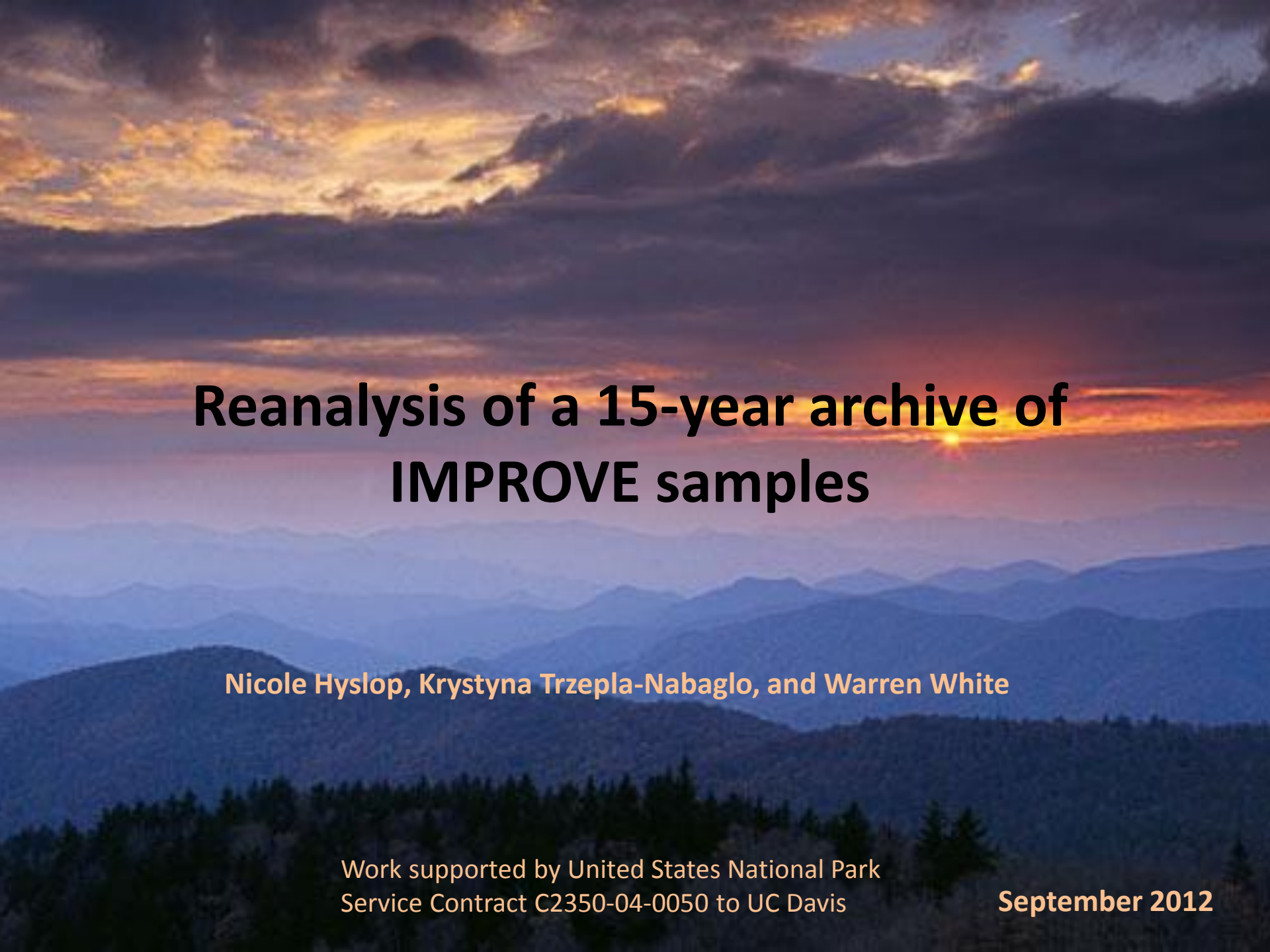




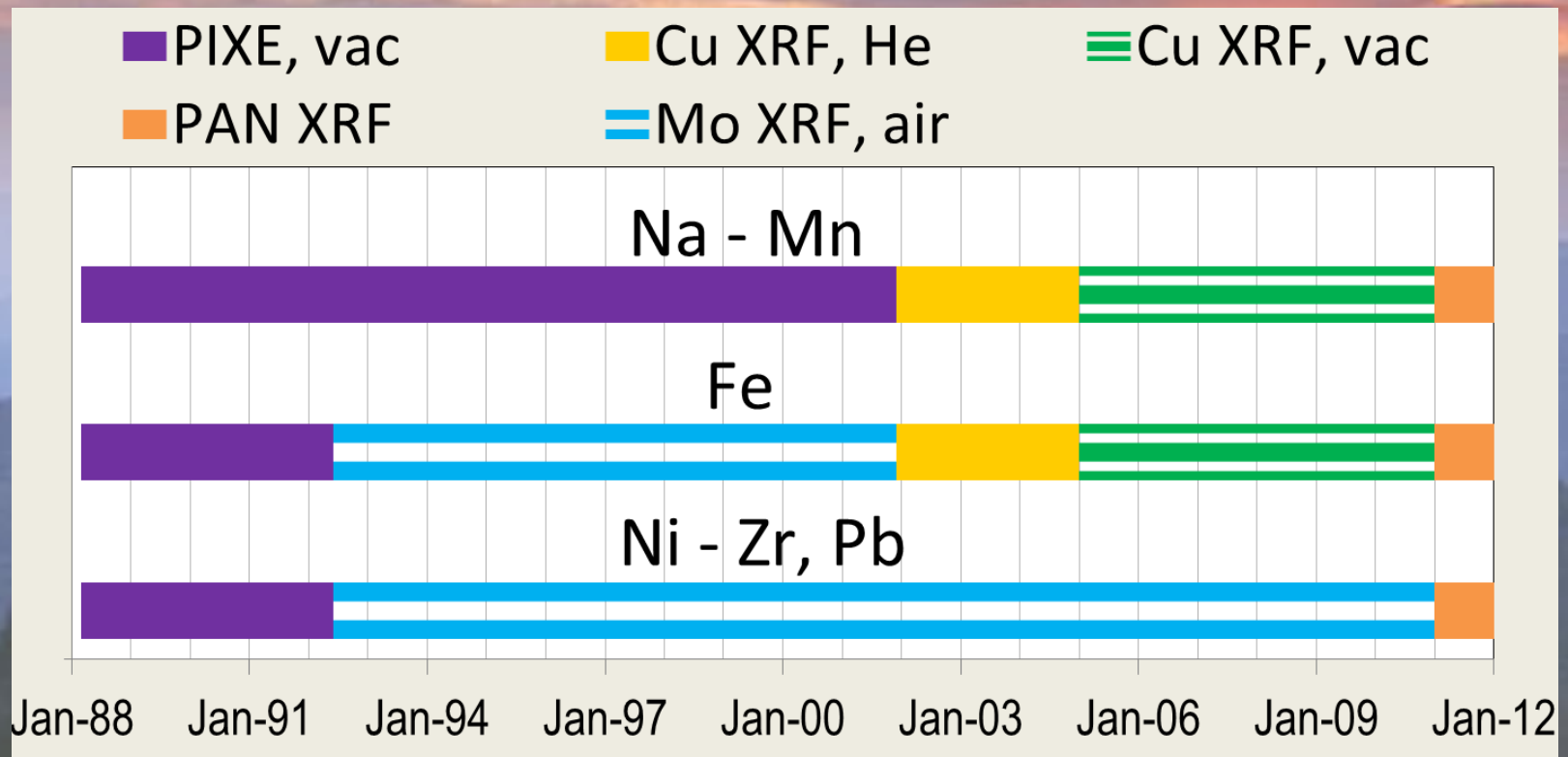
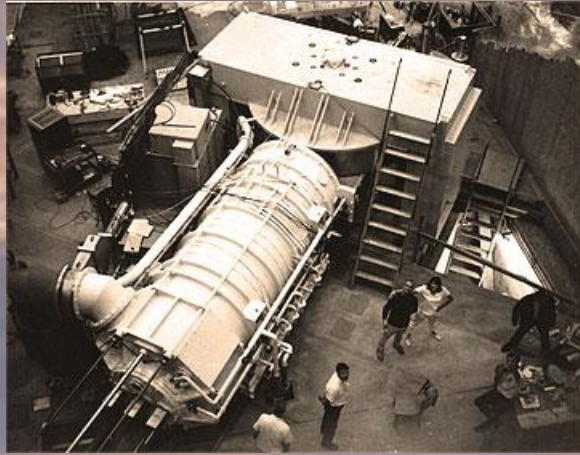
# **Reanalysis of a 15-year archive of IMPROVE samples**

**Nicole Hyslop, Krystyna Trzepla-Nabaglo, and Warren White**

Work supported by United States National Park  
Service Contract C2350-04-0050 to UC Davis

**September 2012**

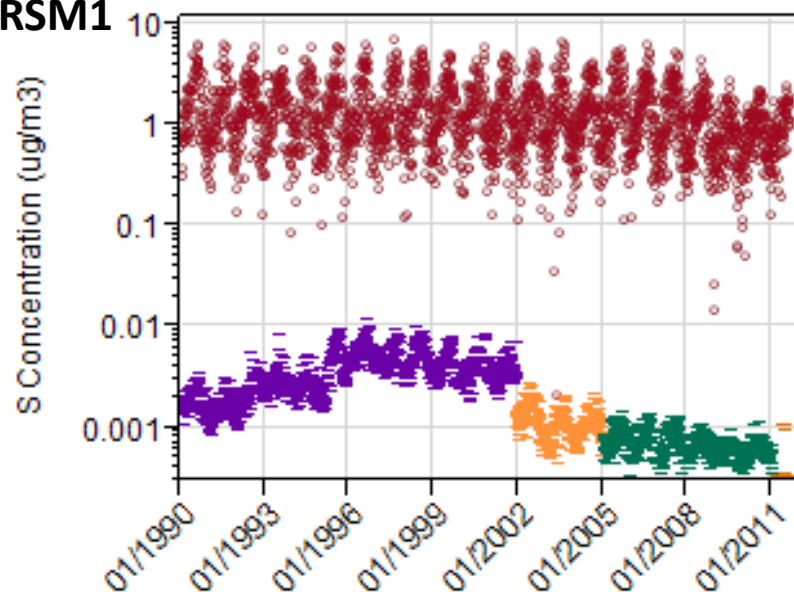
# IMPROVE Elemental Analysis Methods



# ORIGINAL CONCENTRATION MEASUREMENTS

Data downloaded from VIEWS website  
<http://views.cira.colostate.edu/web/DataWizard/>

