

IMPROVE Aerosol Measurements: Overview and Updates

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National Ambient Air Monitoring Conference

St. Louis, MO

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IMPROVE Network

- Interagency **M**onitoring of **P**rotected **V**isual **E**nvironments
- Cooperative effort started in 1988 with ~30 sites
 - Expanded in 2000 to >170 sites
- Designed to monitor visibility-reducing particulate matter (PM) pollution in Class I areas
- Sponsors contribute ~\$37k/year/site for
 - Sampler loan and repairs/upgrades, filter samples, lab analyses, data validation and delivery

Current Sponsors

- U.S. Environmental Protection Agency
- U.S. National Park Service
- U.S. Forest Service
- U.S. Fish & Wildlife Service
- Various State Governments & Tribes
- Environment Canada
- South Korea Ministry of Environment

Most samplers are located in National Parks & other remote areas

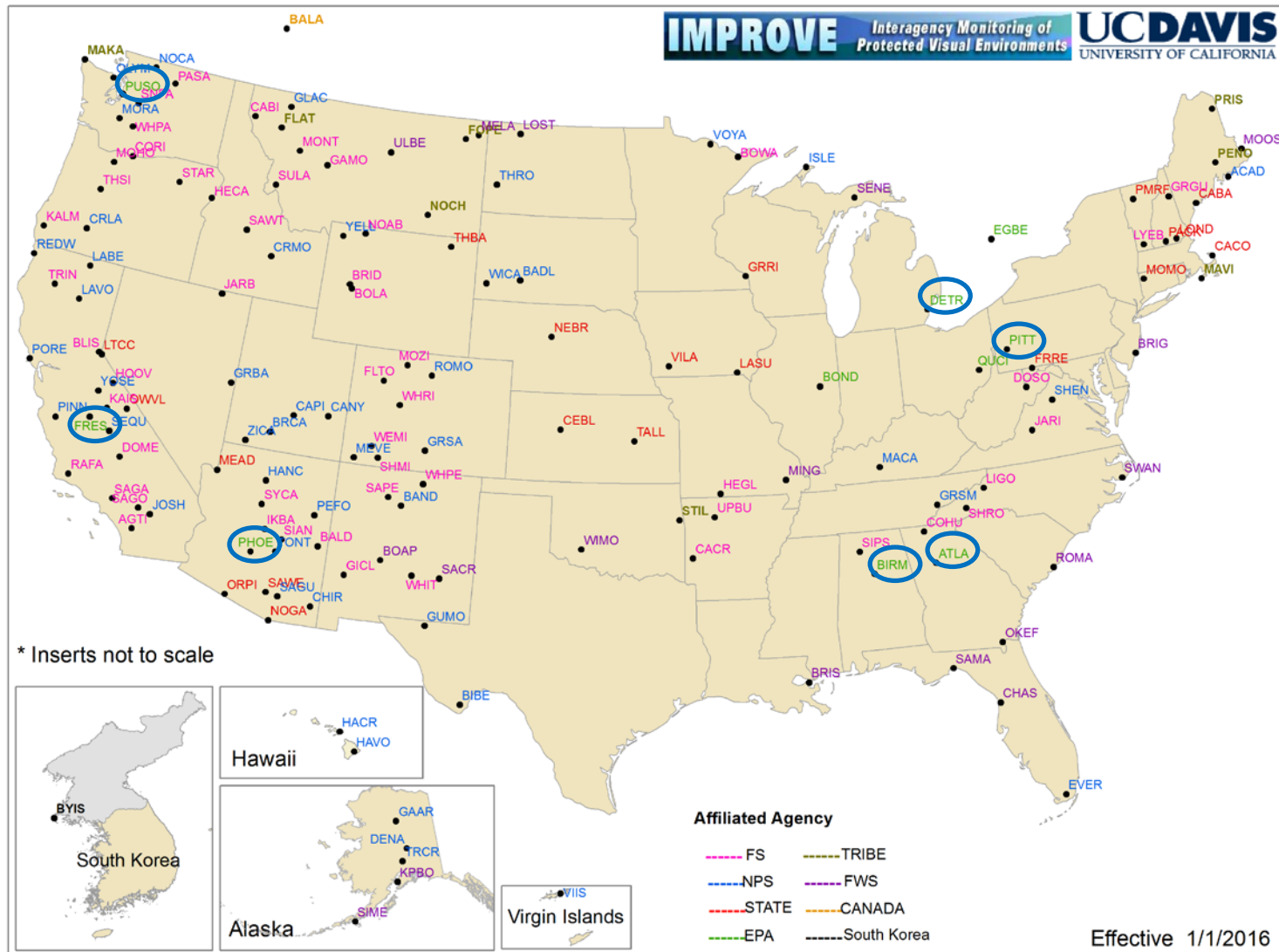


A few samplers are collocated with urban network samplers.



The IMPROVE network maintains 156 sites.

Sites collocated with CSN samplers circled in blue.



IMPROVE sampler

- Designed by UC-Davis for clean environments
 - High flow rate – 23 L/min
 - Small filter – 25 mm diameter concentrates the sample
- 4 samples collected every 3 days
 - PM_{2.5} Teflo[®] PTFE filter analyzed by gravimetry, XRF, and laser absorption by UCD
 - PM_{2.5} nylon filter analyzed by ion chromatography at RTI
 - PM_{2.5} quartz filter analyzed for carbon by DRI
 - PM₁₀ Teflo[®] PTFE filter analyzed by gravimetry by UCD

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Recent IMPROVE Sampler Enhancements

Joshua S. Grant, Christopher D. Wallis, Jose W. Mojica, Nicole P. Hyslop
Crocker Nuclear Laboratory, University of California, Davis



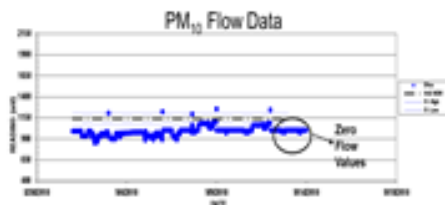
Since the 1970s, the IMPROVE Air Quality Group has collected and analyzed particulate matter. The group routinely monitors visibility-impacting pollution in Schedule I areas as part of EPA's Regional Haze Program and includes 150 national sampling sites, plus three international sites in Canada and South Korea.

Flow Control Valve Reconfiguration and Critical Orifice Deployment

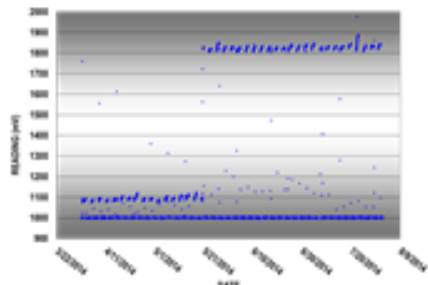
- Previously, noisy transducer flow data was difficult to differentiate flow from non-flow data
- Orifice area was previously determined empirically; with critical orifice the orifice area is known
- New flow calibration equation is less sensitive to changes in valve needle
- Obstructions in valve are easier to clear in new design



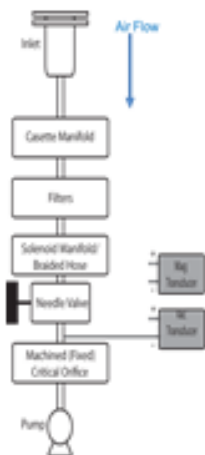
Modified CPC fitting and critical orifice installation tool



Messy transducer data from previous configuration showing flow values vs. zero flow values are hard to distinguish.



Transducer data from new configuration showing distinct flow values vs. zero flow values



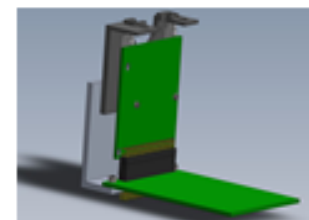
New configuration of flow control valve and flow path of PM10 Module

CFLASH Memory Card Reader Redesign

- Before redesign, yearly average lost data due to memory card writing errors was 4.3%
- New design transmits data over PCB traces rather than ribbon
- After redesign, yearly average lost data due to memory cards is 1.9%



Previous ribbon CFLASH reader



New ribbonless CFLASH reader design

Version III Controller Development

- New digital sensors and pressure transducers are less susceptible to analog noise
- Open source Linux-based microcontroller (Beaglebone Black) for keeping software up to date and easily developed
- Communication through Controller Area Network (CAN), Serial Peripheral Interface (SPI), Universal Serial Bus (USB), I2C, and RJ-45
- Hardware supports networked data transfer for real-time instrument monitoring and remote control
- Modern interface enables user instructions and troubleshooting guidance with high definition images and video
- Modular card design will significantly reduce expensive shipping costs for replacement of specific components



Data Validation and Analysis

- UC-Davis performs data validation for entire network
- Review flow rates immediately upon data receipt
- Review data from different perspectives (space, time) to identify contamination, interferences, patterns, and trends

Data Visualization Web Apps

Flow Rates

Site
HANC1

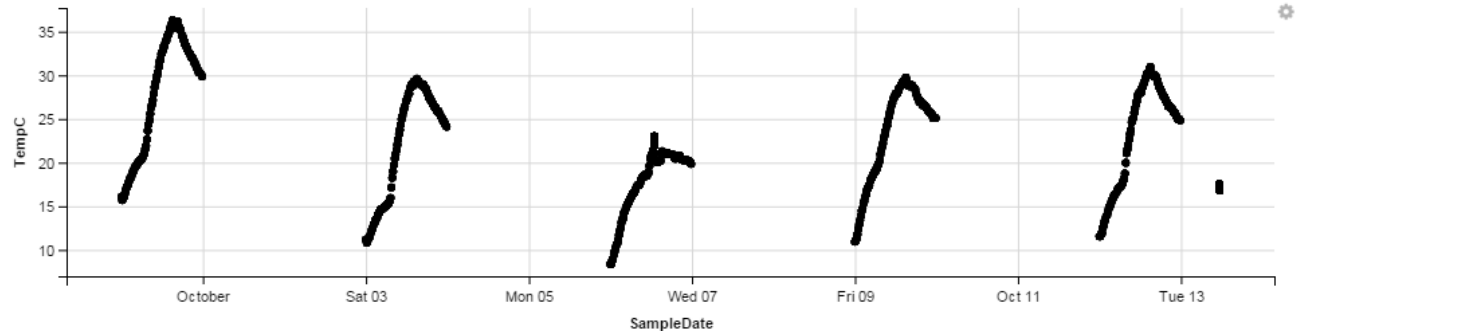
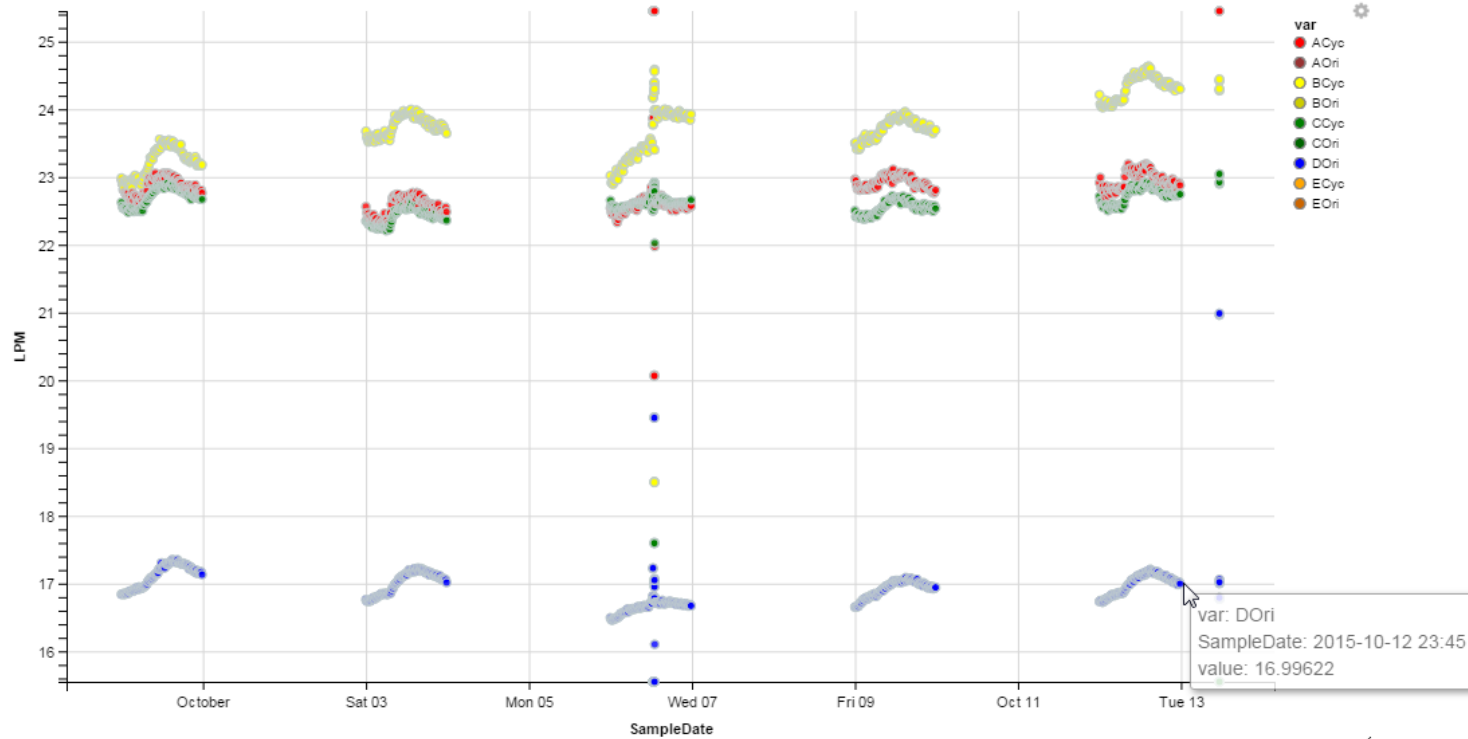
Date Range
2015-09-30 to 2015-10-28

