

Comparison of the STN and IMPROVE Networks for Mass and Selected Chemical Components

Paul Solomon, ORD
Tracy Klamser-Williams, ORIA
Peter Egeghy, ORD
Dennis Crumpler, OAQPS
Joann Rice , OAQPS

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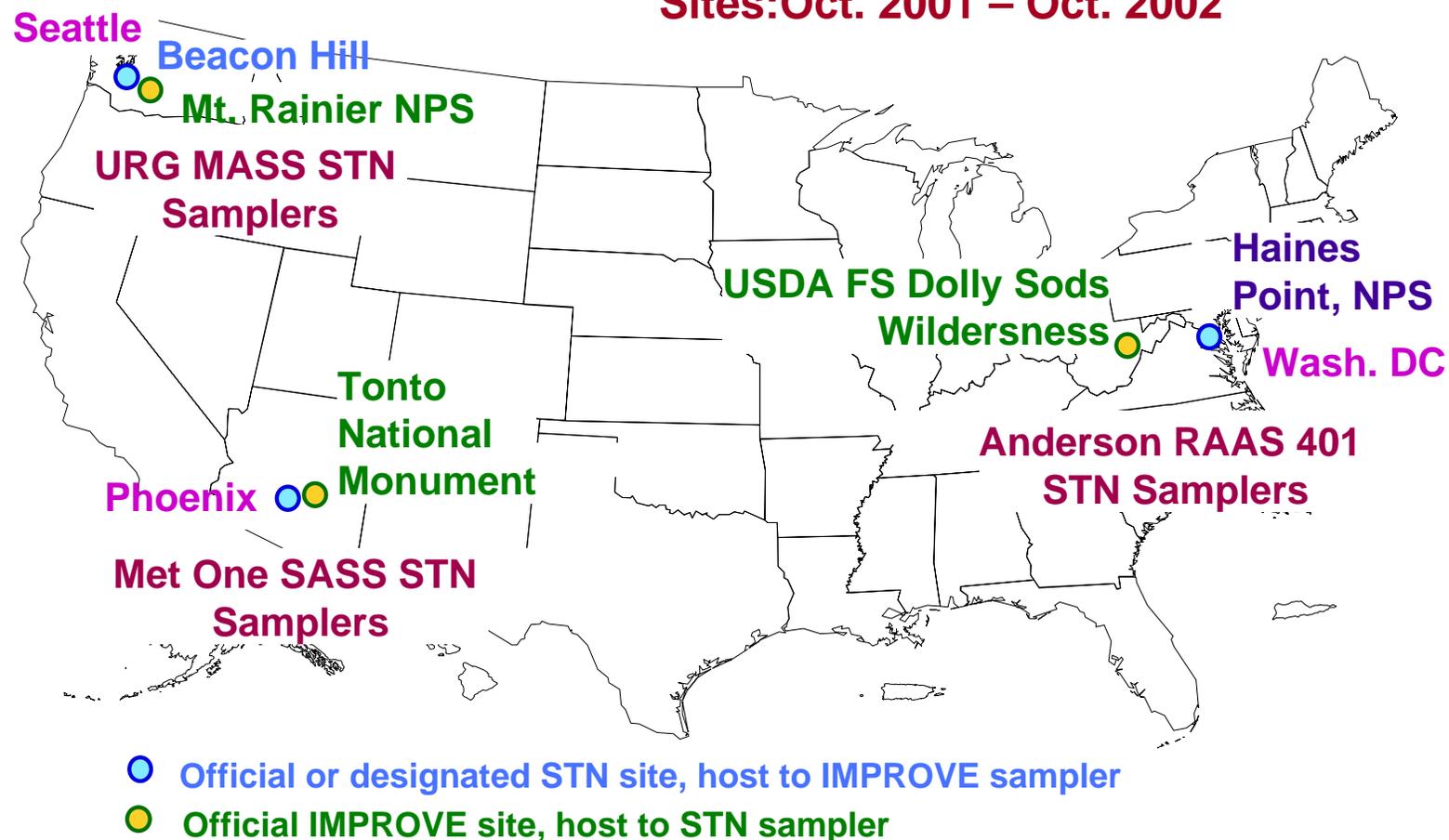
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STN-IMPROVE Comparison Study Approach

Operated According to Each Network's Protocols

STN/IMPROVE Monitoring Intercomparison

Sites: Oct. 2001 – Oct. 2002



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Over Arching Questions

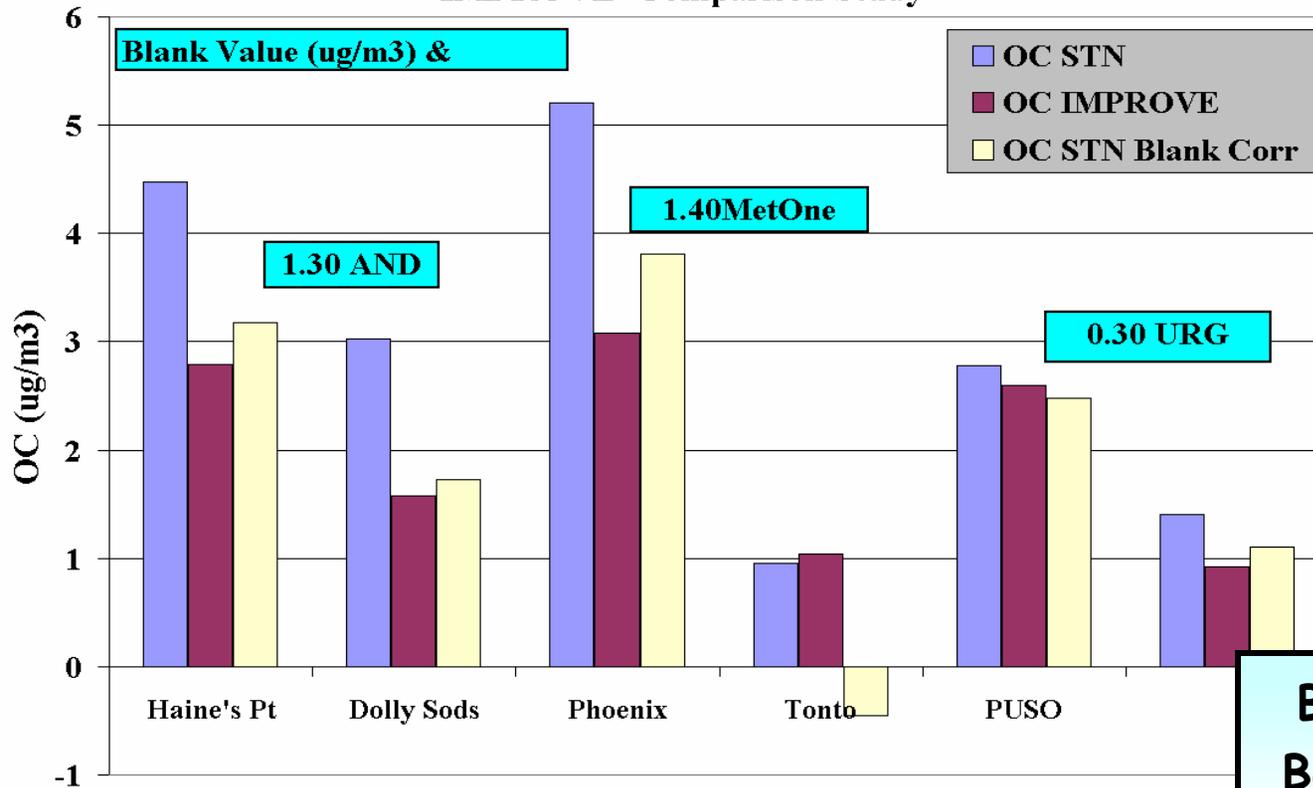
- Is there a Bias Between the Two Networks and for Which Species?
 - ✓ If Yes, How Large?
- Can We Identify the Reason for the Bias?
 - ✓ If Yes, Can We Make Improvements to Existing Protocols in Either/Both Networks to Reduce The Bias and Overall Uncertainty in the Results

Changes To Data Since Last Report

- UC Davis & RTI Examined Data to Ensure Explainable Outliers Were Removed
 - ✓ Overall, At Least Several Hundred Data Points Have Been Removed that Passed Normal Network Quality Assurance. This Was Due to Ability to Compare Data Sets.
- STN-OC was Blank Corrected
- Values Equal to and Below the MDL Were Removed Before Statistics Were Calculated
 - ✓ Many High or Low Ratios Were Due to Species Near or Below the MDL
- Initiated Examination of Seasonal Data

STN-OC Blank Corrections ($\mu\text{g}/\text{m}^3$)

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



Based on
October
Data Set

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

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

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MLD Estimates (ng/m³)

Species	MDL AND	MDL URG	MDL MetOne	MDL IMPROVE
PM2.5**	300	300	750	315
OC	130	60	150	240
EC	130	60	150	70
SO4	11	5	12	42
NO3	8	3	8	29
NH4	15	7	17	2
S	3	3	7	2
Si	3	3	8	4
Ca	1	1	3	0.6
Fe	0.8	0.8	2.0	0.1
Cr	0.6	0.6	1.6	0.3
Se	0.9	0.9	2.1	0.0
As	1.0	1.0	2.5	0.2
Cu	0.5	0.5	1.4	0.1
Pb	2.2	2.2	5.5	0.1
Mn	0.9	0.9	2.3	0.3
Zn	0.6	0.6	1.5	0.1

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Previous Expectations of Comparability¹

Ratio of Test Sampler to Reference Sampler

Species	Expert Panel	4-City Study	Atlanta
	Ratio 1 ± X%		
Mass	10	10	20
SO₄²⁻ or S	5	10	10
NO₃⁻	10	15	35
NH₄⁺	10	10	15
OC		15	20
EC		15	20
Trace Elements		15	30

¹ EPA's Expert Chemical Speciation Panel (Koutrakis 1999), 4-City Study Results (Solomon et al. 2000), Atlanta Supersites Integrated Comparison Study (Solomon et al. 2003)

Previous Expectations of Comparability¹

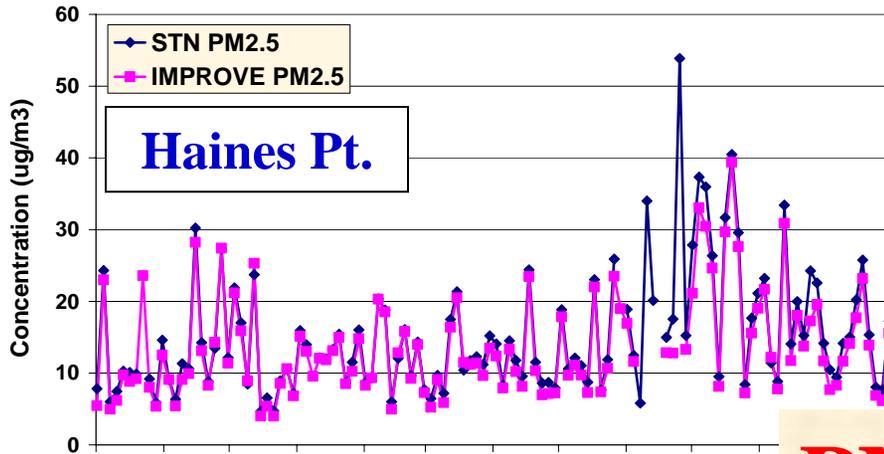
Regression Coefficient for Test Sampler to Reference Sampler

Species	Expert Panel	4-City Study	Atlanta
	Regression Coefficient		
Mass	≥0.9	≥0.9	≥0.9
SO₄²⁻ or S	≥0.95	≥0.95	≥0.95
NO₃⁻	≥0.9	≥0.9	≥0.20
NH₄⁺	≥0.9	≥0.9	≥0.95
OC		≥0.9	≥0.9
EC		≥0.85	≥0.85
Trace Elements		≥0.85	

