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

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

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STN – IMPROVE Networks Comparison Study

✗ Over Arching Questions

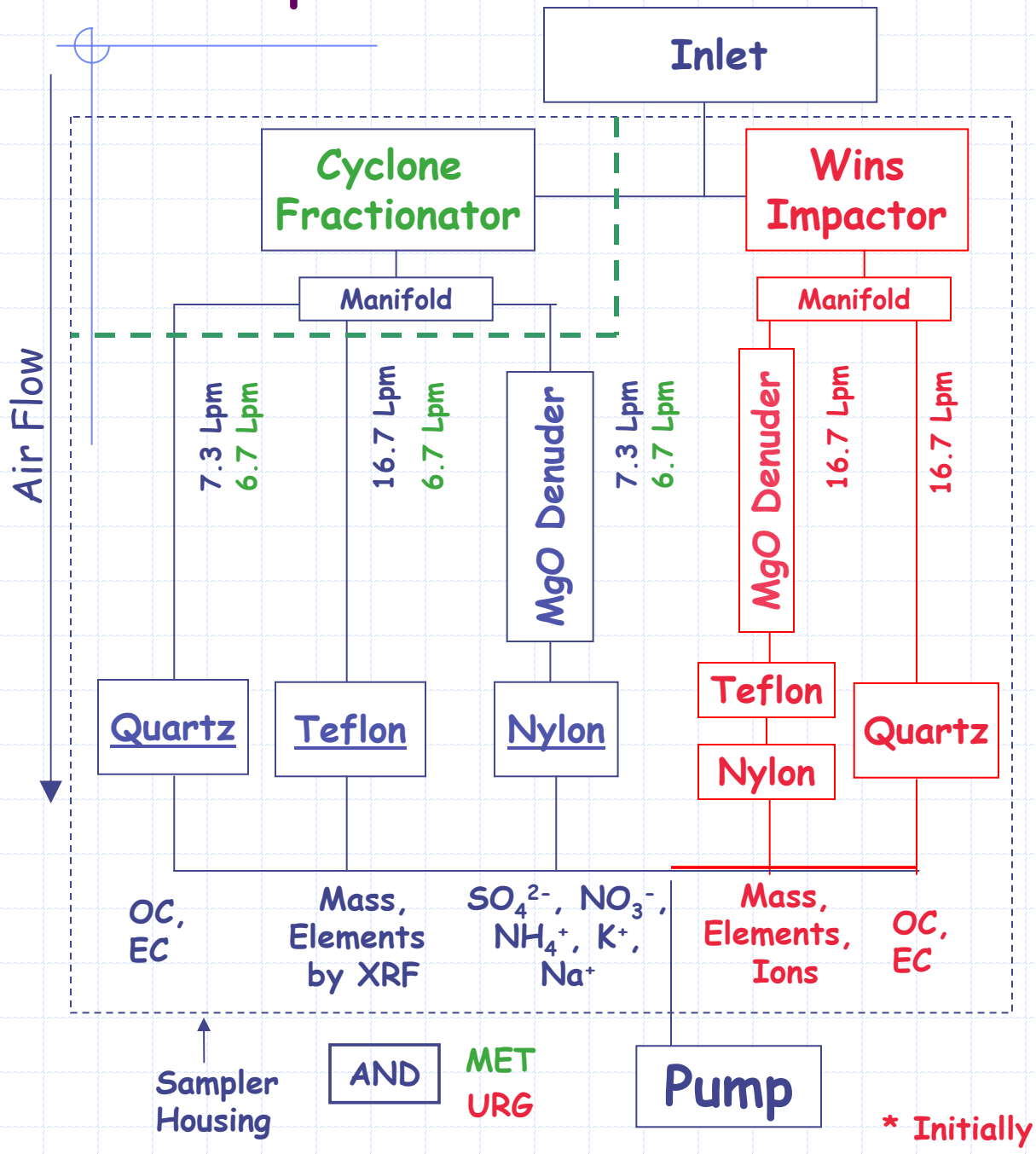
- Is there a Difference Between the Two Networks and for Which Species?
- If Yes, How Large?
- Does Bias Matter Or is Consistency More Important?
  - Do We Need to Know Absolute Concentrations?
    - ✓ If Yes, Which Network Provides EPA the Least Bias Results for Implementation Needs???
  - Is Highly 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
- 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

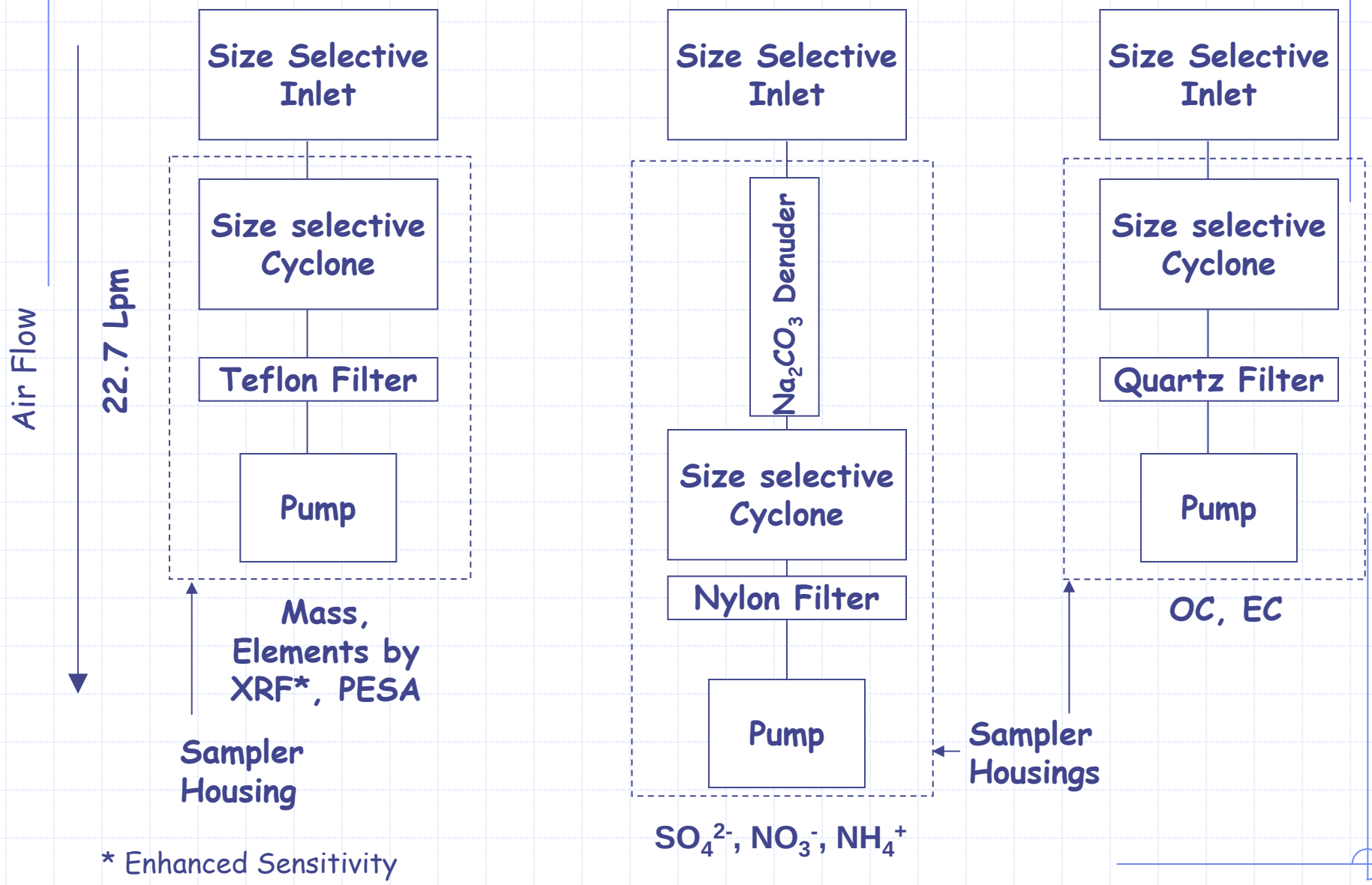
Transfer Lines:
- Wall Losses

Denuders:
- Efficiency
- Capacity
- Selectivity

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

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

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

EPA

X 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

X Between Networks (cont)

- Use of IMPROVE in Urban Areas
  - Higher Flow Rate, Smaller Filters
    - ✓ Filter Clogging Potential
    - ✓ Denuder Capacity and Efficiency
      - o Na_2CO_3 vs MgO
      - o Refurbishing Frequency of Na_2CO_3
    - ✓ Effect on Semi-volatiles

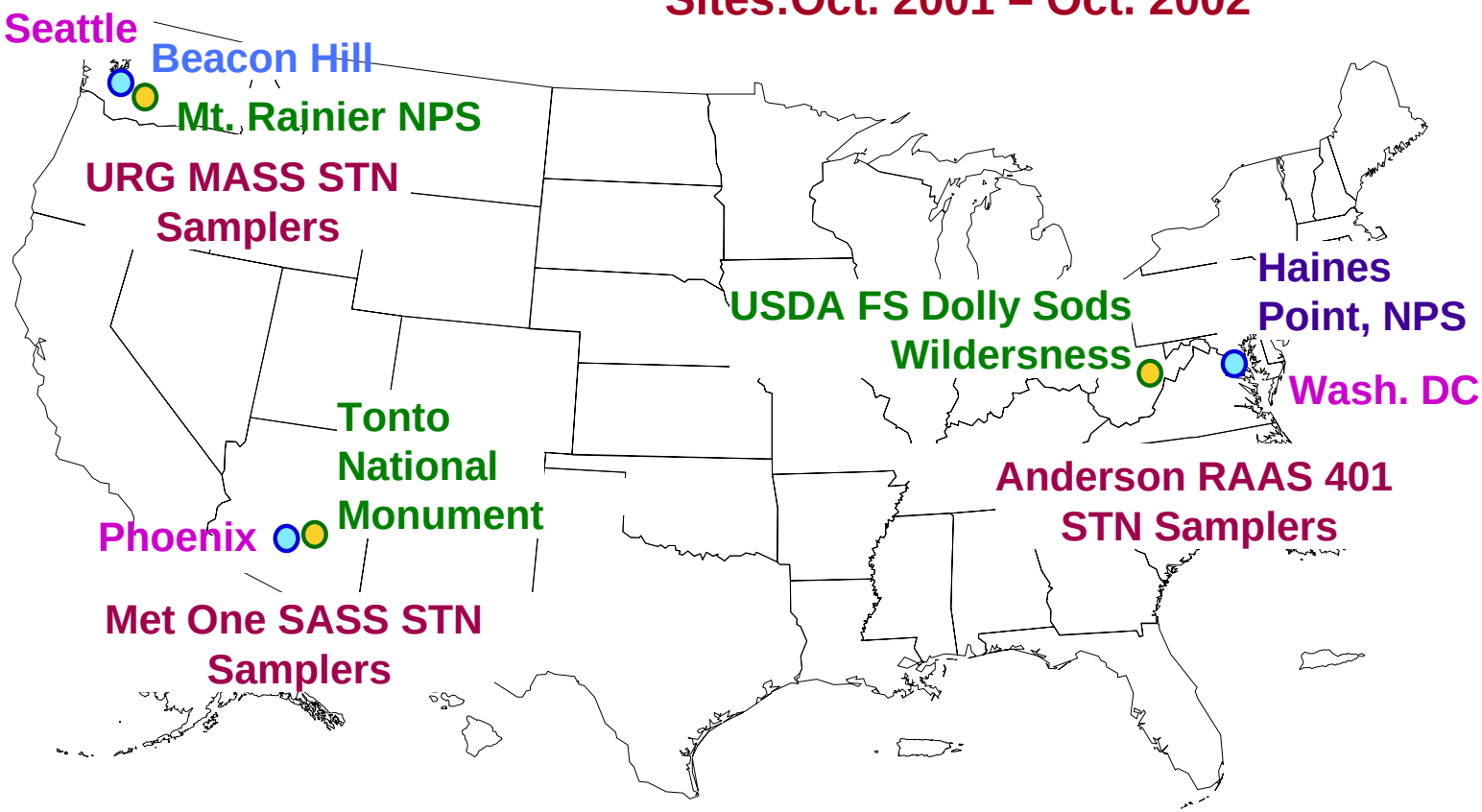
Given All these Differences, Do the Networks Provide Similar Results for Mass and the Components of Mass

?

