Laboratory Research to Evaluate and Improve XRF measurements

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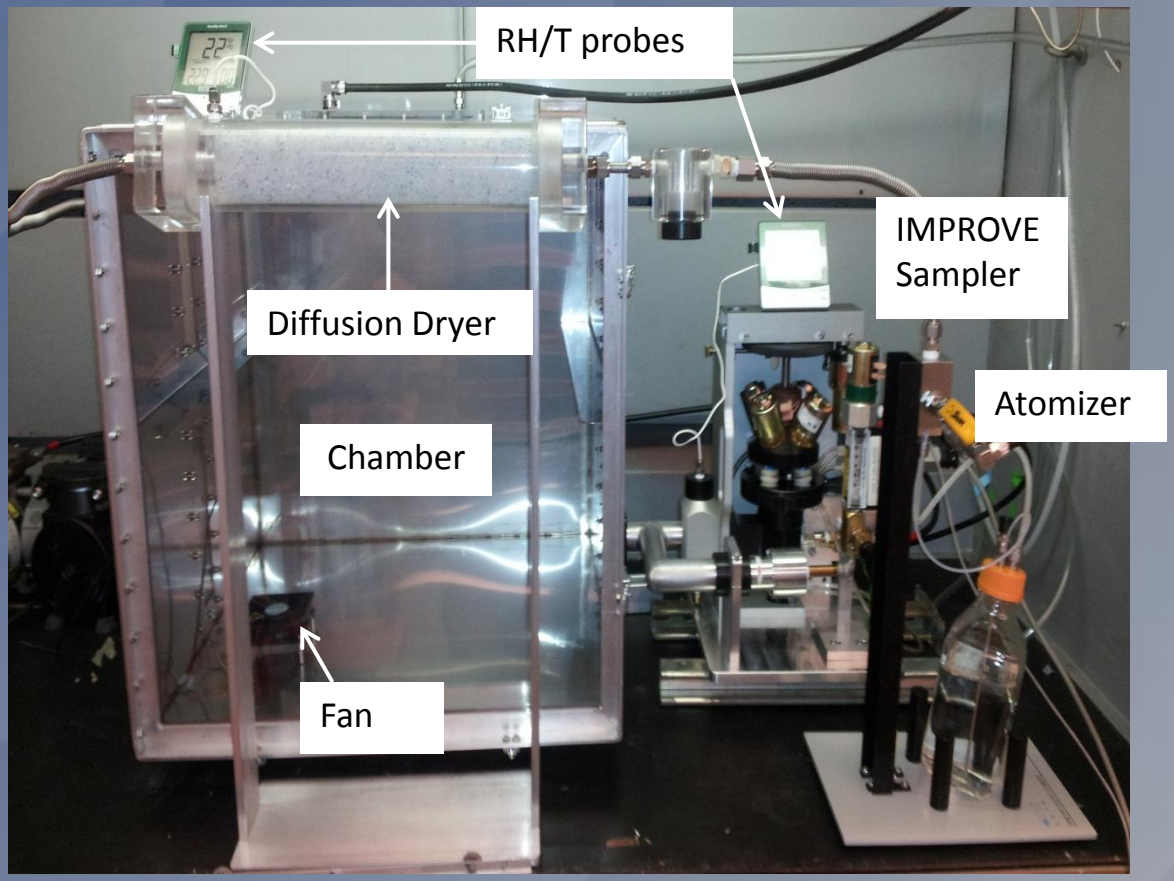
Research Projects

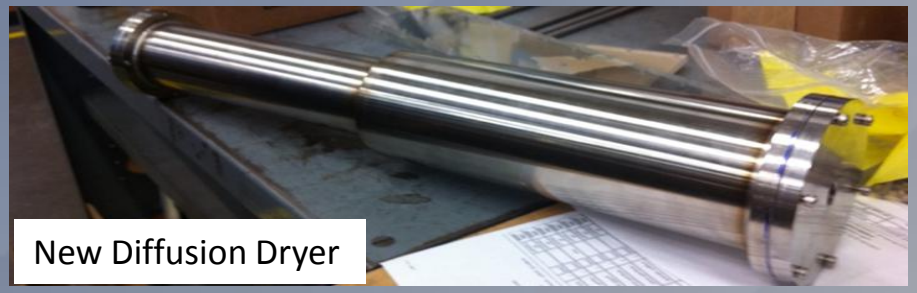
- Single element standards for XRF measurements using the PanAlytical Epsilon 5 XRF instruments
- Error in Si and Al in IMPROVE historical data
- Estimating sample area for reporting XRF data

Motivation for Single Element Standards

- Commercially available standards for XRF instruments are dissimilar to particulate matter samples in chemical composition, substrate, and geometry
- S, Na and Cl standards have been made, used to calibrate the Epsilon 5 instruments, and recently recertified
- Silicon (Si)
  - Si present in soil
  - Commercial XRF standards higher than the 95th percentile of IMPROVE data
- Phosphorous (P)
  - Nutrient, of interest related to water bodies
  - Commercial XRF standards concentration are 20 times higher than maximum IMPROVE masses, are non stoichiometric and not certified

Instrumental Setup - Si and P

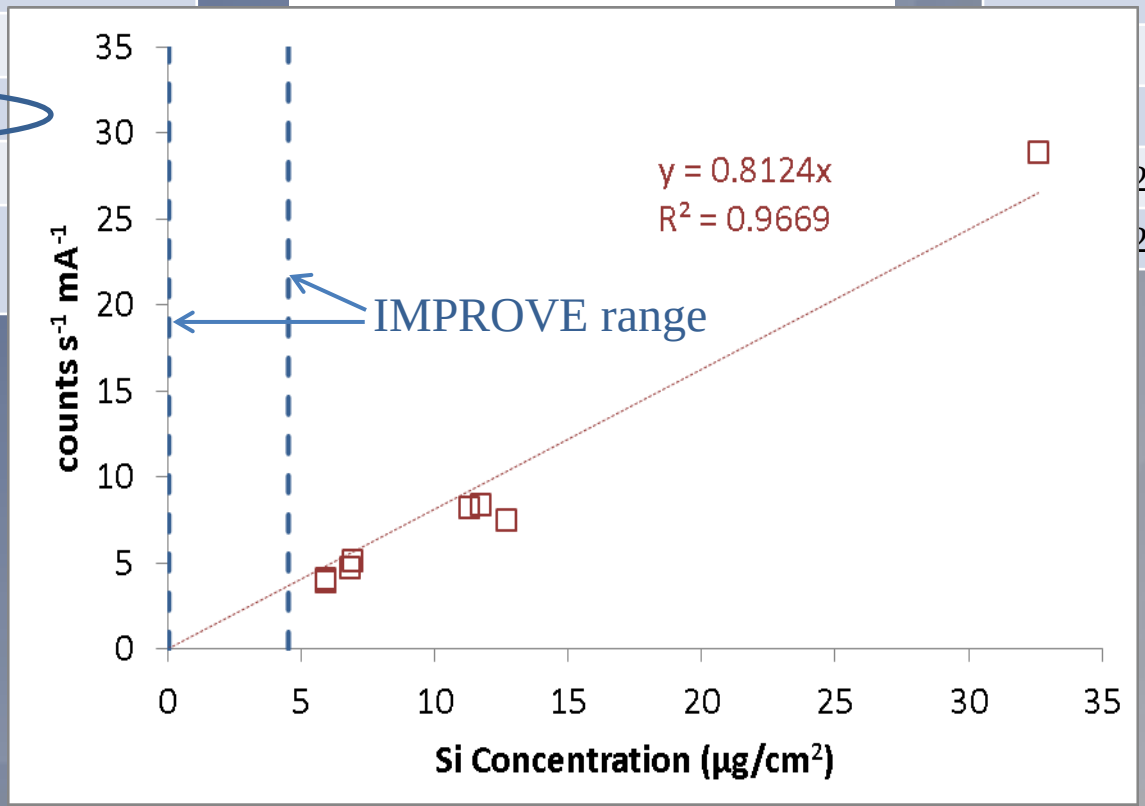




Silicon Commercial XRF Standards

Silicon concentrations IMPROVE (Jan to Oct 2011) (µg/cm²)	
Mean	1.2
Min Conc.	0.0001
5th percentile	0.03
25th percentile	0.17
50th percentile	0.48
75th percentile	1.21
95th percentile	4.5
Max Conc.	51.2
Number of samples (N)	15852