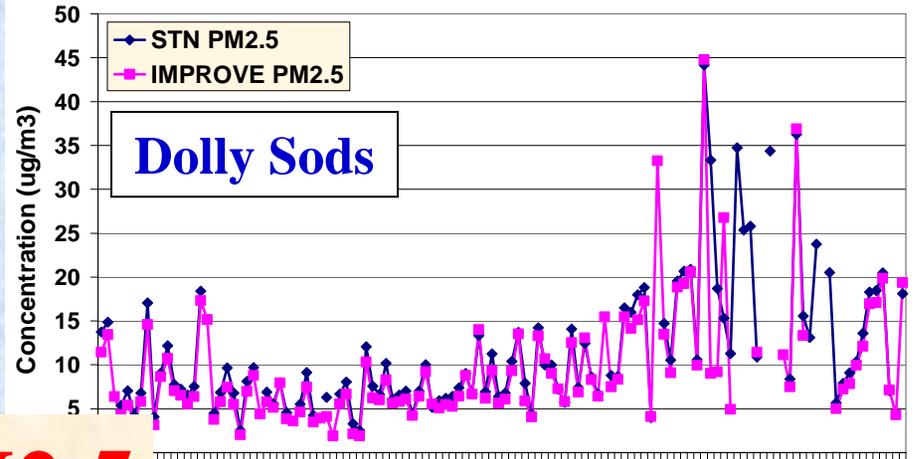
¹ EPA's Expert Chemical Speciation Panel (Koutrakis 1999), 4-City Study Results (Solomon et al. 2000), Atlanta Supersites Integrated Comparison Study (Solomon et al. 2003)

Daily Absolute Comparisons

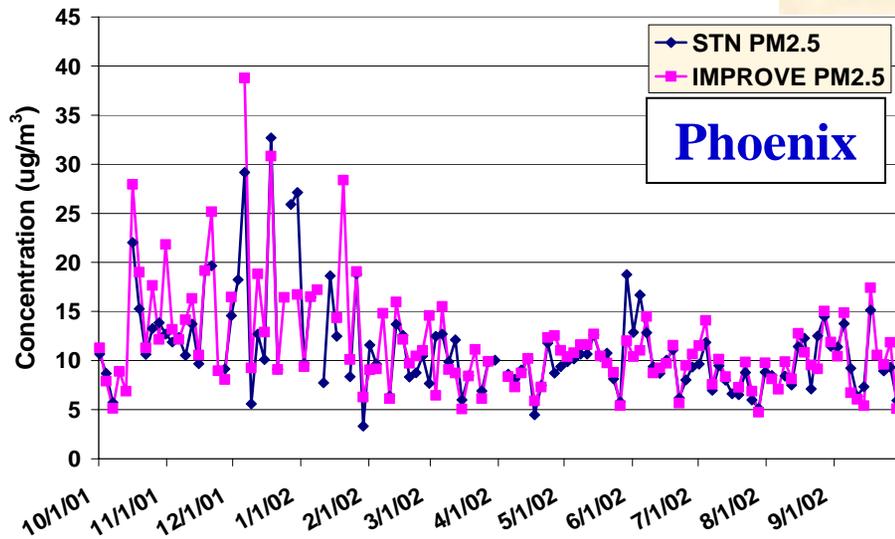
Chemical Speciation for STN vs. IMPROVE for Particulate Matter 2.5 at Washington-Haine's Pt from 10-01 to 9-02



Chemical Speciation for STN vs. IMPROVE for PM2.5 at Dolly Sods from 10-01 to 9-02

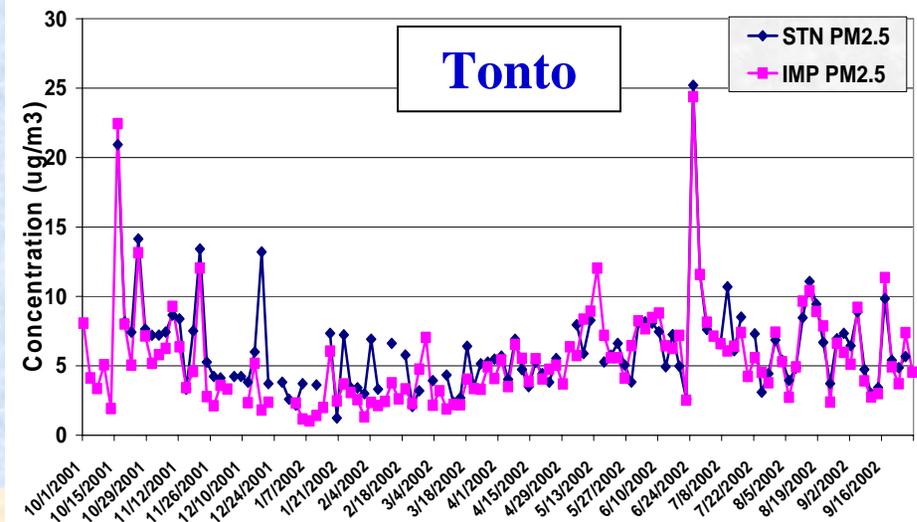


Chemical Speciation for STN vs. IMPROVE Particulate Matter 2.5 at Phoenix 10-01 to 9-02



PM2.5

Chemical Speciation for STN vs. IMPROVE for Particulate Matter 2.5 at Tonto

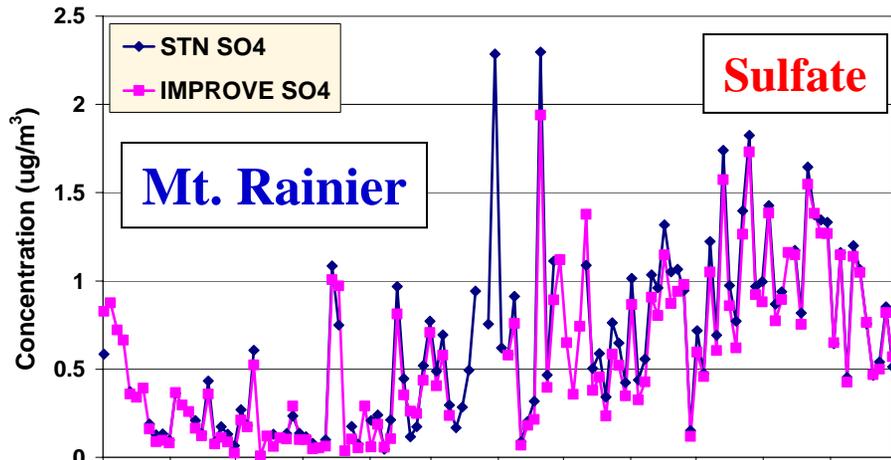


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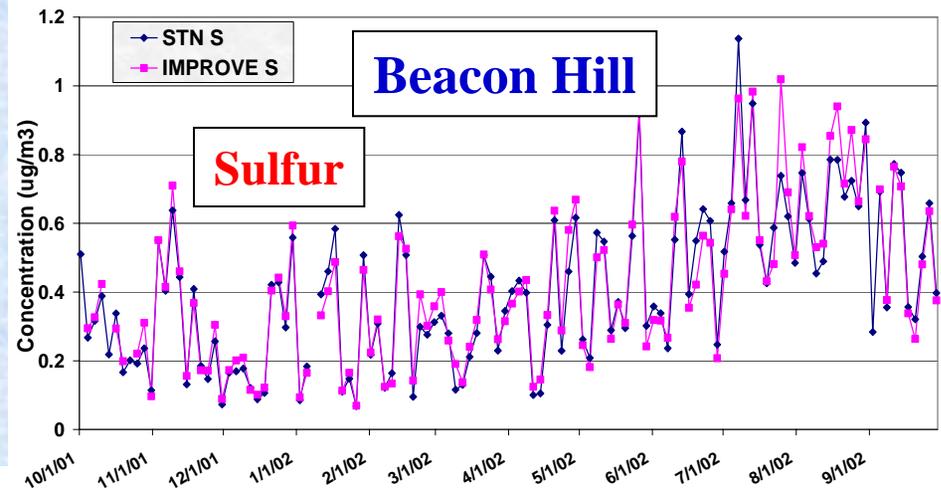
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Daily Absolute Comparisons

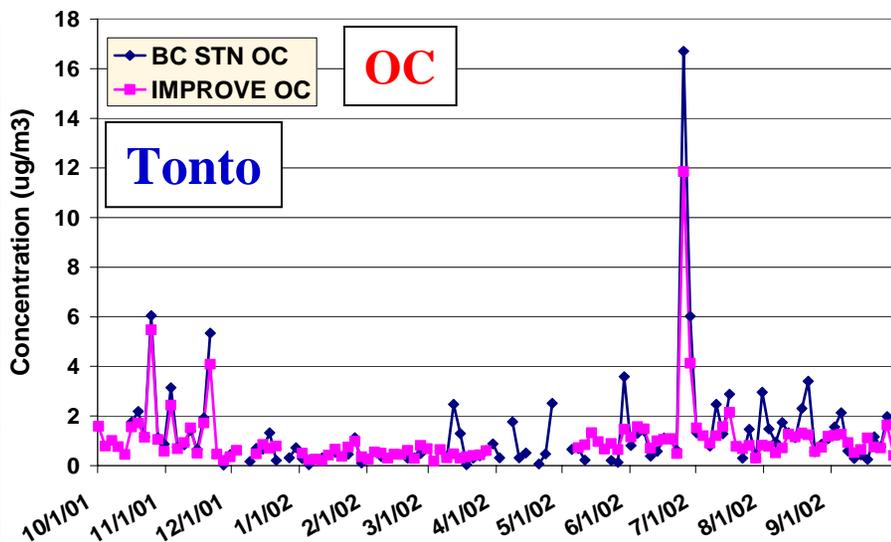
Chemical Speciation for STN vs. IMPROVE for Sulfate at Mt. Rainier from 10-01 to 9-02



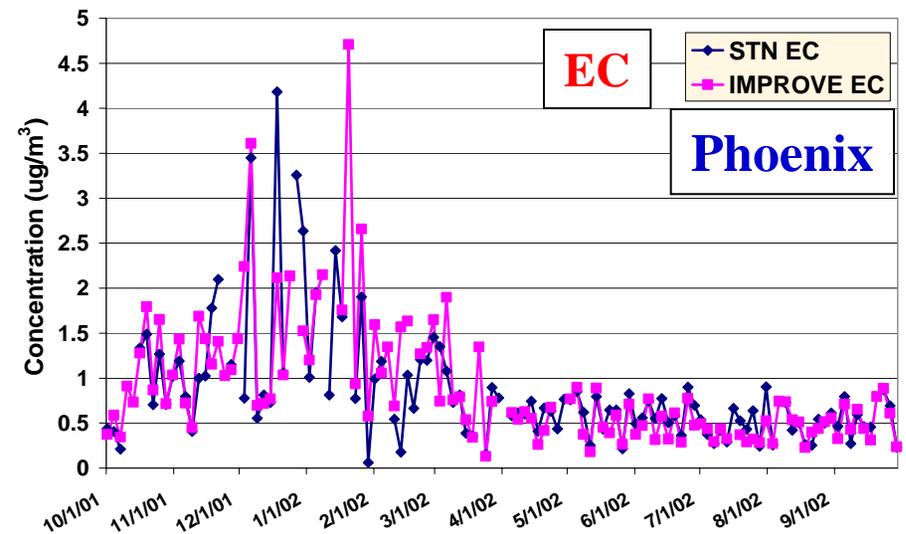
Chemical Speciation for STN vs. IMPROVE for Sulfur at Puget Sound- Beacon Hill from 10-01 to 9-02



Chemical Speciation for STN vs. IMPROVE for Blank Corrected OC for STN vs. OC for IMPROVE 9-01 to 10-02