Methods Comparison Study: STN-IMPROVE

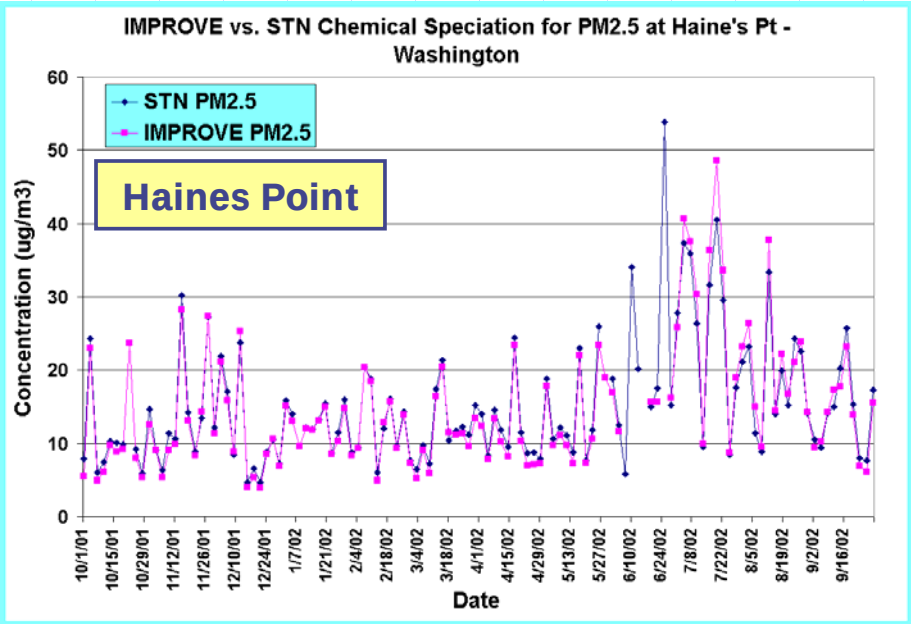
Operated According to Each Network's Protocols

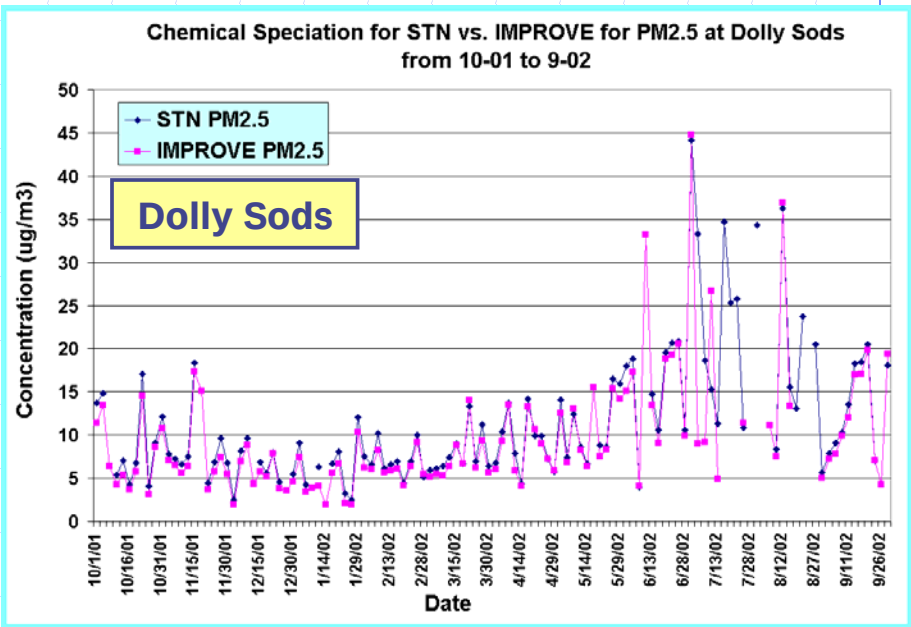
STN/IMPROVE Monitoring Intercomparison Sites:Oct. 2001 – Oct. 2002

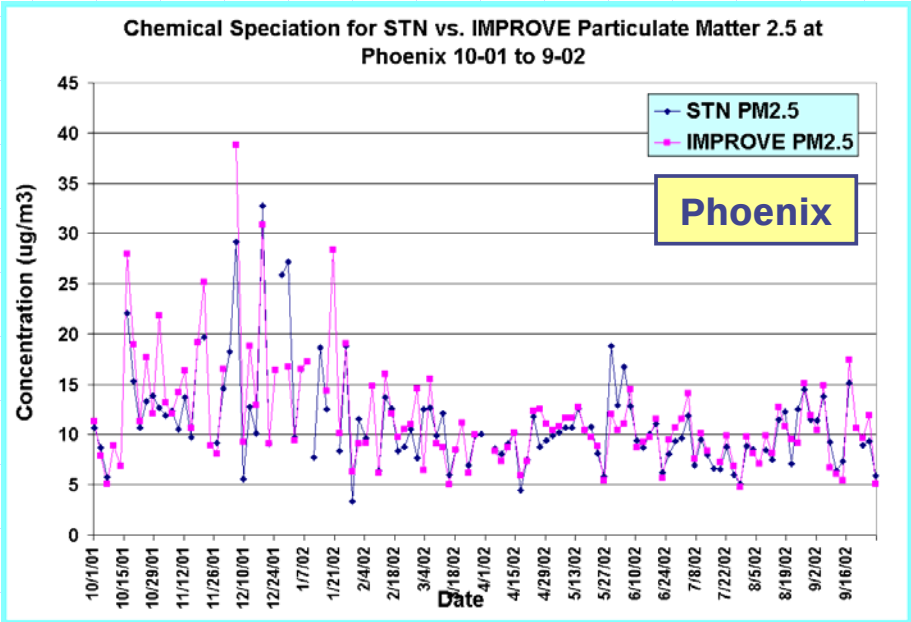


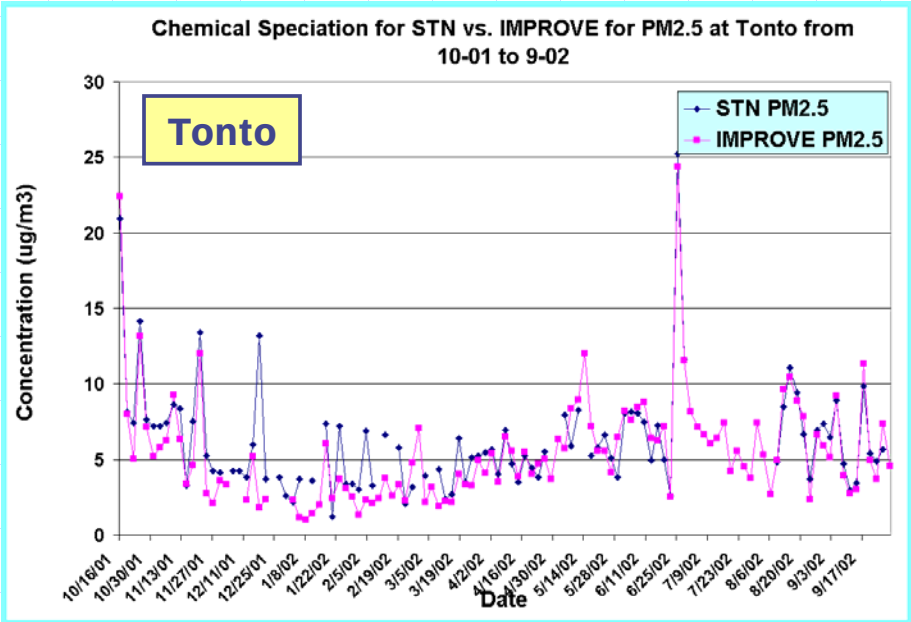
- Official or designated STN site, host to IMPROVE sampler
- Official IMPROVE site, host to STN sampler

Urban – Rural Temporal Analysis Comparison: PM2.5 Mass

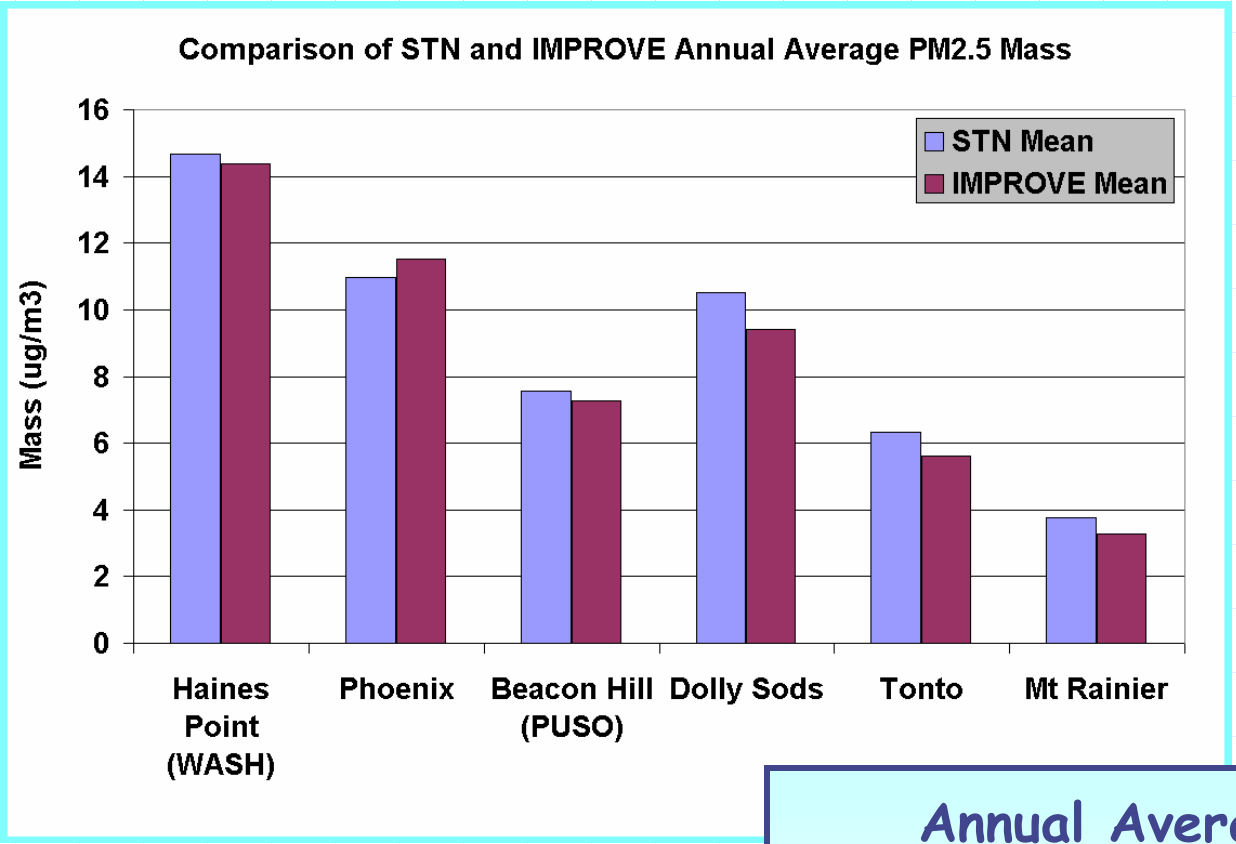








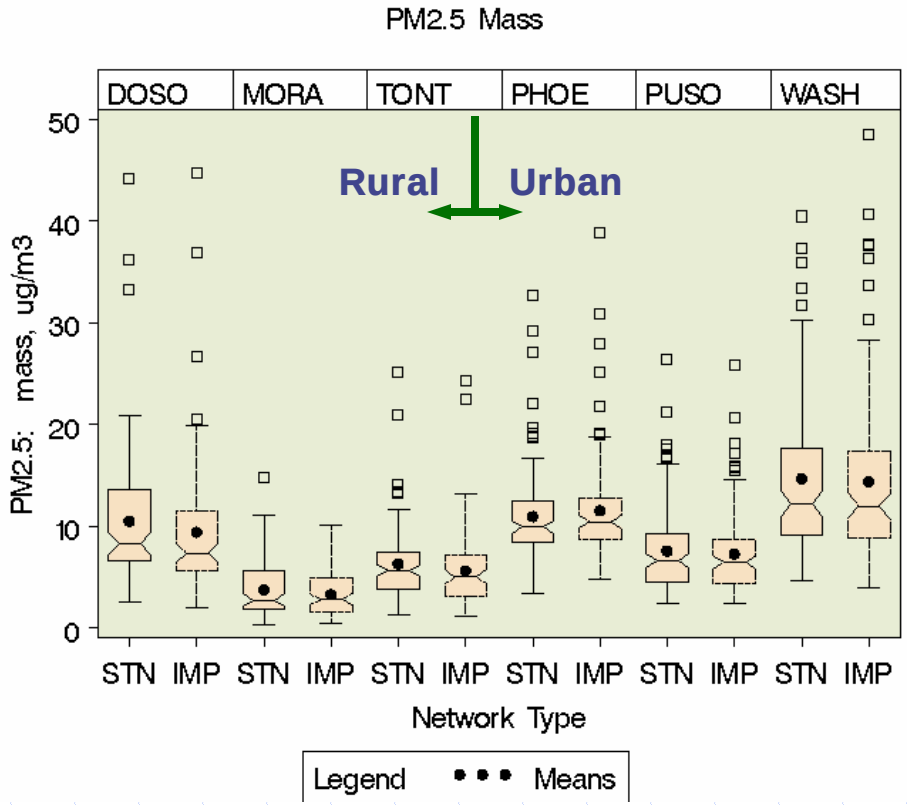
Urban – Rural Comparison of Means: PM2.5 Mass

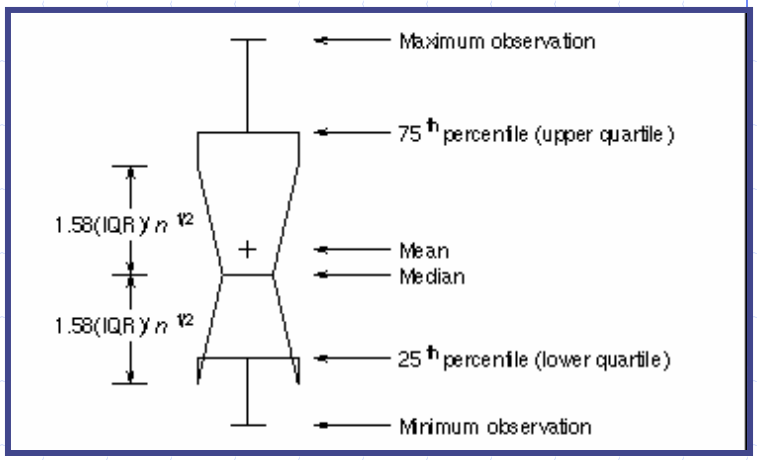


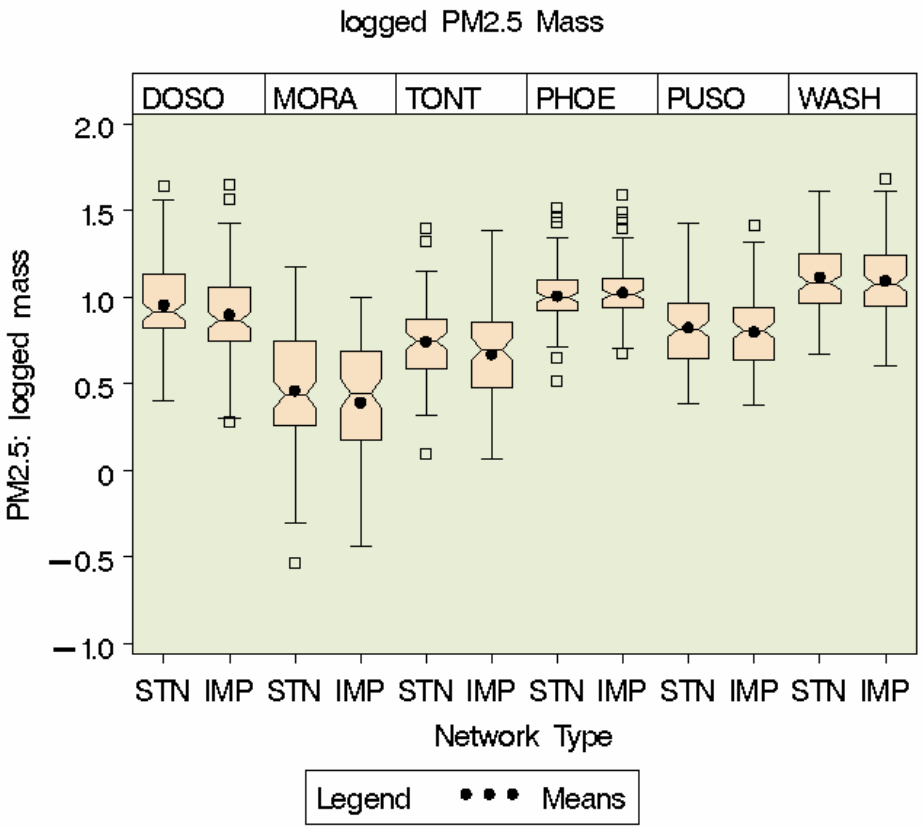
Annual Average Results

- 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)

