IMPROVE Aerosol Measurements: Overview and Updates

Nicole P. Hyslop
University of California, Davis

National Ambient Air Monitoring Conference
St. Louis, MO
August 10, 2016

IMPROVE Network

- Interagency Monitoring of Protected Visual Environments
- 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

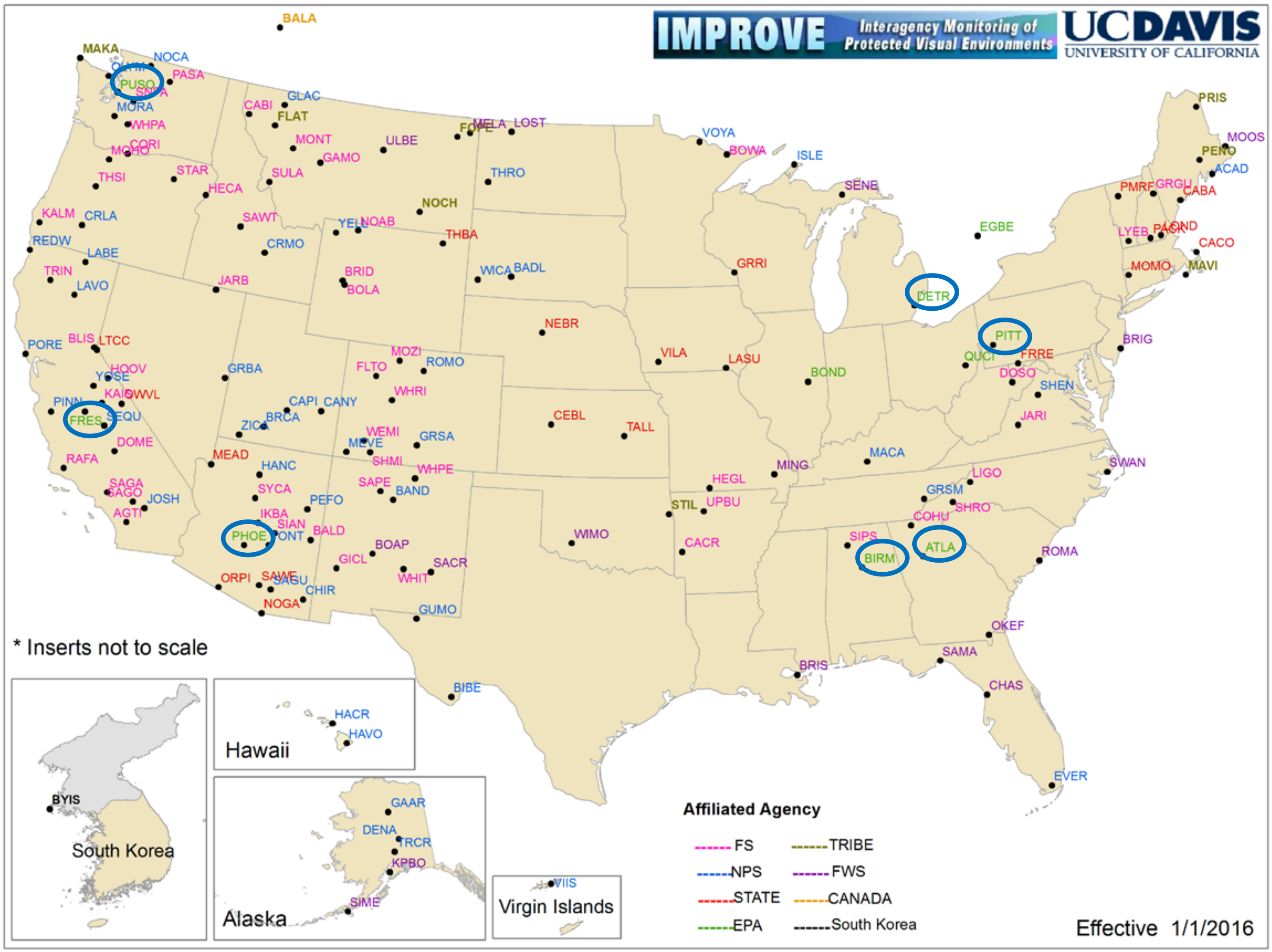
- U.S. Environmental Protection Agency
- U.S. National Park Service
- U.S. Forest Service
- U.S. Fish & Wildlife Service
- Various State Governments & Tribes
- Environment Canada
- South Korea Ministry of Environment

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.

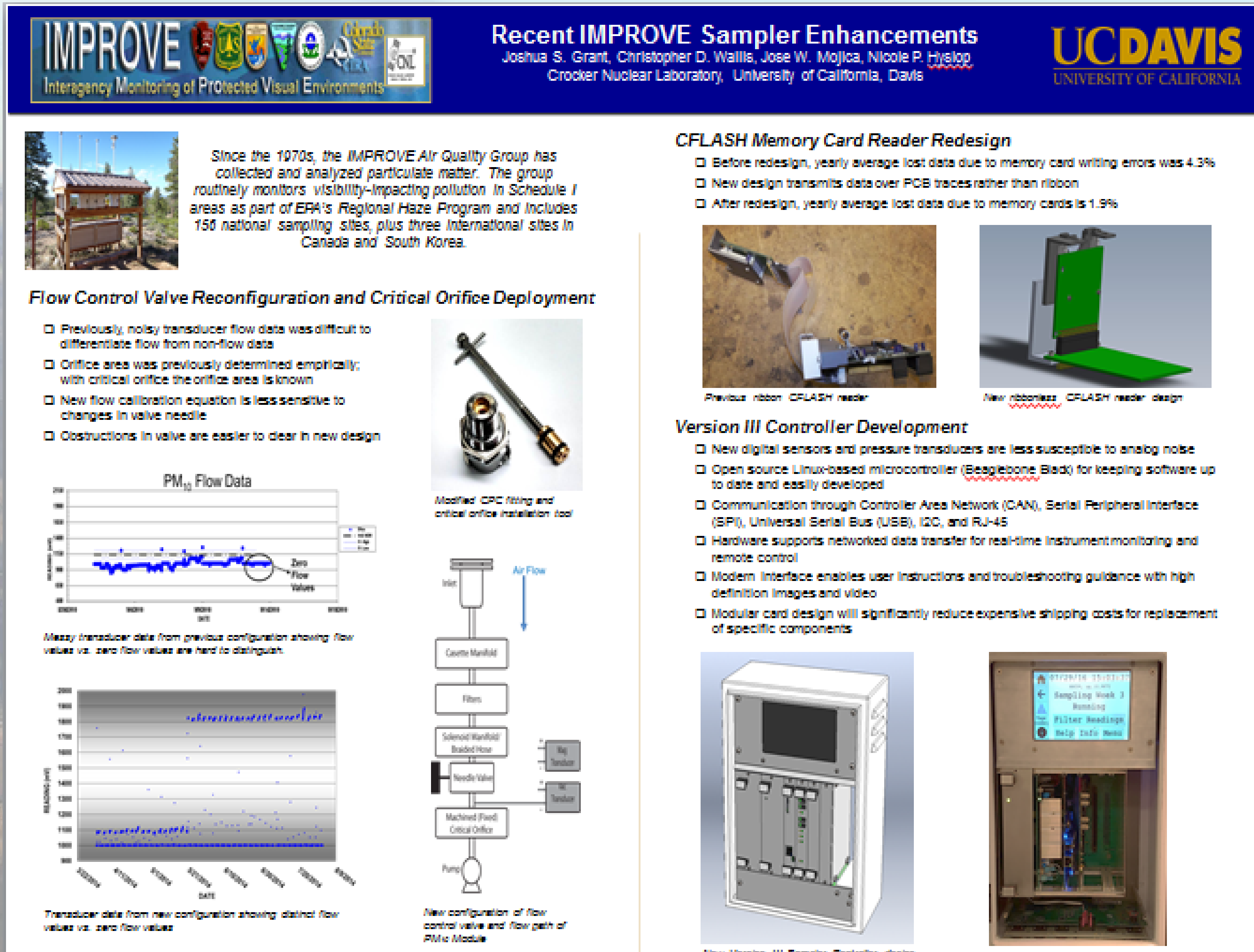
Sites collocated with CSN samplers circled in blue.



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
  - PM_{10} Teflo® PTFE filter analyzed by gravimetry by UCD

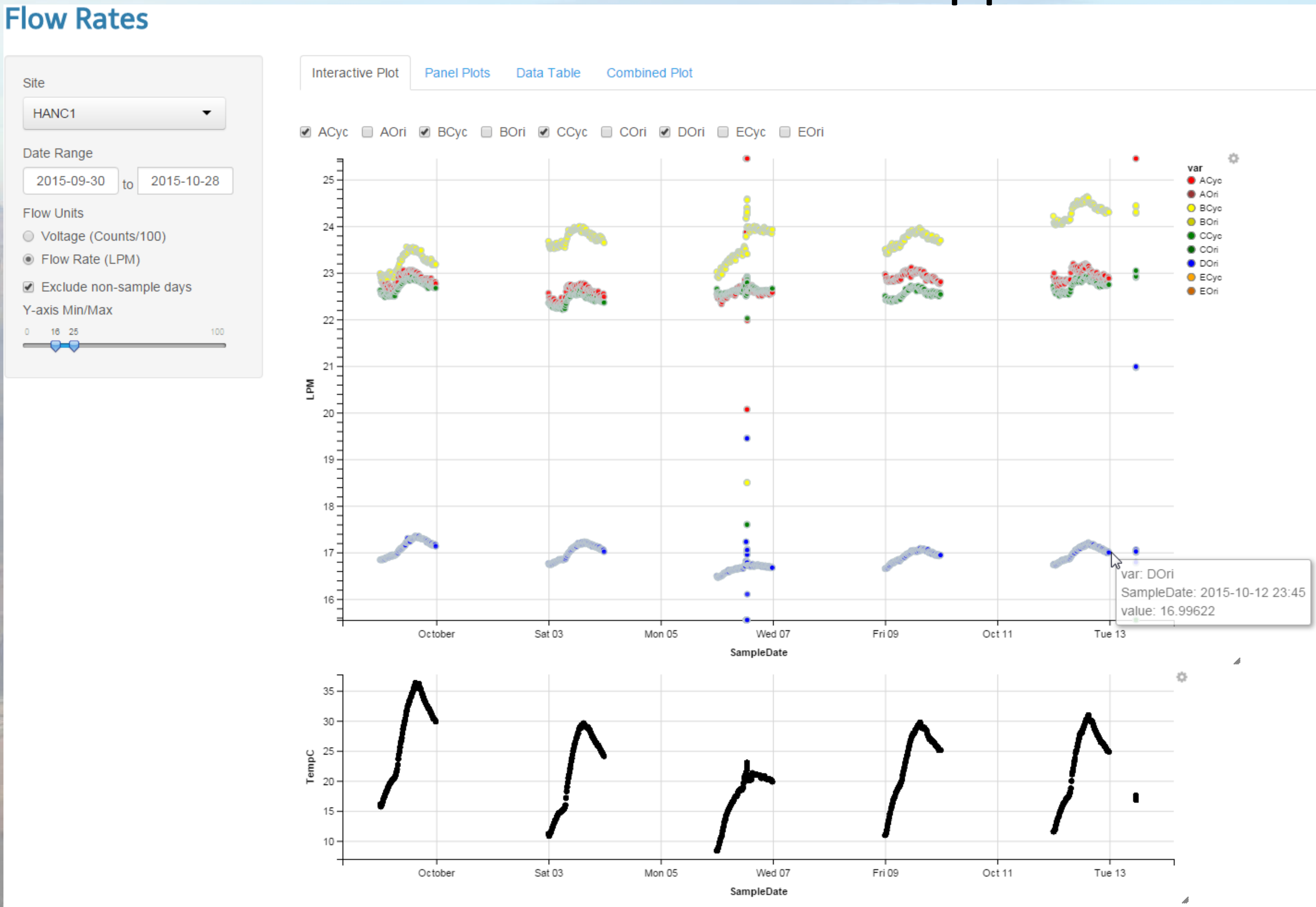
Visit Our Poster!



Data Validation and Analysis

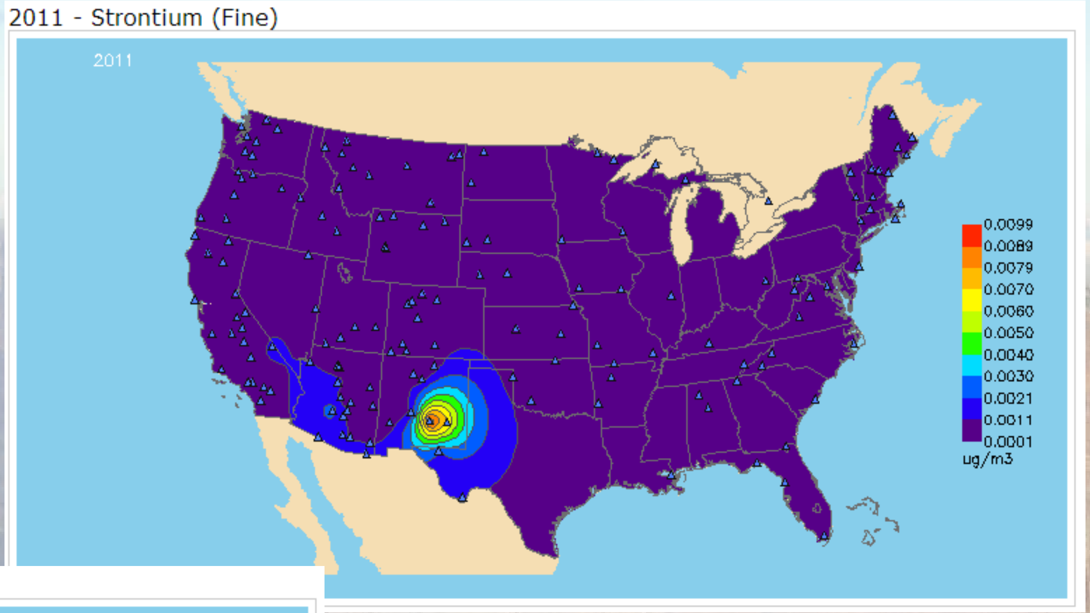
- UC-Davis performs data validation for entire network
- Review flow rates immediately upon data receipt
- Review data from different perspectives (space, time) to identify contamination, interferences, patterns, and trends