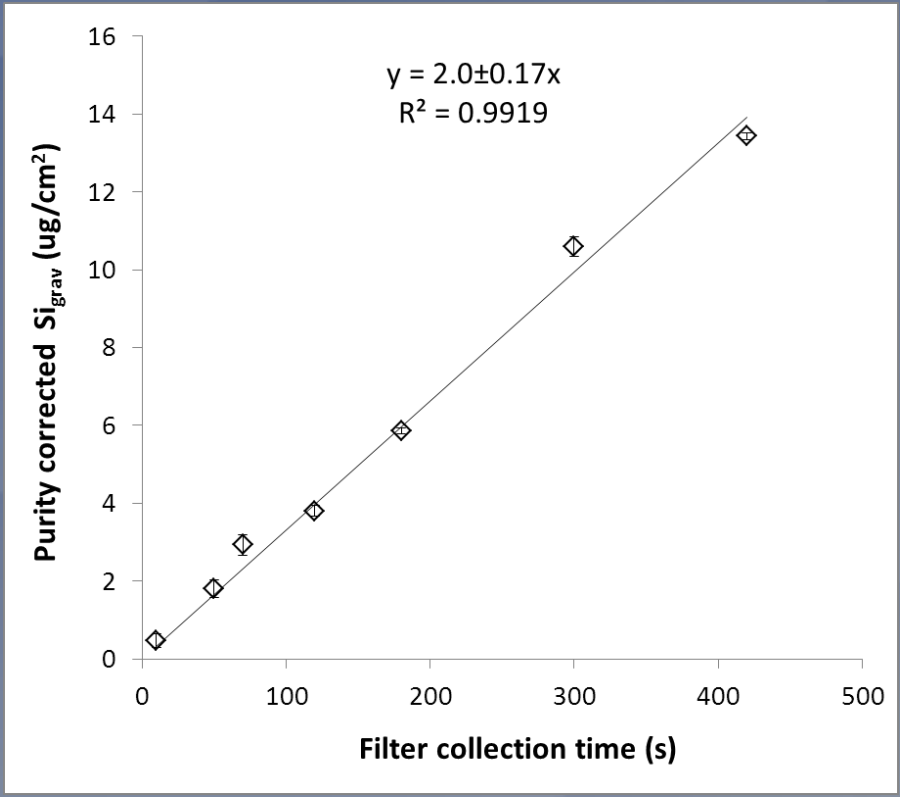
Commercial Si XRF standards

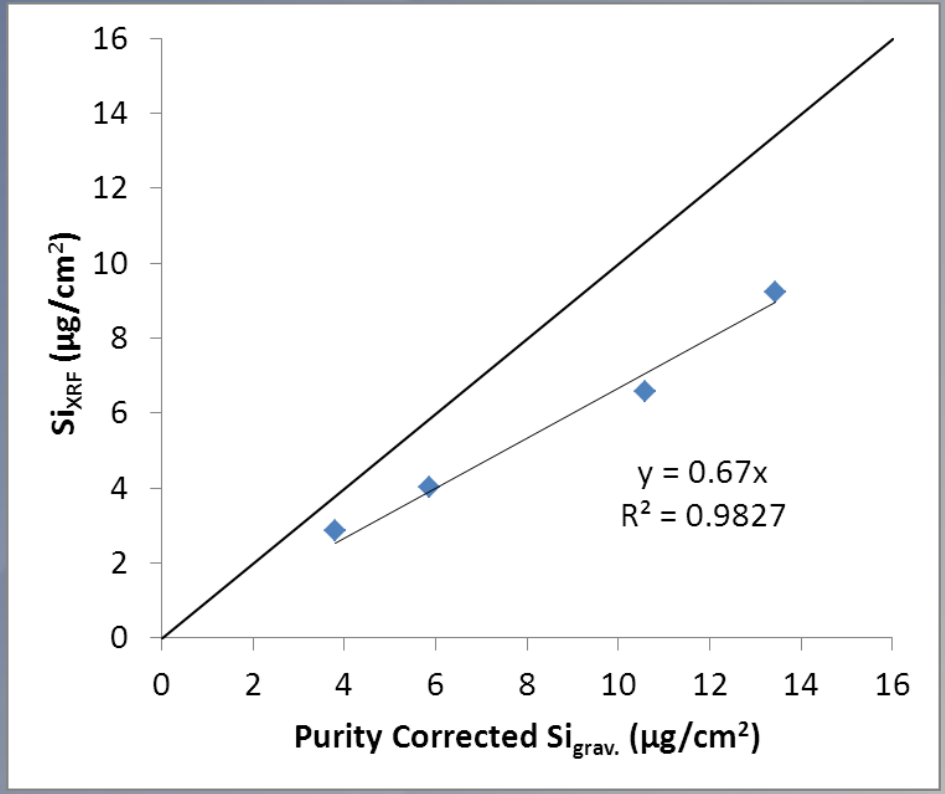


Commercial XRF Si standards (µg/cm²)		
Compound	**Mass**	**Cert.**
SiO	32.6	5%
SiO	12.7	5%
SiO	11.7	5%
SiO	11.3	5%
SiO	6.9	RM
SiO	6.8	RM
2783	5.884	2.7%
2783	5.884	2.7%

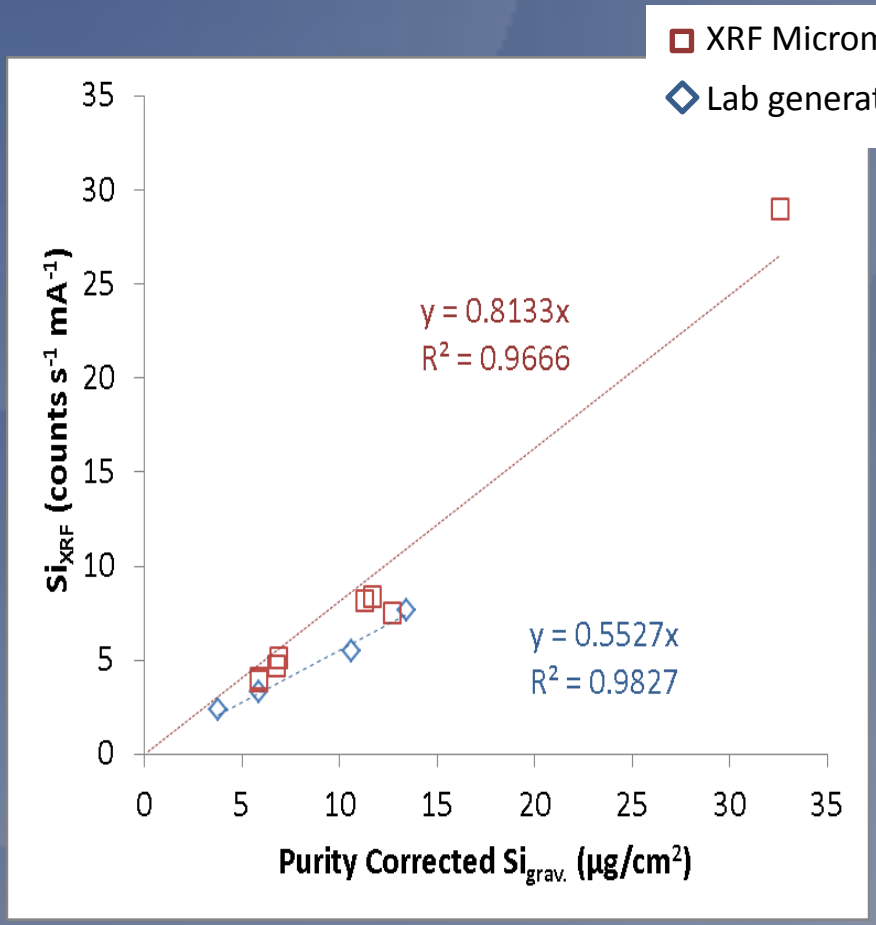
Laboratory Generated Silicon Standards

- A suspension of SiO_2 (99.5 %, purity) nanoparticle (~20 nm)
- Gravimetric deposits of 0.5-13.4 µg Si/cm^2
- IMPROVE 50th percentile = 0.5 µg Si/cm^2
- Dryness of SiO_2 deposits confirmed using IR