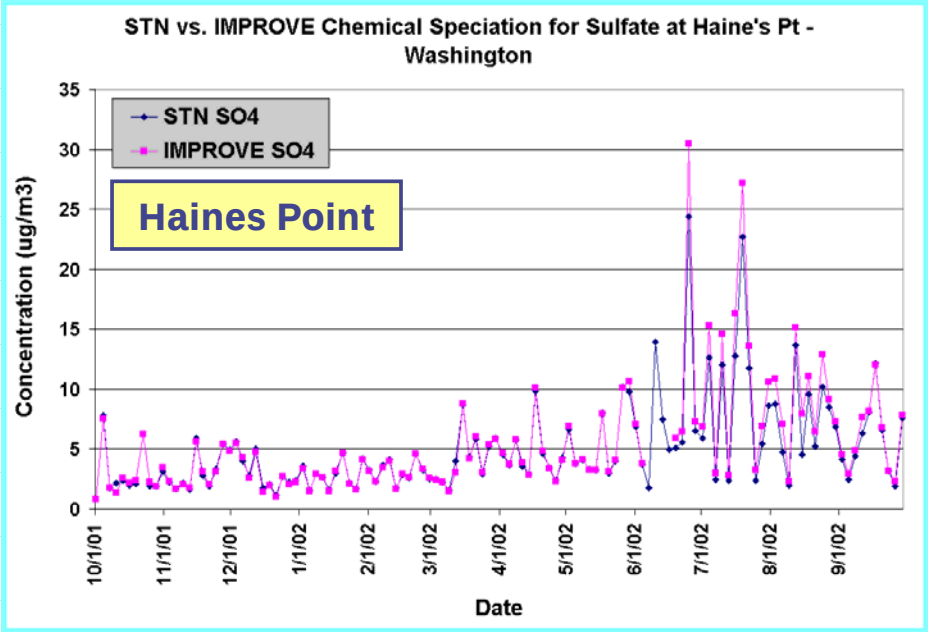


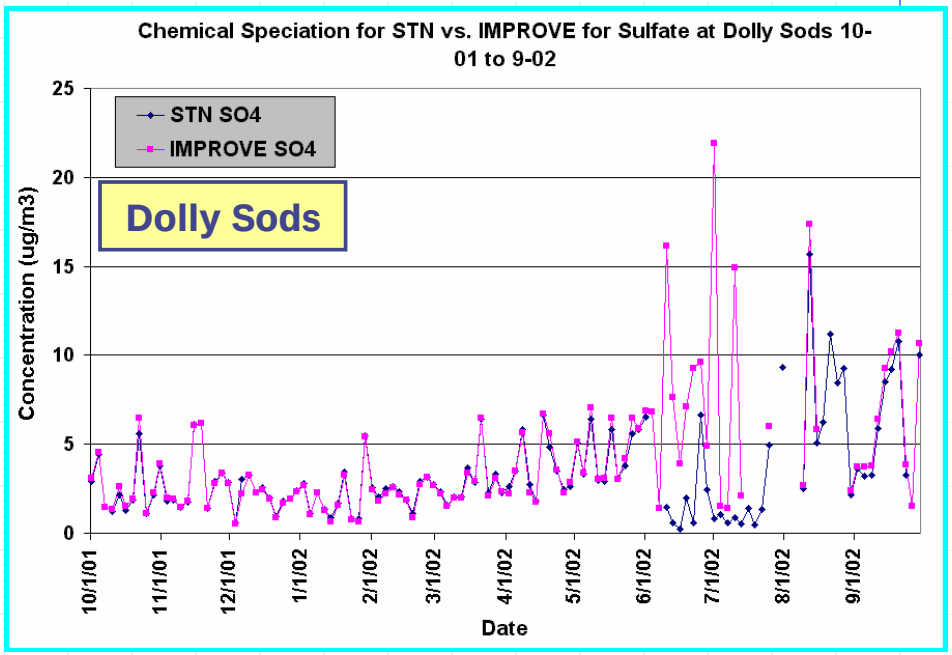


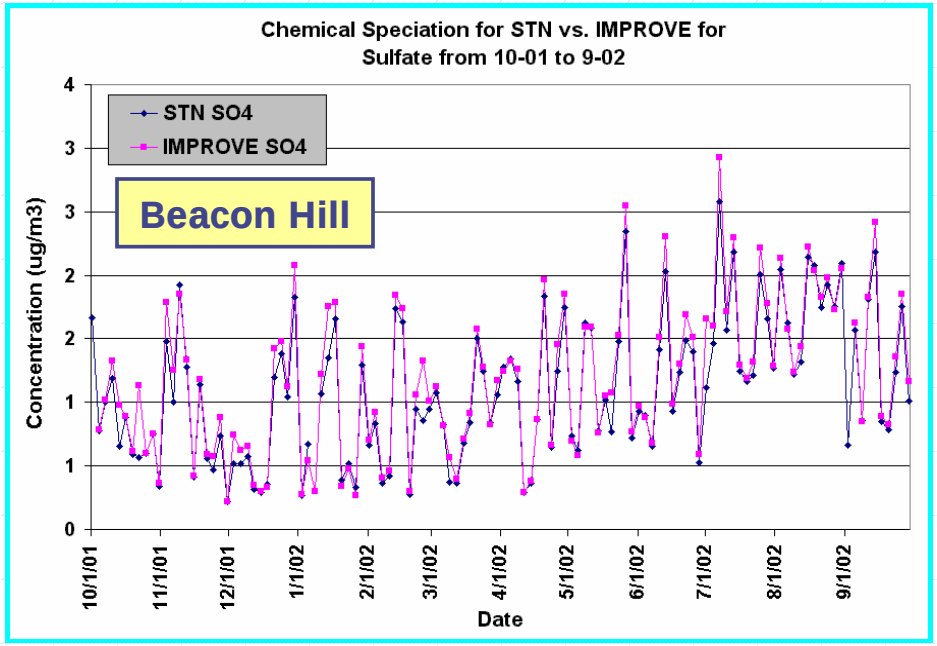


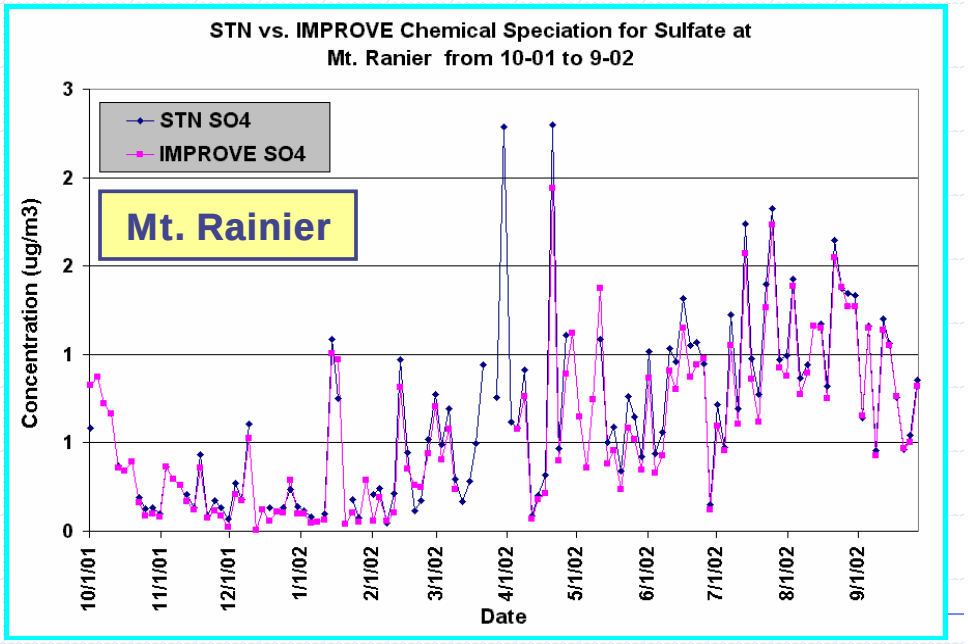
- Log Normal if Mean Is Greater Than Median
- If Notches Do Not Overlap – Distribution Median is Different (95% Confidence Limit
- Data As Supplied by Network
- Oct 01 – Sept 02
- Investigation of Outliers Continuing

Urban – Rural Temporal Analysis Comparison: Sulfate

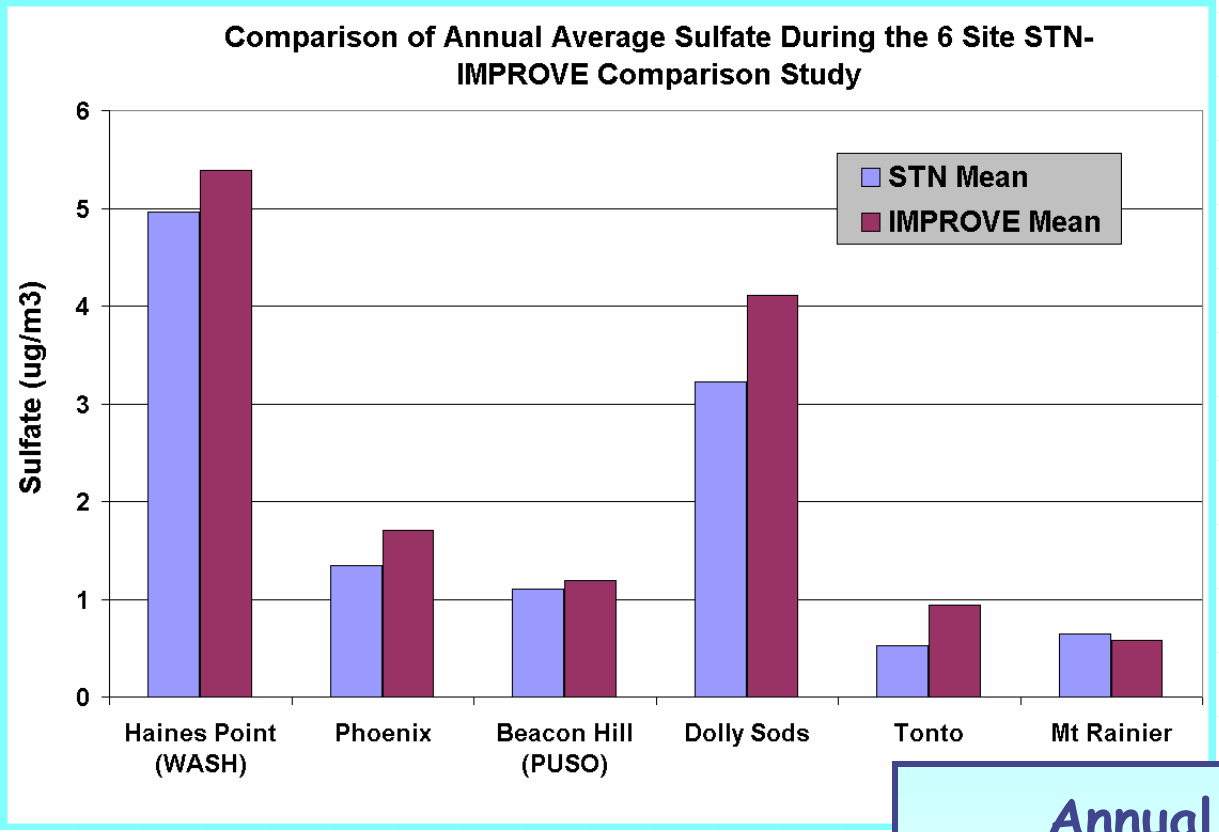








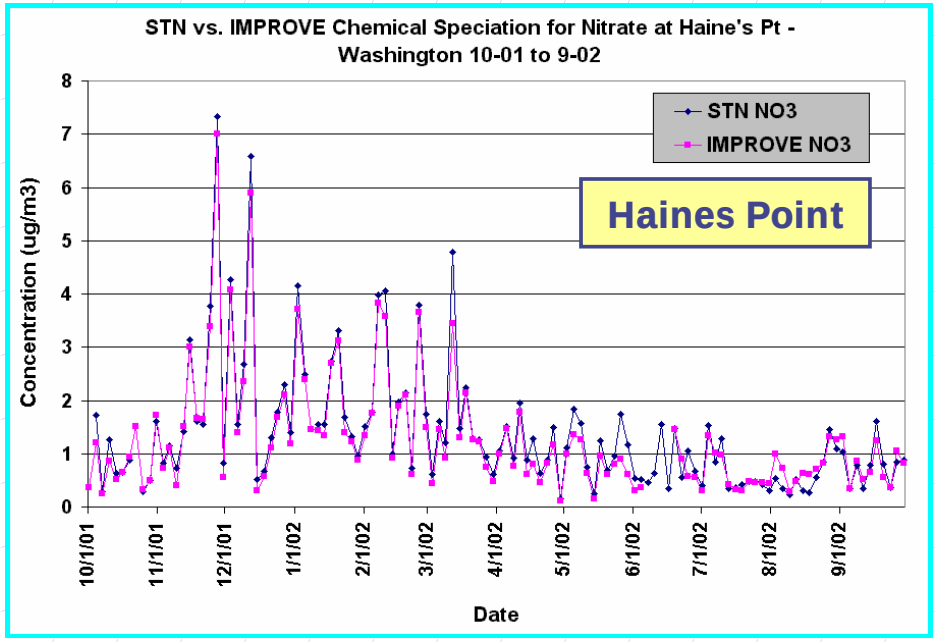
Urban – Rural Comparison of Means: Sulfate