Flow Units
 Voltage (Counts/100)
 Flow Rate (LPM)
 Exclude non-sample days

Y-axis Min/Max
0 16 25 100

Interactive Plot Panel Plots Data Table Combined Plot

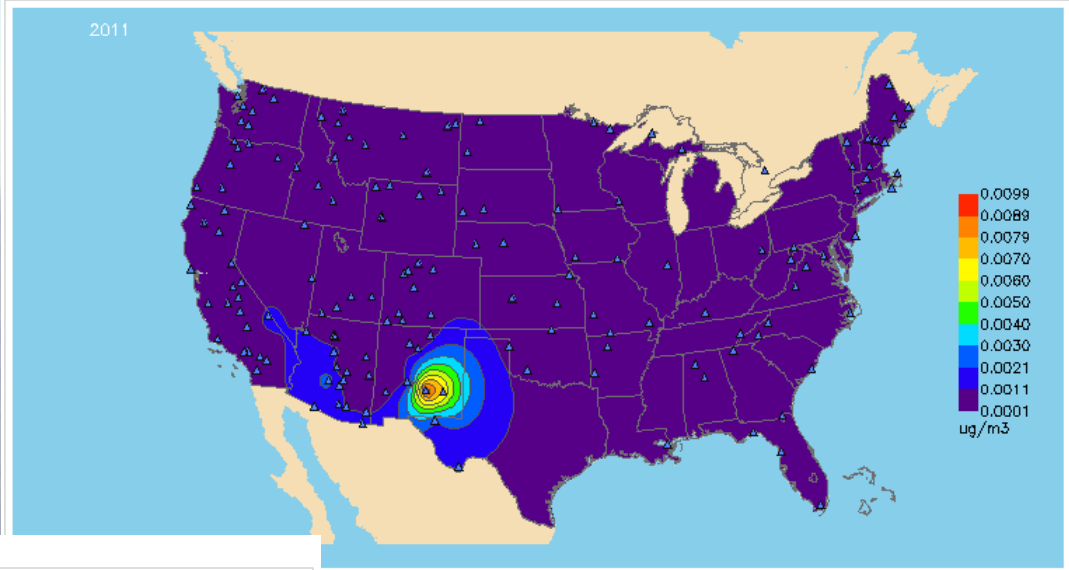
ACyc AOri BCyc BOri CCyc COri DOri ECyc EOri



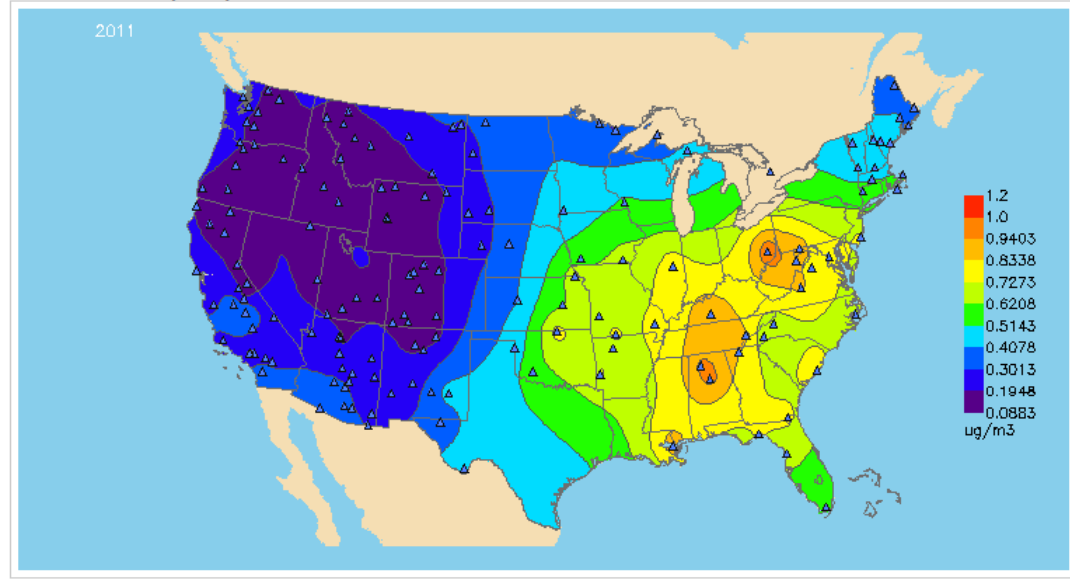
Spatial Context Important for Validation

- Contour maps of annual average $PM_{2.5}$ Sr (right) and S (below) concentrations

2011 - Strontium (Fine)

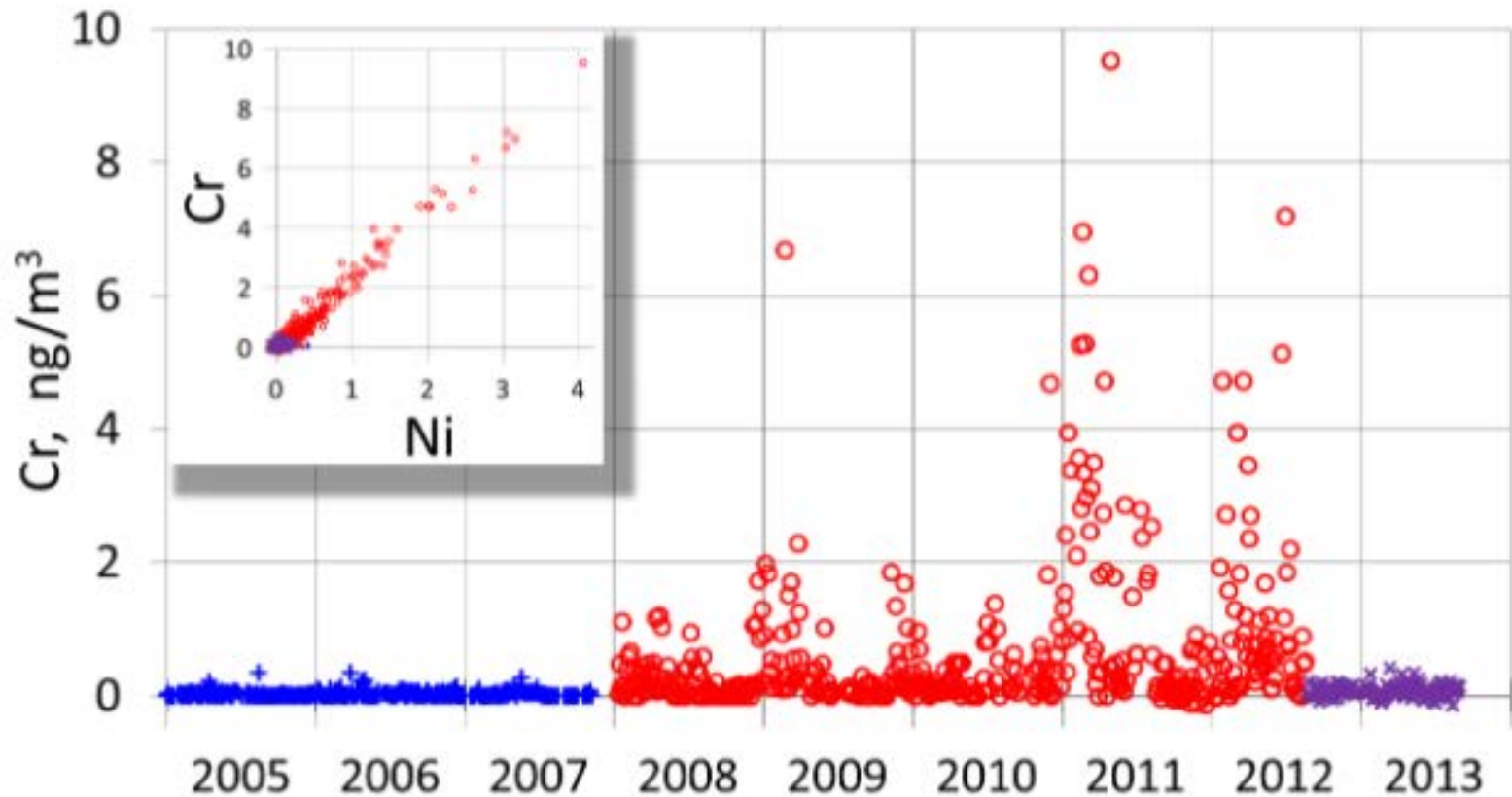


2011 - Sulfur (Fine)



- Dots represent sites
- Sometimes we discover unique sources of trace elements

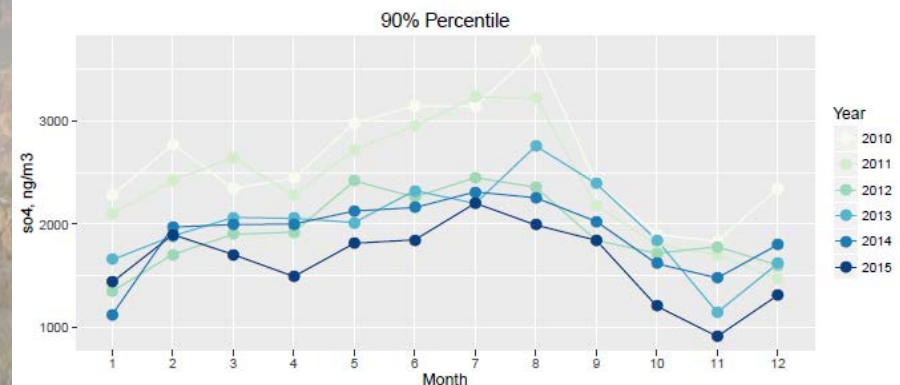
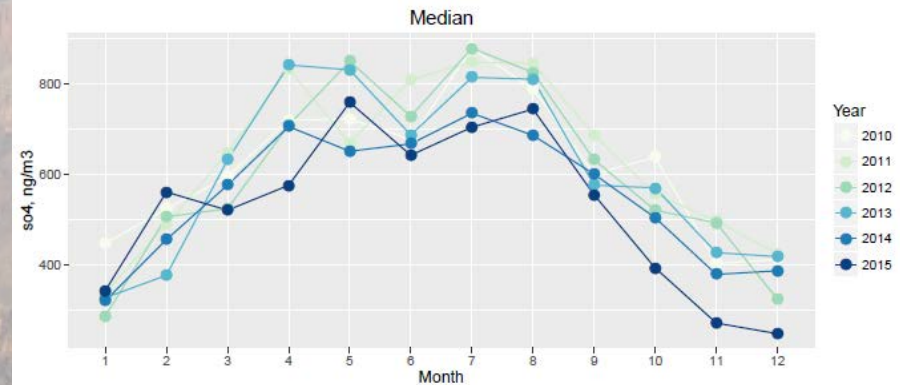
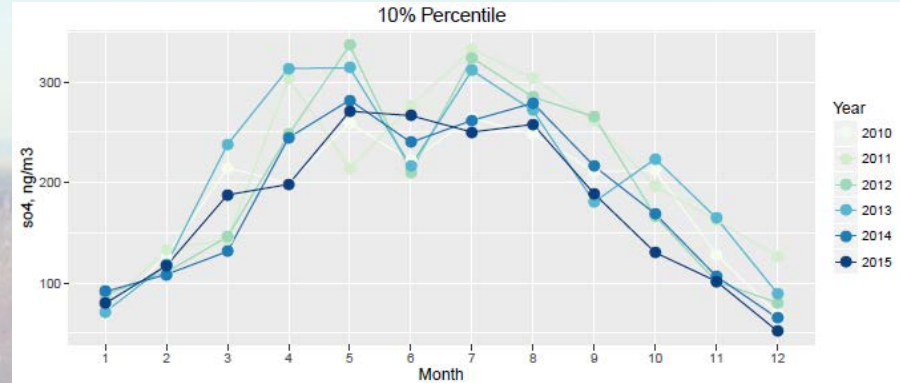
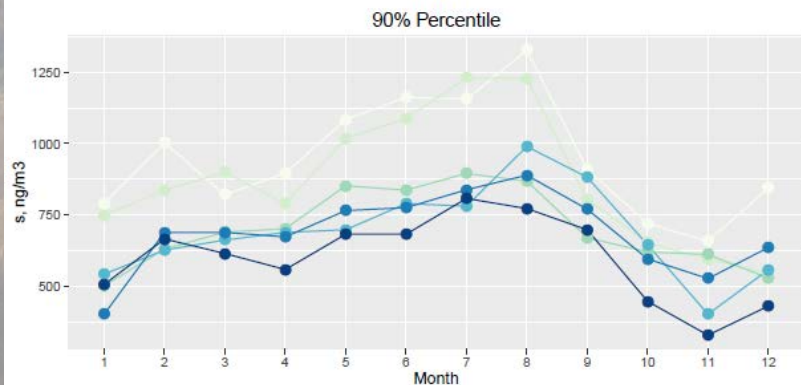
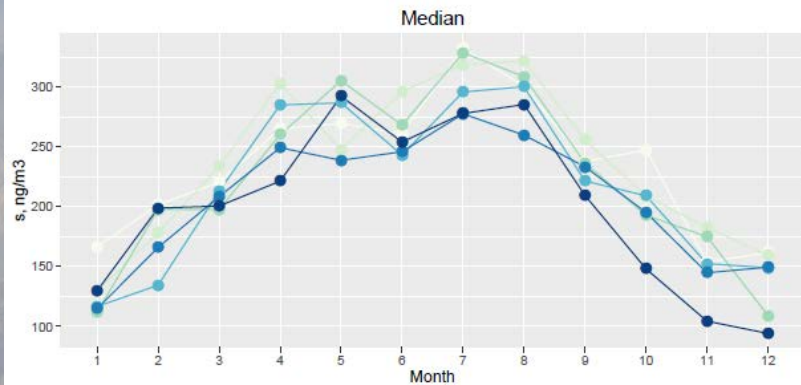
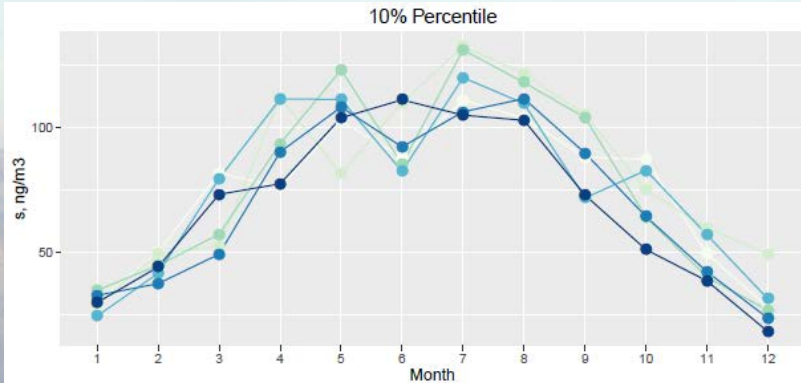
Sometimes we identify contamination



