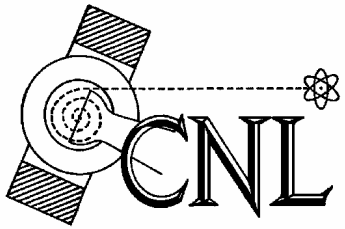
IMPROVE
Particle Monitoring Network:
Special Studies

Chuck McDade, Lowell Ashbaugh, &
Ann Dillner
Crocker Nuclear Laboratory
University of California, Davis
Acadia National Park, July 2005



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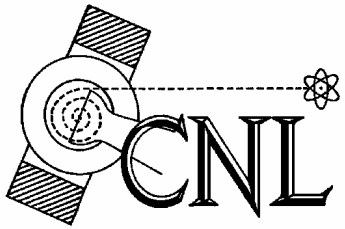

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NITRIC ACID DENUDER EFFICIENCY STUDIES

San Gorgonio
July 2003

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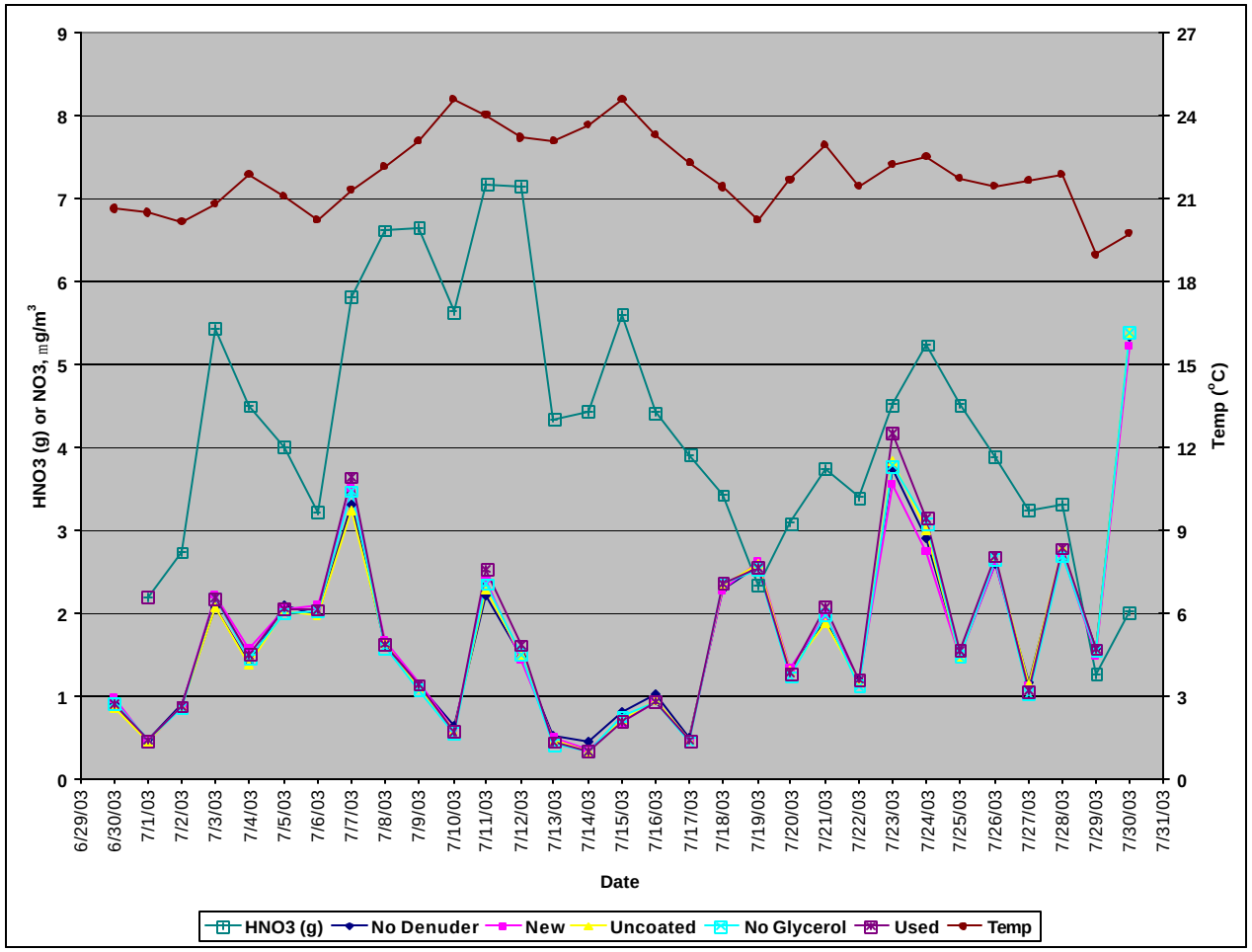

CSU Laboratory Tests

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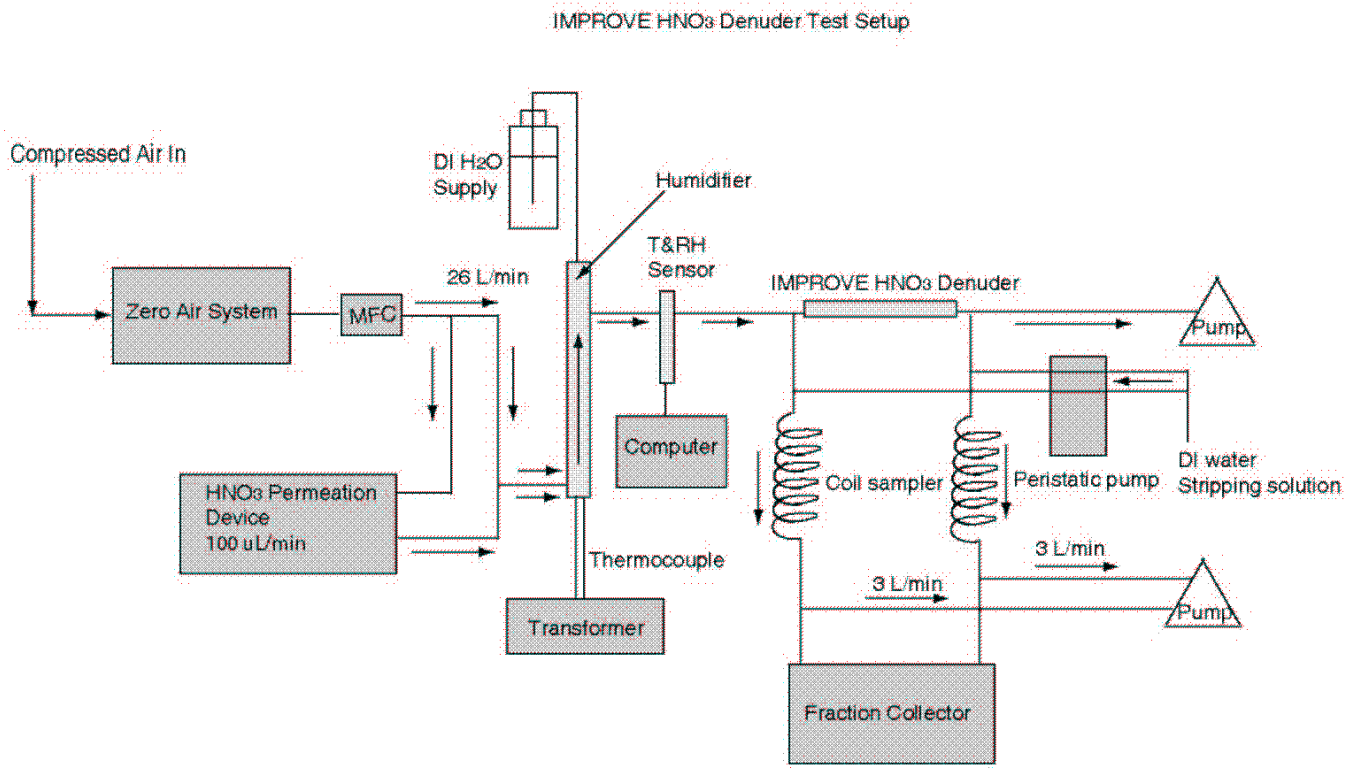

Tests of New & Used Denuders

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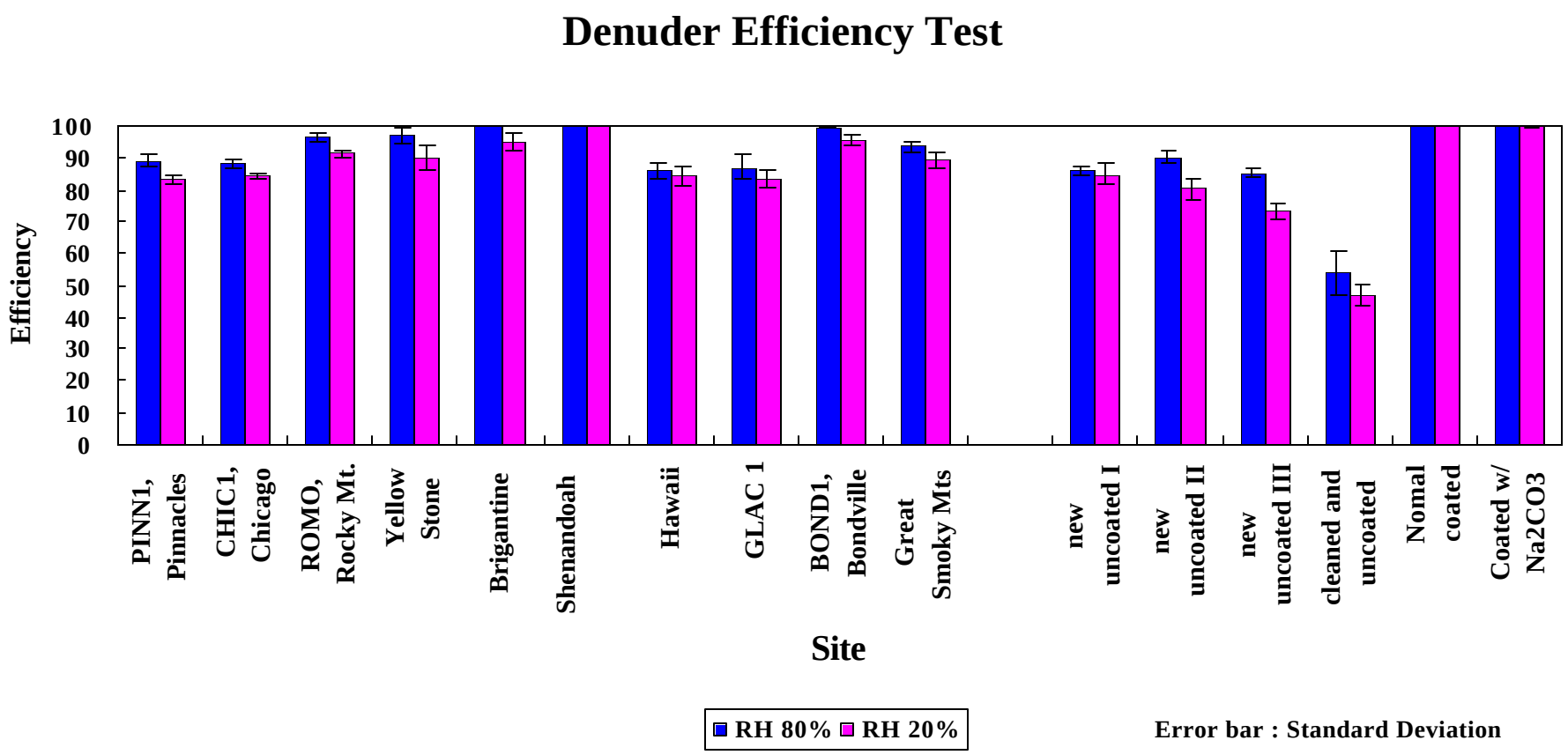

Tests of Freshly Coated Denuders

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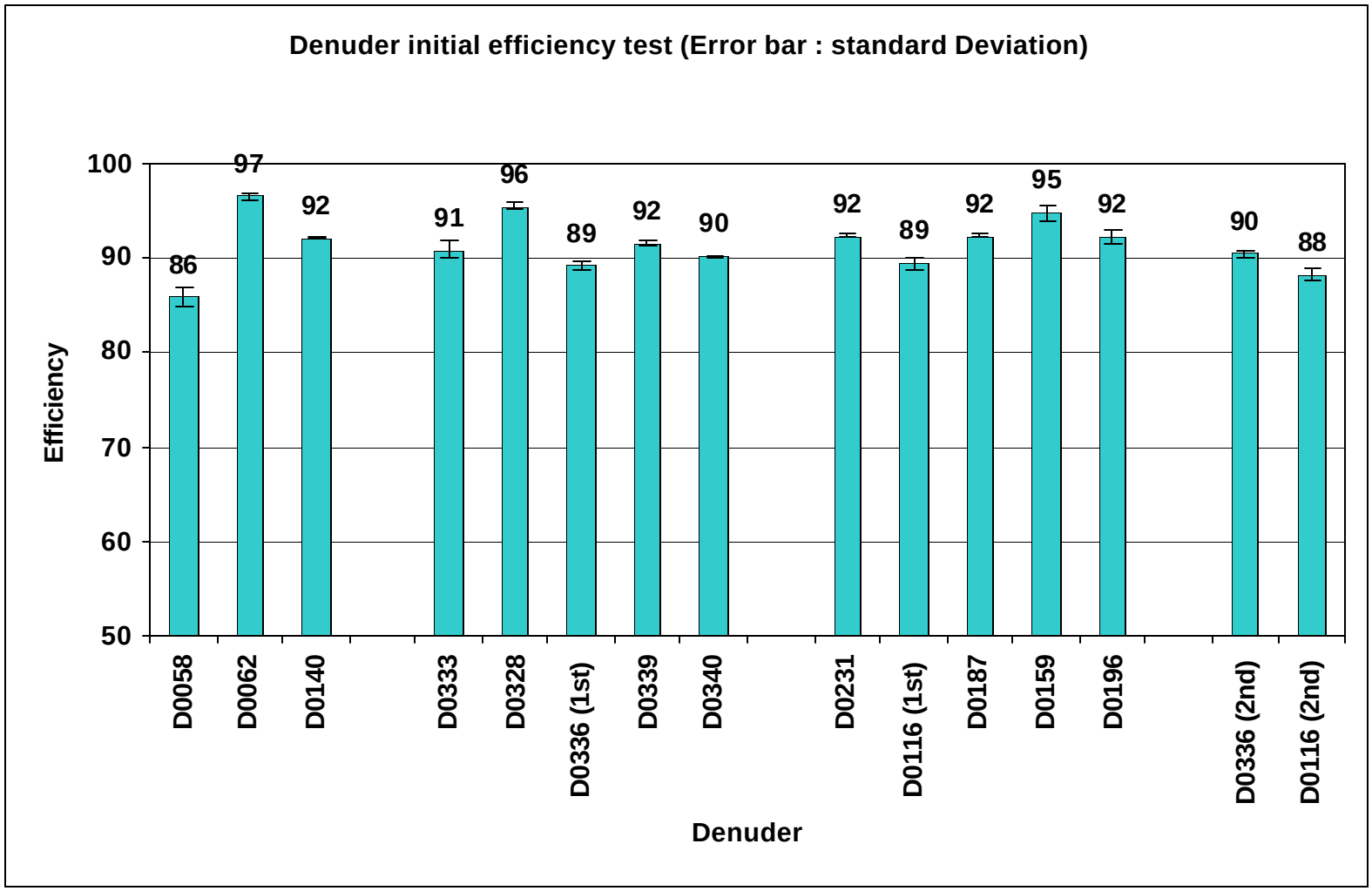

Interim Findings

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- Denuders have a typical efficiency around 90%, but variable among individual denuders
- Efficiencies of new & used denuders do not differ appreciably ----all are around 90%
- Tests suggest that denuder capacity is sufficient for a year in the field (~ 90% efficiency is maintained throughout)

Upcoming Work

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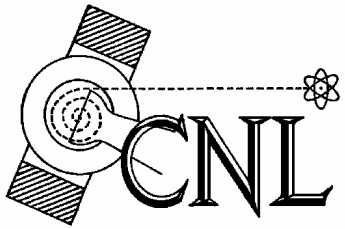
- Conduct some lab tests at lower nitric acid concentrations, closer to ambient
- Assess denuding efficiency of entire sampler (denuder plus aluminum tubing)
- Investigate improved coating techniques or different coatings (e.g., MgO)



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GREAT SMOKY MOUNTAINS AMMONIA STUDY

Motivation

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- Ammonium measured at a few sites
  - Acidity of particles
  - Stoichiometric ratios of ammonium, sulfate and nitrate
- Difficulties in measuring ammonium
  - Contamination
    - Human breath
    - Ammonia gas in atmosphere
  - Loss of ammonium from nylon filters
- Can ammonium be accurately measured -
  - Using current IMPROVE protocol?
  - Using a reasonable modification to IMPROVE protocol?
  - Using extreme modifications to IMPROVE protocol?

Methods

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- Great Smoky Mtns IMPROVE site – lots of ammonium
- Samples
  - every day
  - 24-hours
  - July 19 – August 18, 2004
- IMPROVE Samplers
  - Eight B (ions) modules
  - One set of PM2.5 modules
  - One set of speciated PM10 modules
- Techniques used to reduce contamination and loss
  - Gloves and masks, acid strips and ice in shipping container

URG Sampler

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- URG sampler
- Same sampling times
- Minimizes both contamination and loss
- Quantitative measure of ammonium

URG and IMPROVE Data

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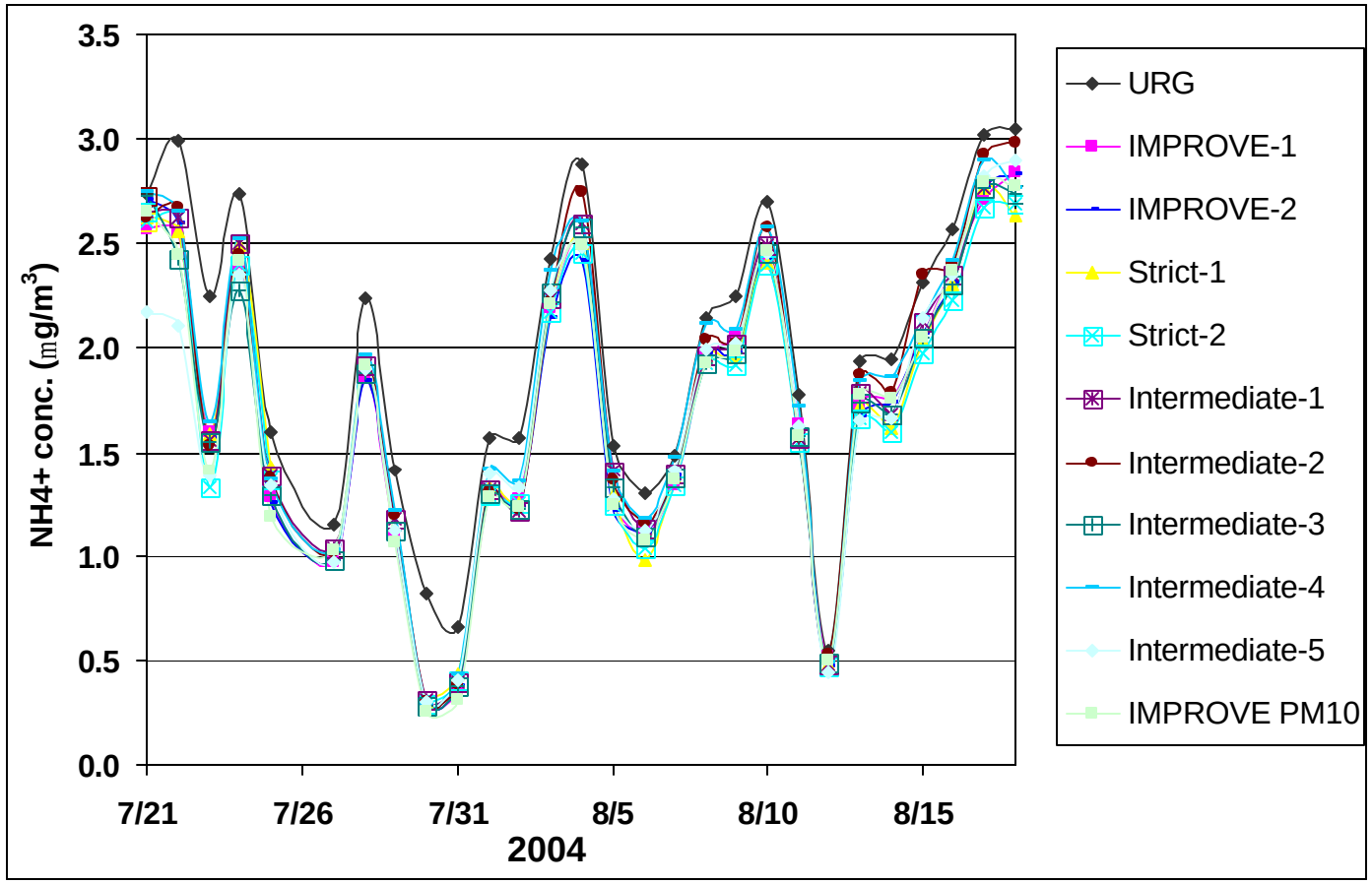

