

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

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## ◀ 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

◀◀ Inlet\* to Data Base

- ❖ 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

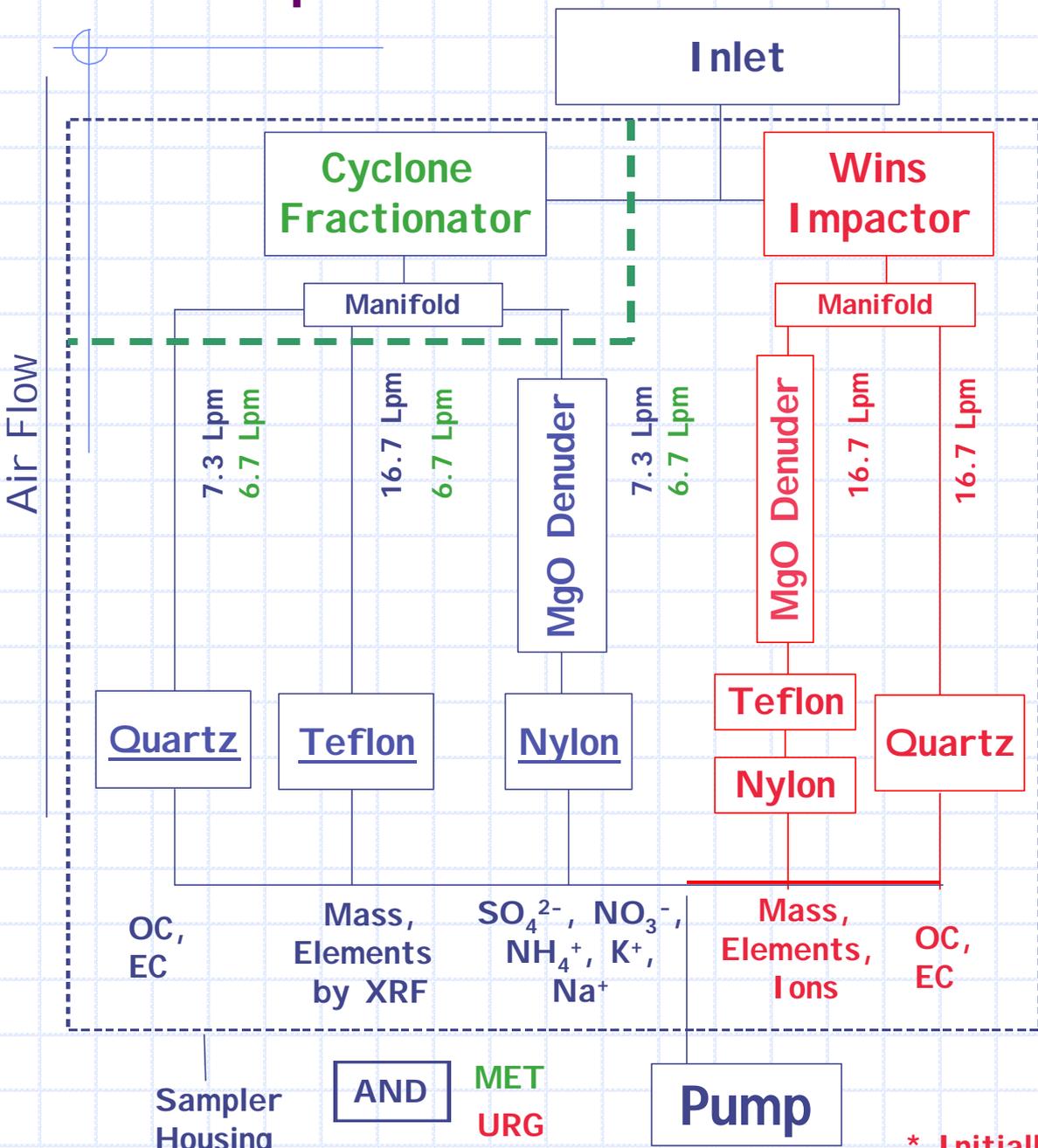
Manifold: Wall Losses

Transfer Lines:  
 Wall Losses

Denuders:  
 Efficiency  
 Capacity  
 Selectivity

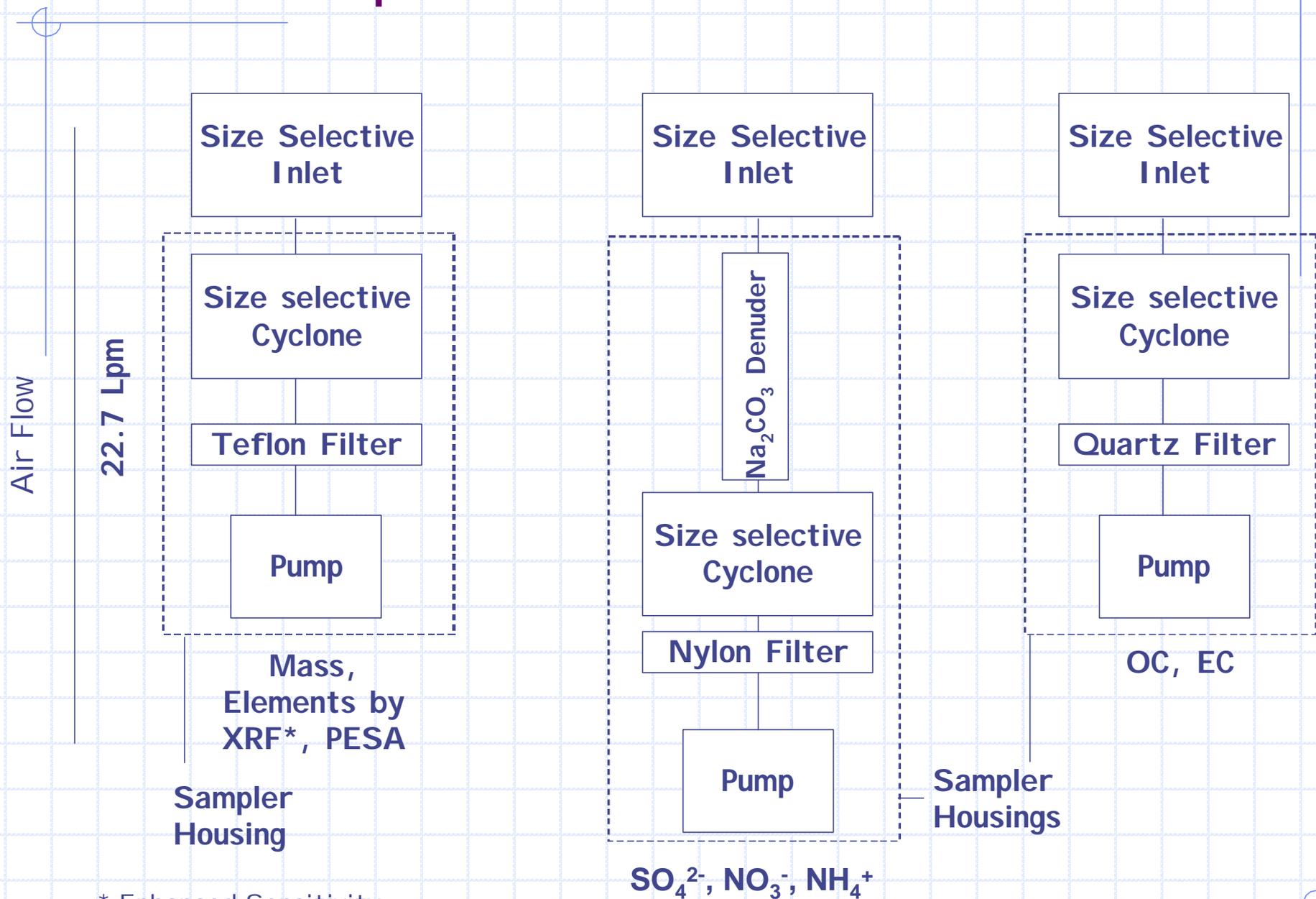
Filter - Inert  
 Loss of Volatiles  
 Blank Levels  
 Flow Rate/Face  
 Velocity

Filter - Reactive  
 Efficiency  
 Capacity  
 Selectivity  
 Stability  
 Blank Levels



\* Initially MgO

# IMPROVE Sample Collection



\* Enhanced Sensitivity

# 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\*

\* Not an Exhaustive List

### ❖ 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

# How Might Protocols Affect Results

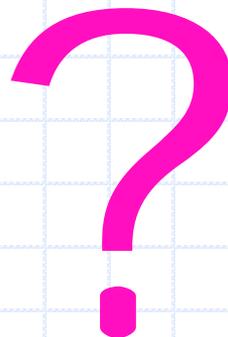
## ◀ Between Networks (cont)

### ❖ Use of IMPROVE in Urban Areas

#### ➤ Higher Flow Rate, Smaller Filters

- ✓ Filter Clogging Potential
- ✓ Denuder Capacity and Efficiency
  - $\text{Na}_2\text{CO}_3$  vs  $\text{MgO}$
  - Refurbishing Frequency of  $\text{Na}_2\text{CO}_3$
- ✓ Effect on Semi-volatiles

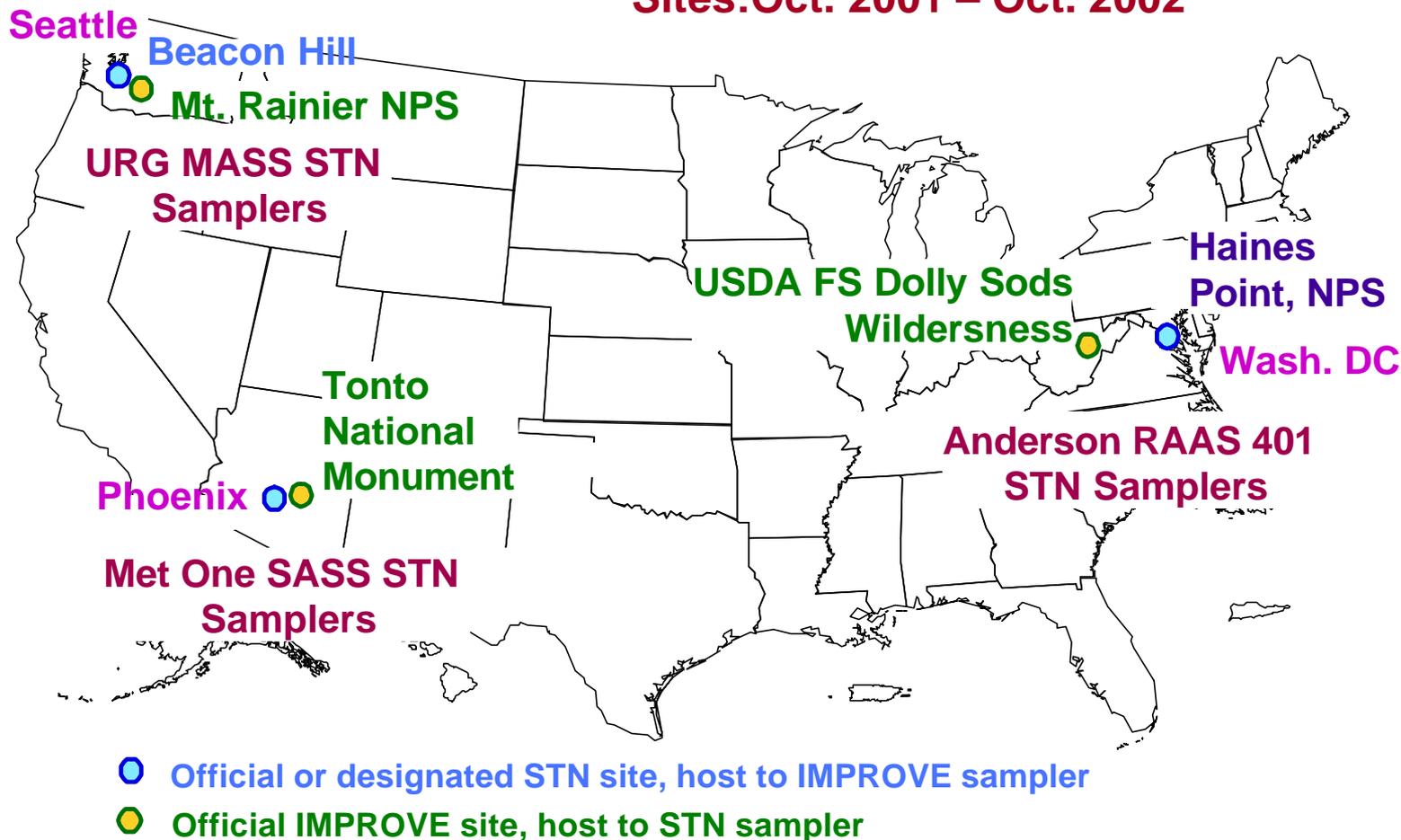
Given All these Differences, Do the  
Networks Provide Similar Results for  
Mass and the Components of Mass