Carbon at Phoenix from 10-01 to 9-02

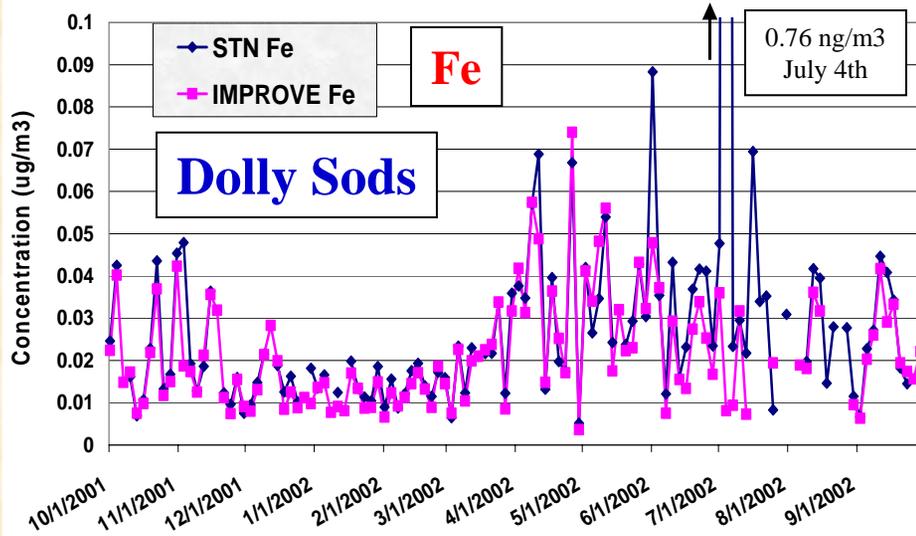


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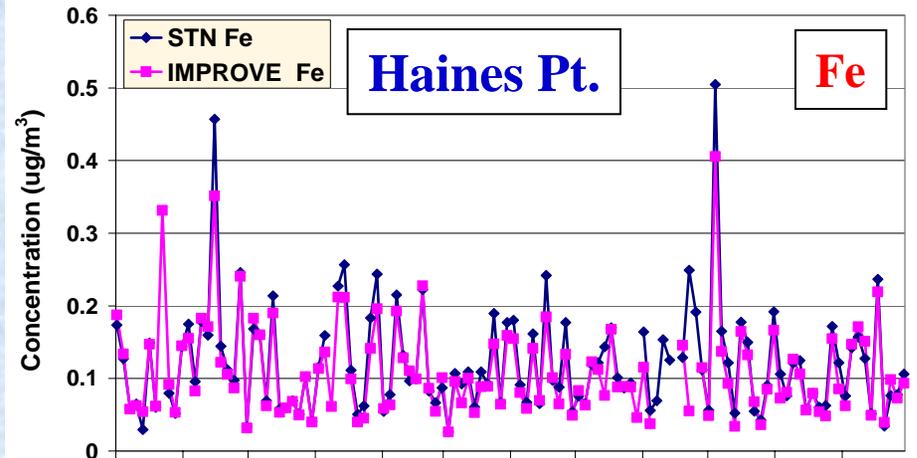
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Daily Absolute Comparisons

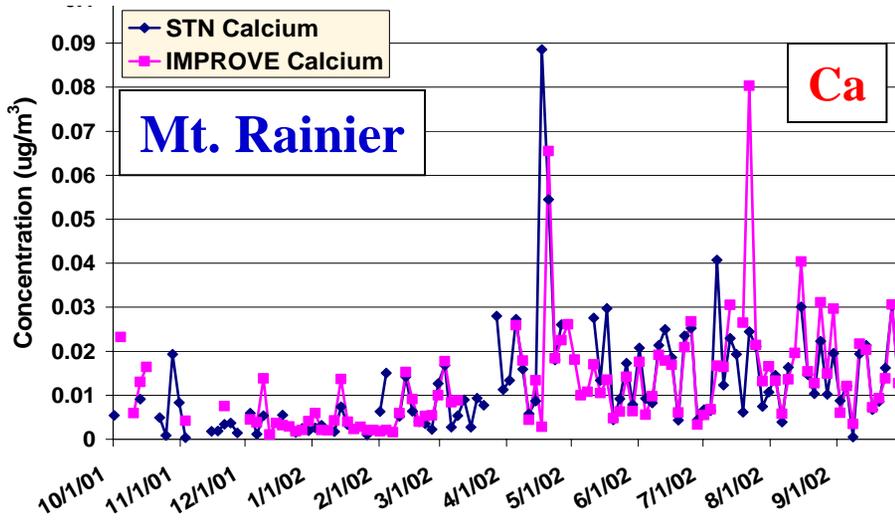
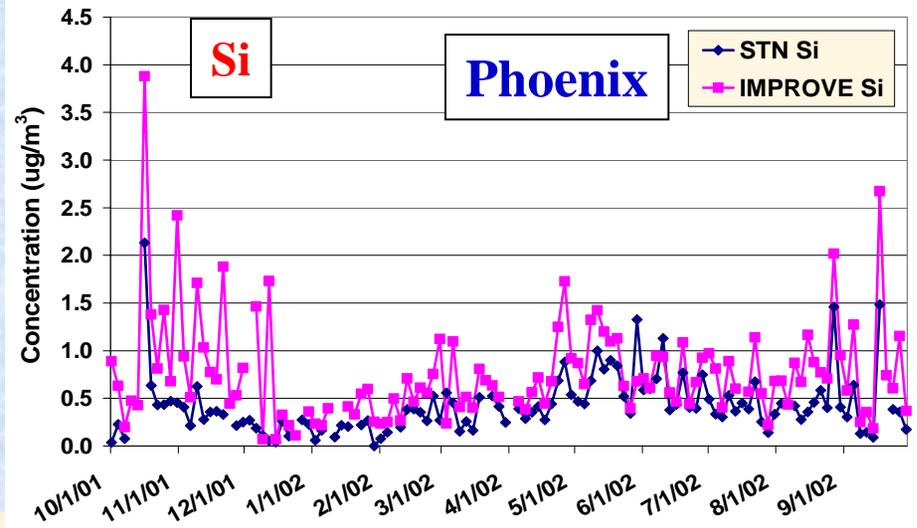
STN vs. IMPROVE Chemical Speciation for Iron at Dolly Sods from 10-01 to 9-02



Chemical Speciation for STN vs. IMPROVE for Iron at Washington-Haine's Pt from 10-01 to 9-02



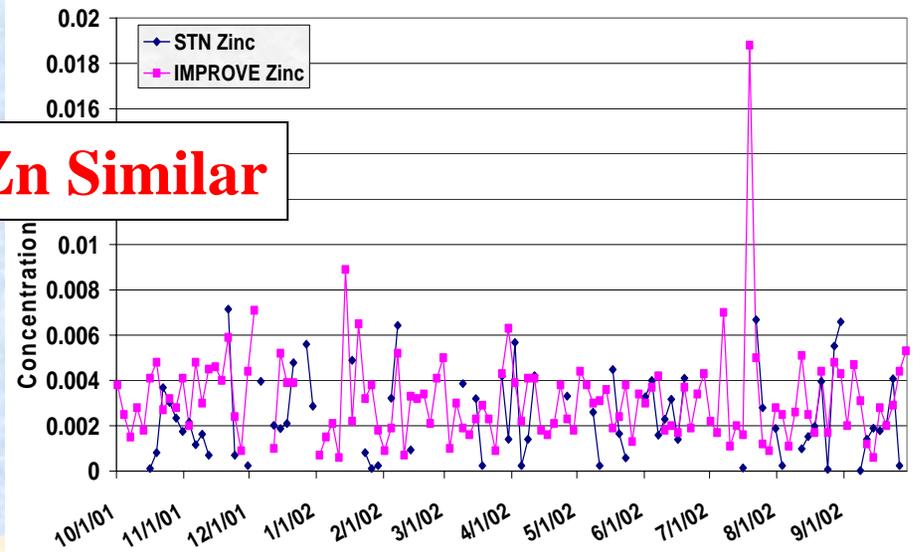
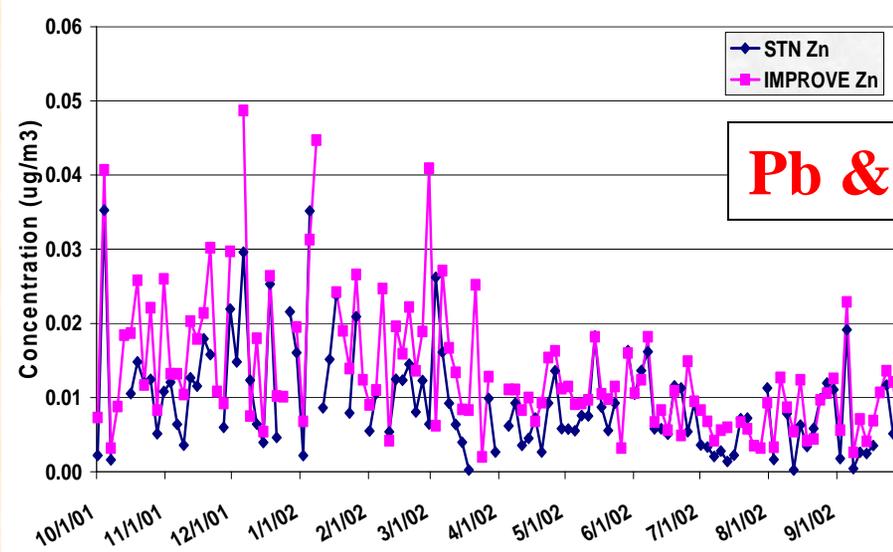
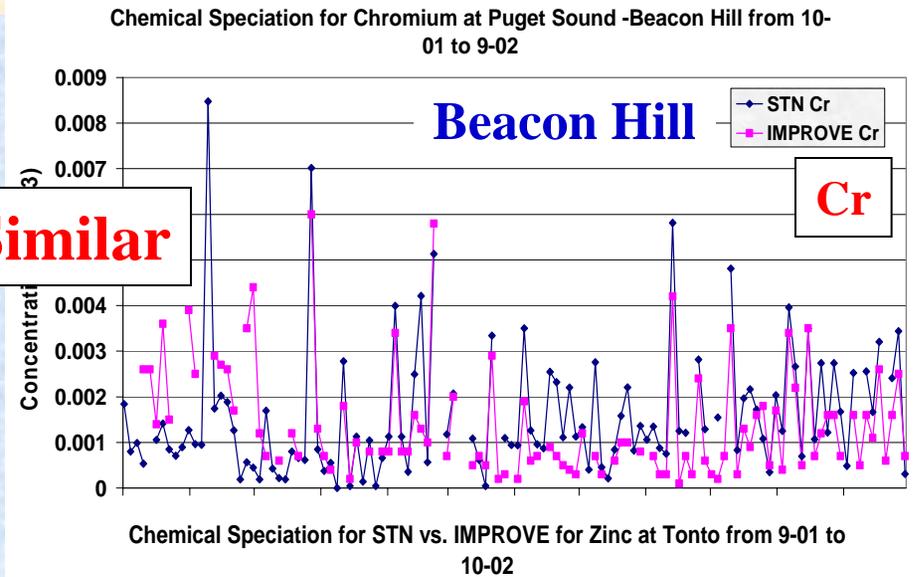
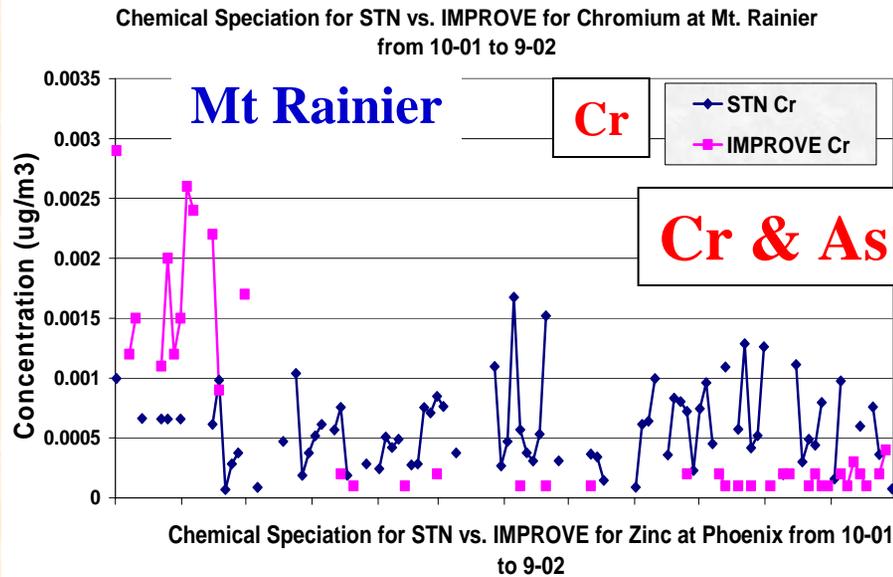
Chemical Speciation for STN vs. IMPROVE for Silicon at Phoenix from 10-01 to 9-02