Strict Controls Vs IMPROVE

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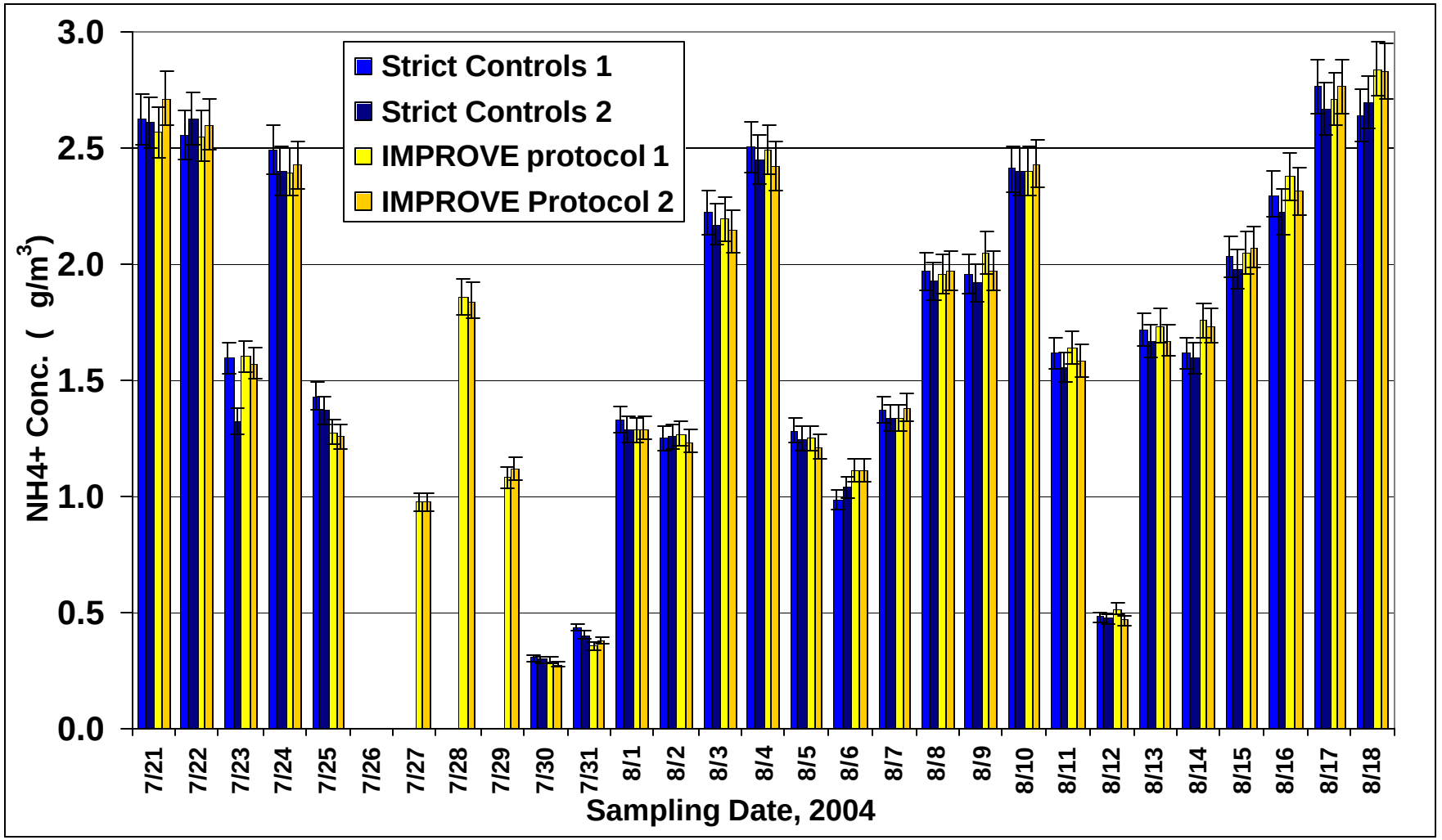

IMPROVE vs. URG

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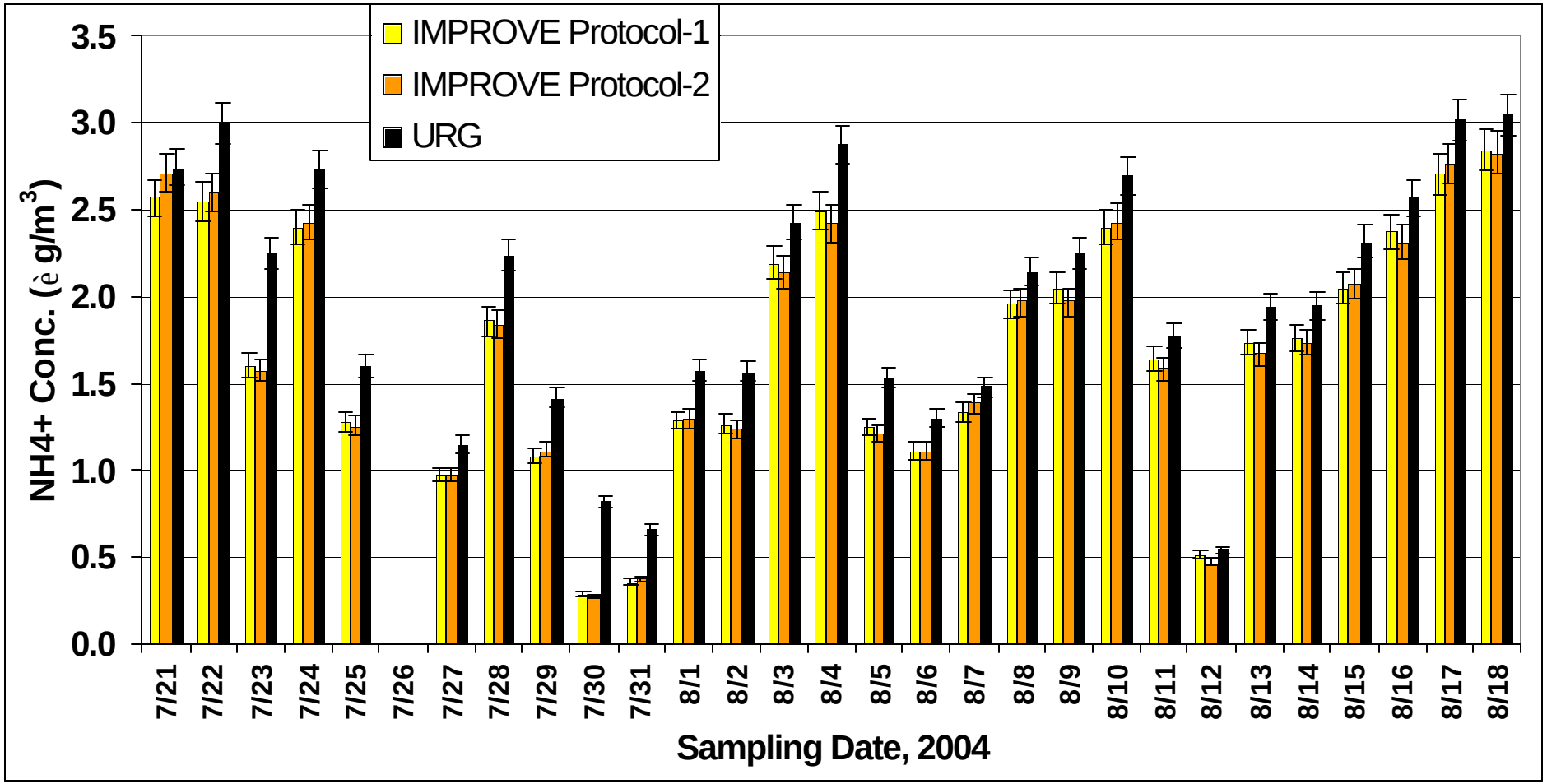

Ammonia Study

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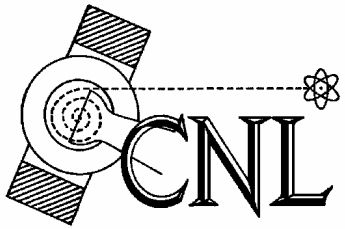
- IMPROVE protocol methods do not contaminate nylon filters with ammonium
- IMPROVE concentrations are less than URG sampler by $0.3 \pm 0.15\ \mu g/m^3$
- IMPROVE is biased low – not quantitative



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NYLON FILTER TESTS

Nitrate measurements have shown unusual patterns at some sites

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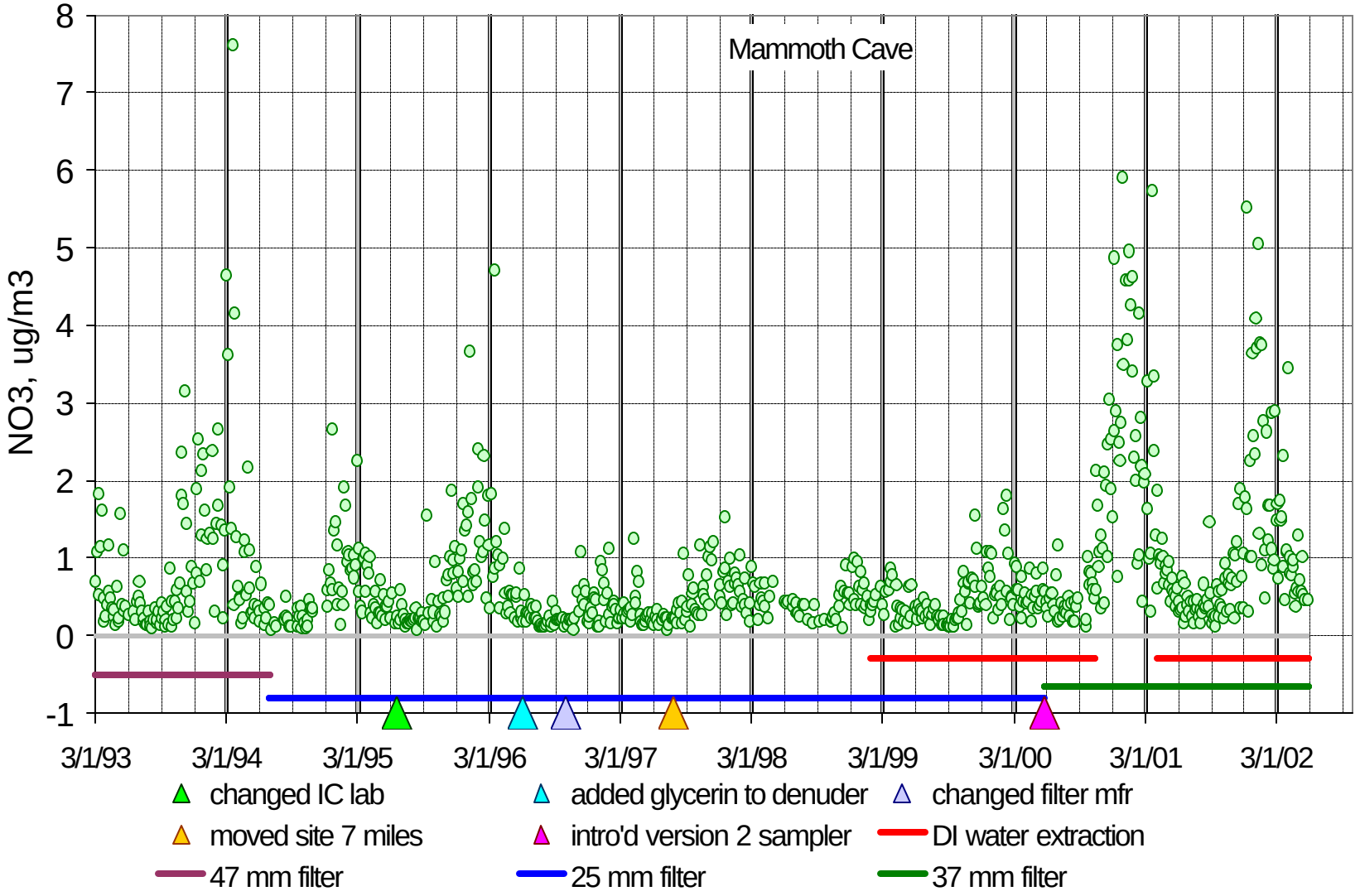

Objective

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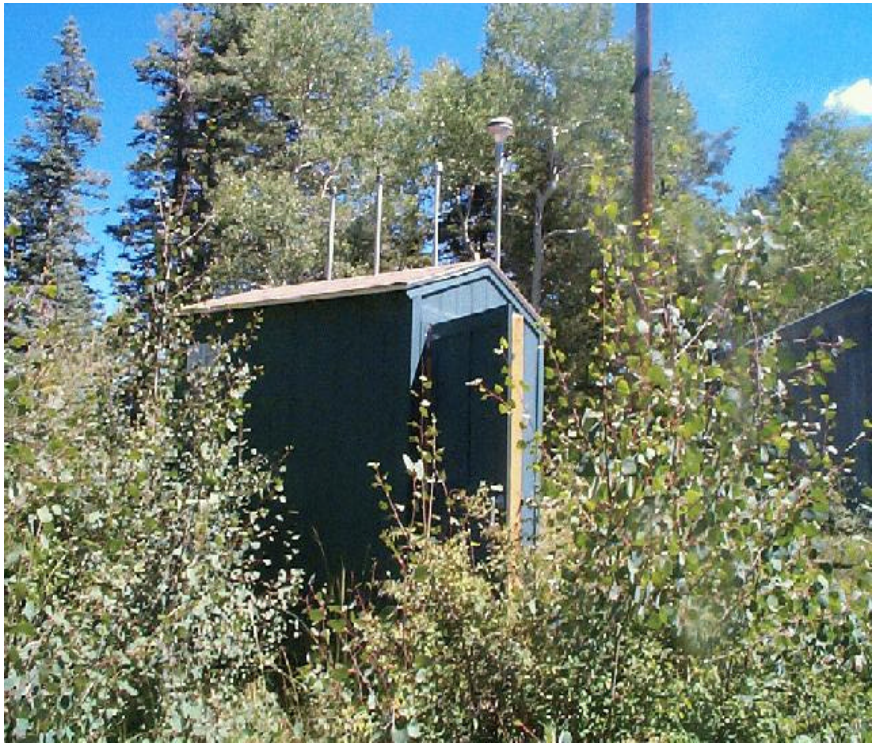
- Evaluate the difference in collection efficiency of nitrate particles on nylon filters
- IMPROVE purchases nylon filters to last about one year
  - Since December 1995, over 20 different nylon filter lots have been used



Sampling

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- Sampling conducted on the roof of EUIII in Davis, CA
- 28 days of 24-hour samples, April-May 2004
- Samples begin at 2300 hr
- Eight modules sampled concurrently

Sampling Trains

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A	B	
HNO_3 Denuder	HNO_3 Denuder	-Removes $HNO_3(g)$
↓	↓	
NH_3 Denuder	NH_3 Denuder	-Removes $NH_3(g)$
↓	↓	
	Teflon Filter	-Collects particles
↓	↓	
Nylon Filter	Nylon Filter	-Collects Nitrate
↓	↓	
Citric Acid Filter	Citric Acid Filter	-Collects NH_3

Sampler Configuration

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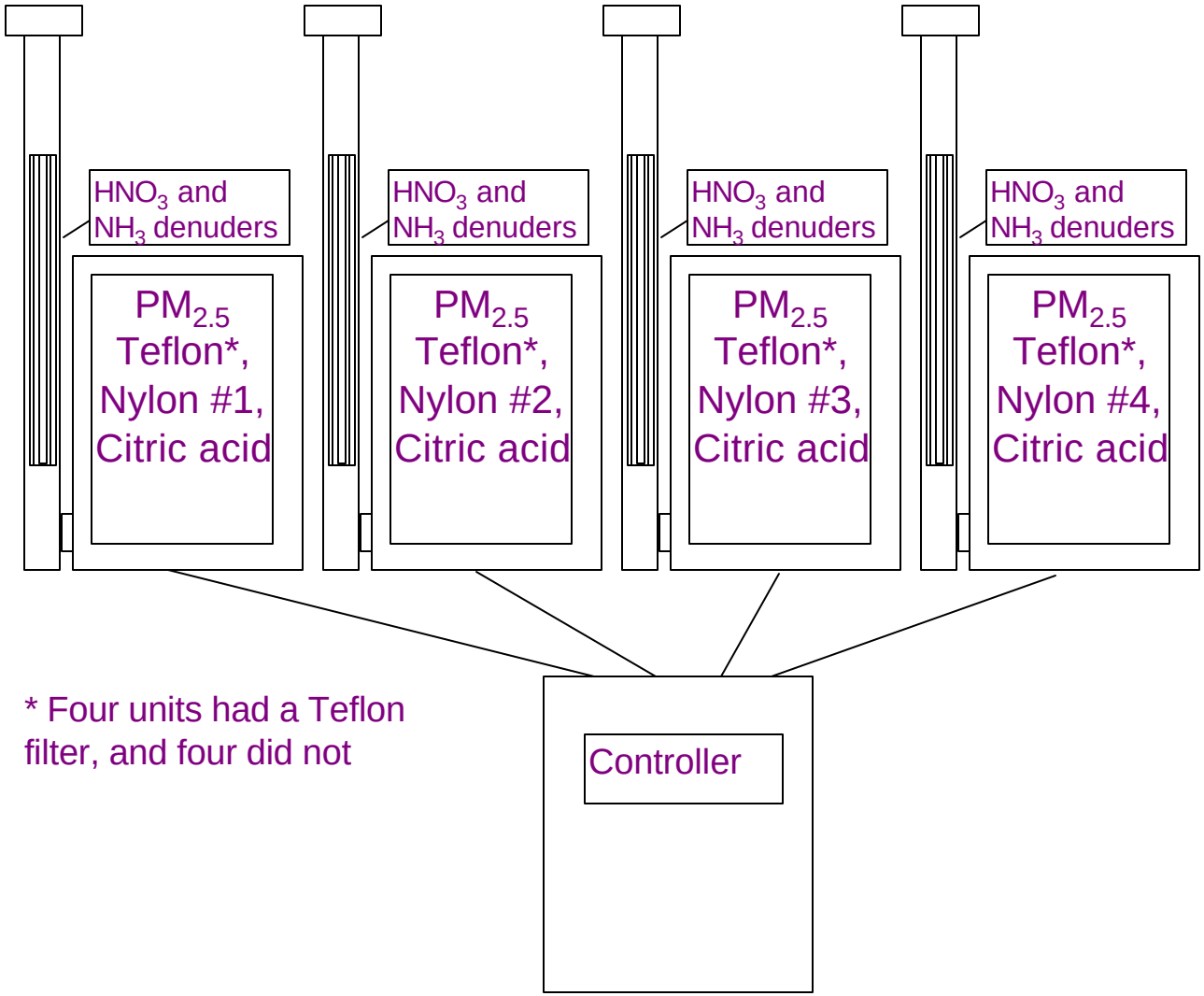

* Four units had a Teflon filter, and four did not

Nylon Filters

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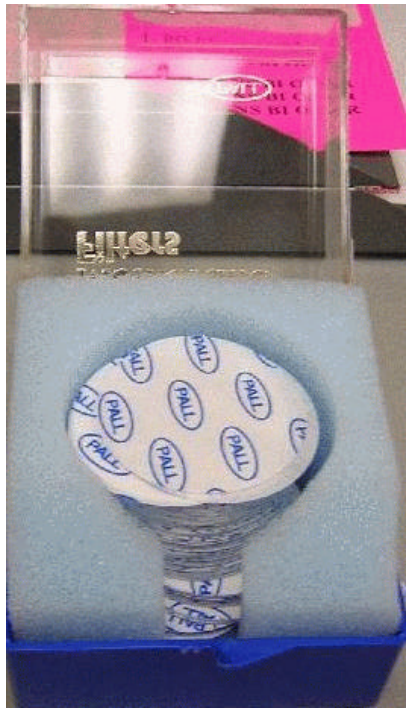
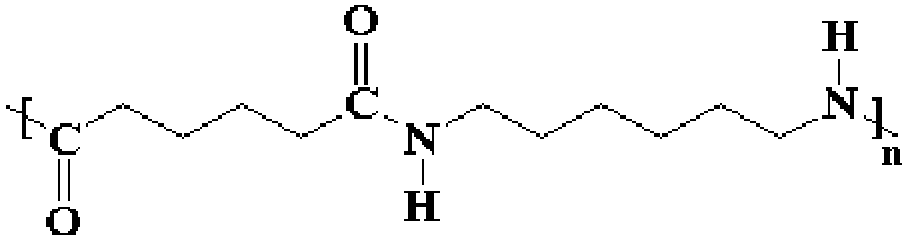
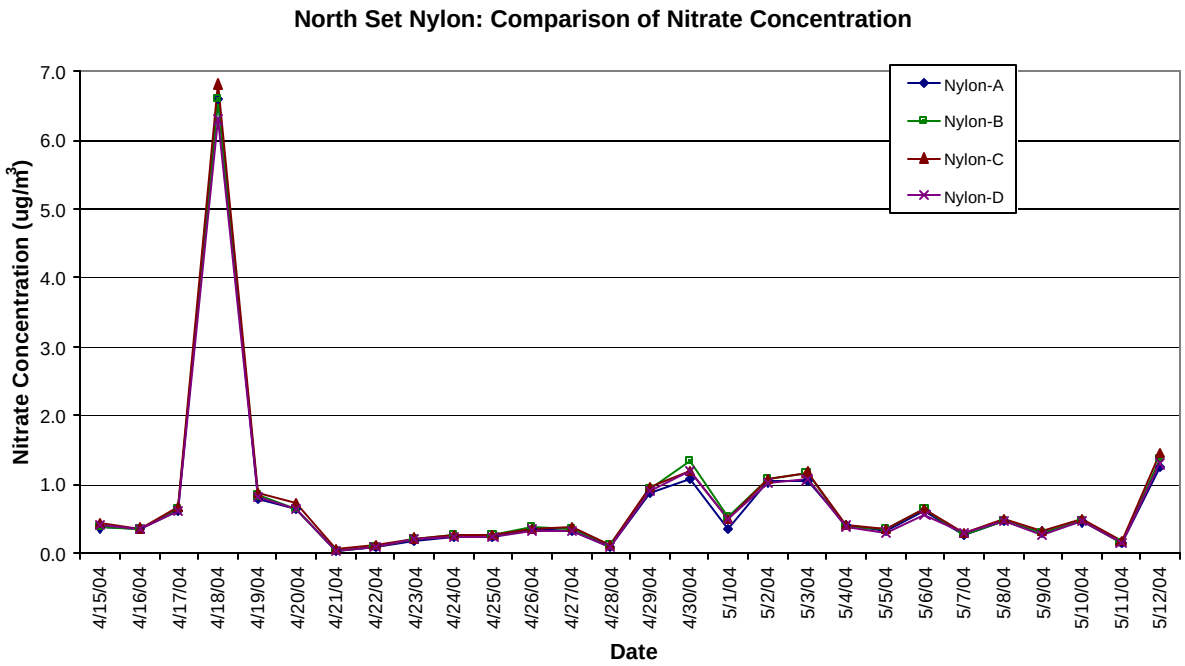
- Four Different Nylon filter lots tested
  - Magna Nylon, GE Osmonics, BK05161B, used 08/18/01-08/30/02
  - Magna Nylon, GE Osmonics, BK09061E, used 08/30/02-01/01/04
  - Nylasorb, Pall Gelman, BNC1716, used 01/01/04-02/11/05
  - Nylon, Advantec MFS Inc., 201622, never used in IMPROVE
- Filter lots often have visible and texture differences
- All made from nylon 6,6