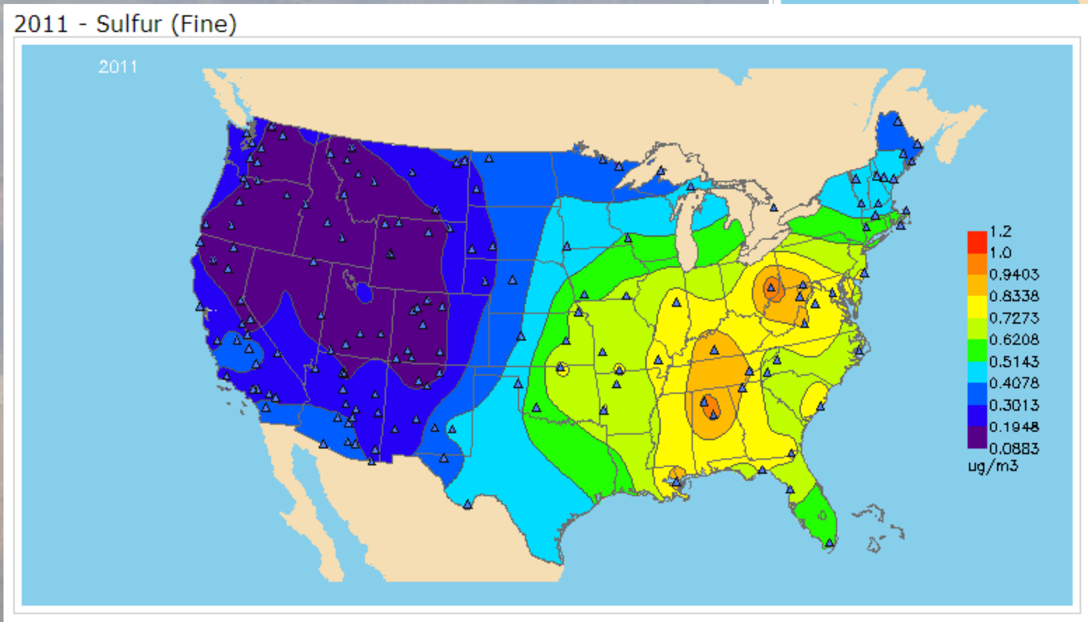
Data Visualization Web Apps



Spatial Context Important for Validation

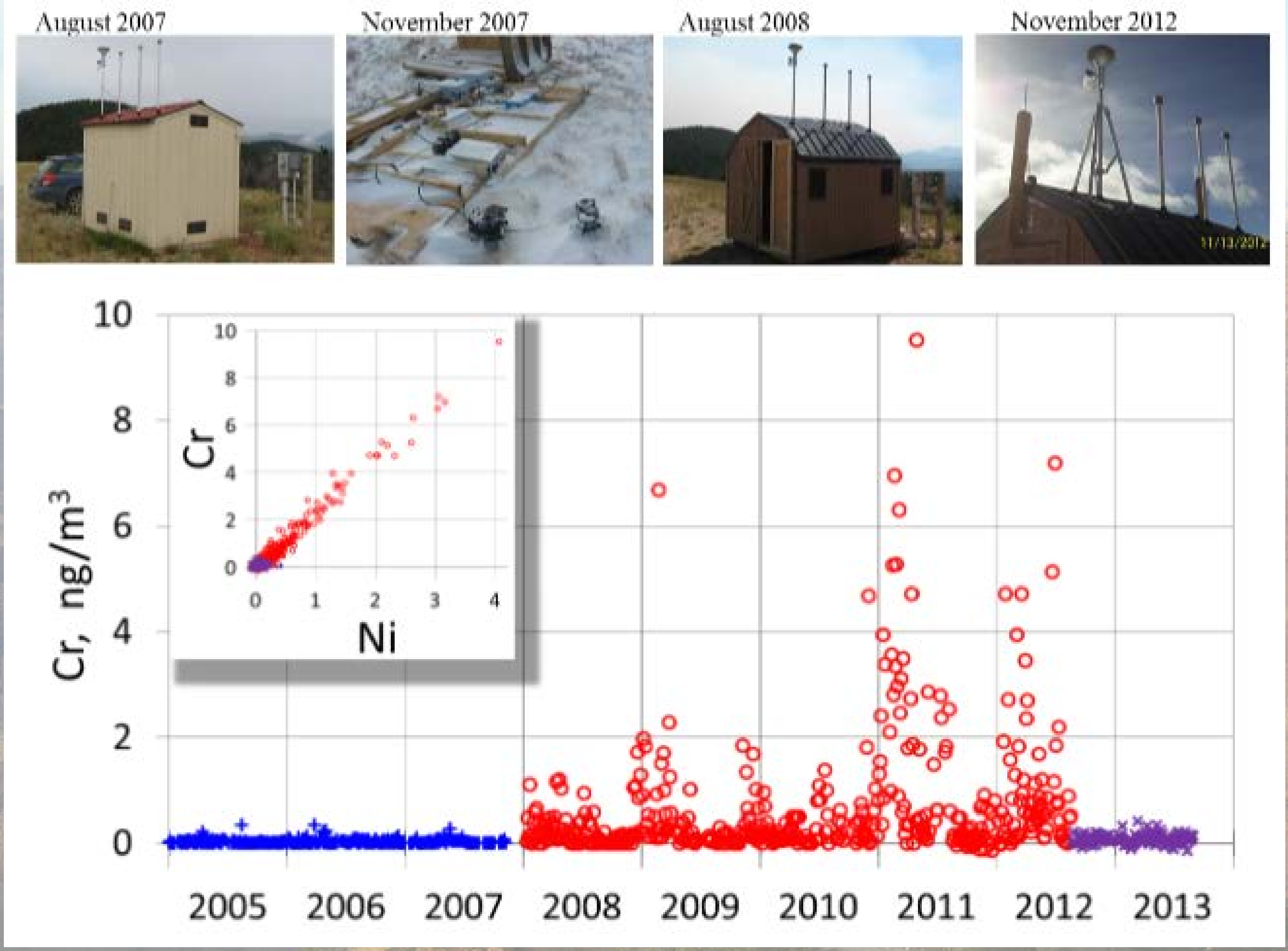
- Contour maps of annual average $PM_{2.5}$ Sr (right) and S (below) concentrations





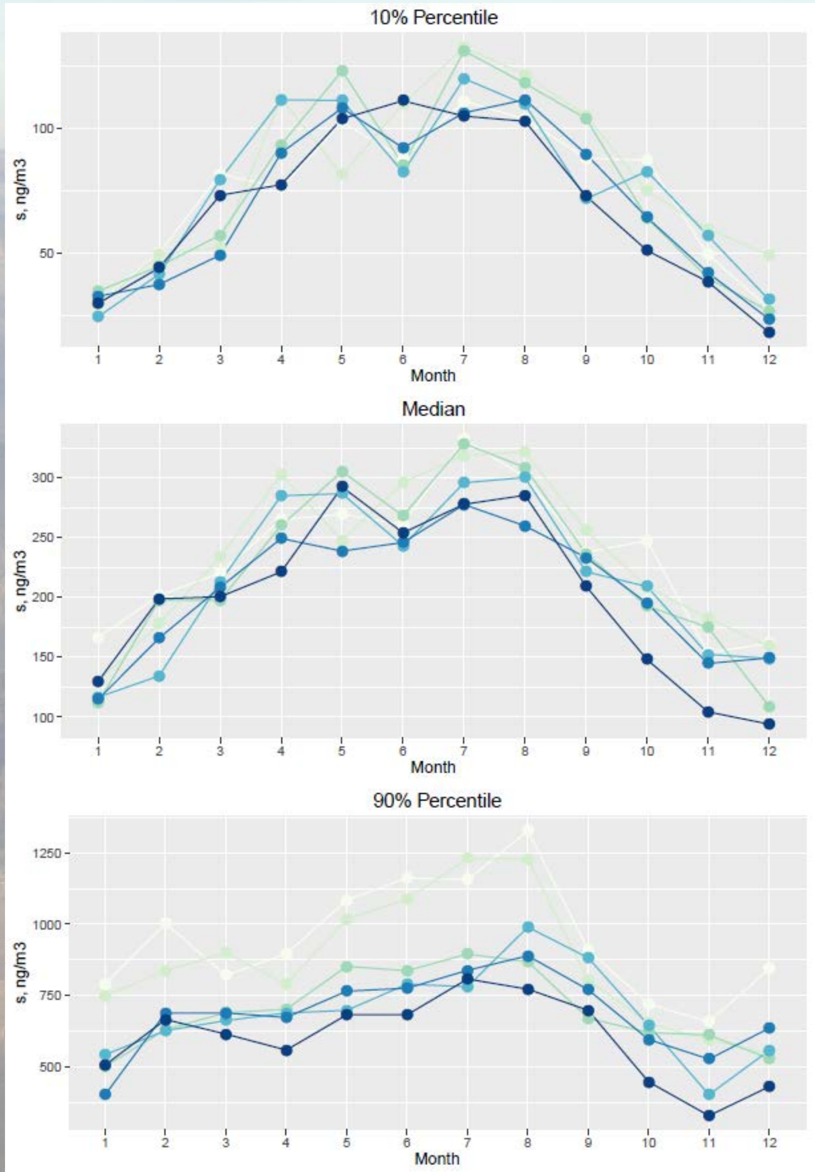
- Dots represent sites
- Sometimes we discover unique sources of trace elements

