have Similar Concentrations
- Urban Site Levels Exceed Rural Sites by 200-500%
- Rural Sites Tend to Agree Better Than Urban Sites Before Blank Correction
- Blank Correction Improves Agreement at Urban and Rural Sites

Blank Correcting Improved the Comparison Between STN and IMPROVE at Most Locations

Comparison of Annual Average OC During the Six Site STN-IMPROVE Comparison Study

<table>
<thead>
<tr>
<th>Location</th>
<th>OC STN</th>
<th>OC IMPROVE</th>
<th>OC STN Blank Corr</th>
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<tbody>
<tr>
<td>Haine's Pt</td>
<td>3.5</td>
<td>2.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Dolly Sods</td>
<td>2.8</td>
<td>2.3</td>
<td>1.0</td>
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<tr>
<td>Phoenix</td>
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<tr>
<td>Tonto</td>
<td>1.5</td>
<td>1.0</td>
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</tr>
<tr>
<td>PUSO</td>
<td>2.2</td>
<td>1.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Urban - Rural Temporal Analysis Comparison: EC

Chemical Speciation for STN vs. IMPROVE for Elemental Carbon at Haine’s Pt from 10-01 to 9-02

Chemical Speciation for STN vs. IMPROVE Elemental Carbon for Dolly Sods from 10-01 to 9-02

Chemical Speciation for STN vs. IMPROVE for Elemental Carbon from 10-01 to 9-02

STN vs. IMPROVE Chemical Speciation for Elemental Carbon at Dolly Sods

Locations:
- Haines Point
- Dolly Sods
- Beacon Hill
- Mt Rainier
Urban - Rural Comparison of Means: EC

Annual Average Results
- EC Data Did Not Require Blank Correction
- Factor of 2 Not Observed Between STN and IMPROVE At Urban Sites
- Urban Sites Are ~ 2X Rural Sites
- Better Agreement Is Observed at Rural Sites Than Urban
- QA Is In Process to Ensure This Is Valid Data
Urban – Rural Temporal Analysis Comparison: Fe

1. IMPROVE vs. STN Chemical Speciation for Haine’s Pt - Washington
   - **Haines Point**

2. STN vs. IMPROVE Chemical Speciation for Iron at Dolly Sods from 10-01 to 9-02
   - **Dolly Sods**

3. Chemical Speciation for IMPROVE vs. STN at Phoenix from 10-01 to 9-02
   - **Beacon Hill**

4. Chemical Speciation for STN vs. IMPROVE for Iron at Tonto from 10-01 to 9-02
   - **Mt Rainier**
Urban - Rural Comparison of Means: Fe

Annual Average Results
- Concentrations are Higher in Urban Areas Than Rural Areas
- Phoenix Has the Highest Concentrations, Mt. Rainier the Lowest
- With the Exception of Phoenix and Tonto Agreement is Similar Between Rural and Urban Sites
- QA Is in Progress to Ensure This Is Valid Data
Urban - Rural Temporal Analysis Comparison: Arsenic

- **Haines Point**
  - STN vs. IMPROVE Chemical Speciation for Arsenic at Haine's Pt - Washington

- **Beacon Hill**
  - Chemical Speciation for STN vs. IMPROVE for Arsenic at Puget Sound-Beacon Hill from 10-01 to 9-02

- **Dolly Sods**
  - Chemical Speciation for STN vs. IMPROVE for Arsenic at Dolly Sods 10-01 to 9-02

- **Mt Rainier**
  - STN vs. IMPROVE Chemical Speciation for Arsenic at Mt. Rainier
Frequency Distributions Analysis: Arsenic

- Distributions at a Given Sites Are Not Similar Between Networks
- Notches Do Not Overlap at Any of the Sites
- Cr Similar to As
Urban - Rural Temporal Analysis Comparison: Zn & Pb

Haines Point

Chemical Speciation for STN vs. IMPROVE for Zinc at Haine’s Pt - Washington

Zn

Dolly Sods

Chemical Speciation for STN vs. IMPROVE for Zinc at Dolly Sods from 10-01 to 9-02

Phoenix

Chemical Speciation for STN vs. IMPROVE for Lead at Phoenix from 10-01 to 9-02

Pb

Tonto

Chemical Speciation for STN vs. IMPROVE for Lead at Tonto from 10-01 to 9-02
Distributions at a Given Site Are Similar Between Networks

However, Notches Do Not Always Overlap*

Pb Similar to Zn
Urban - Rural Temporal Analysis Comparison:

- Concentrations at Rural Sites Were Lower Than Urban Sites for Most Species at Most Sites
- Less Consistency (Greater Scatter) Was Observed at Rural Sites Than Urban Sites Between Networks
- Higher Data Capture Was Observed at Urban Sites
- Mass and Sulfate Agreed Well (typically within 20%) at All Sites
- Nitrate Agreed Better at Rural Sites Than Urban Sites, Which May Be Due to Differences in Denuder Protocols
- Organic Carbon Agreed Better After STN Data Were Blank Corrected, IMPROVE Was Already Blank Corrected
- Potentially Toxic Species (As, Cr, Pb, Zn) Showed Greater Scatter and Less Agreement Than Mass and Sulfate
- Higher Concentration Species Agreed Better than Species Observed at Lower Concentrations: MDL & Blanks are Likely an Issue Between Network Agreement
Agreement for Mass and Sulfate Did Not Meet EPA Expert Criteria at All Sites

- Mass: Ratio 1 ± 0.1; \( R^2 > 0.9 \)
- Sulfate Ratio 1 ± 0.05; \( R^2 > 0.95 \)

What Is a Practical Difference?

- Mass & Sulfate ± 1 ug/m³, ± 0.5 ug/m³
- 'Toxic' Species ± 1 ng/m³, ± 0.5 ng/m³
- Other

Criteria Still Need to Be Established for All Species

Site-to-Site Variations Were Observed for All Species, Although Outliers Still Require Verification

Was Observed for Pb and Zn than for As and Cr
Disclaimer

This work has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products do not constitute endorsement or recommendation for use.

Acknowledgements

This work was supported by the National Park Service as well as EPA. Staff from UC Davis and DRI, as well as NPS personnel, have played a significant role in collection and analysis of samples in the IMPROVE Network. Research Triangle Institute has played a significant role in preparing and analyzing samples for the STN network, as well as state site operators who have meticulously been collecting samples since October 2001, which continues to date.
New Urban IMPROVE Sites

- New York City IS 52
- Atlanta S. Dekalb
- Pittsburgh BAPC
- Birmingham
- Detroit-Allen Park
- Chicago
- Houston-Deer Park
- Riverside-Rubidoux
- Fresno First St.
Urban IMPROVE Site Criteria

- PM2.5 TRENDS Site
- Representative distribution of STN monitors
- Broad geographic representation
- Location likely to be non-attainment
- State or local agency willing to run both instruments
- Power and Space available
- Particular components of PM2.5 of interest, e.g. high nitrate site, wood smoke or diesel carbon, crustal, etc.
Next Steps

- Finalize Report on First Year of intercomparison data from 6 sites
- Conduct Study to determine the effects of shipping conditions
- Deploy Urban IMPROVE sites and collect intercomparison data
- Begin analyzing quartz filters from STN sites using IMPROVE protocol
- Sponsor project to specifically look at effect of carbon measurement protocols