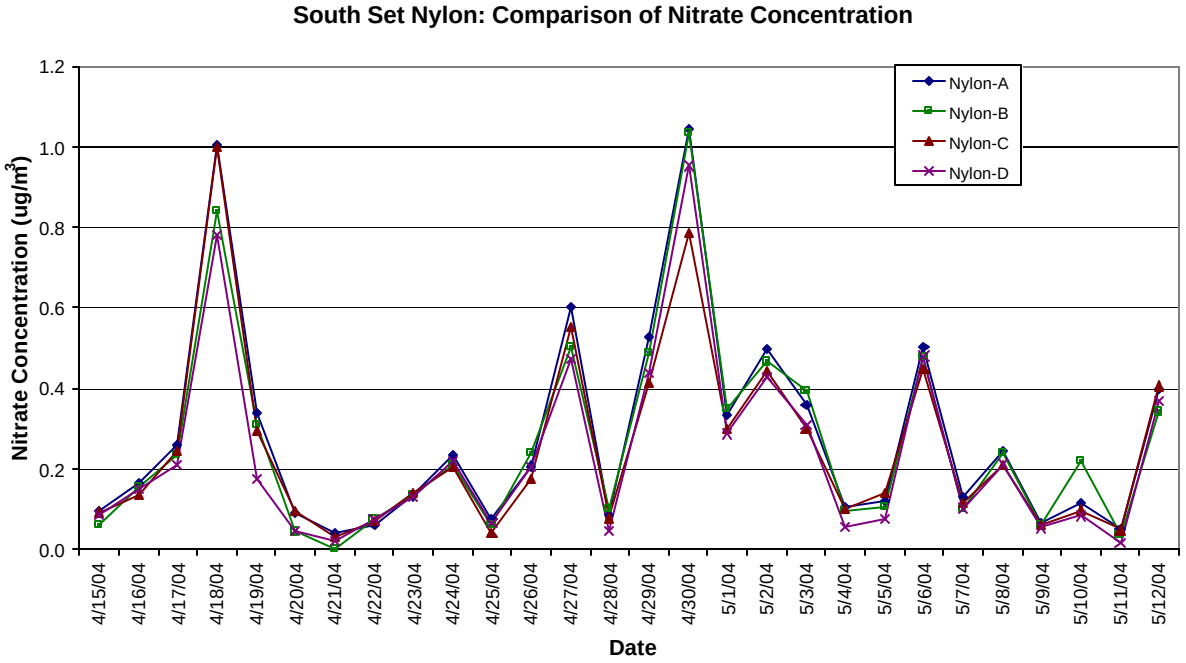






Nitrate concentration measured using four different nylon filters without a Teflon prefilter

Nitrate concentrations measured using four different nylon filters preceded by a Teflon filter (note difference in concentration scale)



Mean Total Nitrate Concentration

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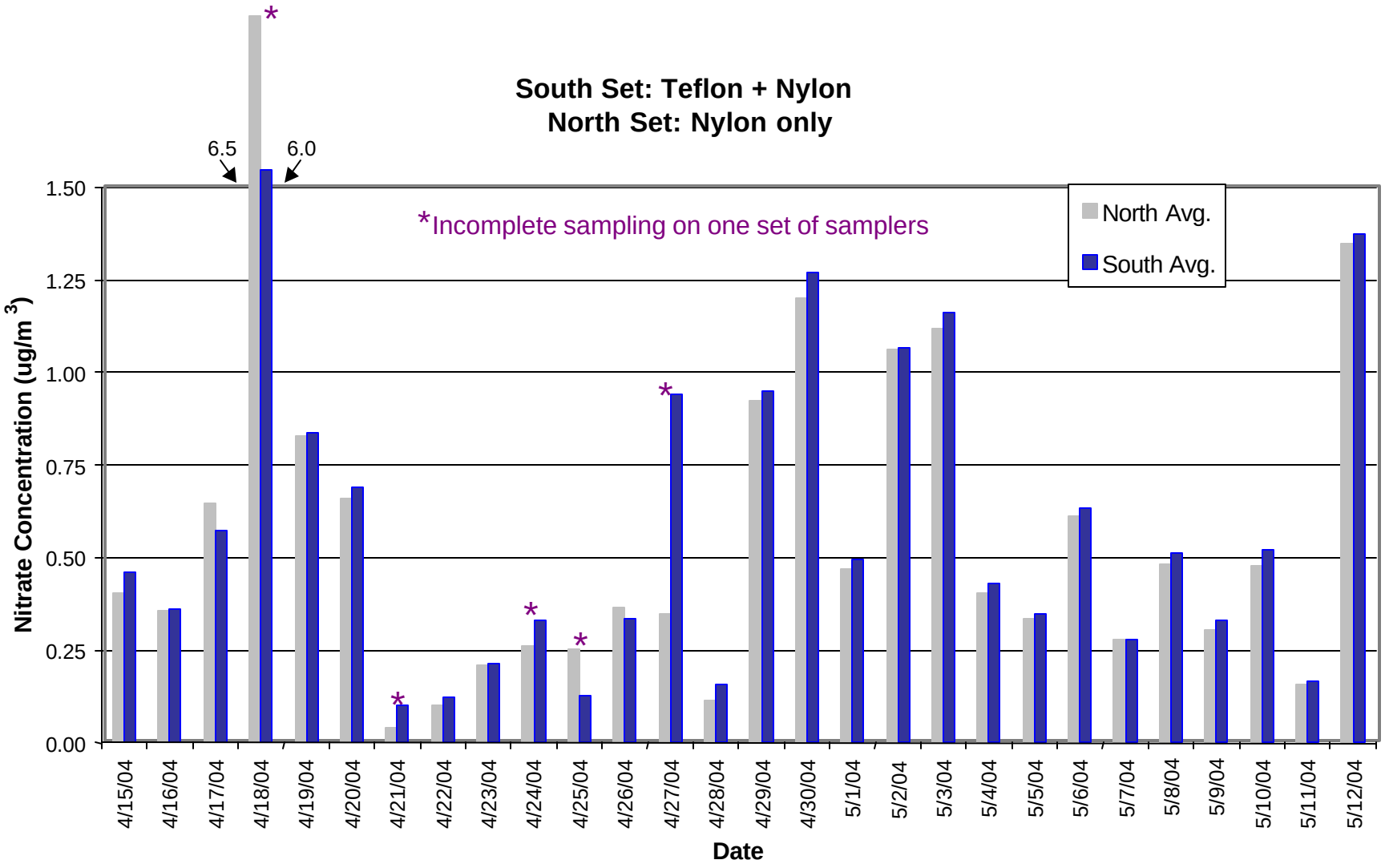

Conclusions

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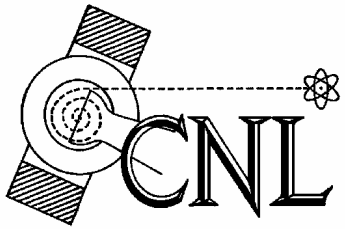
- Nylon filters tested were virtually identical in their nitrate collection characteristics.
  - We were unable to test filters used prior to August 2001 because they were no longer available.
  - The few nitrate differences that were observed occurred when one set of samplers did not run all 24 hours – differences were consistent with higher concentrations at night and lower concentrations during the day.



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MOBILE LABORATORY

IMPROVE Mobile Laboratory

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- Cooperative effort – UCD & CSU
- To be used for special studies
- Delivery expected late summer 2005

Mobile Lab Details

- International truck + 20’ custom truckbody
- Three power options: landline, onboard generator, inverter/battery system
- Air-ride suspension for smooth ride for delicate instrumentation
- Rear power liftgate for loading instruments
- Underbody storage boxes for pumps, etc.
- Split design-chemistry lab and aerosol lab
- Modular, reconfigurable instrumentation

“Green” Diesel Retrofit

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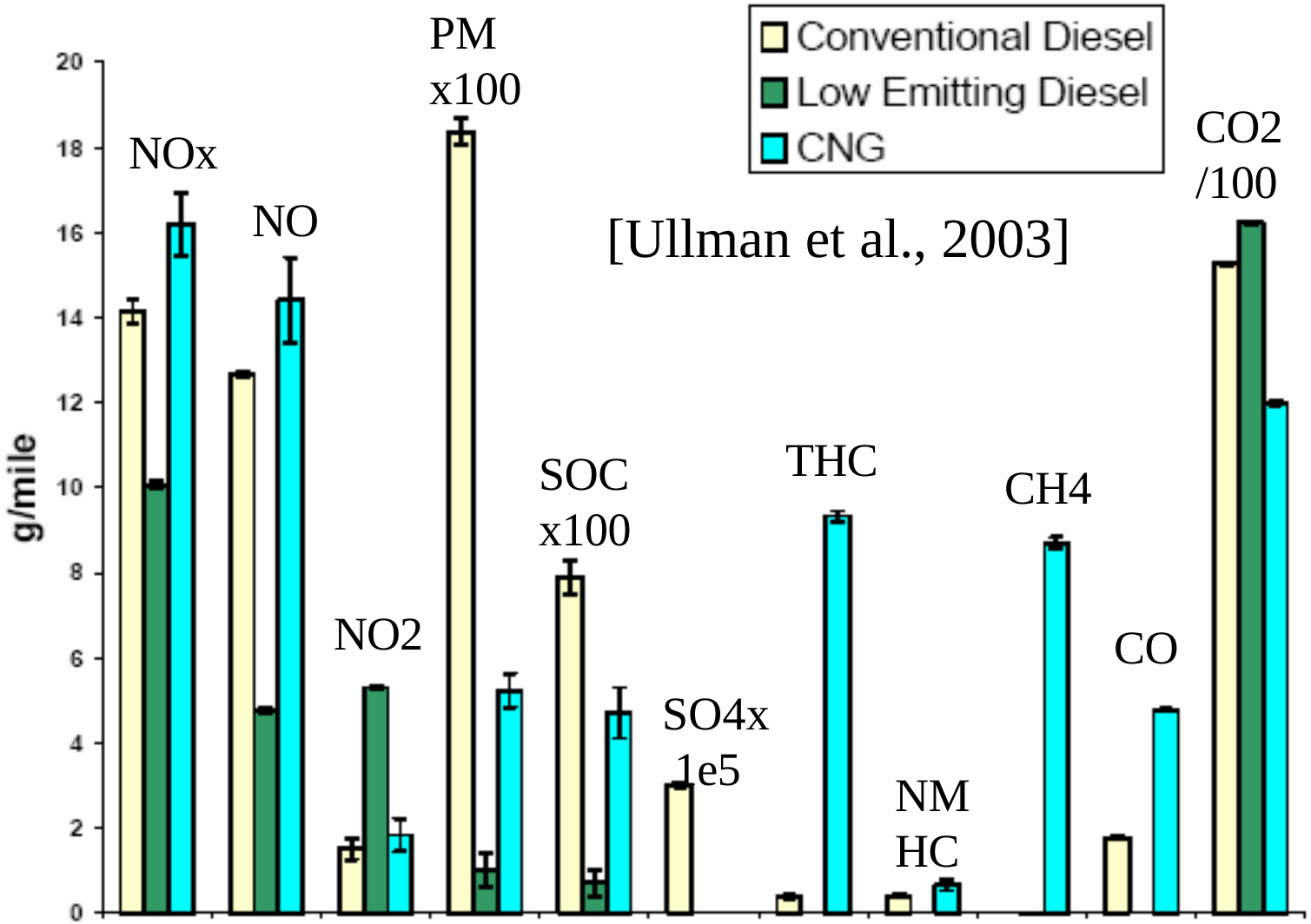
- Future retrofit of continuously regenerating catalyzed particulate filter
- Will be cleaner than CNG (w/low sulfur diesel in 2007)
- Diesel also uses 40-60% less fossil fuel per mile than gas engines
- Other diesel benefits-greater engine longevity (0.5 million miles) and more torque
- Also allows use of electrical generator

Green Diesel Emissions



- Big improvement, especially in PM emissions
- Important for on-road and stationary sampling using self-generator power

Mobile Lab Instrumentation

Online Ions and Carbon

Dry Particle Sizing System

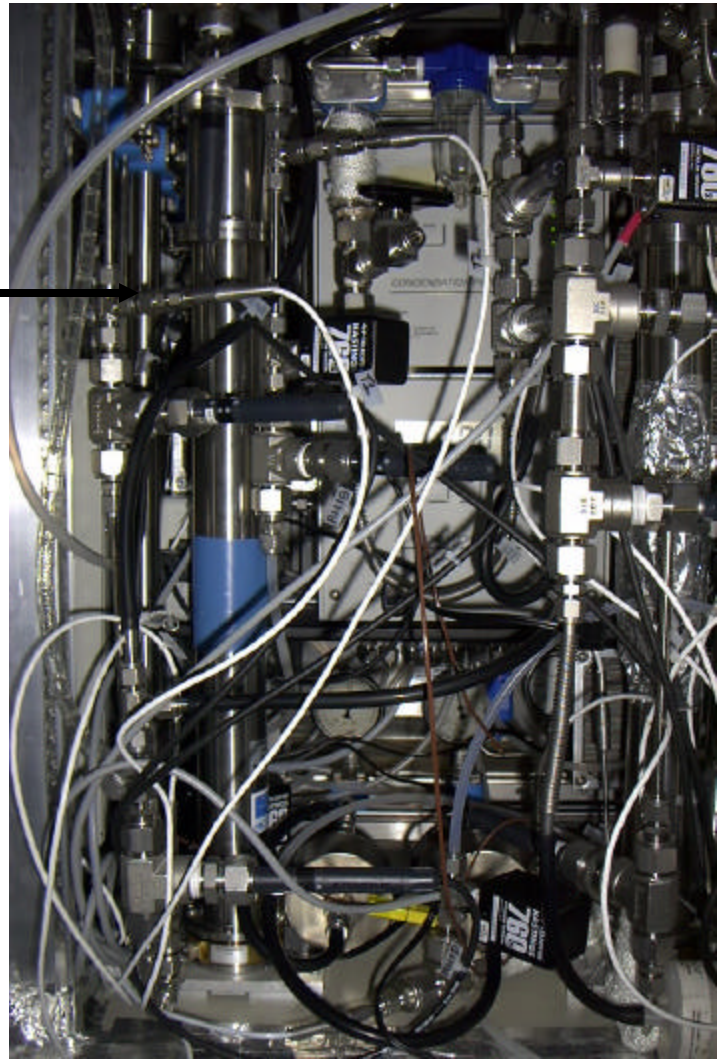
Trace Gases (CO, O3, NH3/NO/NO2)

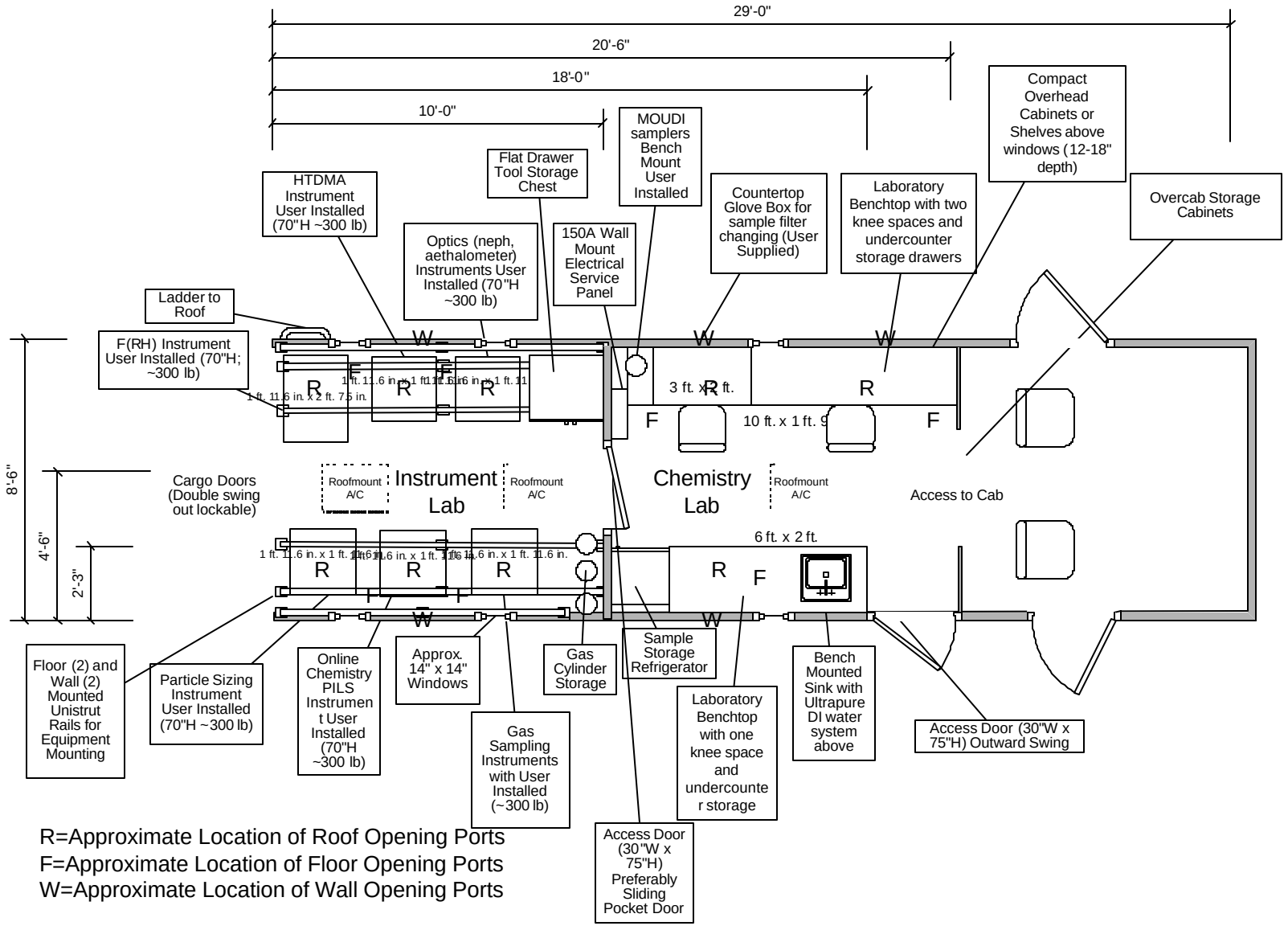
- Light Scattering, Microbalance, MOUDIs, IMPROVE Sampler, Met Station

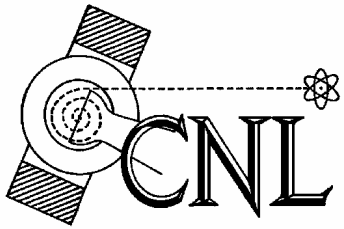
HTDMA-CSU Version 3.0

HTDMA

Control and Measurement Electronics, Pneumatics, Pumps, Aerosol Generation




29'-0"
20'-6"
18'-0"
10'-0"
MOUDI samplers Bench Mount User Installed
Compact Overhead Cabinets or Shelves above windows (12-18" depth)
Flat Drawer Tool Storage Chest
HTDMA Instrument User Installed (70"H ~300 lb)
Optics (neph, aethalometer) Instruments User Installed (70"H ~300 lb)
150A Wall Mount Electrical Service Panel
Countertop Glove Box for sample filter changing (User Supplied)
Laboratory Benchtop with two knee spaces and undercounter storage drawers
Overcab Storage Cabinets
Ladder to Roof
F(RH) Instrument User Installed (70"H; ~300 lb)
3 ft. x 2 ft.
10 ft. x 1 ft. 9
8'-6"
4'-6"
2'-3"
Cargo Doors (Double swing out lockable)
Roofmount A/C
Instrument Lab
Roofmount A/C
Chemistry Lab
Roofmount A/C
Access to Cab
6 ft. x 2 ft.
Floor (2) and Wall (2) Mounted Unistrut Rails for Equipment Mounting
Particle Sizing Instrument User Installed (70"H ~300 lb)
Online Chemistry PILS Instrument User Installed (70"H ~300 lb)
Approx. 14" x 14" Windows
Gas Sampling Instruments with User Installed (~300 lb)
Gas Cylinder Storage
Sample Storage Refrigerator
Laboratory Benchtop with one knee space and undercounter storage
Bench Mounted Sink with Ultrapure DI water system above
Access Door (30"W x 75"H) Outward Swing
Access Door (30"W x 75"H) Preferably Sliding Pocket Door
R=Approximate Location of Roof Opening Ports
F=Approximate Location of Floor Opening Ports
W=Approximate Location of Wall Opening Ports



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IMPROVE vs. STN SAMPLER COMPARISON

Scope of the Analysis

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- New data recently available, from Year 2 of comparison
- Broad-brush analysis today, focusing on Year 1 versus Year 2
- More detailed analyses to follow later in 2005

STN/IMPROVE Intercomparison

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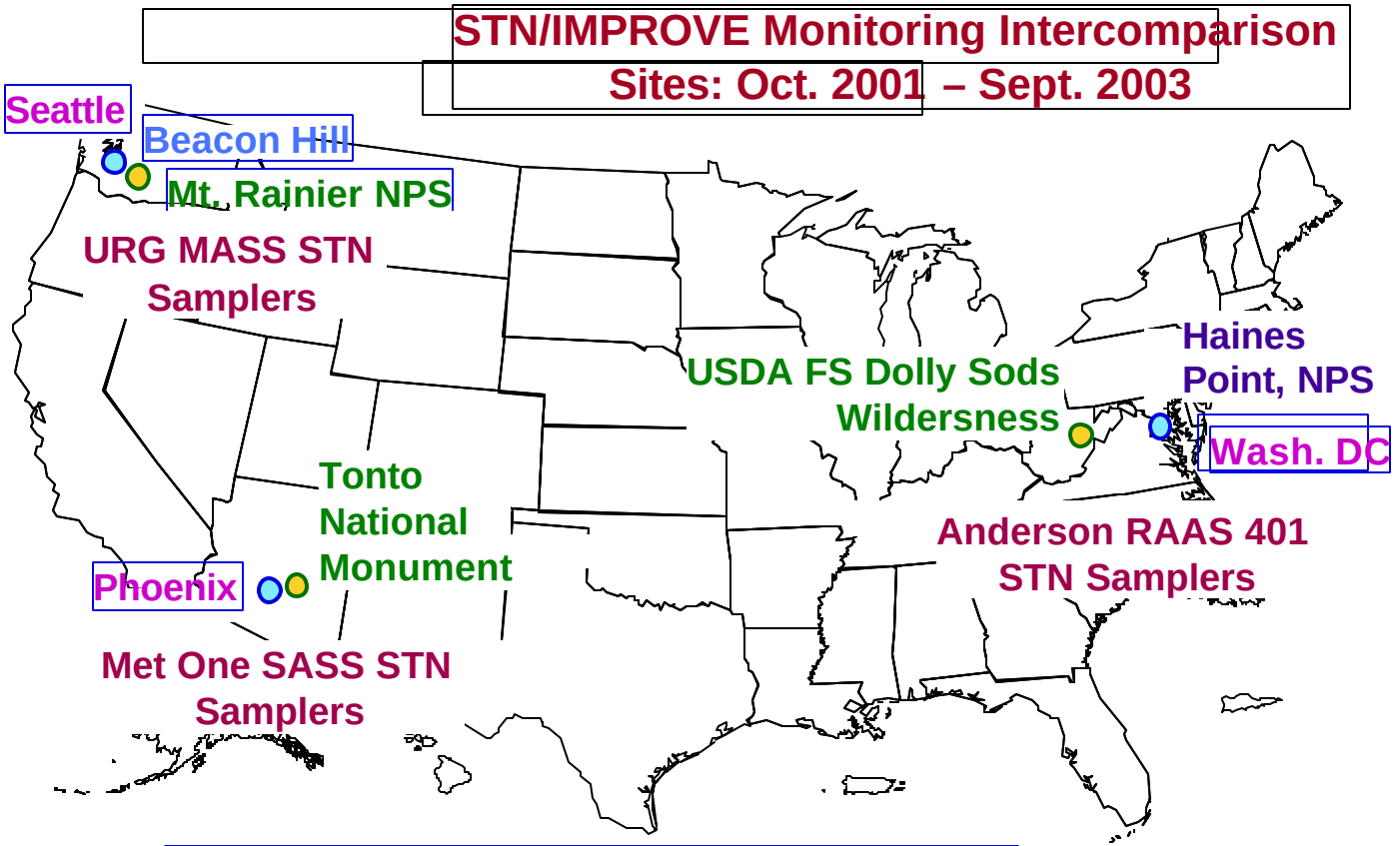
Operated According to Each Network's Protocols



What do we know?