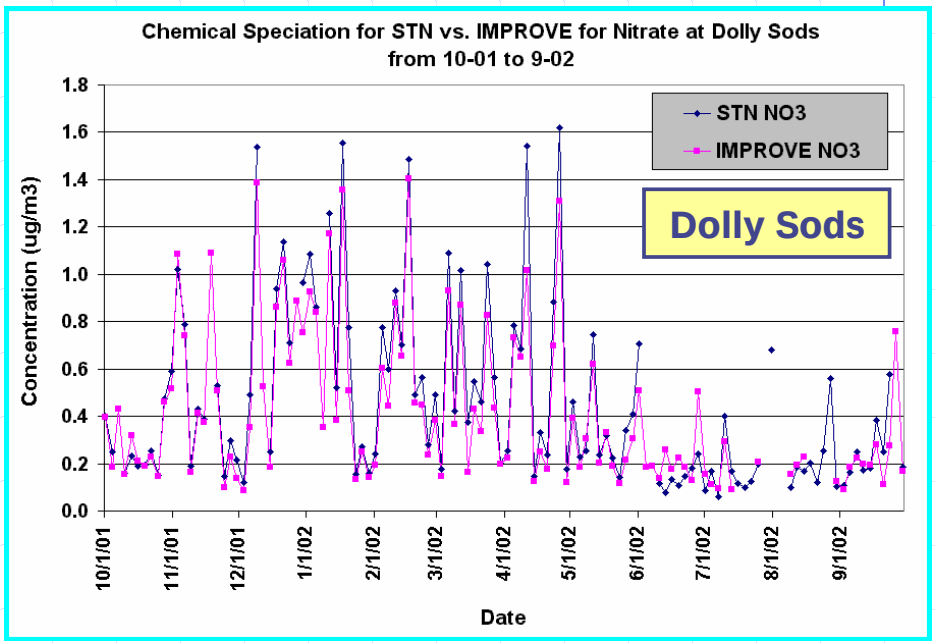


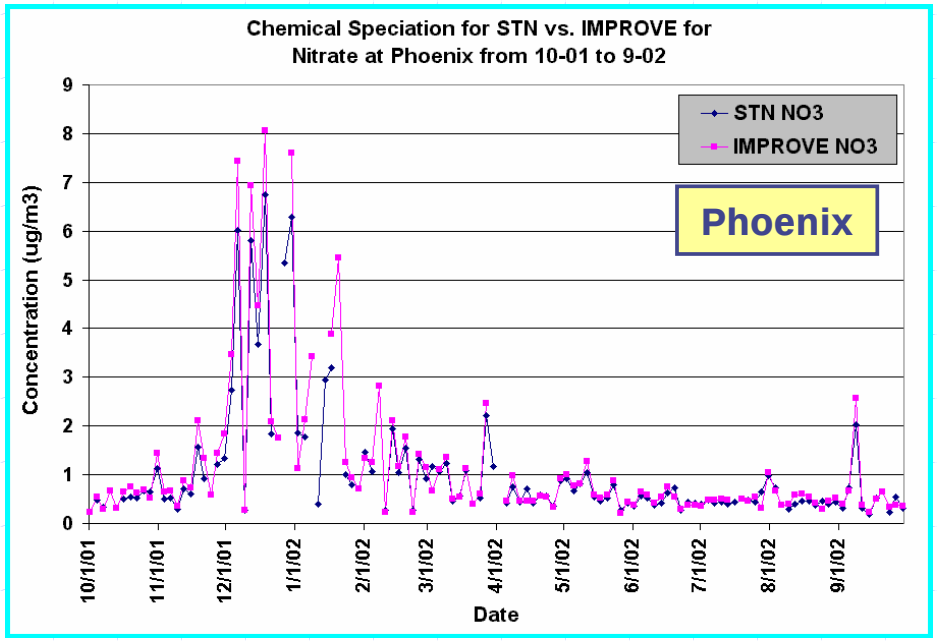
Annual Average Results

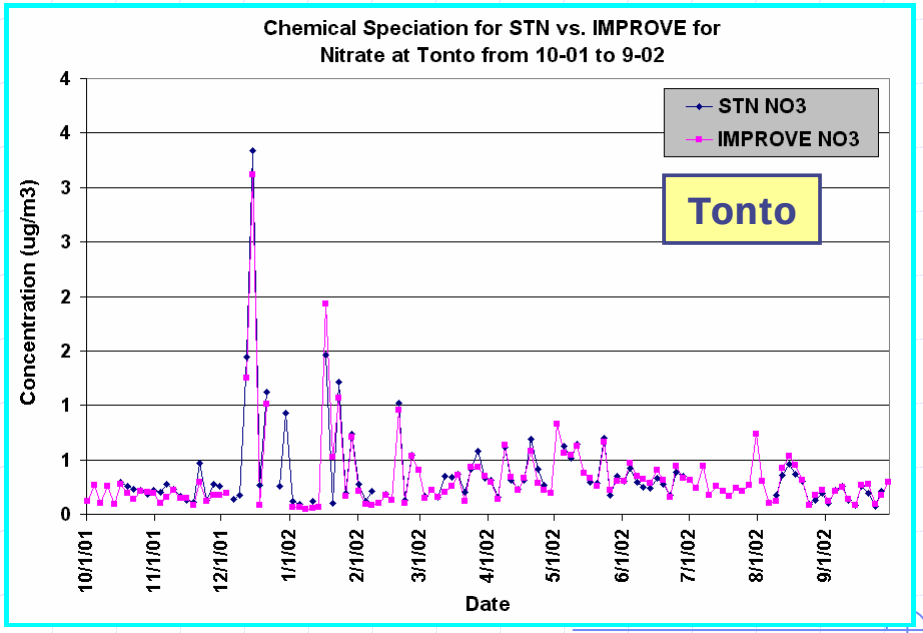
- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 35->200%
- There Is Better Agreement at Urban Sites, and May be Related to Higher Pollution Levels

Urban – Rural Temporal Analysis Comparison: Nitrate

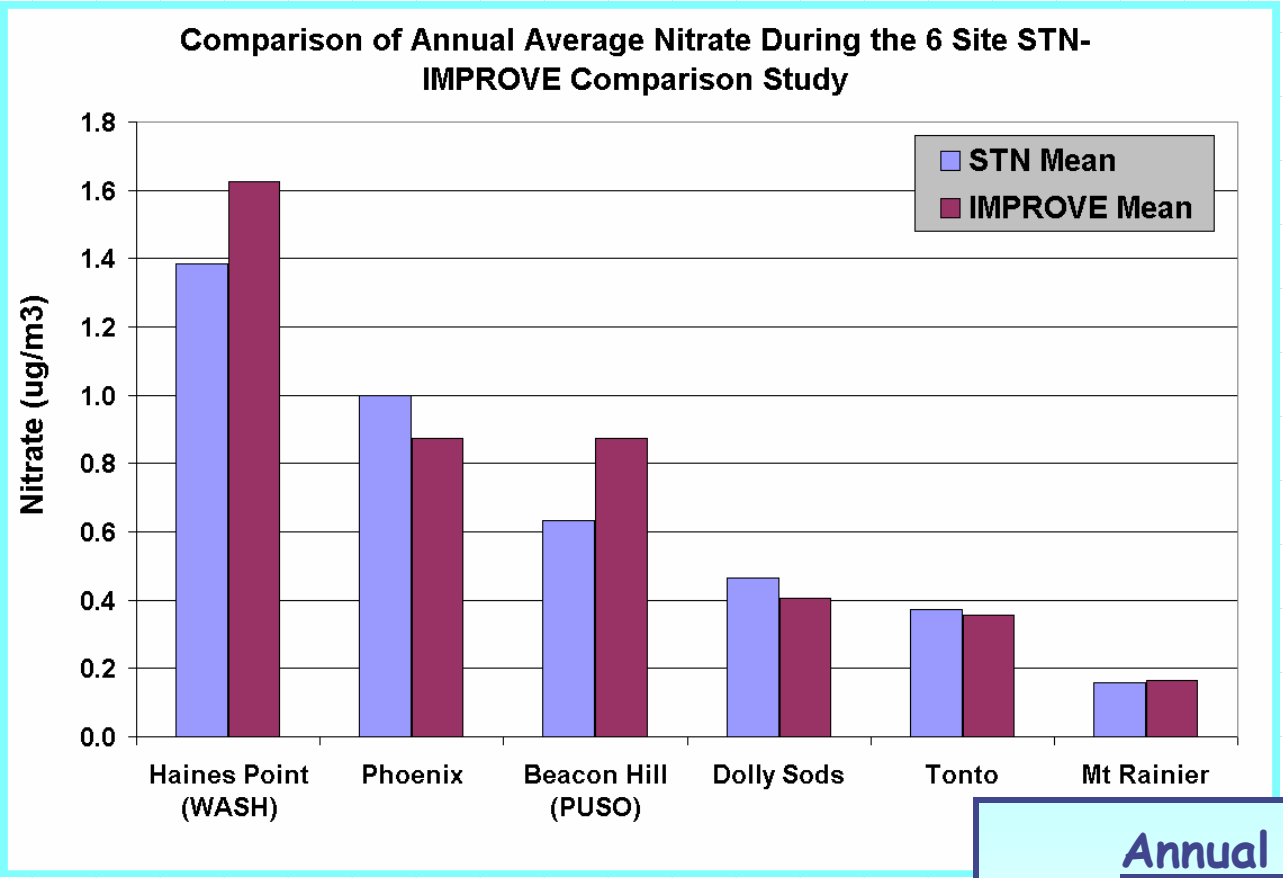








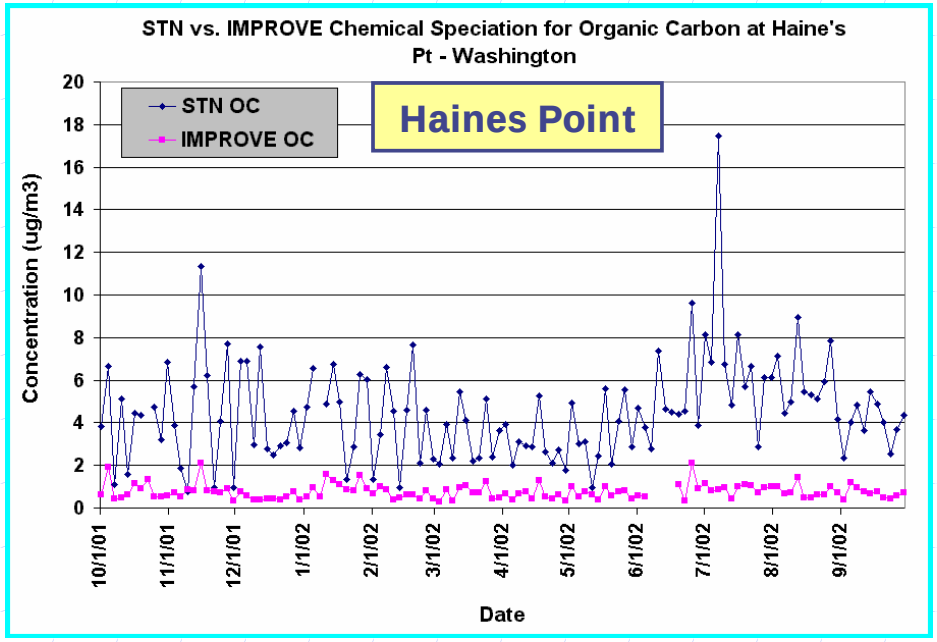
Urban – Rural Comparison of Means: Nitrate