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Daily Absolute Comparisons

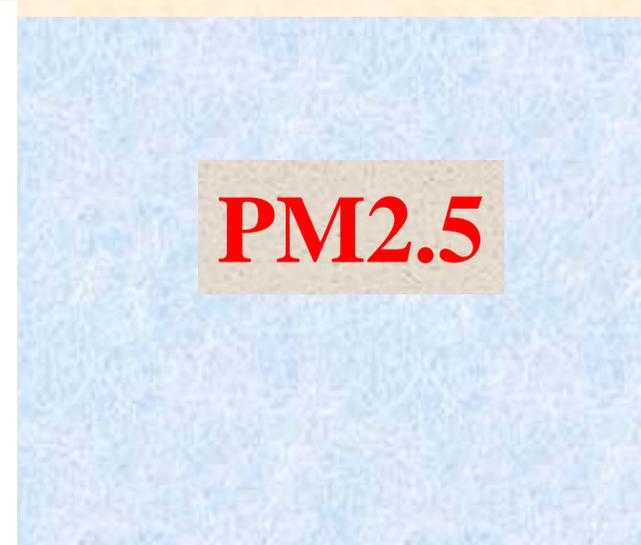
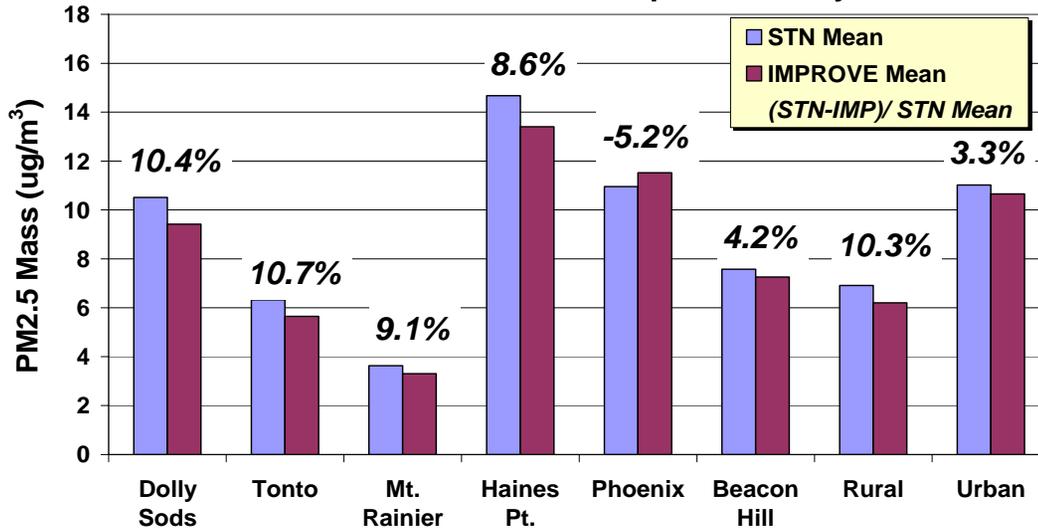


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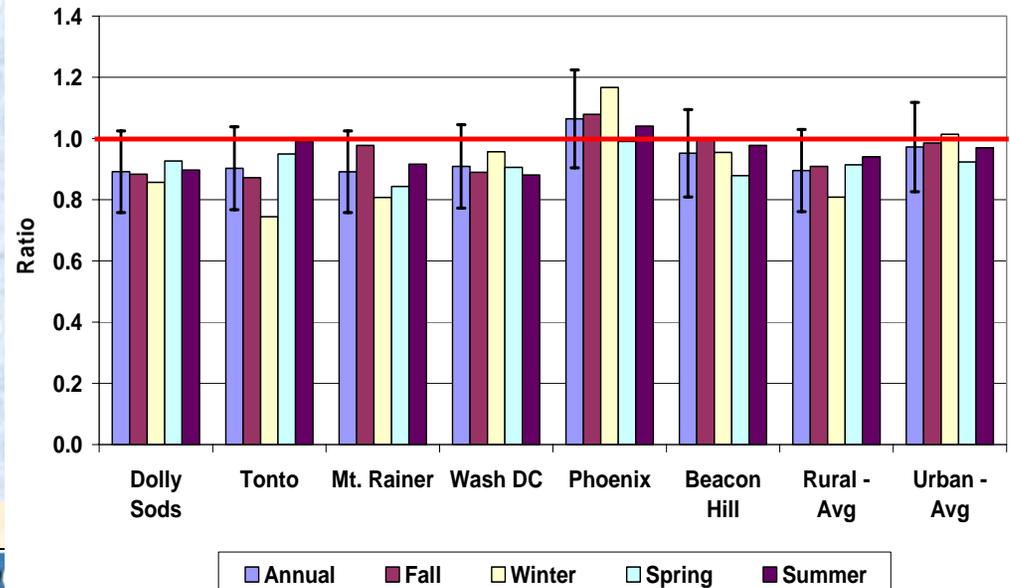
Annual Average & Seasonal Comparisons

Comparison of Annual Average PM2.5 Mass During the 6 Site STN-IMPROVE Comparison Study



Previous Speciation Monitor Comparability Results = Ratio 10-20%; Error Bars = 15%

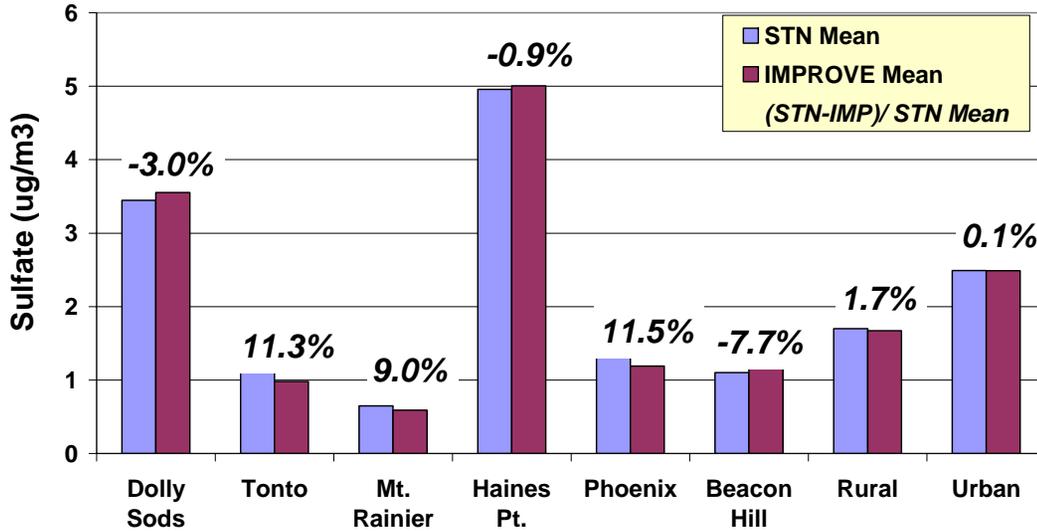
PM2.5 Seasonal Mean Ratio (IMP/STN)



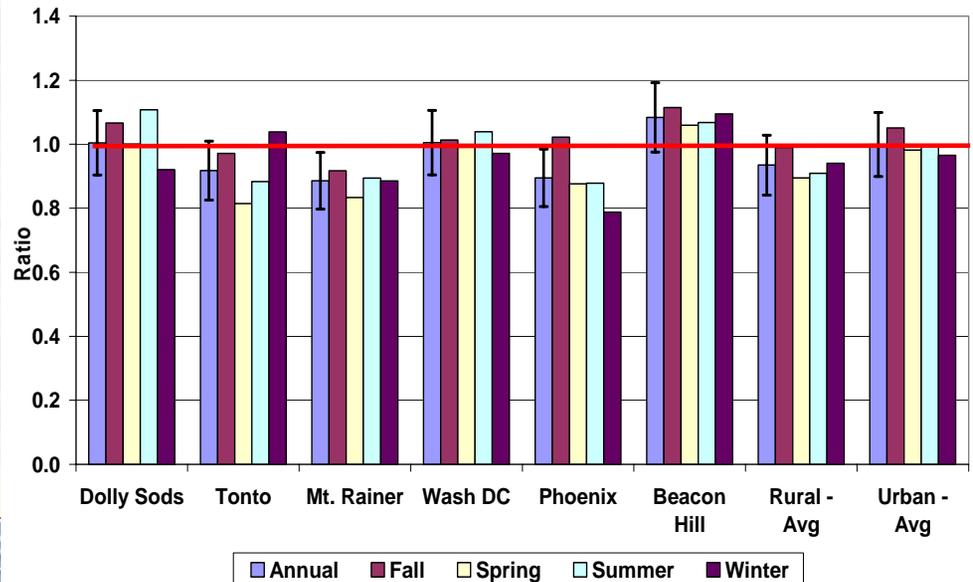
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Annual Average & Seasonal Comparisons

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



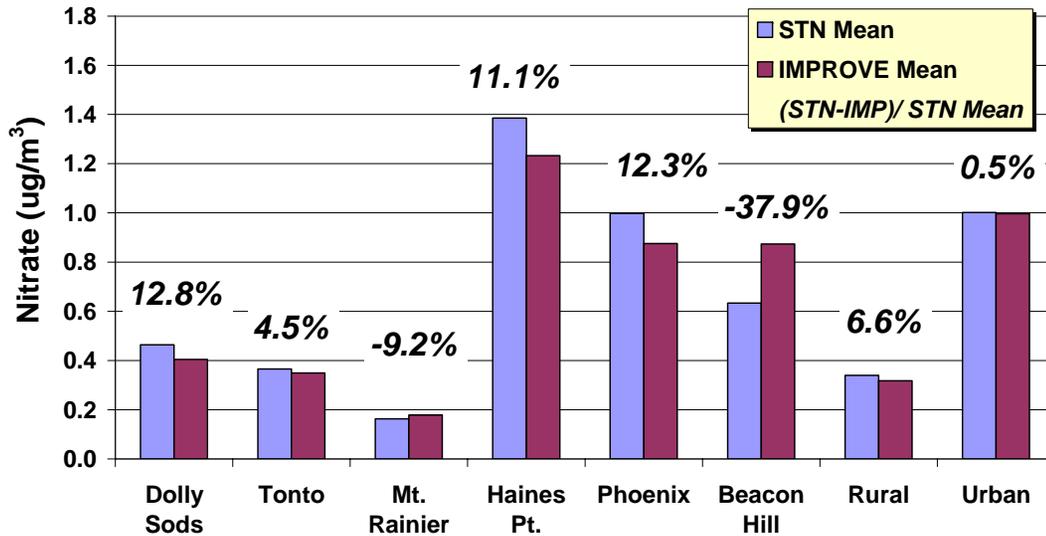
Sulfate Seasonal Mean Ratio (IMP/STN)