Data Validation Across Years

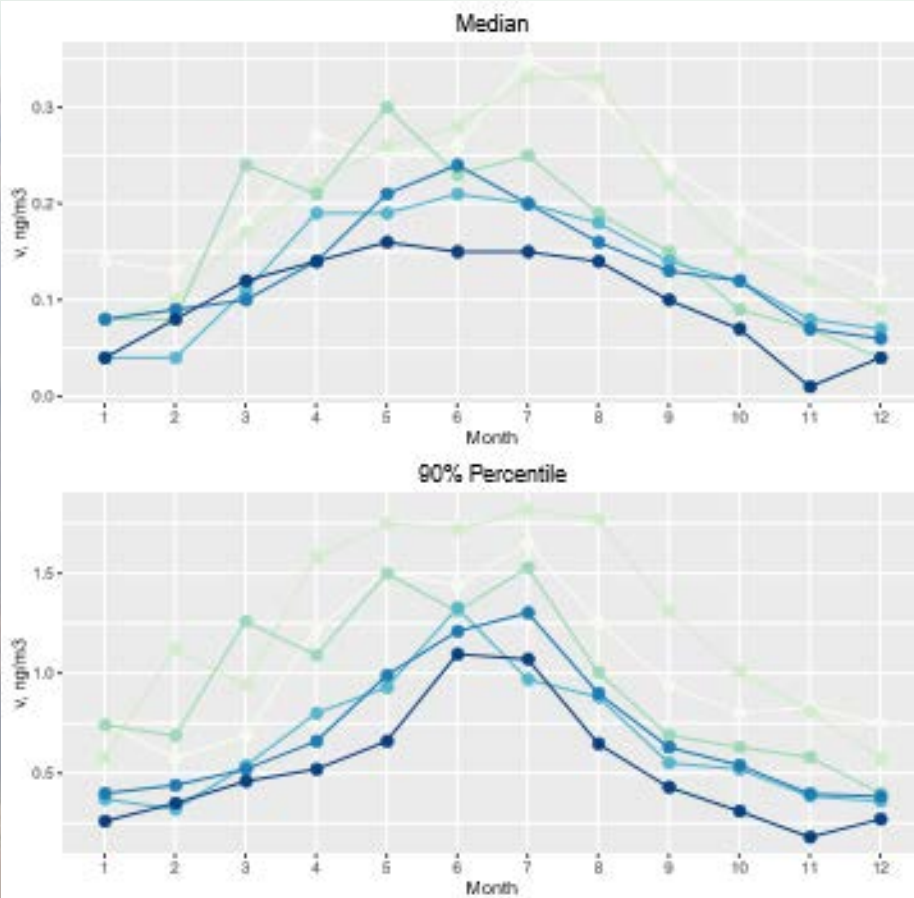
Sulfur by XRF

Sulfate by IC

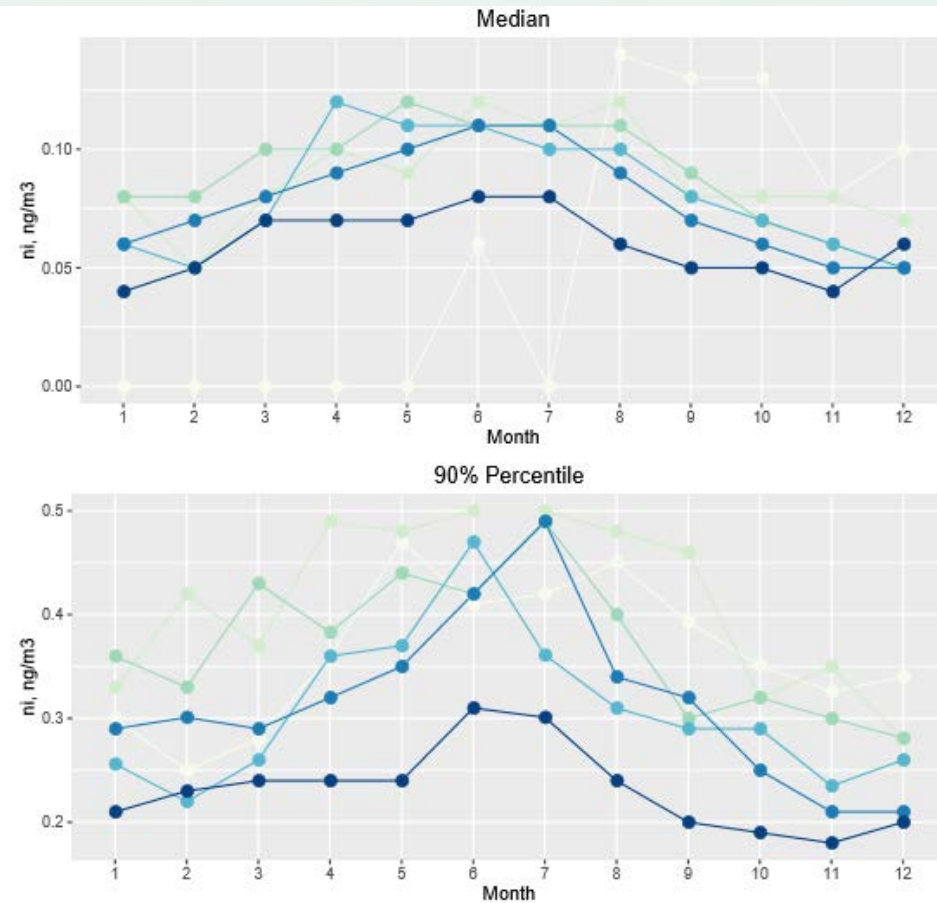


Sometimes we find trends in atmosphere!

Vanadium



Nickel



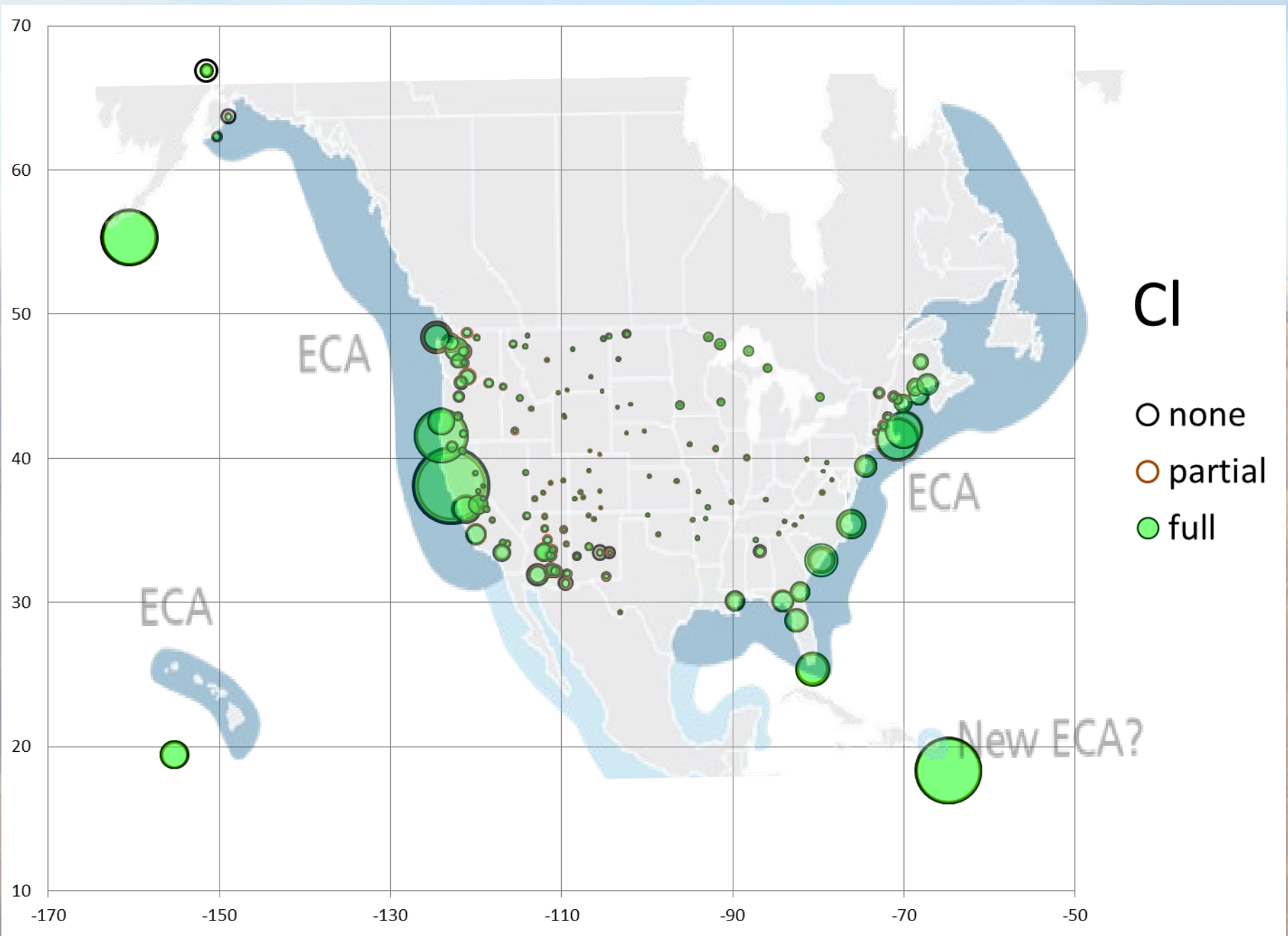
- Nickel and vanadium are tracers for bunker fuel

Table 1

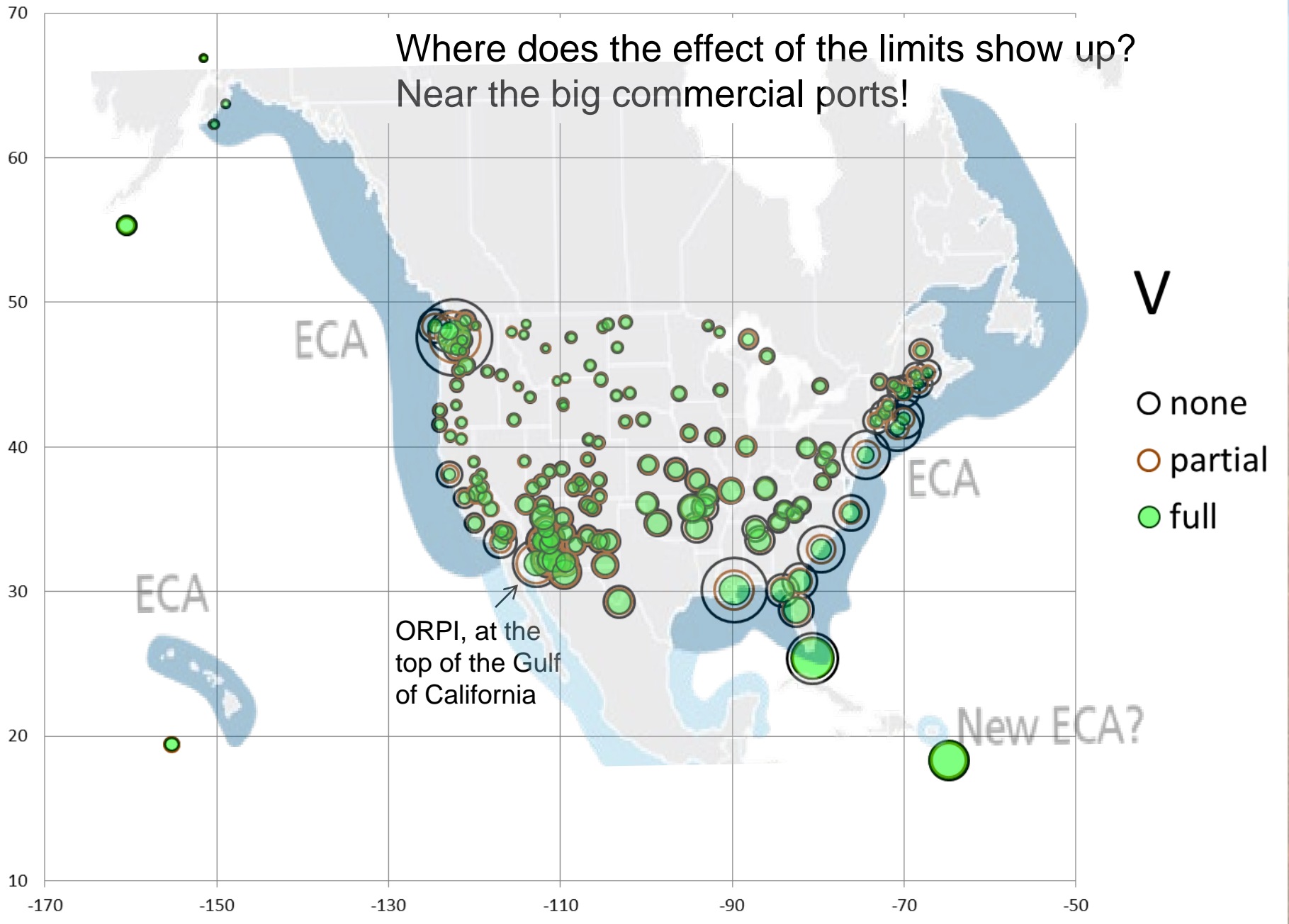
Bunker Fuel Regulations		
Outside an ECA established to limit SOx and particulate matter emissions	Inside an ECA established to limit SOx and particulate matter emissions	ARB's California OGV Fuel Requirement Percent Sulfur Content Limit
4.50% sulfur prior to January 1, 2012	1.50% sulfur prior to July 1, 2010	Phase I effective July 1, 2009: Marine gas oil (DMA) at or below 1.5% sulfur; or Marine diesel oil (DMB) at or below 0.5% sulfur
3.50% sulfur on and after January 1, 2012	1.00% sulfur on and after July 1, 2010	Phase I effective August 1, 2012: Marine gas oil (DMA) at or below 1.0% sulfur; or Marine diesel oil (DMB) at or below 0.5% sulfur
0.50% sulfur on and after January 1, 2020 ^{1,2}	0.10% sulfur on and after January 1, 2015	Phase II effective January 1, 2014: Both marine gas oil (DMA) and marine diesel oil (DMB) at or below 0.1% sulfur

¹ depending on the outcome of a review, to be concluded by 2018, as to the availability of the required fuel oil, this date could be deferred to January 1, 2025.

² European Union Directive 2012/33/EU mandates a maximum fuel sulfur content of 0.5% to be burned in ships in the European Economic Zone in areas outside of ECAs, beginning in 2020.



Where does the effect of the limits show up?
Near the big commercial ports!



ECA

V

- none
- partial
- full

ECA

ECA

New ECA?