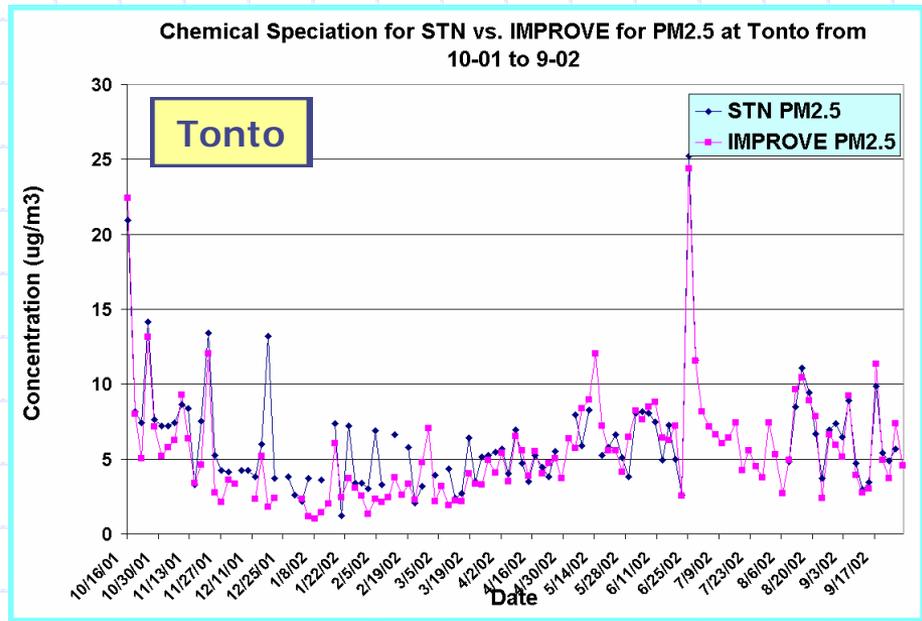
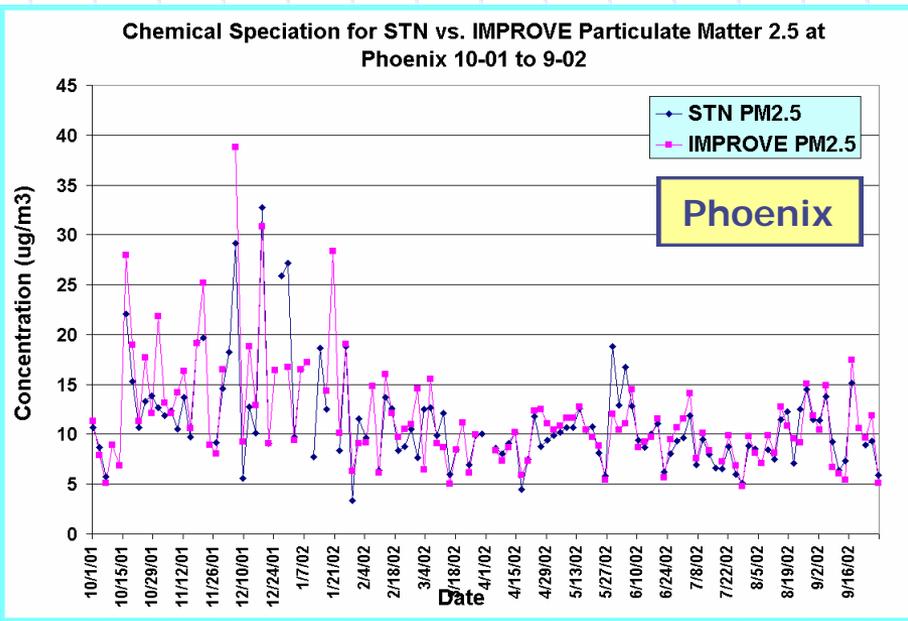
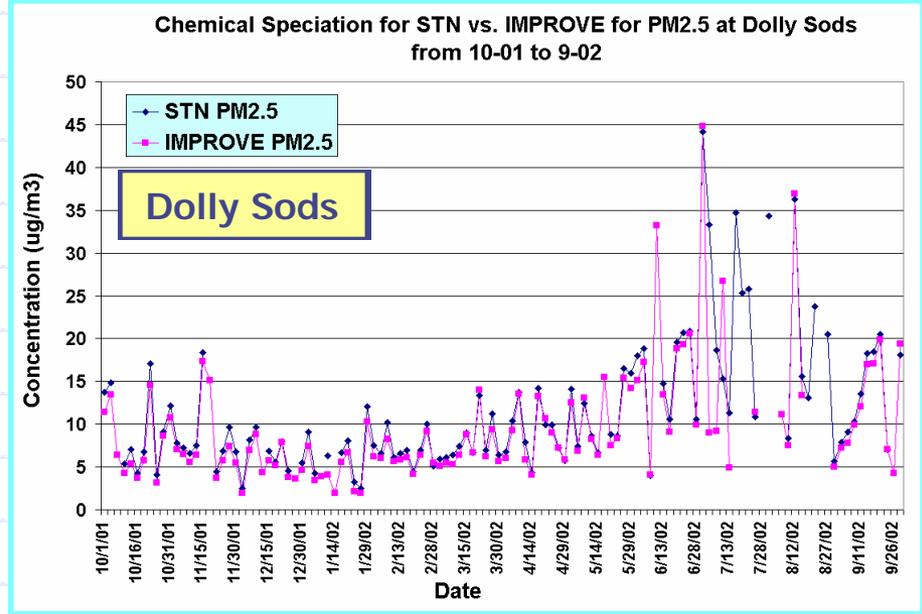
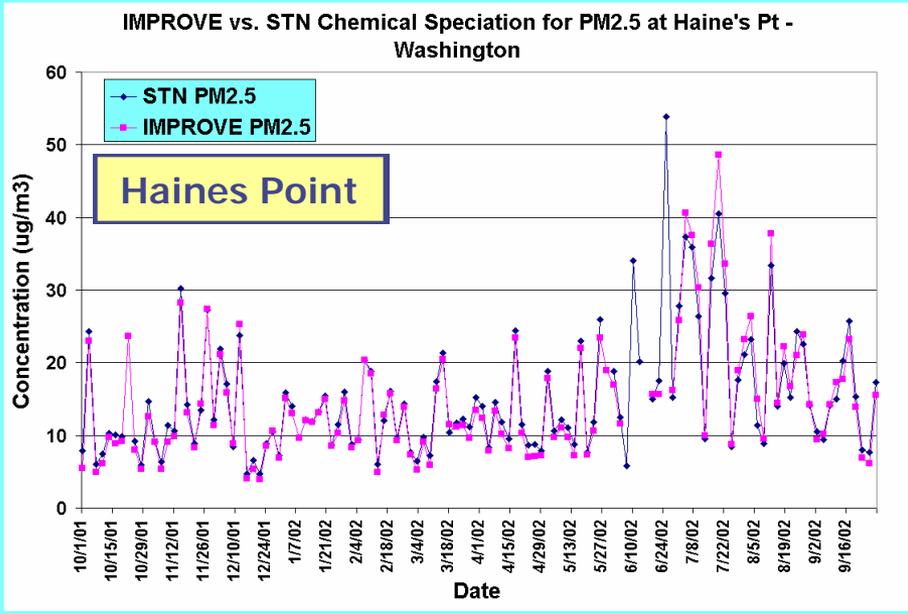
# Methods Comparison Study: STN-IMPROVE

Operated According to Each Network's Protocols

## STN/IMPROVE Monitoring Intercomparison Sites: Oct. 2001 – Oct. 2002



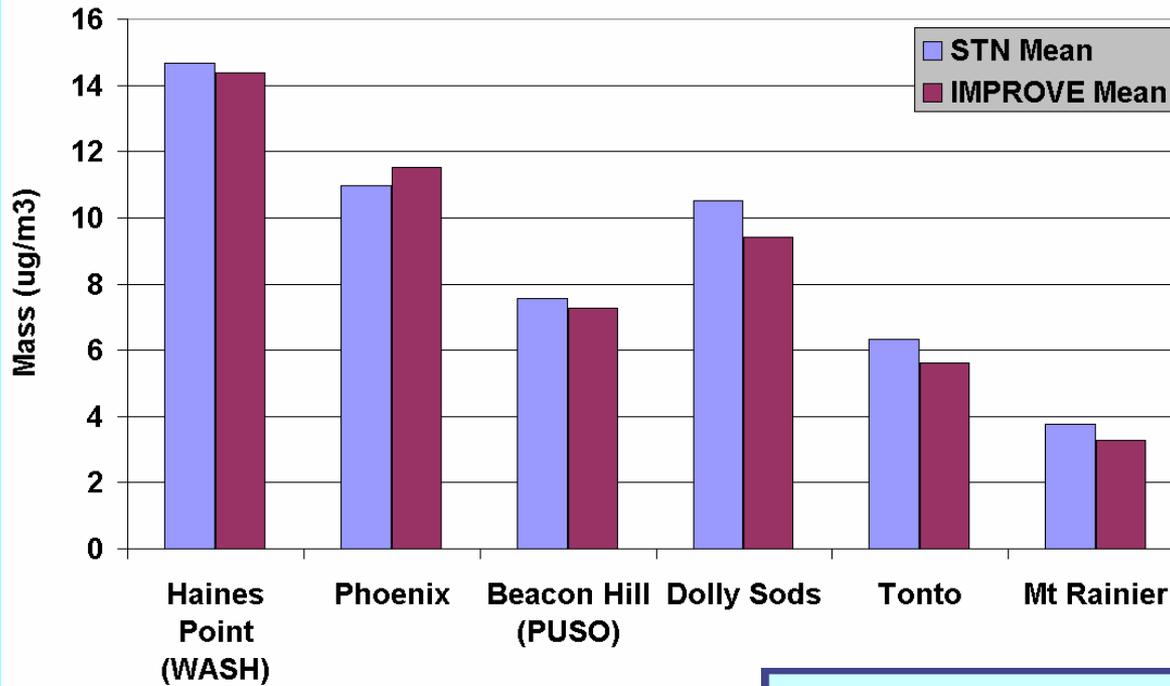
# Urban - Rural Temporal Analysis Comparison: PM2.5 Mass



# Urban - Rural Comparison of Means: PM2.5 Mass



Comparison of STN and IMPROVE Annual Average PM2.5 Mass

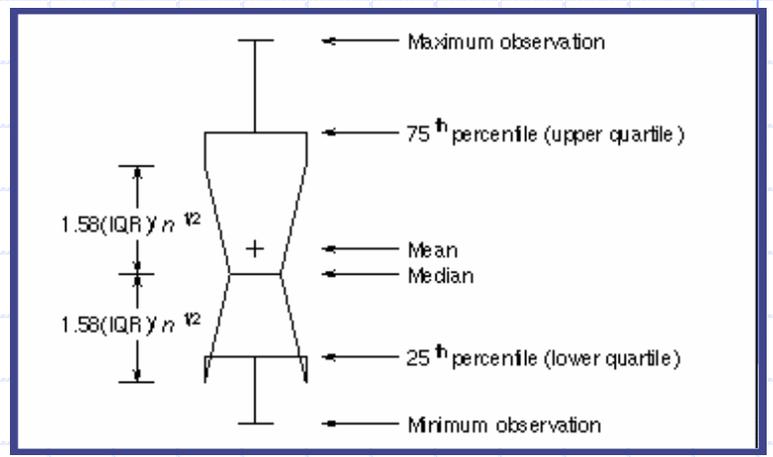
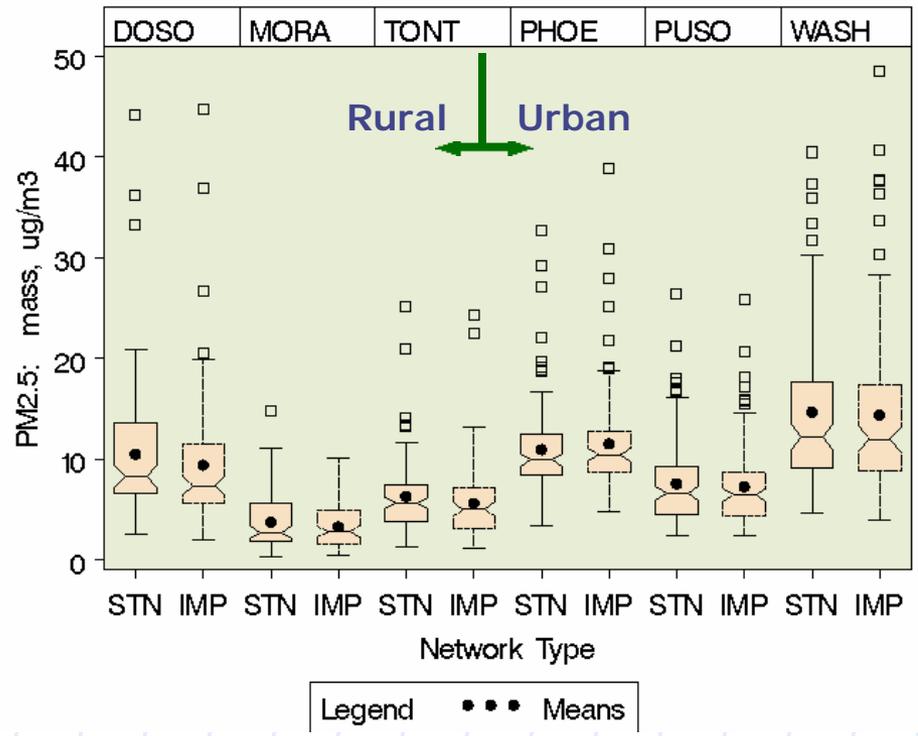