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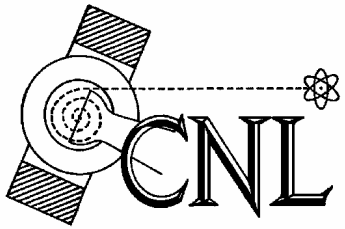
- Year 2 looks much like Year 1
- Major components of the aerosol agree well between STN and IMPROVE
- OC differs because techniques are different
- Many soil elements differ (due to cutpoints?)
- Comparing near the MDL can be misleading, and many measurements are near the MDL



Major Aerosol Components

Fine Mass (PM2.5)

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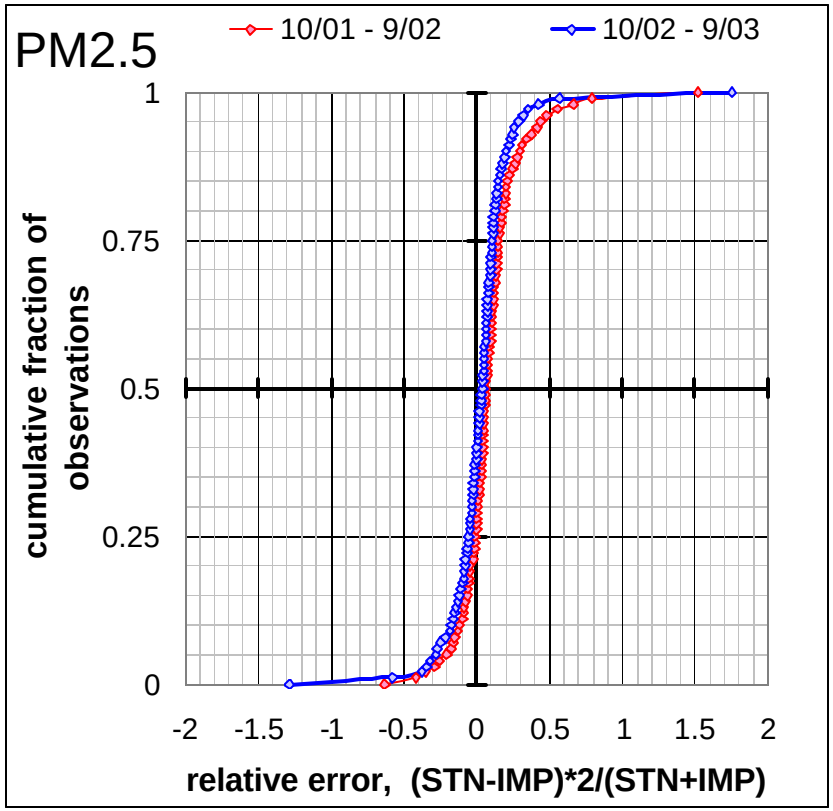

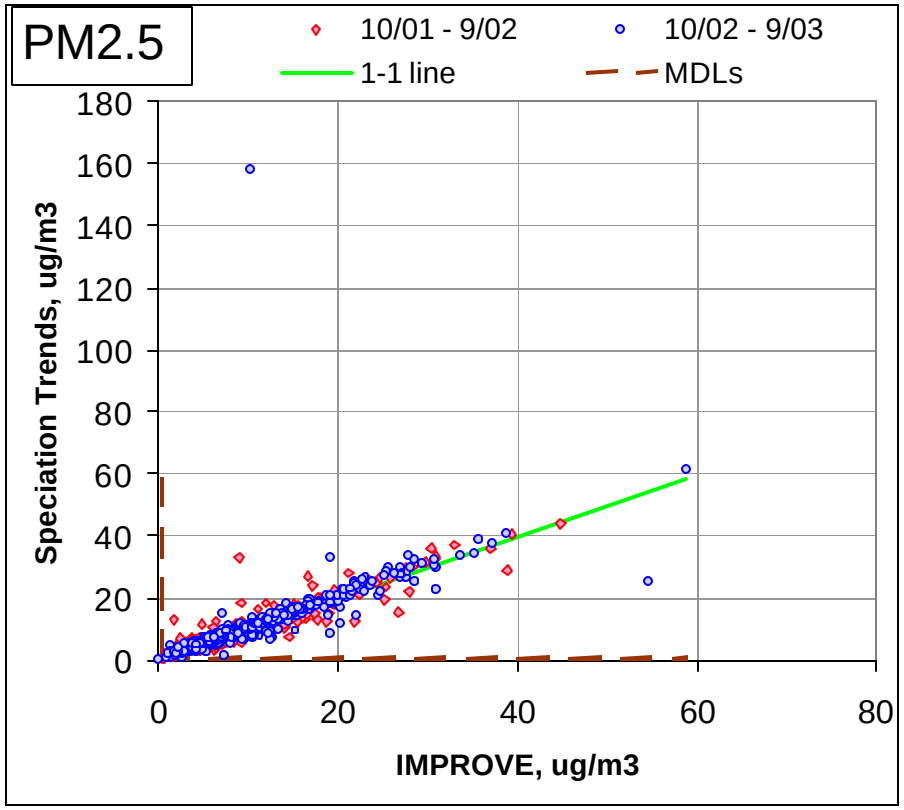

Sulfur

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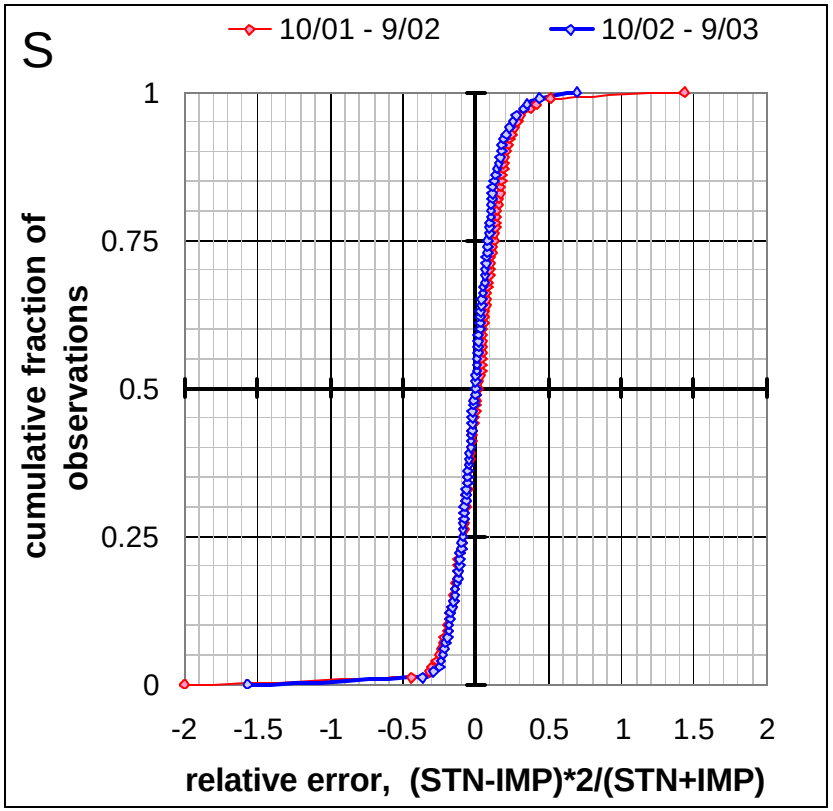

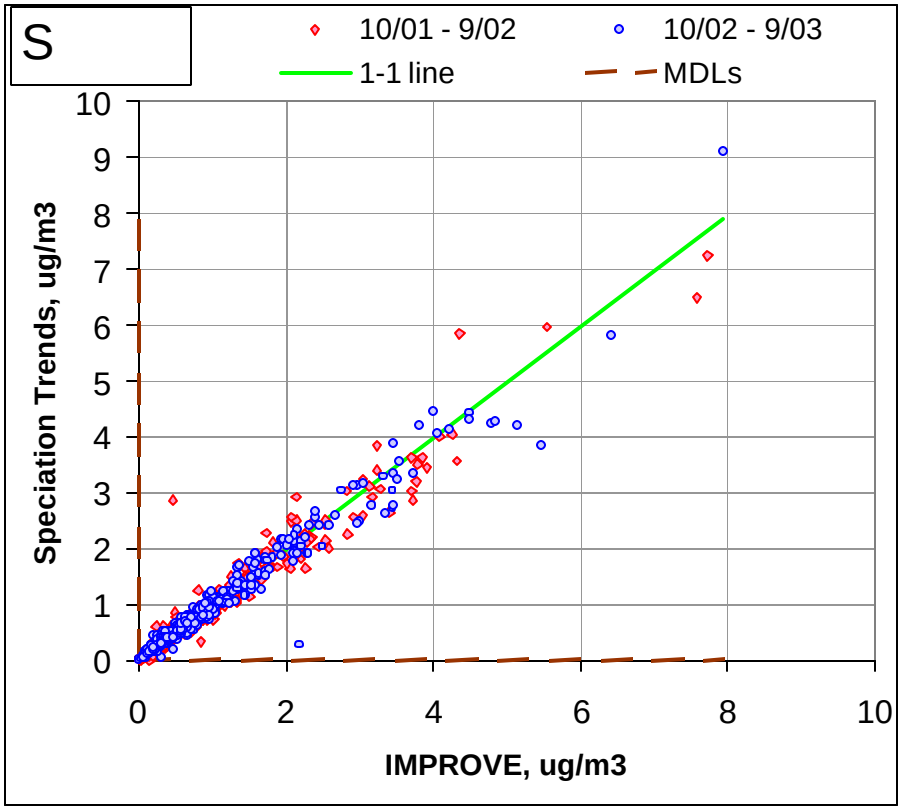

Sulfate

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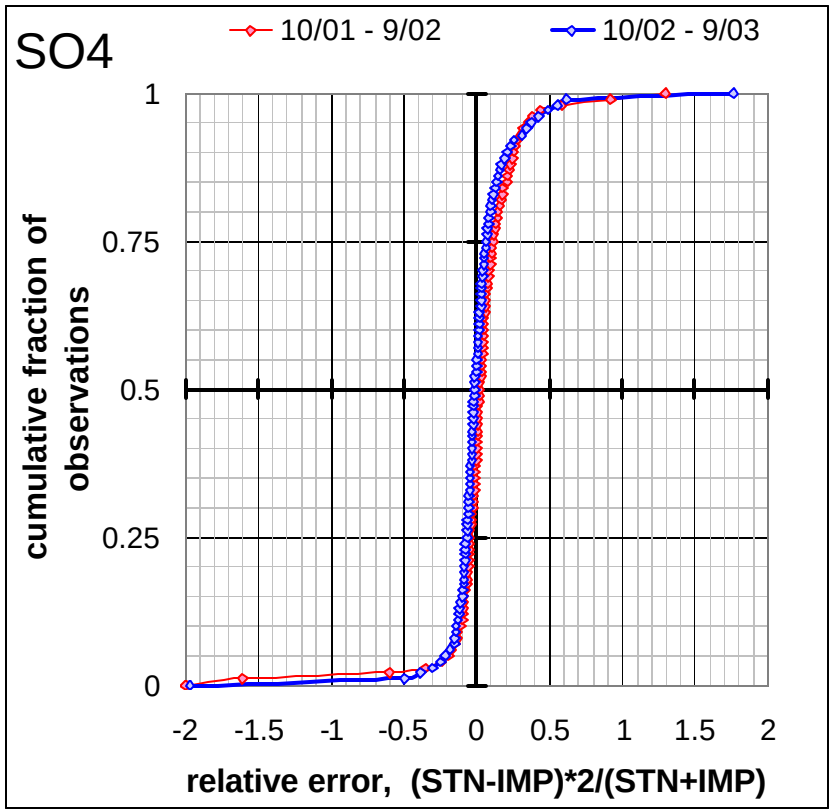

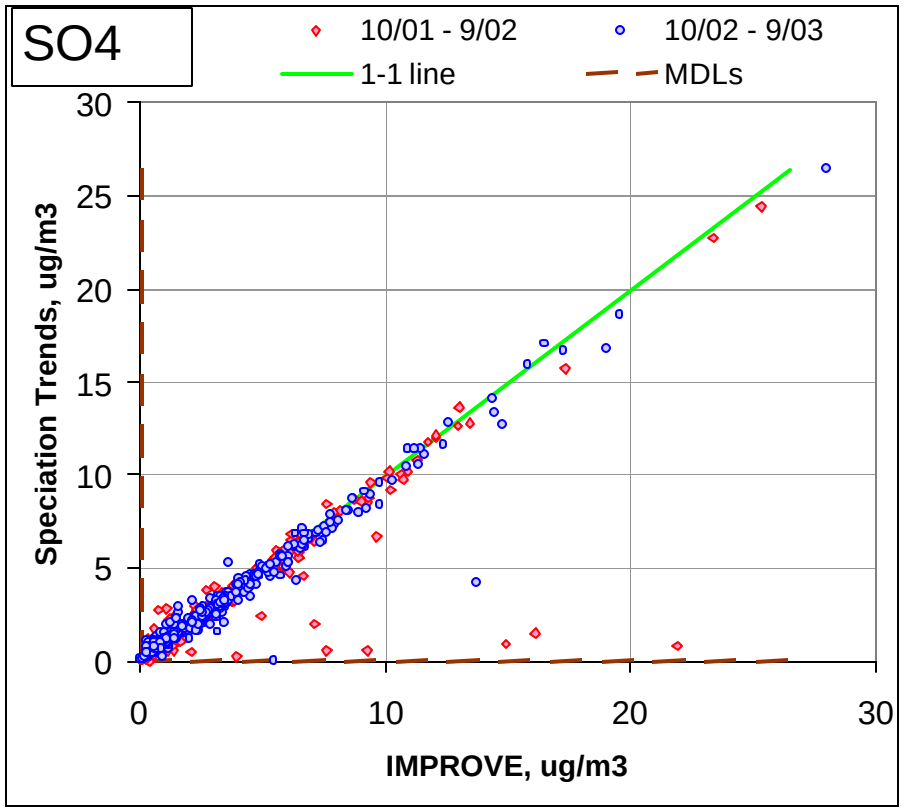

Nitrate

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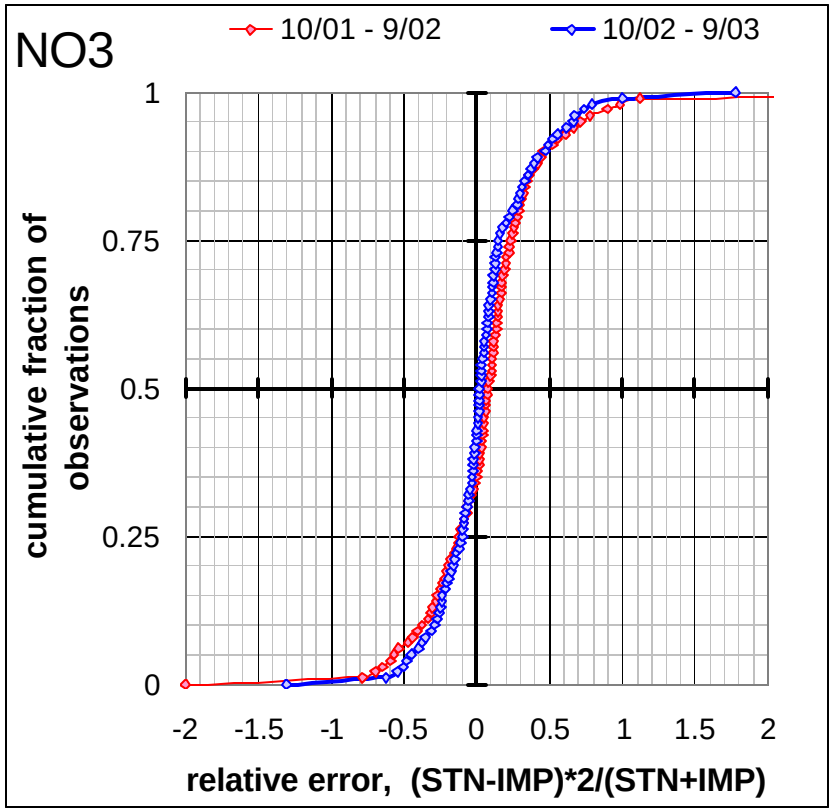

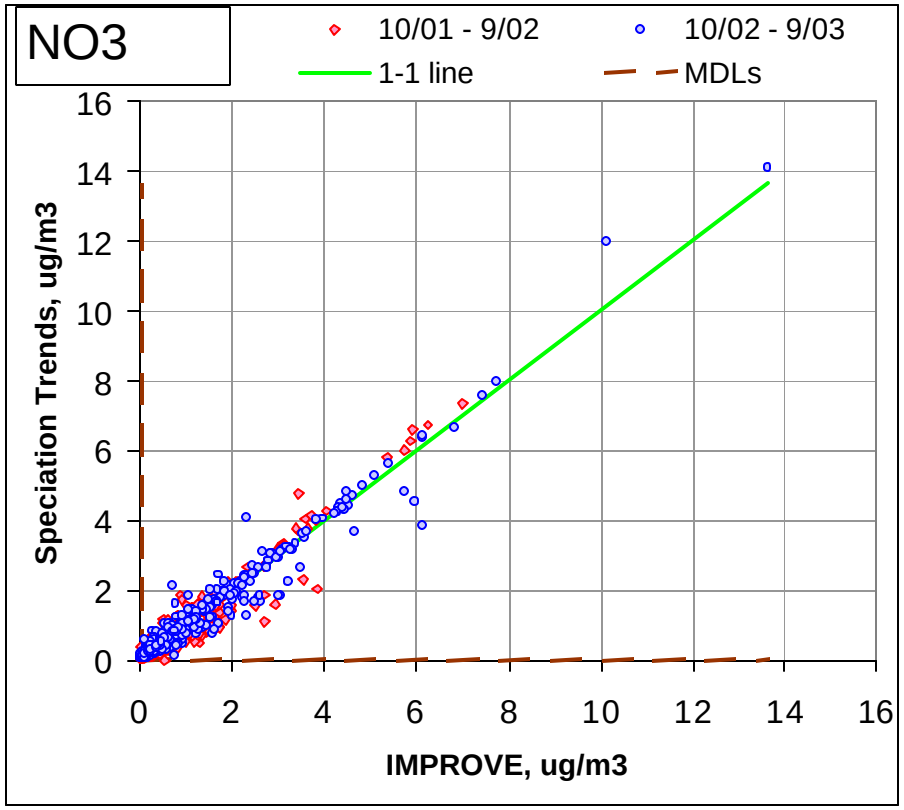

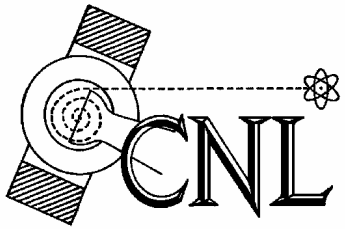

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Elemental & Organic Carbon

Techniques differ between STN & IMPROVE

- Temperature profiles for sample heating not identical
- IMPROVE corrects for artifacts, STN does not