ORPI, at the top of the Gulf of California

70
60
50
40
30
20
10

-170 -150 -130 -110 -90 -70 -50



IMPROVE Reinvestment and Data Analysis

Investigations can lead to better
understanding and improvements of the
measurements

Aerosol generation system

Dilution Air

IMPROVE PM2.5 Module

Atomizer

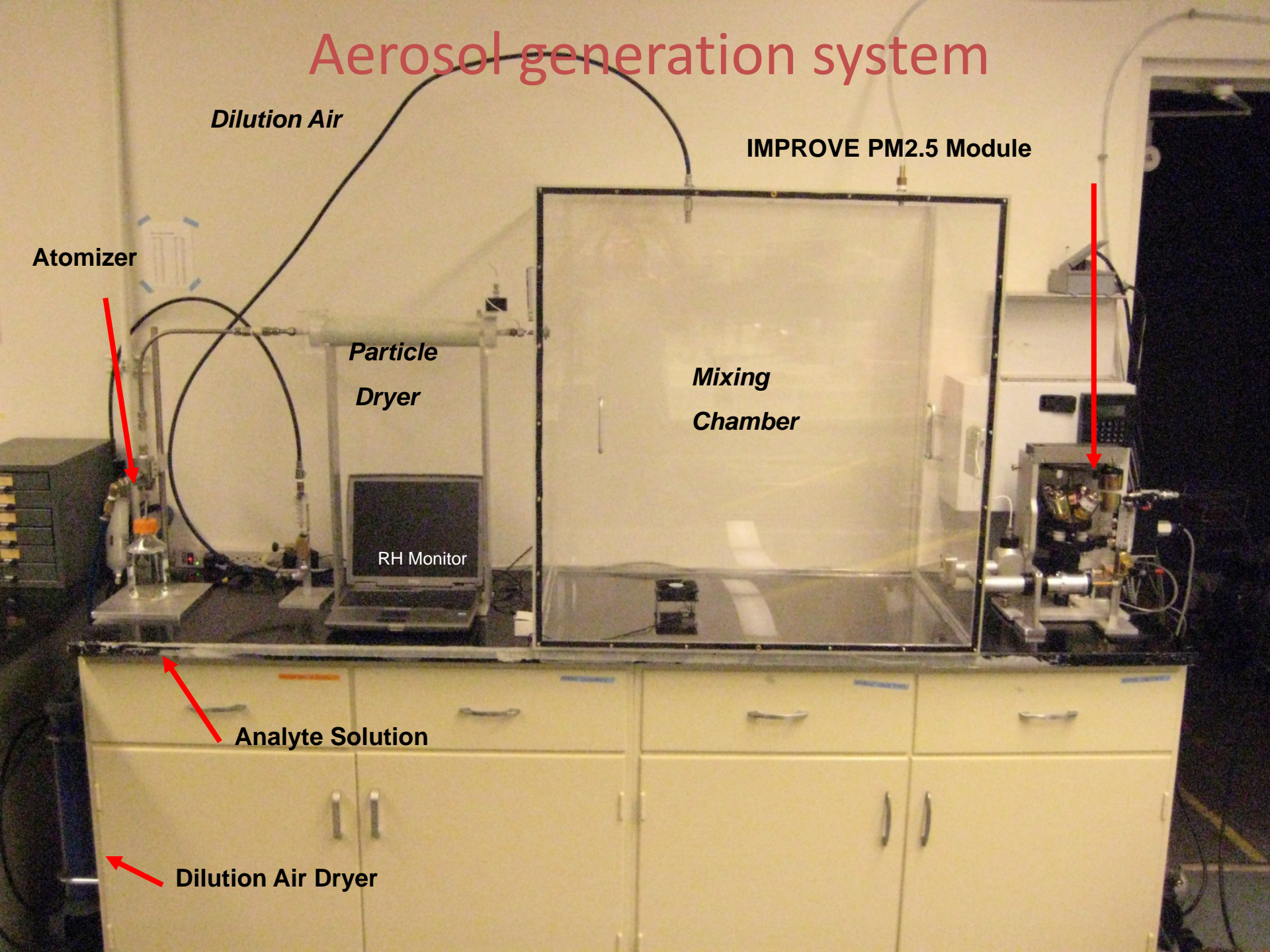
*Particle
Dryer*

*Mixing
Chamber*

RH Monitor

Analyte Solution

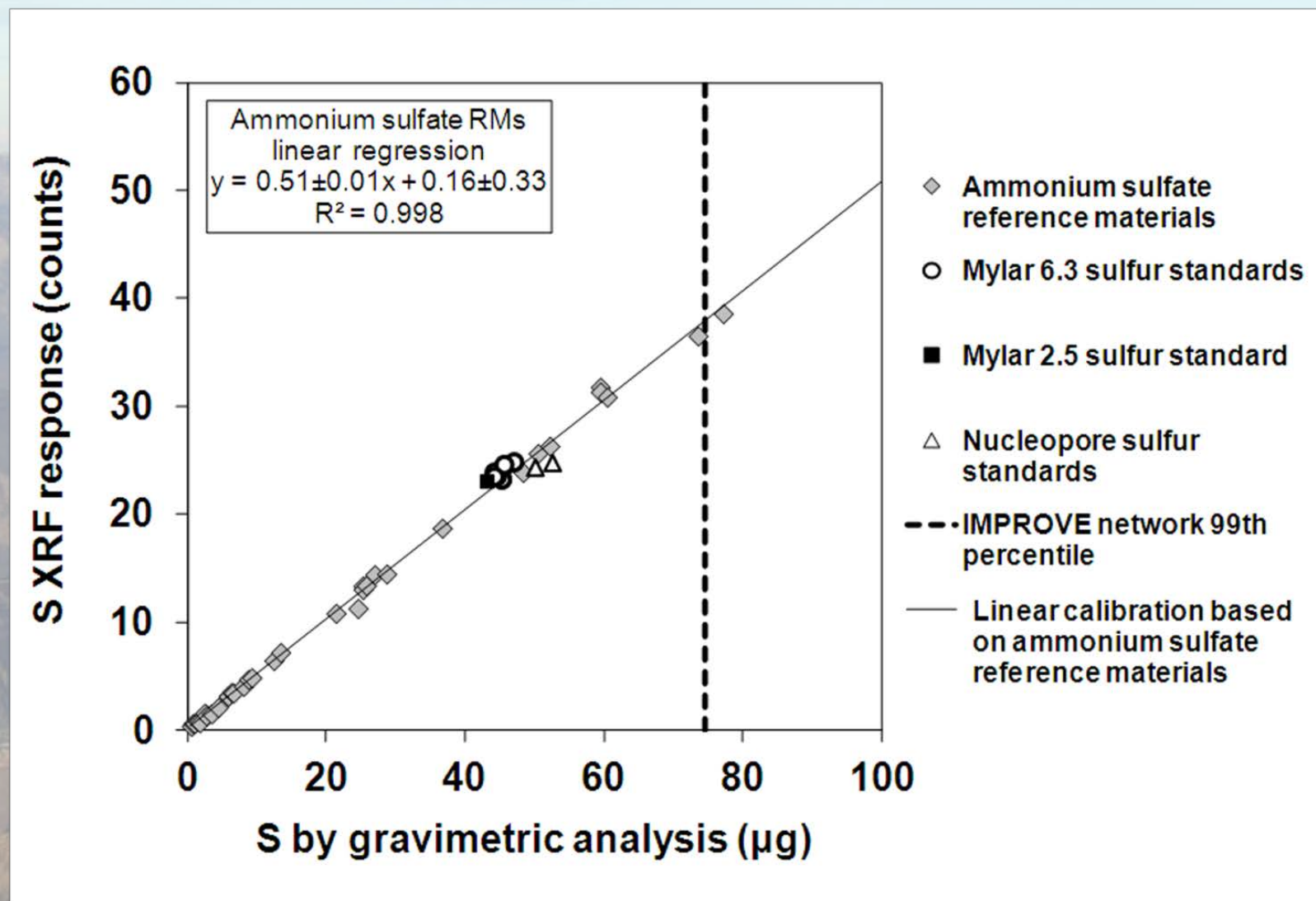
Dilution Air Dryer



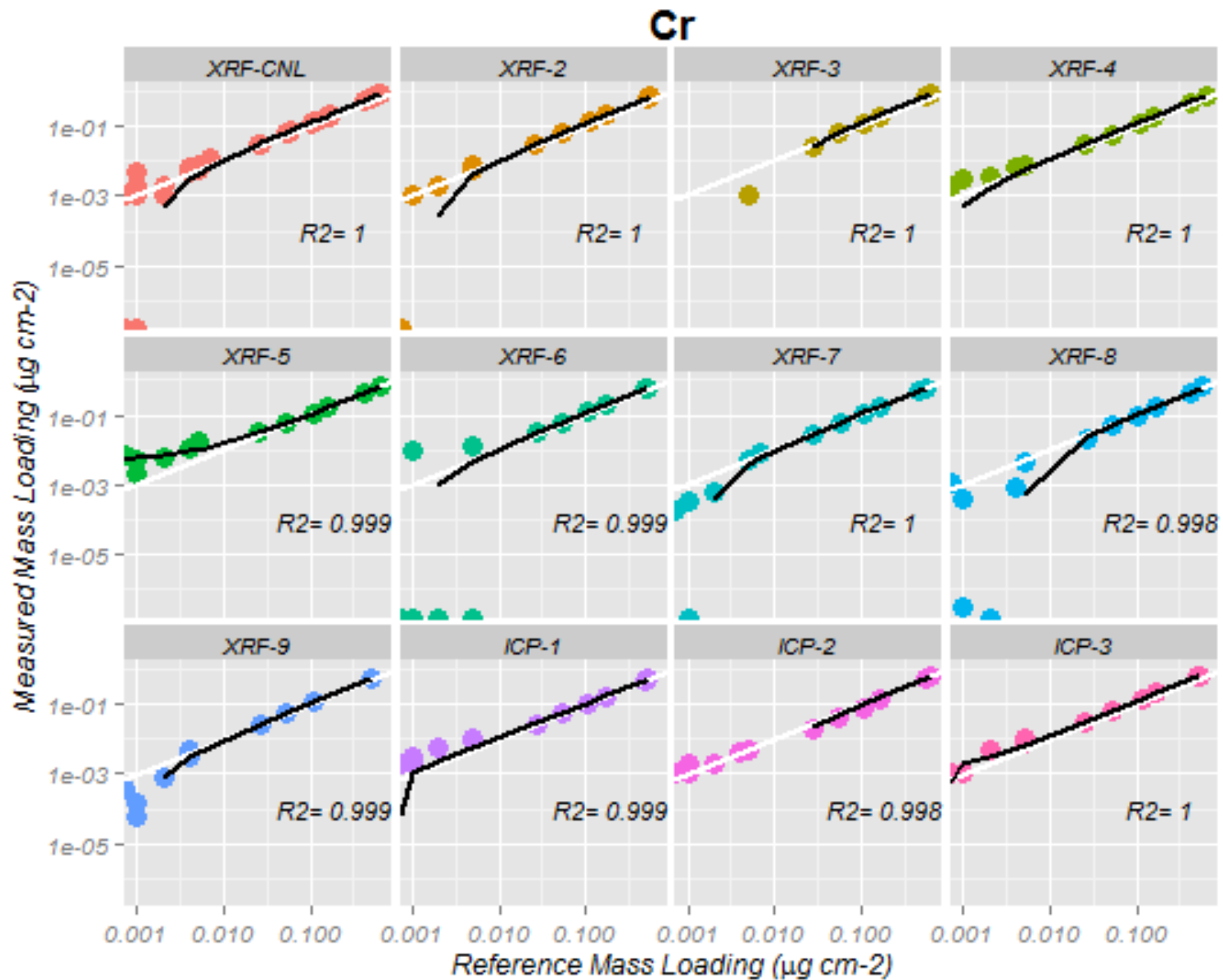
Creating XRF Calibration Reference Filters

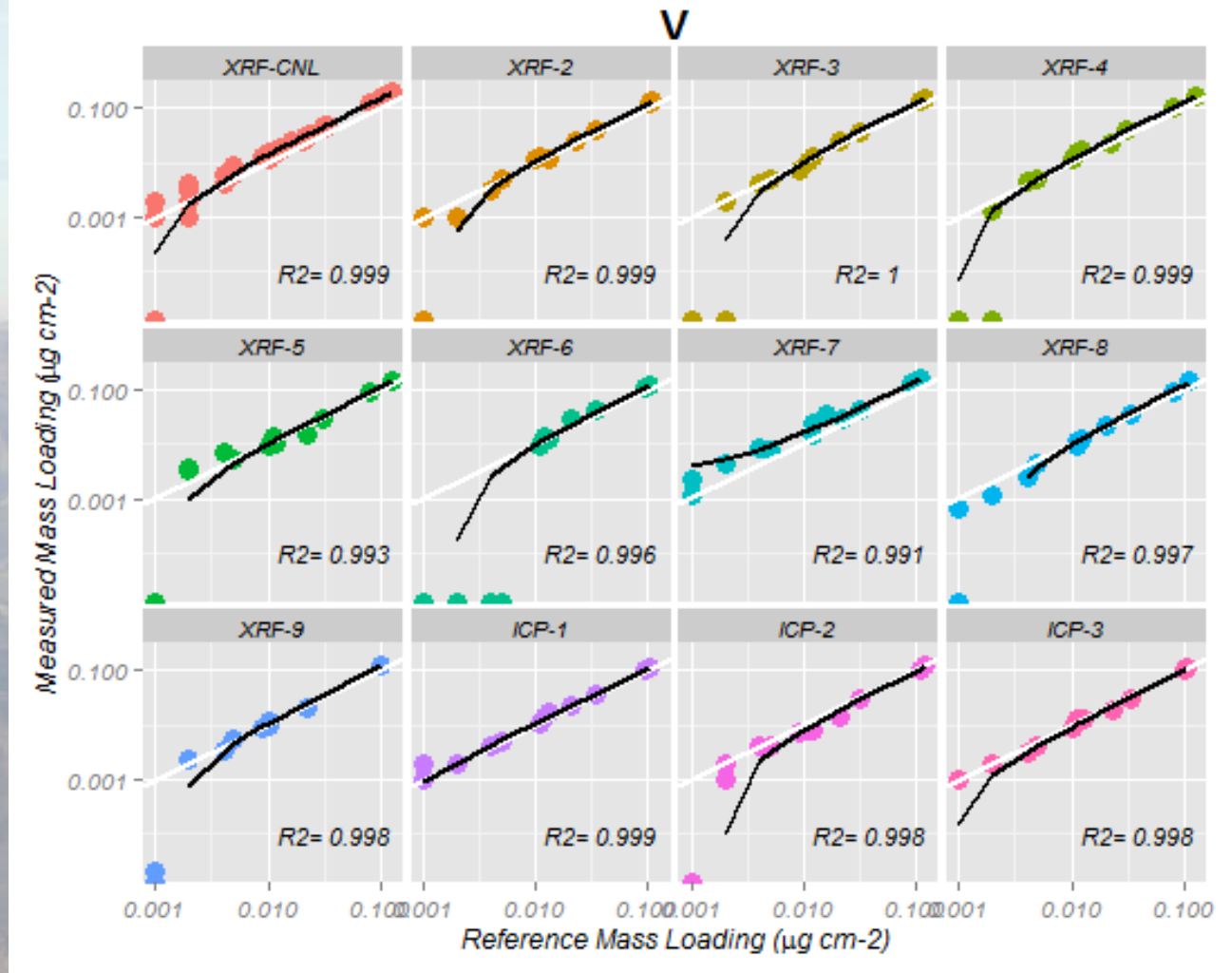
- Reference filters prepared using IMPROVE or Partisol[®] sampler
- Provides reference filters at relevant concentrations
- XRF benchmark independent of Micromatter Inc. (commercially available) standards
- Single-compound reference filters for S, Na, Cl, Pb, and K are used in current UC-Davis XRF calibrations
- Multi-element reference filters are also under development
 - used to check stability of XRF measurements

Sulfur Reference Filters



Multi-Element Reference Filters Analyzed by 12 Labs





- Eventually plan to use ME reference filter to explore interferences, matrix effects, and calibrate the instrument

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IMPROVE



Interagency Monitoring of Protected Visual Environments

Developing Single and Multi-element Reference Materials for Evaluating XRF Measurements of Atmospheric Aerosols

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Objective: To generate single and multi-element reference materials (RMs) on Polytetrafluoroethylene (PTFE, Teflon) filters using aerosol chamber at CNL-UC Davis (Fig.1), and utilize them in calibration and quality control (QC) of EDXRF analyzers in order to address the limitations of available resources.