Sometimes we identify contamination

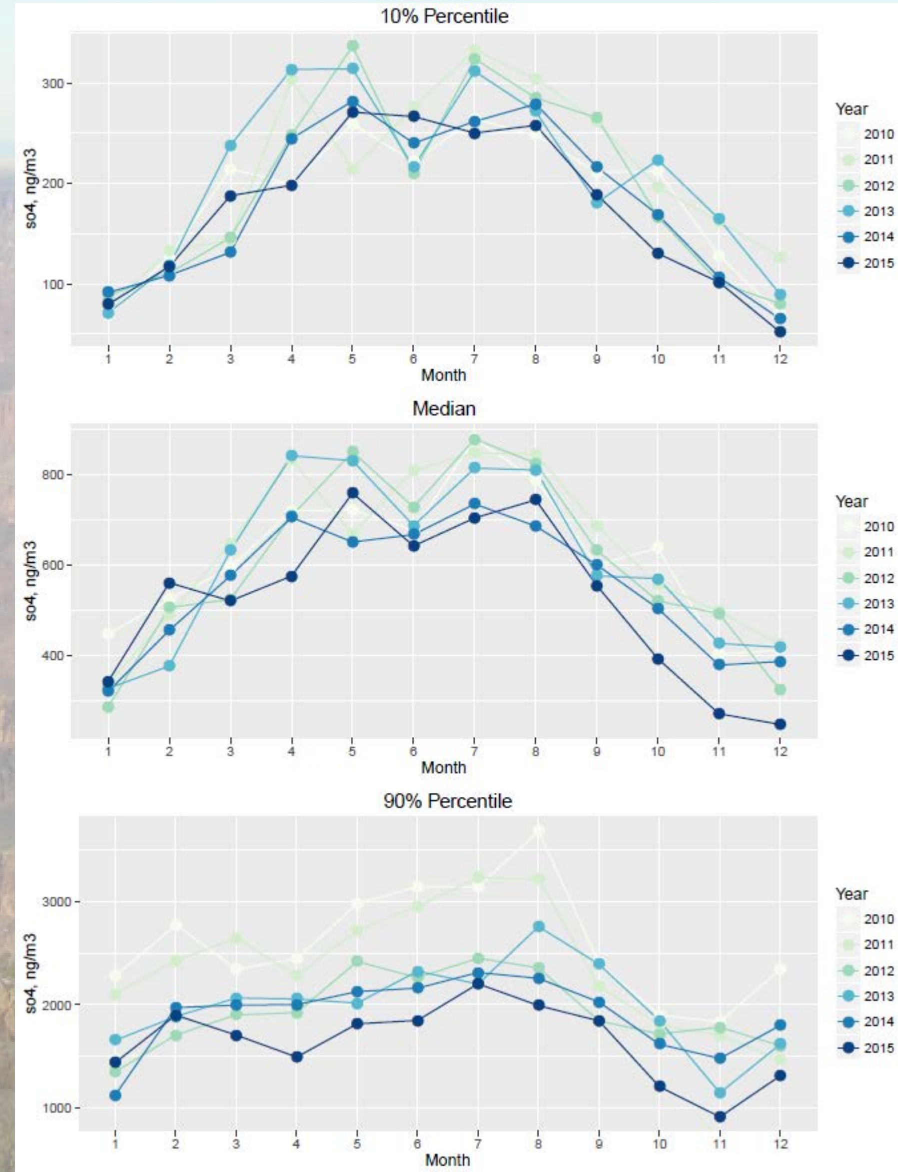


Data Validation Across Years

Sulfur by XRF



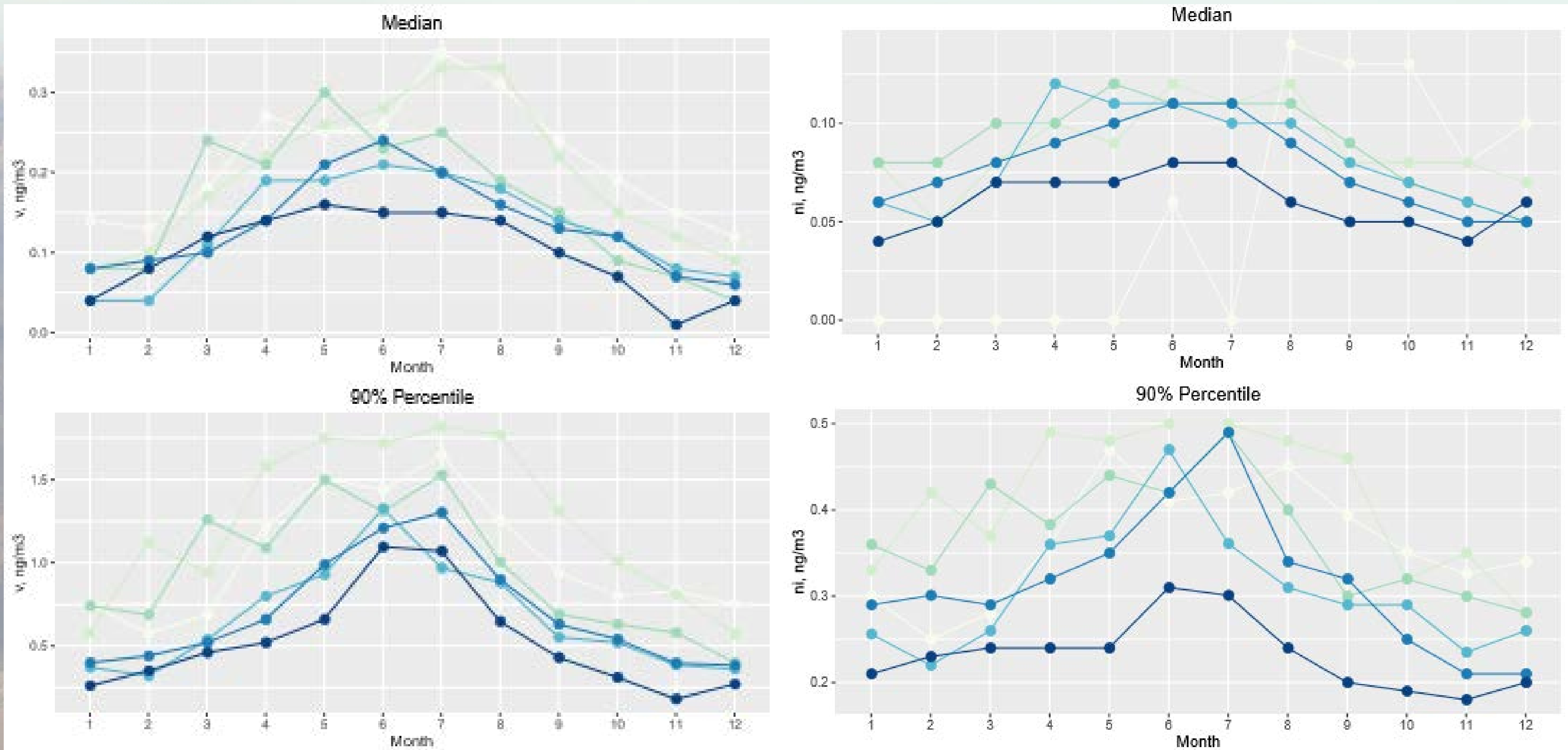
Sulfate by IC



Sometimes we find trends in atmosphere!

Vanadium

Nickel



- Nickel and vanadium are tracers for bunker fuel

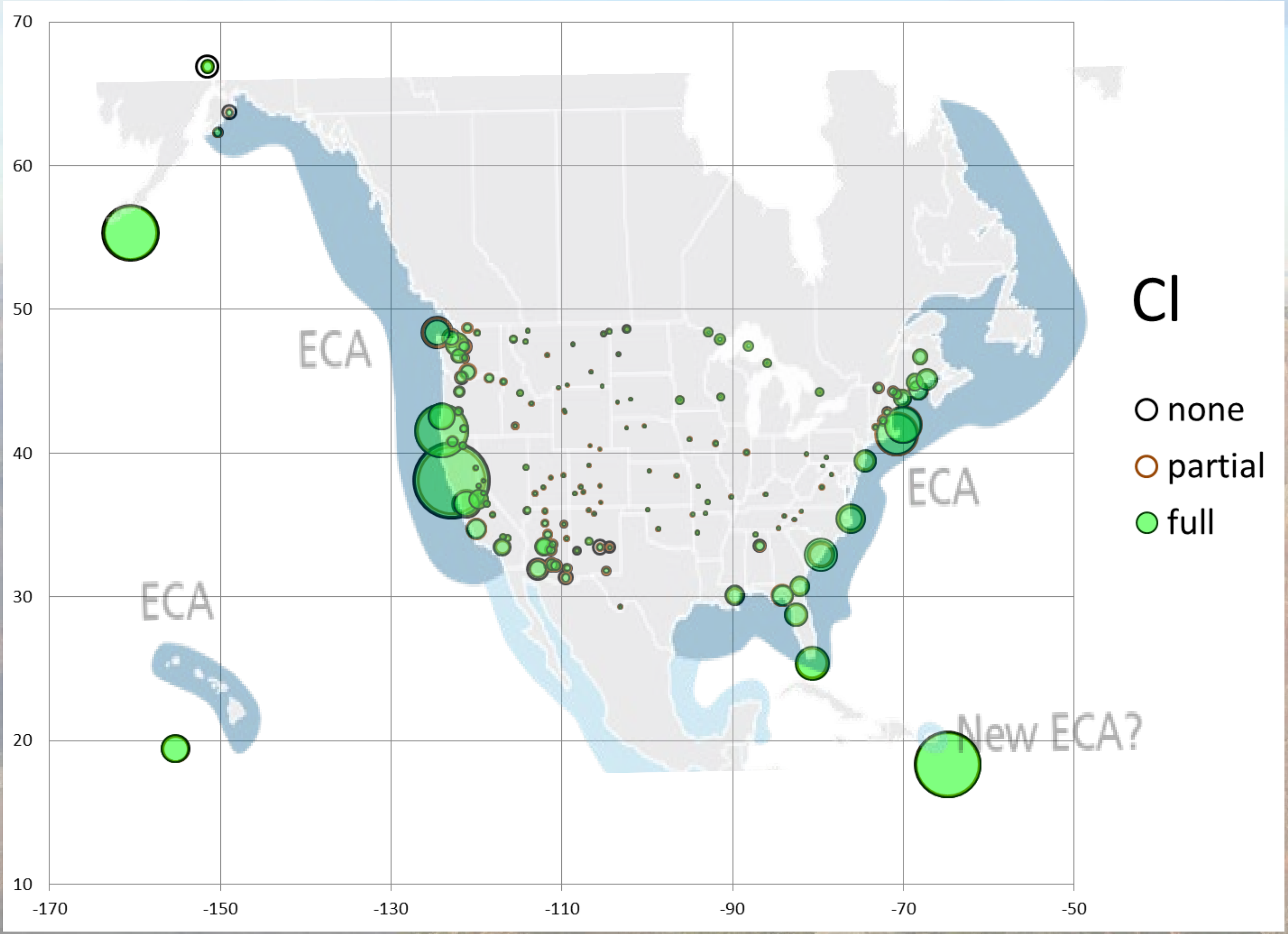
From http://www.turnermason.com/index.php/all-in-the-family-what-is-happening-with-the-bunkers/

Table 1

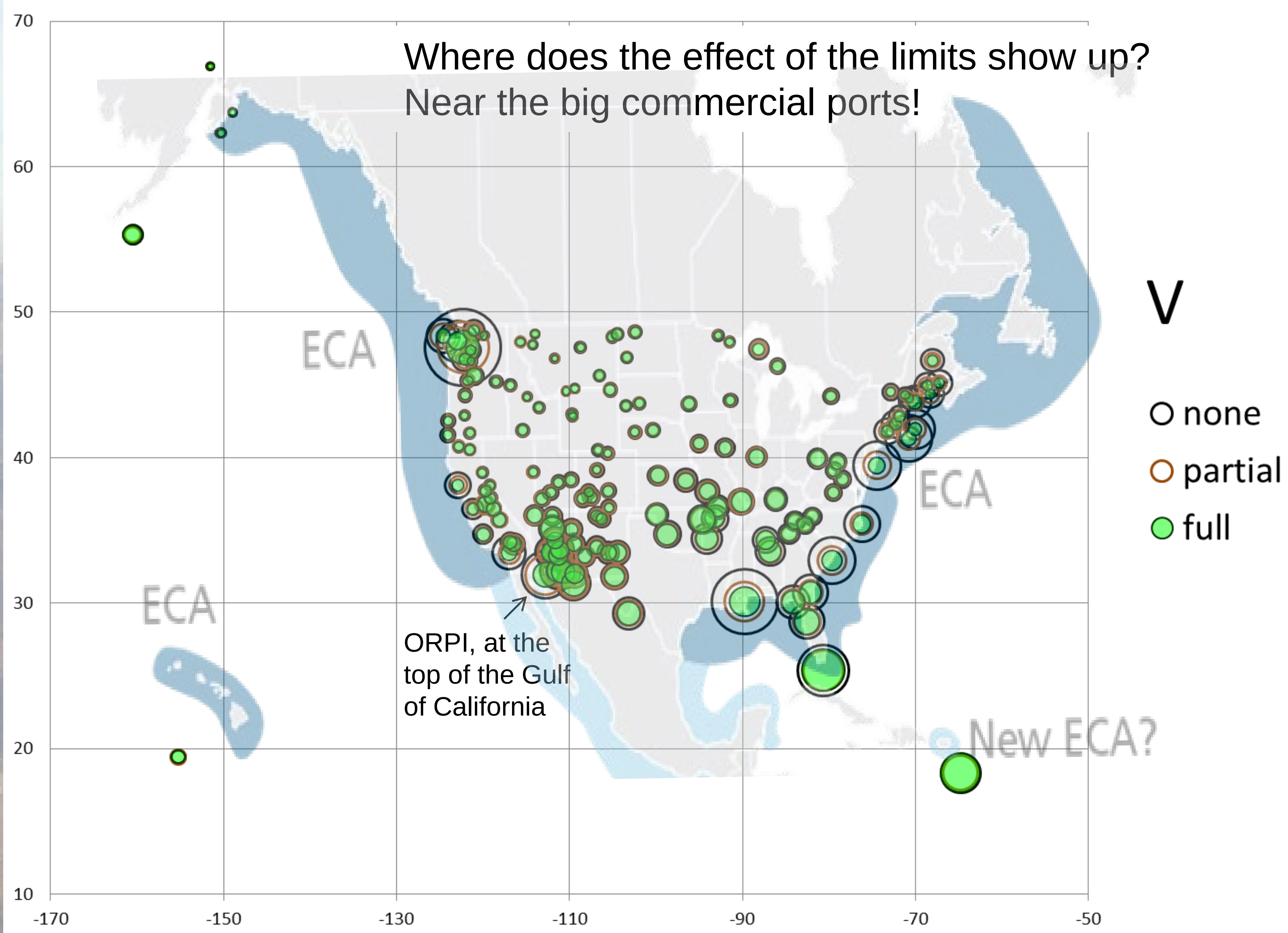
Bunker Fuel Regulations		
Outside an ECA established to limit SOx and particulate matter emissions	**Inside an ECA established to limit SOx and particulate matter emissions**	**ARB's California OGV Fuel Requirement Percent Sulfur Content Limit**
4.50% sulfur prior to January 1, 2012	1.50% sulfur prior 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 January1, 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.



Cl
none
partial
full
ECA
ECA
ECA
New ECA?
70
60
50
40
30
20
10
-170
-150
-130
-110
-90
-70
-50

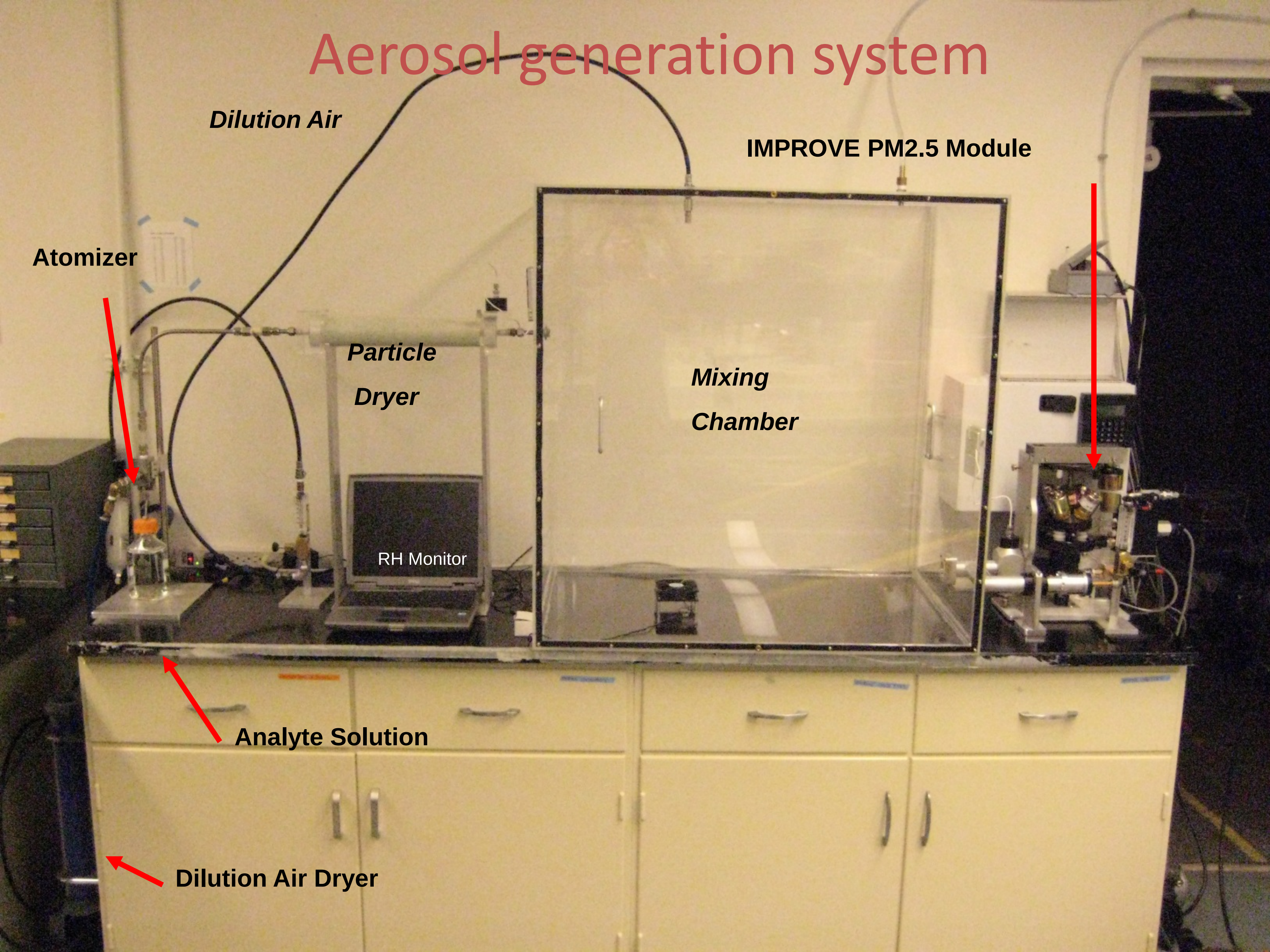


Where does the effect of the limits show up?
Near the big commercial ports!
ECA
ECA
ECA
New ECA?
ORPI, at the top of the Gulf of California
V
none
partial
full
70
60
50
40
30
20
10
-170
-150
-130
-110
-90
-70
-50