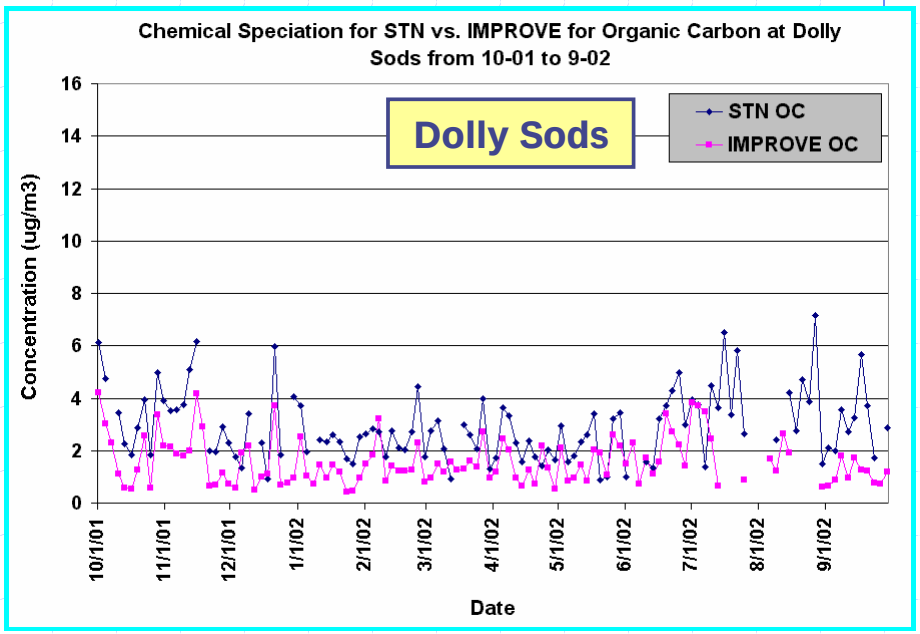


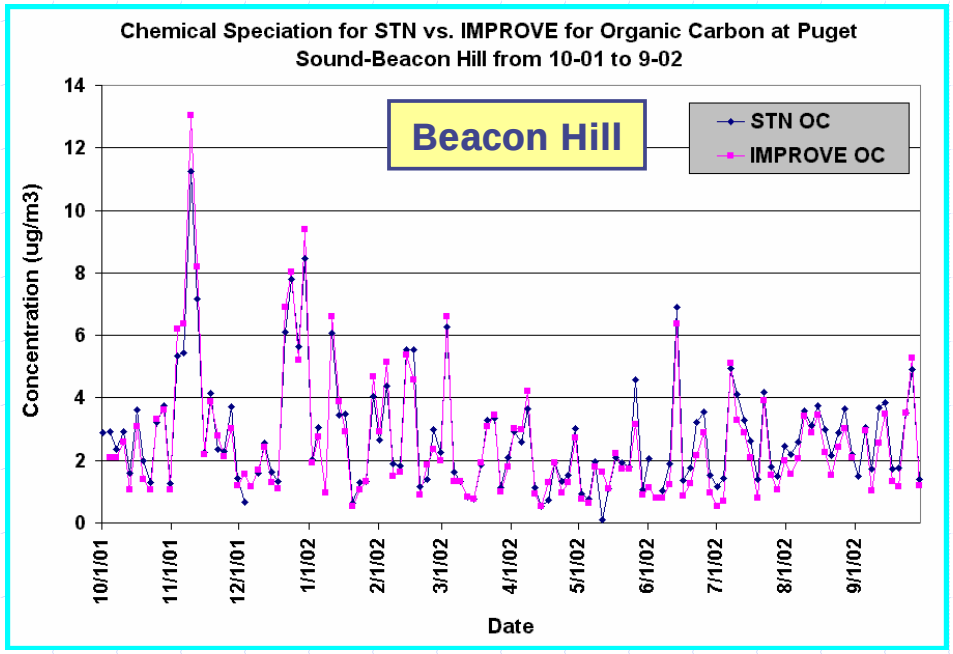
Annual Average Results

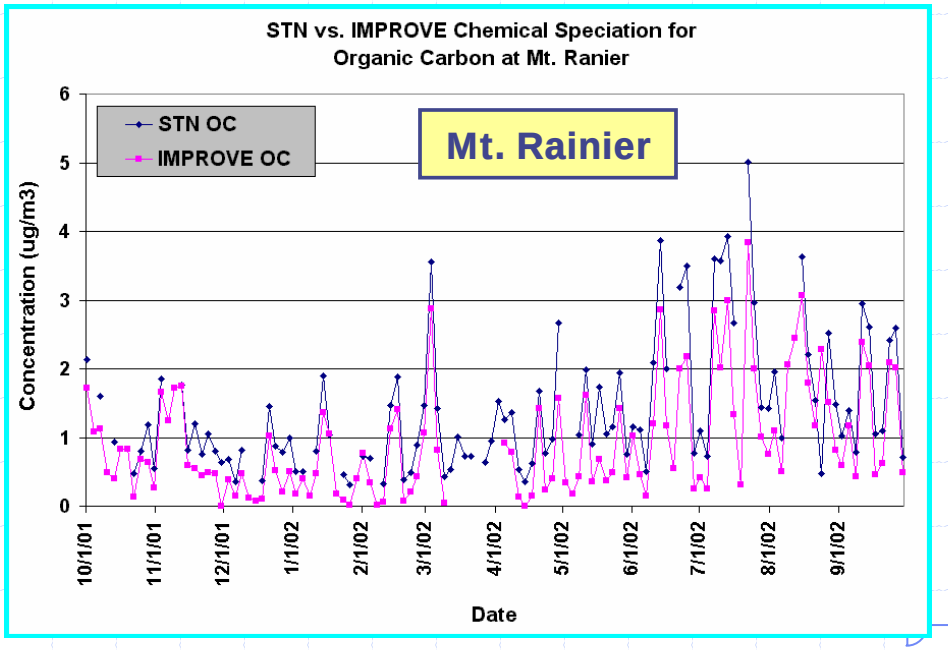
- East Coast Sites Have Higher Conc. Than West Coast Sites
- Urban Site Levels Exceed Rural Sites by 200-400%
- Rural Sites Tend to Agree Better Than Urban Sites, Which May Be Due to Difference in Denuder Protocols

Urban – Rural Temporal Analysis Comparison: OC

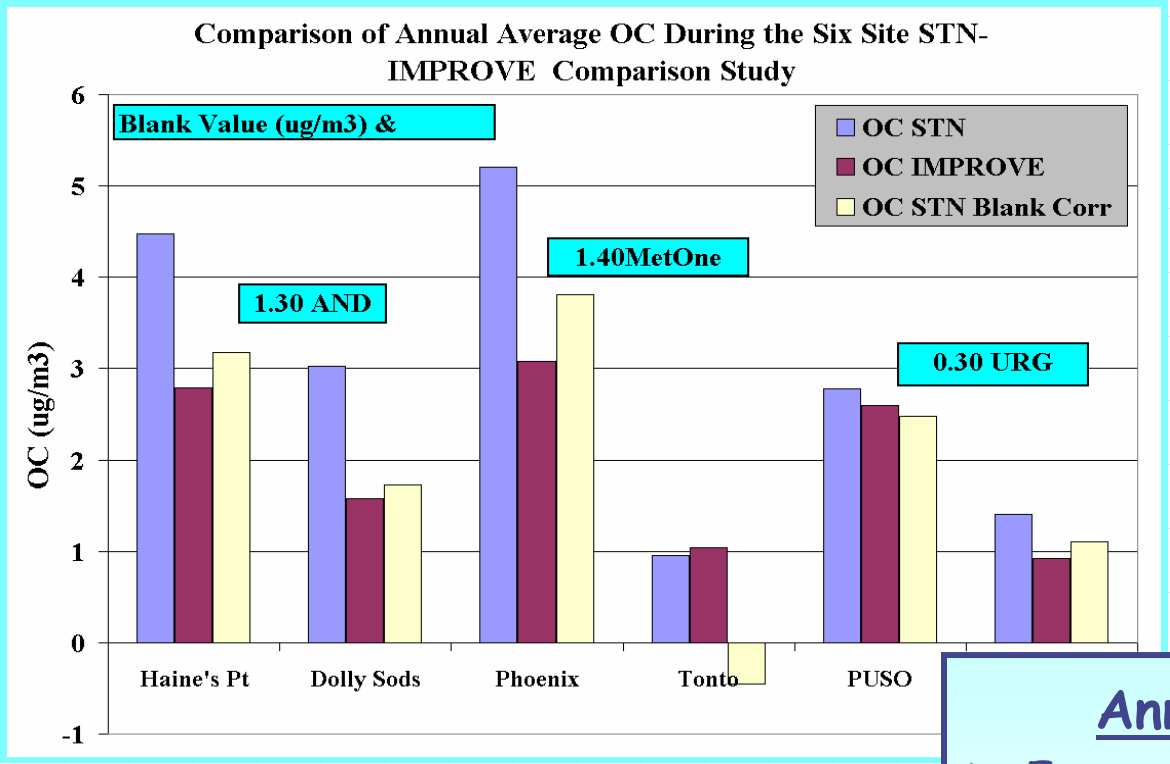








Urban – Rural Comparison of Means: OC



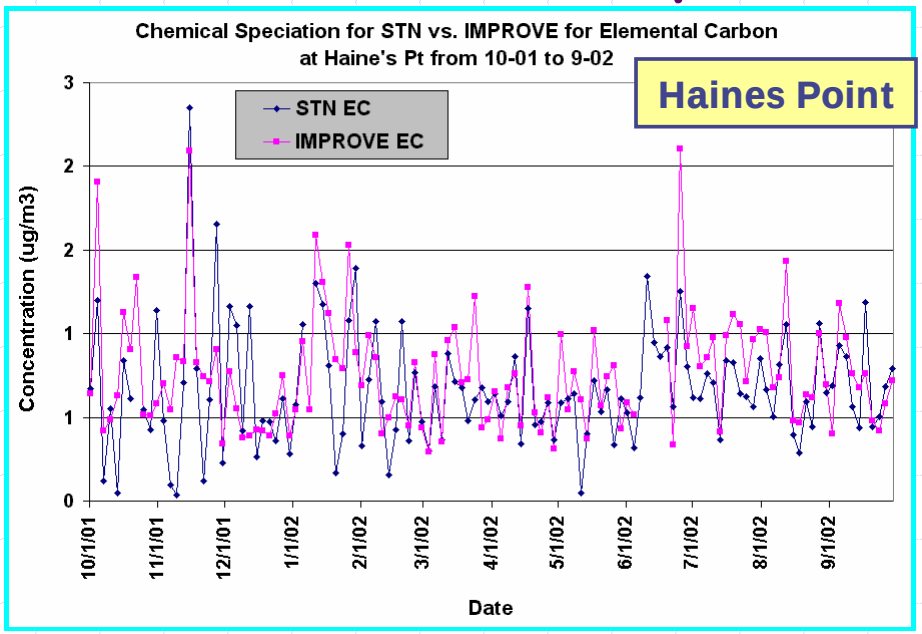
Blank Values Are Based on Trip and Field Blanks for the Averaged Over the Time Period of the Study

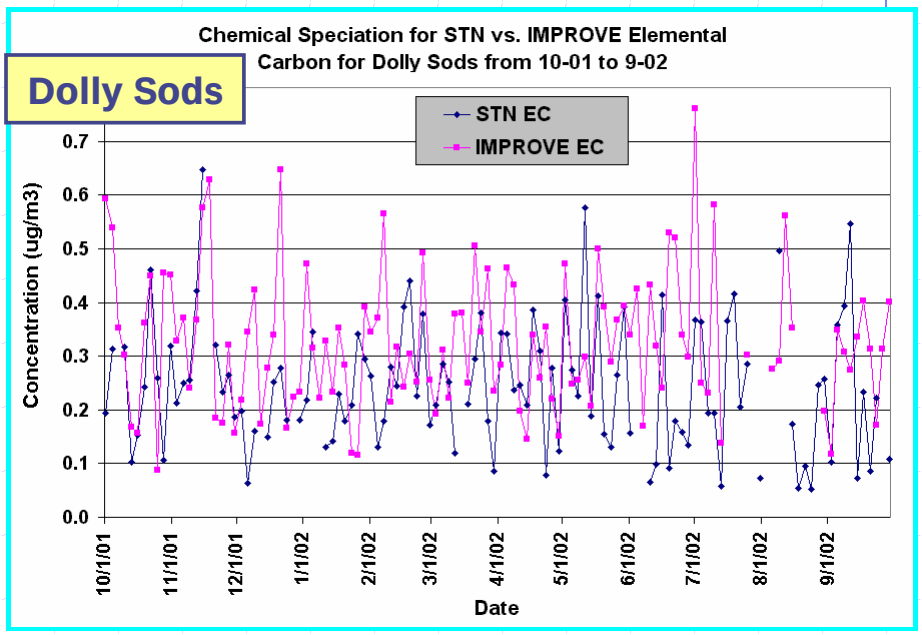
Blank Correcting Improved the Comparison Between STN and IMPROVE at Most Locations

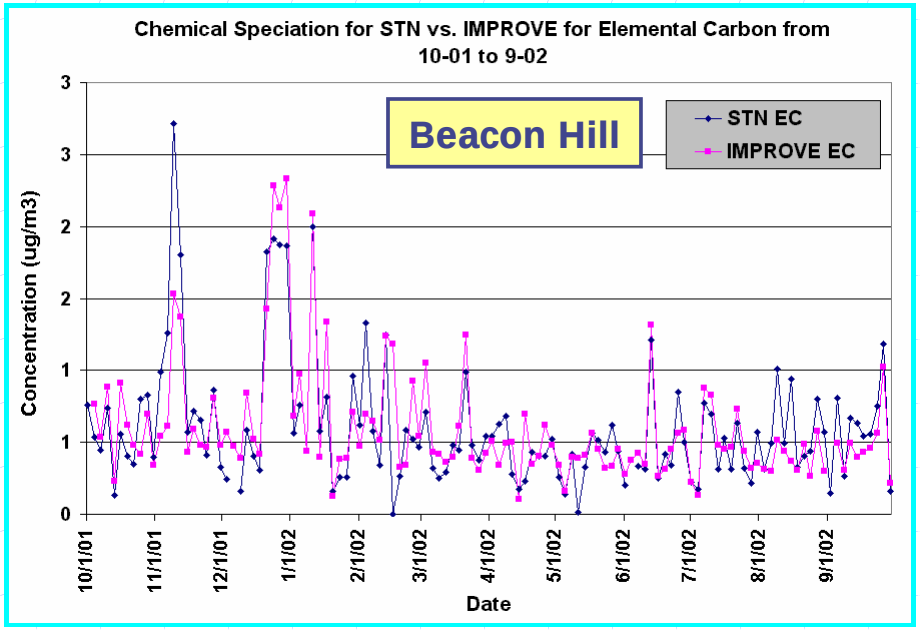
Annual Average Results

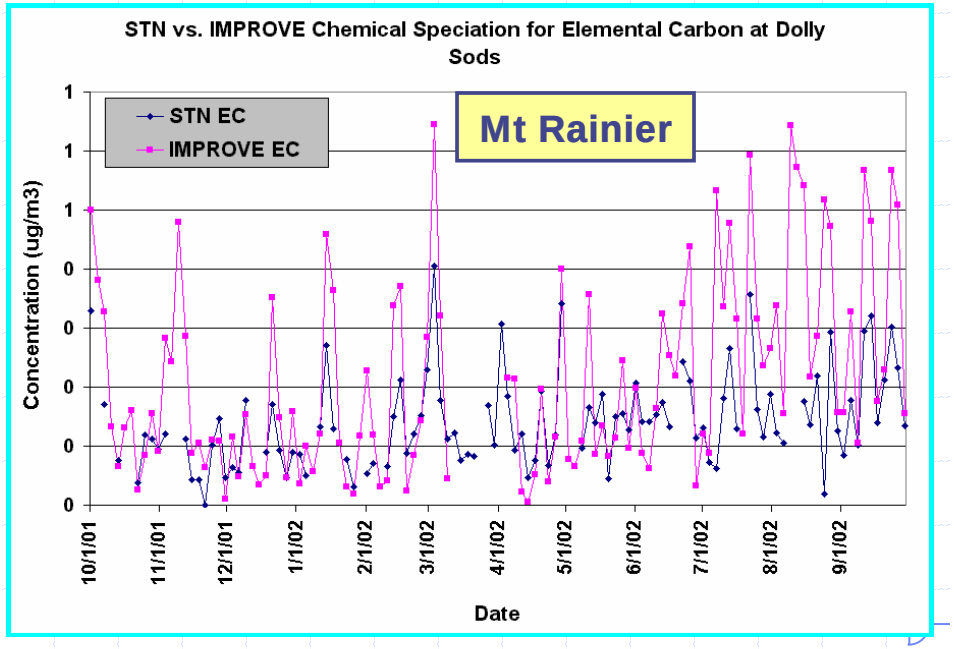
- East and West Coast Sites Can Have Similar Concentrations
- Urban Site Levels Exceed Rural Sites by 200-500%
- Rural Sites Tend to Agree Better Than Urban Sites Before Blank Correction
- Blank Correction Improves Agreement at Urban and Rural Sites