Previous Speciation Monitor Comparability Results = Ratio 10%; Error Bars = 10%

Annual Average & Seasonal Comparisons

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

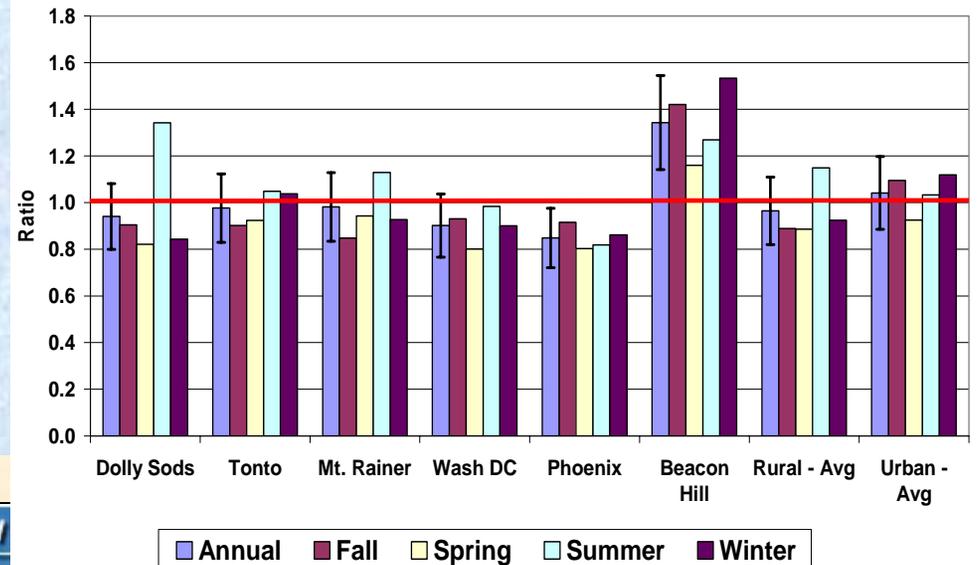


Nitrate

**Previous Speciation Monitor Comparability Results = Ratio 15-35%*;
Error Bars = 15%**

***Range Function of Sampling Method**

Nitrate Seasonal Mean Ratio (IMP/STN)

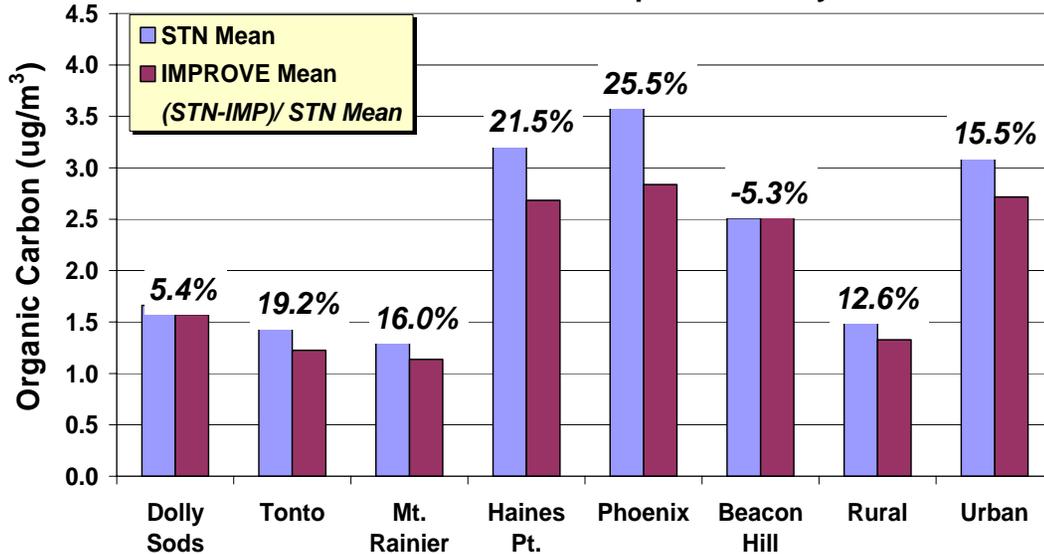


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Annual Average & Seasonal Comparisons

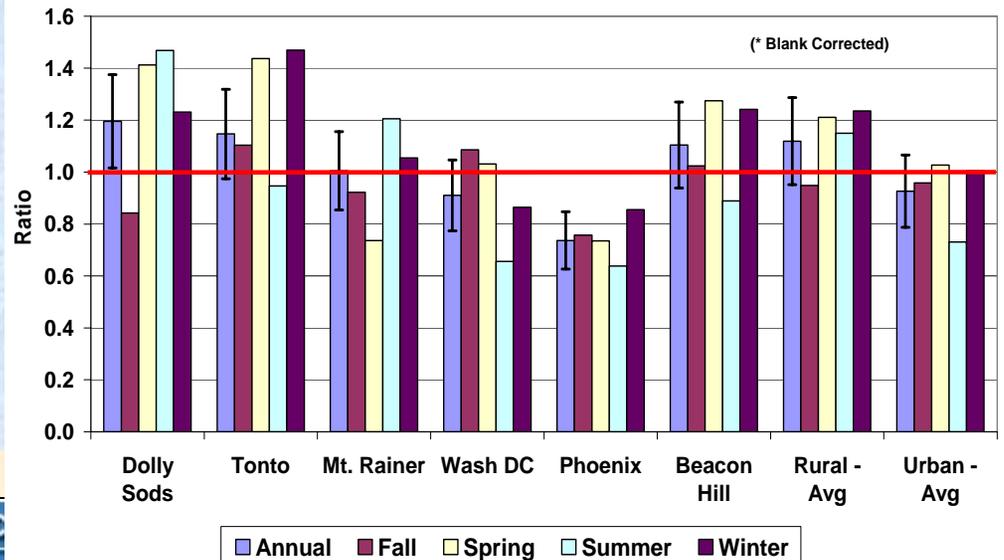
Comparison of Annual Average Organic Carbon During the 6 Site STN-IMPROVE Comparison Study



Organic Carbon

Previous Speciation Monitor Comparability Results = Ratio 15%; Error Bars = 15%

Organic Carbon* Seasonal Mean Ratio (IMP/STN)

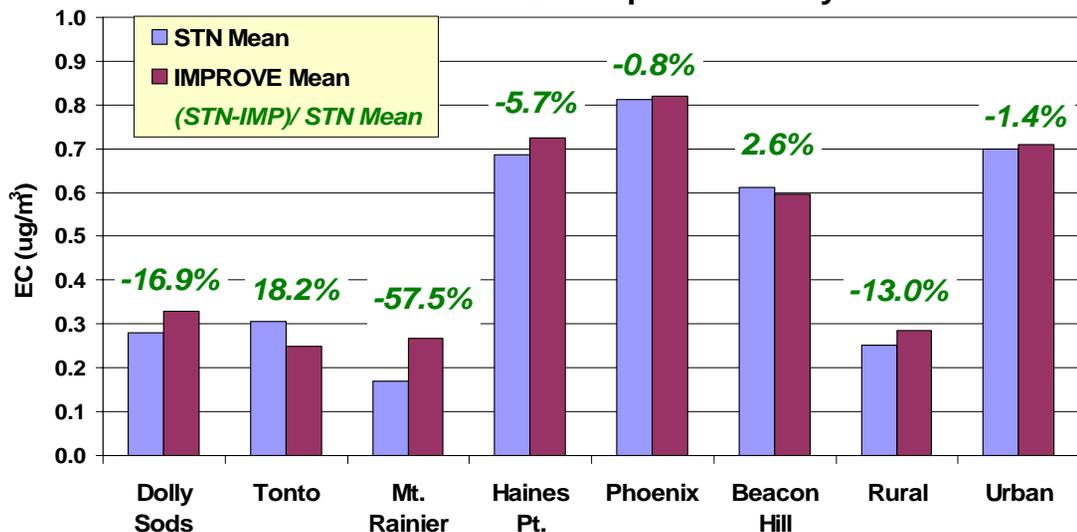


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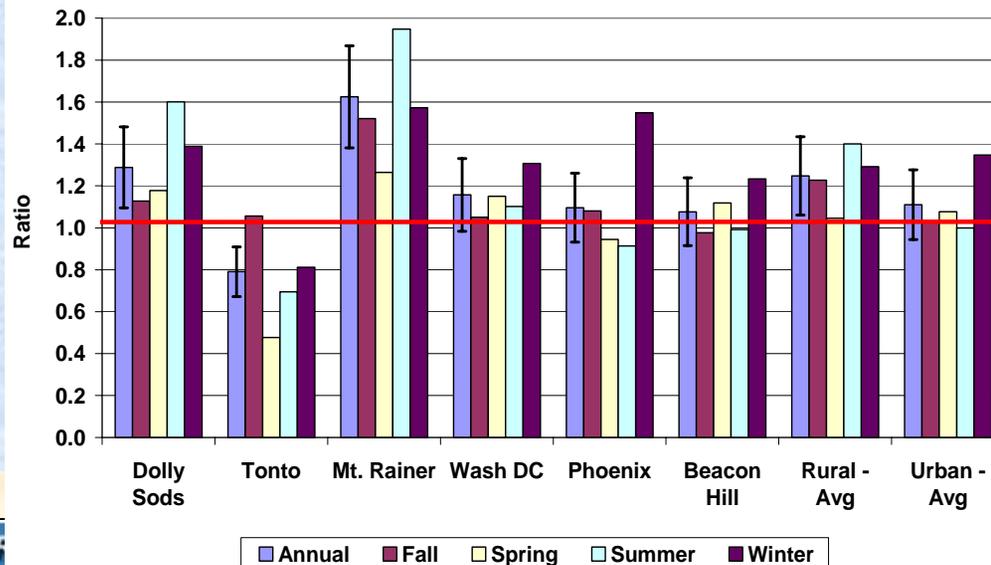
Annual Average & Seasonal Comparisons

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



Elemental Carbon

Elemental Carbon Seasonal Mean Ratio (IMP/STN)



Previous Speciation Monitor Comparability Results = Ratio 15%*; Error Bars = 15%

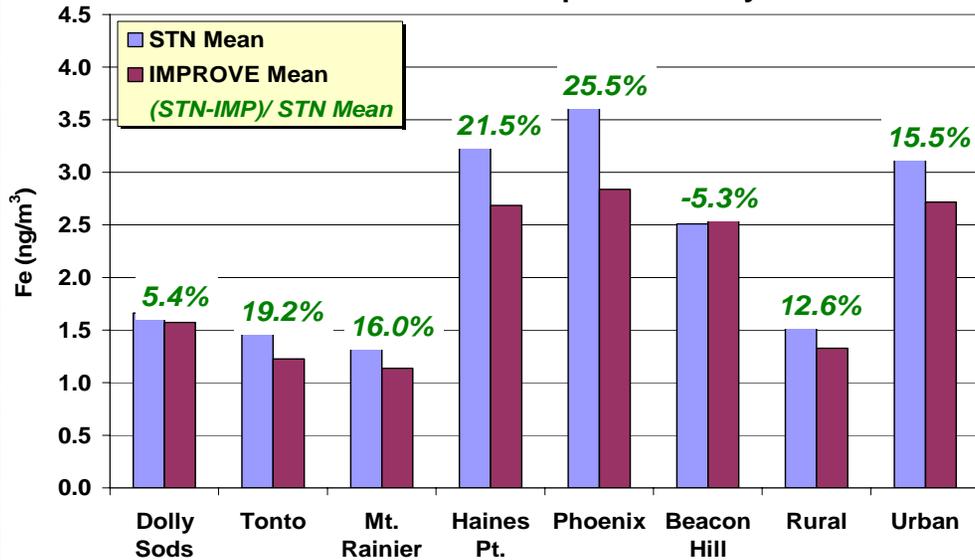
*Employing Same Analytical Method

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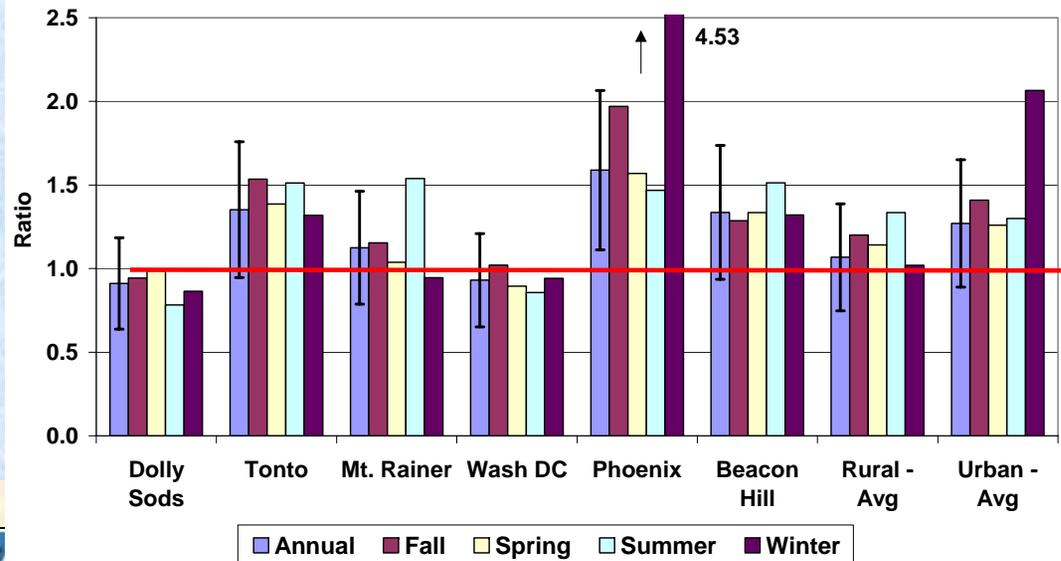
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Annual Average & Seasonal Comparisons