Elemental Carbon

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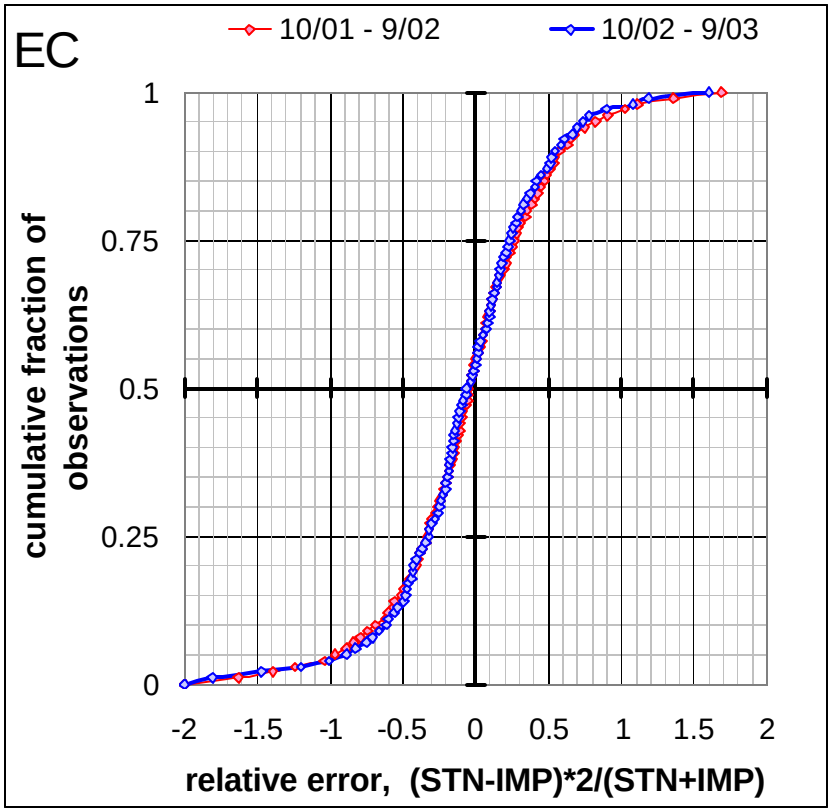

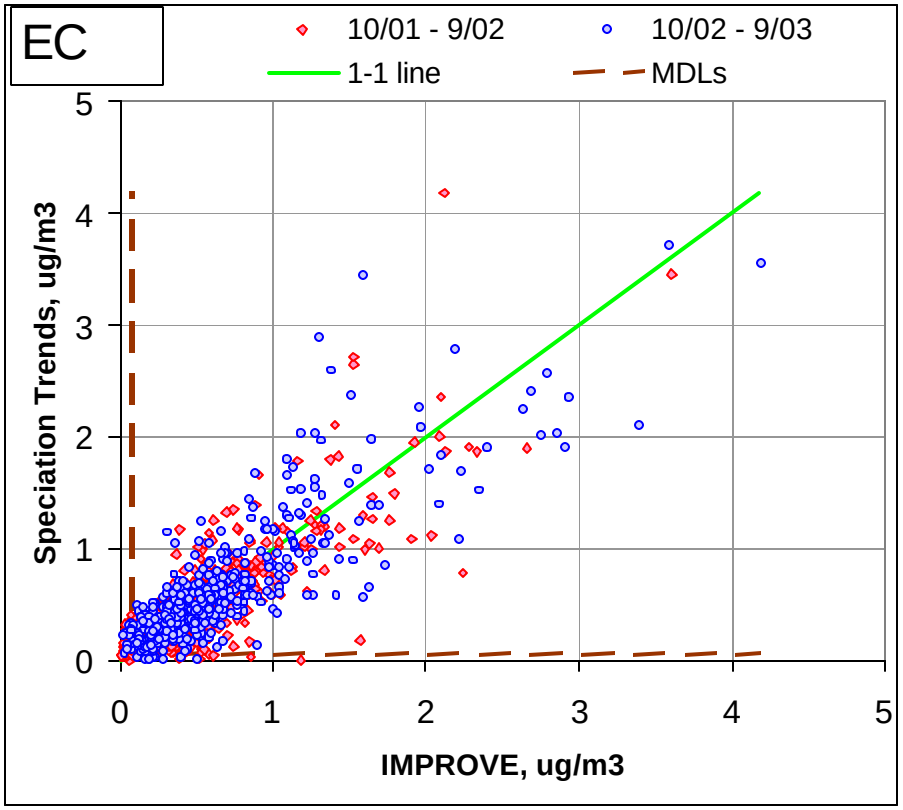

Organic Carbon

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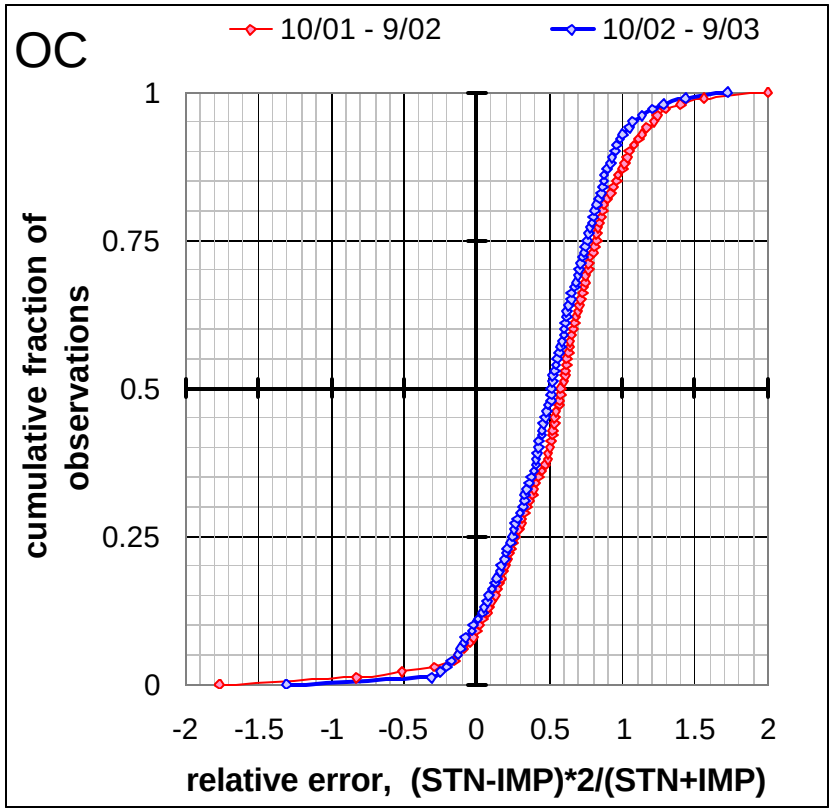

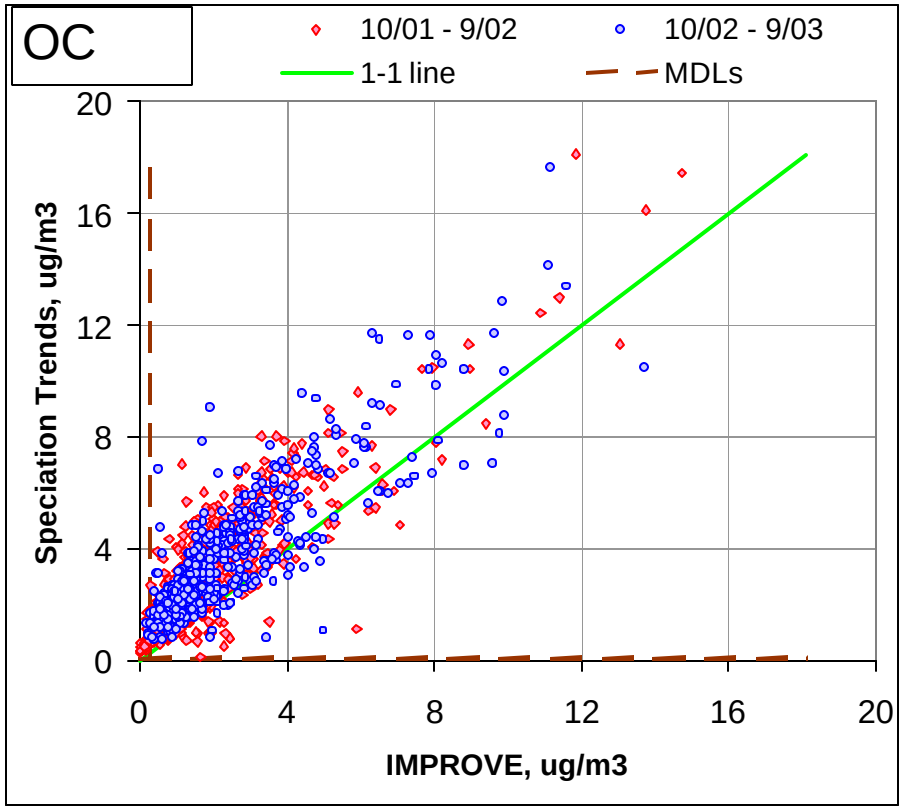

Soil Elements

Some differences; IMPROVE generally higher

- Different cutpoints may be the cause (to be investigated)

Calcium

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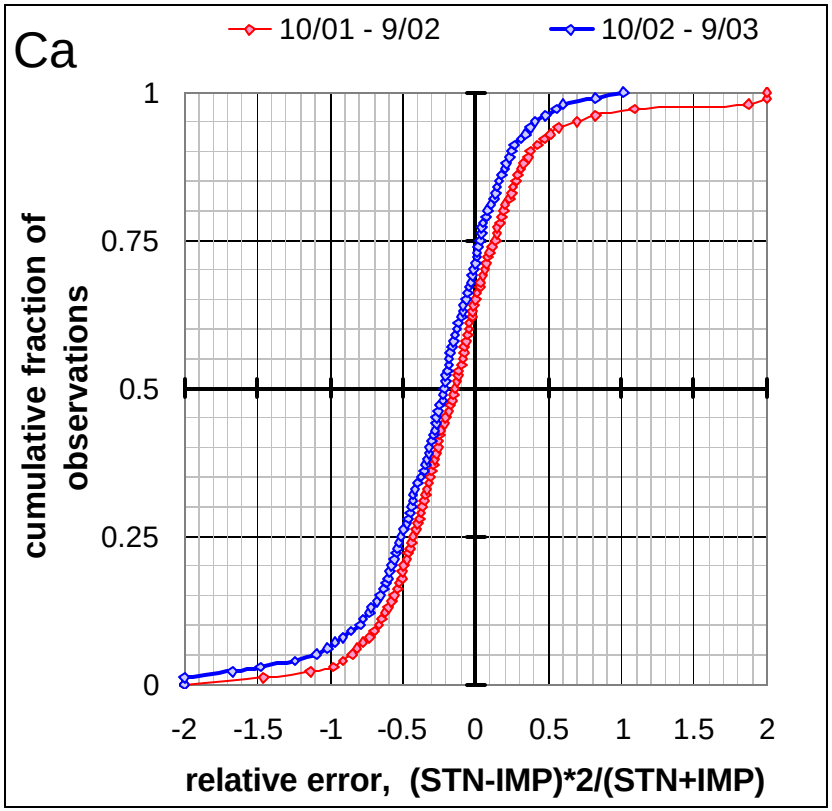
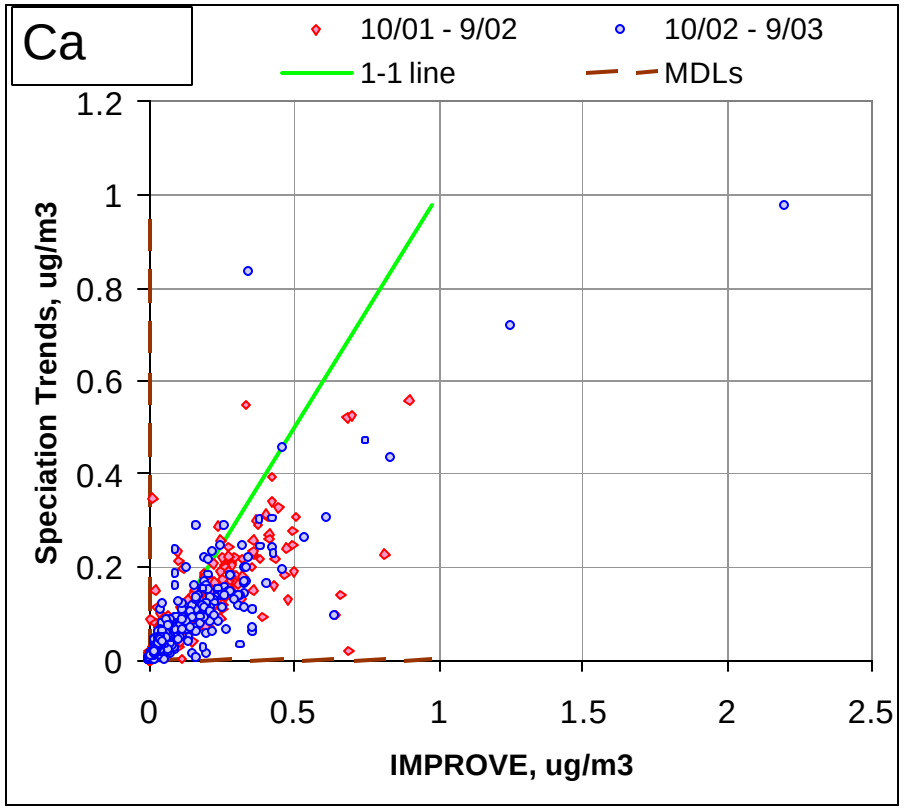
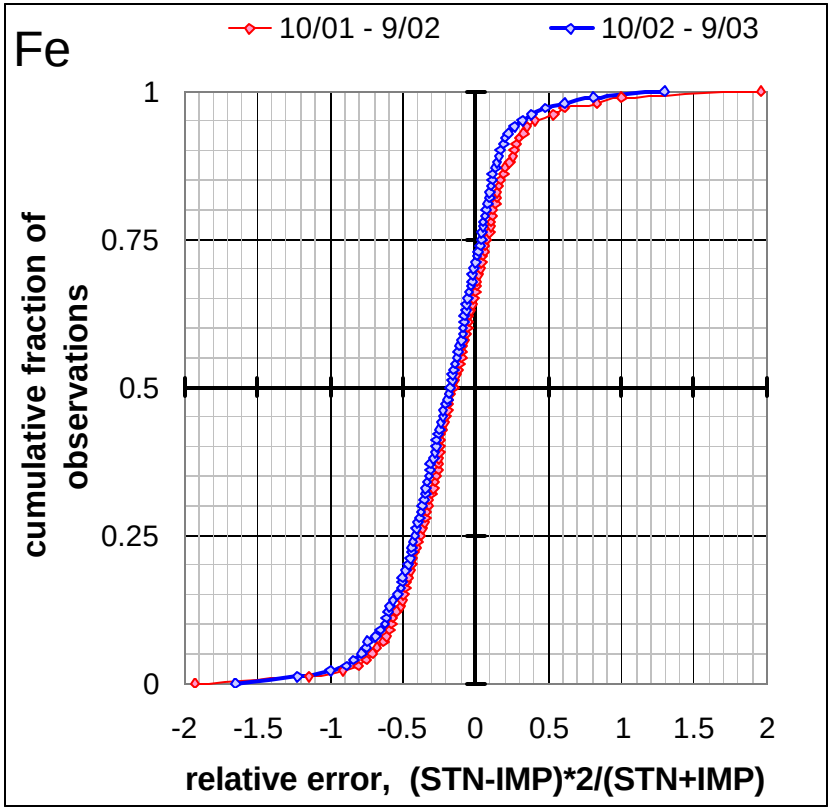
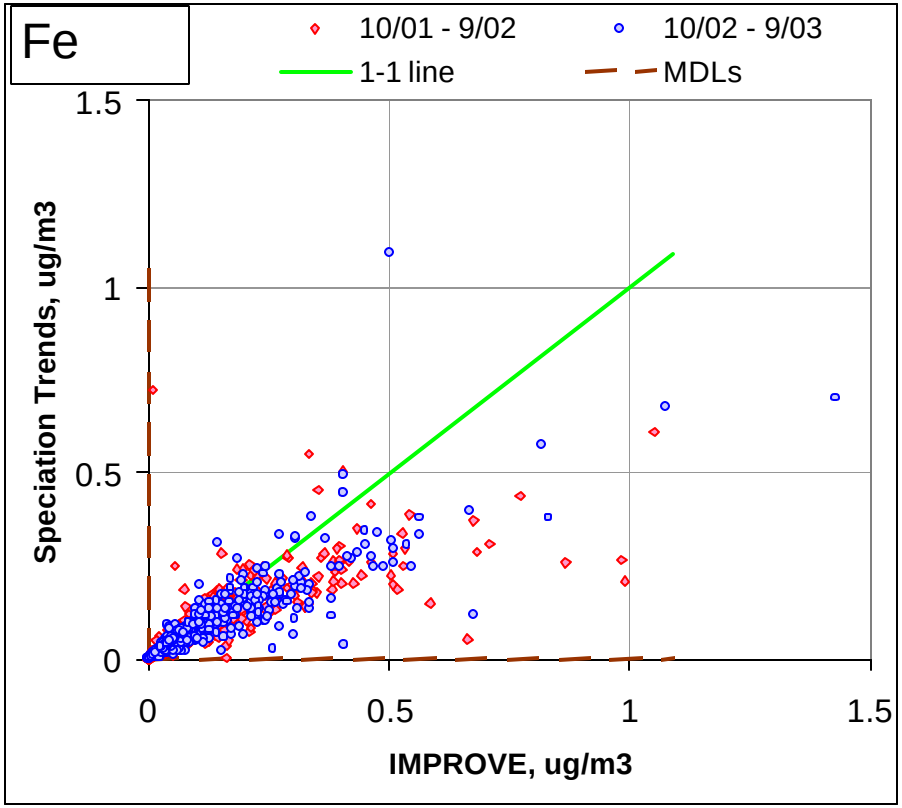




Iron


Fe
10/01 - 9/02
10/02 - 9/03
cumulative fraction of observations
1
0.75
0.5
0.25
0
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
relative error, (STN-IMP)*2/(STN+IMP)


Fe
10/01 - 9/02
10/02 - 9/03
1-1 line
MDLs
Speciation Trends, ug/m3
1.5
1
0.5
0
0
0.5
1
1.5
IMPROVE, ug/m3

Silicon

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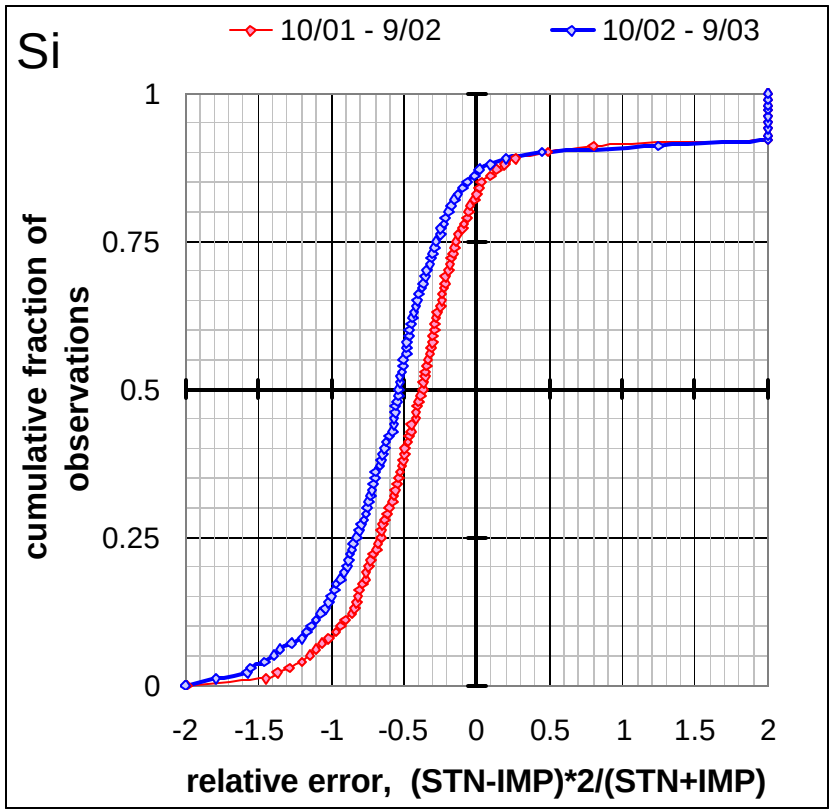