Urban – Rural Temporal Analysis Comparison: EC

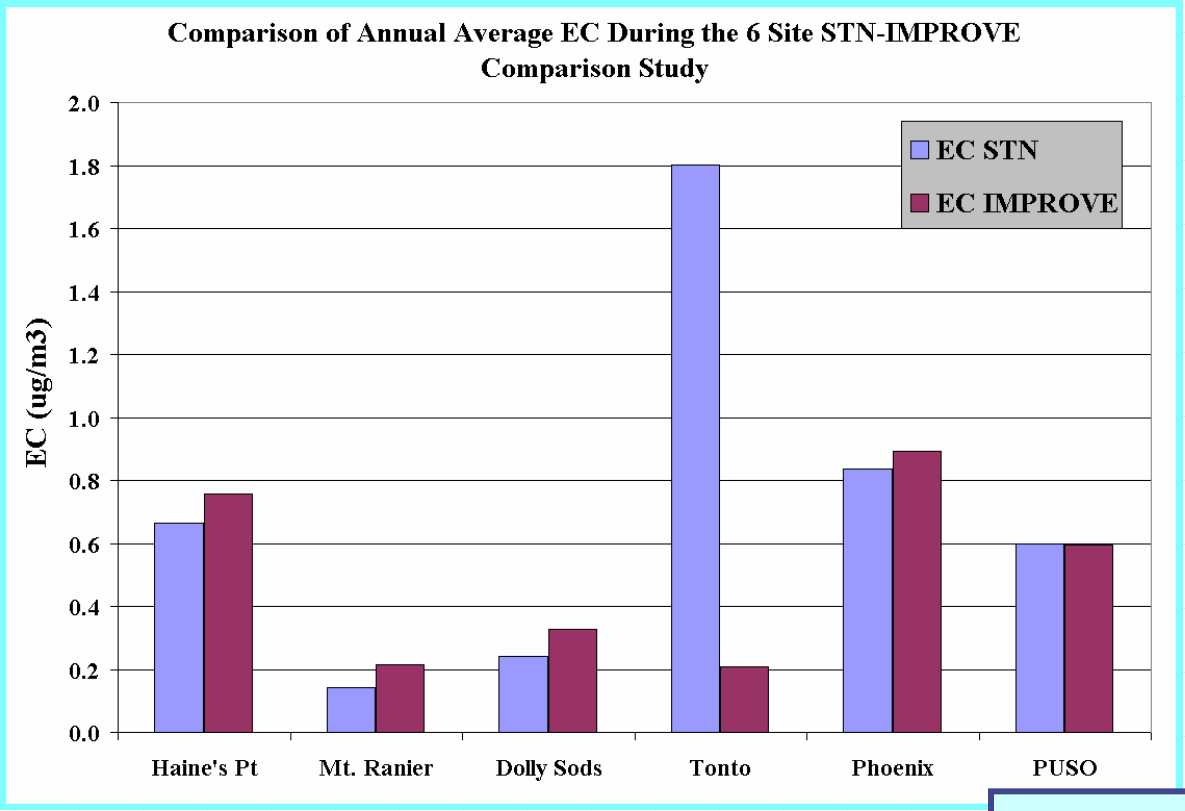








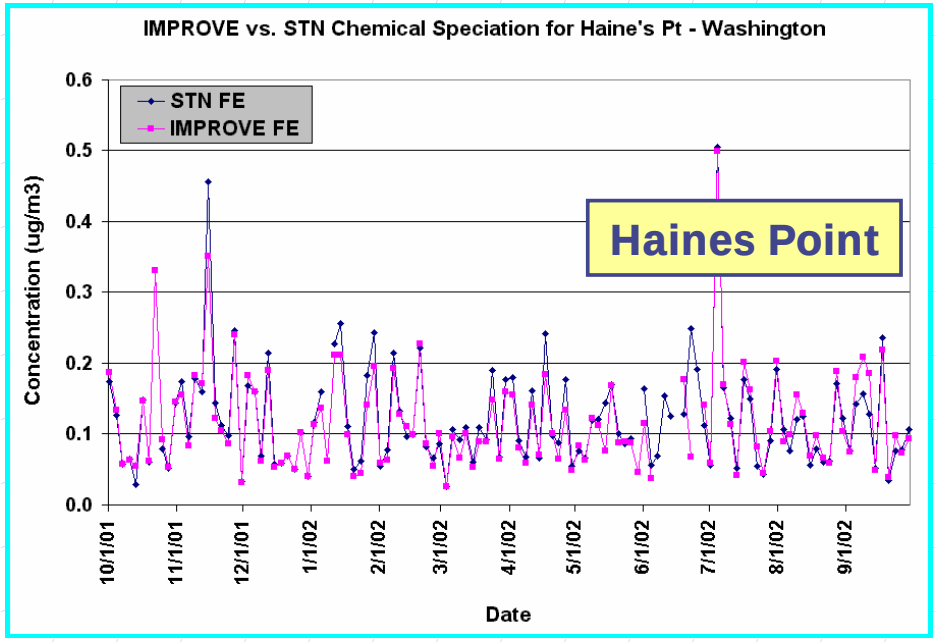
Urban – Rural Comparison of Means: EC

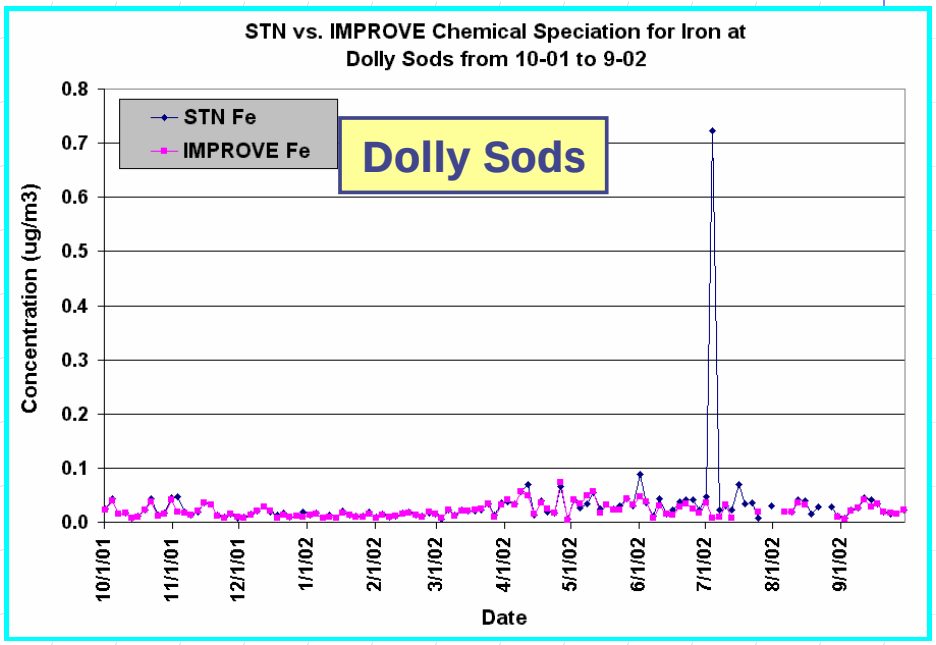


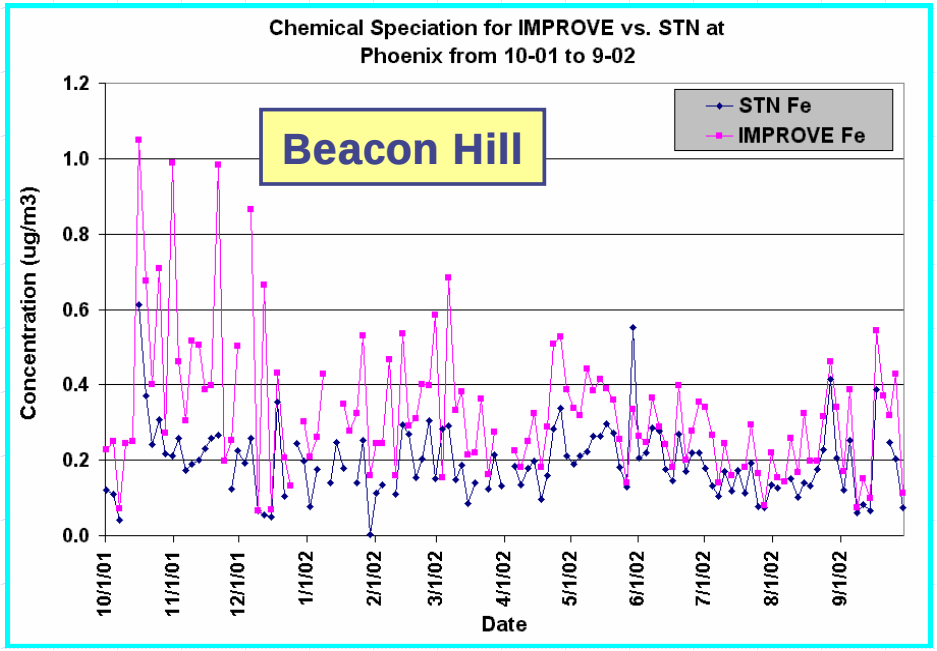
Annual Average Results

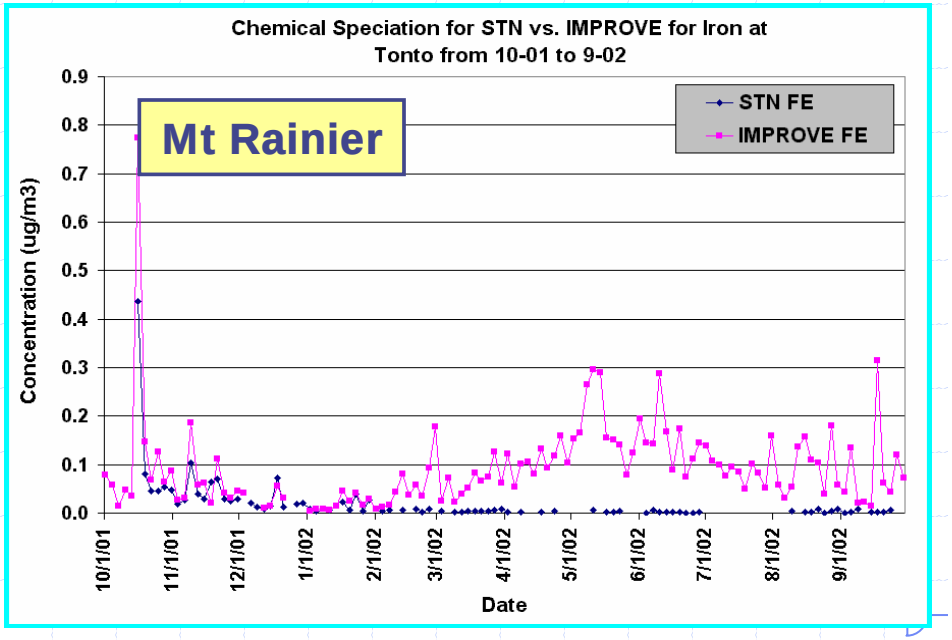
- EC Data Did Not Require Blank Correction
- Factor of 2 Not Observed Between STN and IMPROVE At Urban Sites
- Urban Sites Are ~ 2X Rural Sites
- Better Agreement Is Observed at Rural Sites Than Urban
- QA Is In Process to Ensure This Is Valid Data