## Annual Average Results

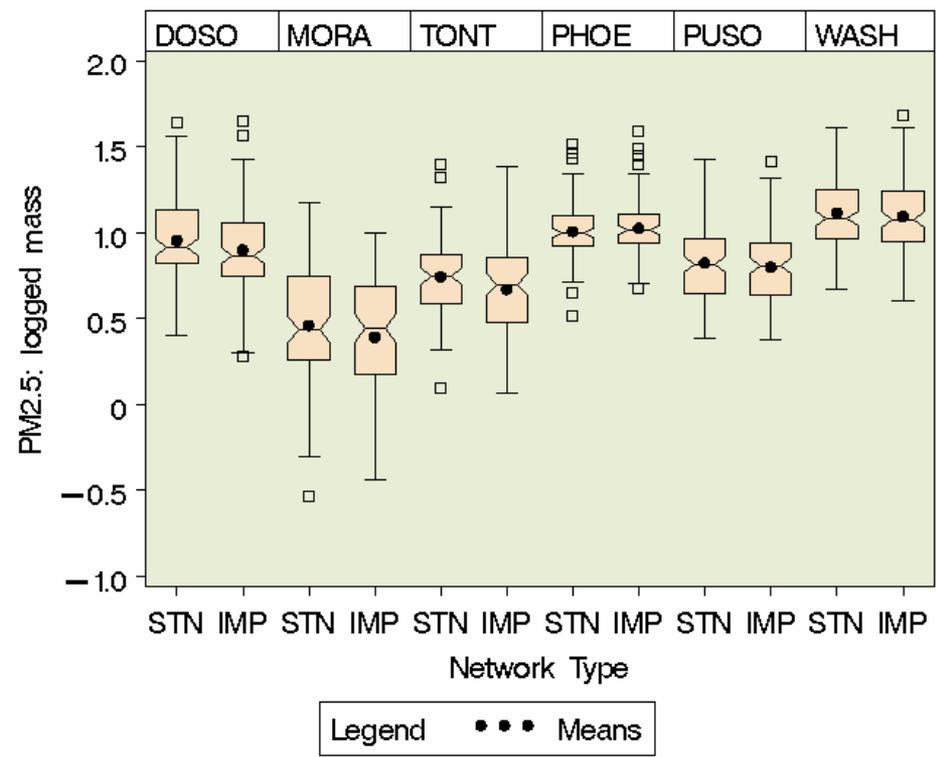
- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 50-100%
- There Is Better Agreement at Urban Sites, but Not Necessarily Due Just to Higher Pollution Levels

# Frequency Distributions Analysis: Mass (Paired Values)

PM2.5 Mass



logged PM2.5 Mass

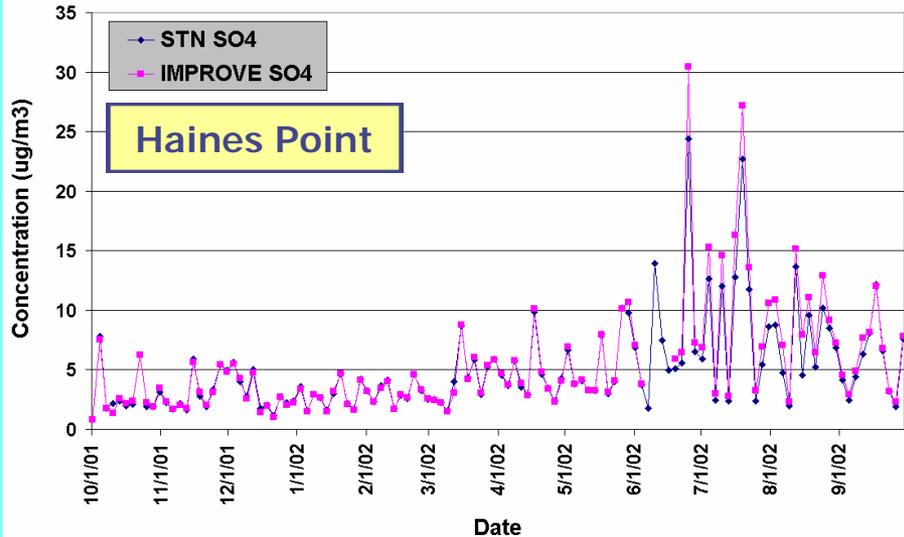


- Log Normal if Mean Is Greater Than Median
- If Notches Do Not Overlap - Distribution Median is Different (95% Confidence Limit)
- Data As Supplied by Network
- Oct 01 - Sept 02
- Investigation of Outliers Continuing

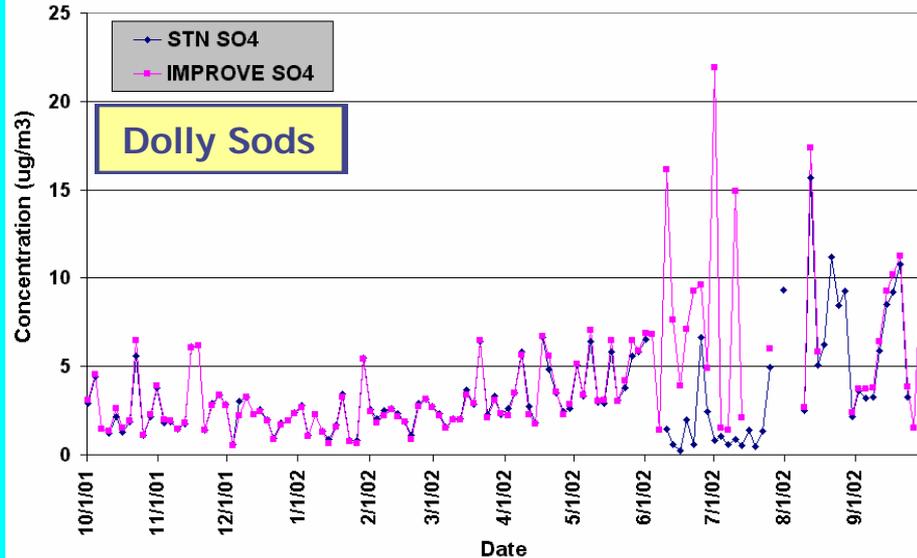
# Urban - Rural Temporal Analysis Comparison: Sulfate



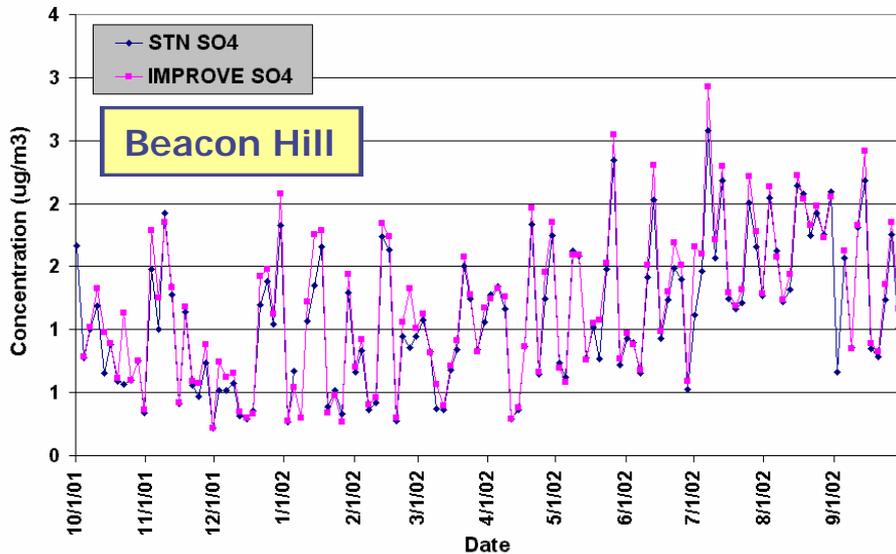
STN vs. IMPROVE Chemical Speciation for Sulfate at Haine's Pt - Washington



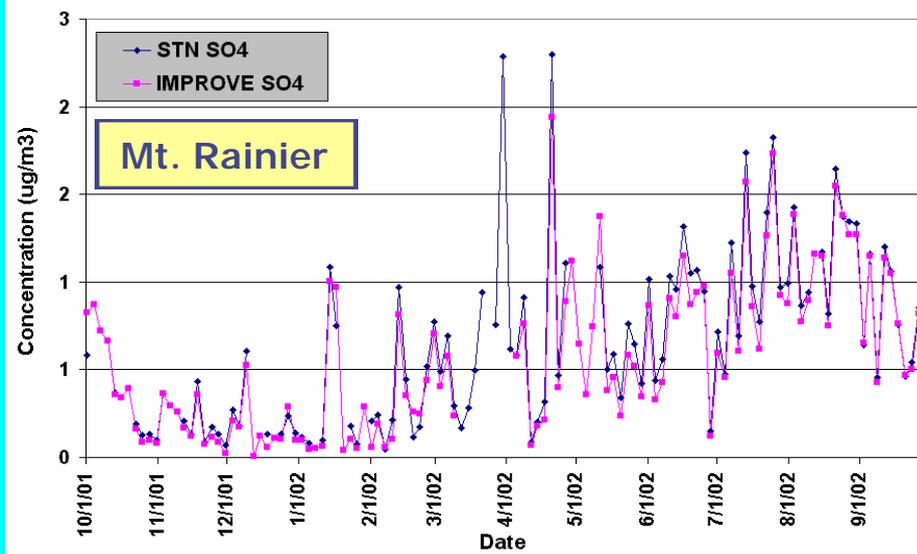
Chemical Speciation for STN vs. IMPROVE for Sulfate at Dolly Sods 10-01 to 9-02



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

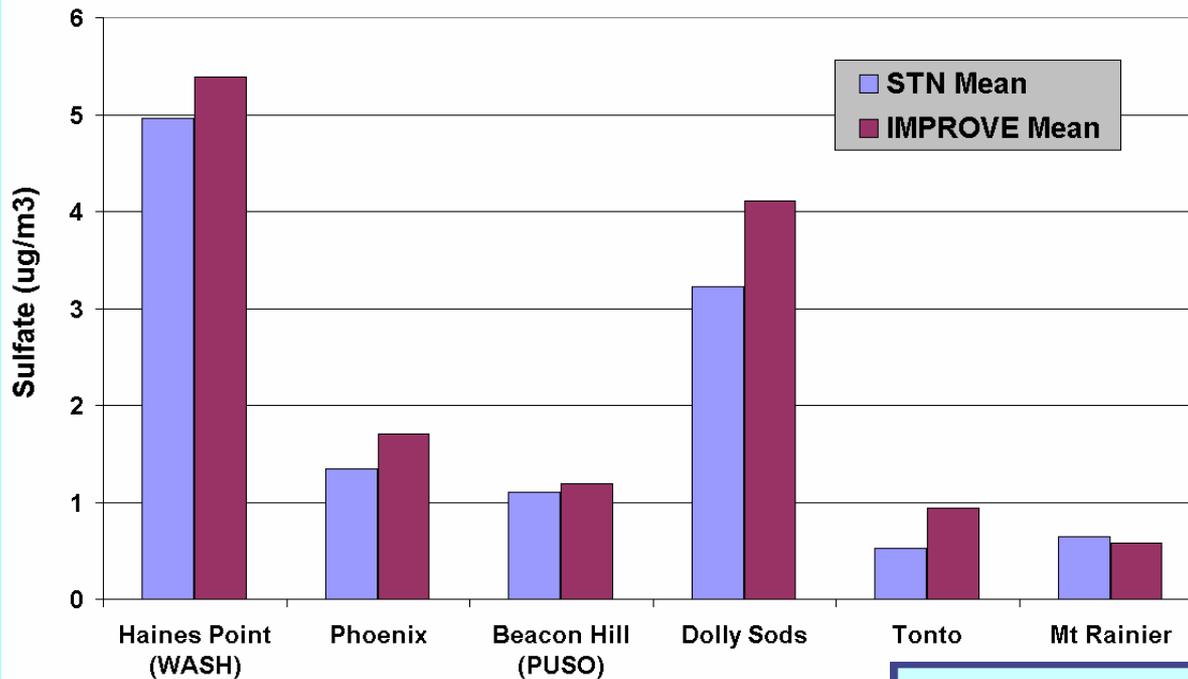


STN vs. IMPROVE Chemical Speciation for Sulfate at Mt. Rainier from 10-01 to 9-02