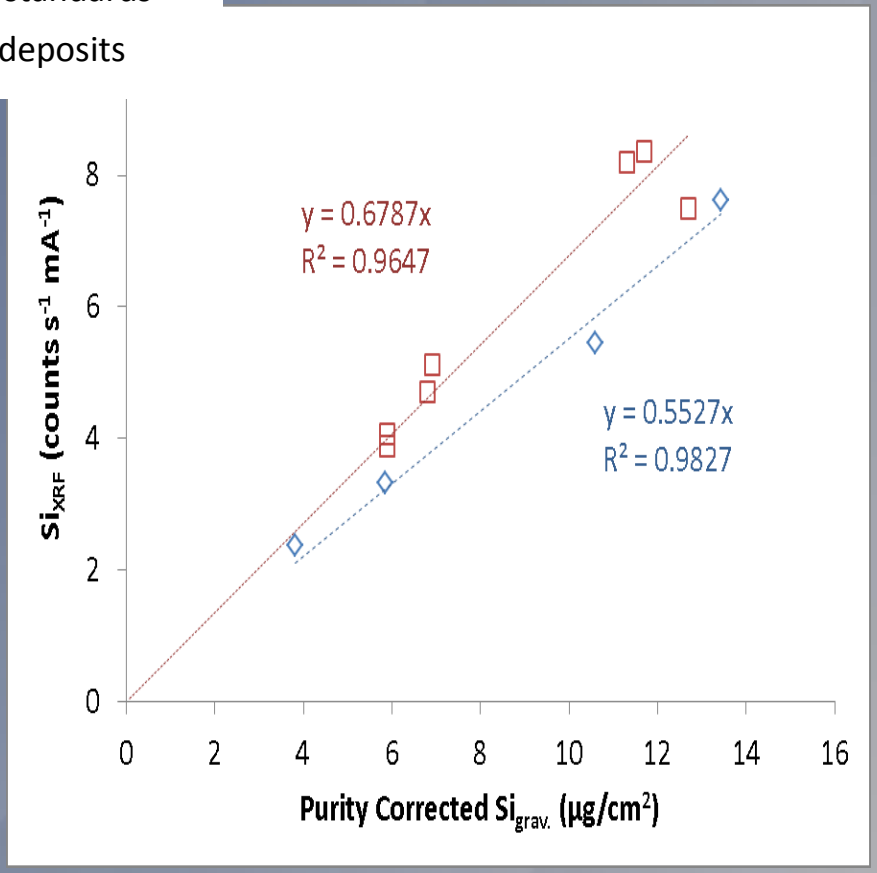




Silicon XRF vs. Gravimetric Results

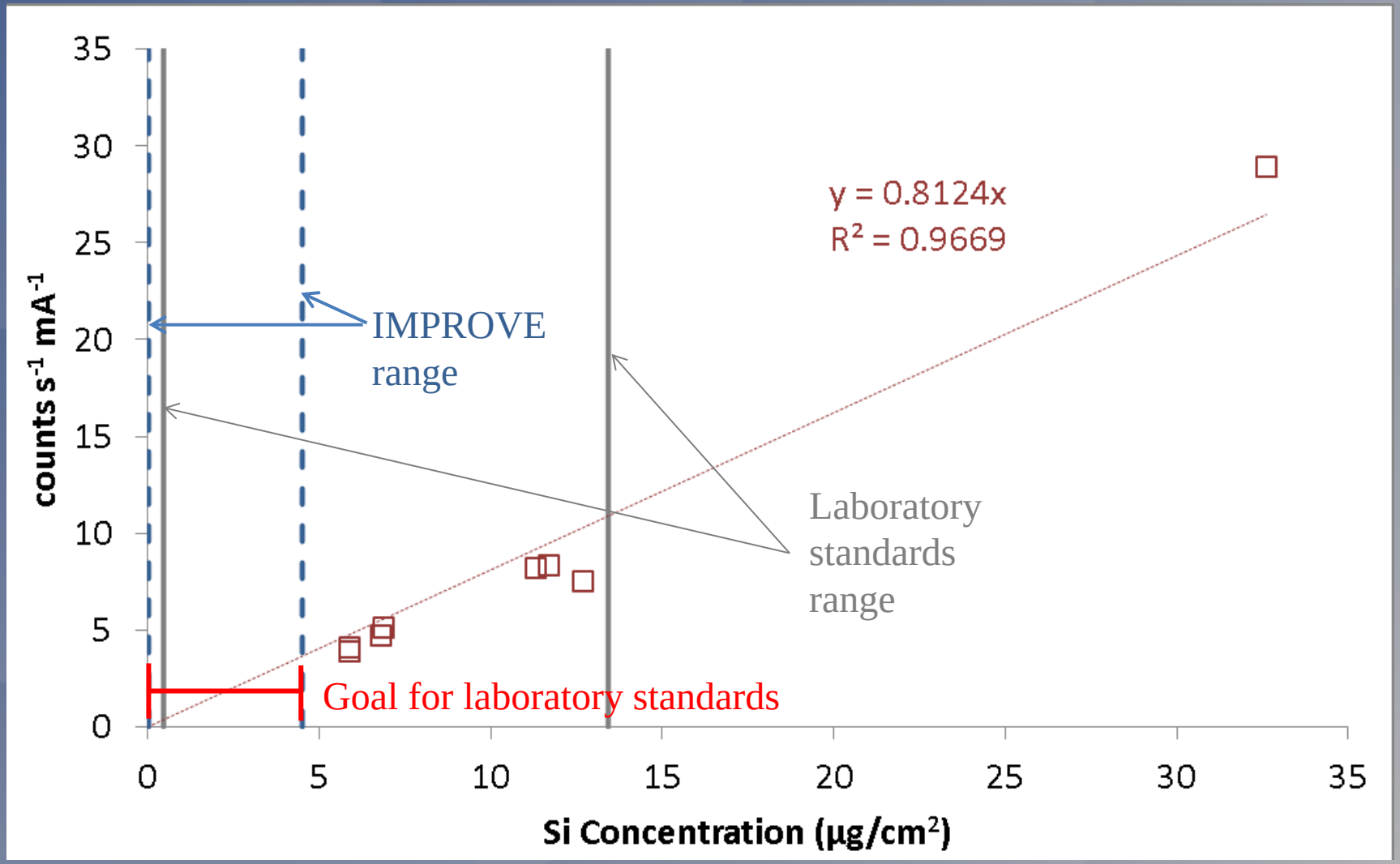


Si counts on Epsilon 5 vs. Si gravimetric data for commercial and lab standards. 32% difference in slope



Si counts on Epsilon 5 excluding highest commercial standard vs. Si gravimetric data. 19% difference in slope