Materials & Method: High purity salts and nanoparticles for single compound RMs (SE-RMs)
Certified multi-elemental solutions containing 28 elements for multi-element RMs (ME-RMs).

Certified or Reference loadings of RMs:

- The loadings of SE-RMs (C_{cer}) are certified gravimetrically using a balance with 0.1 μg sensitivity
- The ME-RMs reference loading of element i ($C_{ref,i}$) was assigned assuming :
 1. The elemental ratios in solutions are preserved onto ME-RMs
 2. The potassium (K) measurement by UCD-EDXRF, $C_{K,UCD-EDXRF}$ (Epsilon 5, Panalytical Inc, the Netherlands) is accurate to be <10%. These assumptions resulted in estimated uncertainties below 10%.

$$C_{ref,i} = C_{(K,UCD-EDXRF)} \cdot \frac{i_{solution}}{K_{solution}}$$

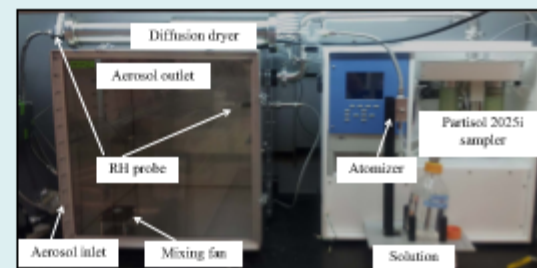


Fig.1. The aerosol generation and sampling system

Data Evaluation:

1. Agreement between certified loadings of SE-RMs and EDXRF: Linear regression, bias and E_n number (ISO/IEC 17043, 2010):
U: Expanded uncertainty by GUM (2008)
2. Linear regression between reference loading of ME-RMs (x) and lab (y),
3. z-score (ISO 13528:2005): Loadings in $\mu\text{g}/\text{cm}^2$ converted to $\mu\text{g}/\text{g}$ for 12 ME-RMs in interlaboratory comparison

\bar{C} : outlier-excluded mean

$\hat{\sigma}$: outlier-excluded standard deviation

$$E_n = \frac{|C_{EDXRF} - C_{cer}|}{\sqrt{U_{C(EDXRF)}^2 + U_{C(cer)}^2}}$$

When $E_n \leq 1$, C_{EDXRF} and C_{cer} are equivalent

$$z = \frac{C_{lab} - \bar{C}}{\hat{\sigma}}$$

For good interlaboratory comparability, $|z| \leq 3$

Results and Discussion

➤ The SE-RMs could be generated successfully for Na, Al, Si, S, Cl, K, Ti, Fe, Zn and Pb with loadings almost spanning the range of two large US atmospheric PM monitoring networks, namely IMPROVE (Interagency Monitoring of PROTECTED Visual Environments) and CSN (Chemical Speciation Network) (Fig.2.-Left) while the loadings of ME-RMs spanned the range of both networks (Fig.2-Right).

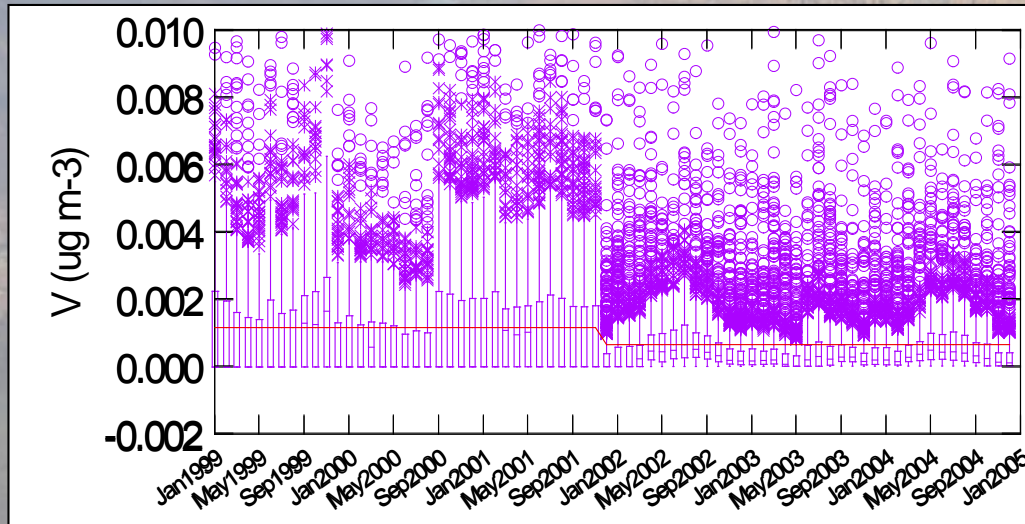
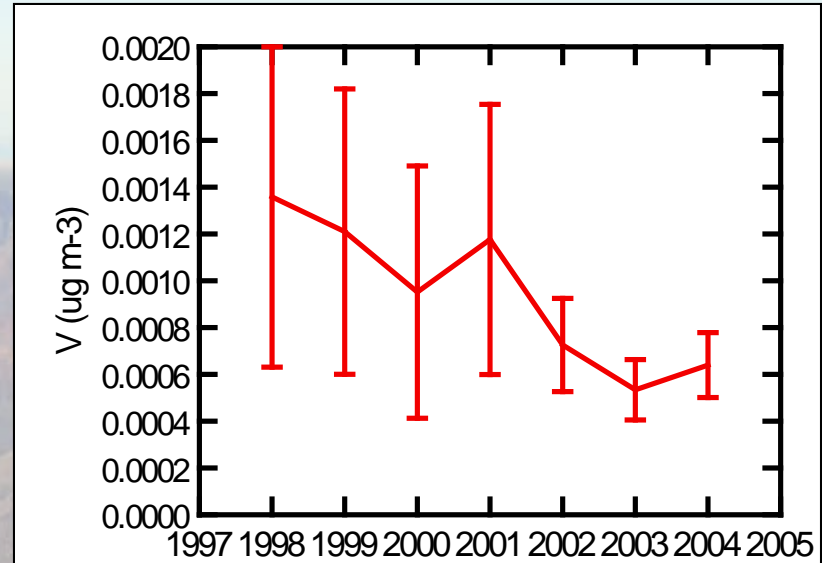
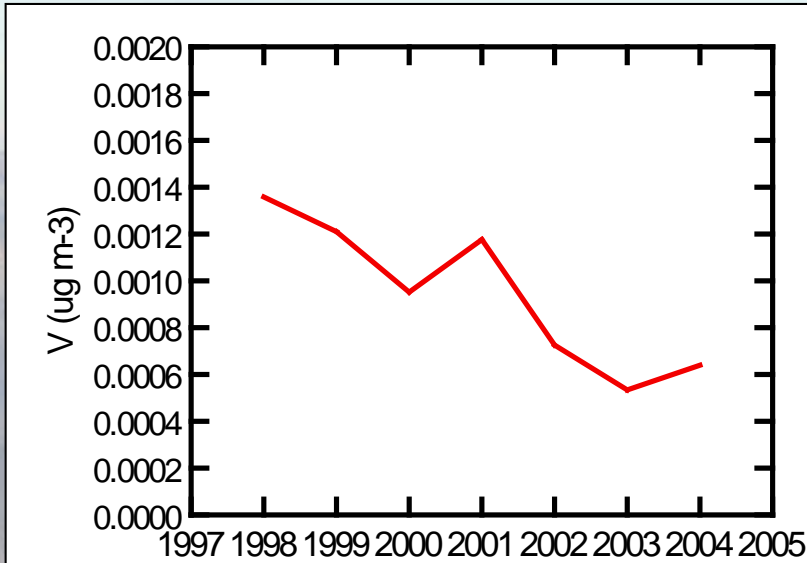
Interlaboratory Comparison of ME-RMs

An interlaboratory comparison study of ME-RMs were conducted with participation of 9 XRF and 3 ICP-MS laboratories

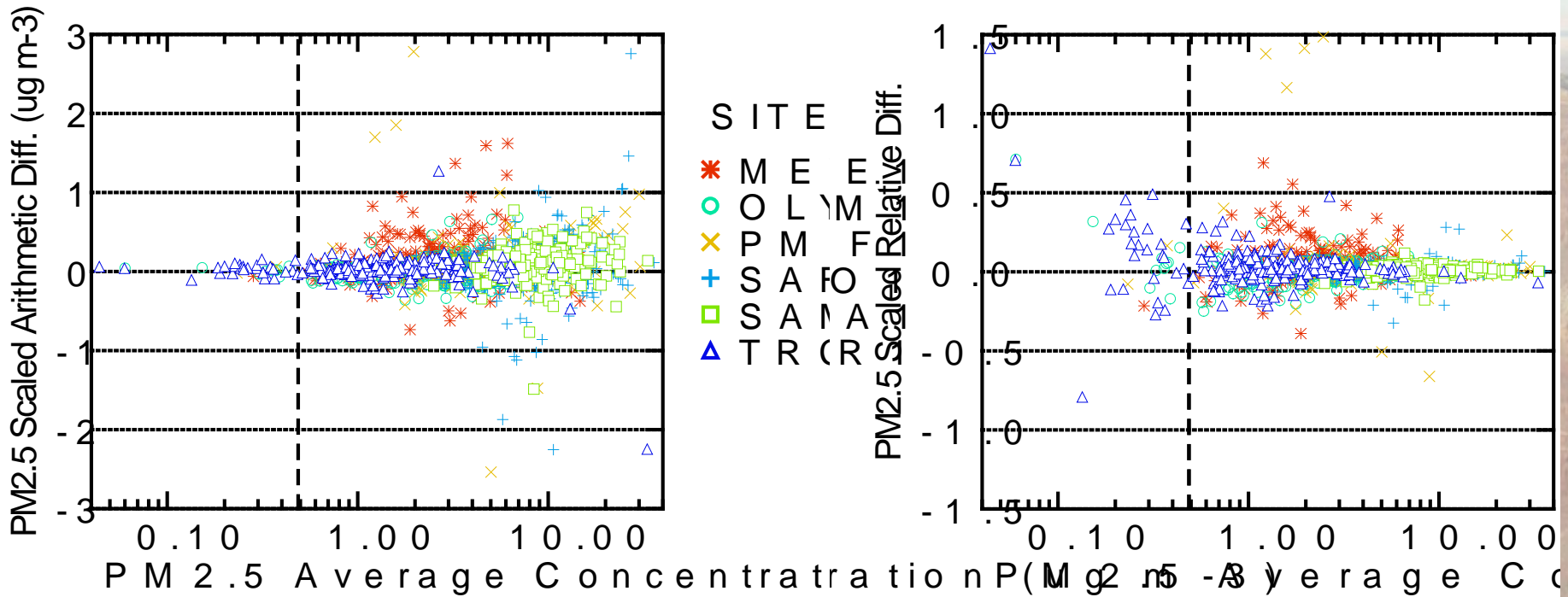
- The slopes of reference vs. labs are mostly within 20% of unity ($R^2 > 0.95$) (Fig.6)
- Participating labs are mostly in good agreement ($|z| \leq 3$) (Fig.7)



Different views, same data



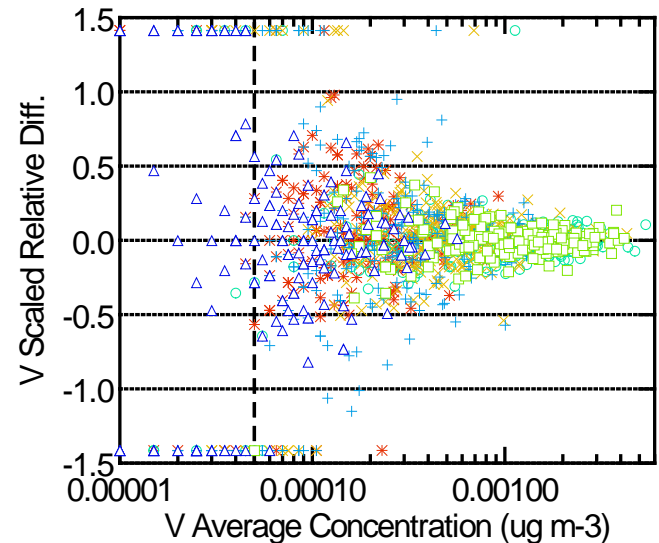
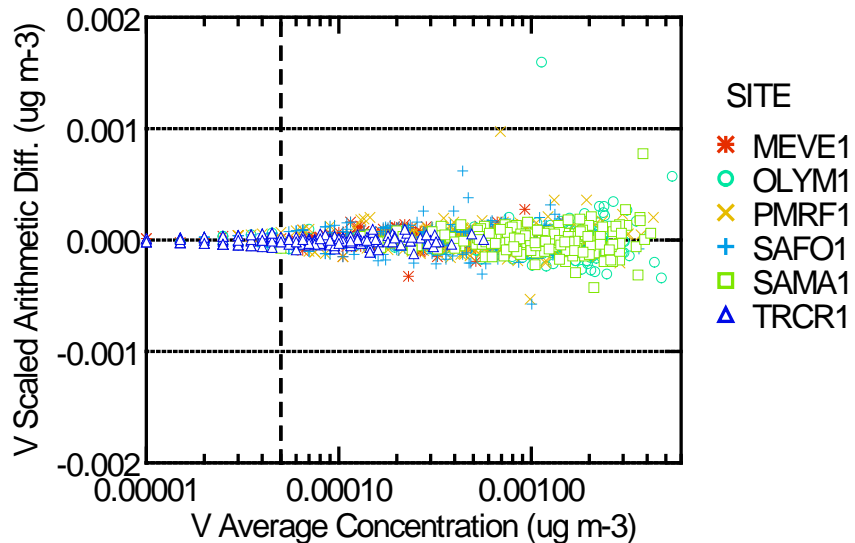
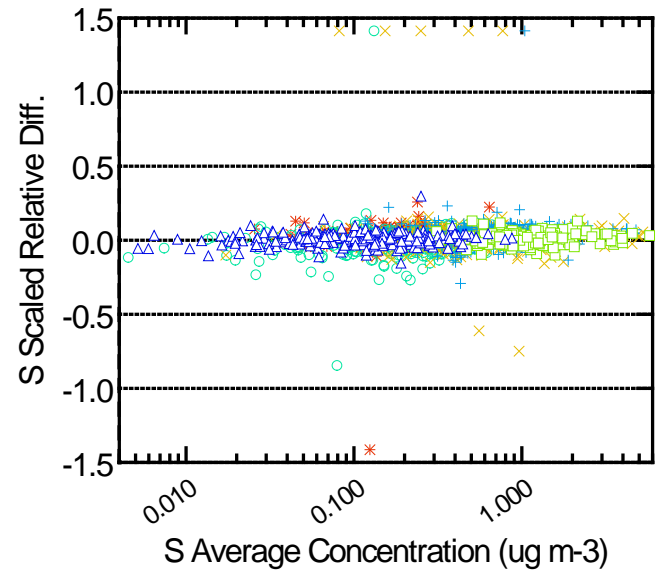
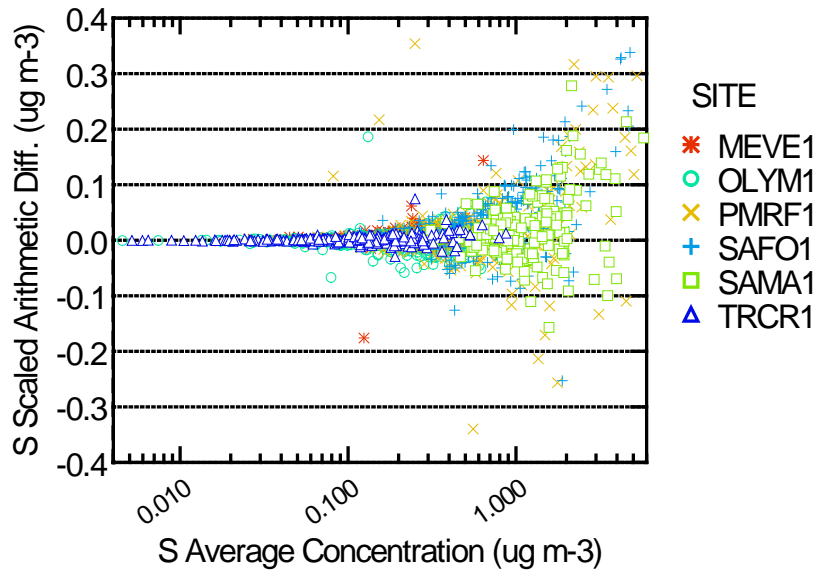
Collocated IMPROVE PM_{2.5} Data