IMPROVE Reinvestment and Data Analysis

Investigations can lead to better understanding and improvements of the measurements

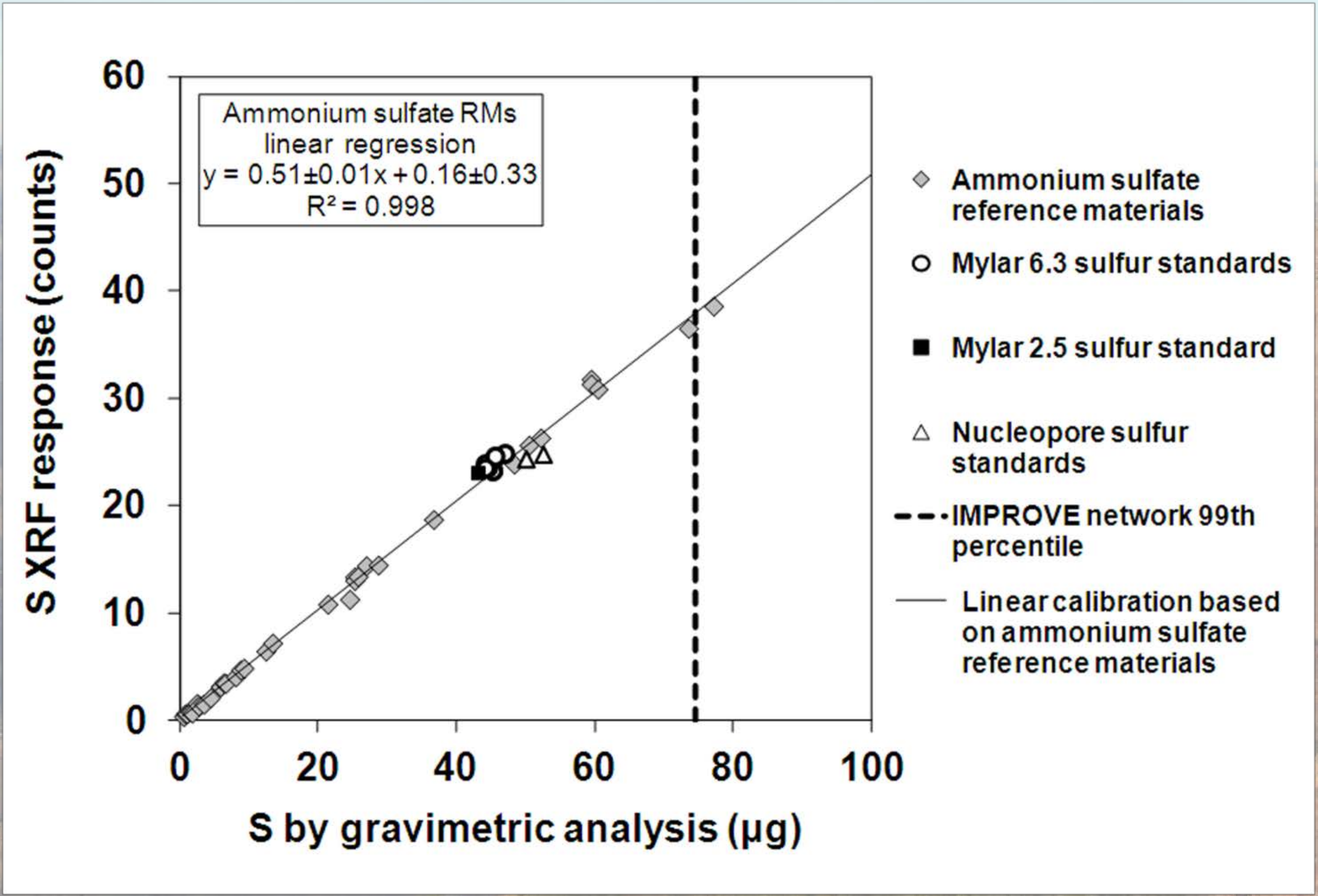
Aerosol generation system



Creating XRF Calibration Reference Filters

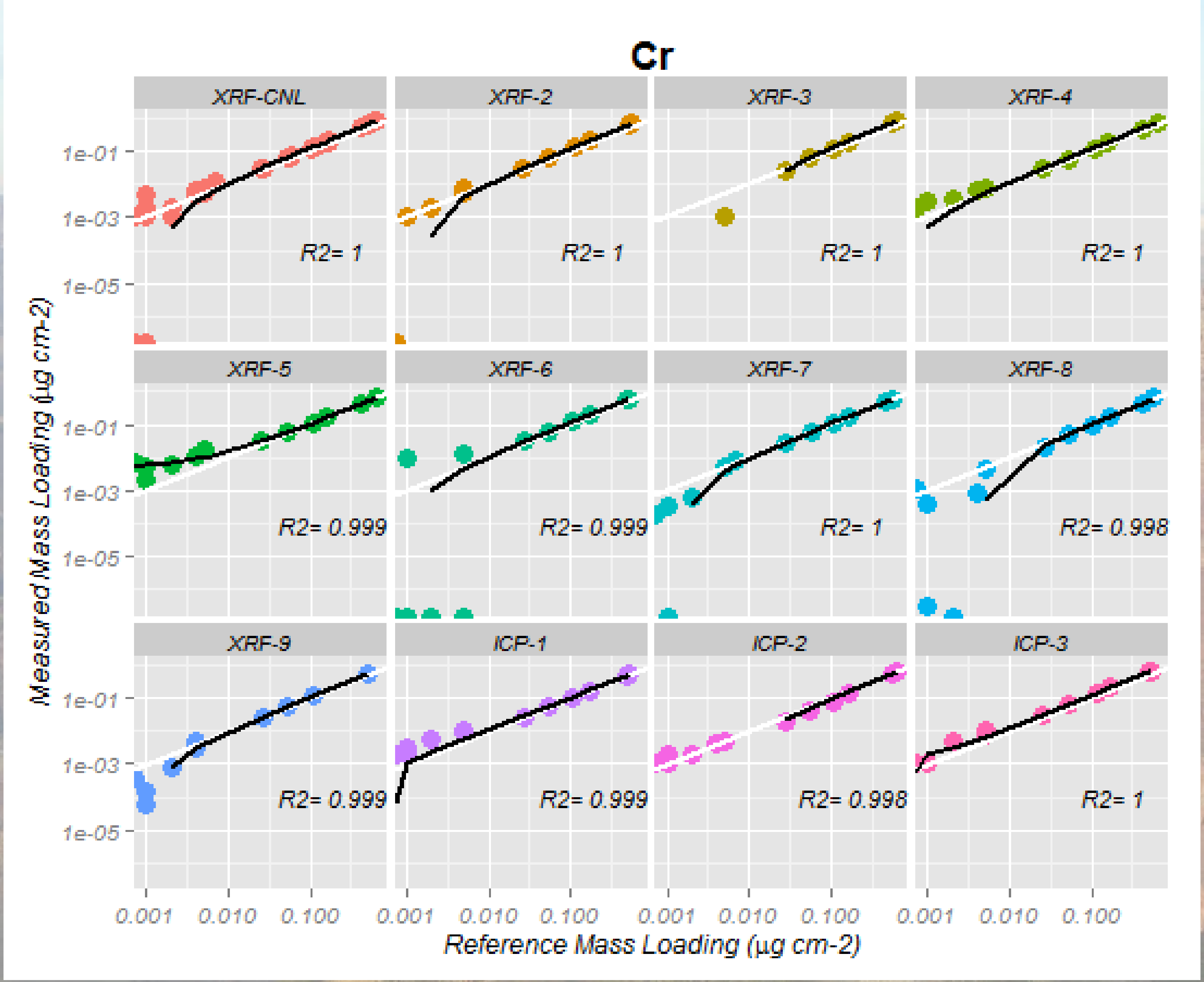
- Reference filters prepared using IMPROVE or Partisol® sampler
- Provides reference filters at relevant concentrations
- XRF benchmark independent of Micromatter Inc. (commercially available) standards
- Single-compound reference filters for S, Na, Cl, Pb, and K are used in current UC-Davis XRF calibrations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

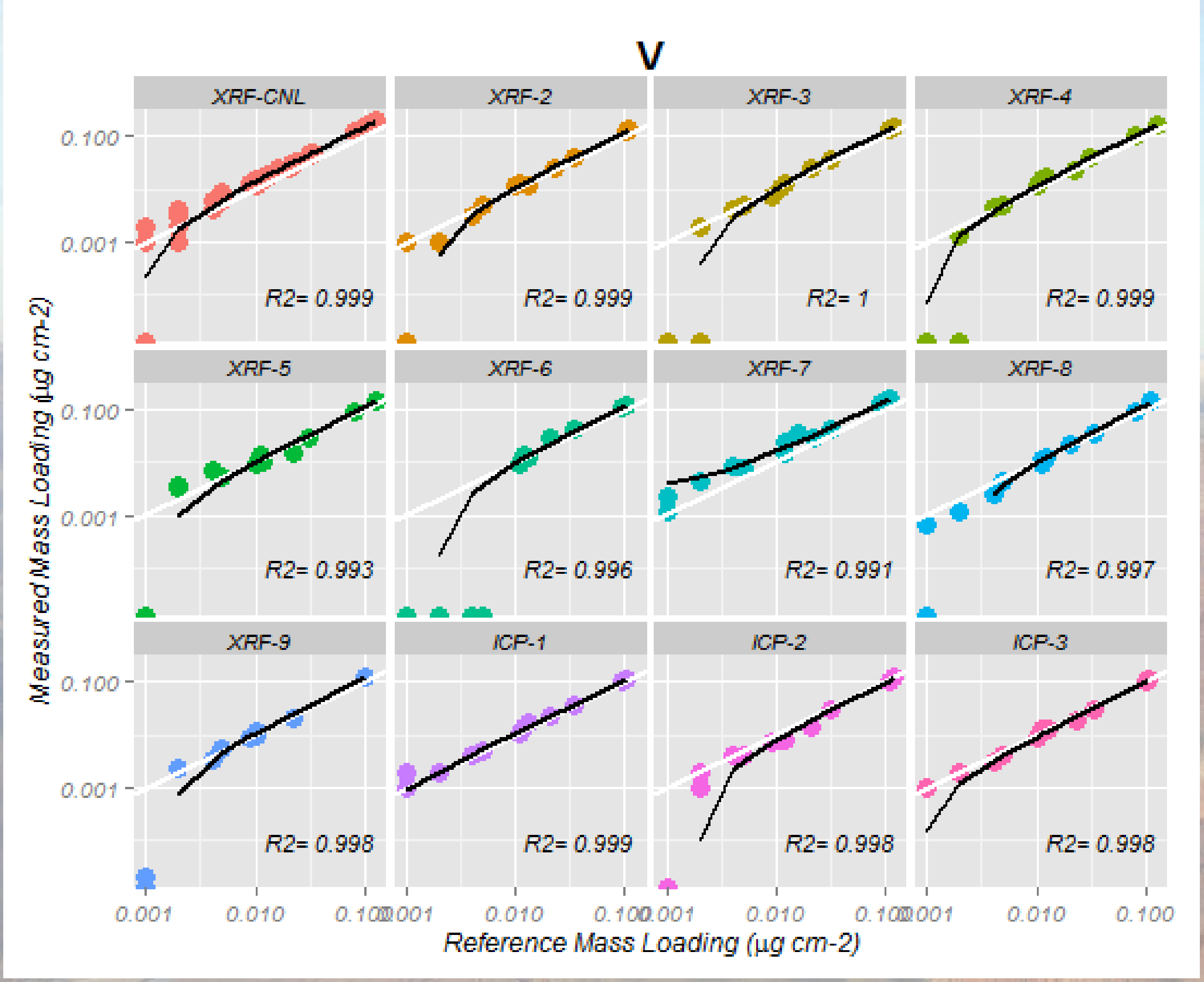
Sulfur Reference Filters



Indresand, H.; White, W. H.; Trzepla, K.; Dillner, A. M. *X-Ray Spectrometry* **2013**. doi: 10.1002/xrs.2456.

Multi-Element Reference Filters Analyzed by 12 Labs





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

Visit Our Poster!

IMPROVE
Interagency Monitoring of Protected Visual Environments

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

Krystyna Trzepla, Sinan Yatkin, Warren White, Nicole Hyslop
Crocker Nuclear Laboratory, University of California, Davis, California, 95616, USA

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).

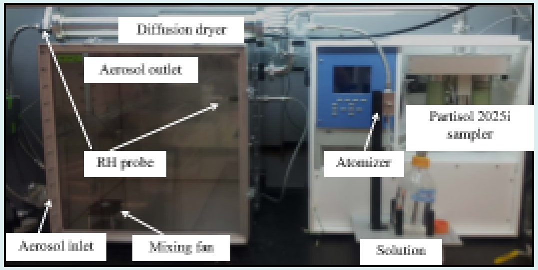


Fig.1. *The aerosol generation and sampling system*

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, $C_{K,UCD\text{-}EDXRF}$ (Epsilon 5, Panalytical Inc, the Netherlands) is accurate to be <10%. These assumptions resulted in estimated uncertainties below 10%.