Si Summary and Future Work



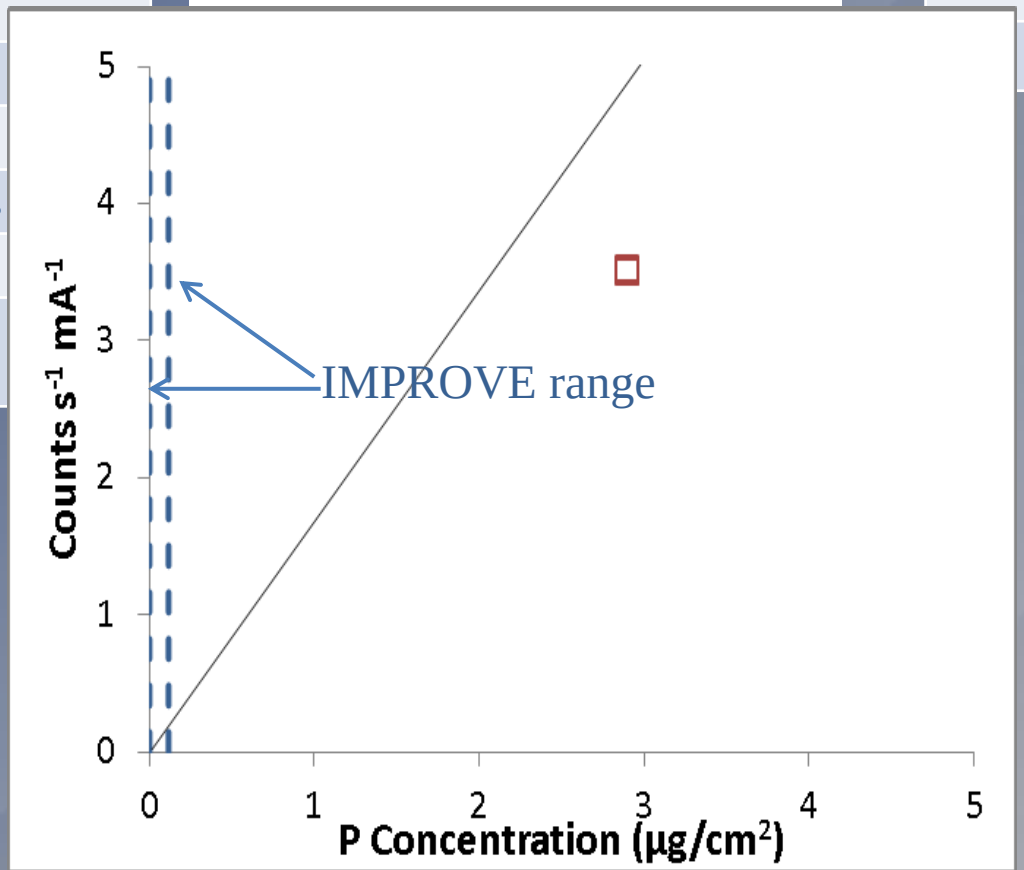
- TiO_2 (~21 nm) standards to determine if detection of nanoparticles is accurate
- Second compound/salt for Si deposition, possible analysis by alternate method
- Expanding the mass range of the current deposits (25^{th} to 99^{th} percentile, some higher)

Phosphorous Commercial XRF Standards

Phosphorous concentrations IMPROVE (Jan to Oct 2011) (µg/cm²)	
Mean	0.29
Min Conc.	6.97 X 10^{-5}
5th percentile	0.001
25th percentile	0.006
50th percentile	0.0011
75th percentile	0.03
95th percentile	0.12
Max Conc.	1.86
Number of samples (N)	6114

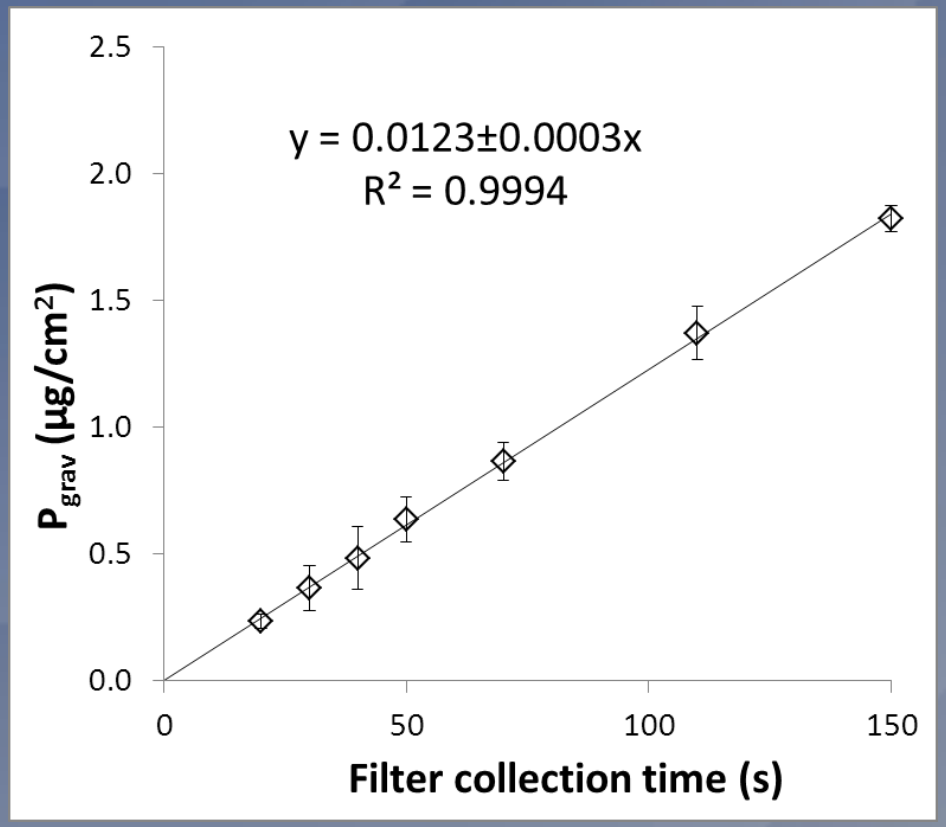
Commercial XRF P standards (µg/cm²)		
Compound	**Mass**	**Cert.**
GaP	14.5	NS
GaP	4.6	NS
GaP	2.9	RM
GaP	2.9	RM