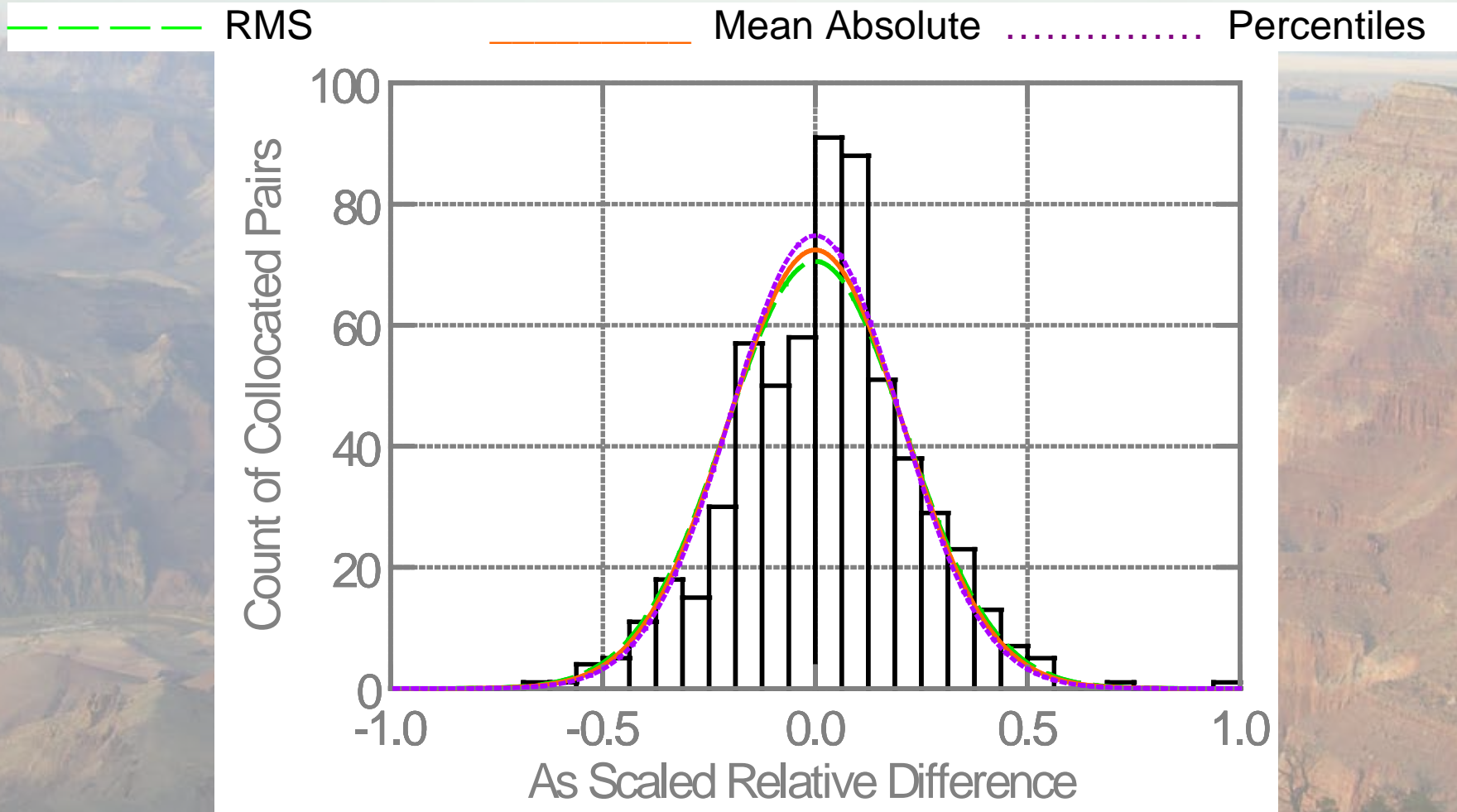
$$\text{Scaled Arithmetic Difference} = \frac{C_1 - C_2}{\sqrt{2}}$$

$$\text{Scaled Relative Difference} = \frac{(C_1 - C_2)/\sqrt{2}}{(C_1 + C_2)/2}$$

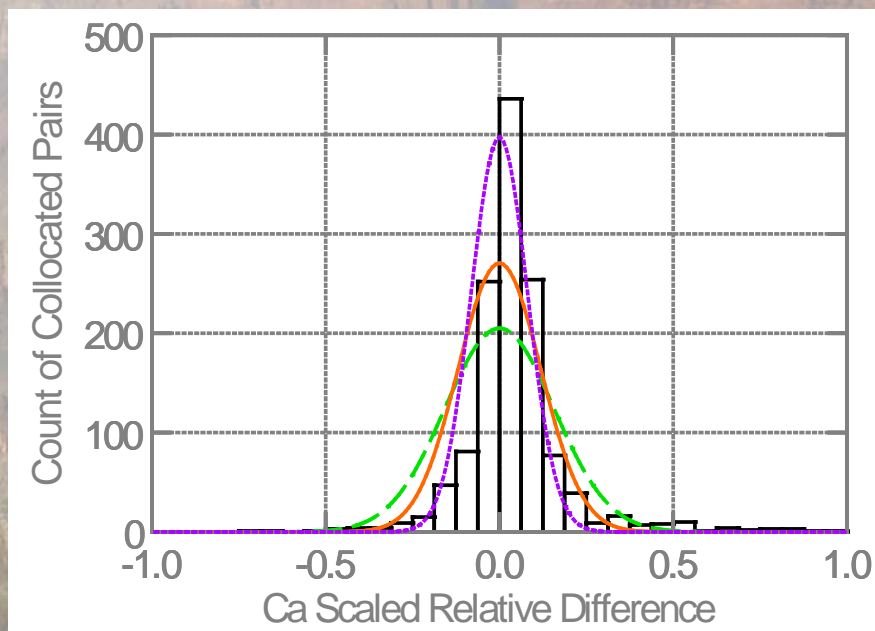
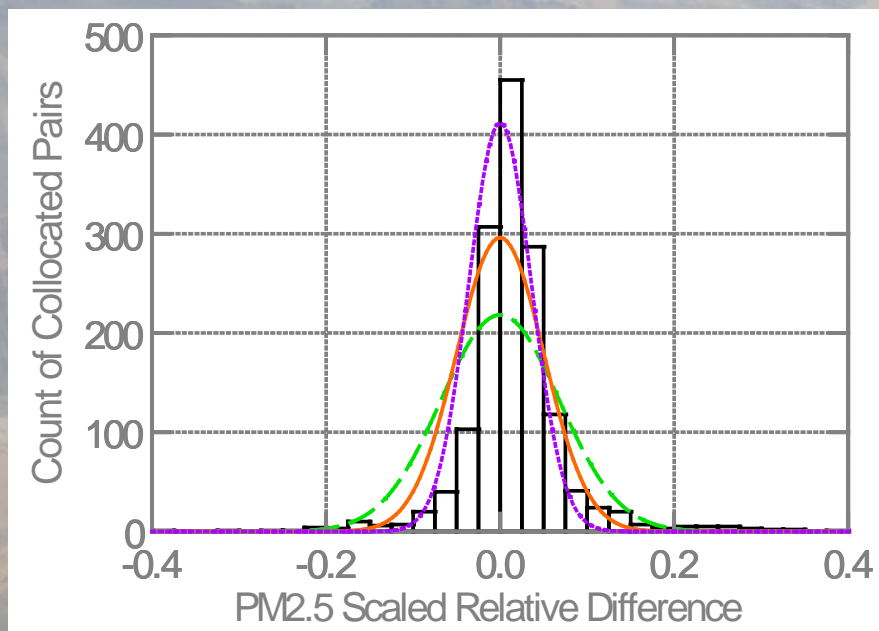
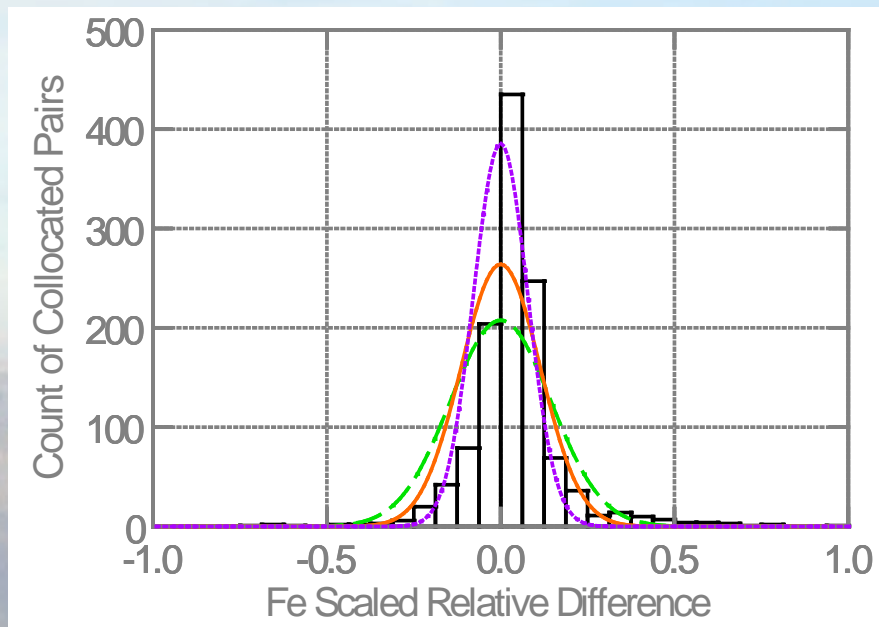
Additive and Multiplicative Errors



Distribution of Differences and Precision Estimates

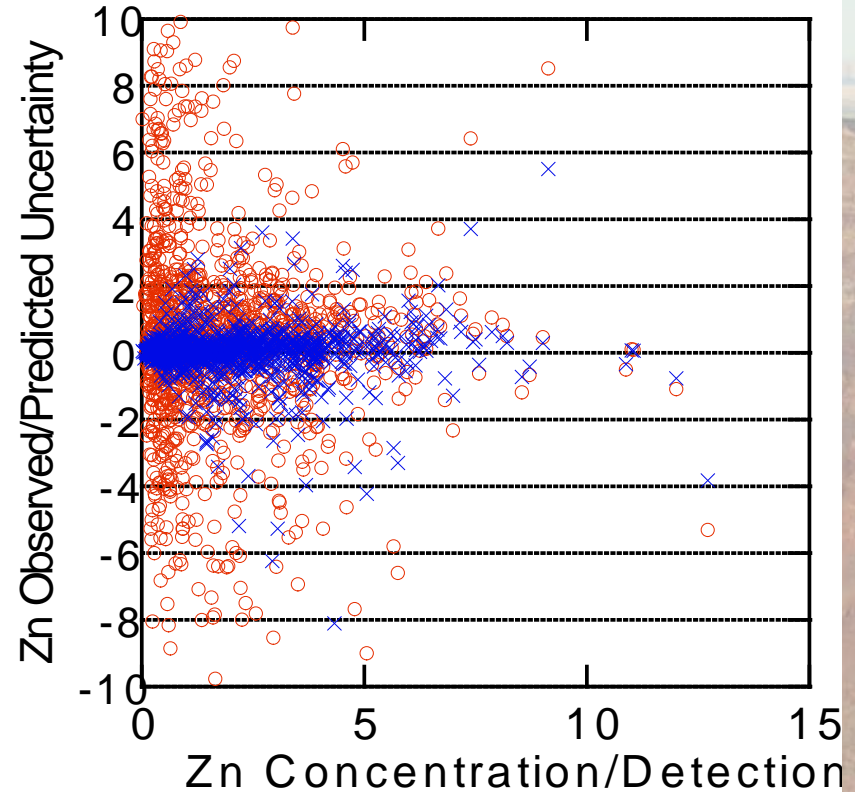
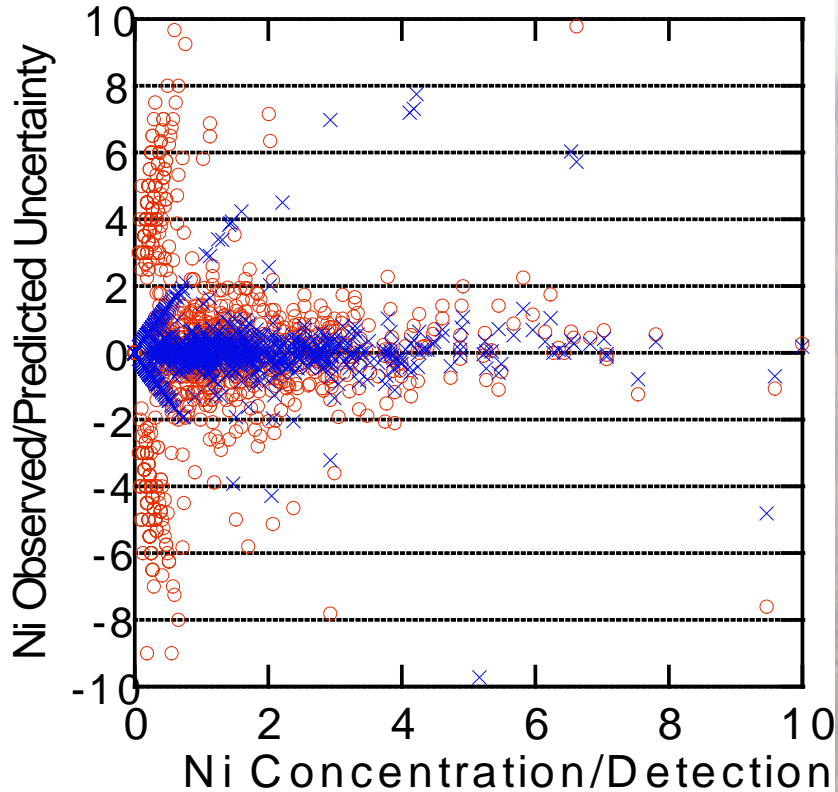