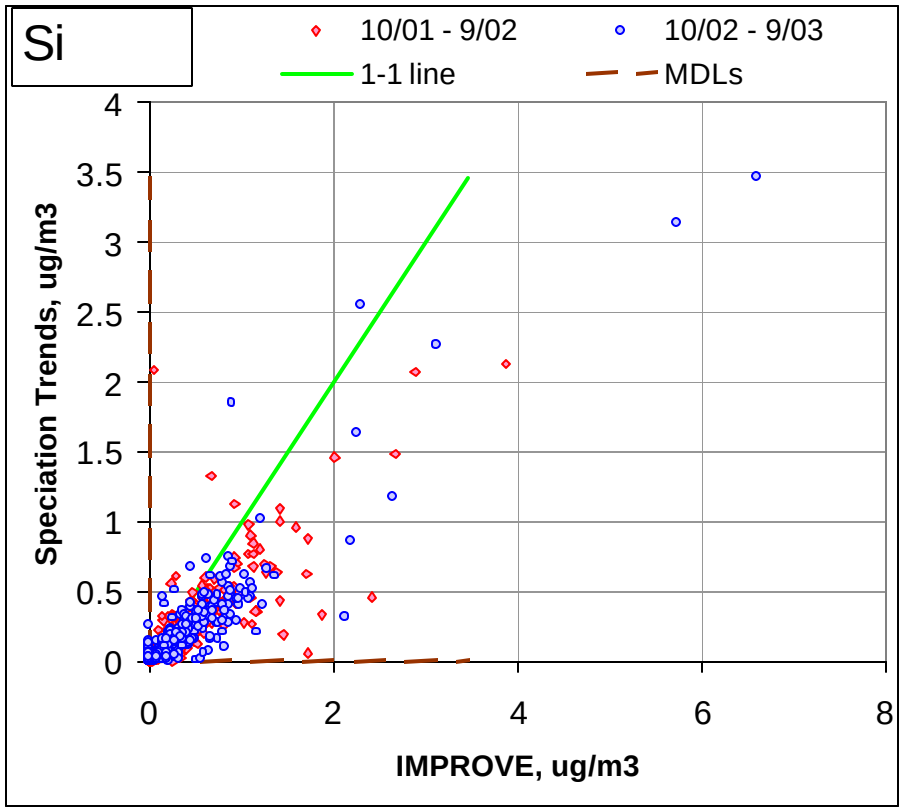

Silicon: Arizona Sites Highlighted

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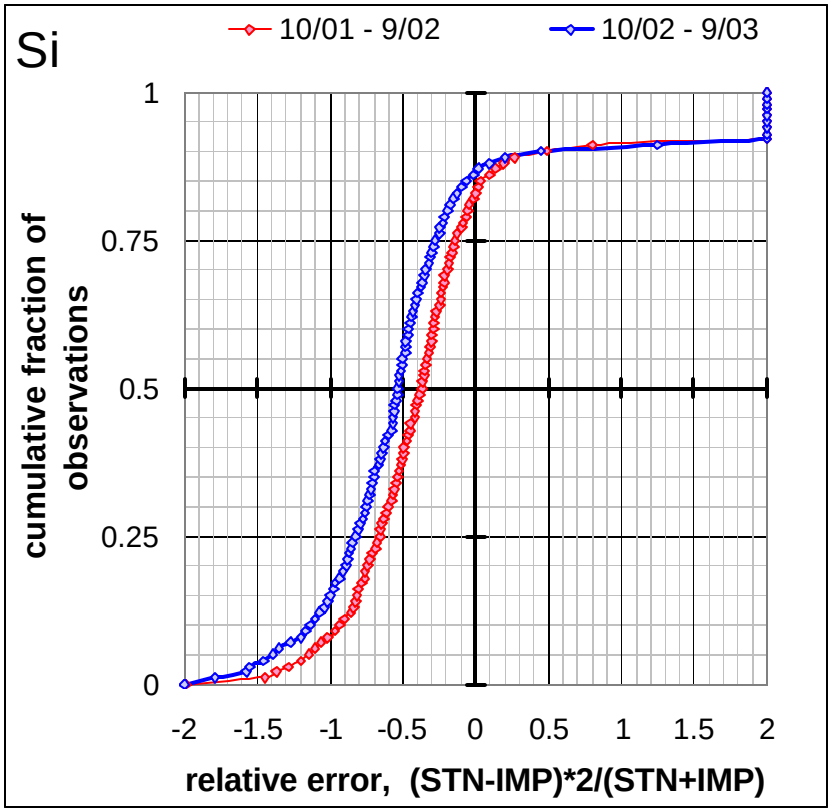

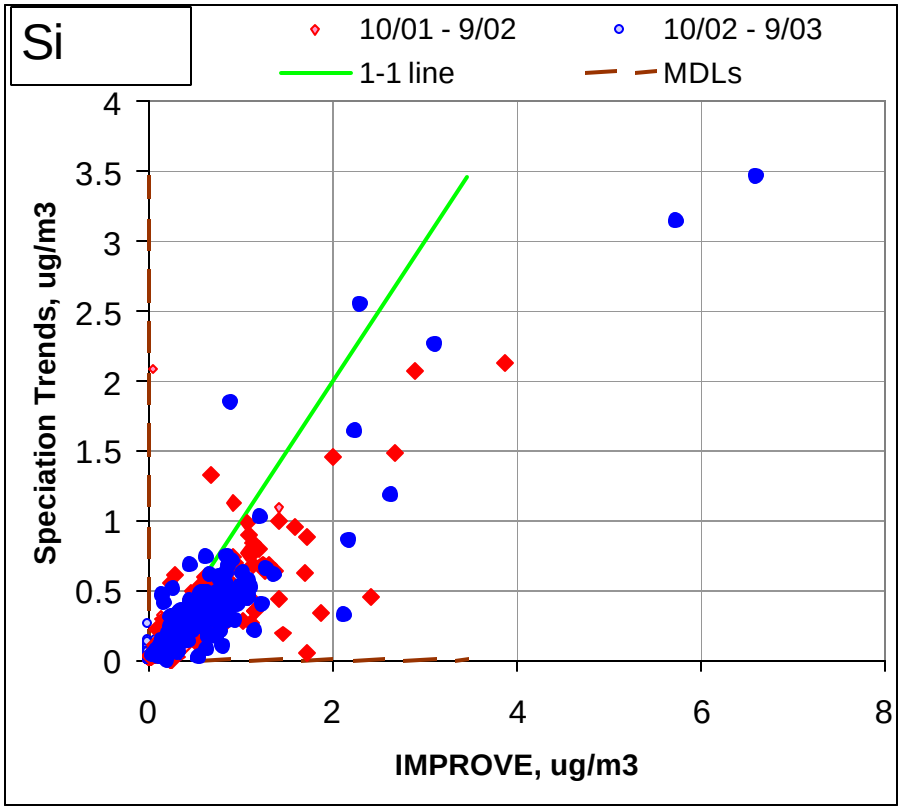

Silicon at Phoenix: Large Deviations are Episodic

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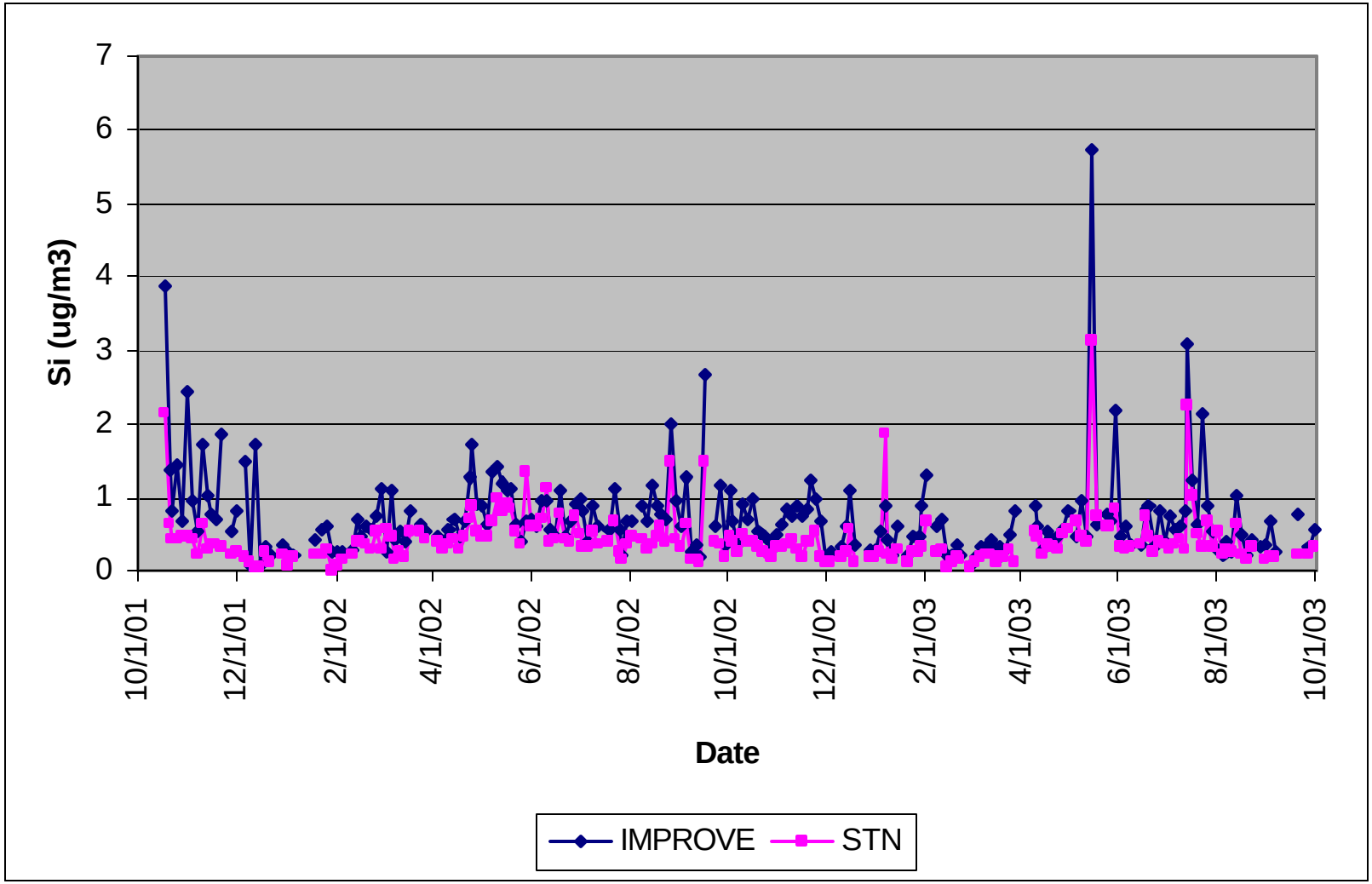

For Some Elements Many Measurements are Near their MDL

Data can be noisy near the MDL

- Comparison behavior can be masked by noise when relative errors are high
- Screening out low concentrations can help

Chromium

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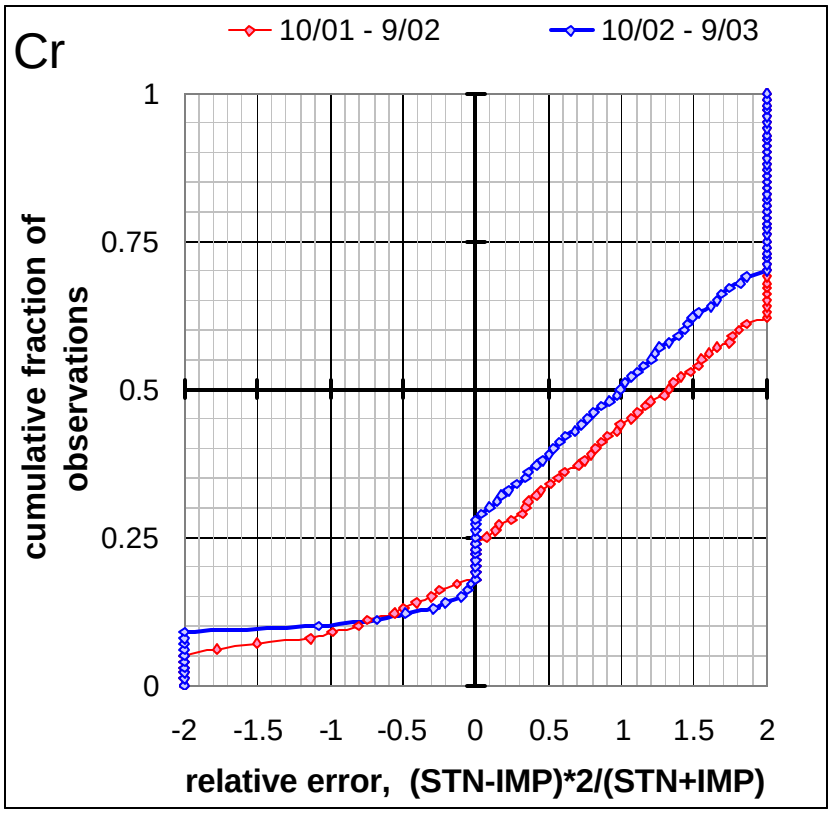

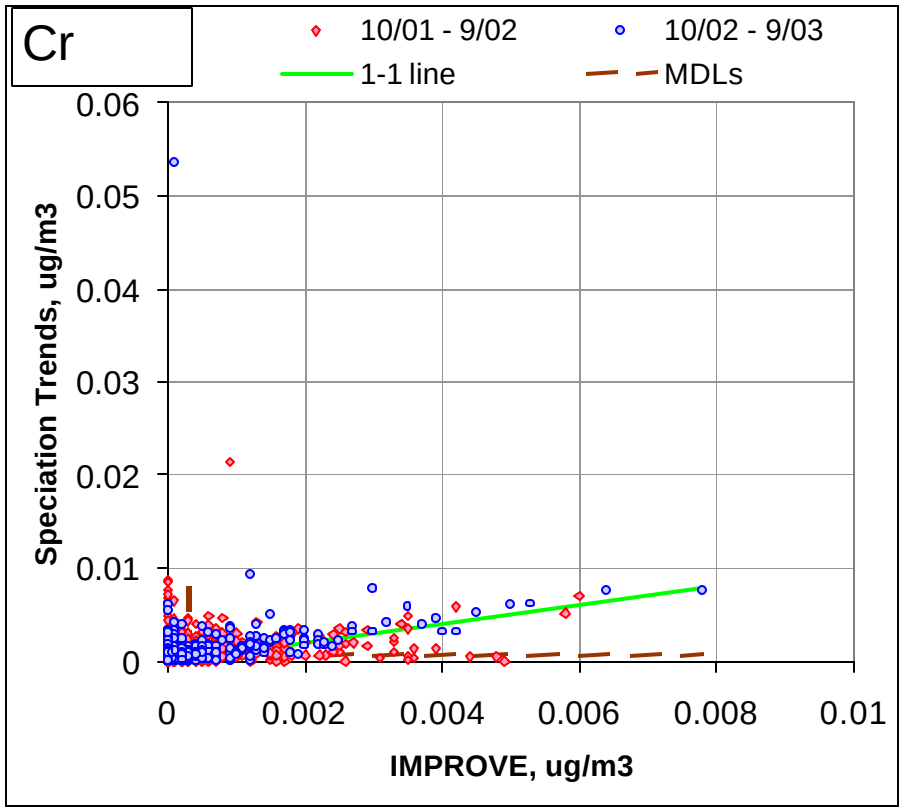

Chromium: >3 x MDL only

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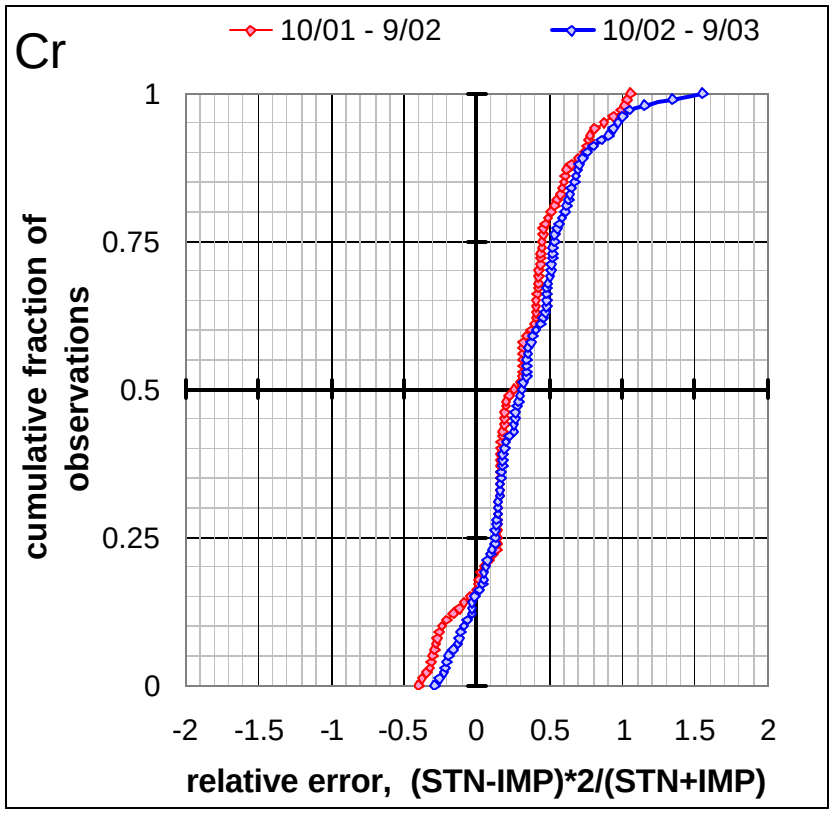

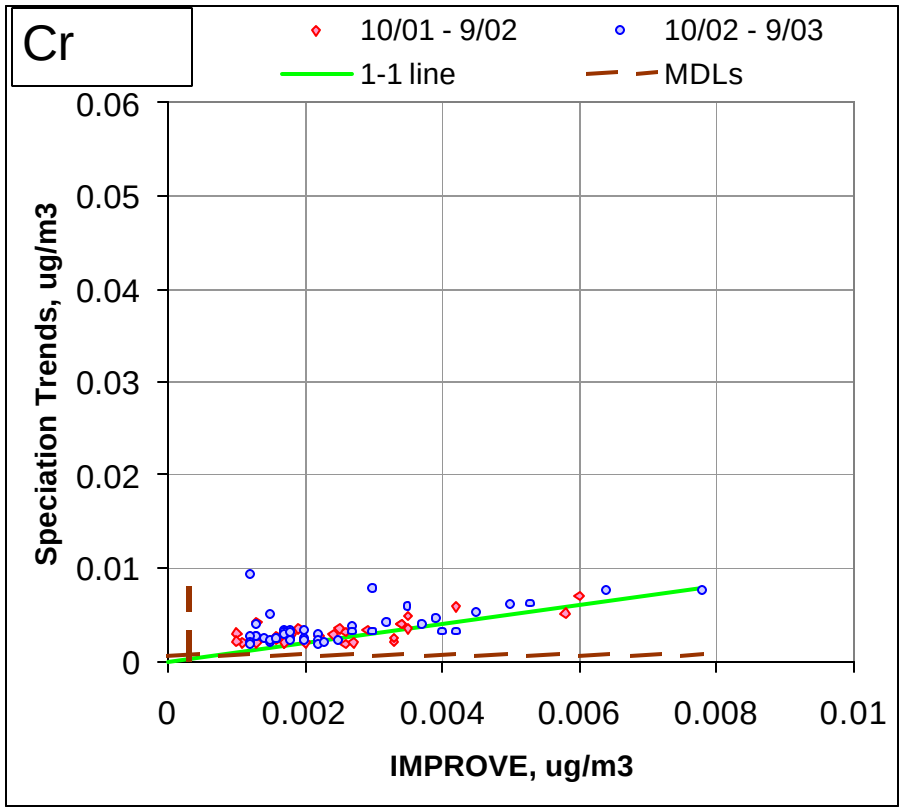

Manganese

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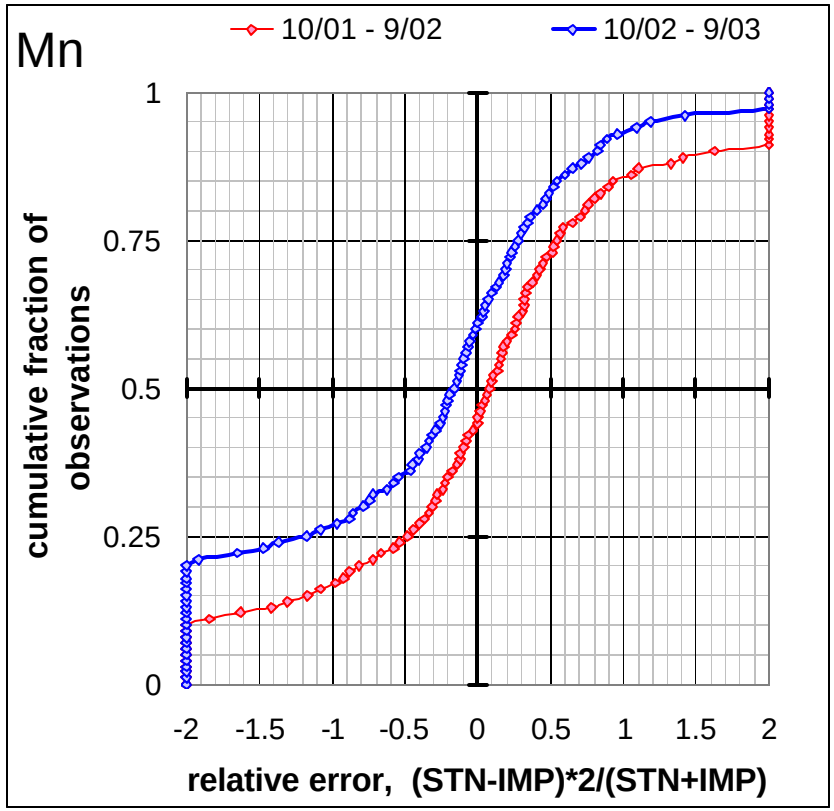
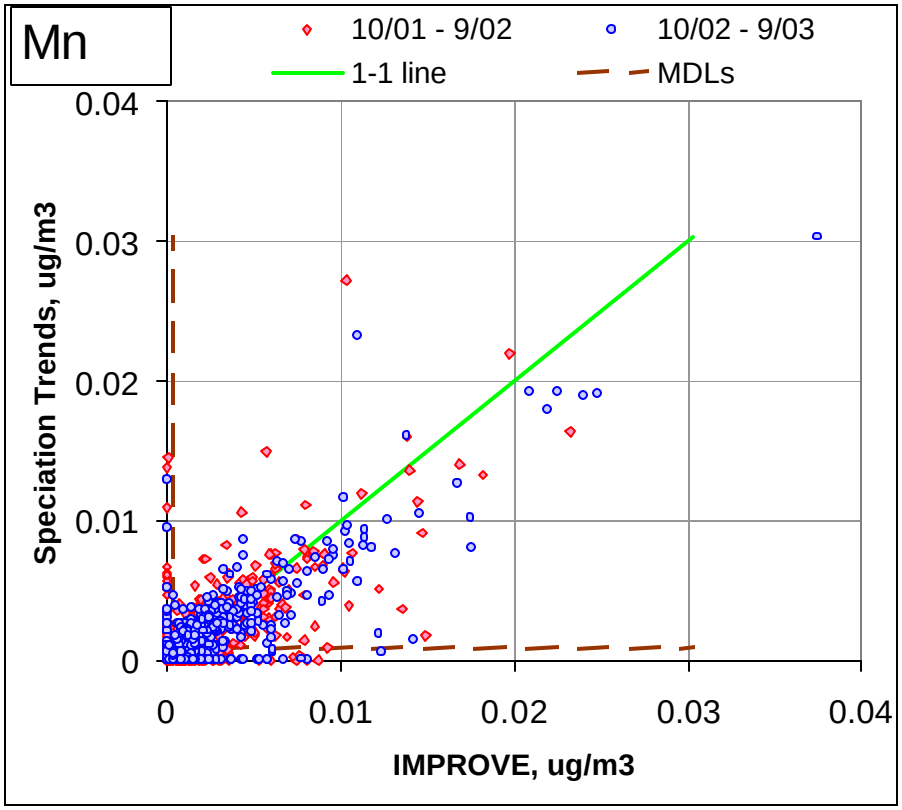
University of California, Davis