# Urban - Rural Comparison of Means: Sulfate

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



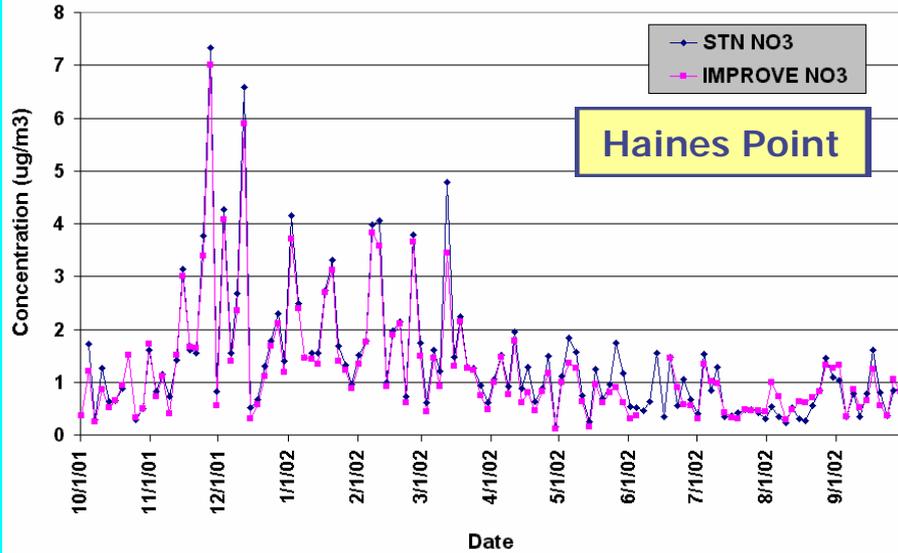
## Annual Average Results

- 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

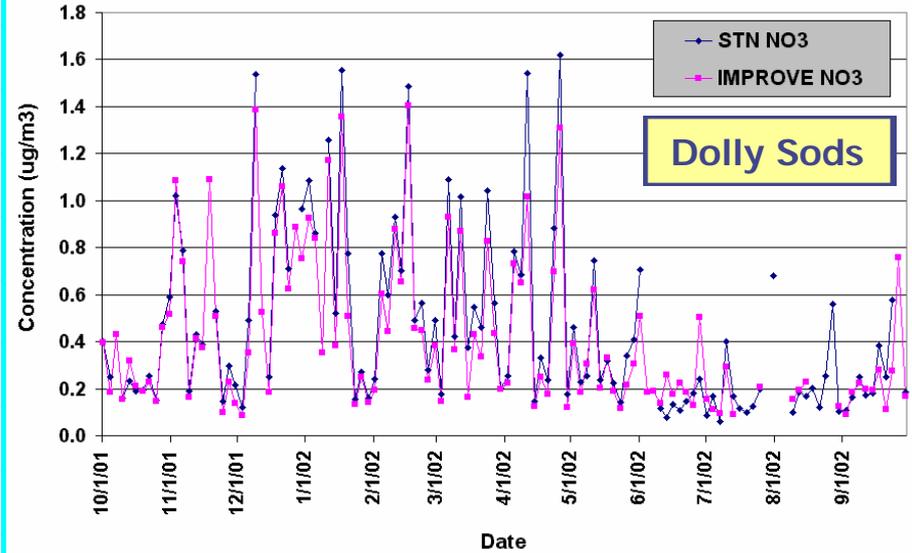
# Urban - Rural Temporal Analysis Comparison: Nitrate



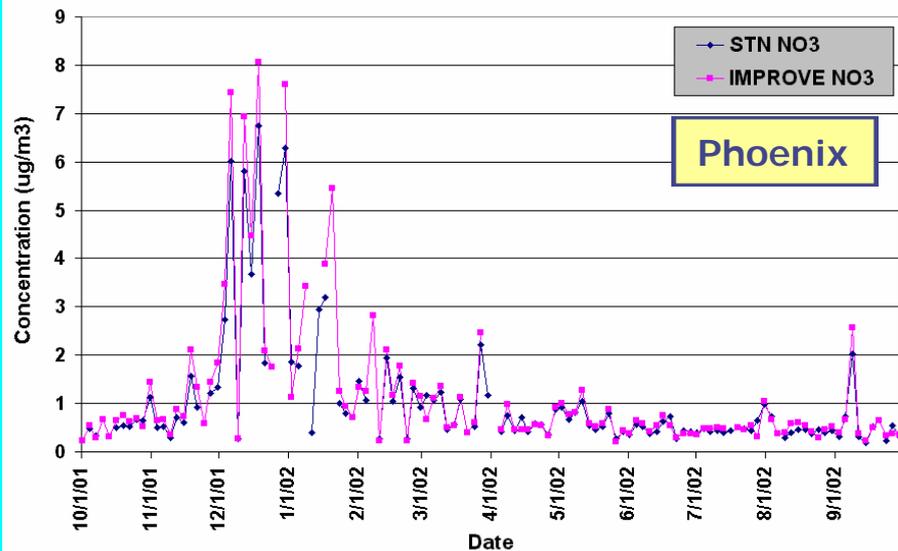
STN vs. IMPROVE Chemical Speciation for Nitrate at Haine's Pt - Washington 10-01 to 9-02



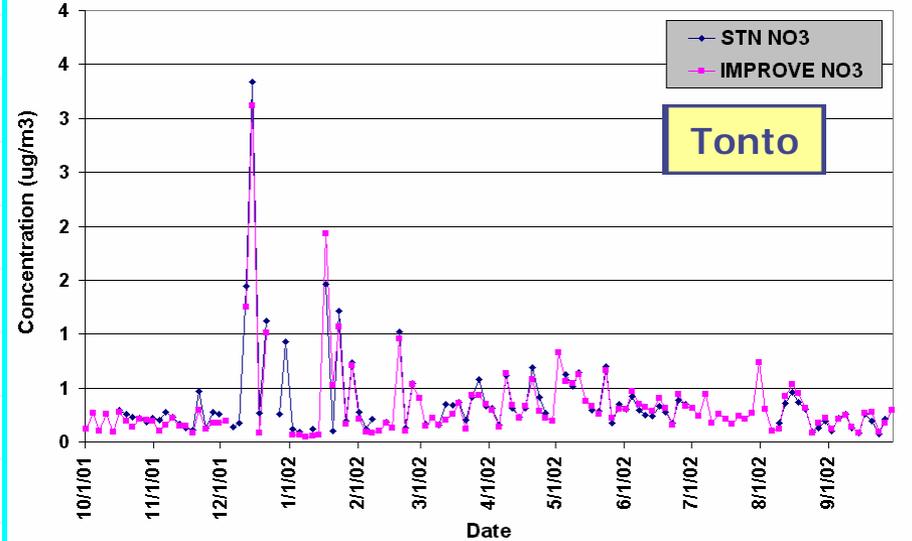
Chemical Speciation for STN vs. IMPROVE for Nitrate at Dolly Sods from 10-01 to 9-02



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



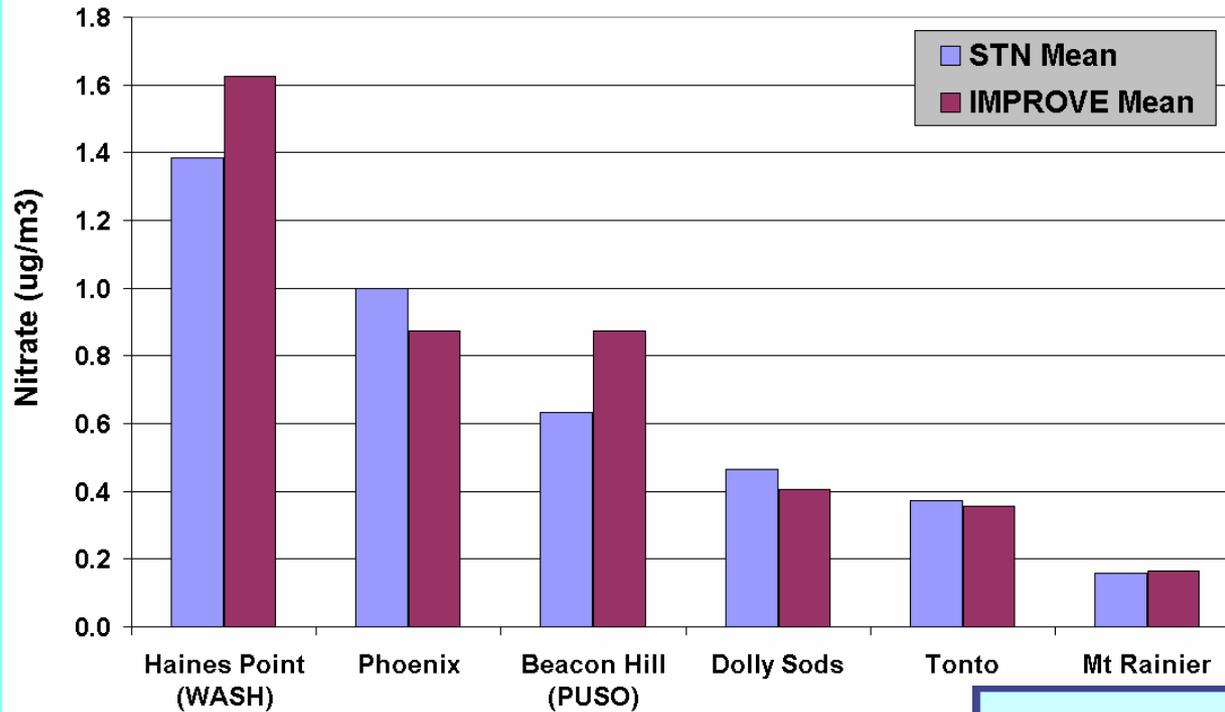
Chemical Speciation for STN vs. IMPROVE for Nitrate at Tonto from 10-01 to 9-02



# Urban - Rural Comparison of Means: Nitrate



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



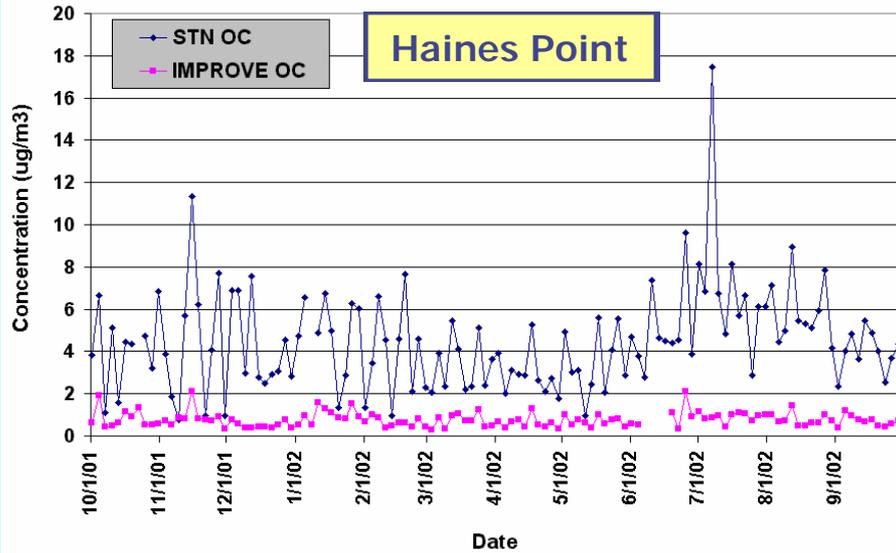
## Annual Average Results

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

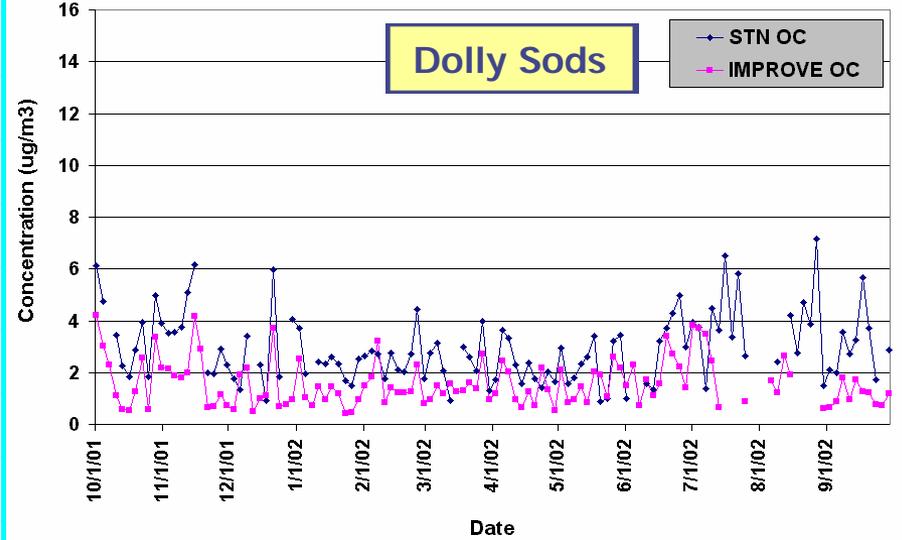
# Urban - Rural Temporal Analysis Comparison: OC