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



Iron Seasonal Mean Ratio (IMP/STN)

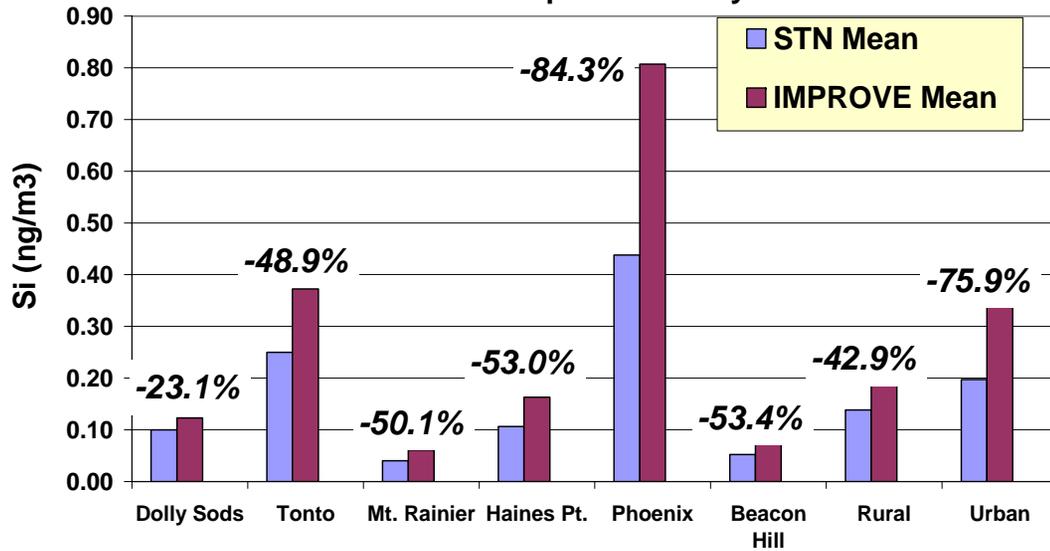


Previous Speciation Monitor Comparability Results =
Ratio 15-30%*;
Error Bars = 30%

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Annual Average & Seasonal Comparisons

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

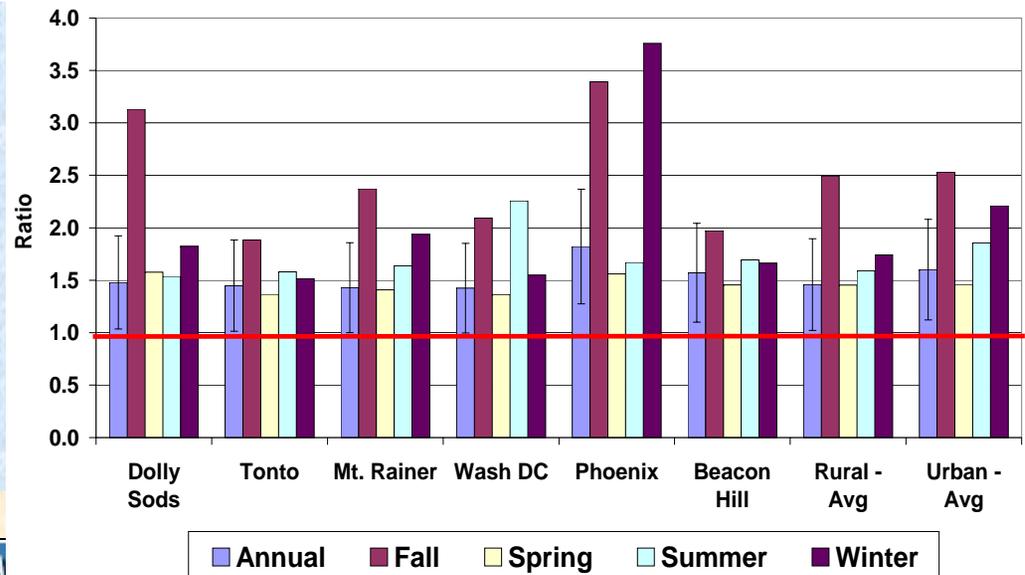


Silicon

*Ca is Similar to Si

Previous Speciation Monitor Comparability Results = Ratio 15-30%*; Error Bars = 30%

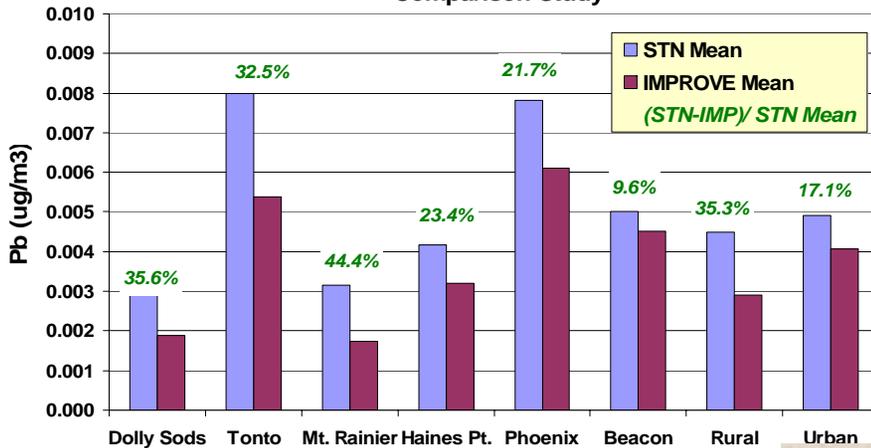
Silicon Seasonal Mean Ratio (IMP/STN)



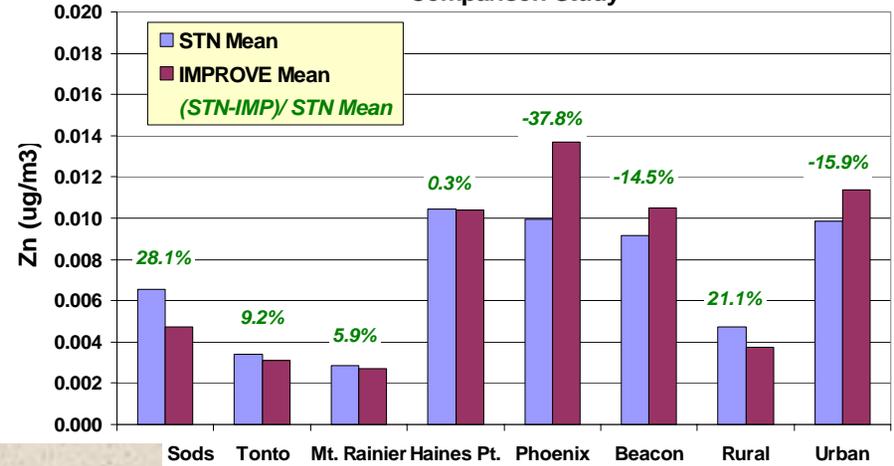
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Annual Average & Seasonal Comparisons

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

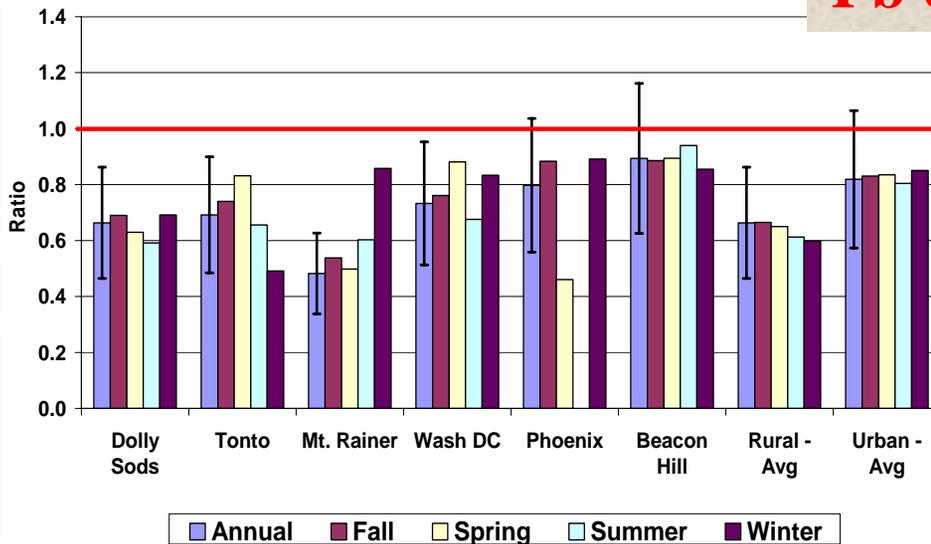


Comparison of Annual Average Zn During the 6 Site STN-IMPROVE Comparison Study

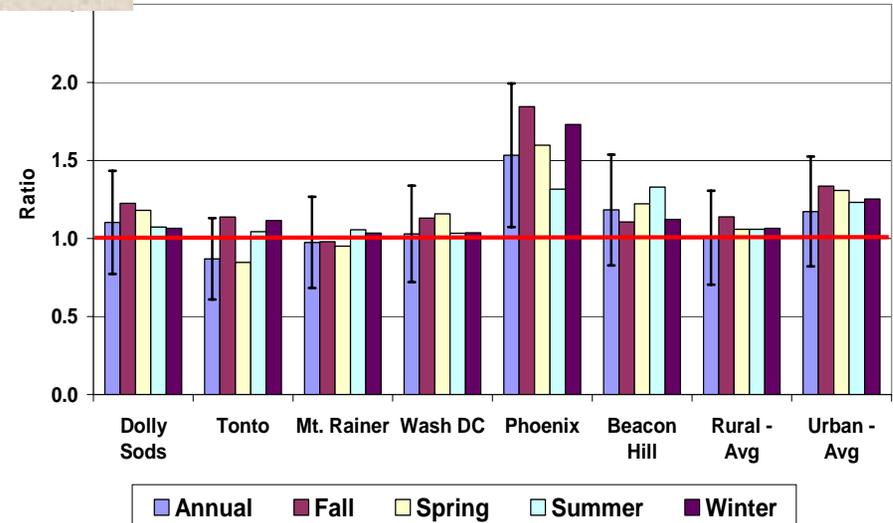


Lead Seasonal Mean Ratio (IMP/STN)

Pb & Zn



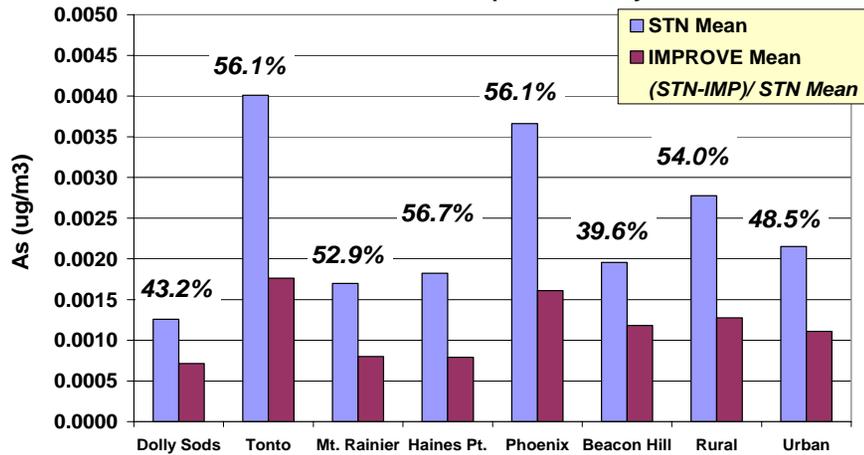
Zinc Seasonal Mean Ratio (IMP/STN)