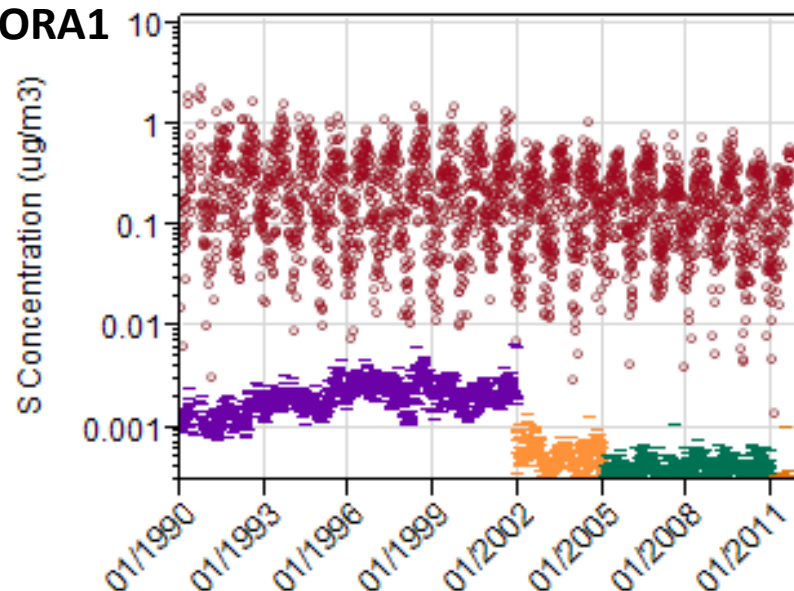
GRSM1



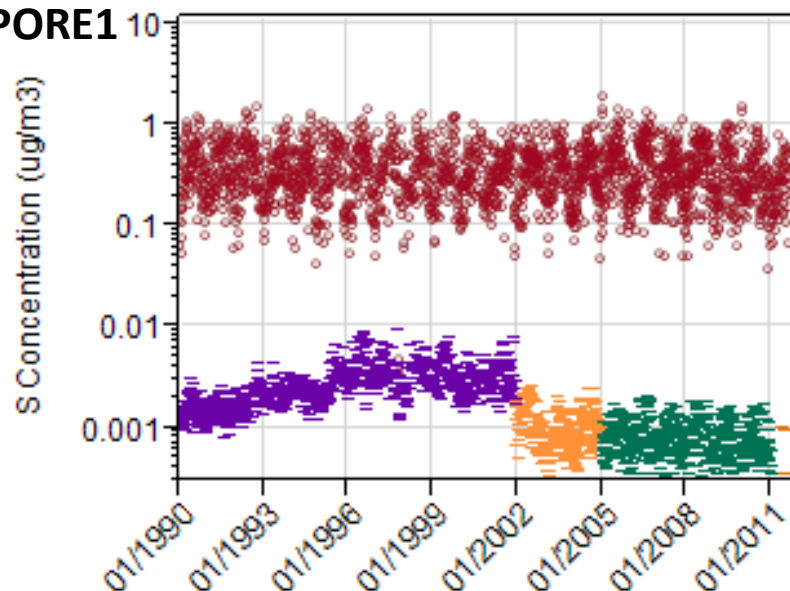
# Analytical Method Changes: Sulfur

-Measured well above detection limits

MORA1

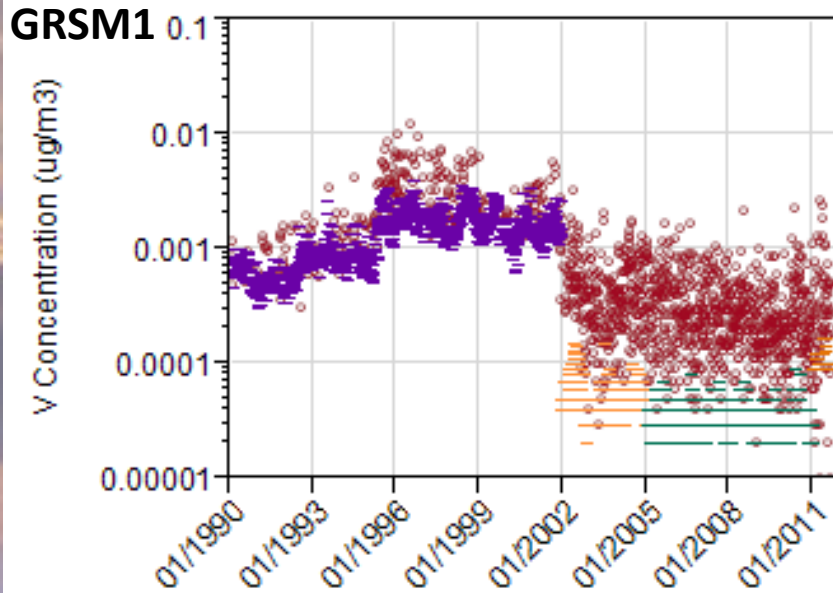


PORE1

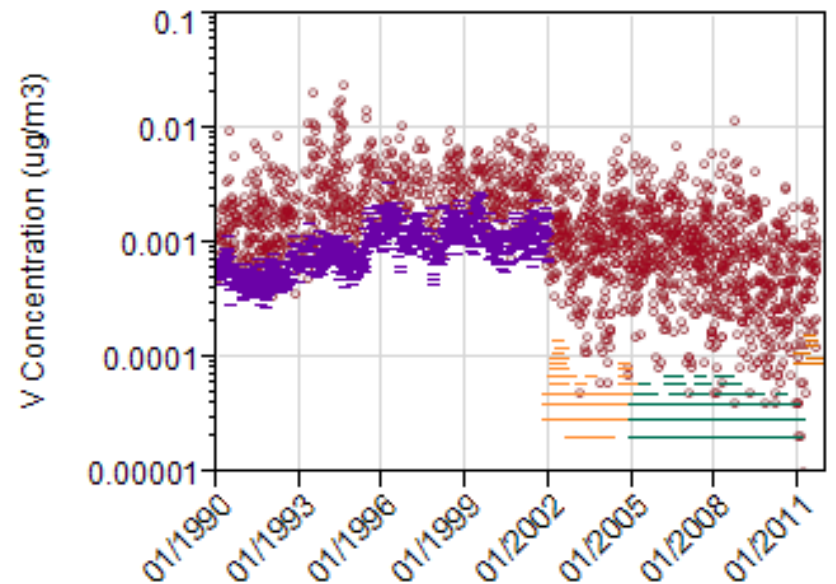
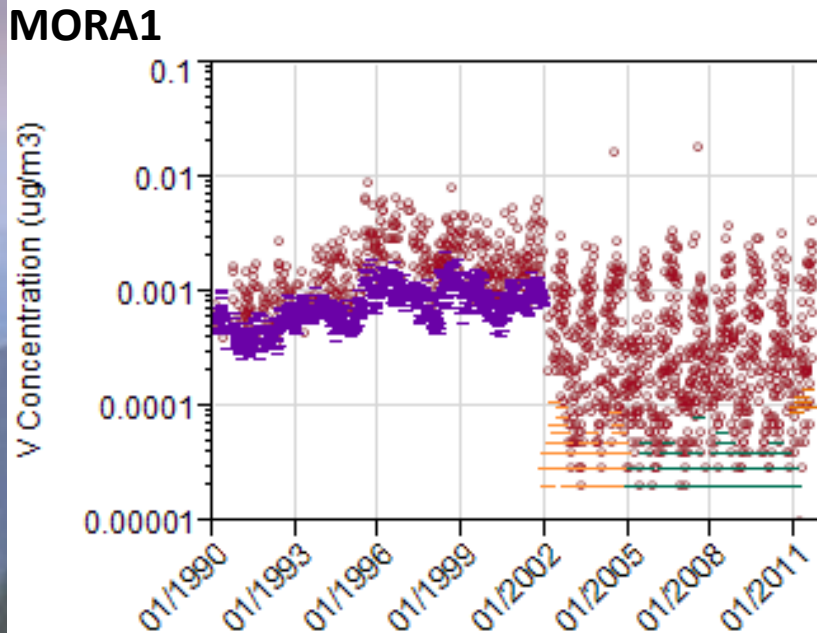


○ Value    — PIXE mdl    — Cu XRF He mdl    — Cu XRF vac mdl    — *PAN mdl*

# Analytical Method Changes: Vanadium

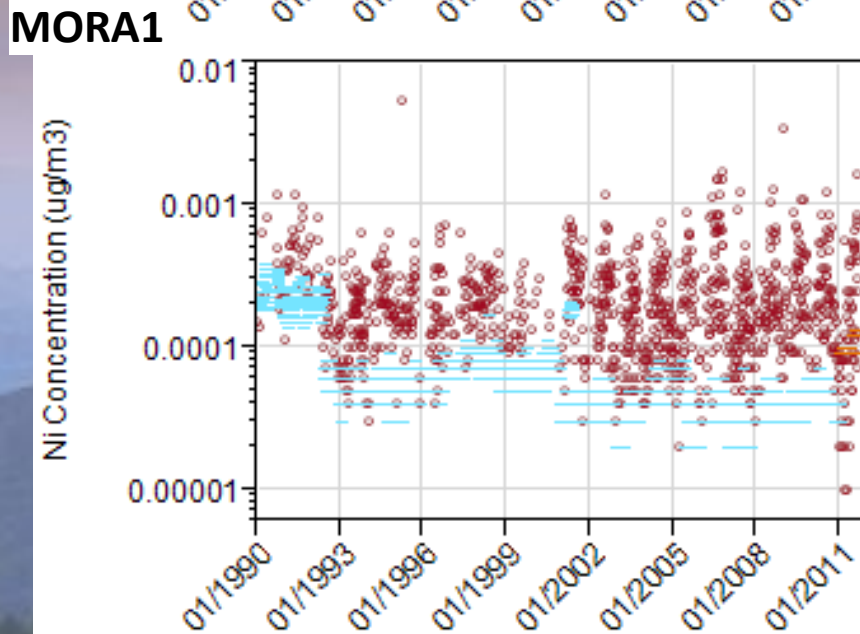
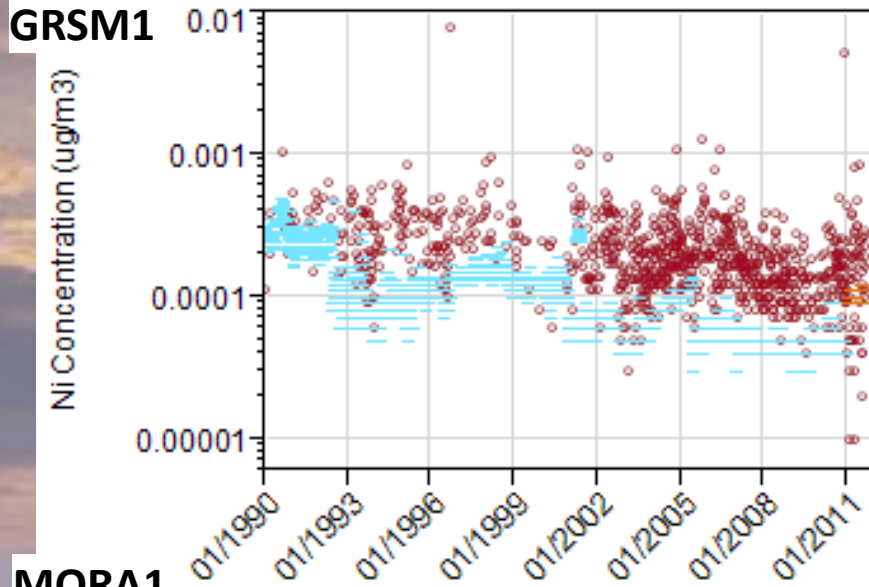