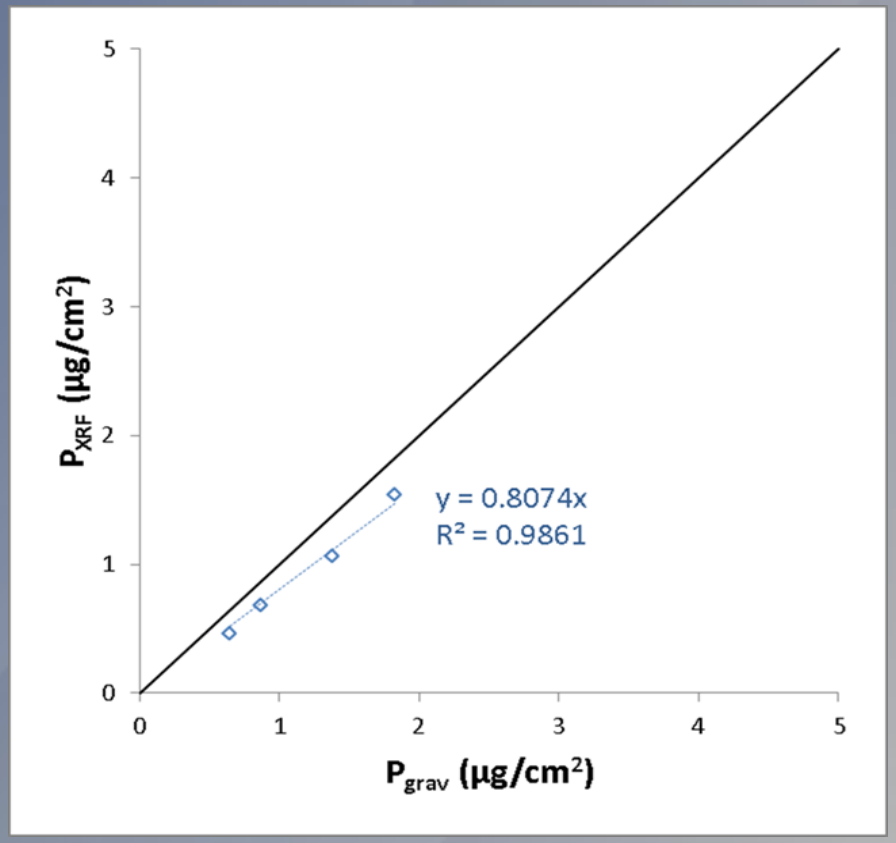
Commercial XRF standards of P



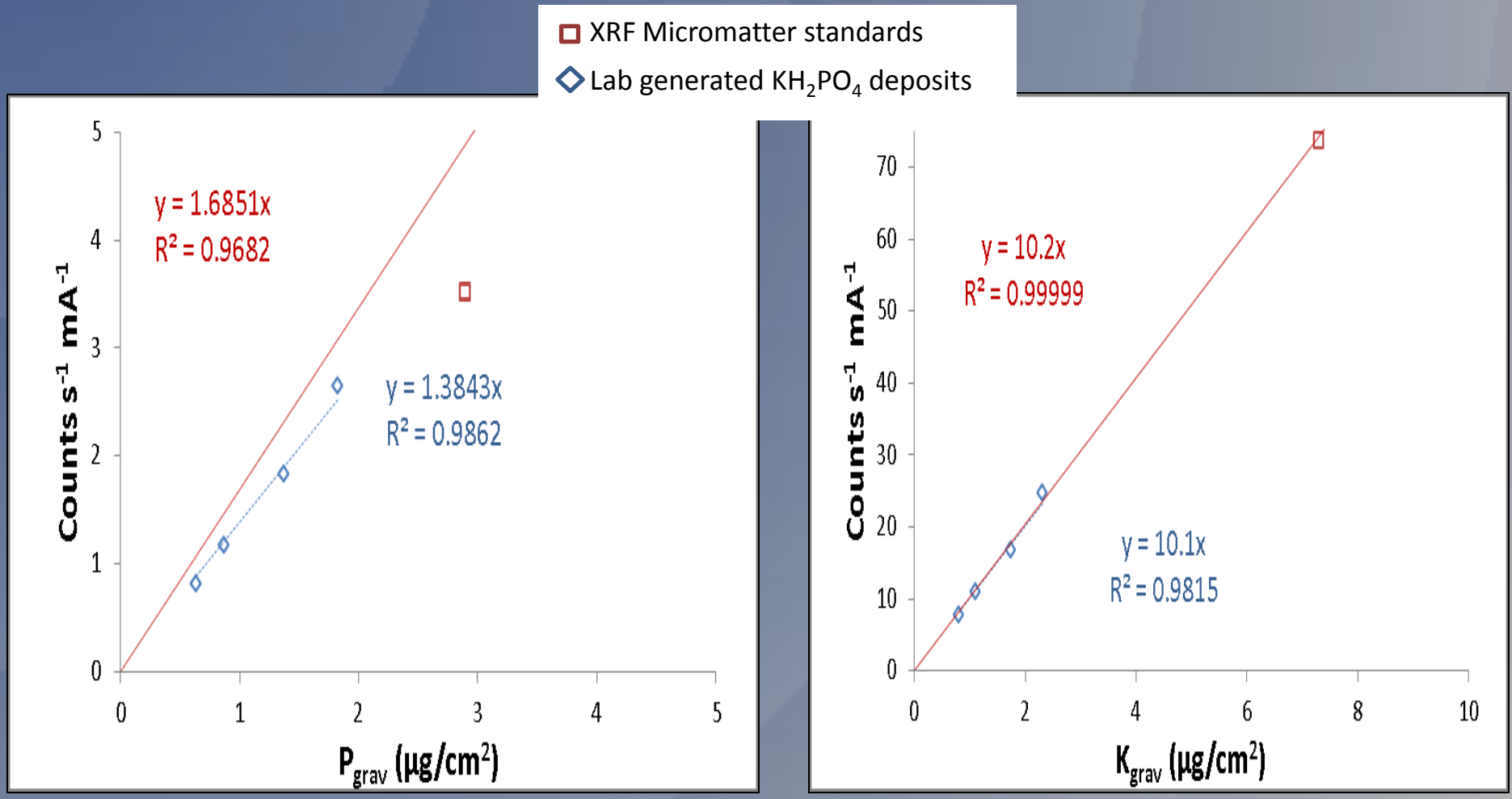
Phosphorous (P)

- 0.004 M solution of KH_2PO_4 (99.995 %, purity)
- Dryness of deposits confirmed using IR



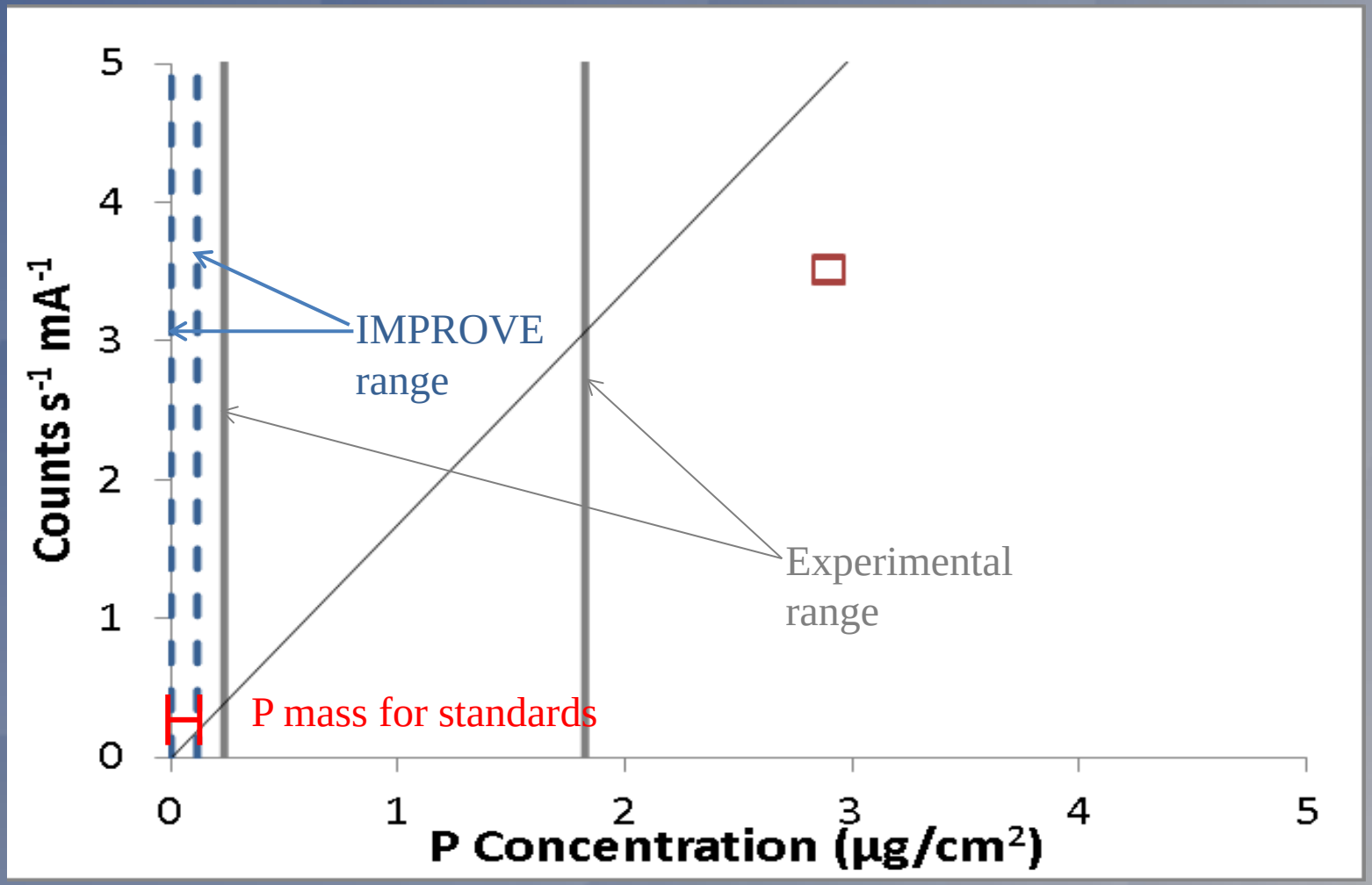


Phosphorous XRF vs. Gravimetric



From XRF analysis the molar ratio of P to K is found to be 0.83, theoretical ratio is 1