Errors: often not normally distributed



Updated Uncertainty Estimates

Notable Improvements in Some Elements

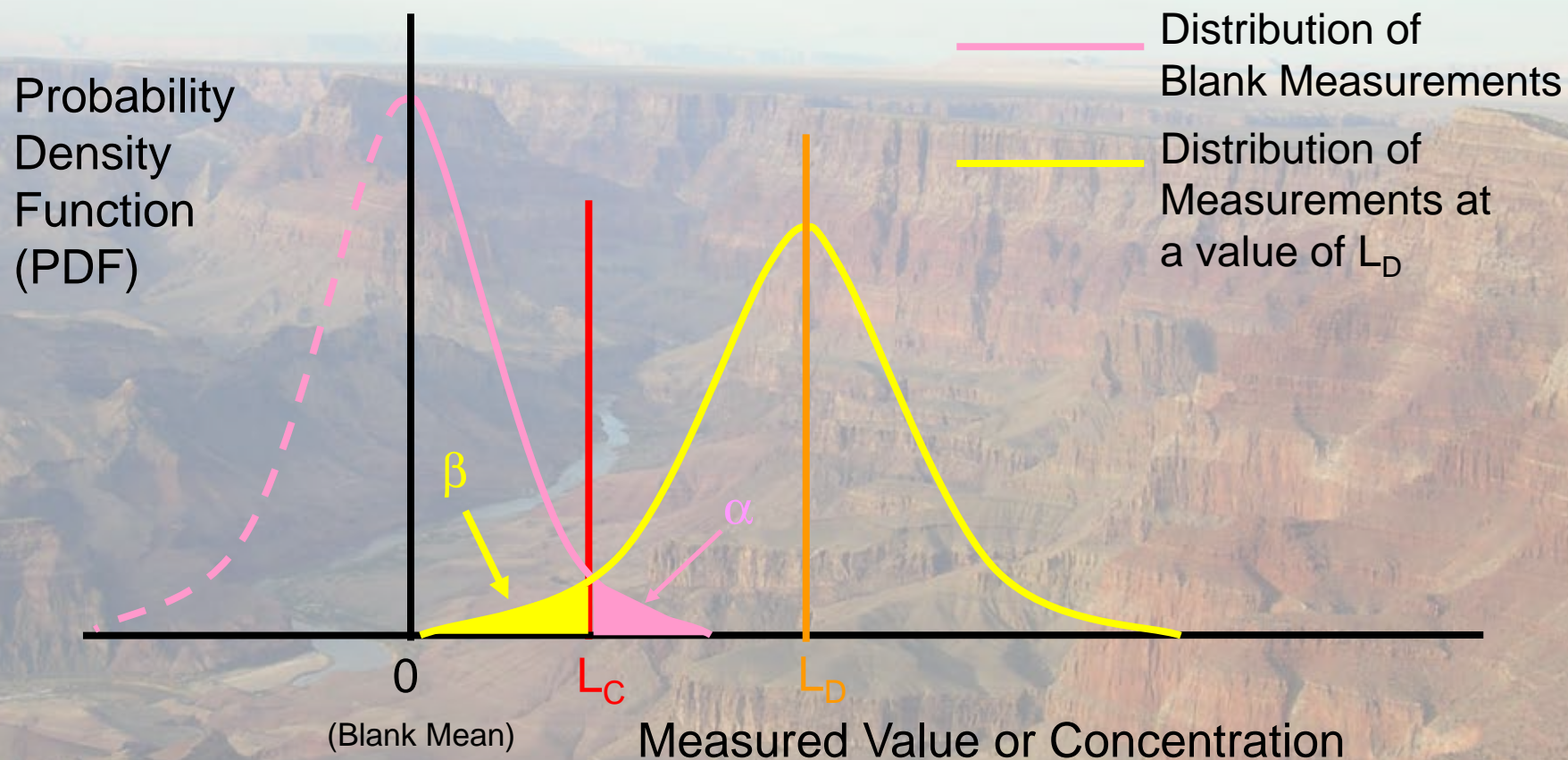


- Existing Uncertainty Estimate
- × Updated Uncertainty Estimate

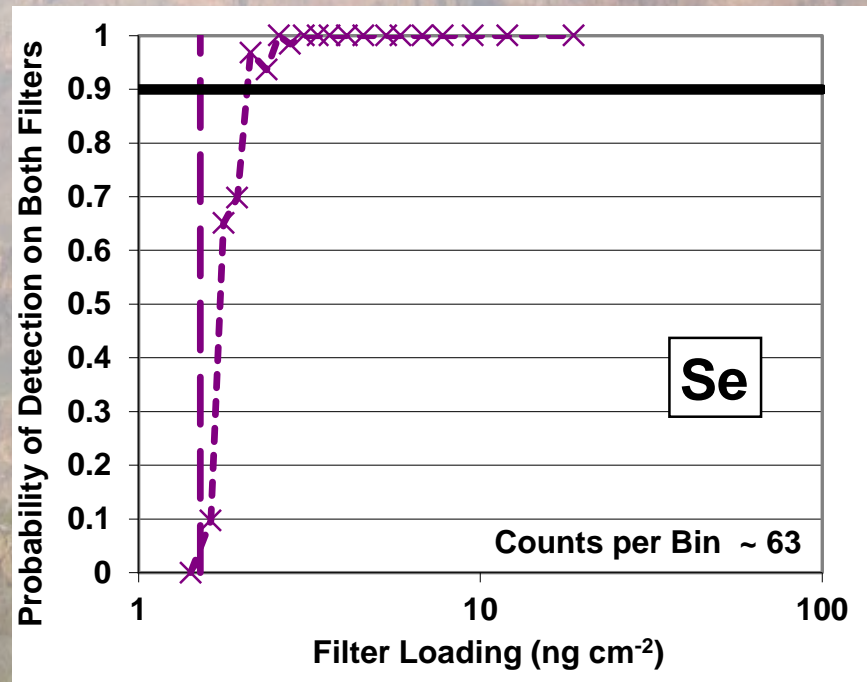
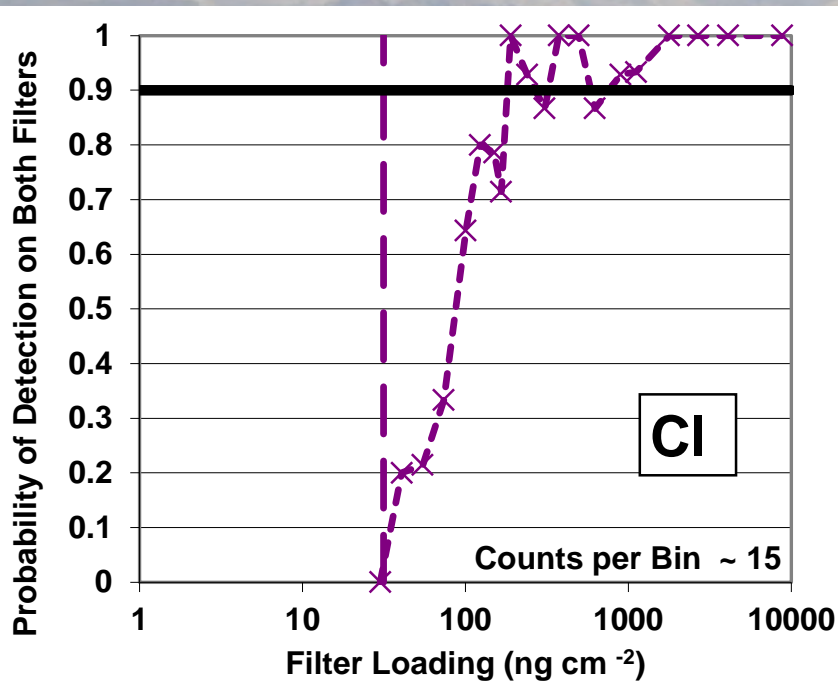
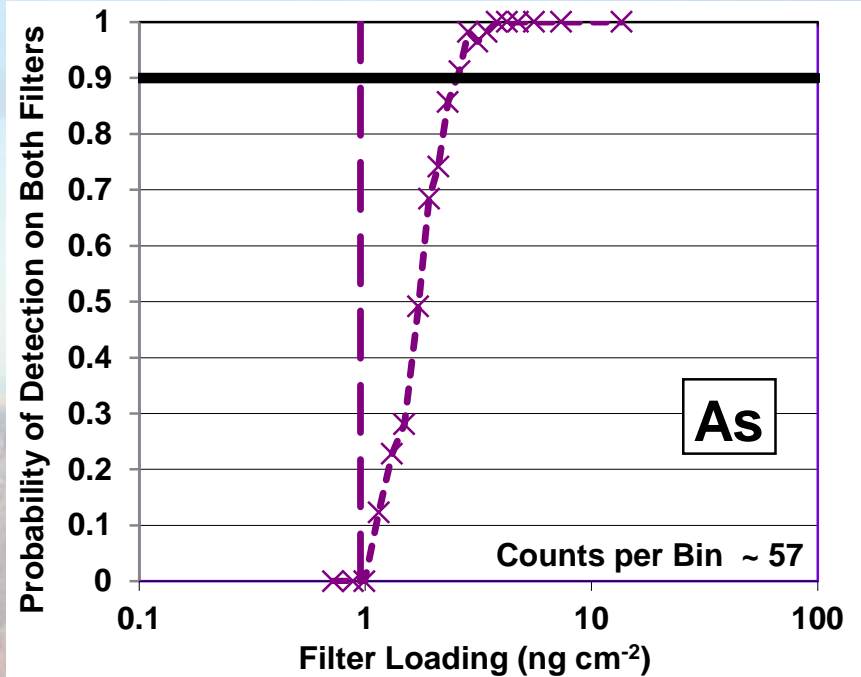
Limits of Detection

	Analyte is not present in sample	Analyte is present in sample
Analyte is measured	Type I error, L_C	Correct decision
Analyte is not measured	Correct decision	Type II error, L_D

Illustration of Type I & II Errors

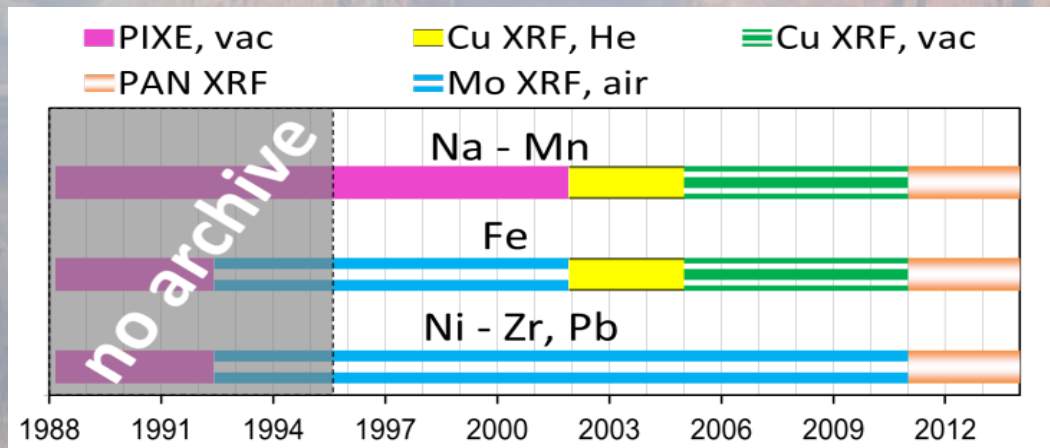


Estimating Detection limits from duplicate measurements



Reanalysis of 15 years of Archived Filters

- Great Smoky Mountains, Mount Rainier, Point Reyes
- Reanalysis under stable conditions and calibration
- Long-term uncertainties not reflected in our precision or collocated measurements

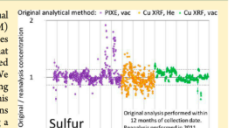


Reanalysis of Archived IMPROVE PM_{2.5} Samples Previously Analyzed over a 15-Year Period

Nicole P. Hyslop,^{*,†} Krystyna Trzepla,[‡] and Warren H. White[‡]

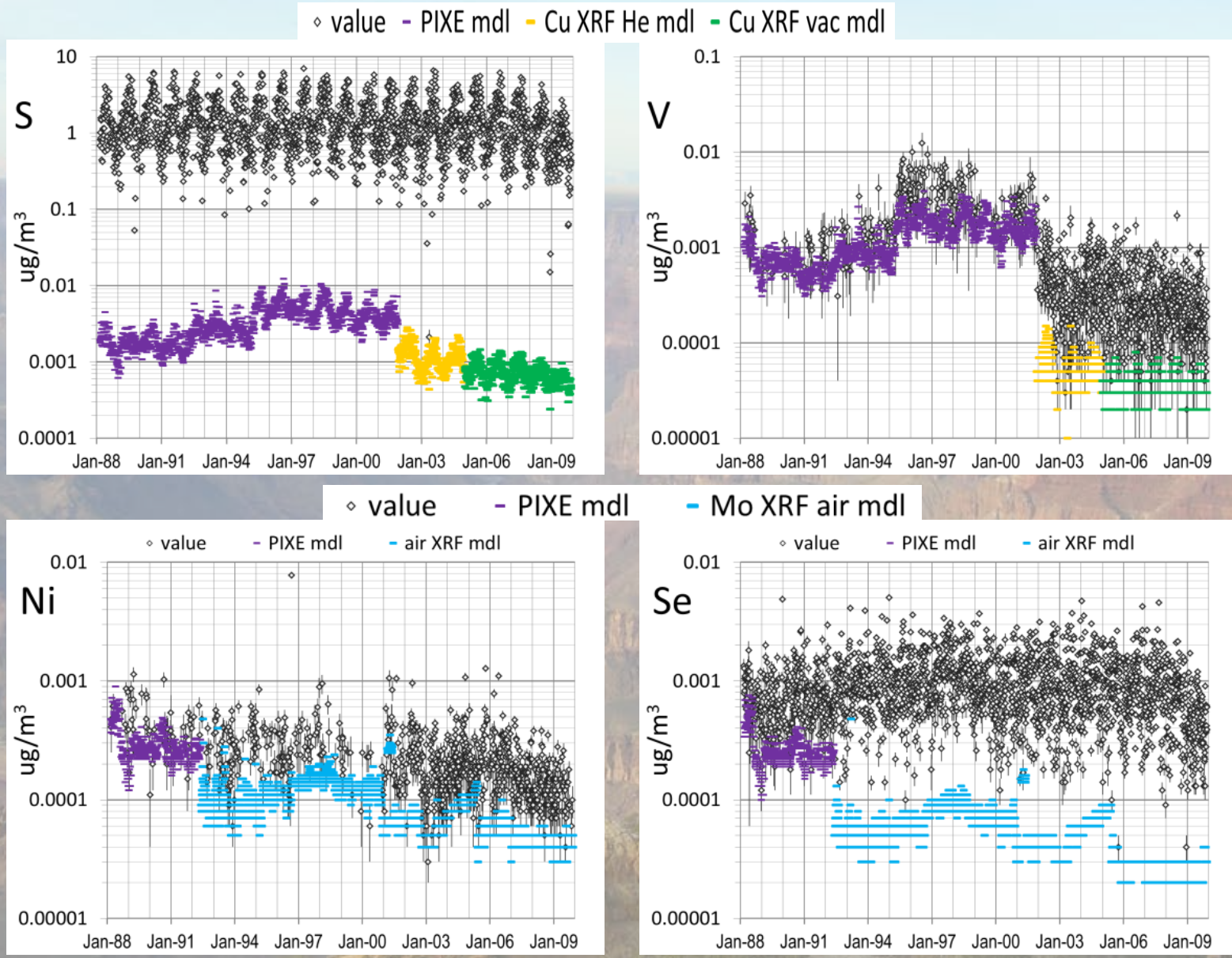
[†]Crocker Nuclear Laboratory, University of California, Davis, California, United States