**PORE1**

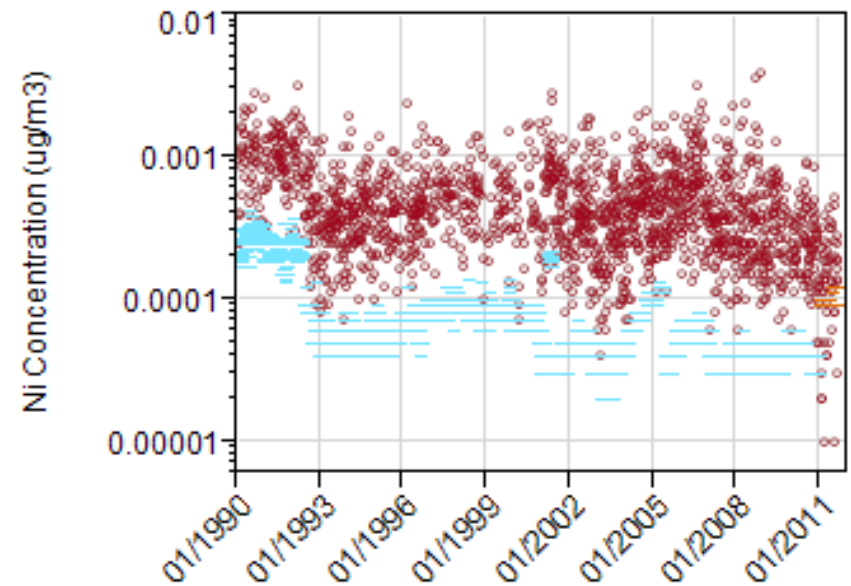


○ Value    — PIXE mdl    — Cu XRF He mdl    — Cu XRF vac mdl    — *PAN* mdl

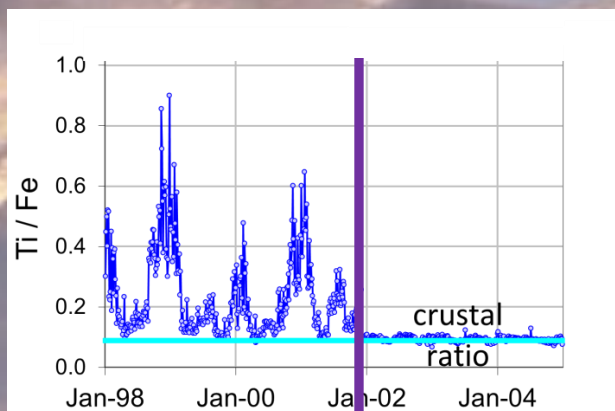
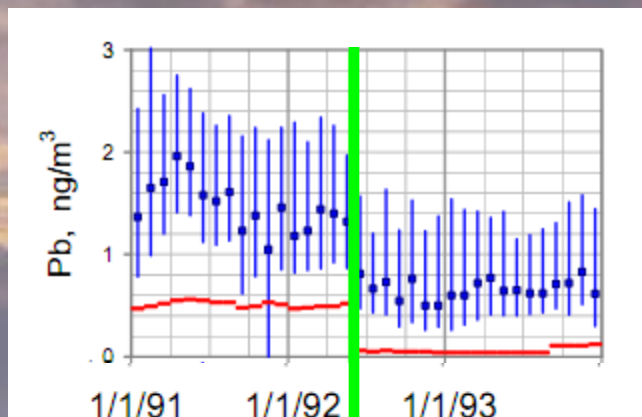
# Analytical Method Changes: Nickel



**PORE1**



○ Value    — Mo XRF air mdl    — PAN XRF mdl



Samples of specific advisories posted at data portal

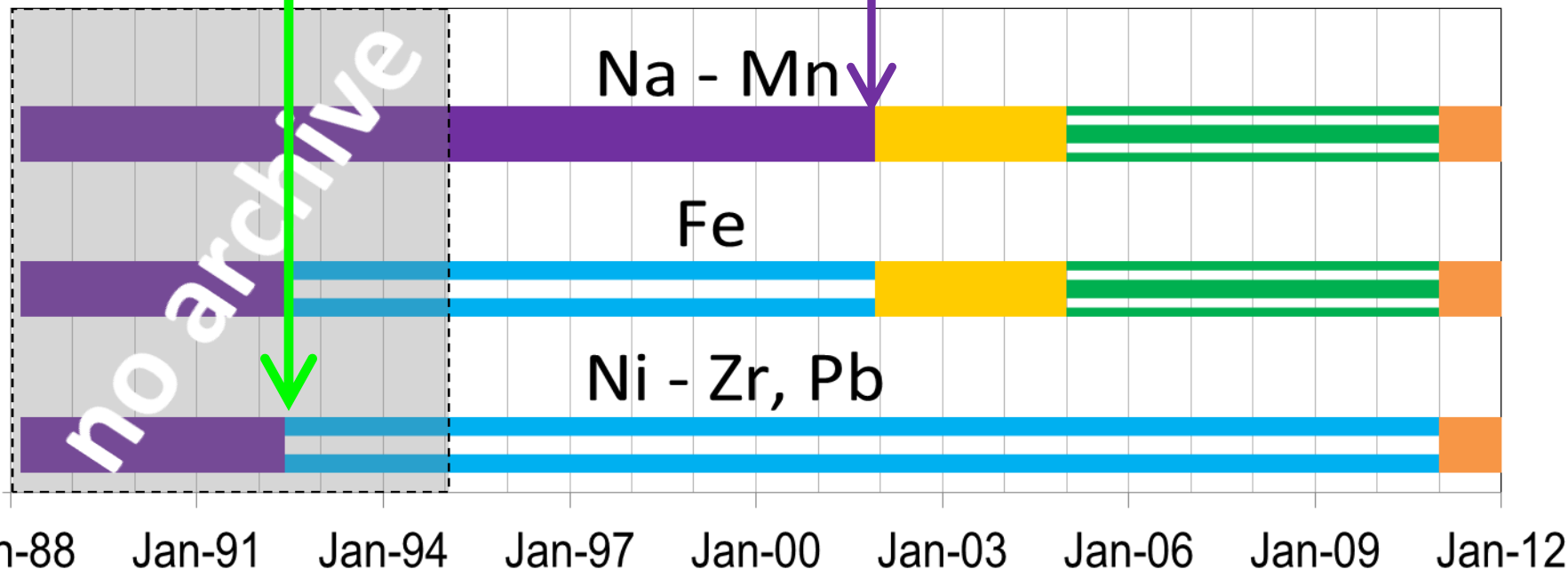
PIXE, vac

PAN XRF

Cu XRF, He

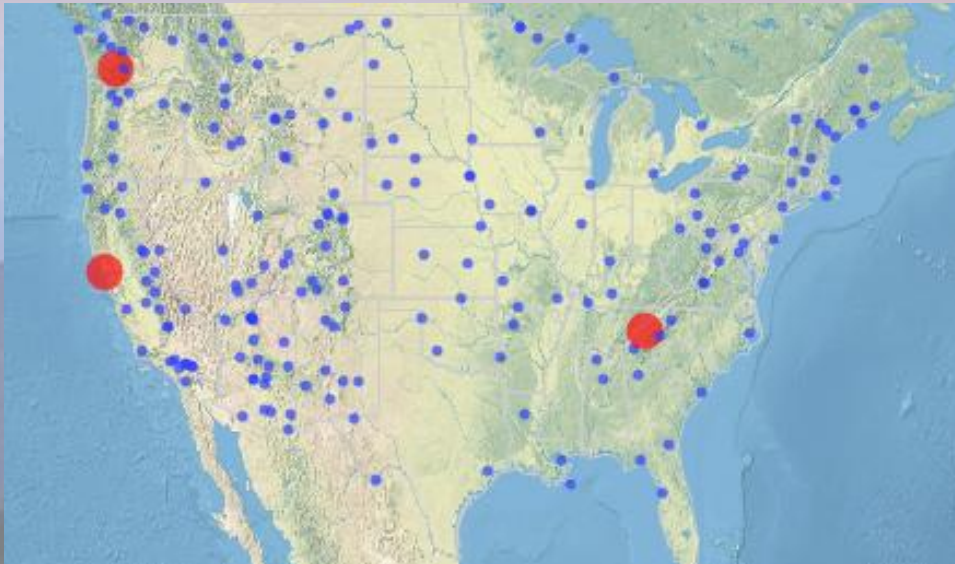
Mo XRF, air

Cu XRF, vac



# Feasibility of Reanalyzing Filters

- The IMPROVE network has
  - Used the same size selective inlets and Teflon filters to collect 24h PM<sub>2.5</sub> samples for elemental analyses
  - Used non-destructive analytical methods on the Teflon filters
- We were able to recover filters back to 1995
- We can analyze archived filters with current analytical protocol in a single analytical batch