Manganese: >3 x MDL only

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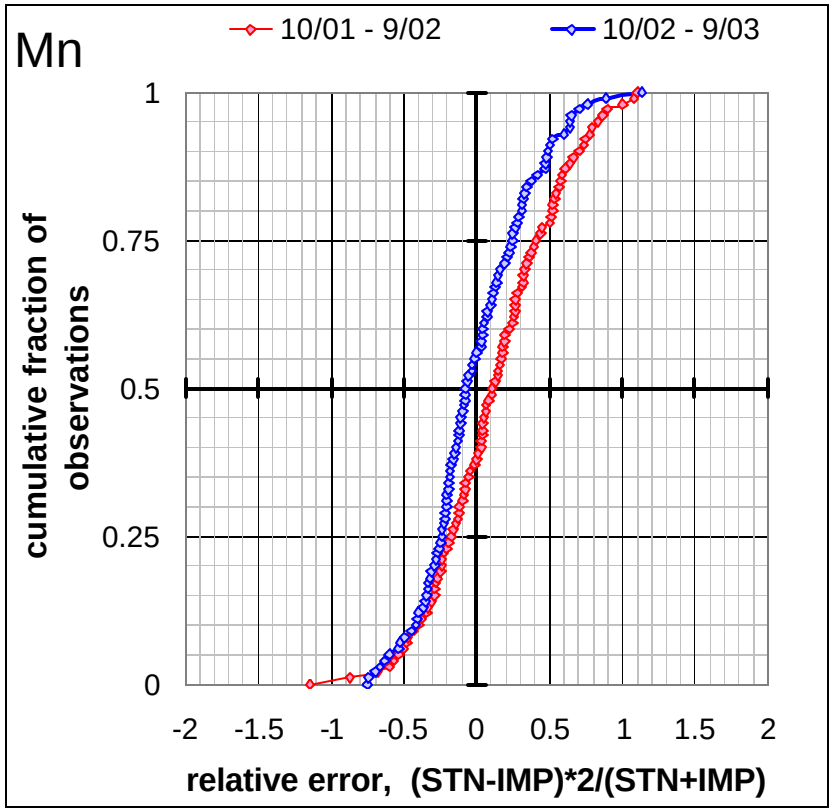

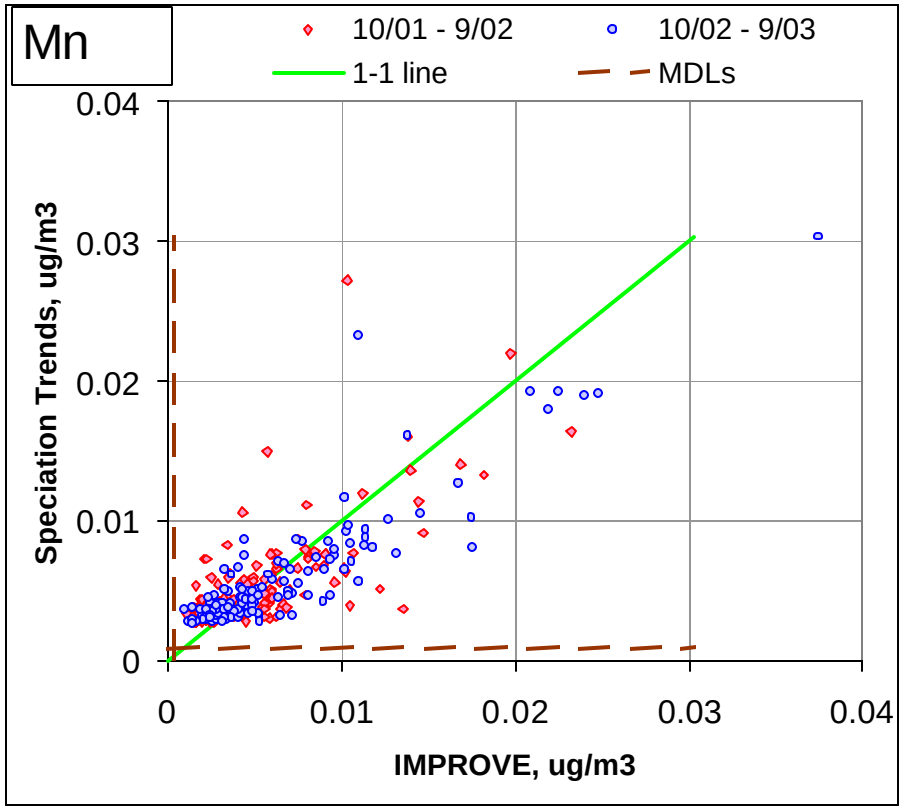

Selenium

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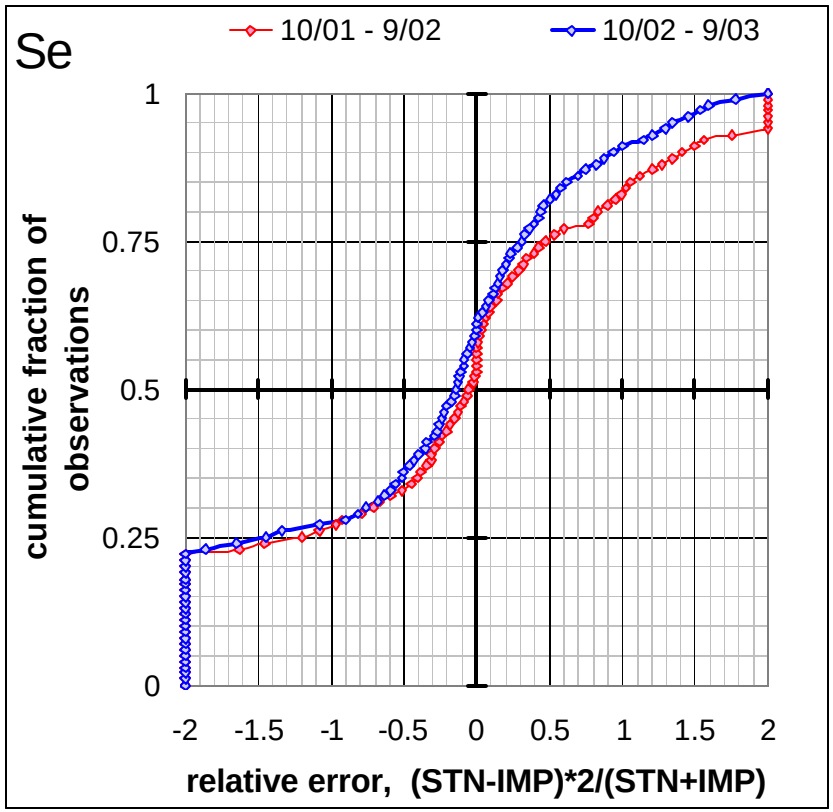

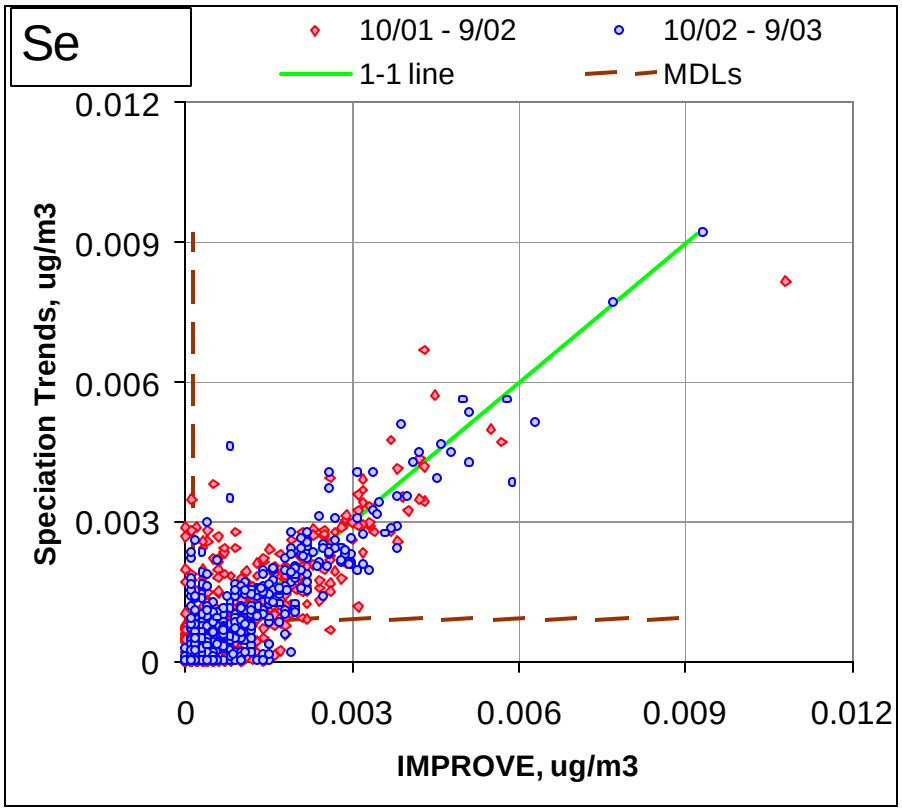

Selenium: >3 x MDL only

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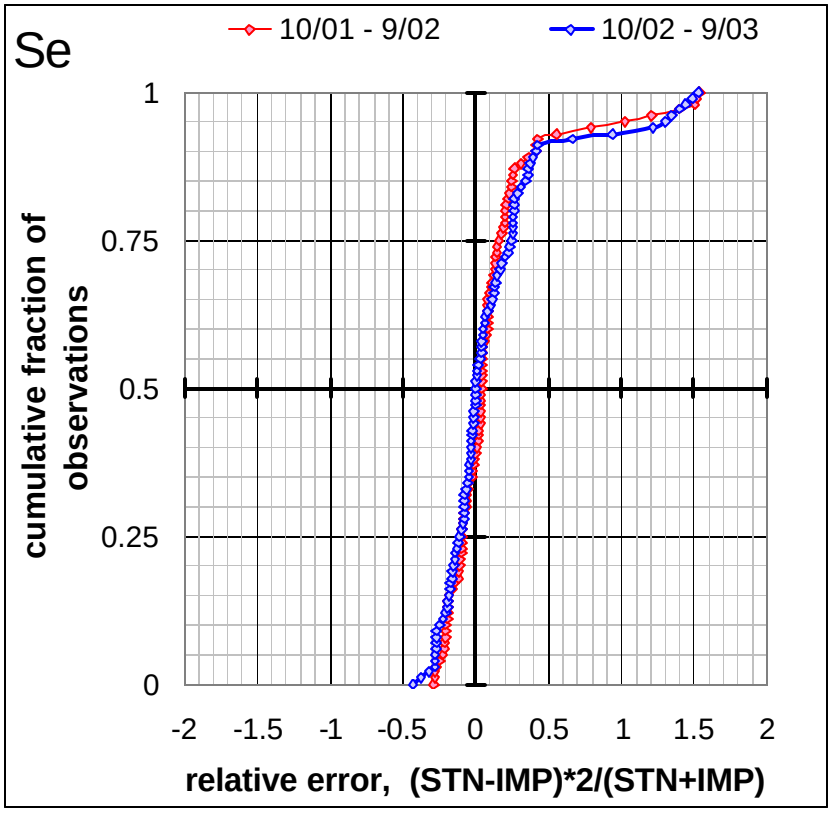

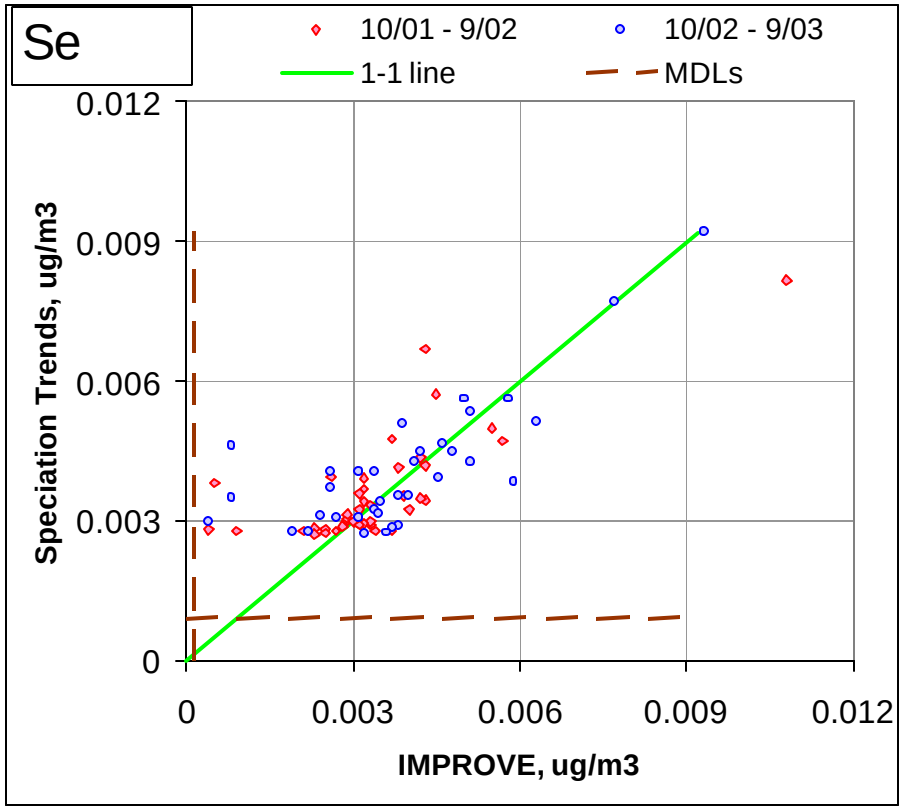

For the Future

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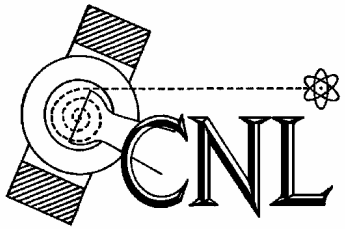
- Develop understanding of differences in measurements (e.g., soil elements)
- Apply further statistical techniques
  - Performance versus expectations
  - Means, medians, standard deviations
- Explore Year 1-to-Year 2 differences
- Add data from current sites and from urban sites established in 2004



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IMPROVE vs. STN XRF COMPARISON

XRF Systems

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STN (RTI)

- Anode X-ray tube
  - High flux rhodium anode X-ray tube
  - Five excitation conditions
- Lithium-drifted silicon detector
- Vacuum system

IMPROVE

- Anode X-ray tube
  - High flux Copper and Molybdenum anode X-ray tubes
- Lithium-drifted silicon detector
- In air and He environment systems

RTI Round Robin Filters

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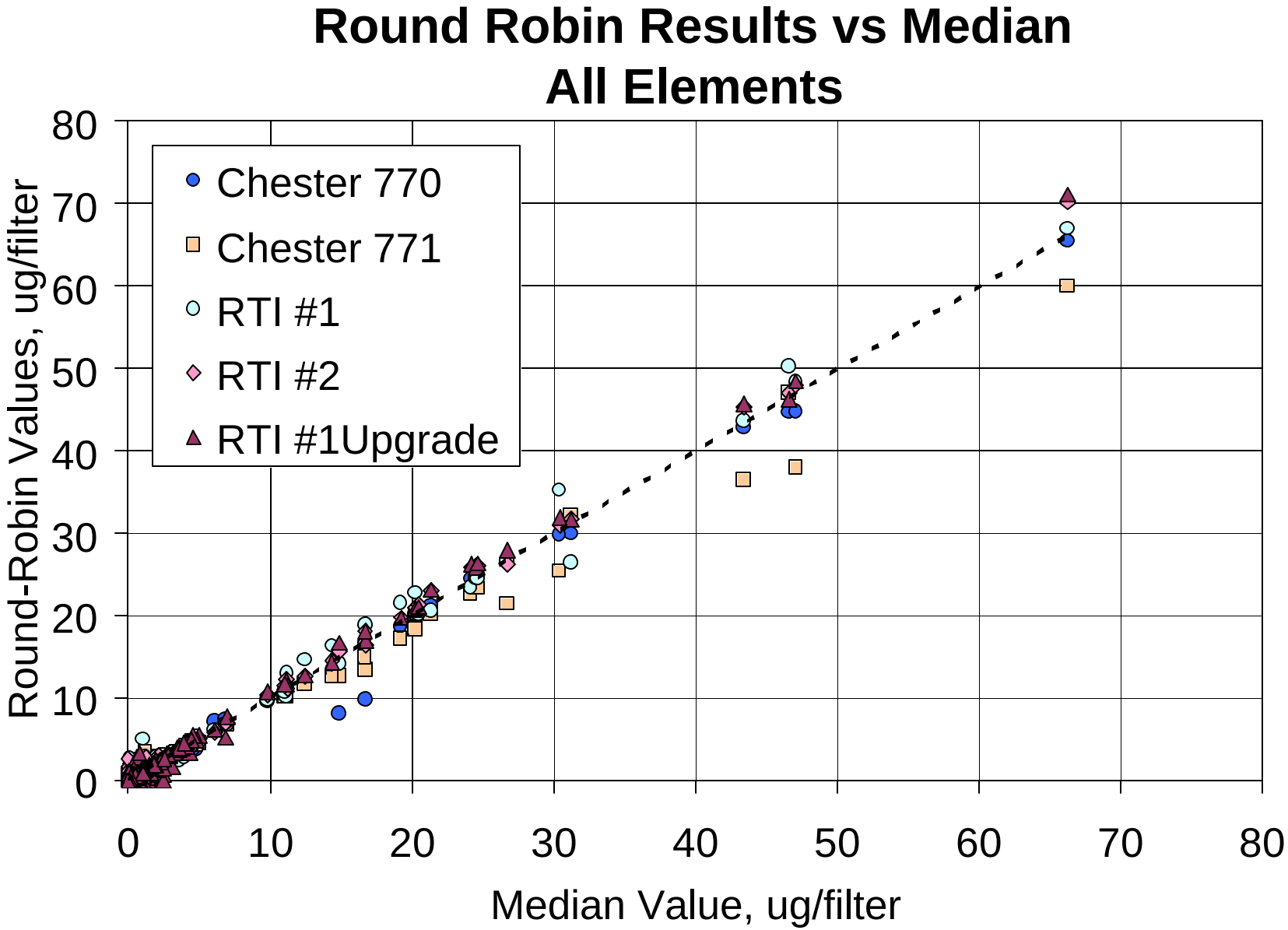
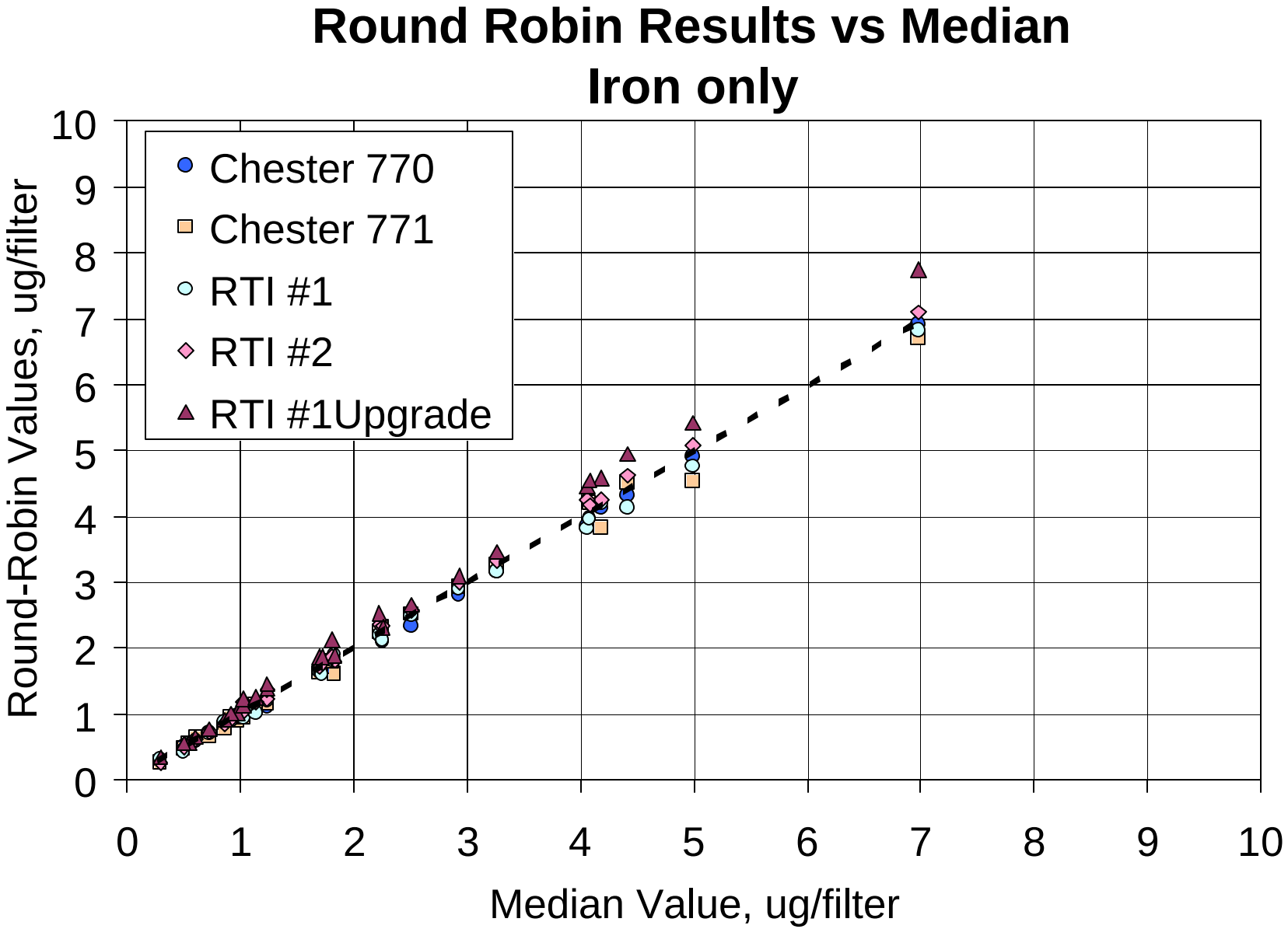
- Over 6 months old but less than 1 year
- Range of elements above analytical uncertainties
- Range of concentrations
- No data validity flags or codes
- In good condition, visually