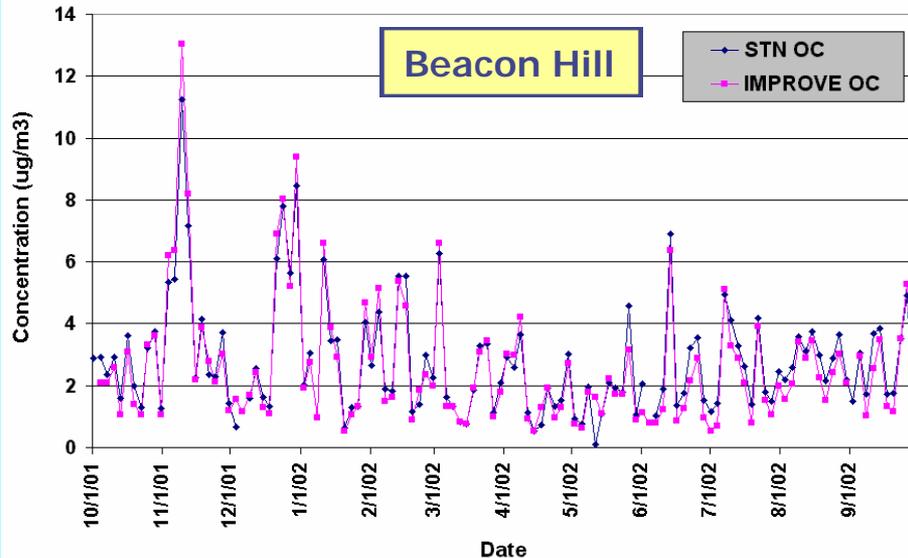
STN vs. IMPROVE Chemical Speciation for Organic Carbon at Haines Pt - Washington



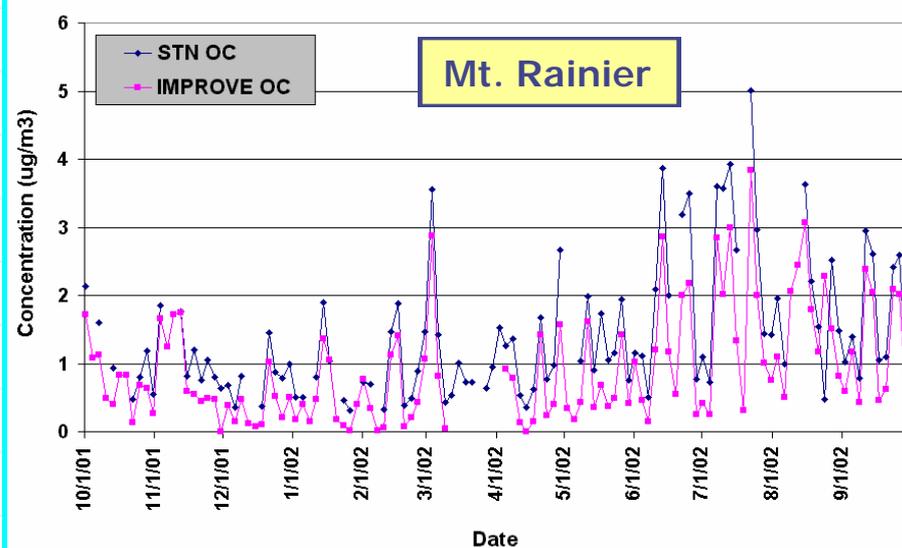
Chemical Speciation for STN vs. IMPROVE for Organic Carbon at Dolly Sods from 10-01 to 9-02



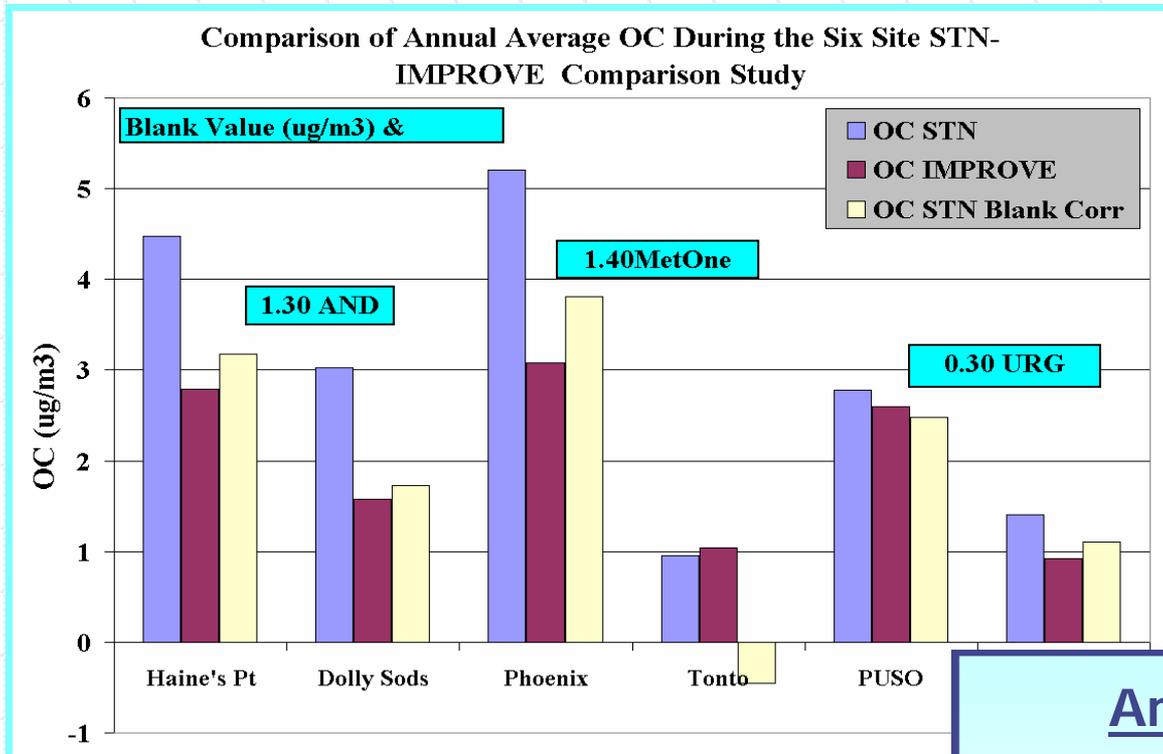
Chemical Speciation for STN vs. IMPROVE for Organic Carbon at Puget Sound-Beacon Hill from 10-01 to 9-02



STN vs. IMPROVE Chemical Speciation for Organic Carbon at Mt. Rainier



# Urban - Rural Comparison of Means: OC

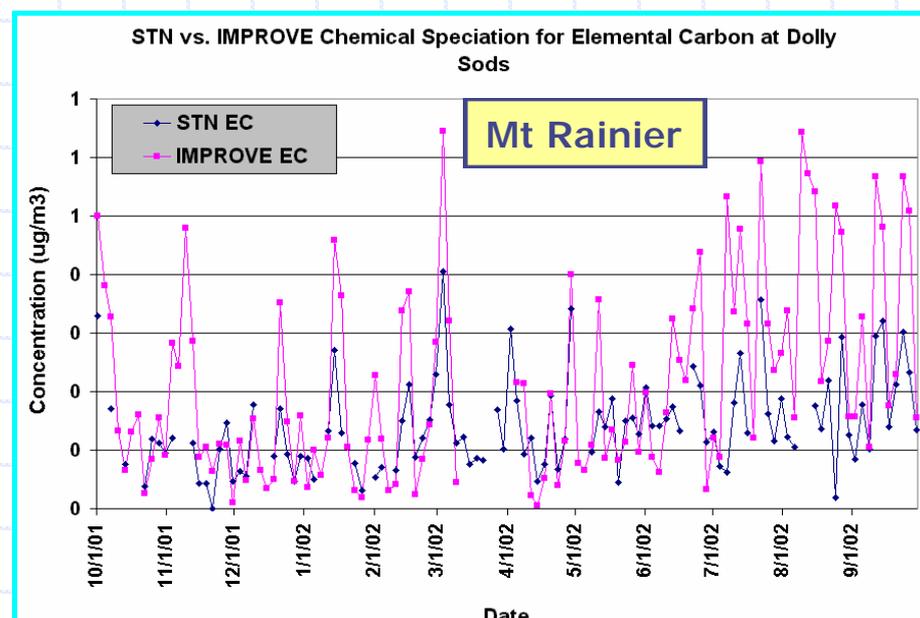
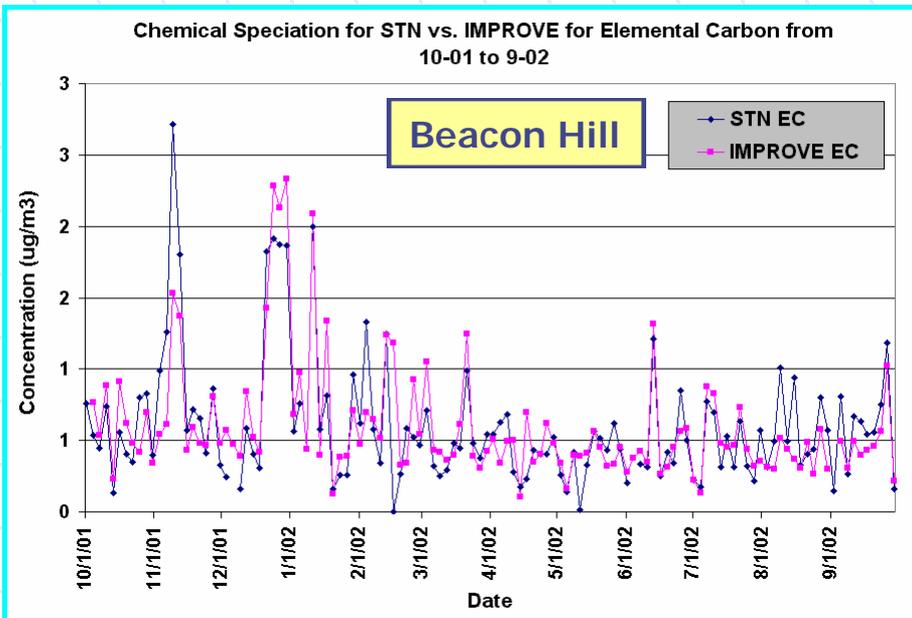
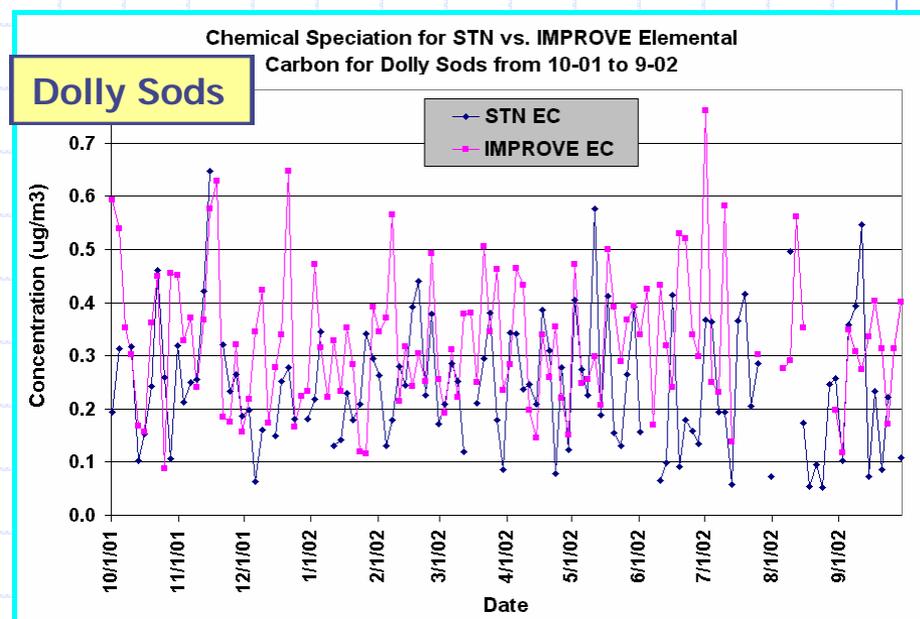
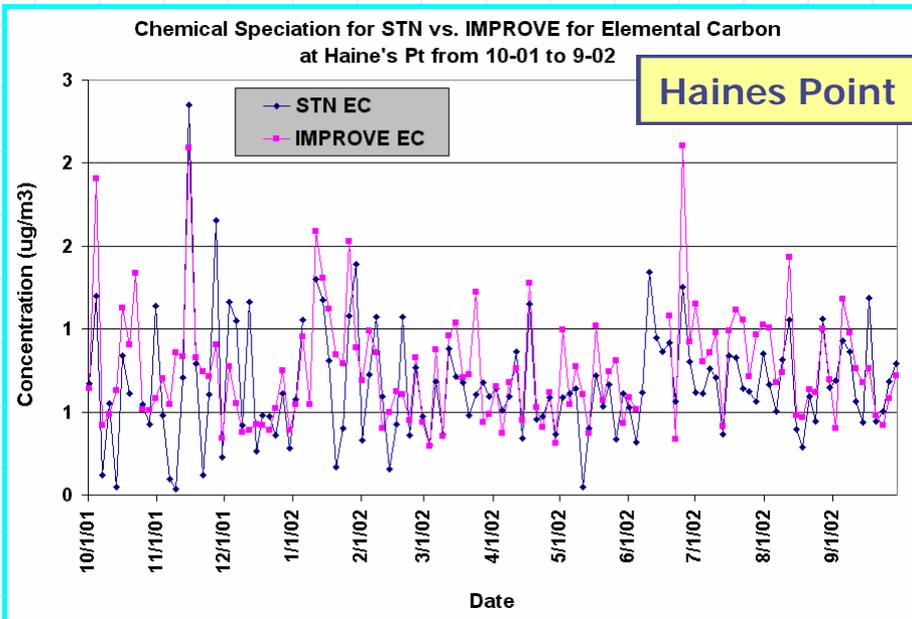