P Summary and Future Work

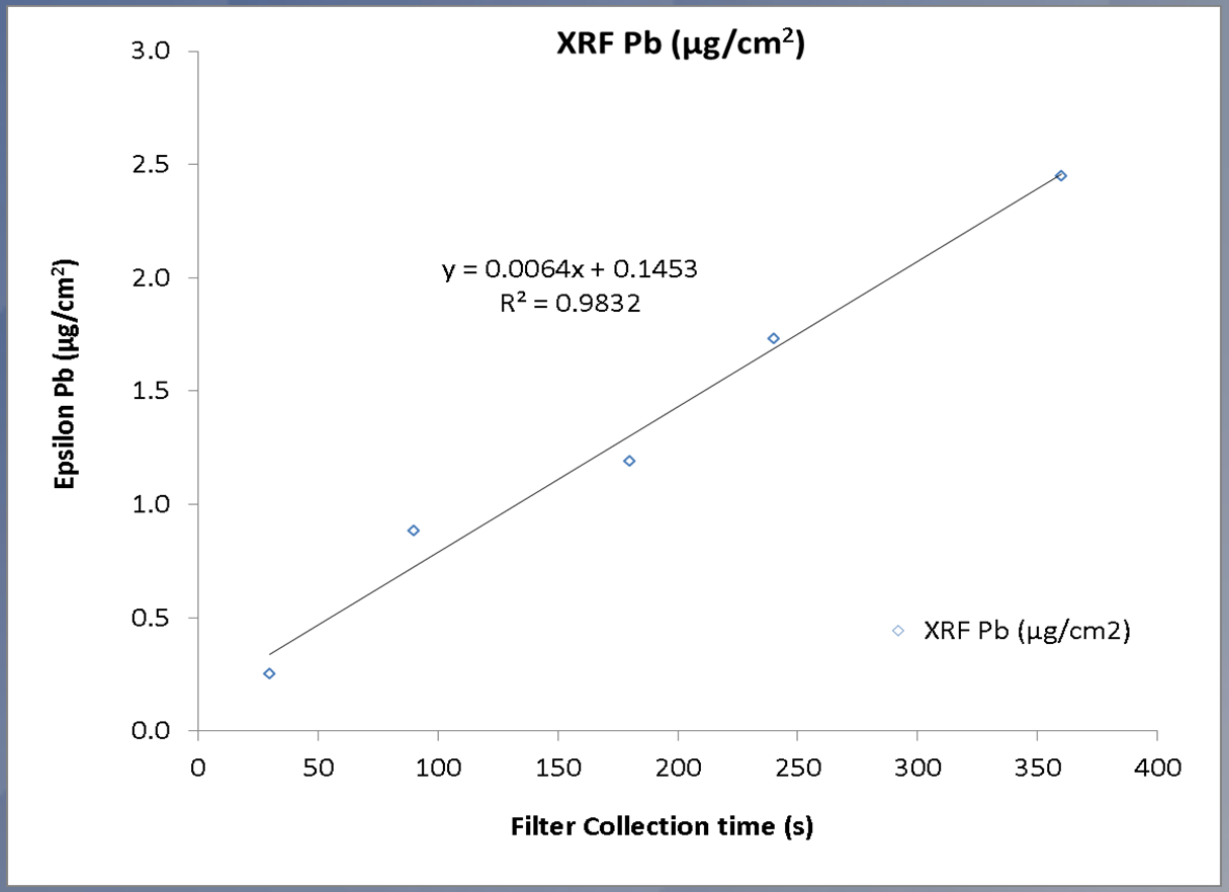


- **K interferes with P measurement; use $BiPO_4$ (10%P) or NH_4PF_6 (20%P)**
- **Analyze filters by IC (at RTI) for PO4 to confirm gravimetric measurements**
- **Lower mass on filter to be in IMPROVE range**
- **Evaluate differences in response in P spectral region for three Ep. 5 XRF instruments**

Lead (Pb) – EPA funded project

- **Objective:** To create Pb deposits on EPA 47mm Teflon filters with for FEM testing and approval, quarterly audit analysis samples and with possible use as SRM
  - FEM testing and approval requires Pb at three levels, **0.1 µg/cm^2, 0.3 µg/cm^2, and 0.75 µg/cm^2,** which correspond to **30%, 100%, and 250%**, of current Pb NAAQS
  - Audit filters are needed at 30-100% of NAAQS Pb and 200-300% of NAAQS Pb
- Lead nitrate and lead acetate have been used to generate these filters
- Initial experiments were performed using IMPROVE PM2.5 sampler
- Partisol 2025 Sampler to generate Pb deposits on 47 mm filters
  - Updated electronics in chamber for better system control and safety in chamber

Lead Acetate Trihydrate ($Pb(CH_3COO)_2.3H_2O$

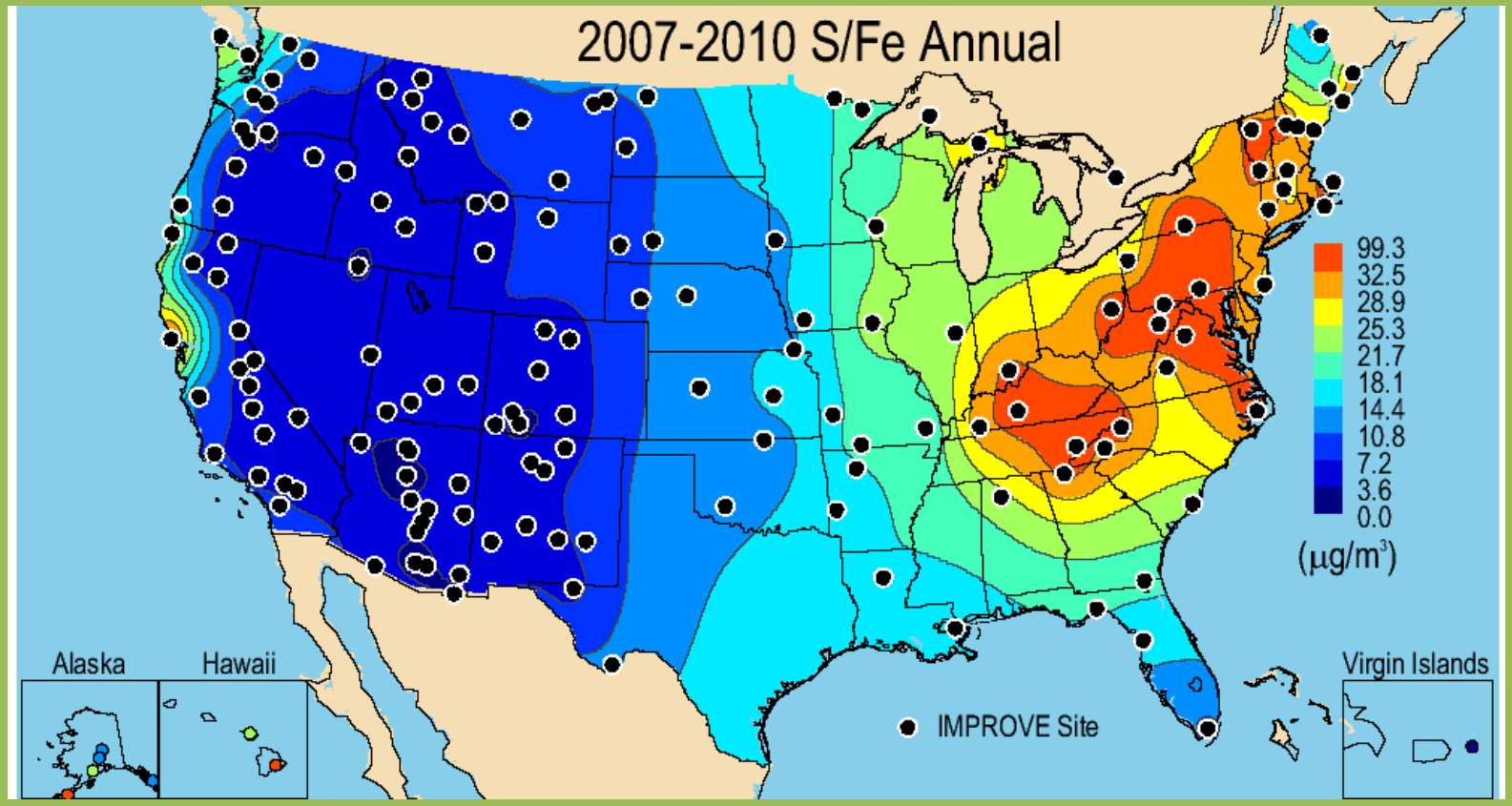


- Achieved mass of 0.25 µg/cm², close to lowest mass required by EPA
- Use lower concentration in atomizer to achiever lower mass on filter
- Water on filter an issue: installed larger dryer, may try other Pb compounds
- Analyze by ICP-MS