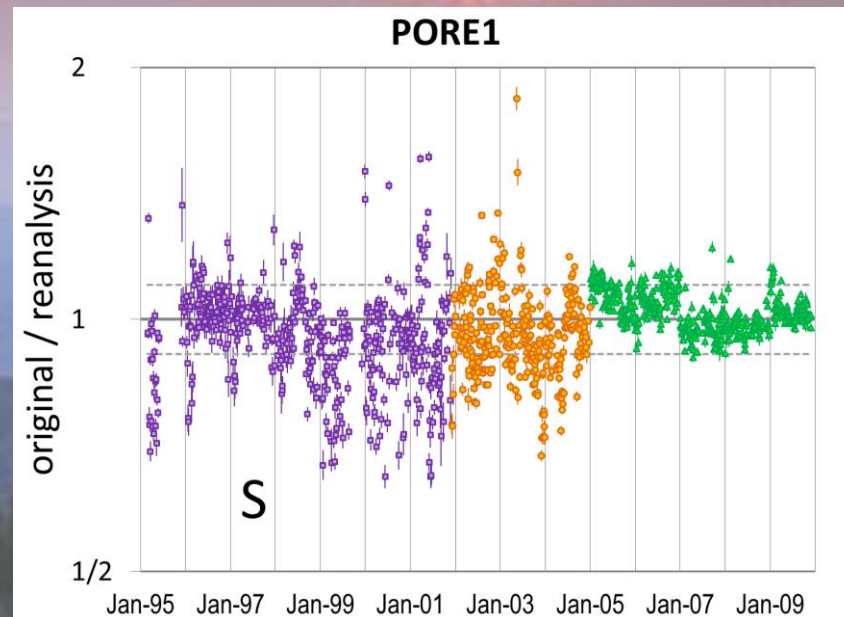
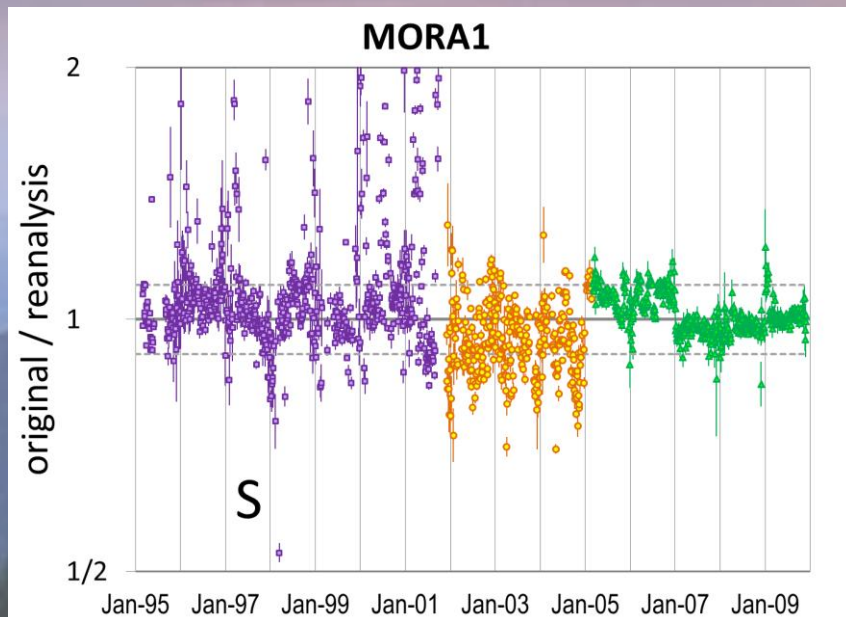
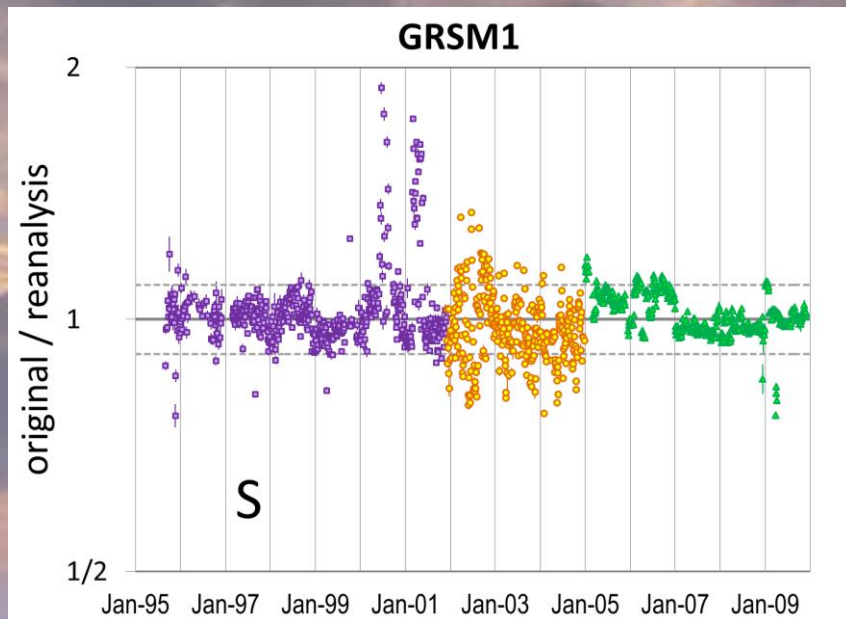
Sites selected for reanalysis:

Great Smoky Mountains (GRSM1)  
Mount Rainier (MORA1)  
Point Reyes (PORE1)

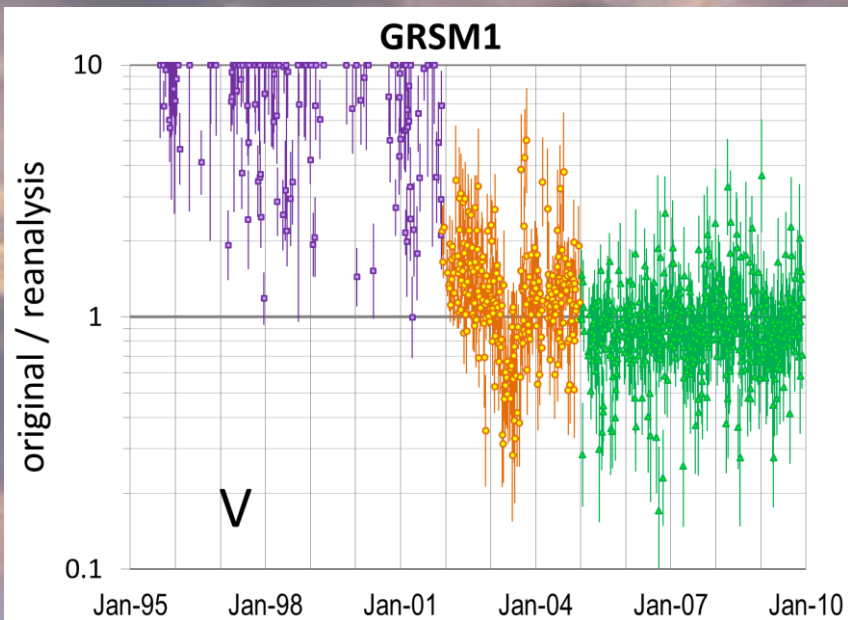
# REANALYSIS RESULTS

Shown as ratios to original concentration measurements

# Reanalysis Results: Sulfur

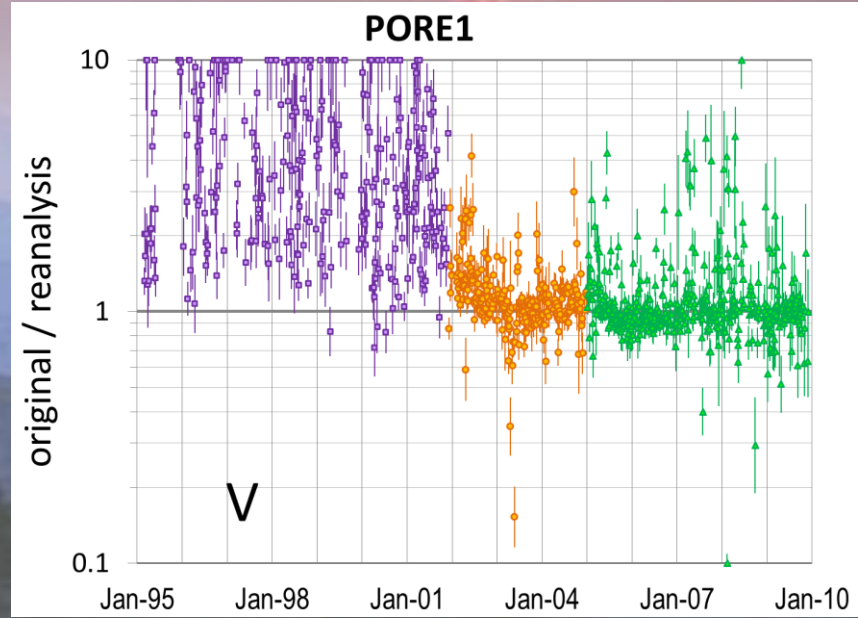
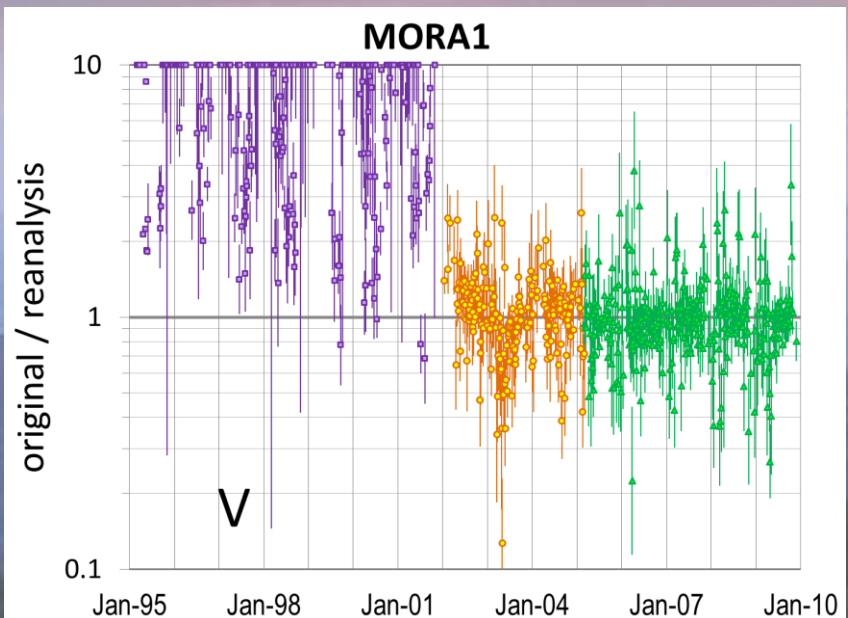