Blank Values Are Based on Trip and Field Blanks for the Averaged Over the Time Period of the Study

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

- ### 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

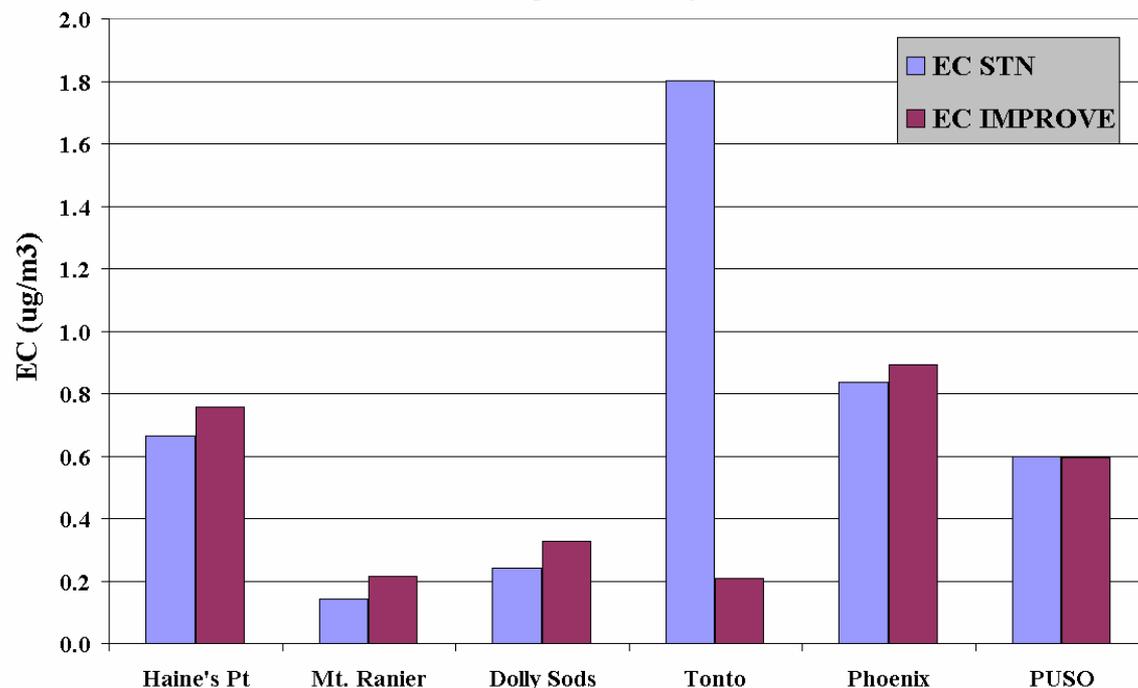
# Urban - Rural Temporal Analysis Comparison: EC



# Urban - Rural Comparison of Means: EC



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



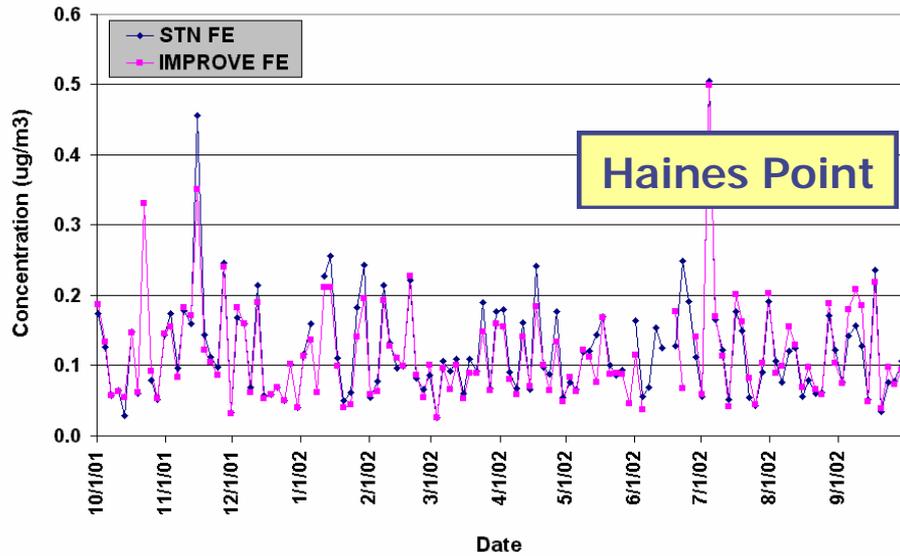
## Annual Average Results

- 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

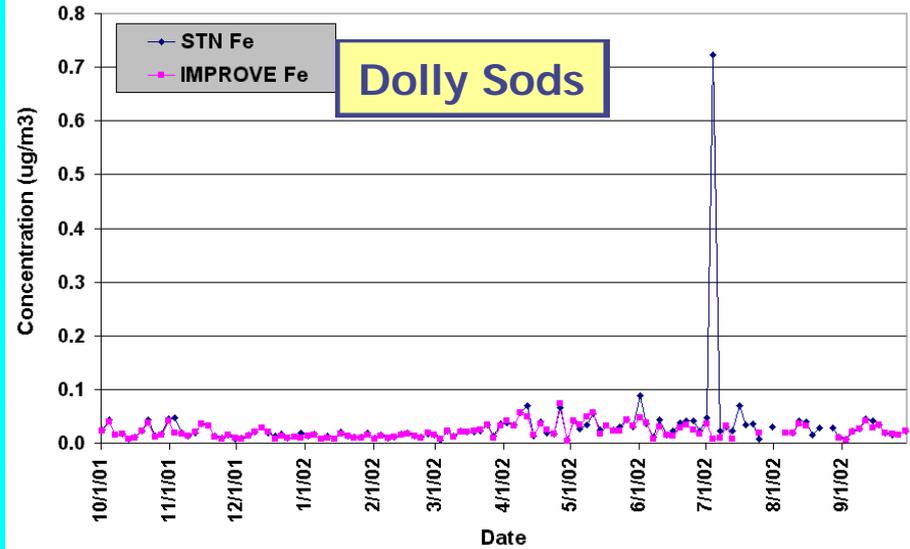
# Urban - Rural Temporal Analysis Comparison: Fe



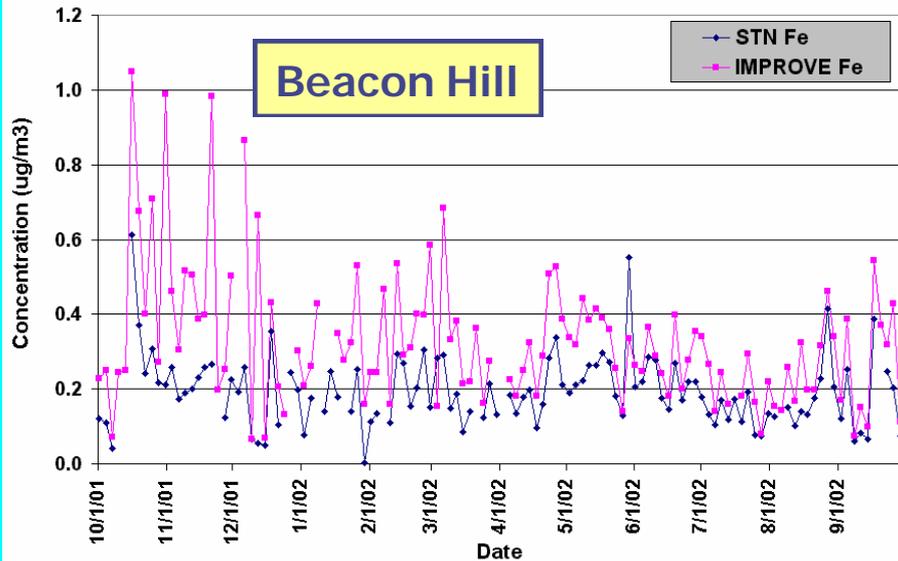
### IMPROVE vs. STN Chemical Speciation for Haine's Pt - Washington



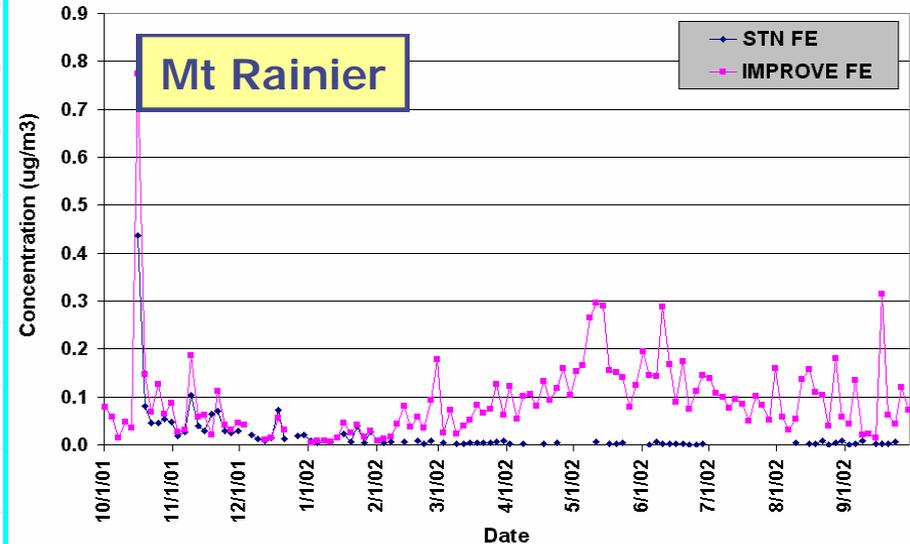
### STN vs. IMPROVE Chemical Speciation for Iron at Dolly Sods from 10-01 to 9-02



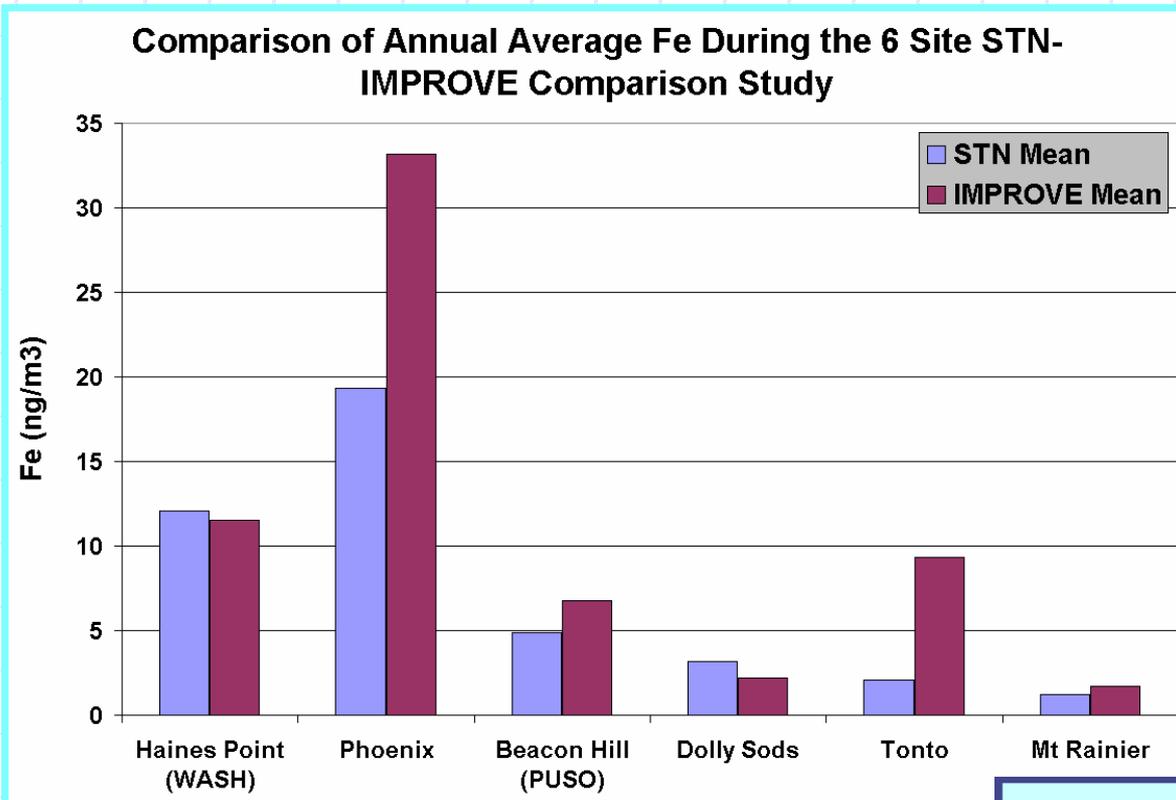
### Chemical Speciation for IMPROVE vs. STN at Beacon Hill from 10-01 to 9-02