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

Data Evaluation:

1. Agreement between certified loadings of SE-RMs and EDXRF: Linear regression, bias and En number (ISO/IEC 17043, 2010):
   U:Expanded uncertainty by GUM (2008)

$$En = \frac{|C_{EDXRF} - C_{cer}|}{\sqrt{U^2_{C(EDXRF)} + U^2_{C(cer)}}}$$

When En ≤1, C_{EDXRF} and C_{cer} are equivalent

2. Linear regression between reference loading of ME-RMs (x) and lab (y),
3. z-score (ISO 13528:2005): Loadings in µg/cm² converted to µg/g for 12 ME-RMs in interlaboratory comparison
   $\bar{C}$: outlier-excluded mean
   $\hat{\sigma}$: outlier-excluded standard deviation

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

For good interlaboratory comparability, |z≤3|

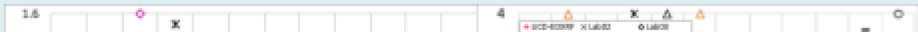
Results and Discussion

- 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 spun the range of both networks (Fig.2-Right).

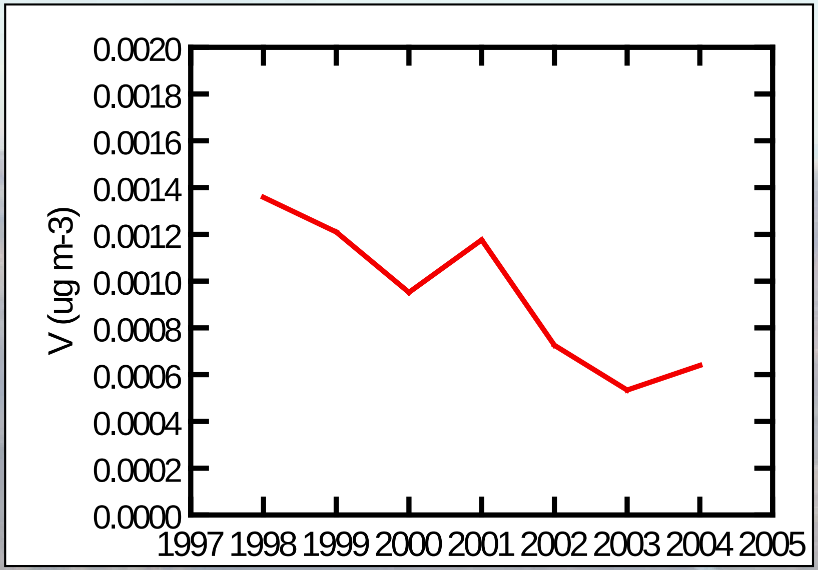
Interlaboratory Comparison of ME-RMs

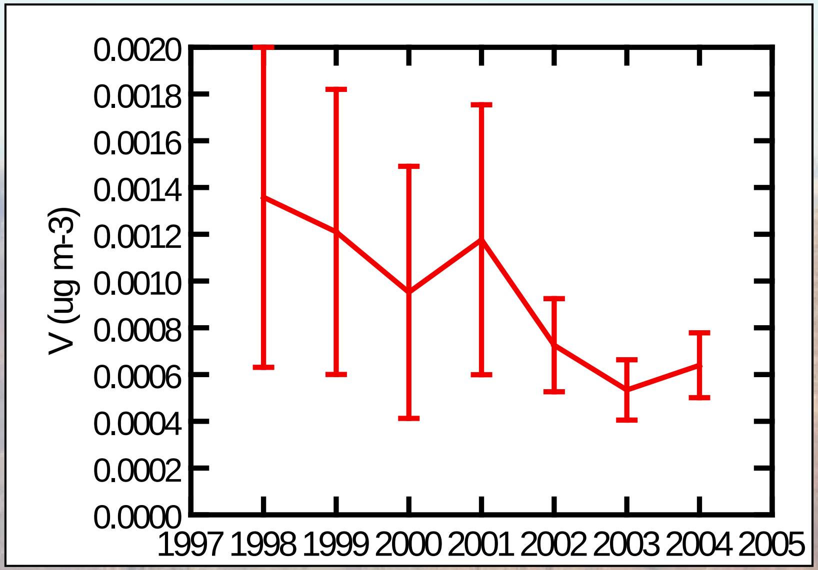
An interlaboratory comparison study of ME-RMs were conducted with participation of 9 XRF and 3 ICP-MS laboratories

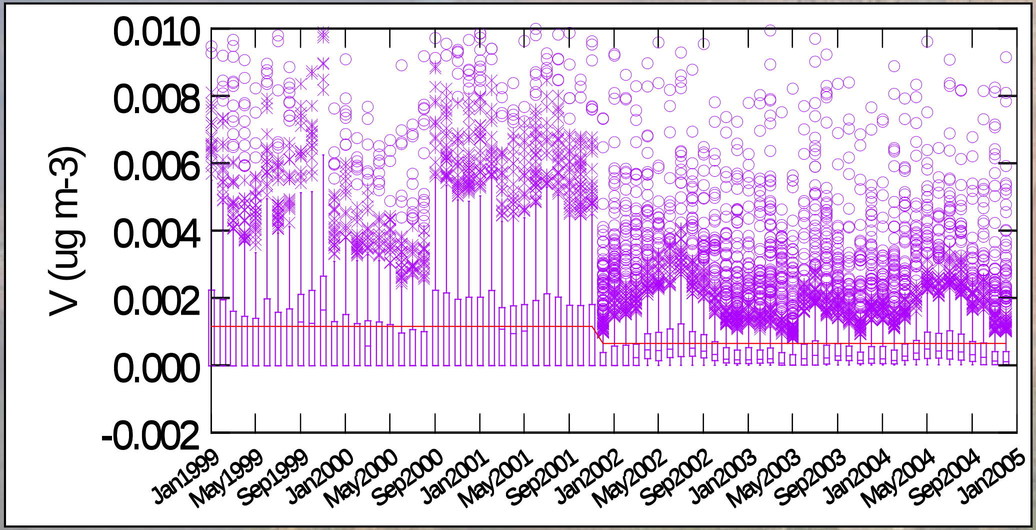
- The slopes of reference vs. labs are mostly within 20% of unity (R^2>0.95) (Fig.6)
- Participating labs are mostly in good agreement (|z≤3|) (Fig.7)