■ PIXE, vac      ● Cu XRF, He      ▲ Cu XRF, vac



# Reanalysis Results: Vanadium

Note change in y-axis scale

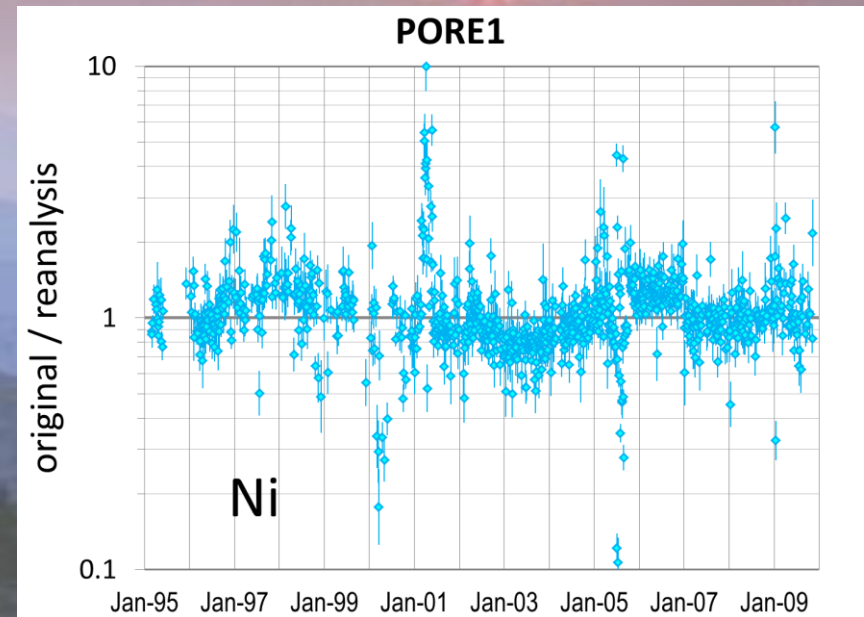
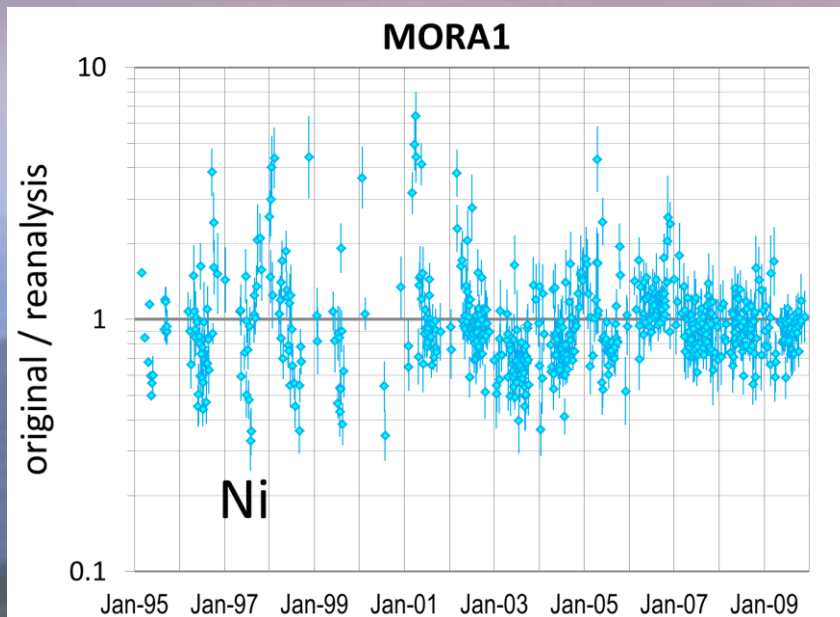
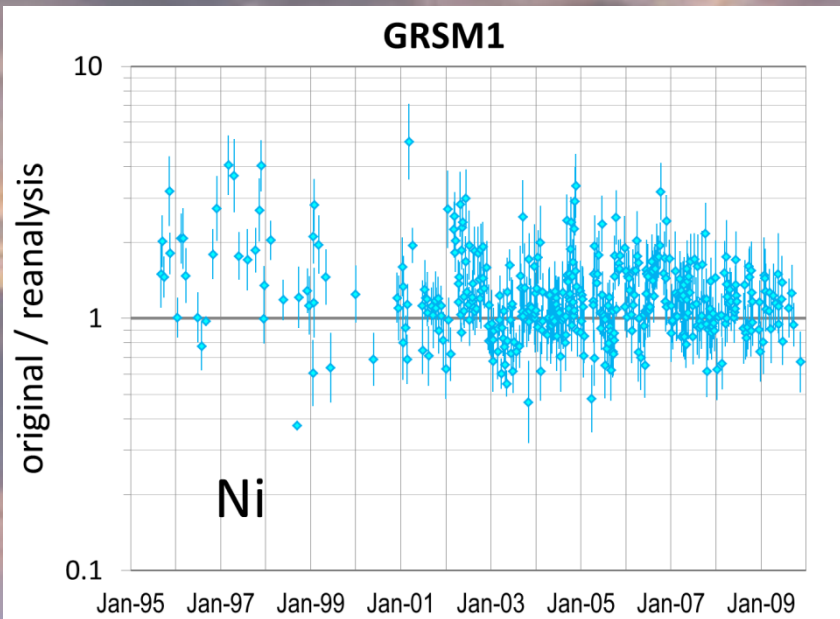


■ PIXE, vac

● Cu XRF, He

▲ Cu XRF, vac

# Reanalysis Results: Nickel



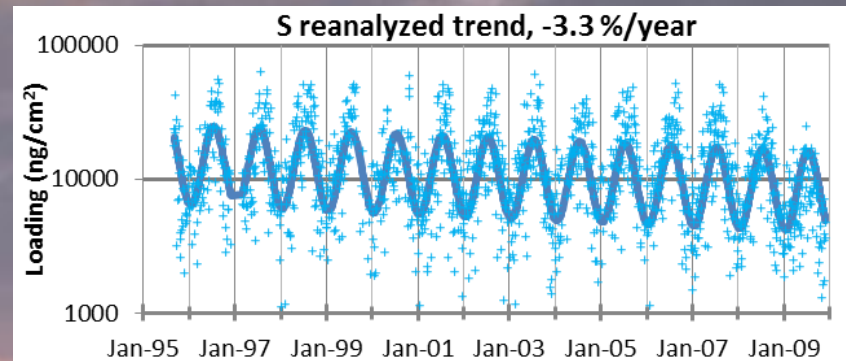
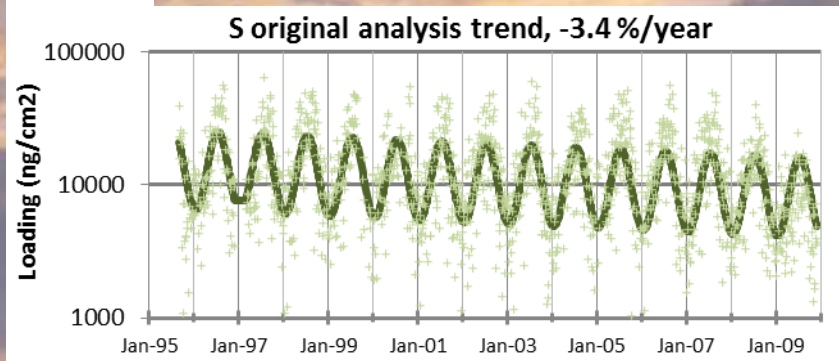
◆ Mo XRF, air

# TRENDS ANALYSIS

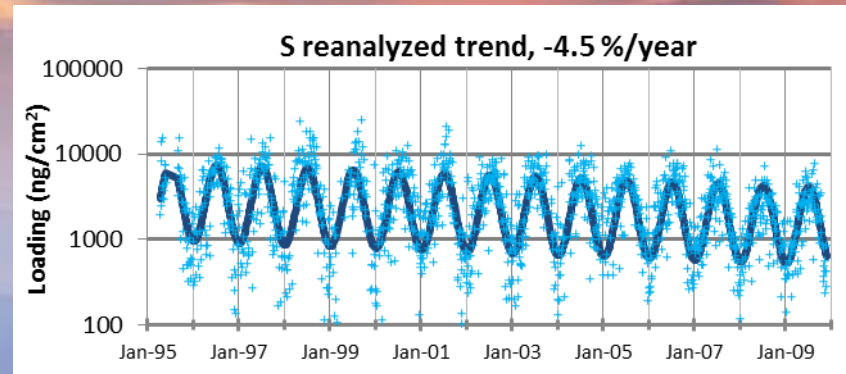
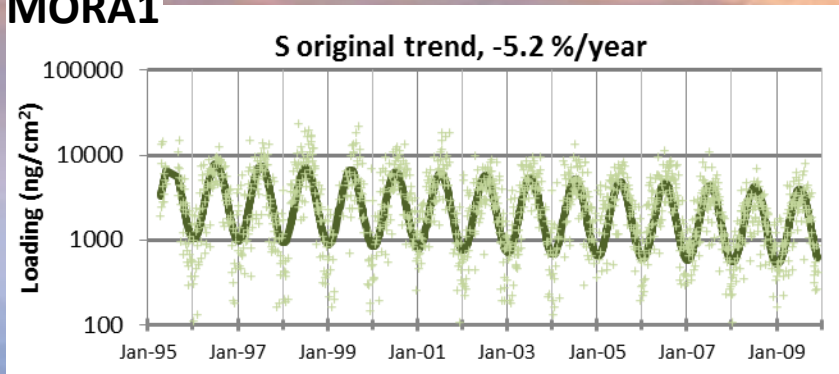
Evaluate trends in original and reanalysis data

# Original and Reanalysis Trends: Sulfur

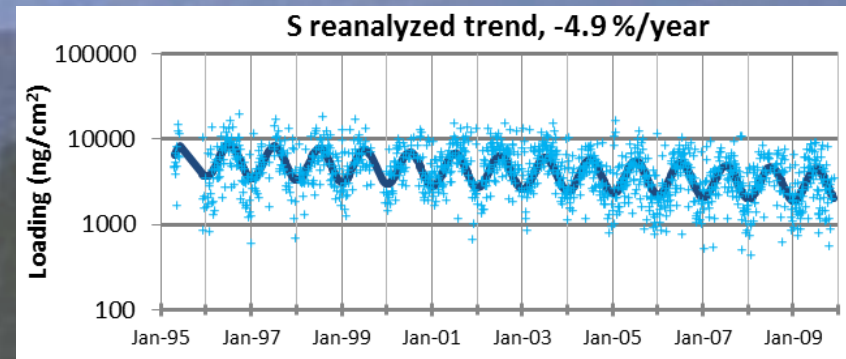
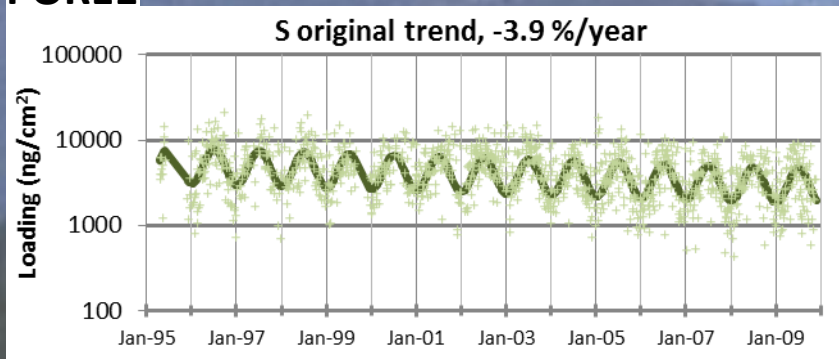
**GRSM1**