Recommendations for using IMPROVE Si and Al data 2002-2010

- Samples with S/Fe < 8 (49% of 2008 data)
  - Si and Al data unaffected by S
- Samples with 8 < S/Fe < 70 (47% of 2008 data)
  - Si mass over reported by up to 100%
  - Al data may have errors up to ±50%
  - Use data with care
- Samples with S/Fe > 70 (4% of 2008 data)
  - Si concentrations are likely over reported by ≥2
  - Al concentrations either over reported by >50% or erroneously reported as below MDL
  - Use data with extreme caution
- Results do not significantly impact RHR

2007-2010 Average S/Fe

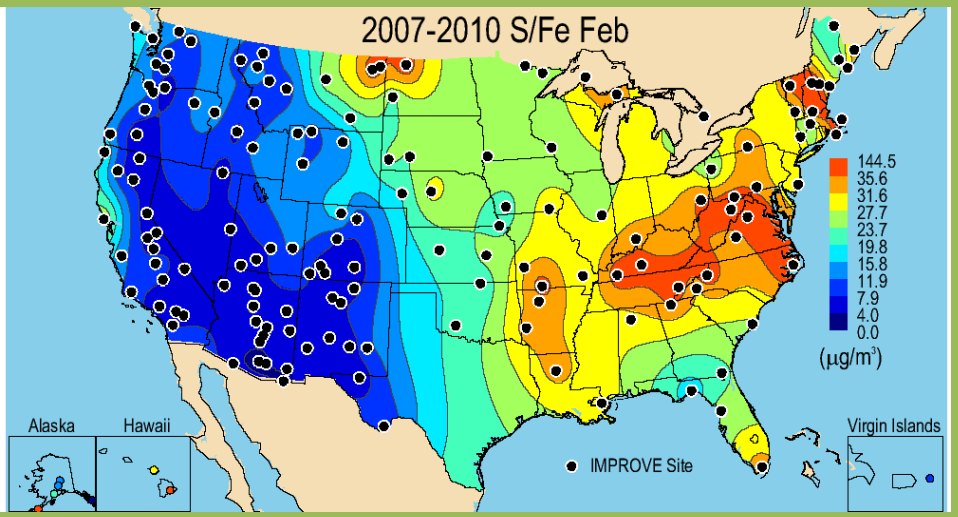


Maps by Jenny Hand

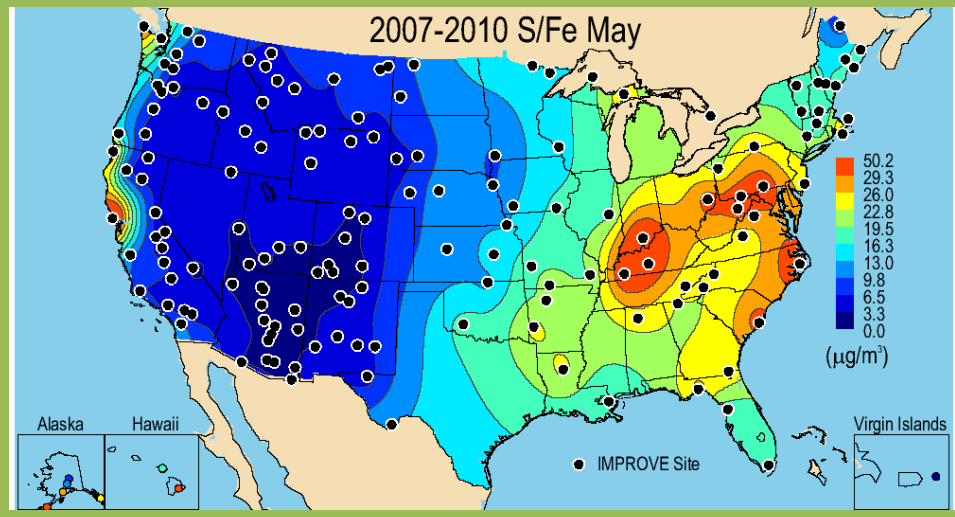
Maps by Jenny Hand

S/Fe By Season

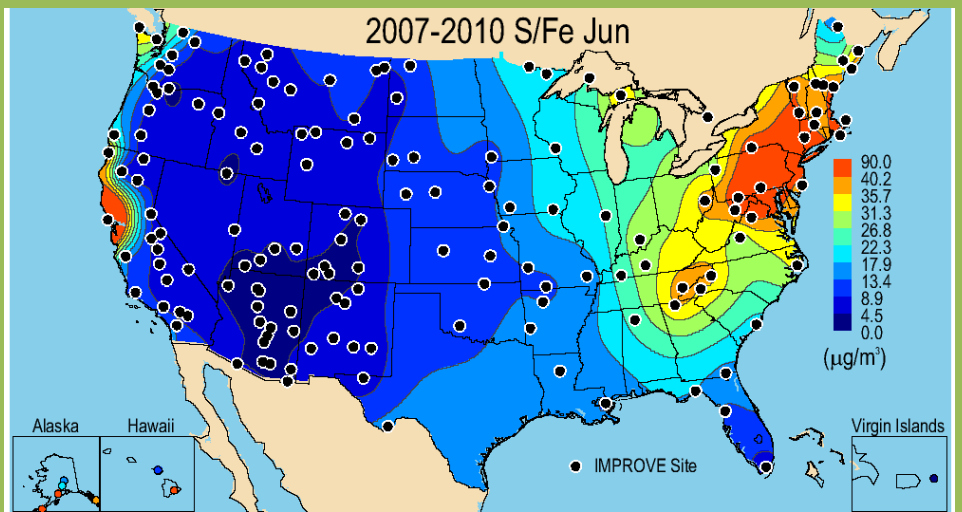