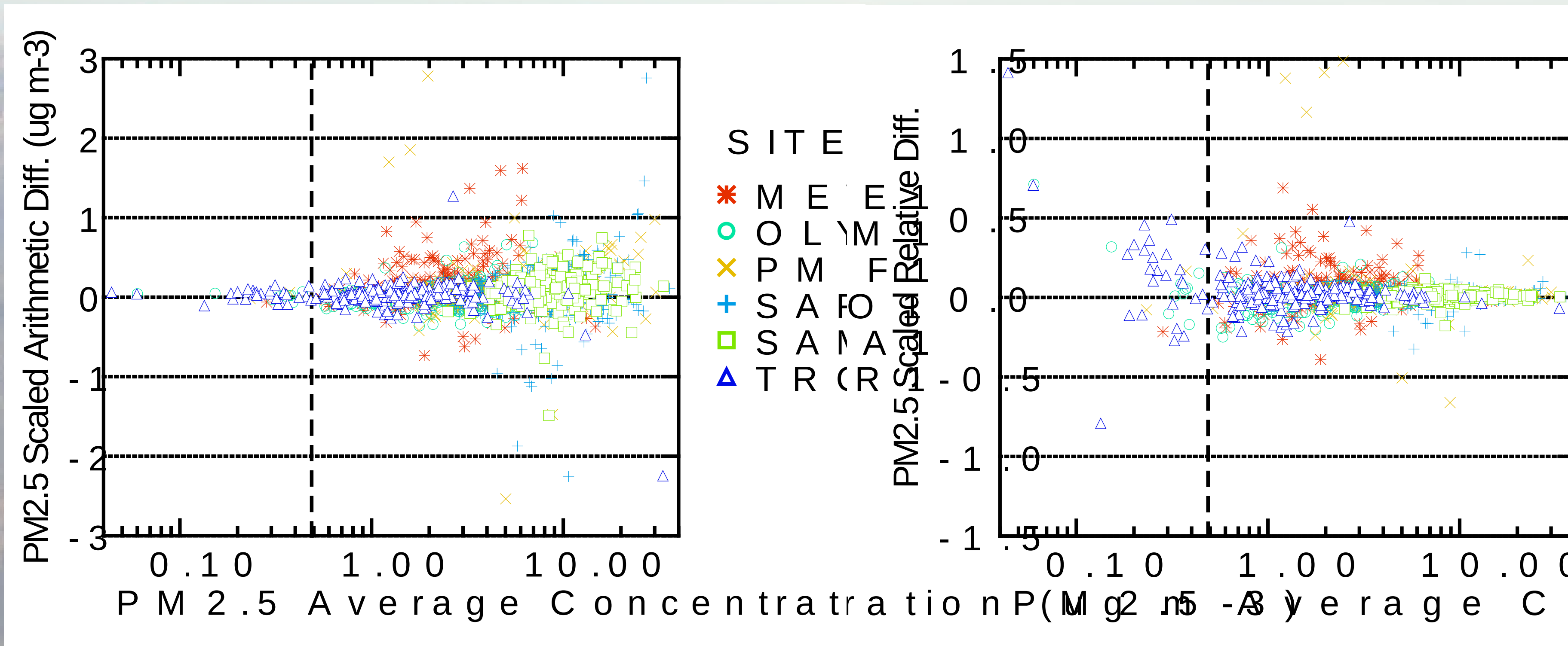
Different views, same data







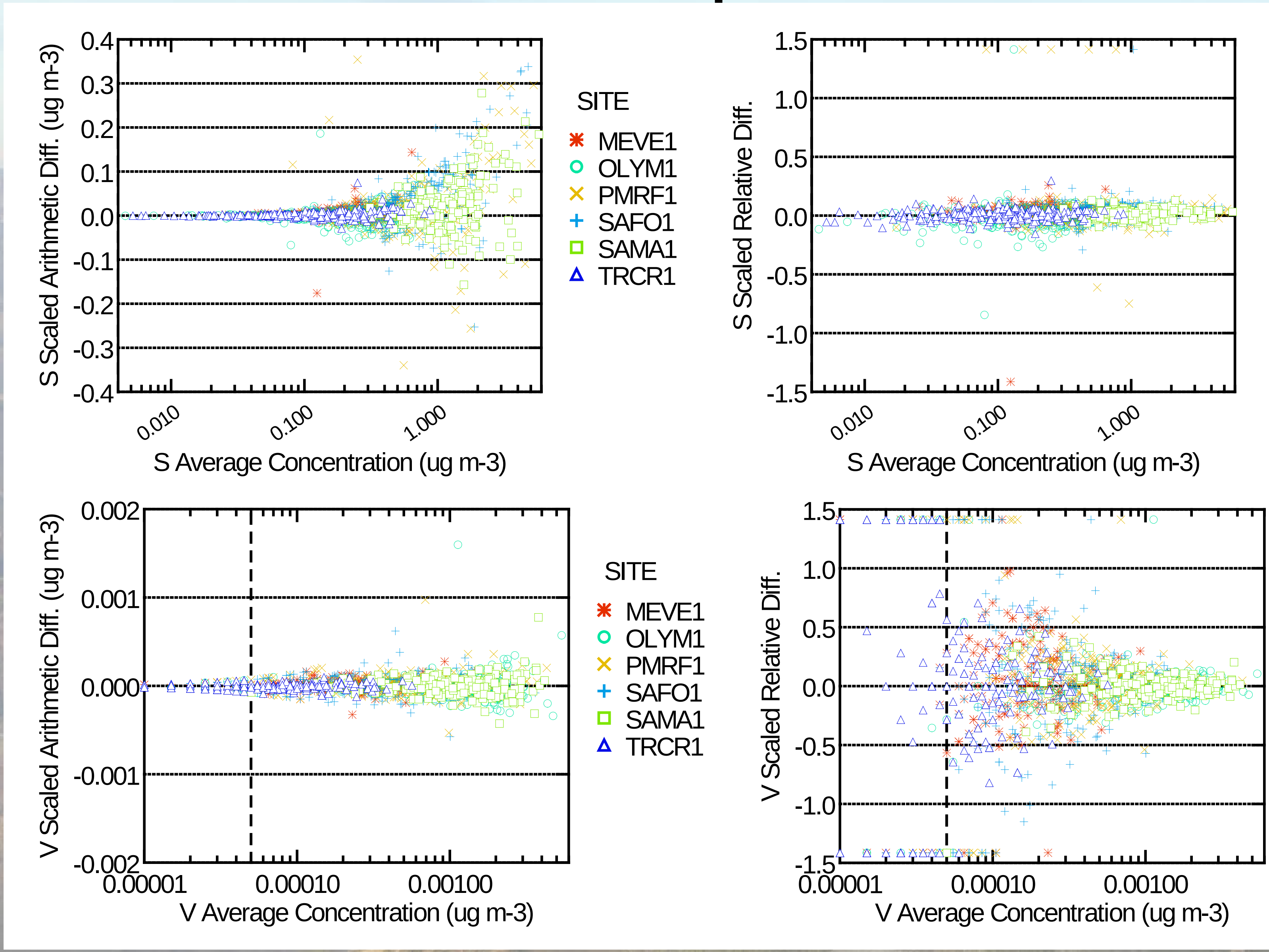
Collocated IMPROVE $PM_{2.5}$ Data



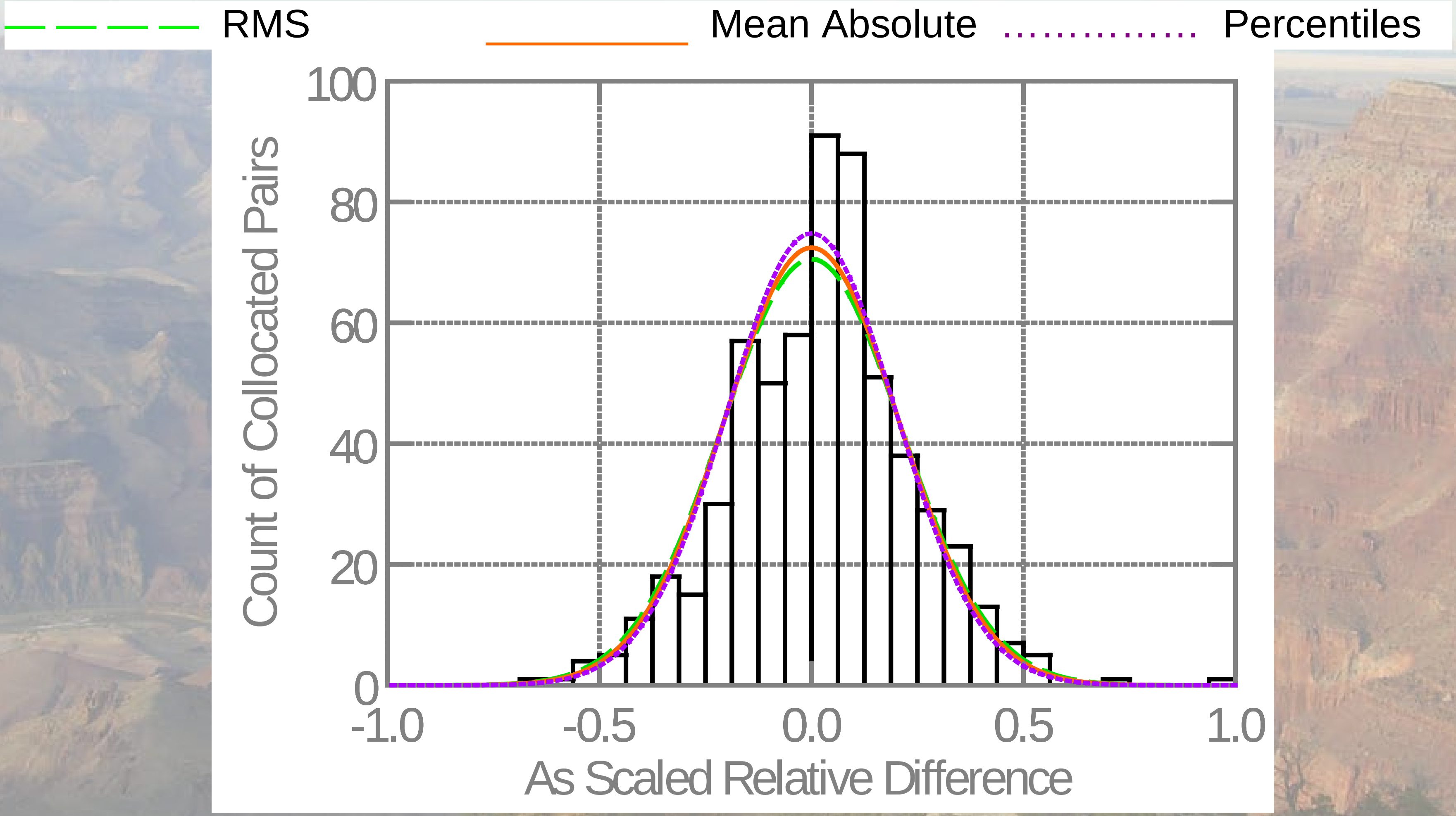
Scaled Arithmetic Difference $= \frac{C_1 - C_2}{\sqrt{2}}$

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

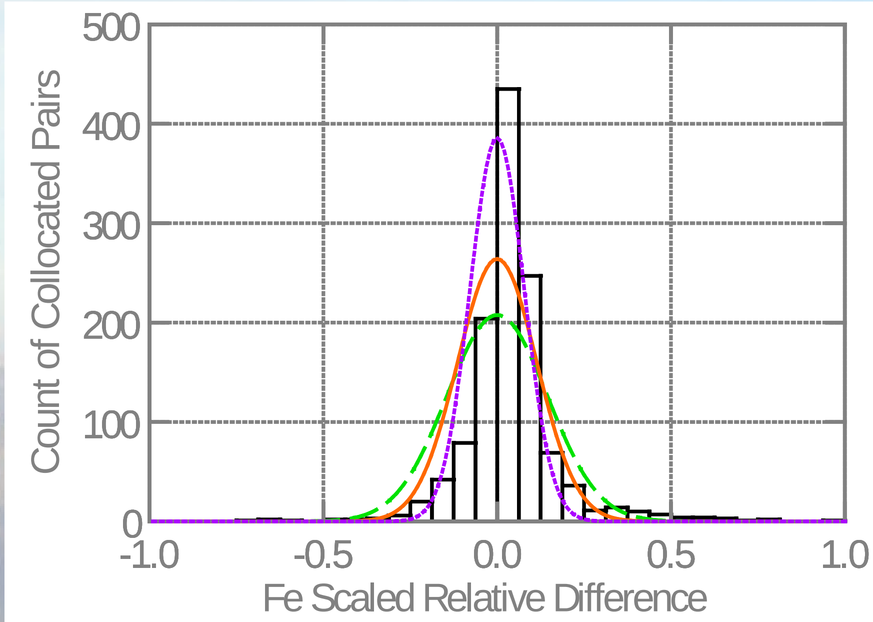
Additive and Multiplicative Errors

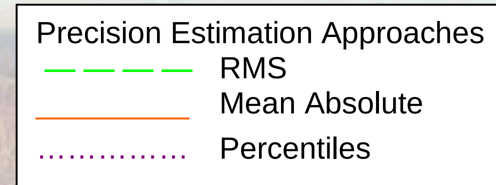


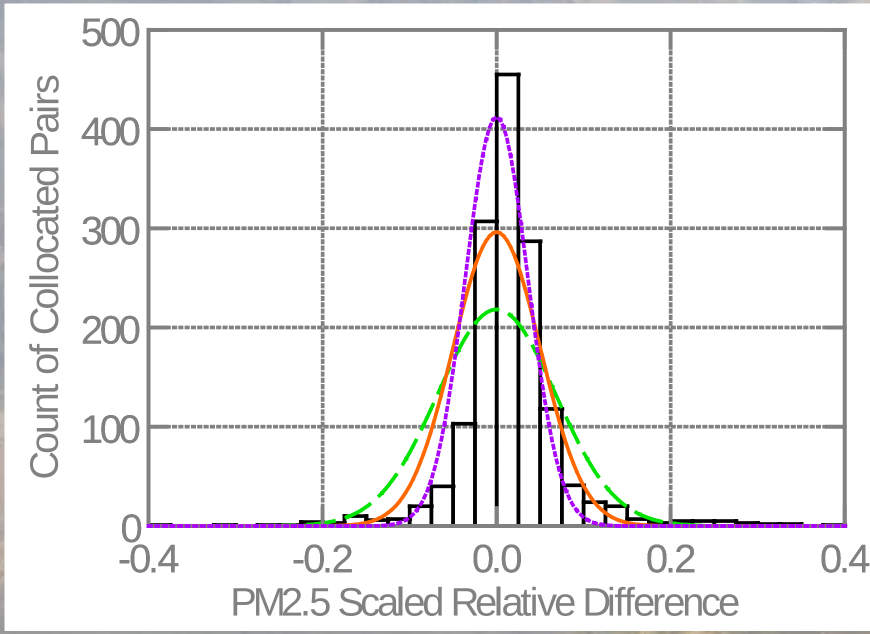
Distribution of Differences and Precision Estimates