ABSTRACT: The IMPROVE (Interagency Monitoring of Protected Visual Environments) network has collected airborne particulate matter (PM) samples at locations throughout the United States since 1988. These samples have been analyzed for elemental content using analytical methods that evolved over the years. Changes in analytical methods sometimes introduced shifts in reported concentrations that are evident in the historical record. We sought to illuminate the effects of methodological changes by reanalyzing archived samples with current methods. To test the feasibility of this approach, the 15-year archive of PM samples from Great Smoky Mountains National Park was selected for reanalysis as a single analytical batch using a



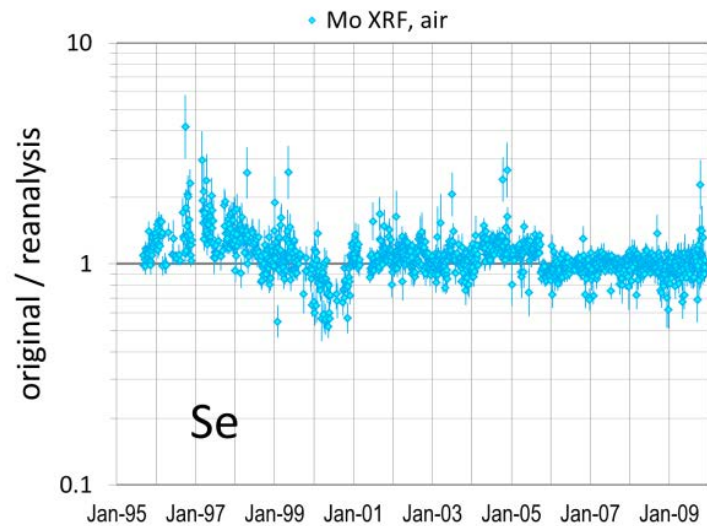
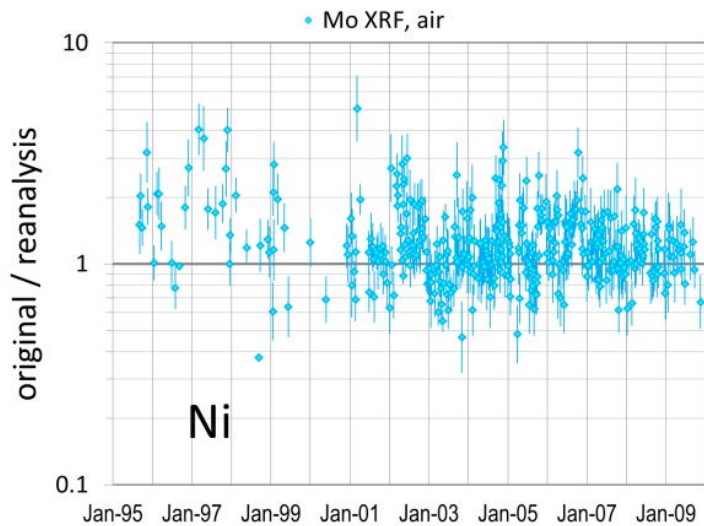
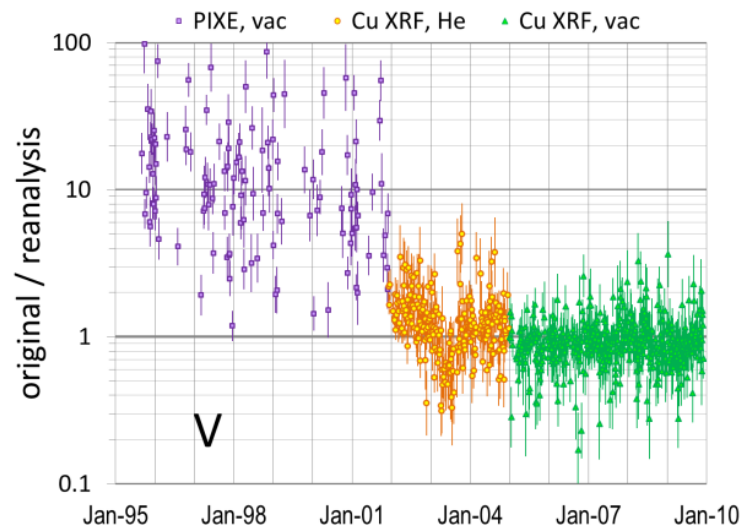
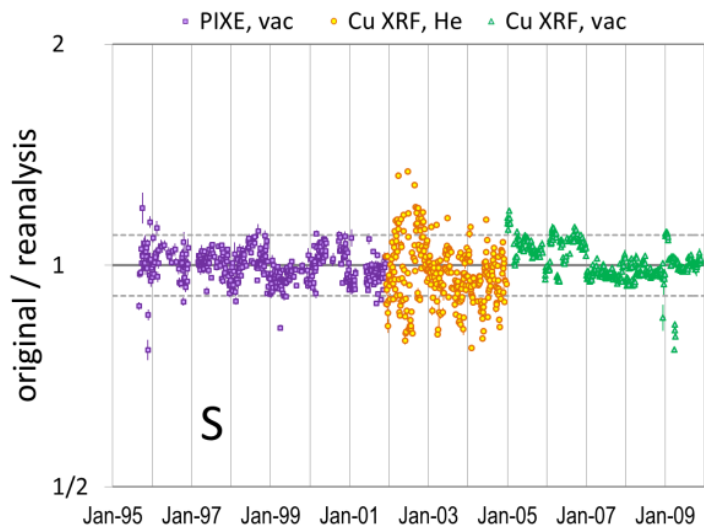
Original Measured Concentrations

Great Smoky Mountains National Park

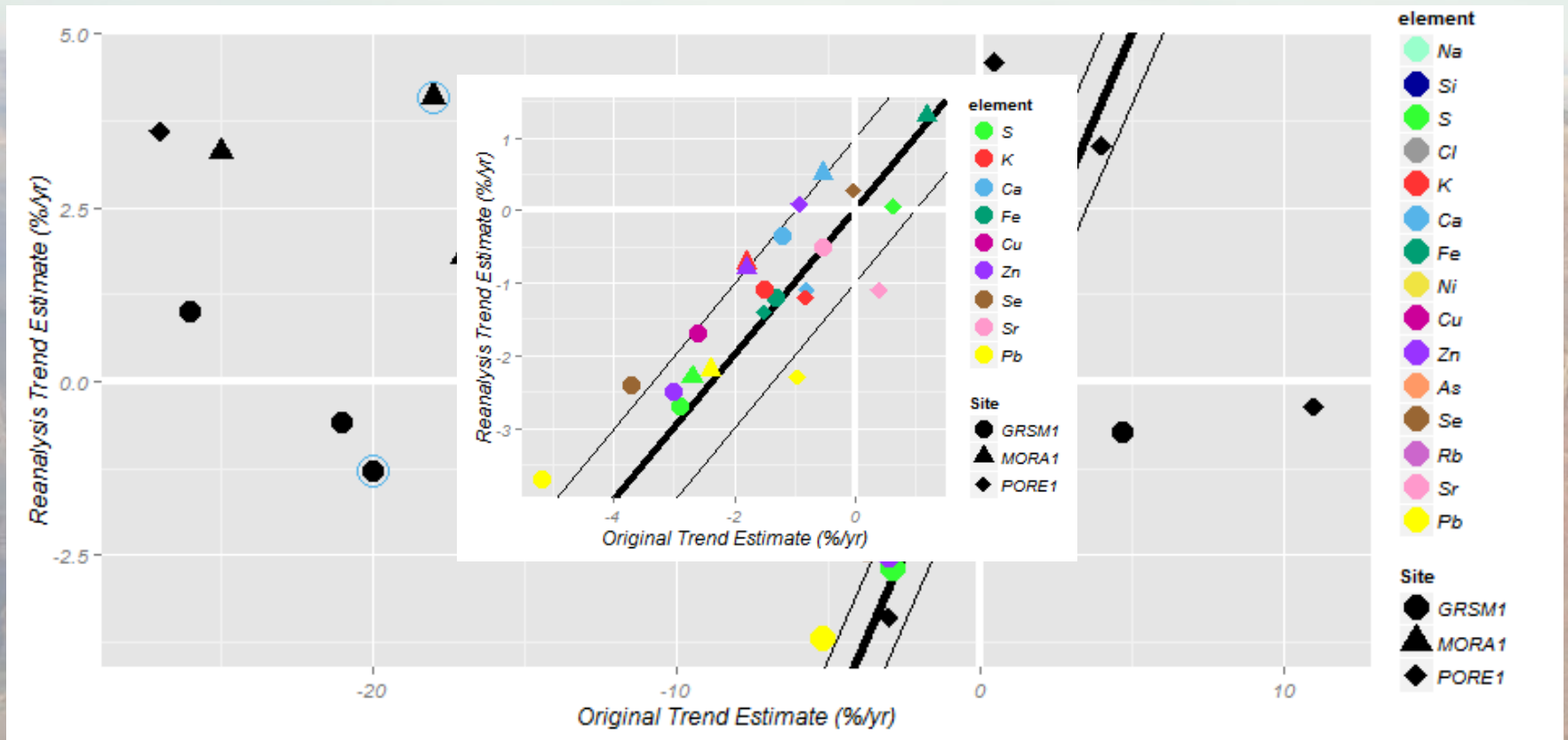


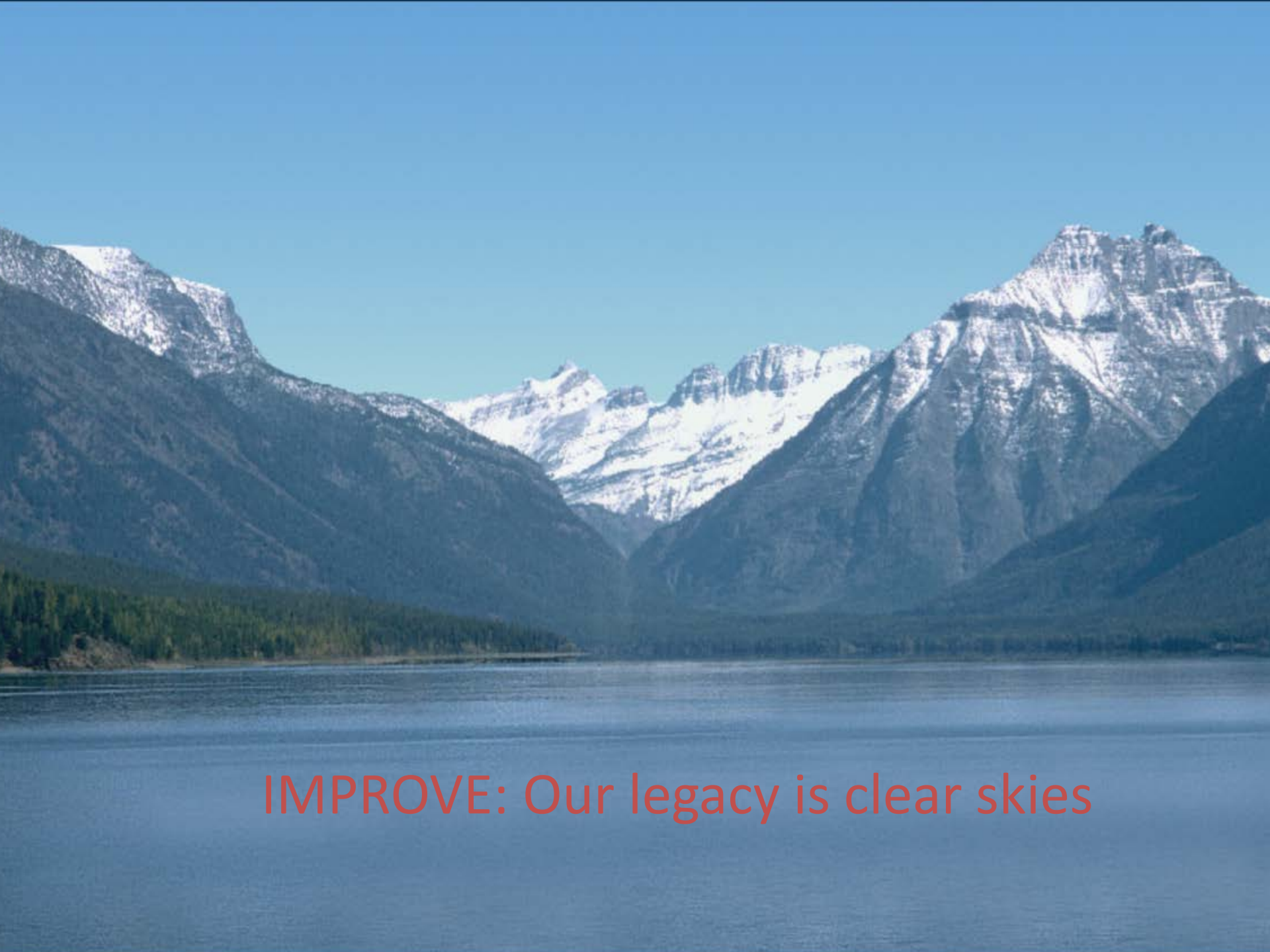
Ratios of Original and Reanalysis Concentrations

Great Smoky Mountains National Park



Trends based on Reanalysis versus Original Results





IMPROVE: Our legacy is clear skies