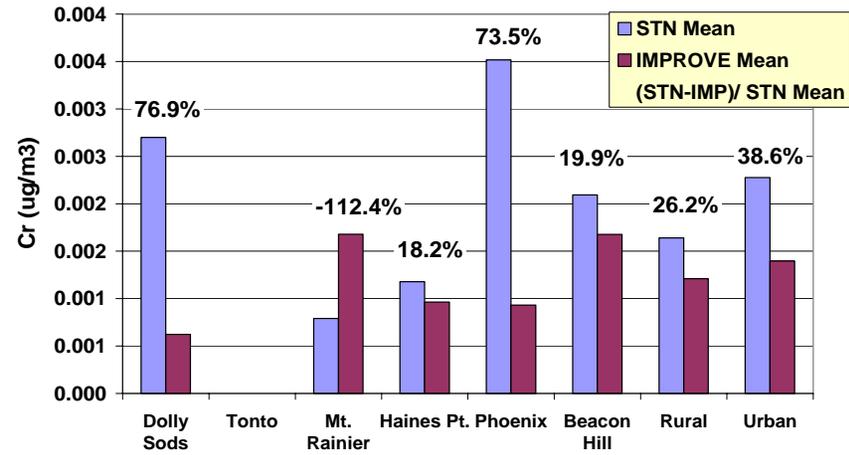
Previous Speciation Monitor Comparability Results =
Ratio 15-30%*; Error Bars = 30%

Annual Average & Seasonal Comparisons

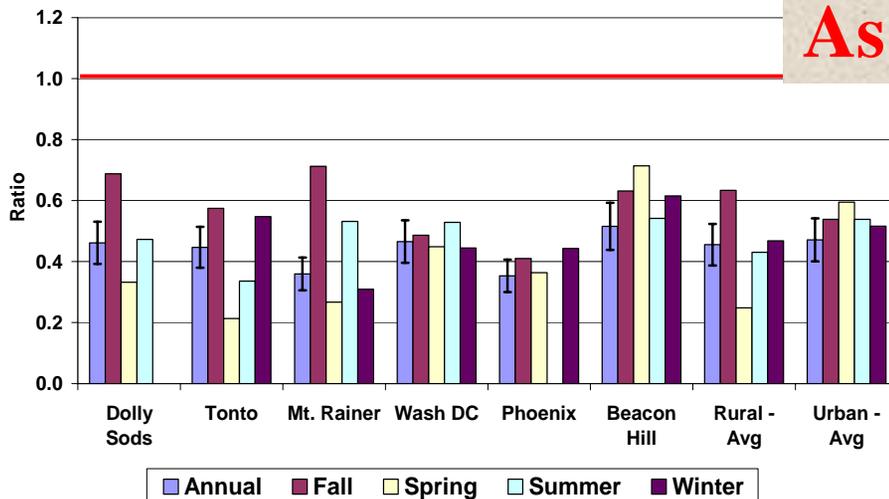
Comparison of Annual Average As During the 6 Site STN-IMPROVE Comparison Study



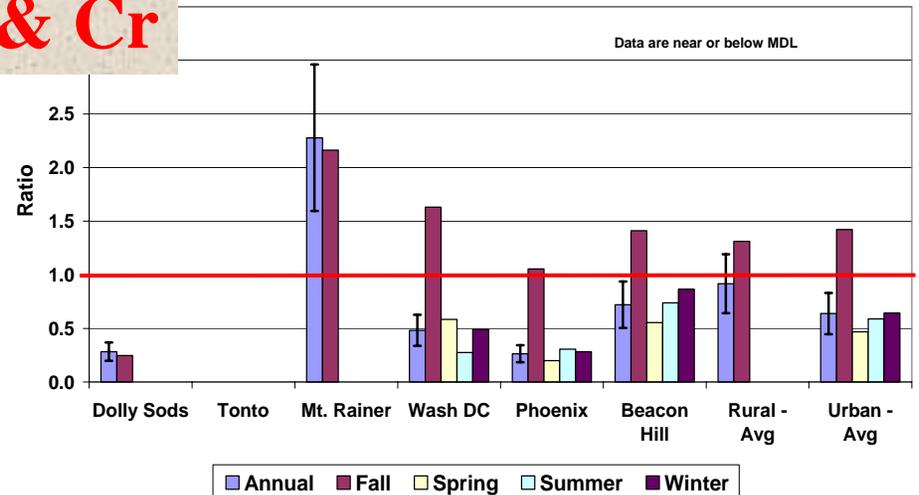
Comparison of Annual Average Cr During the 6 Site STN-IMPROVE Comparison Study



Arsenic Seasonal Mean Ratio (IMP/STN)



Chromium Seasonal Mean Ratio (IMP/STN)

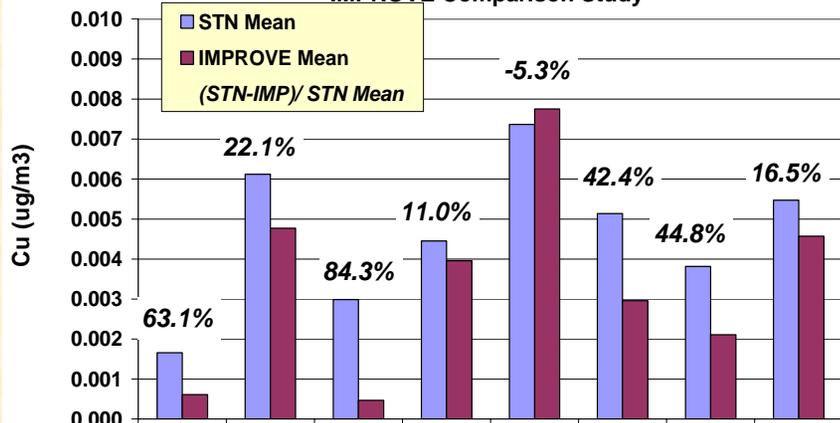


As & Cr

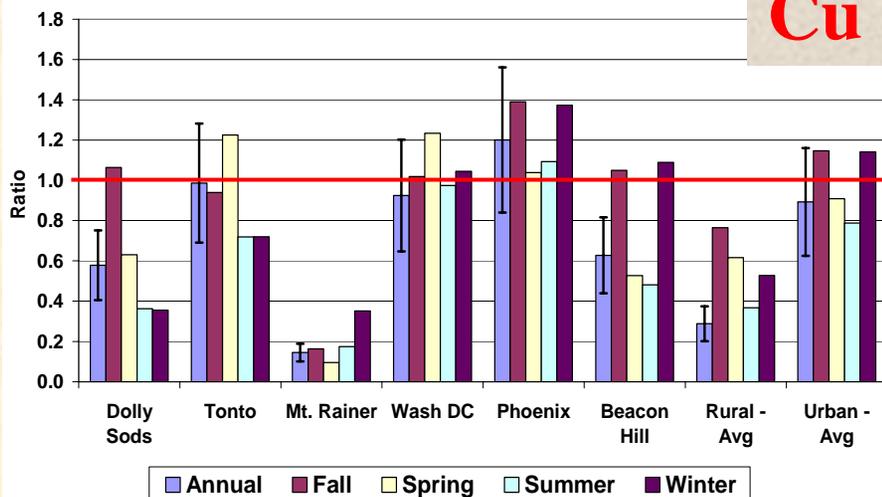
**Previous Speciation Monitor Comparability Results =
Ratio 15-30%*; Error Bars = 30%**

Annual Average & Seasonal Comparisons

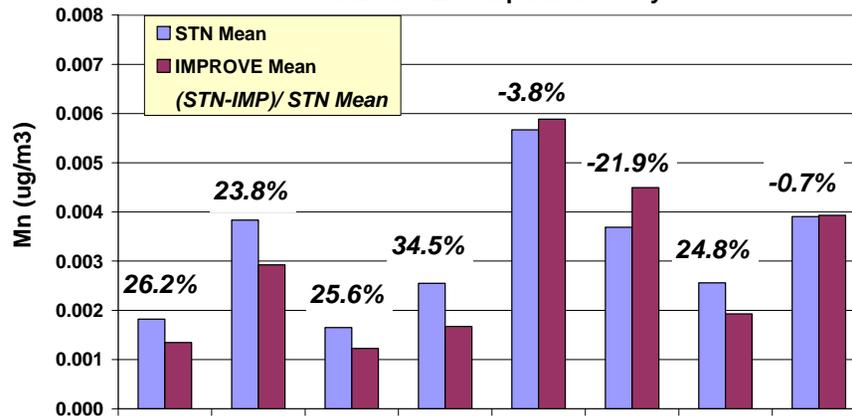
Comparison of Annual Average Cu During the 6 Site STN-IMPROVE Comparison Study



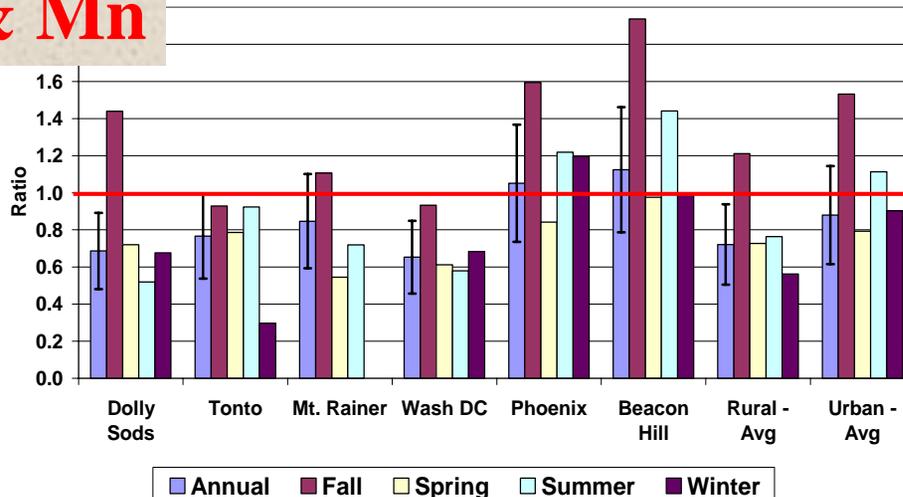
Copper Seasonal Mean Ratio (IMP/STN)



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



Manganese Seasonal Mean Ratio (IMP/STN)