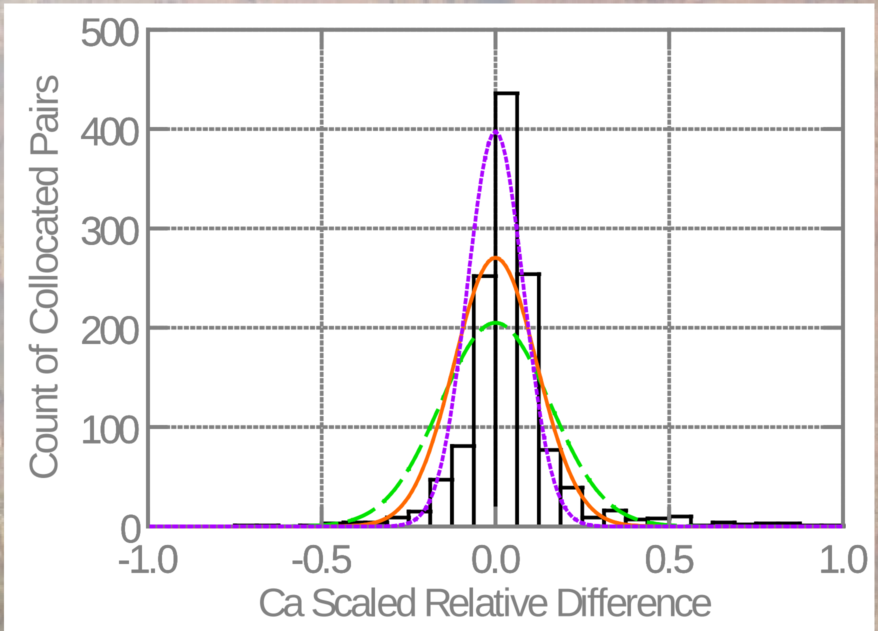


Errors: often not normally distributed



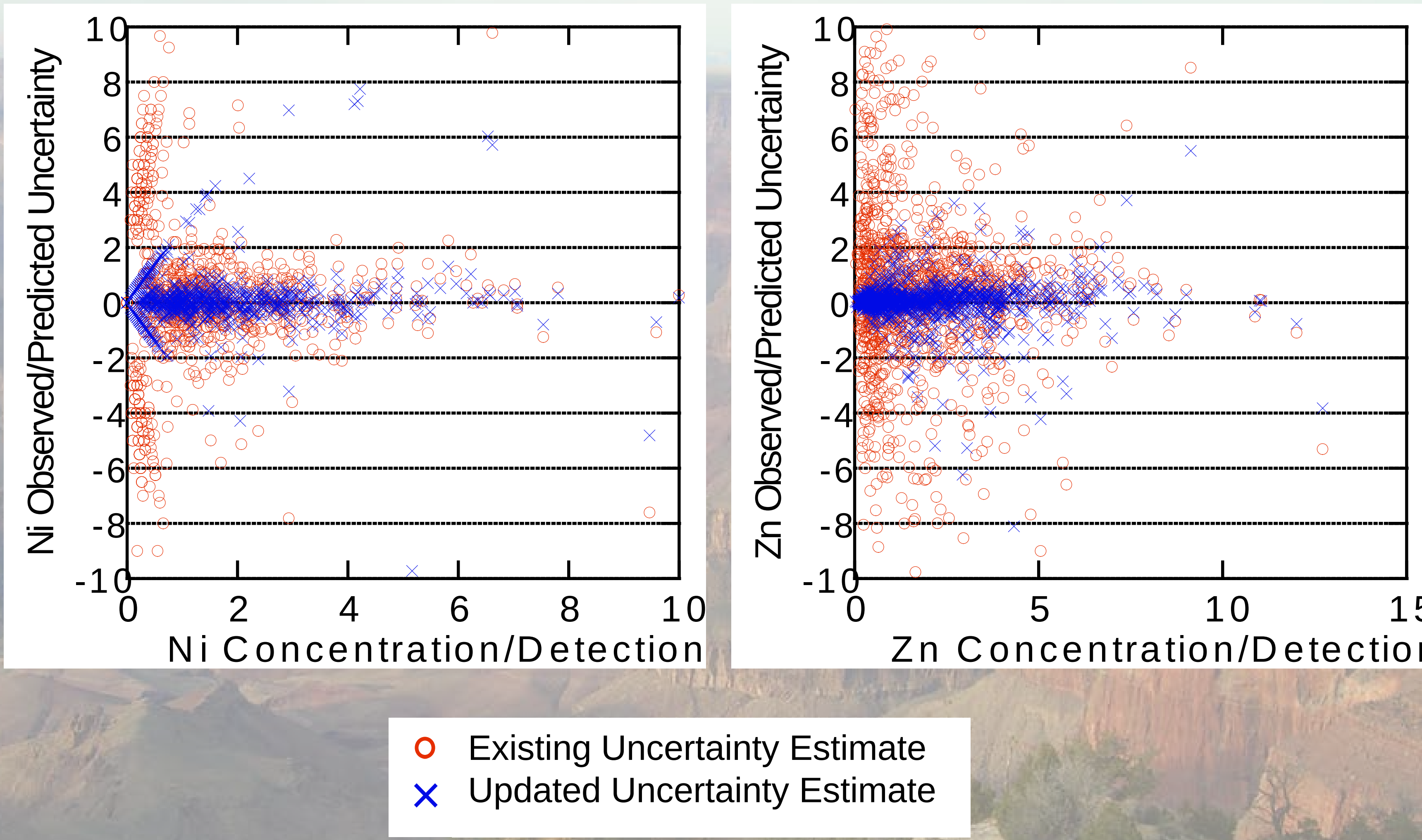






Updated Uncertainty Estimates

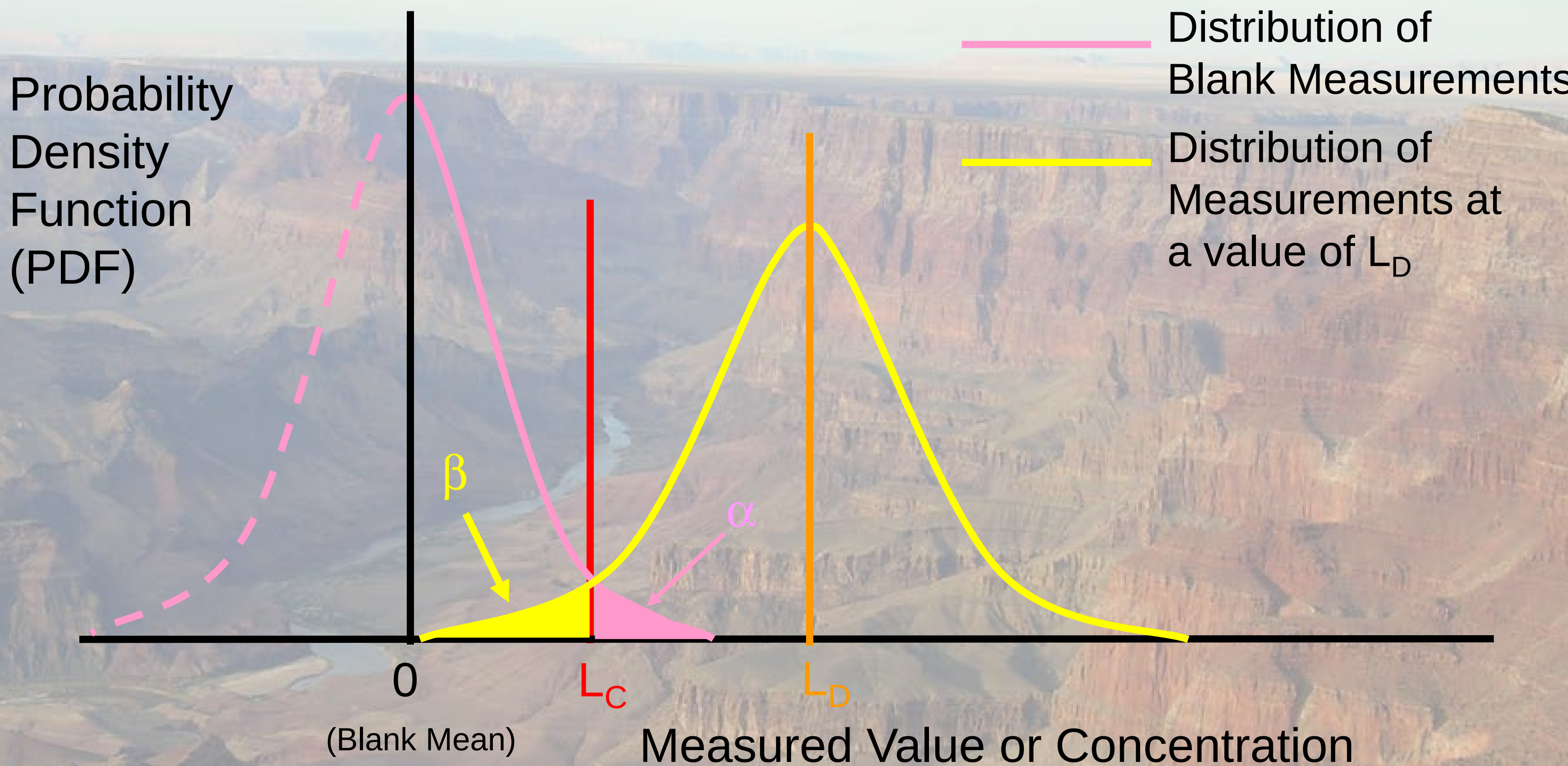
Notable Improvements in Some Elements



Limits of Detection

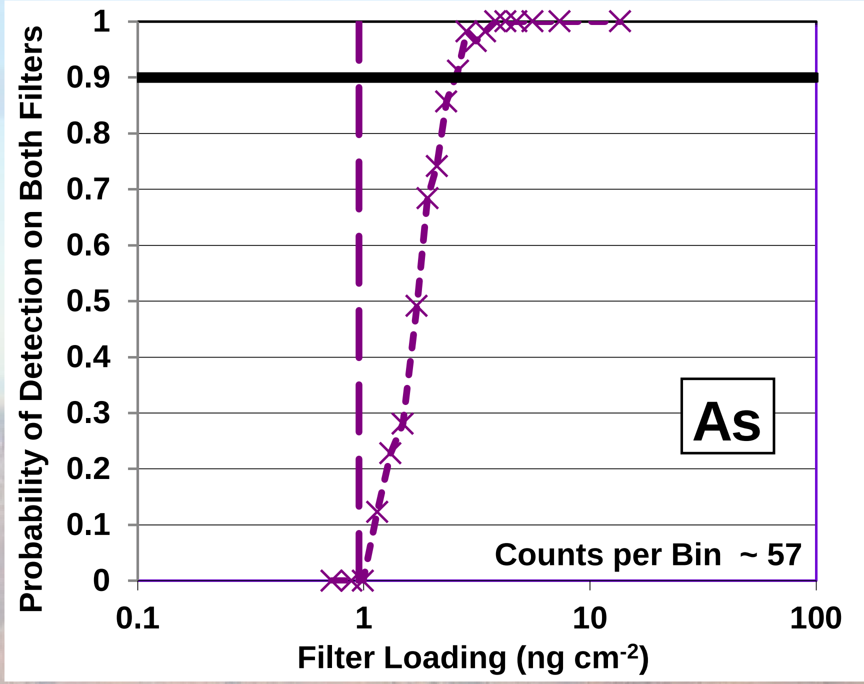
	Analyte is not present in sample	Analyte is present in sample
Analyte is measured	Type I error, L_C	Correct decision
Analyte is not measured	Correct decision	Type II error, L_D

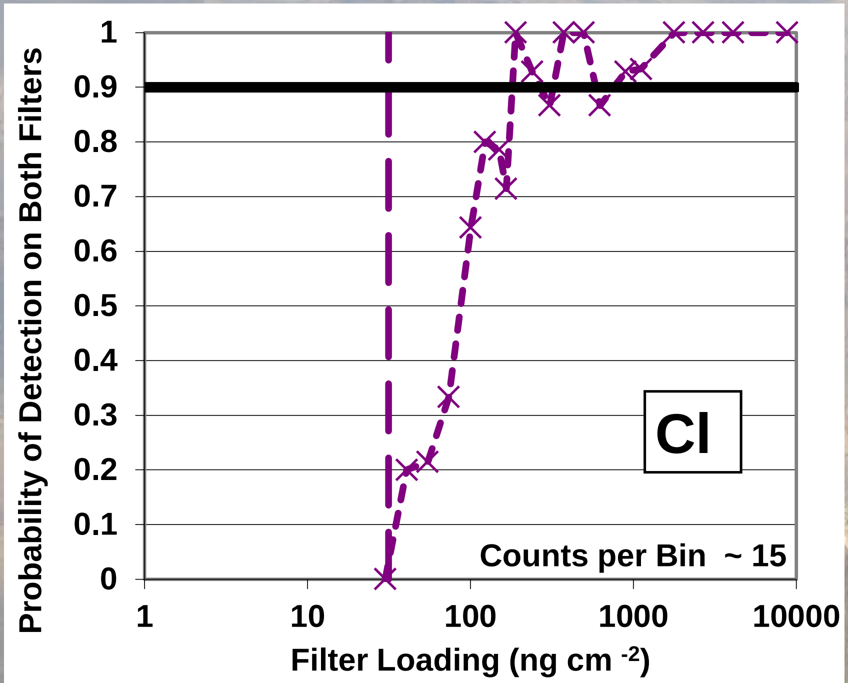
Illustration of Type I & II Errors

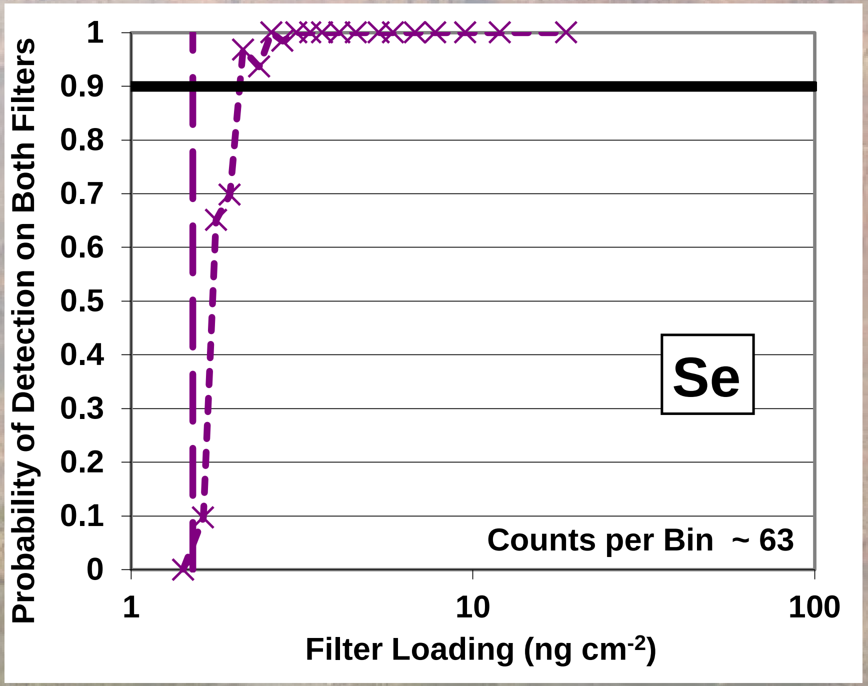


(Currie, 1995)

Estimating Detection limits from duplicate measurements

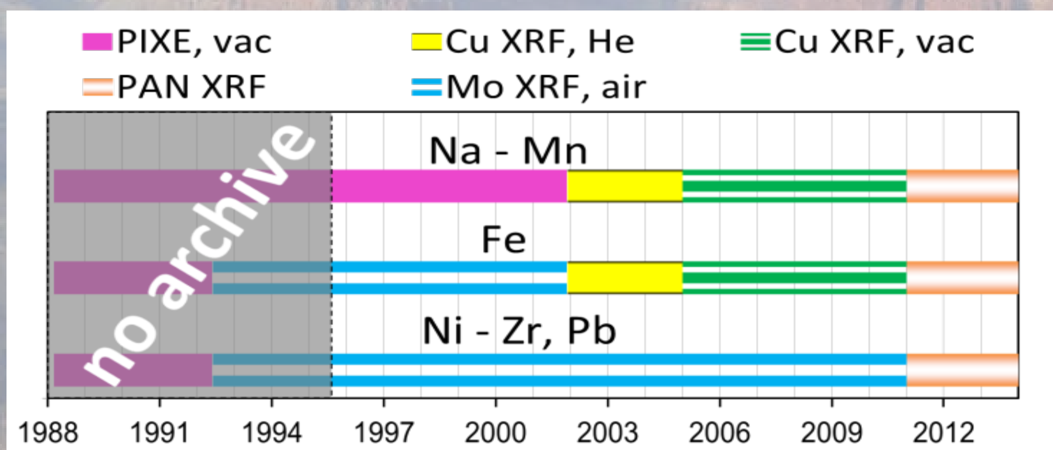


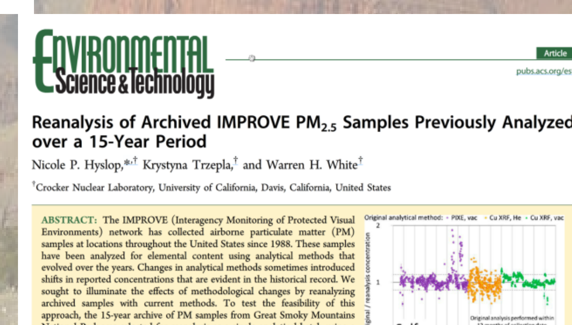




Reanalysis of 15 years of Archived Filters

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




Environmental Science & Technology
Article
pubs.acs.org/est

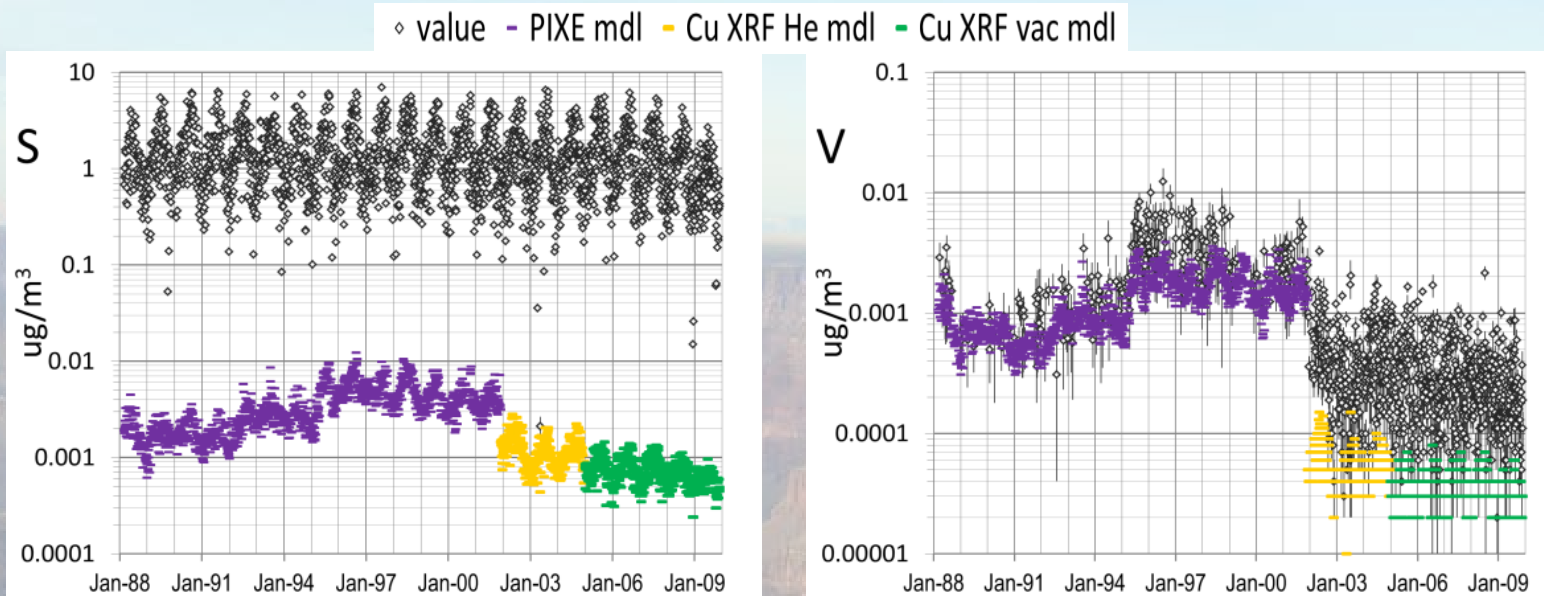
Reanalysis of Archived IMPROVE $PM_{2.5}$ Samples Previously Analyzed over a 15-Year Period