**MORA1**

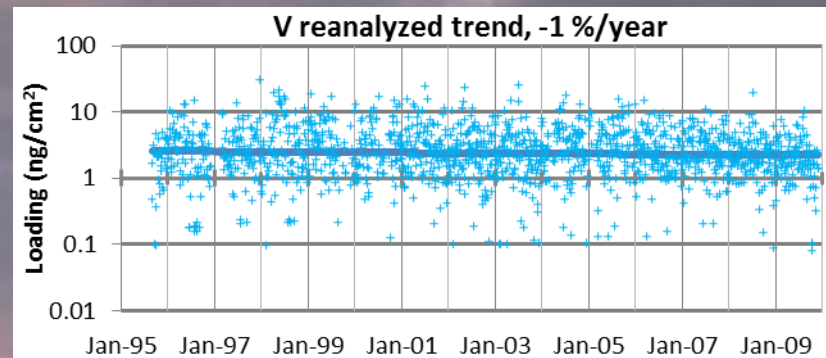
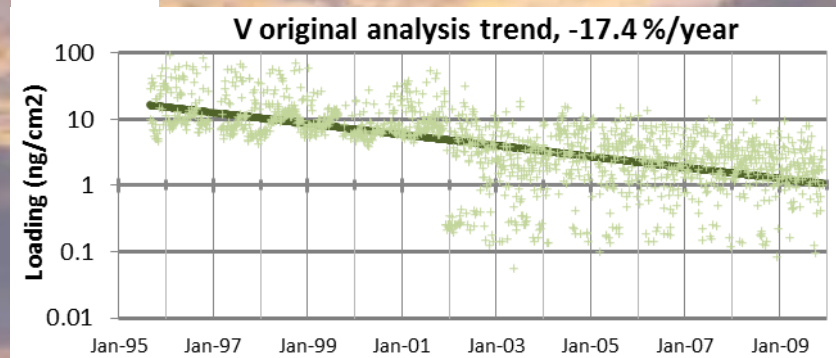


**PORE1**

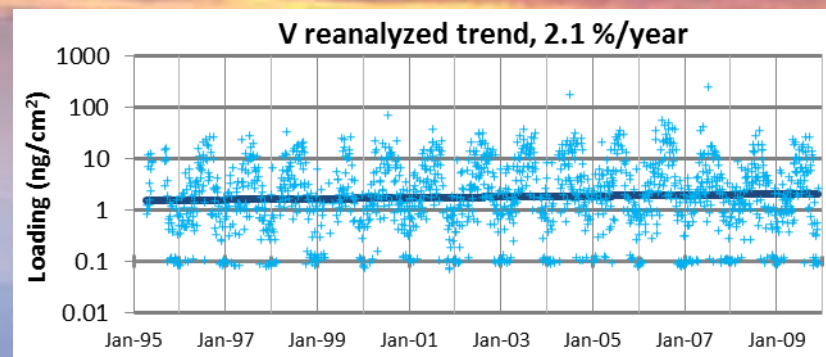
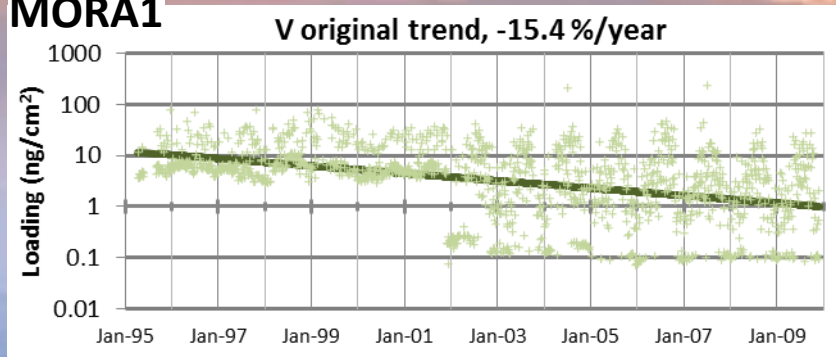


# Vanadium Trends: treatment of non-detects affects trends

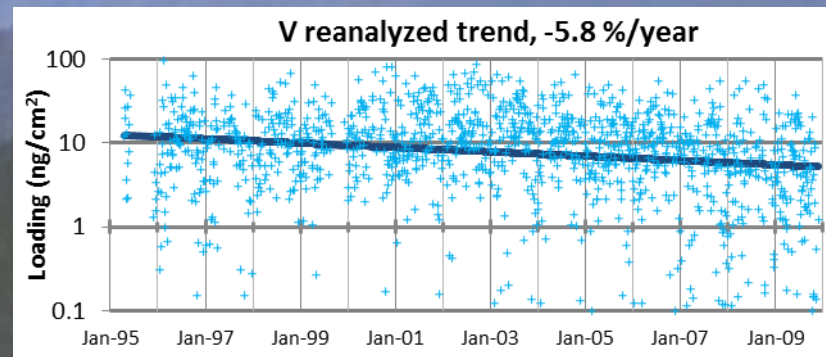
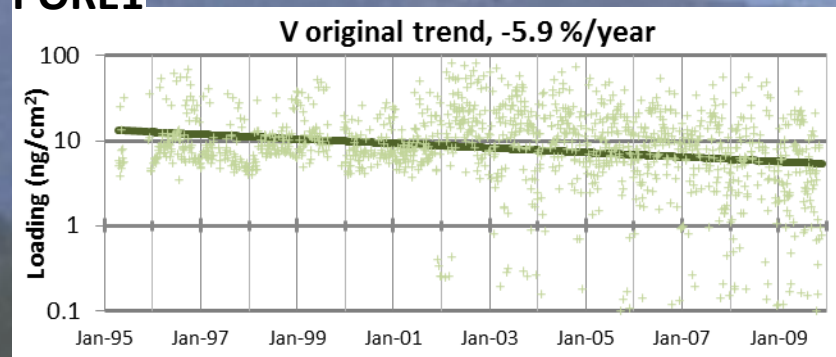
## GRSM1



## MORA1

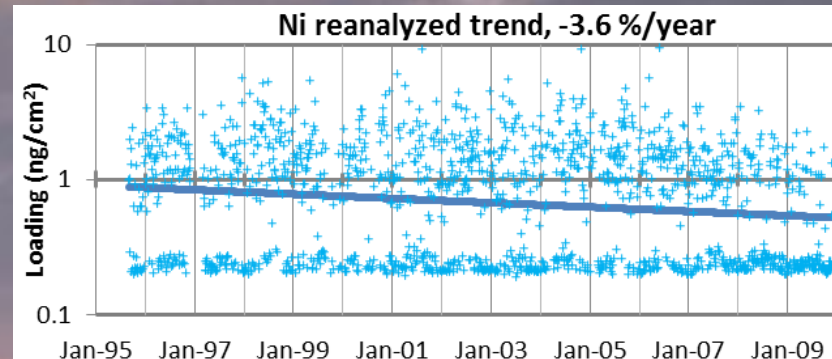
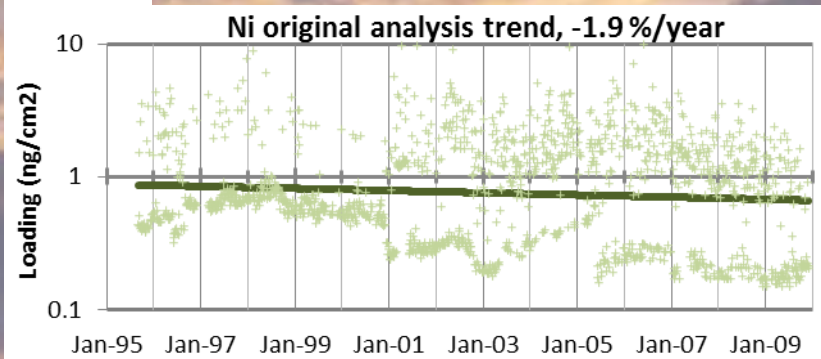


## PORE1

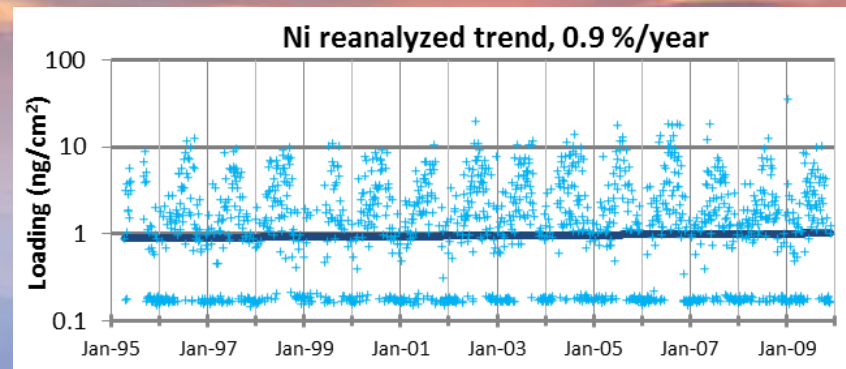
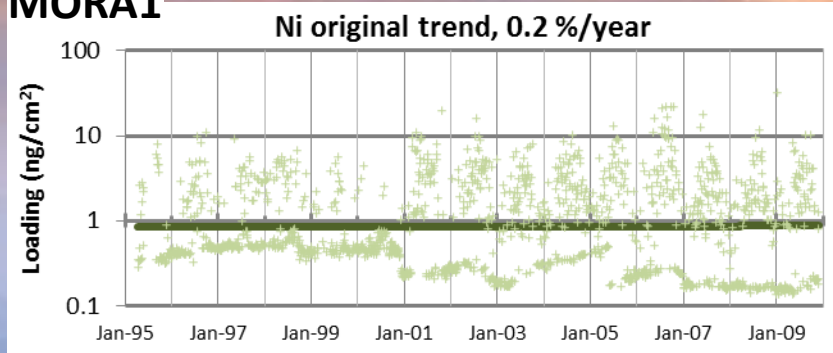


# Original and Reanalysis Trends: Nickel

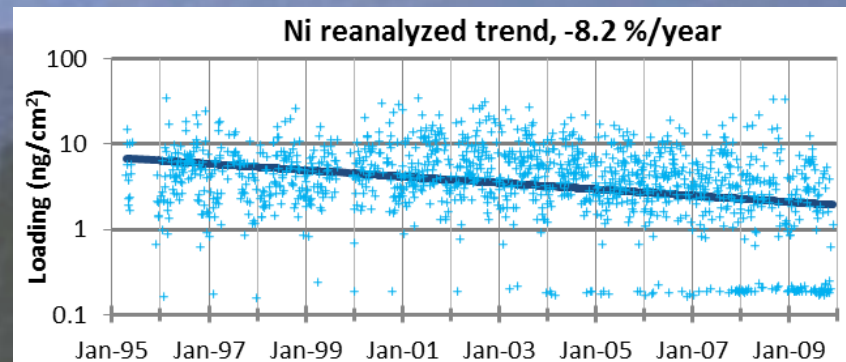
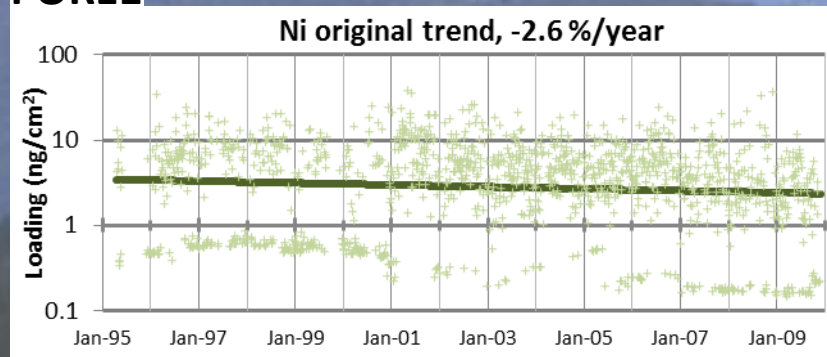
**GRSM1**