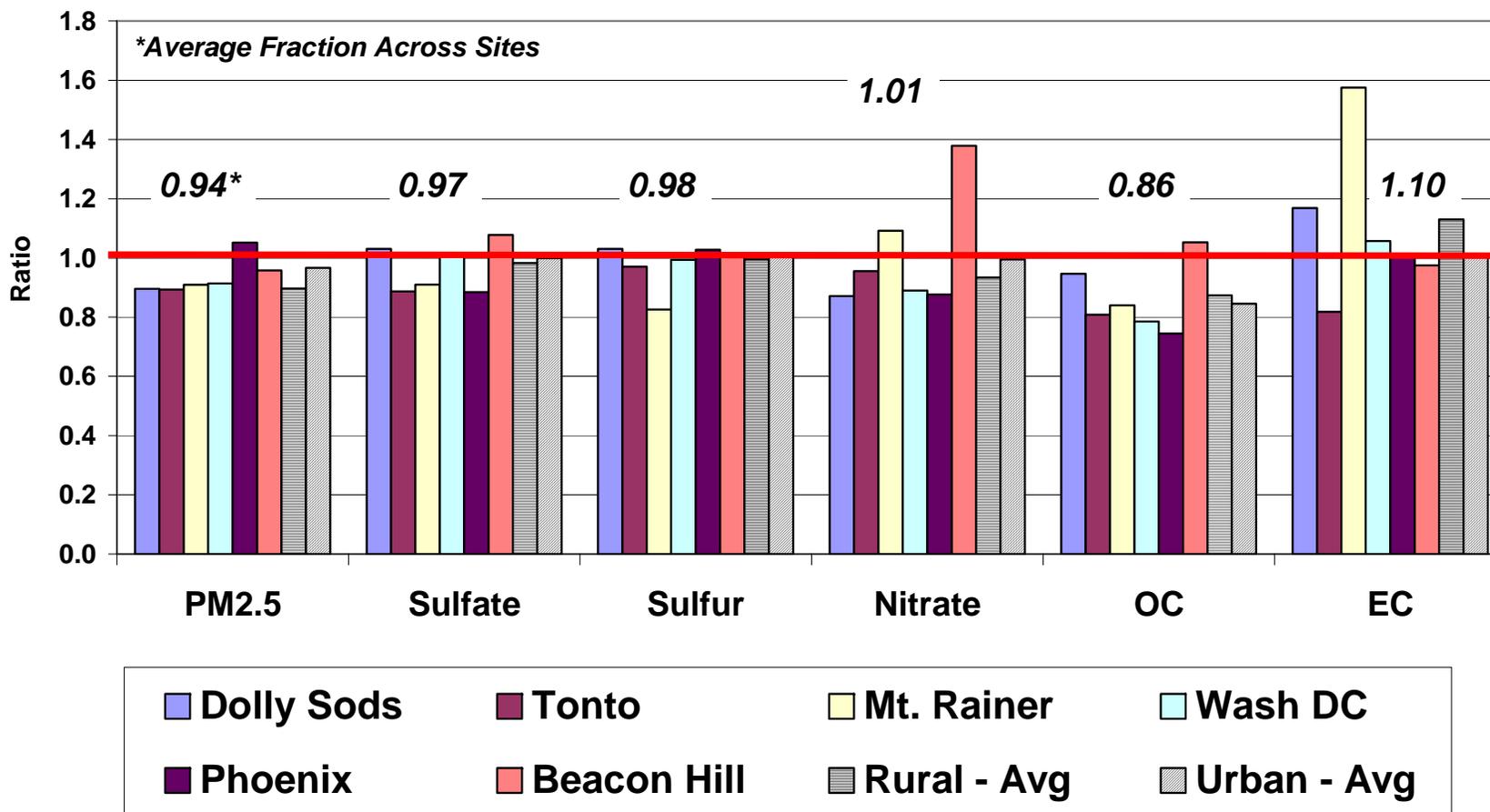
Cu & Mn

Previous Speciation Monitor Comparability Results =
Ratio 15-30%*; Error Bars = 30%

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Relative Annual Average Comparability

Annual Average IMP/STN Ratio of Means for PM2.5 Mass and Major Species



Ratio of Means

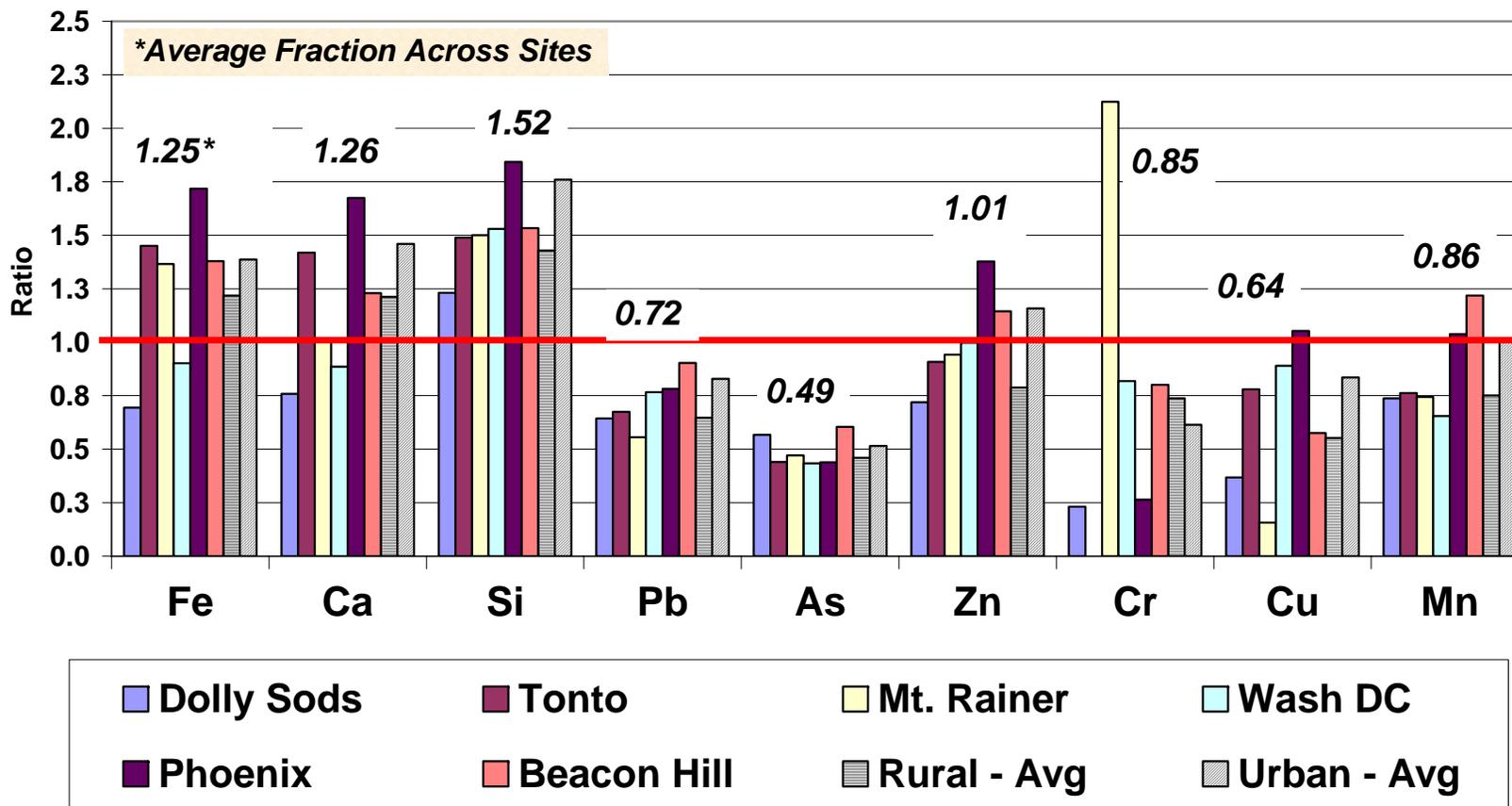
Comparability \pm 15%

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Relative Annual Average Comparability

Annual Average IMP/STN Ratio of Means for PM2.5 Minor and Trace Elements



Ratio of Means

Comparability \pm 30%
Most Species

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Summary & Conclusions

- 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 10%) at All Sites
- Nitrate Agreed Within Expectations (typically within 15%):
 - ✓ Better Agreement at Rural Sites Than Urban Sites, Which May Be Due to Differences in Denuder Protocols;
 - ✓ A Consistent Positive Bias (%) in Nitrate was Observed at Beacon Hill
- Organic Carbon Agreed Well (typically within 15% on Average)
 - ✓ Site-by-Site Comparability was Higher (typically within 25%);
 - ✓ (STN Data Were Blank Corrected)
- Elemental Carbon Agreed Extremely Well.
 - ✓ Urban Sites Within About 5%; Rural Sites Between 20-50%
 - ✓ However, EC Conc. Were Low Overall, and Very Low At Rural Sites

Summary & Conclusions

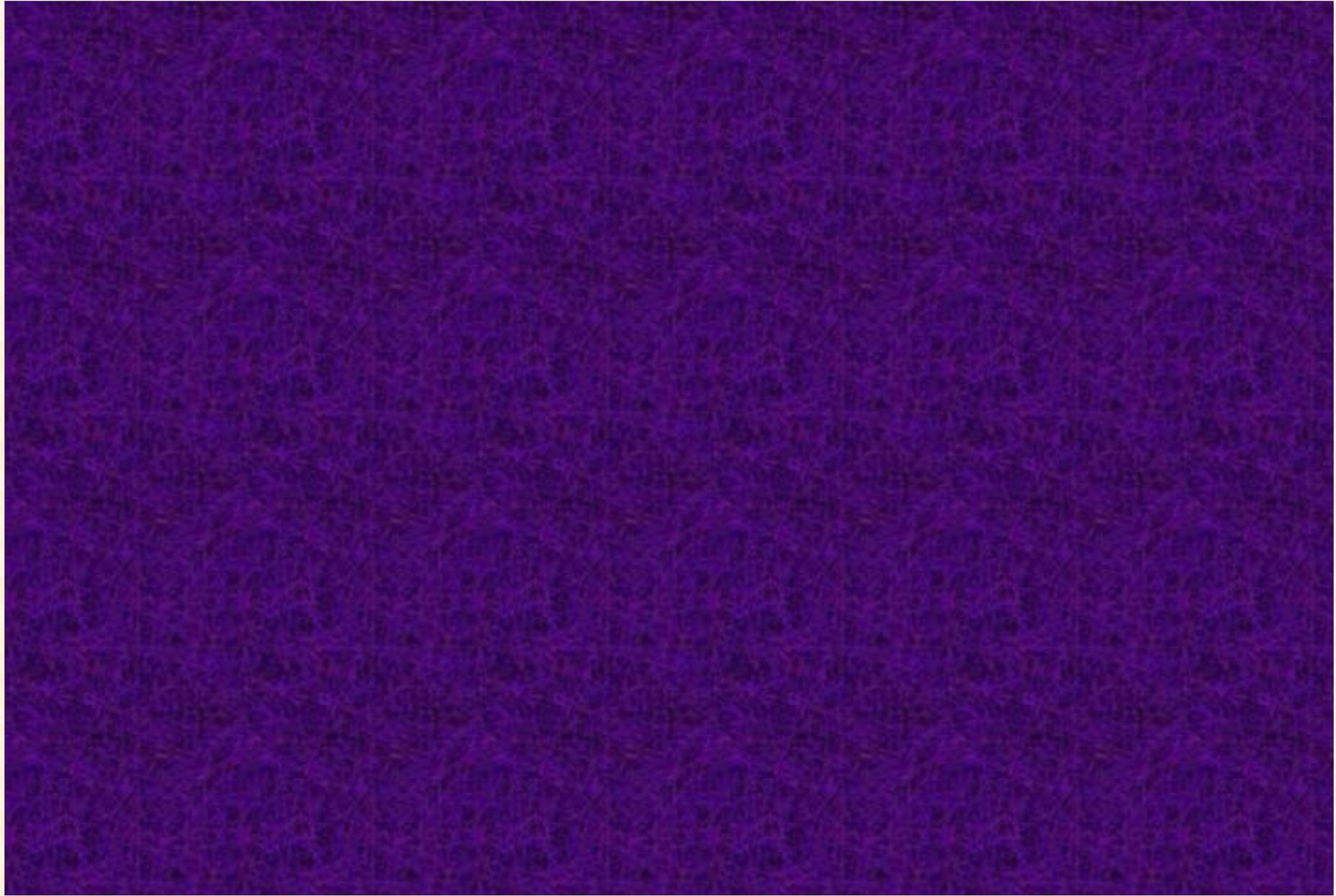
- Potentially Toxic Species (As, Cr, Pb, Zn) Showed Greater Scatter and Less Agreement Than Mass and Sulfate
- Higher Concentration Species Agreed Better than Species Observed at Lower Concentrations: MDL & Blanks are Likely an Issue Between Network Agreement
- Site-to-Site Variations Were Relatively Consistent, With Results From One Network Typically Being Higher than the Other
 - ✓ At Most Sites, Most Species Were Biased Slightly High for STN Relative to IMPROVE
 - ✓ Si and Ca Are the Major Exceptions, Where IMPROVE Is Slightly Higher Than STN.
- **In General, and on Average, Comparison Between Networks was Within Expectations for Most Species at Most Sites**
- Criteria Can Be Established Based On Past Multi-Sampler Comparisons for Chemical Components In Air
- Past Precision Results Need To Be Included in the Analysis

Disclaimer

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

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.



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