Round Robin Results vs Median
All Elements
Chester 770
Chester 771
RTI #1
RTI #2
RTI #1Upgrade
Round-Robin Values, ug/filter
Median Value, ug/filter
0
10
20
30
40
50
60
70
80


Round Robin Results vs Median
Iron only
Chester 770
Chester 771
RTI #1
RTI #2
RTI #1Upgrade
Round-Robin Values, ug/filter
Median Value, ug/filter
0
1
2
3
4
5
6
7
8
9
10

IMPROVE analysis of the STN round robin filters

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- Adaptation of STN 47mm Teflon filters for IMPROVE XRF analysis
- Analysis of 47mm Teflon laboratory blanks
- Analysis of Round Robin filters

Slide Mounts

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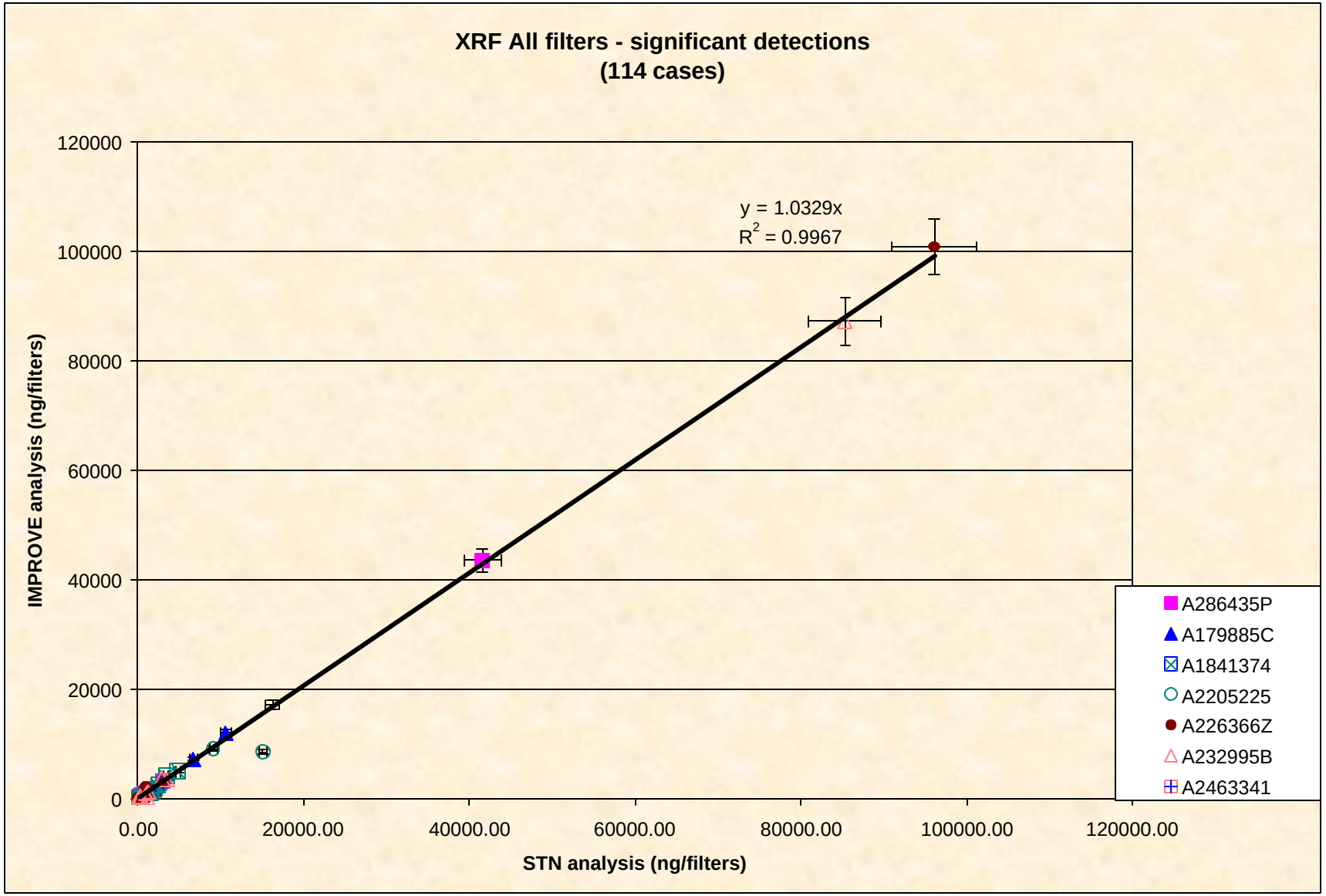
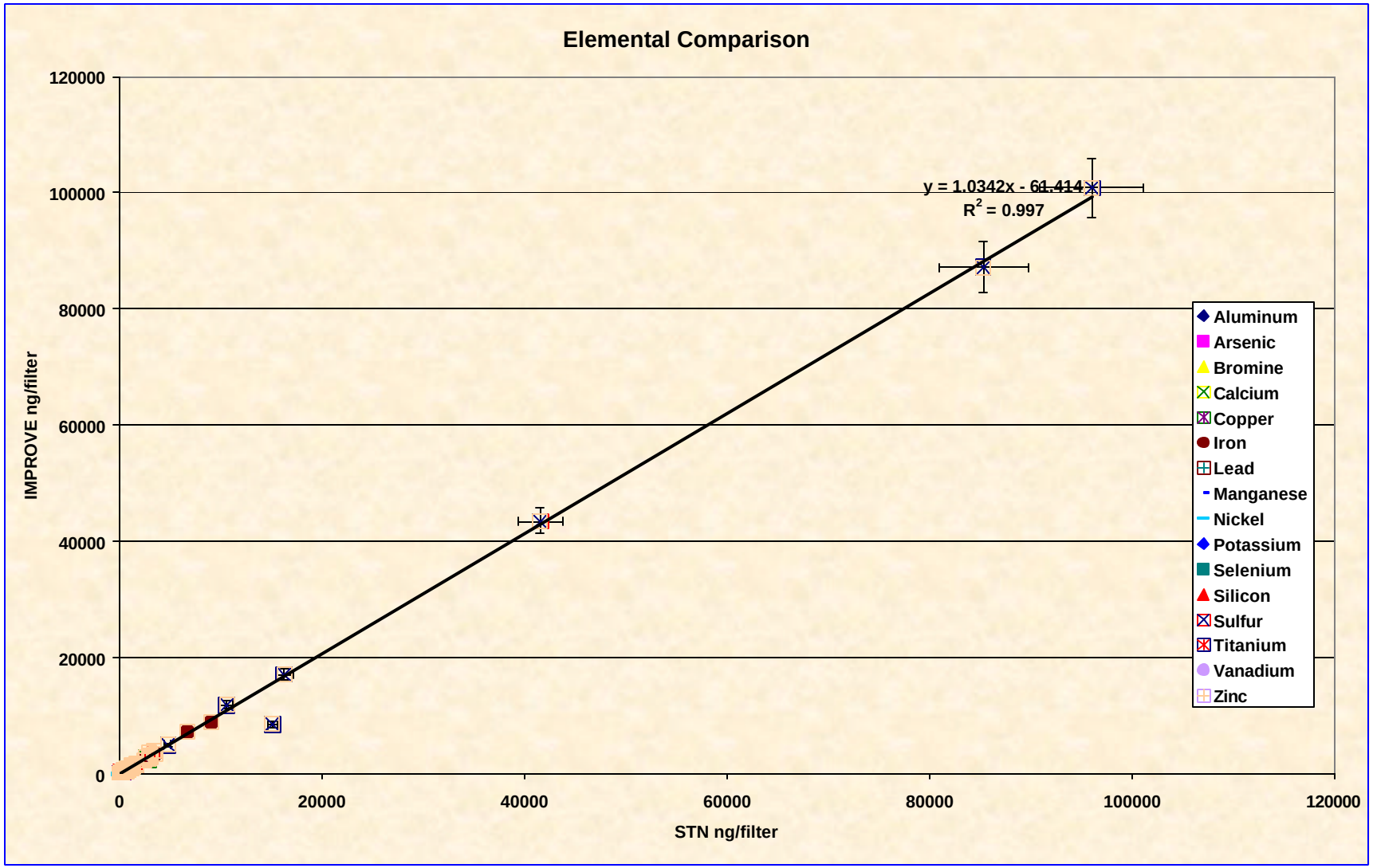
STN (47mm) IMPROVE (25mm)

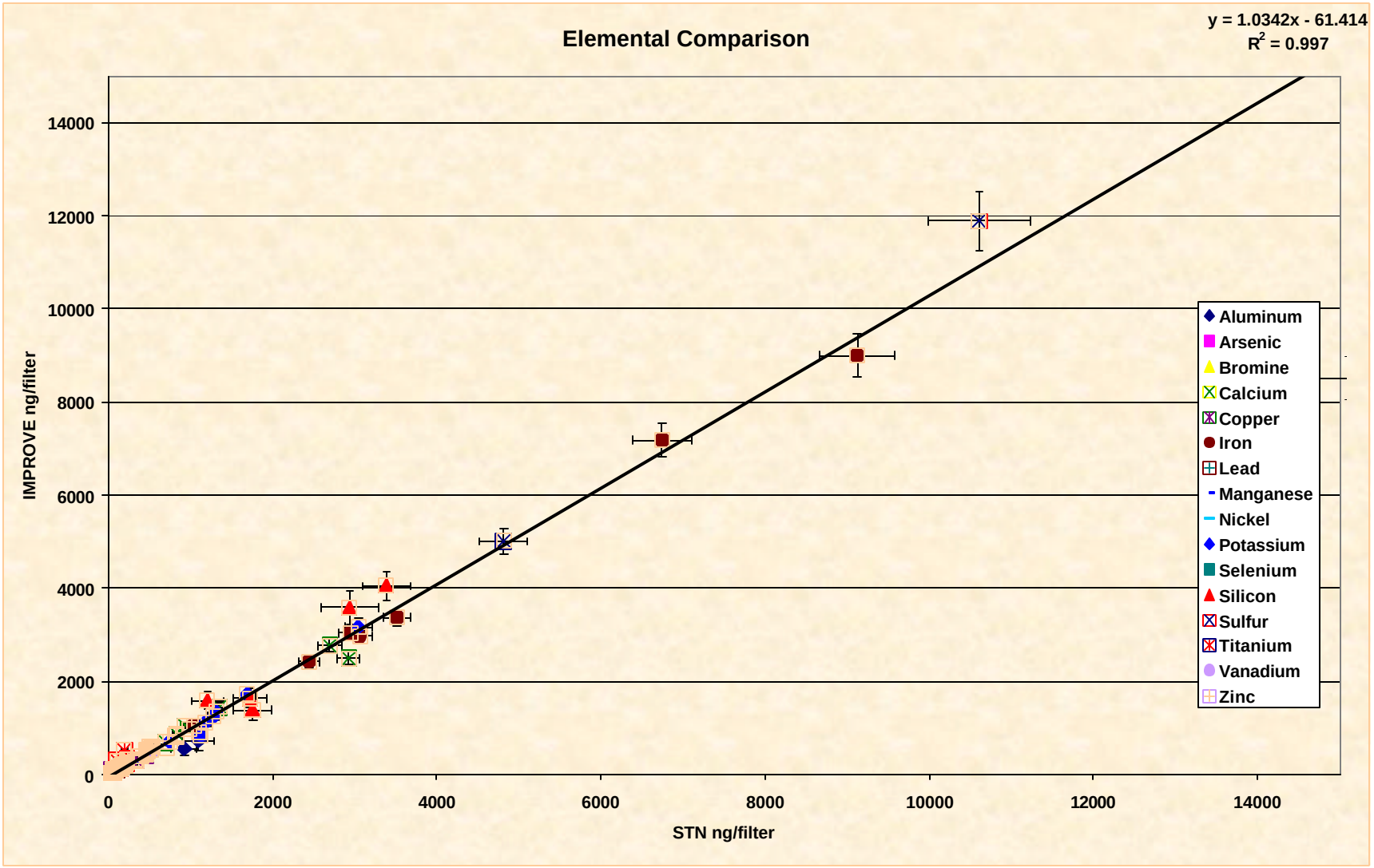
XRF analysis – by filter ID, Significant detection of all elements



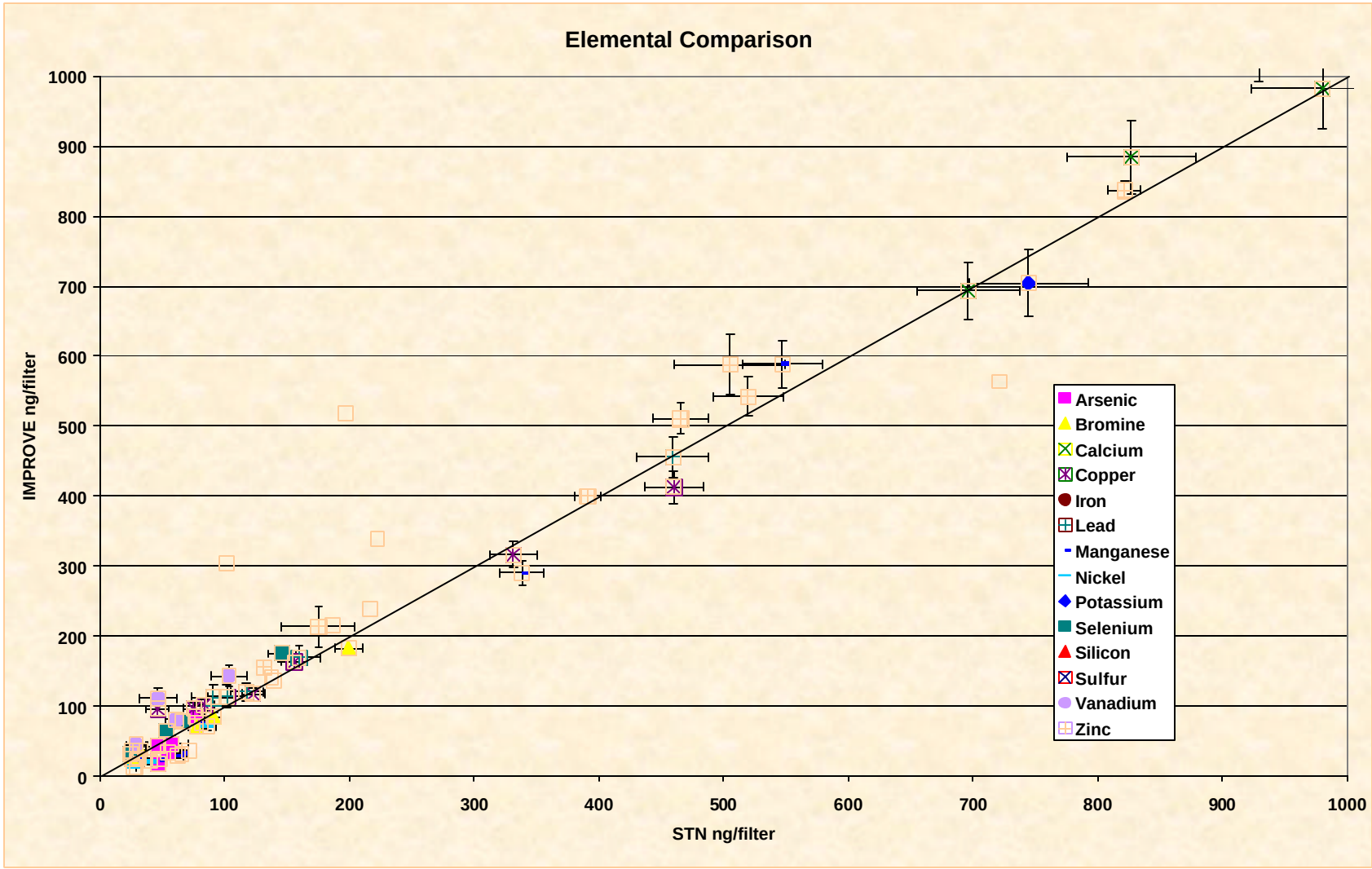
XRF analysis – by element, Significant detection – full scale



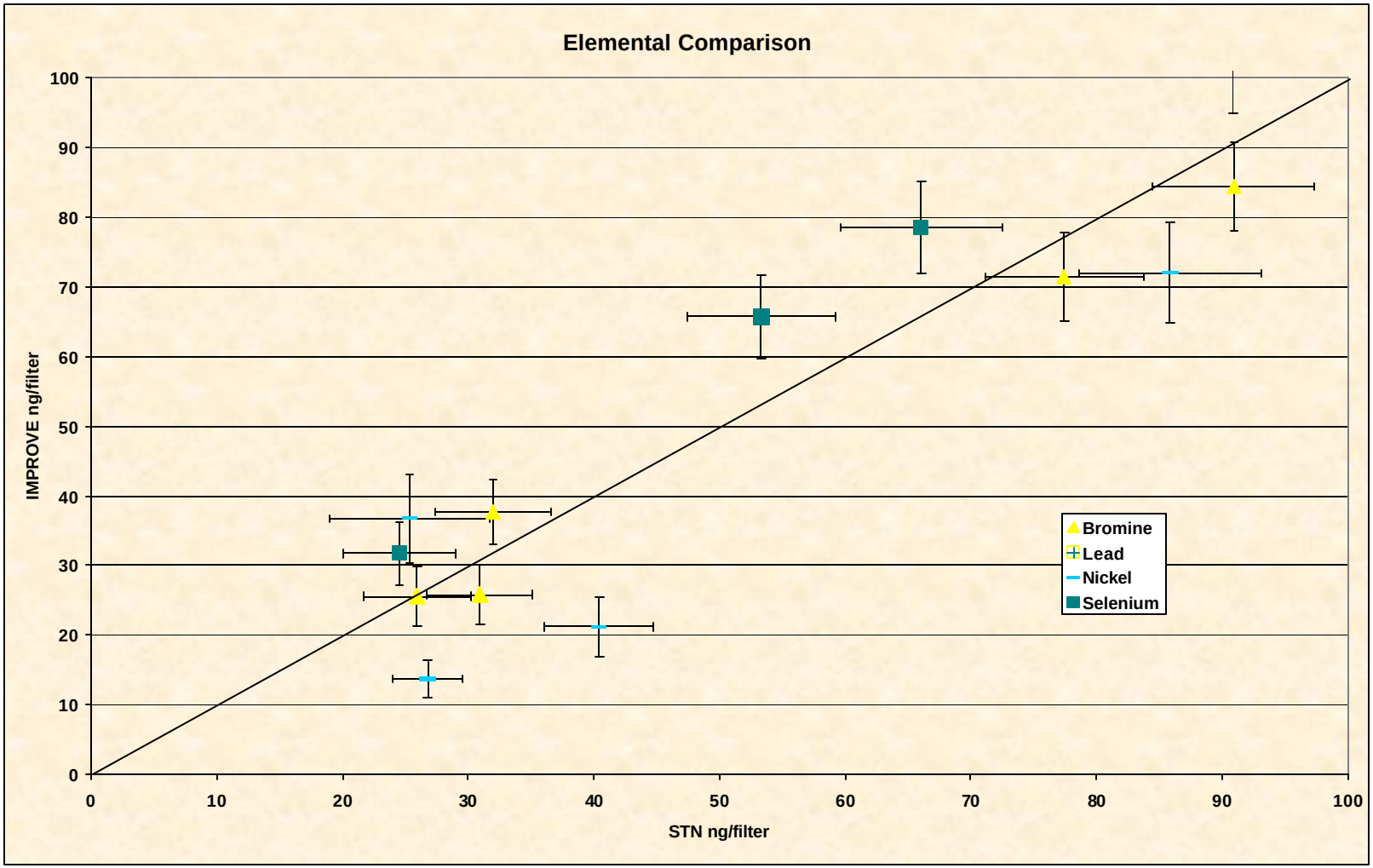
XRF analysis – by element, Significant detection – soil scale



XRF analysis – by element, Significant detection – tracer scale



XRF analysis – by element, near detection limits



Conclusions

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- STN samples are within specifications of IMPROVE XRF analysis system
- General good agreement between STN and IMPROVE XRF analysis. Of the significant detection:
  - 16 Elements reported very good precision

Next Steps

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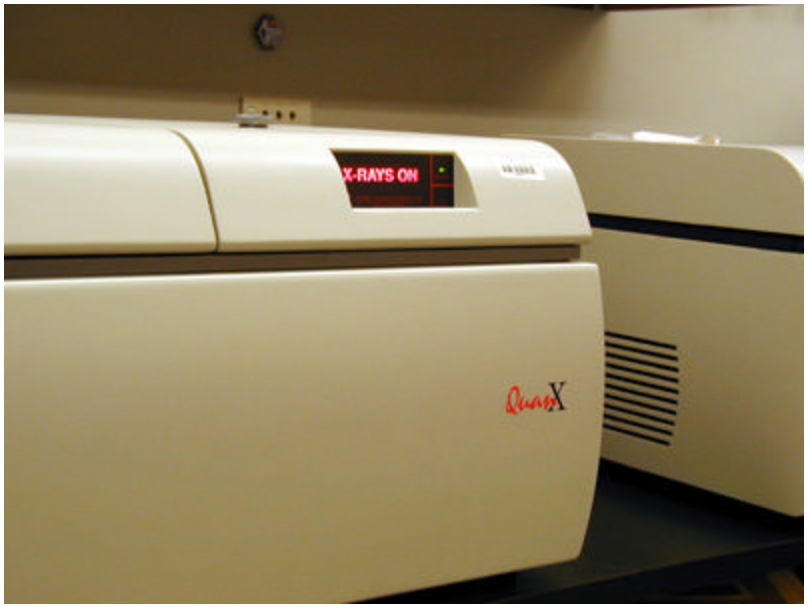
- Analysis of Micromatter standards
- Analysis of NIST samples
- Reanalysis of same filters by RTI
- Developing protocols for round robin tests between IMPROVE and STN networks