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



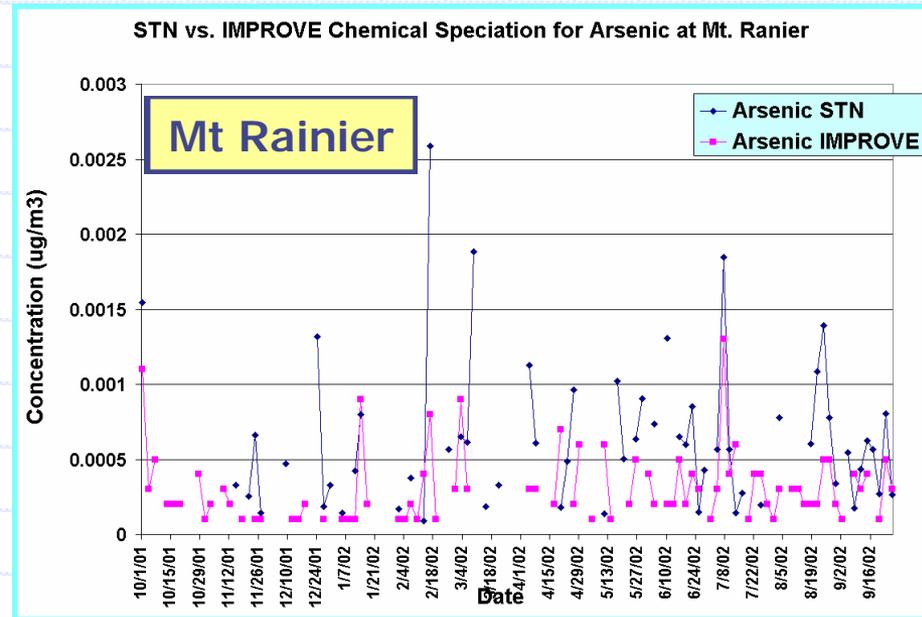
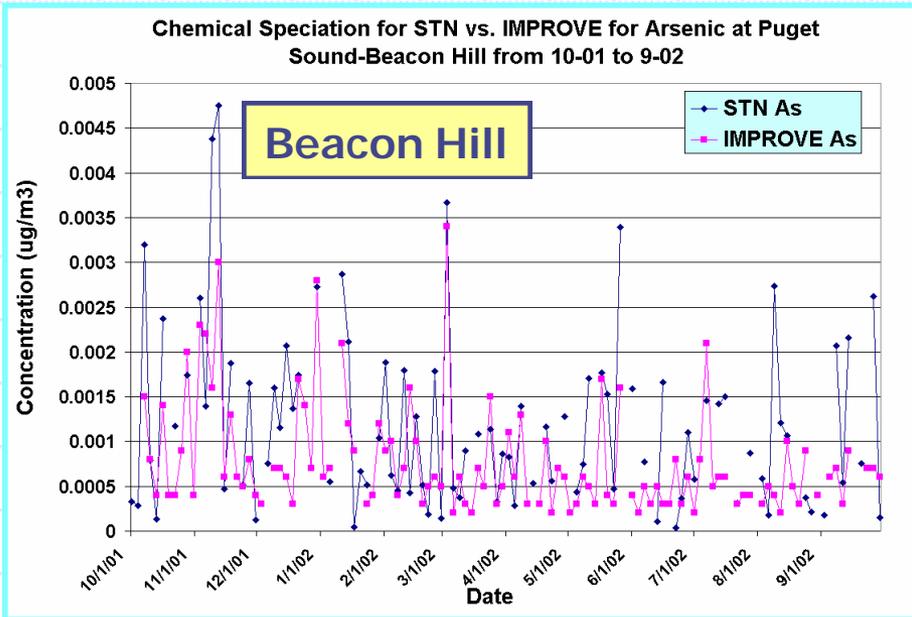
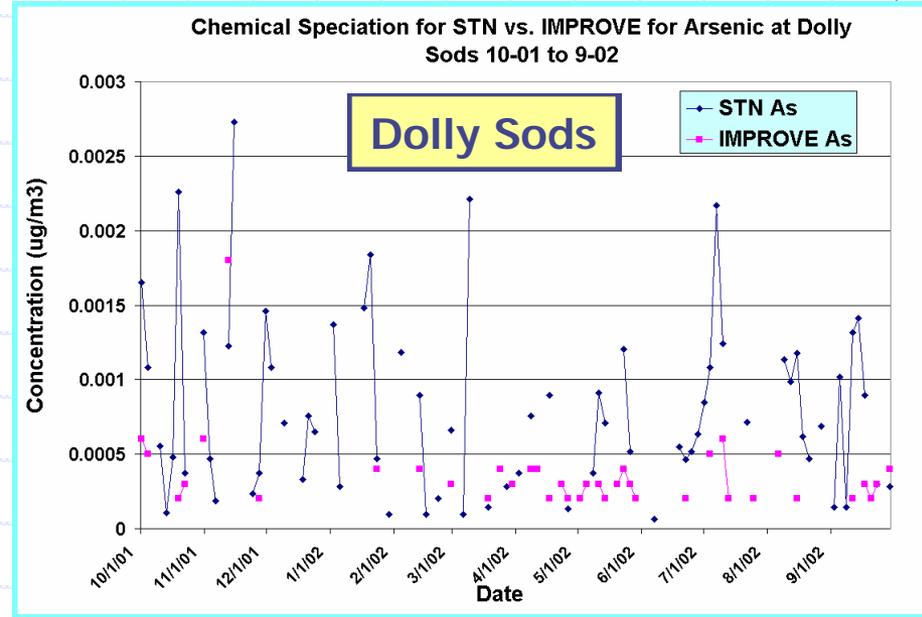
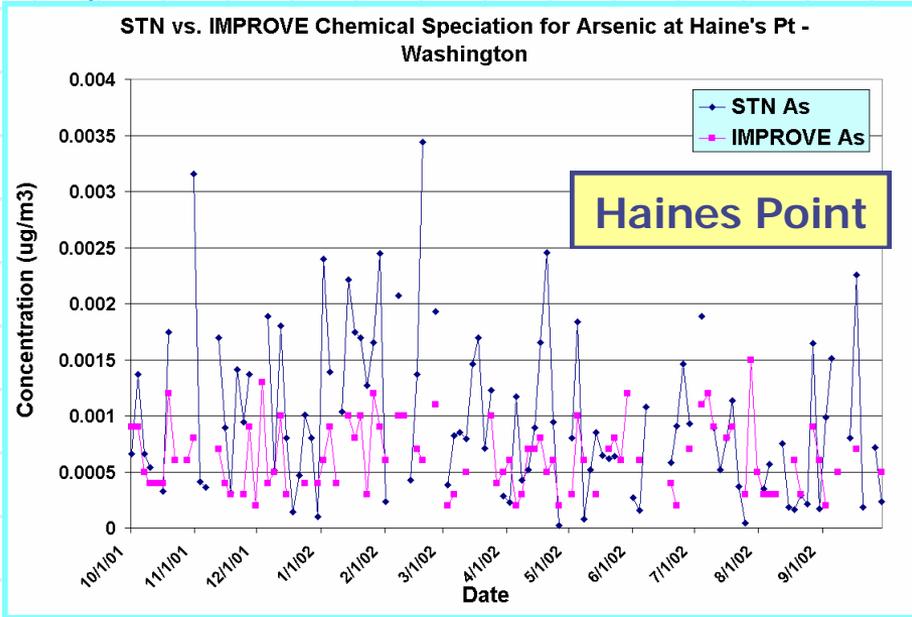
# Urban - Rural Comparison of Means: Fe



## Annual Average Results

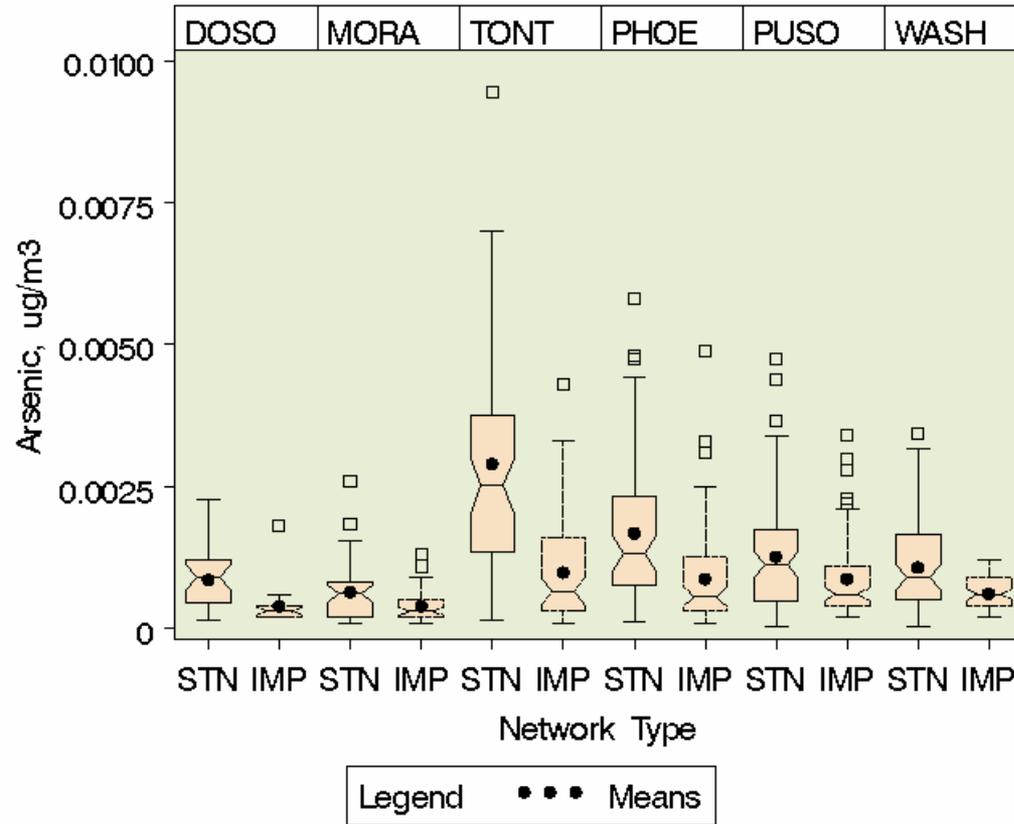
- Concentrations are Higher in Urban Areas Than Rural Areas
- Phoenix Has the Highest Concentrations, Mt. Rainier the Lowest
- With the Exception of Phoenix and Tonto Agreement is Similar Between Rural and Urban Sites
- QA Is in Progress to Ensure This Is Valid Data

# Urban - Rural Temporal Analysis Comparison: Arsenic



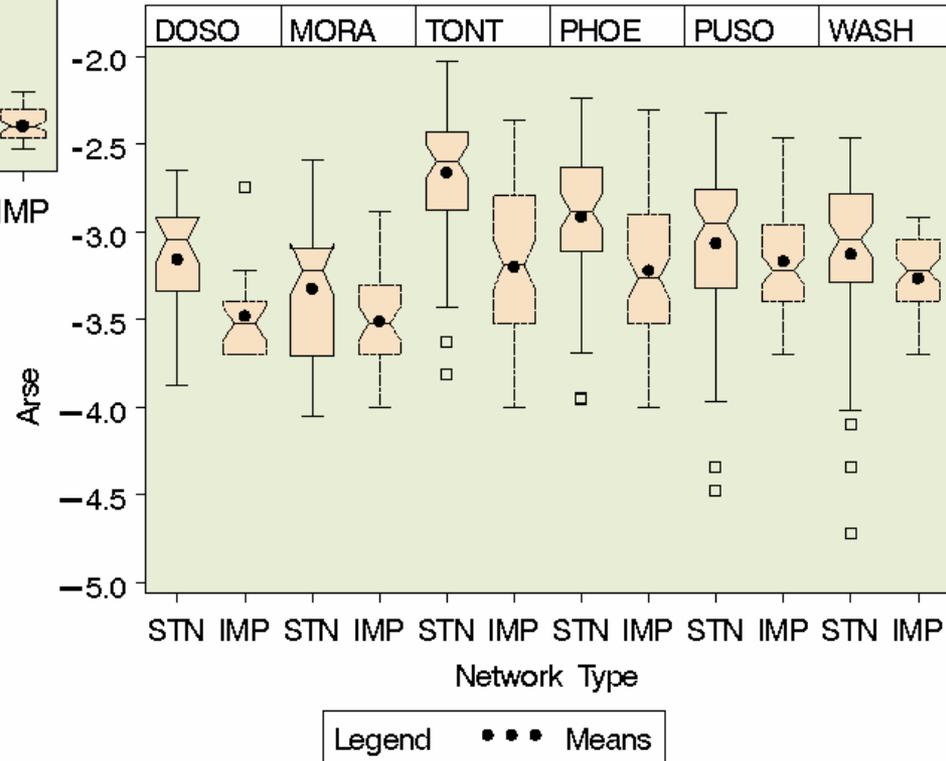
# Frequency Distributions Analysis: Arsenic