Urban – Rural Temporal Analysis Comparison: Fe









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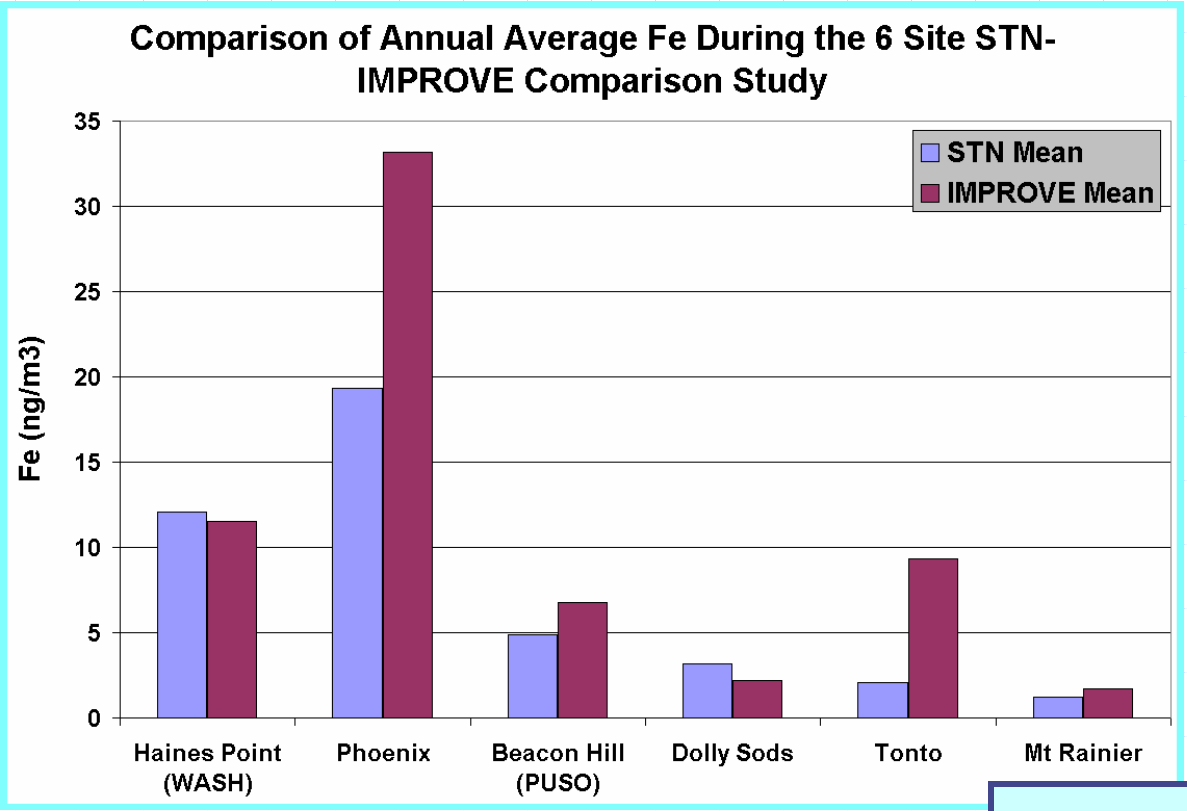
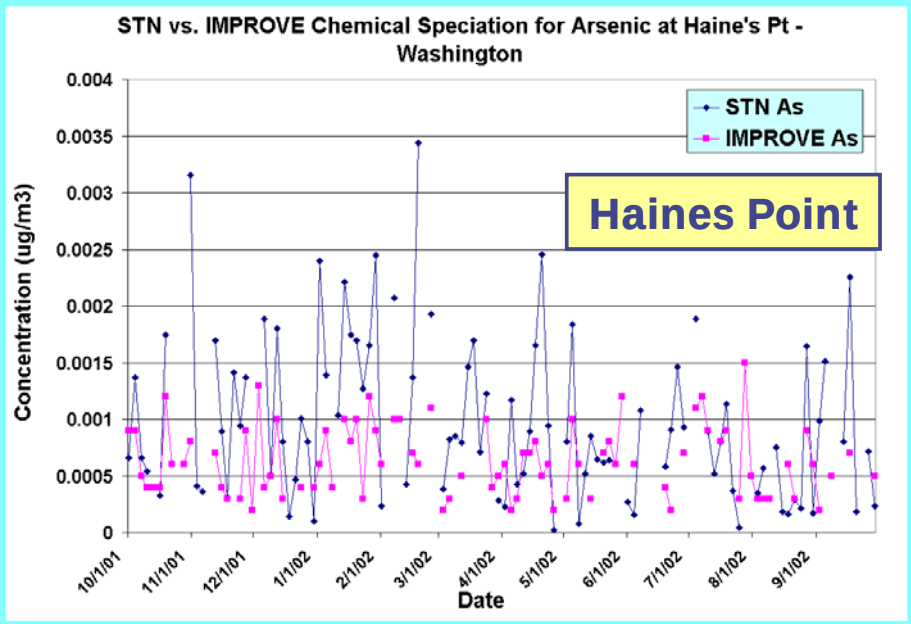
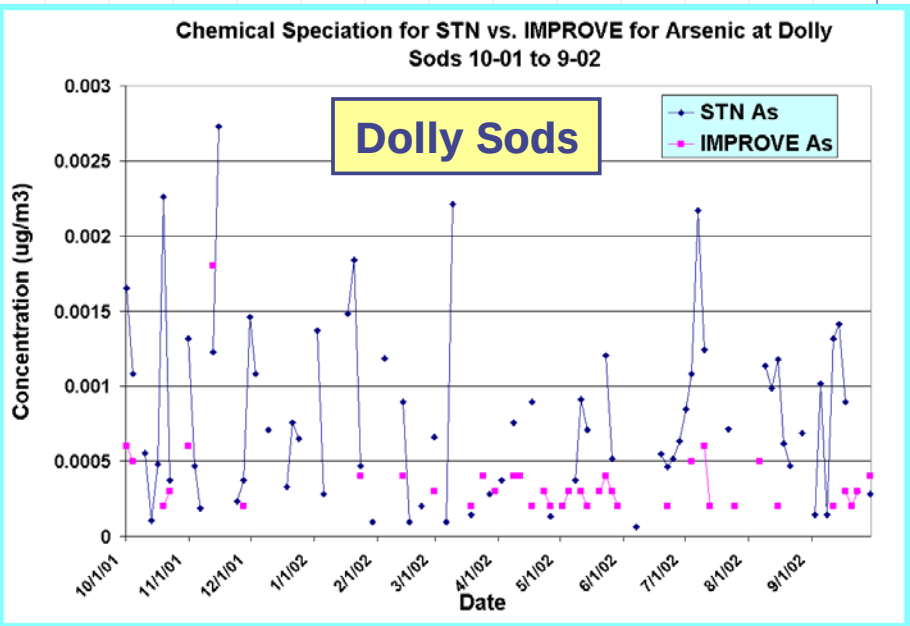


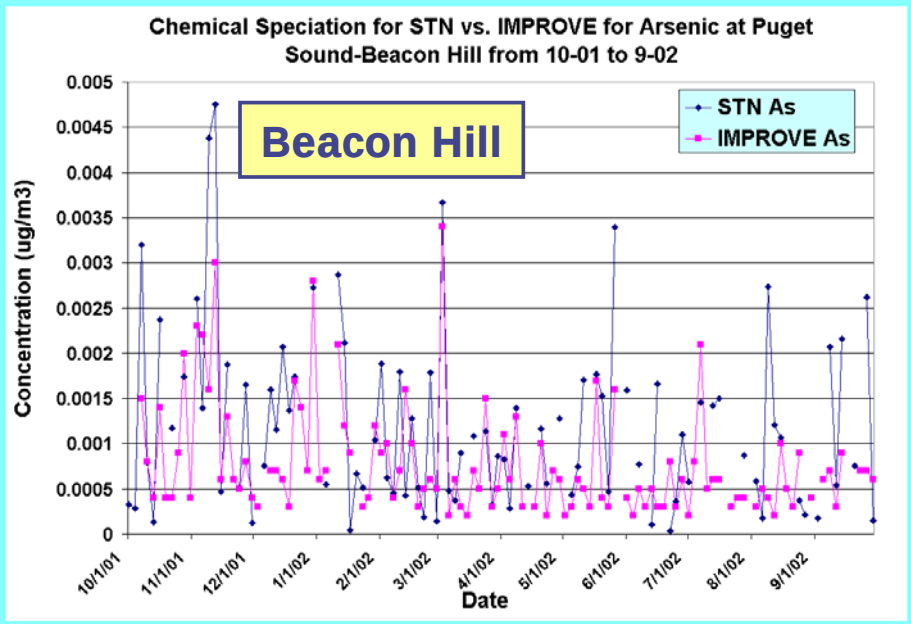
Annual Average Results

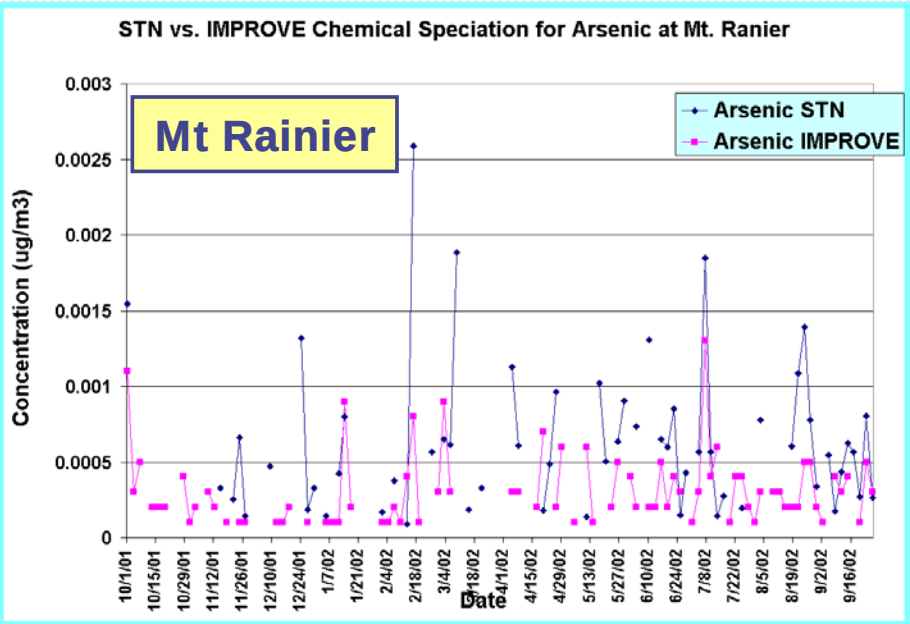
- Concentrations are Higher in Urban Areas Than Rural Areas
- Phoenix Has the Highest Concentrations, Mt. Rainier the Lowest
- With the Exception of Phoenix and Tonto Agreement is Similar Between Rural and Urban Sites
- QA Is in Progress to Ensure This Is Valid Data