**MORA1**

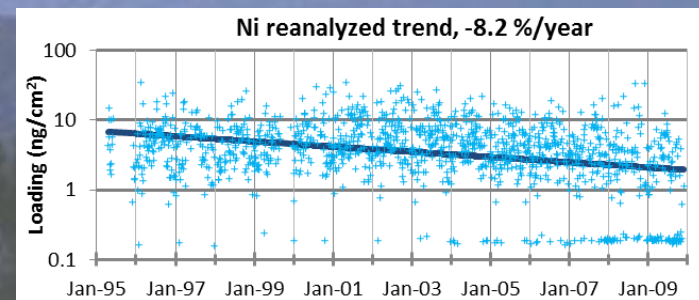
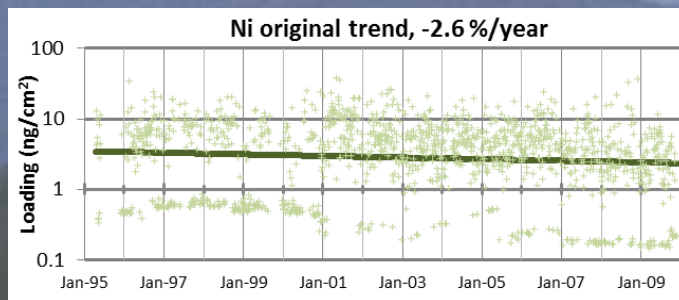
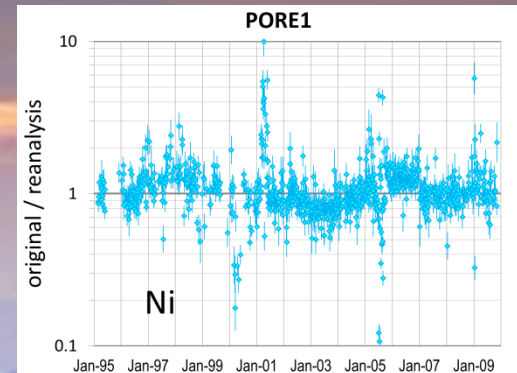
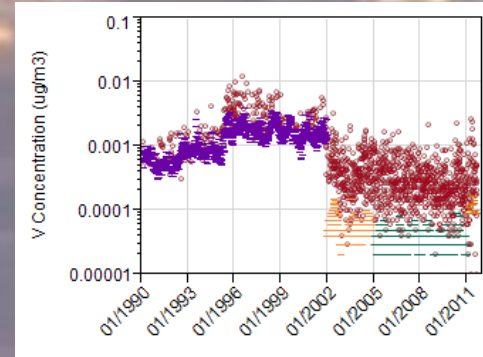


**PORE1**



# Advice for the analyst:

1. Elements measured close to the detection limits are the most sensitive to changes in analytical method
2. Expect shifts in concentrations over time even with consistent methods
3. Trend analyses are particularly sensitive to analytical changes and treatment of data near or below detection limits



# Mauna Loa

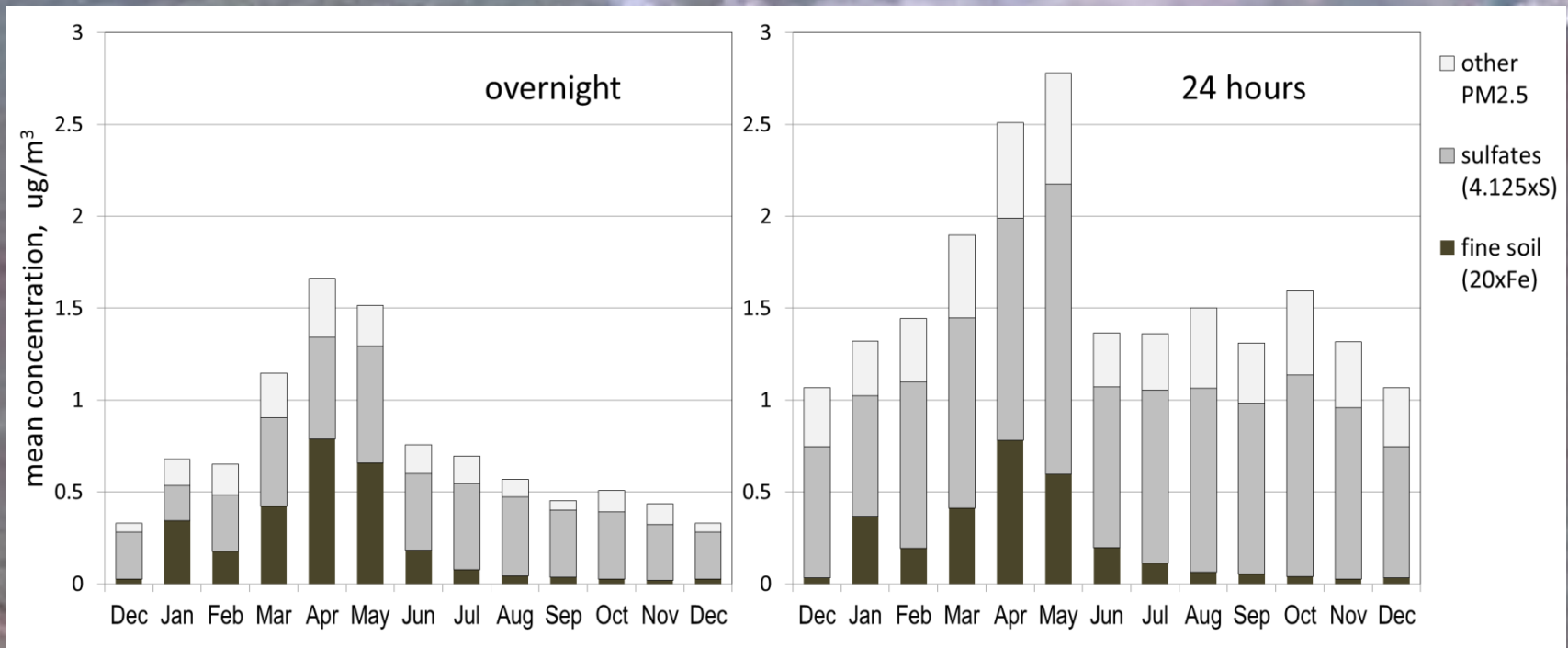
## 20+ Years of (Mostly) Unpublished Data

- Mauna Loa started operating in 1988
- Data have not been reported consistently
- Samples have not been analyzed continuously
- Recently analyzed samples from 2002-2010 on Cu-XRF and Mo-XRF systems
  - Preparing delivery file for 2000-2010

# Overnight and 24-hour Compositions

- MALO has two PM<sub>2.5</sub> modules
  - MALO1: first module runs all the time for 3-4 days
  - MALO2: second module runs only at night for 3-4 days