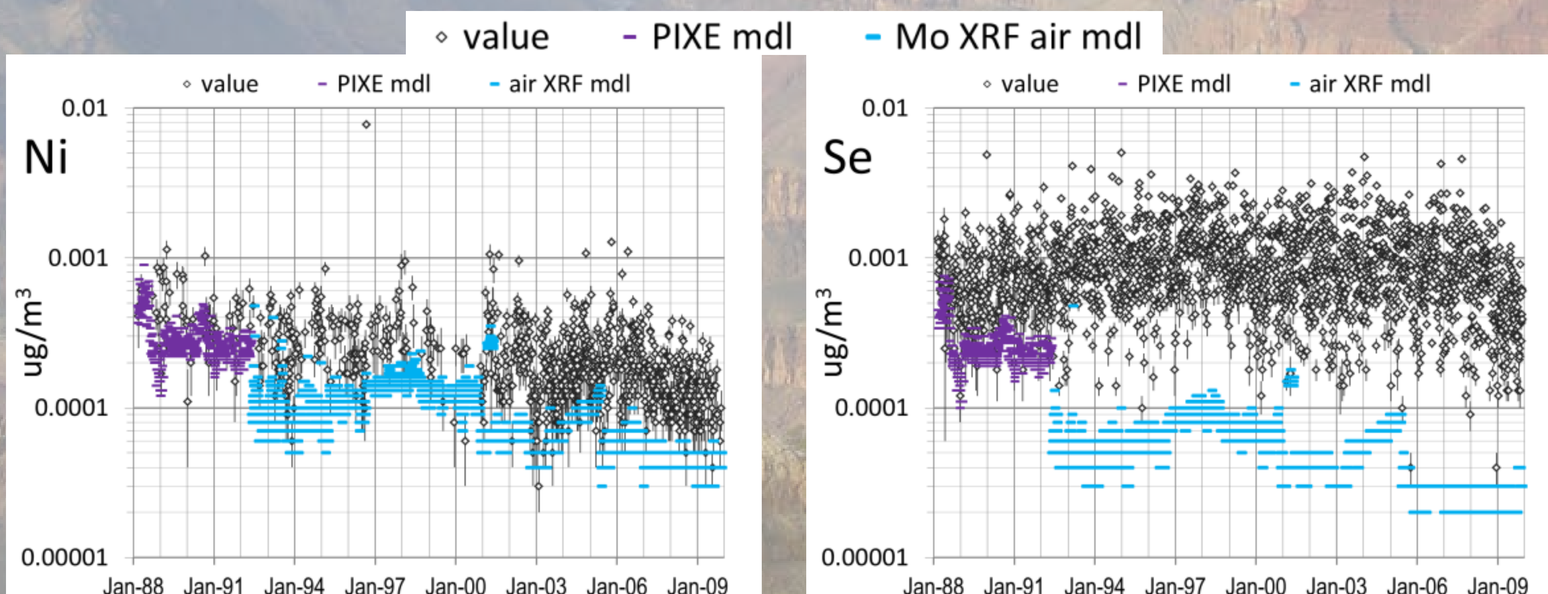
Nicole P. Hyslop,*,† Krystyna Trzepla,† and Warren H. White†
†Crocker Nuclear Laboratory, University of California, Davis, California, United States

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

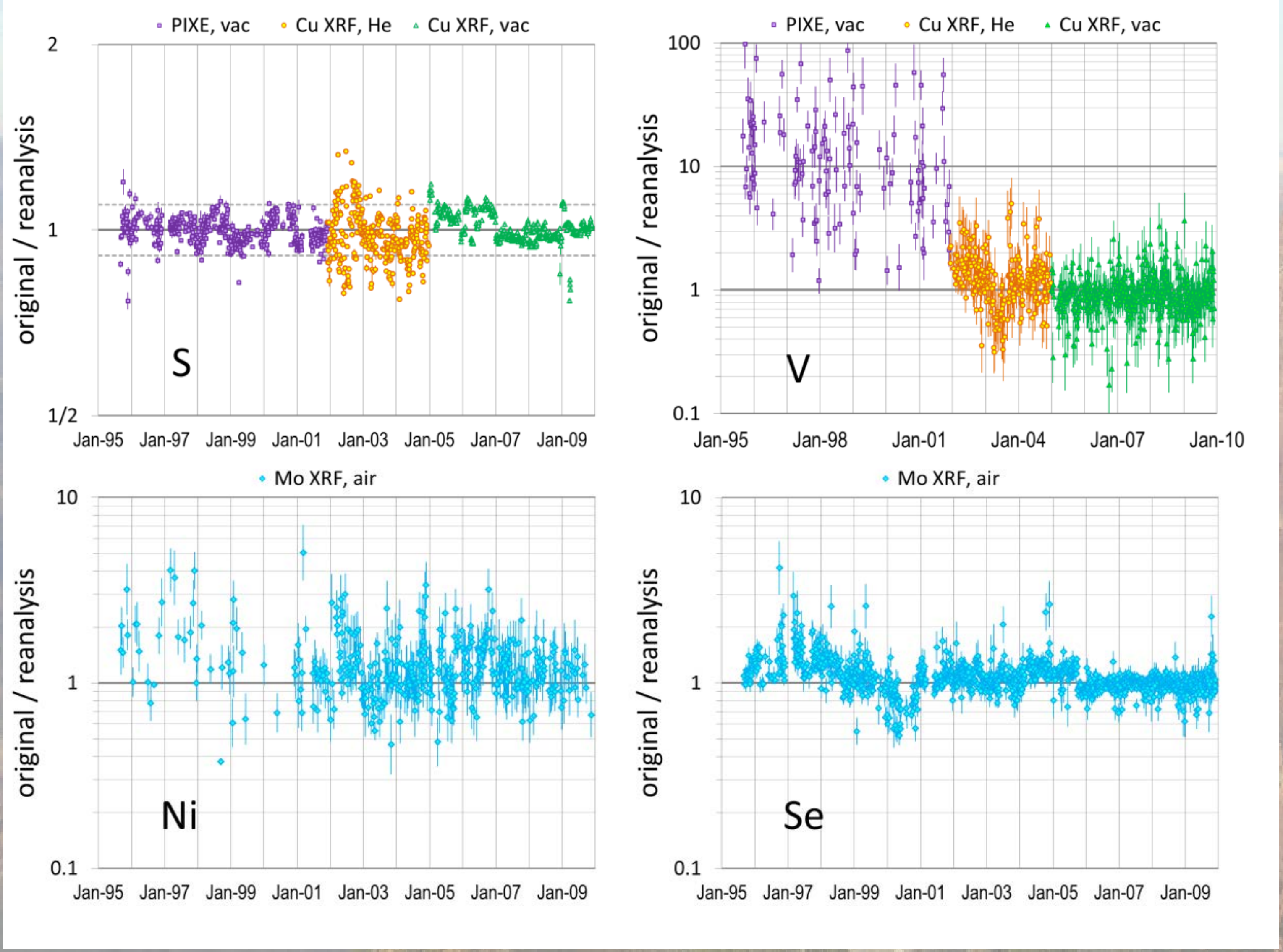
Great Smoky Mountains National Park



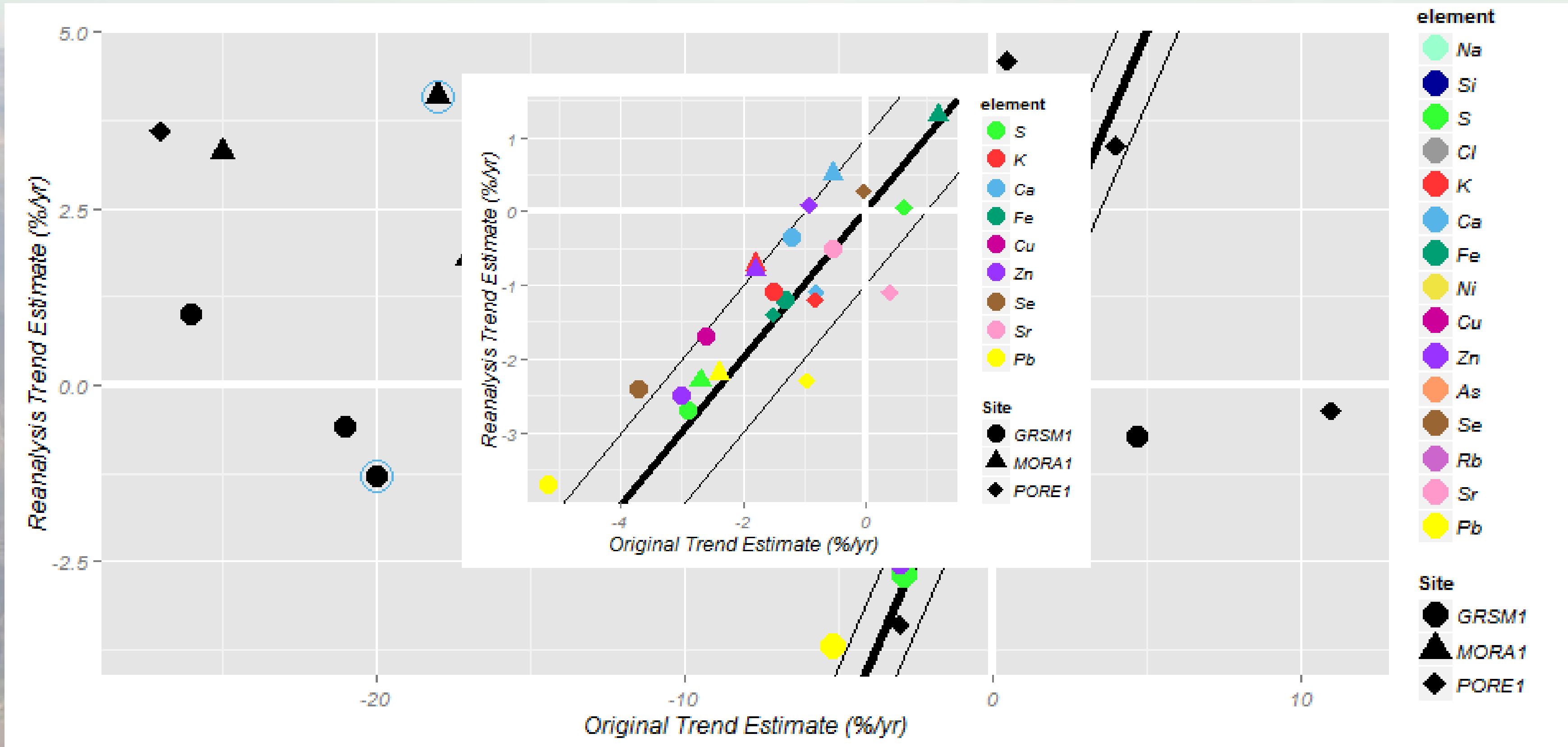


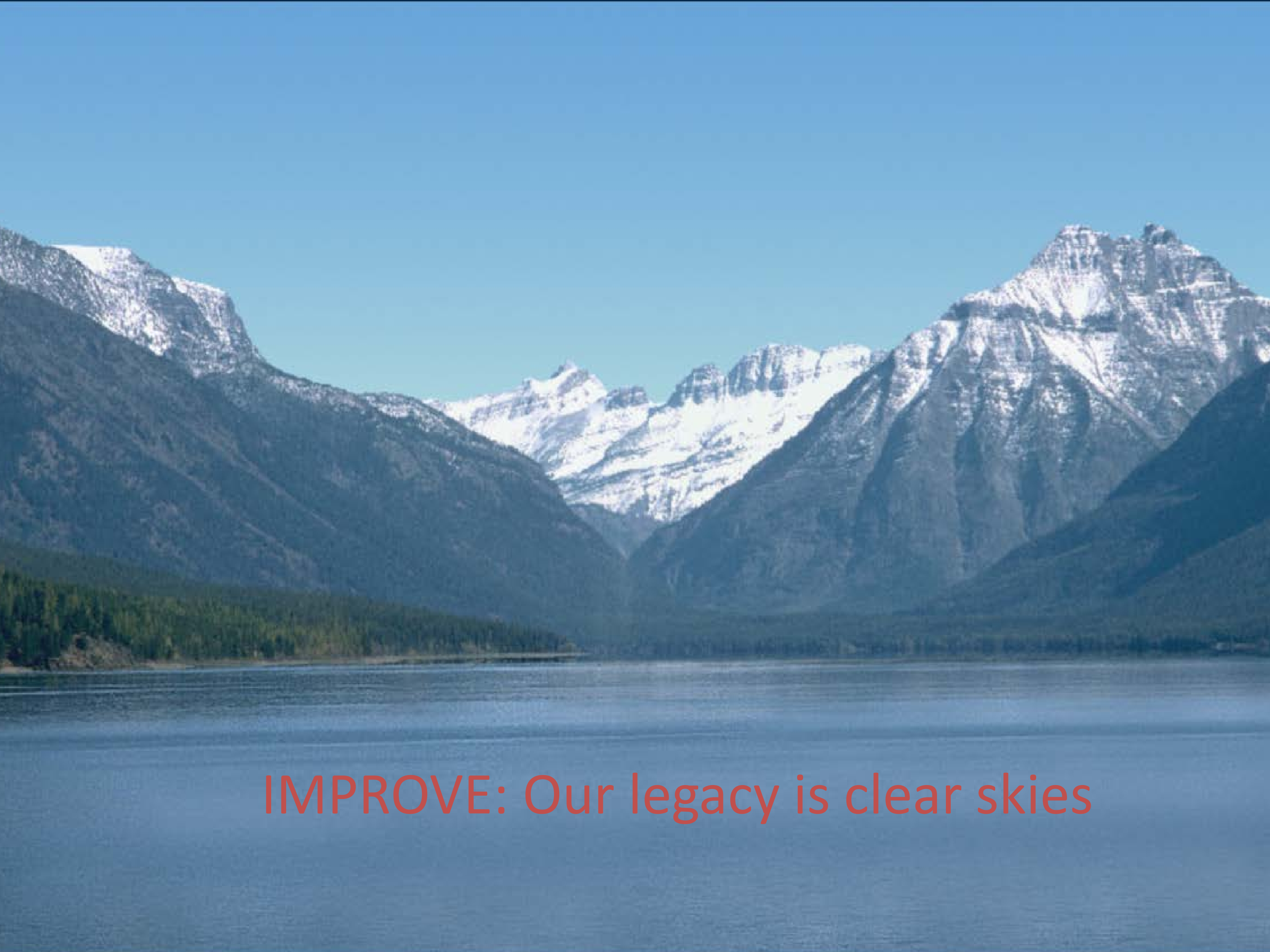
Ratios of Original and Reanalysis Concentrations

Great Smoky Mountains National Park



Trends based on Reanalysis versus Original Results




IMPROVE: Our legacy is clear skies