Urban – Rural Temporal Analysis Comparison: Arsenic

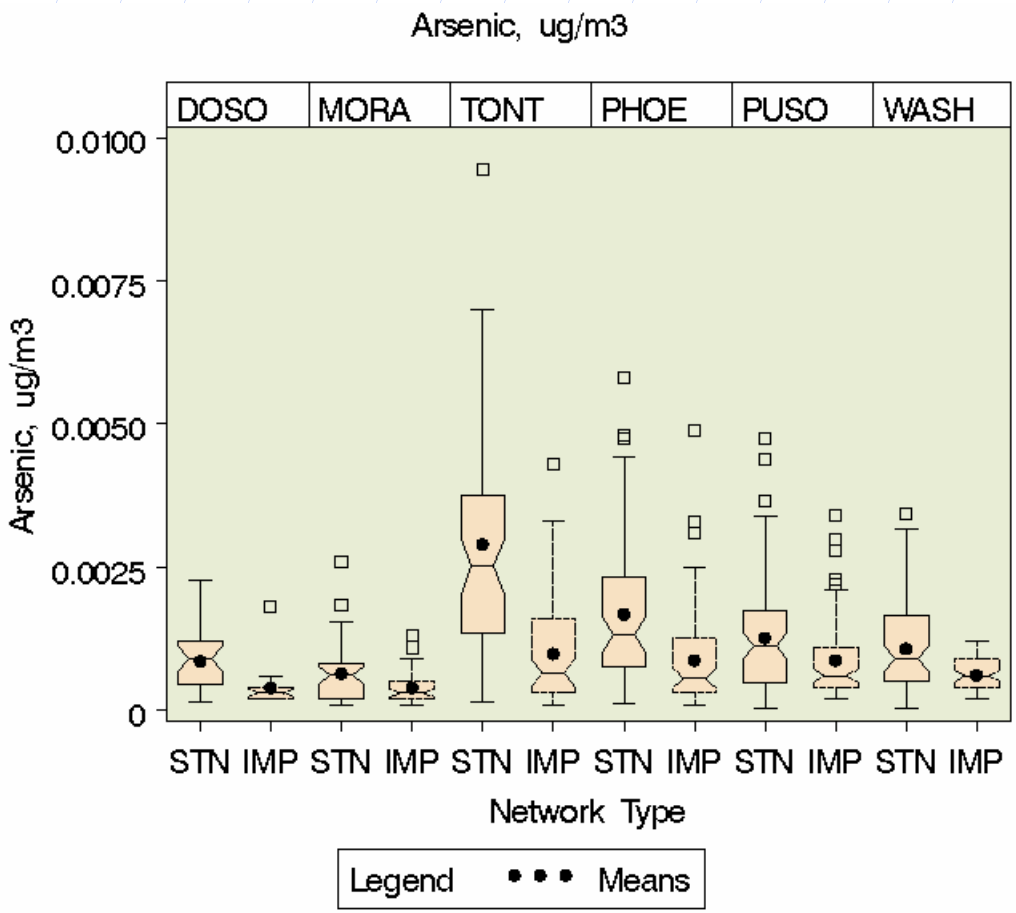




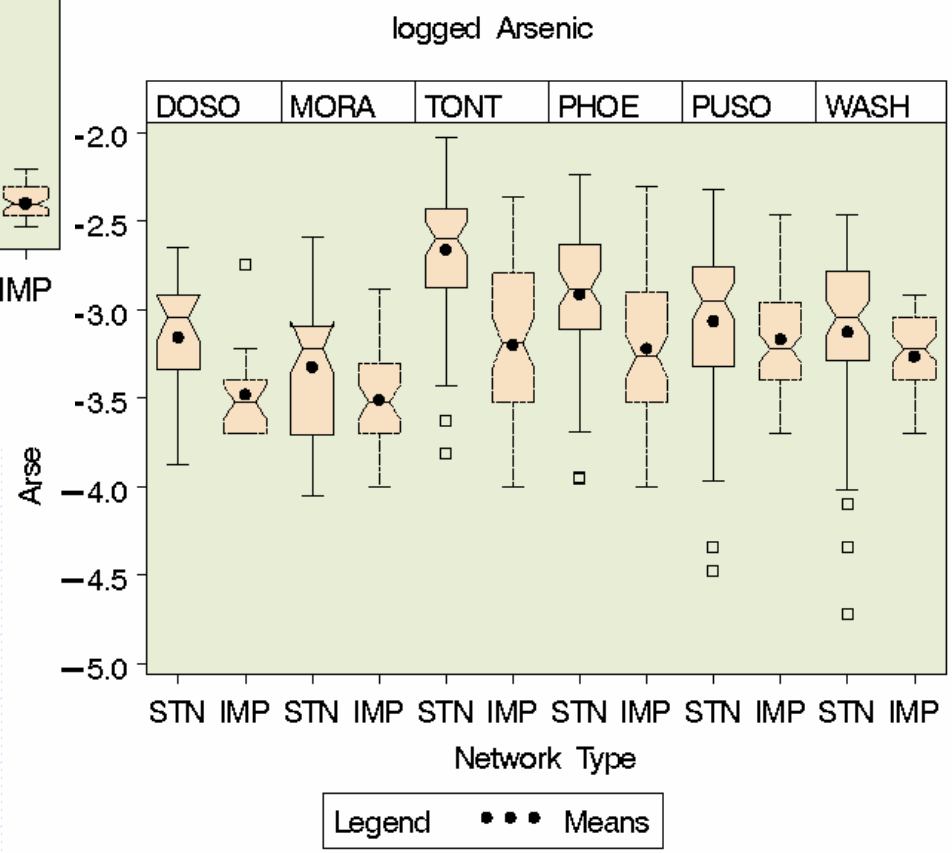




Frequency Distributions Analysis: Arsenic

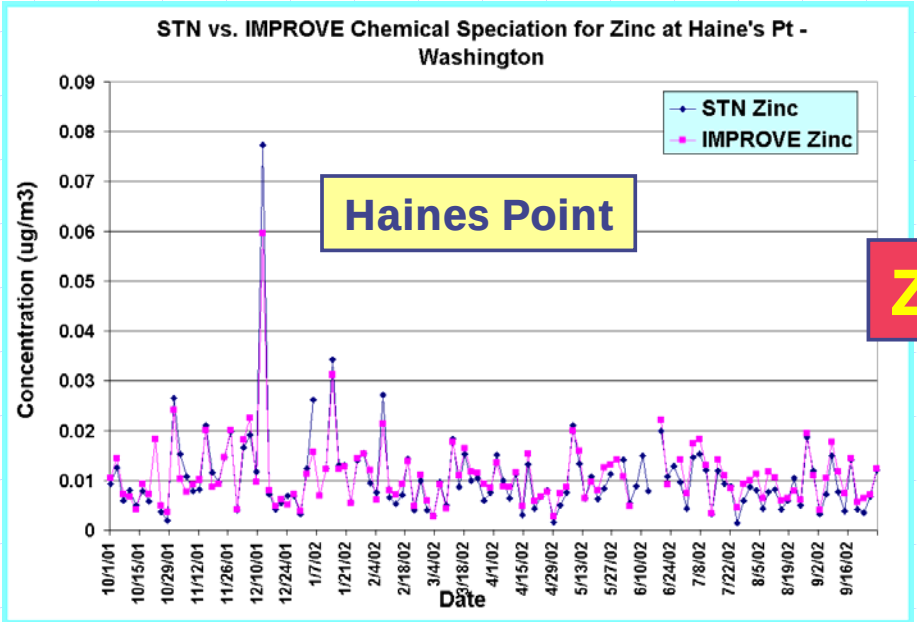


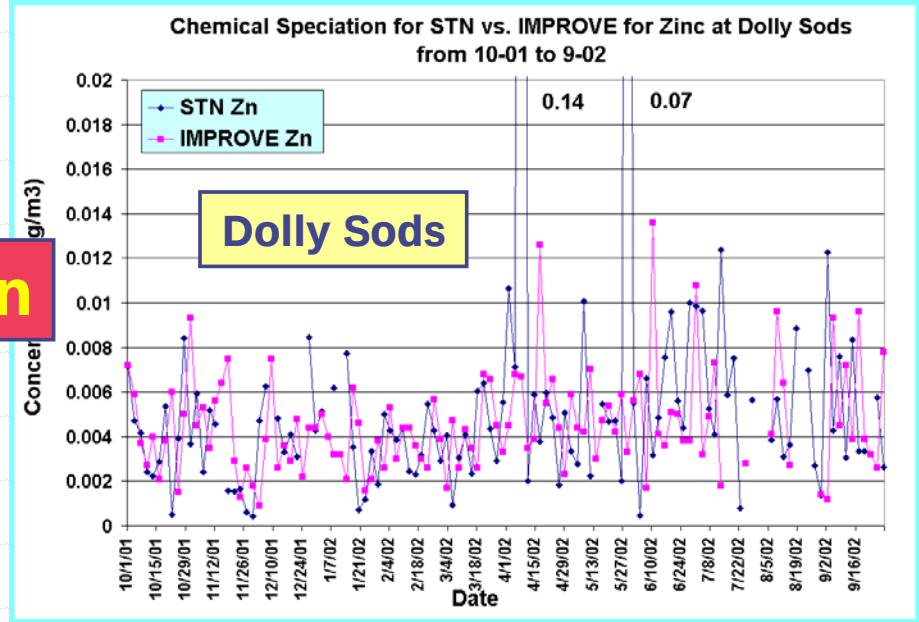
Frequency Distributions – Paired Samplers, All Sites: Arsenic



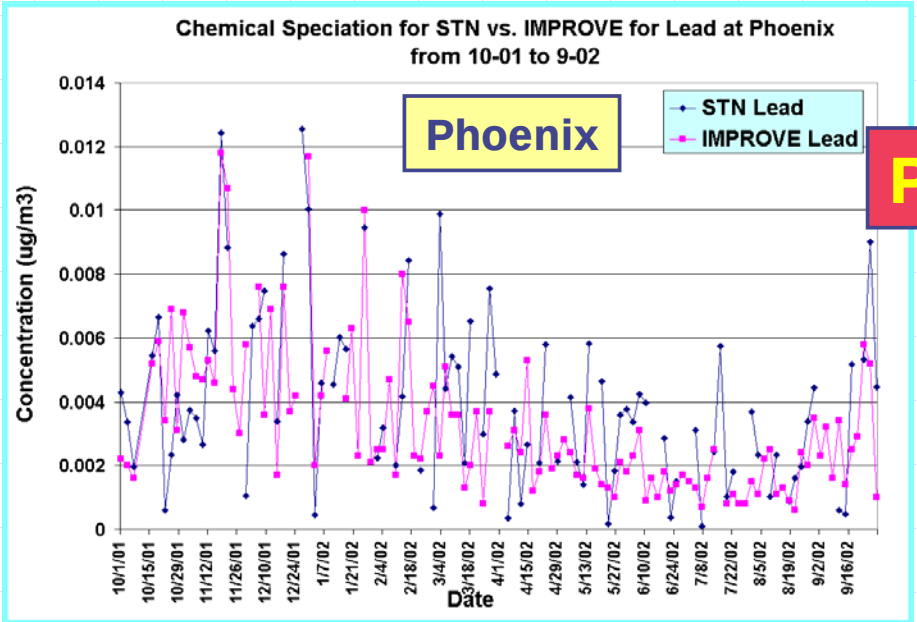
- Distributions at a Given Sites Are Not Similar Between Networks
- Notches Do Not Overlap at Any of the Sites
- Cr Similar to As

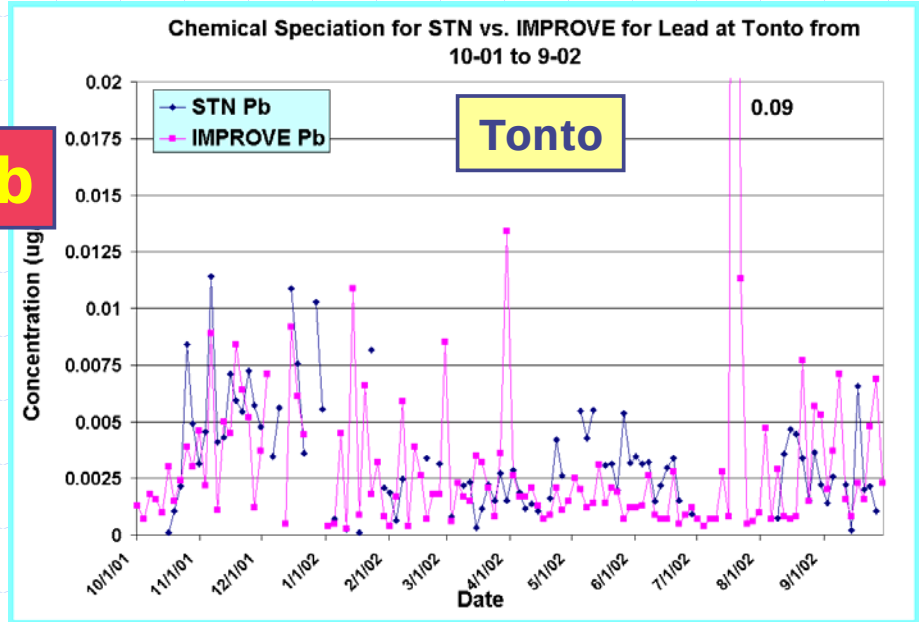
Urban – Rural Temporal Analysis Comparison: Zn & Pb





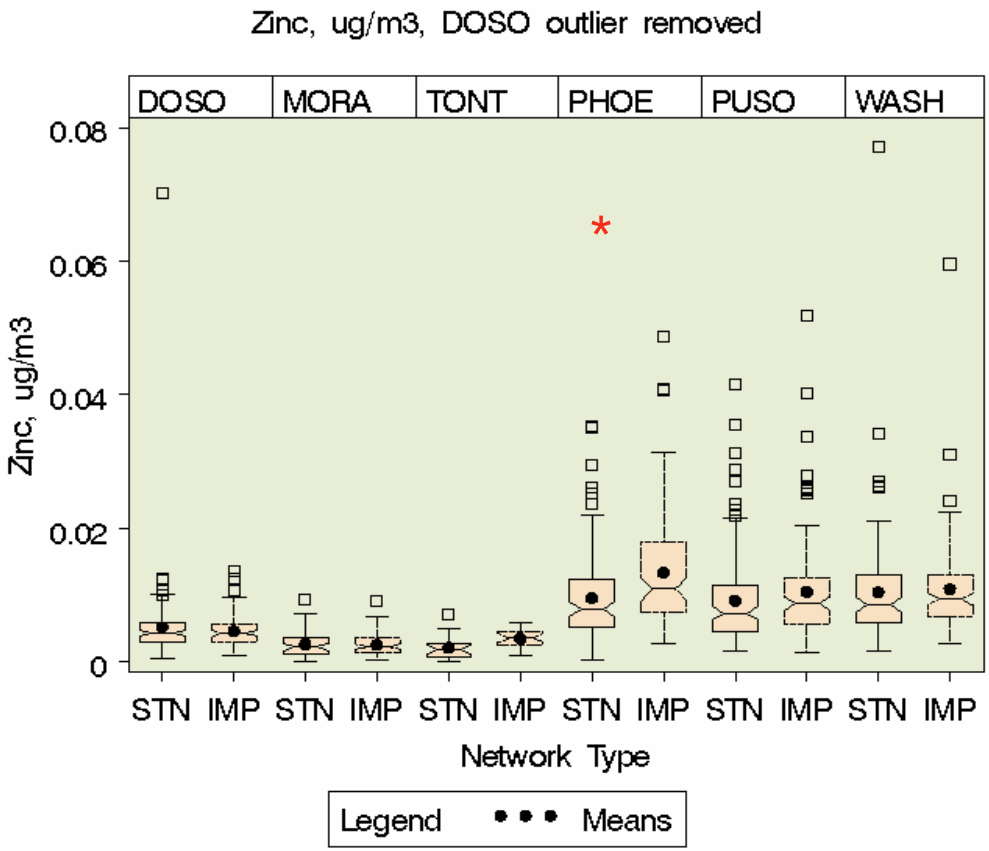
Zn

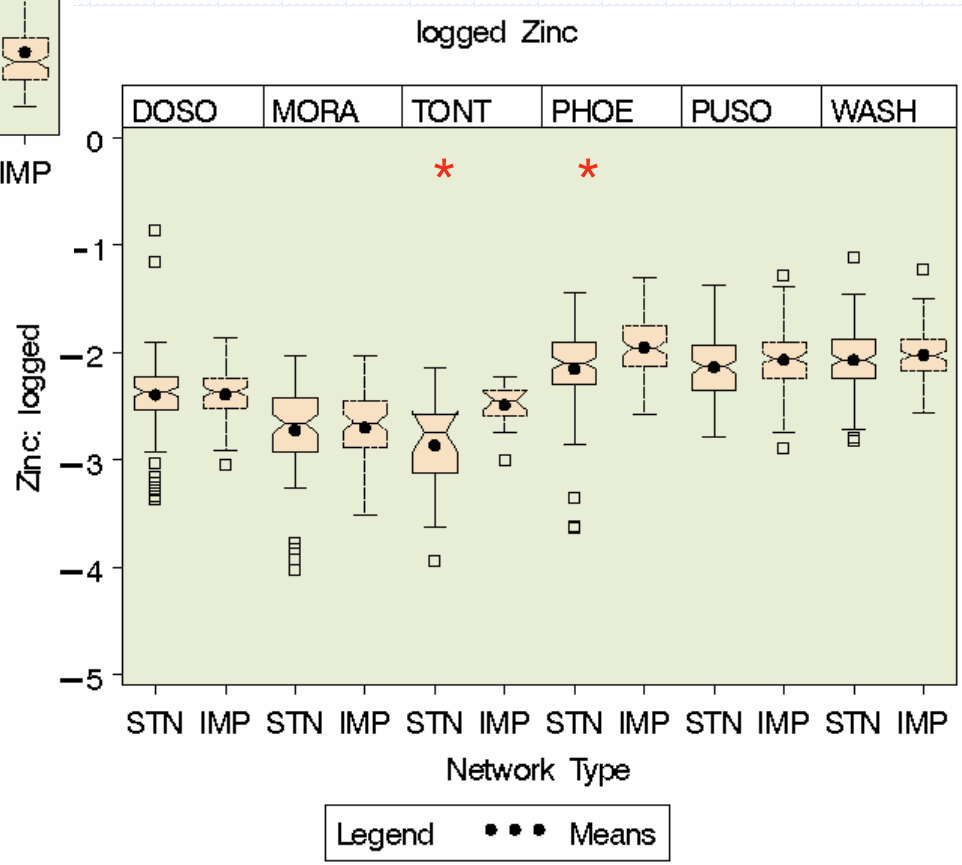




Pb

Frequency Distributions – Paired Samplers, All Sites: 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 ± 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

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