Arsenic, ug/m3



## Frequency Distributions - Paired Samplers, All Sites: Arsenic

logged Arsenic

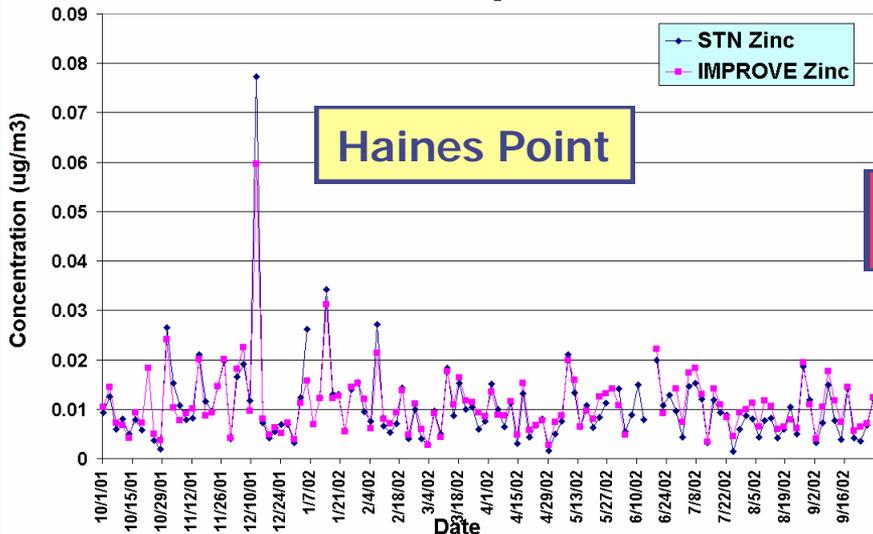


- Distributions at a Given Sites Are Not Similar Between Networks
- Notches Do Not Overlap at Any of the Sites
- Cr Similar to As

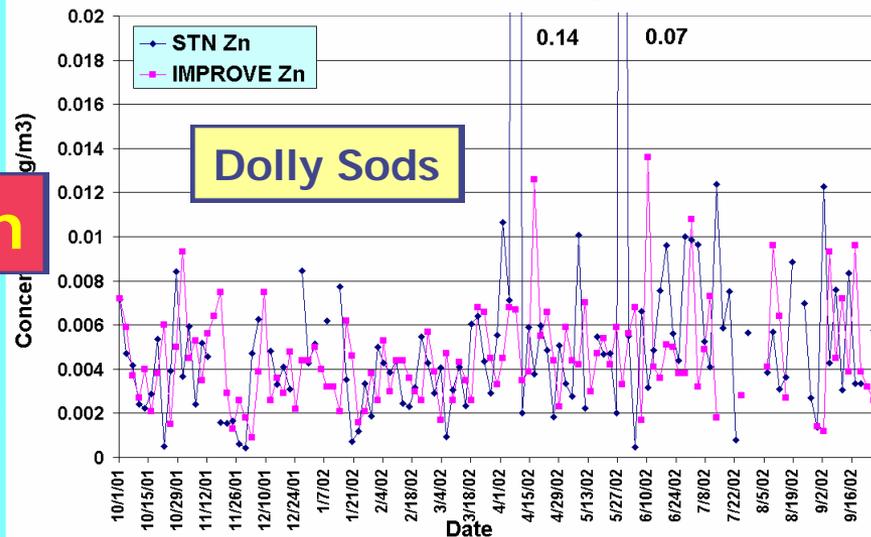
# Urban - Rural Temporal Analysis Comparison: Zn & Pb



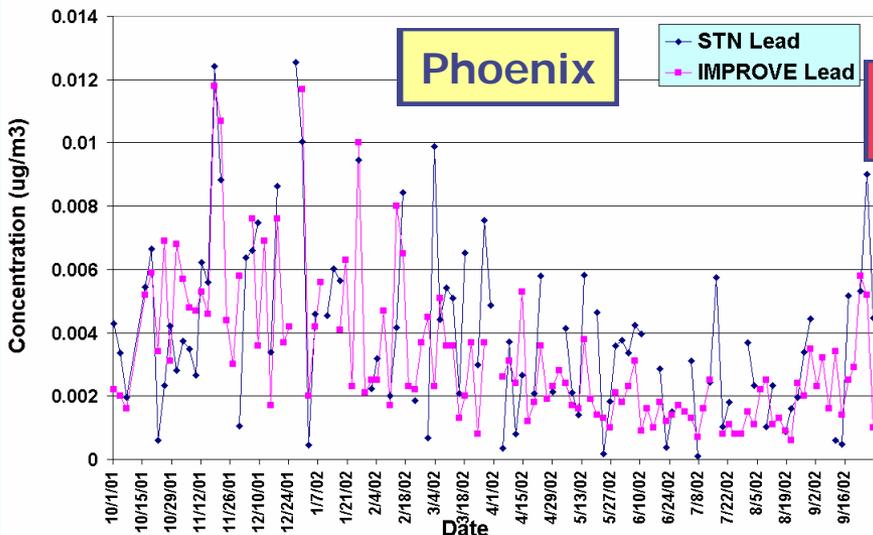
### STN vs. IMPROVE Chemical Speciation for Zinc at Haine's Pt - Washington



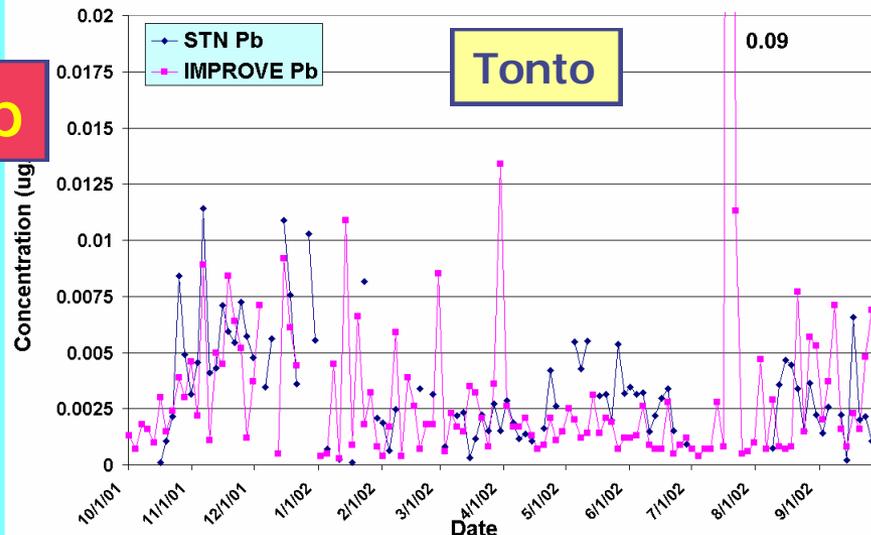
### Chemical Speciation for STN vs. IMPROVE for Zinc at Dolly Sods from 10-01 to 9-02



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

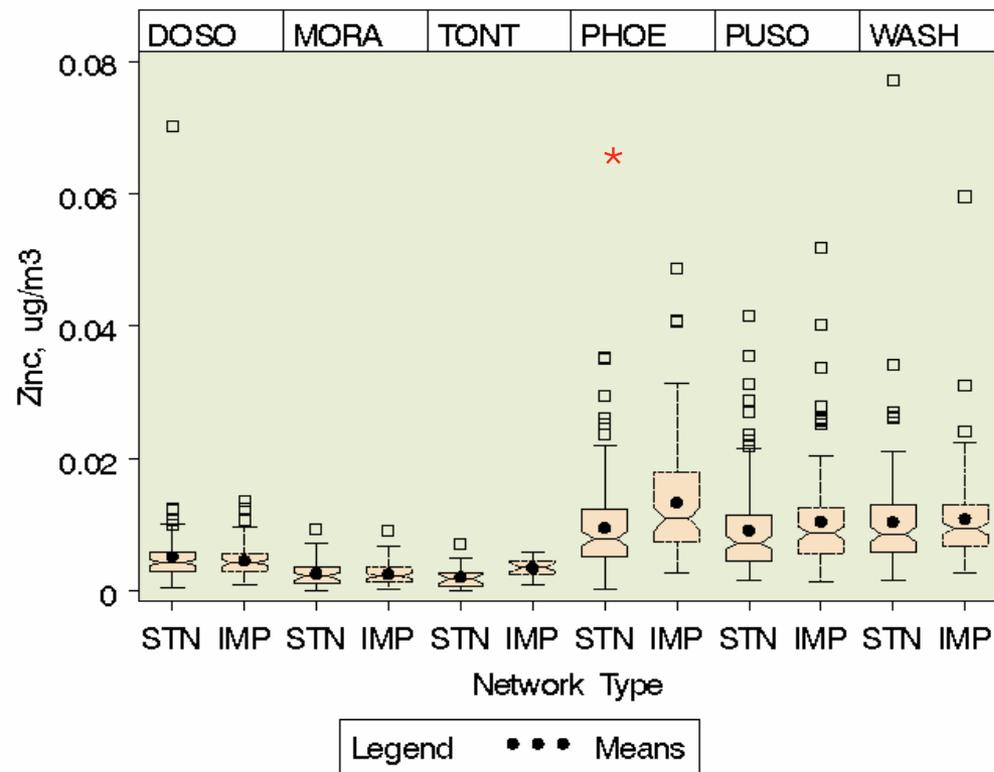


### Chemical Speciation for STN vs. IMPROVE for Lead at Tonto from 10-01 to 9-02

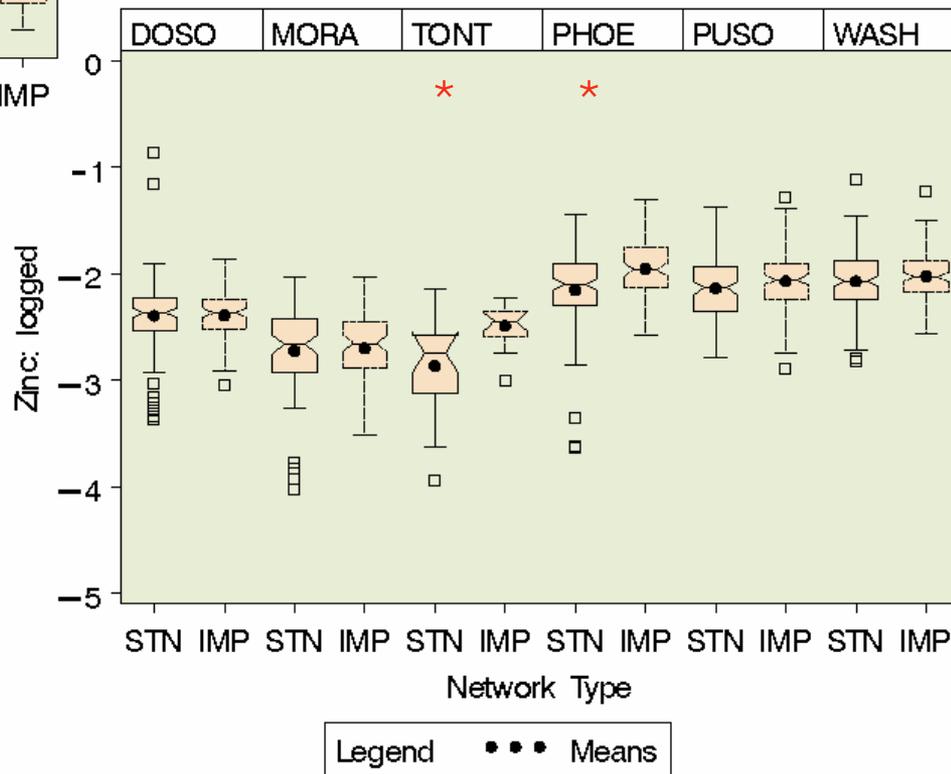


Zinc, ug/m<sup>3</sup>, DOSO outlier removed

# Frequency Distributions - Paired Samplers, All Sites: Zinc



logged Zinc



- 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  $1 \pm 0.1$ ;  $R^2 > 0.9$
- ❖ Sulfate Ratio  $1 \pm 0.05$ ;  $R^2 > 0.95$

◀ What Is a Practical Difference?

- ❖ Mass & Sulfate  $\pm 1 \text{ ug/m}^3$ ,  $\pm 0.5 \text{ ug/m}^3$
- ❖ 'Toxic' Species  $\pm 1 \text{ ng/m}^3$ ,  $\pm 0.5 \text{ ng/m}^3$
- ❖ 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*

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