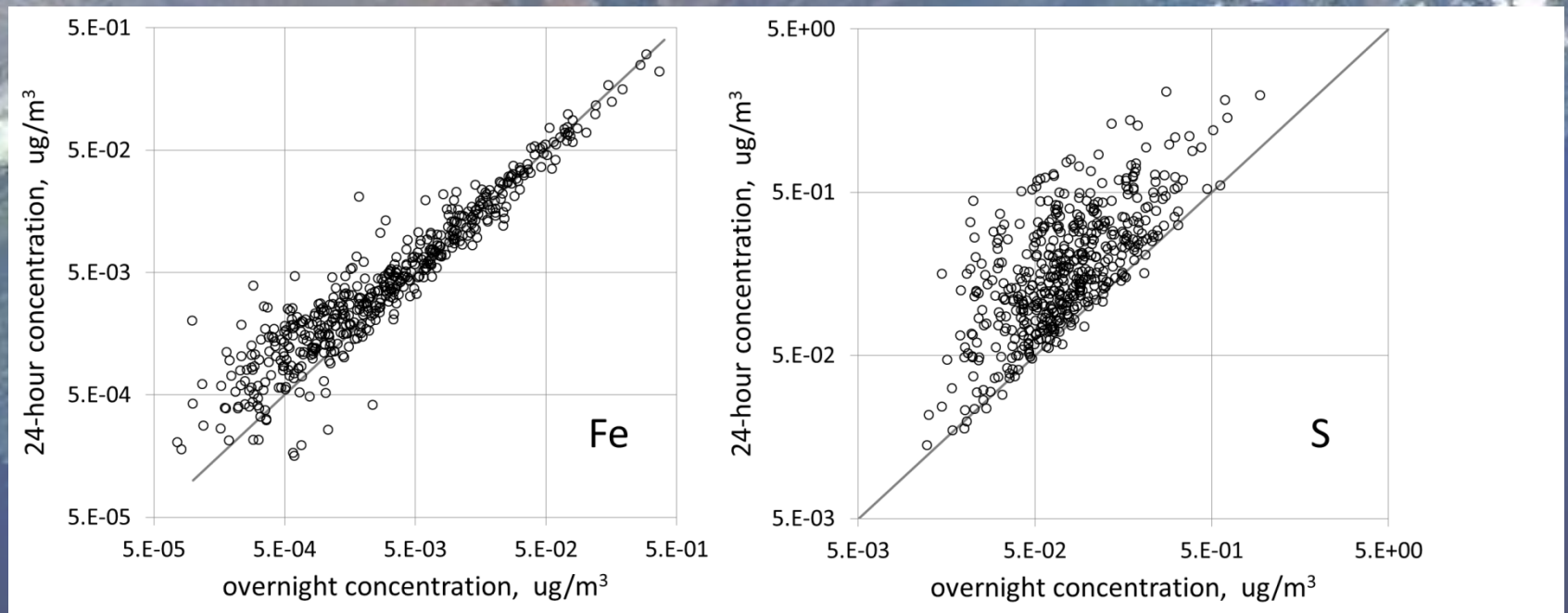
Mauna Loa, 2006 - 2010



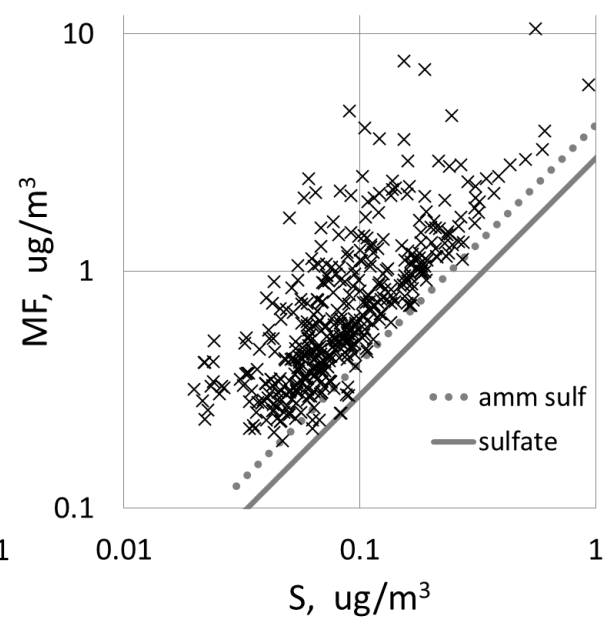
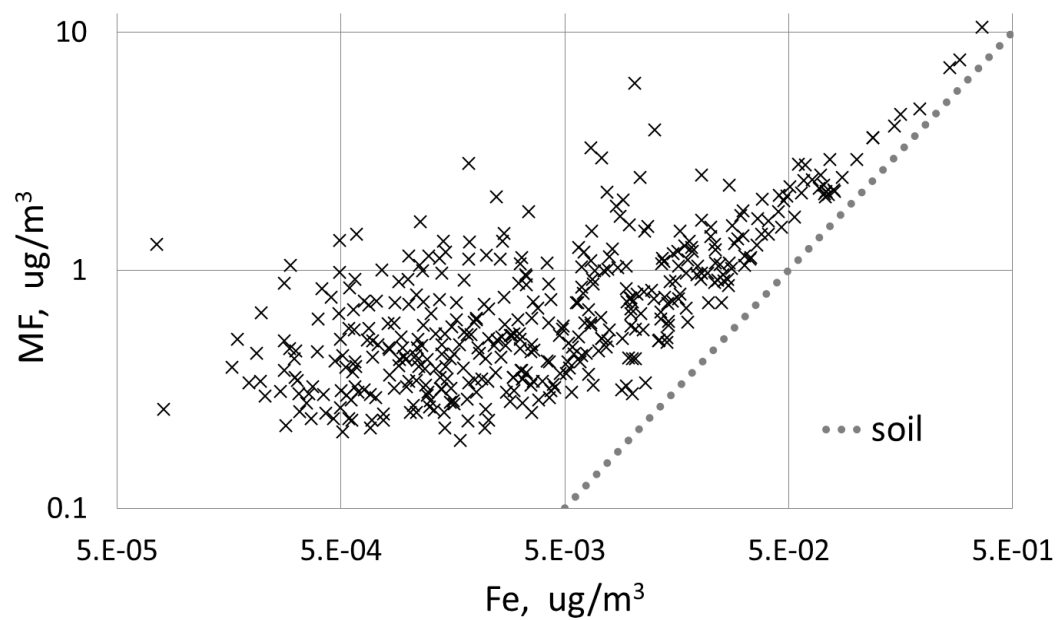
# 24-hr versus Overnight Samples

- Overnight samples create a concentration edge for the 24-hr samples

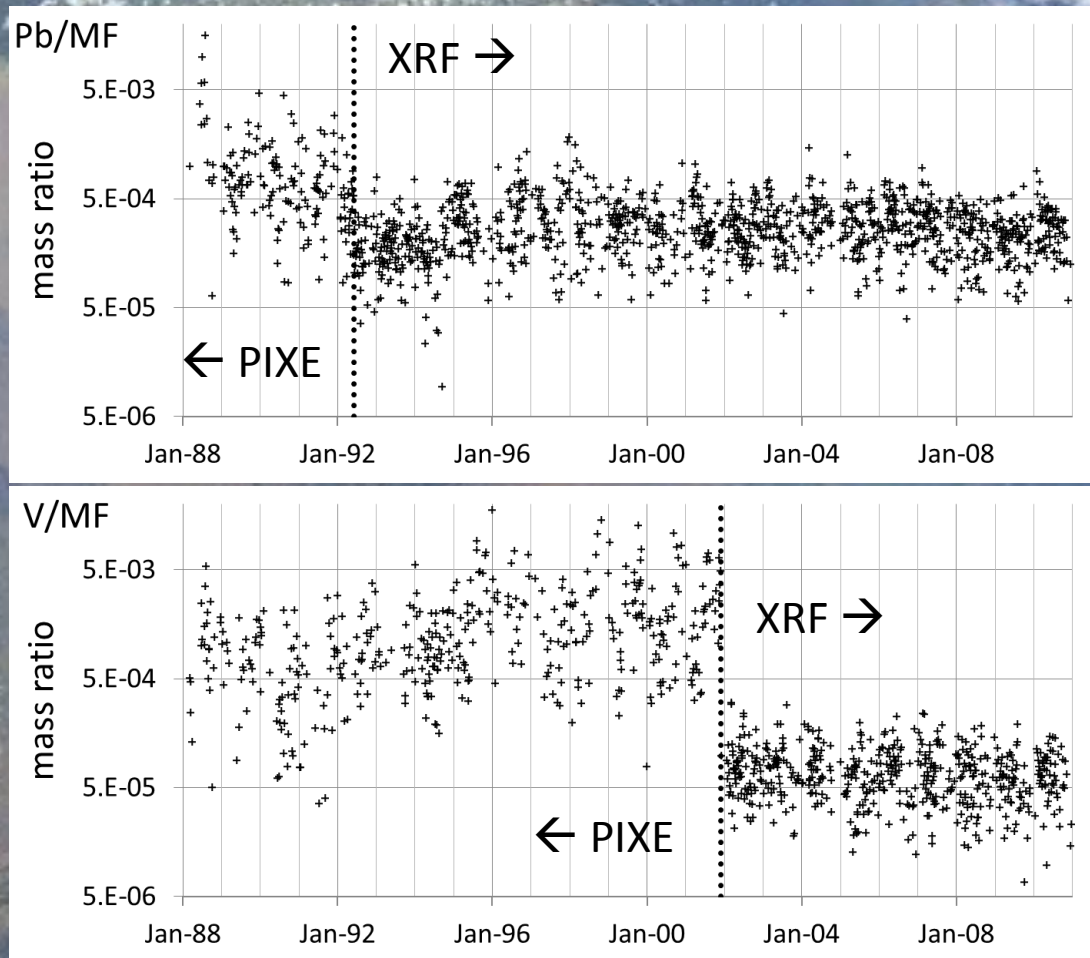
Mauna Loa, 2006 - 2010



Mauna Loa overnight, 2006 - 2010

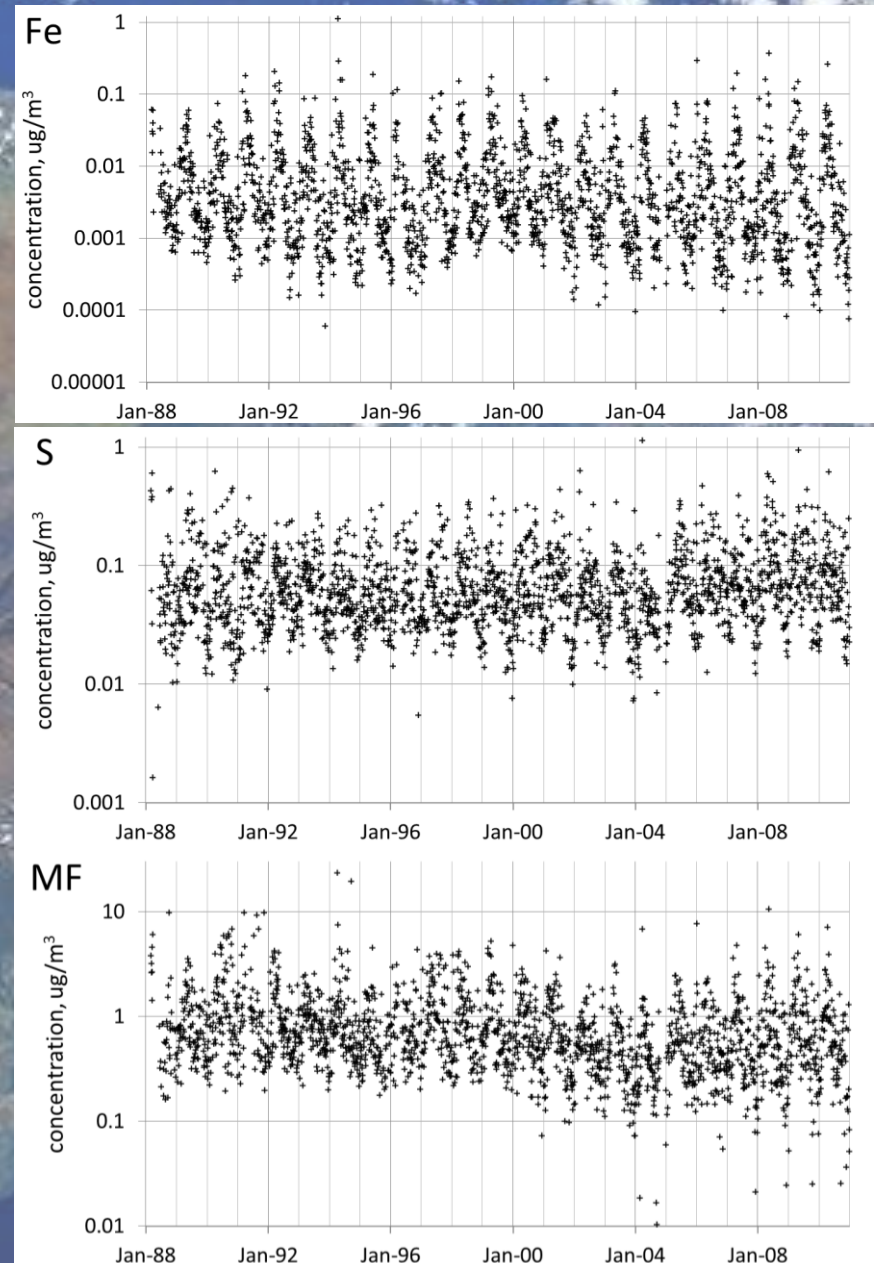


## Mauna Loa overnight



# Long-term trends from the overnight-only module

Mauna Loa overnight



# MALO Plans

- Warren and I are working on a short (technical note) publication on the MALO data set to introduce it to the community.
- MALO data processing is done by hand
  - Current data processing system can't handle the odd schedules
  - Modules are non-standard
  - If these modules will keep running, we need to plan to accommodate them in the new data management system.