Winter



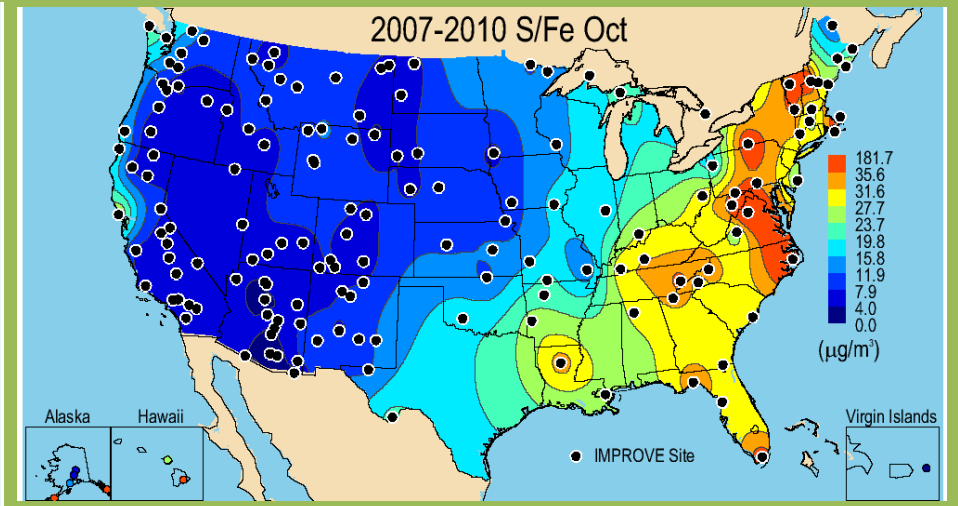
Spring



Summer



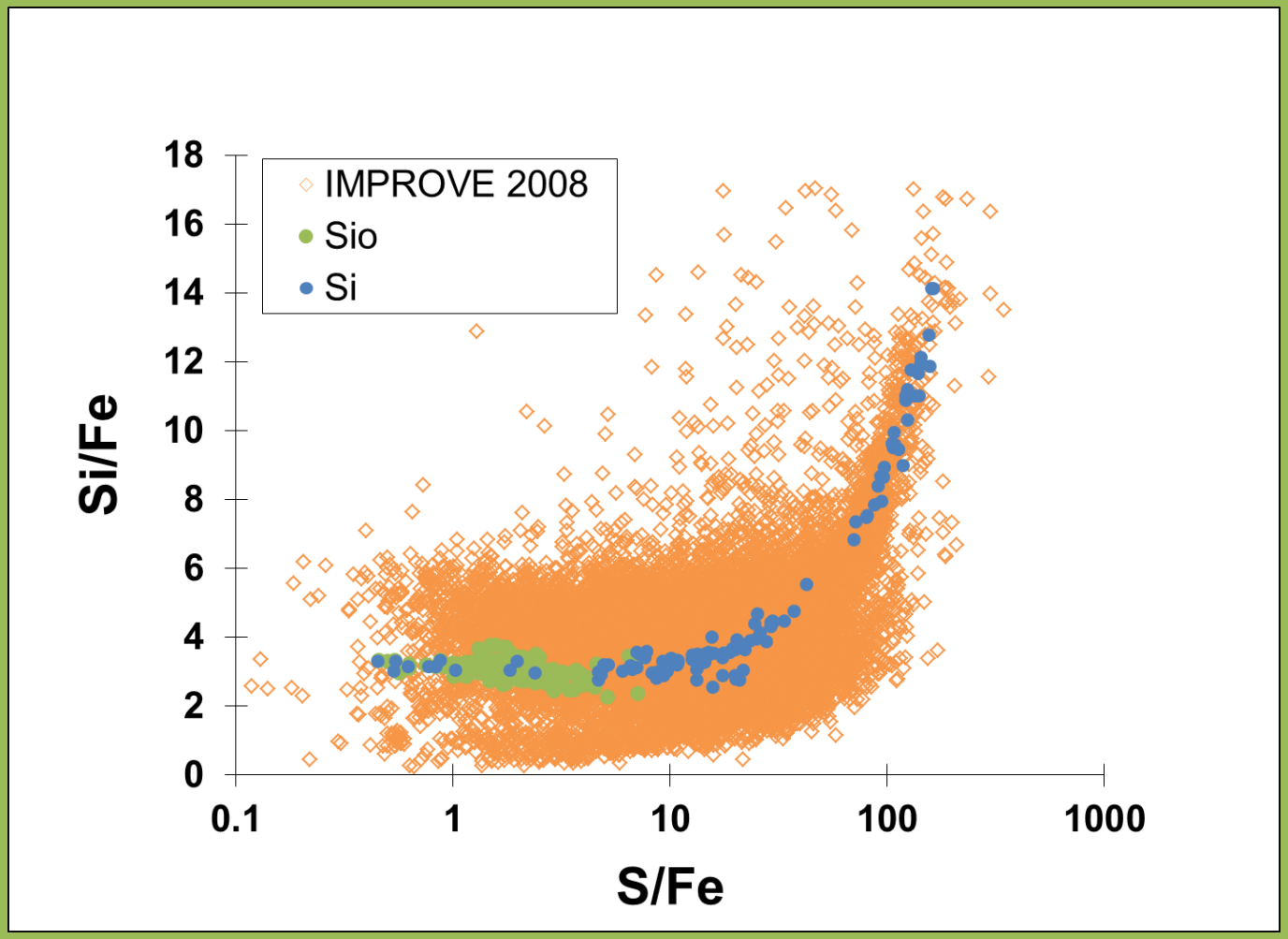
Fall



Analysis does not apply to

- Samples with significant urban influence due to anthropogenic Fe
  - Non-rural sites in IMPROVE
  - EPA's CSN network sites
- Samples analyzed with XRF that has no sulfur tail or has proper correction for the sulfur tail
- IMPROVE samples prior to 12/1/2001 and after 12/31/2010

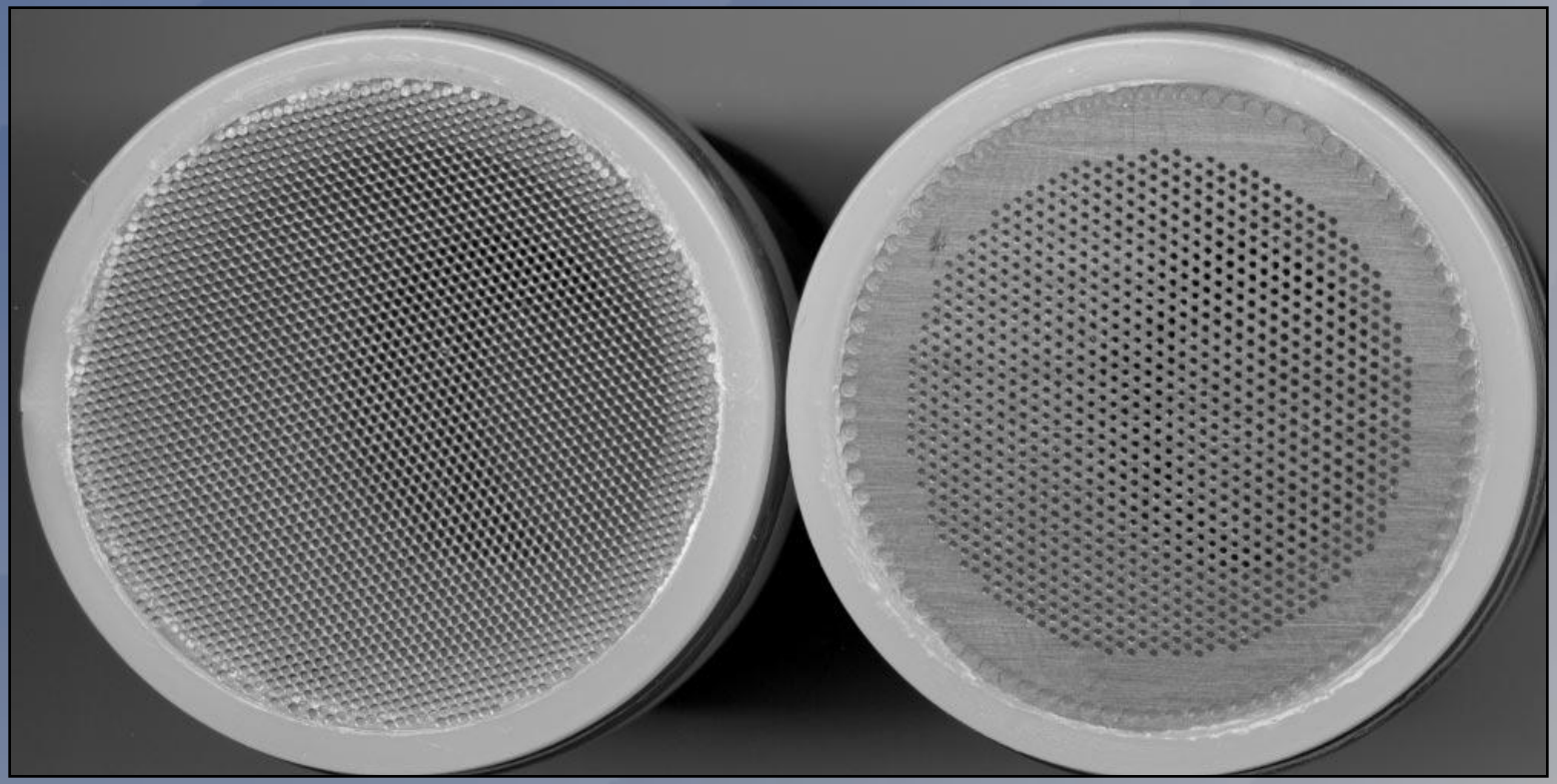
Is your site impacted by urban Fe?



More information

- Indresand H., Dillner, A.M., Atmospheric Environment 61 (2012) 140-147 (emailed to Steering Committee)
- Forthcoming data advisor on the IMPROVE website http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm

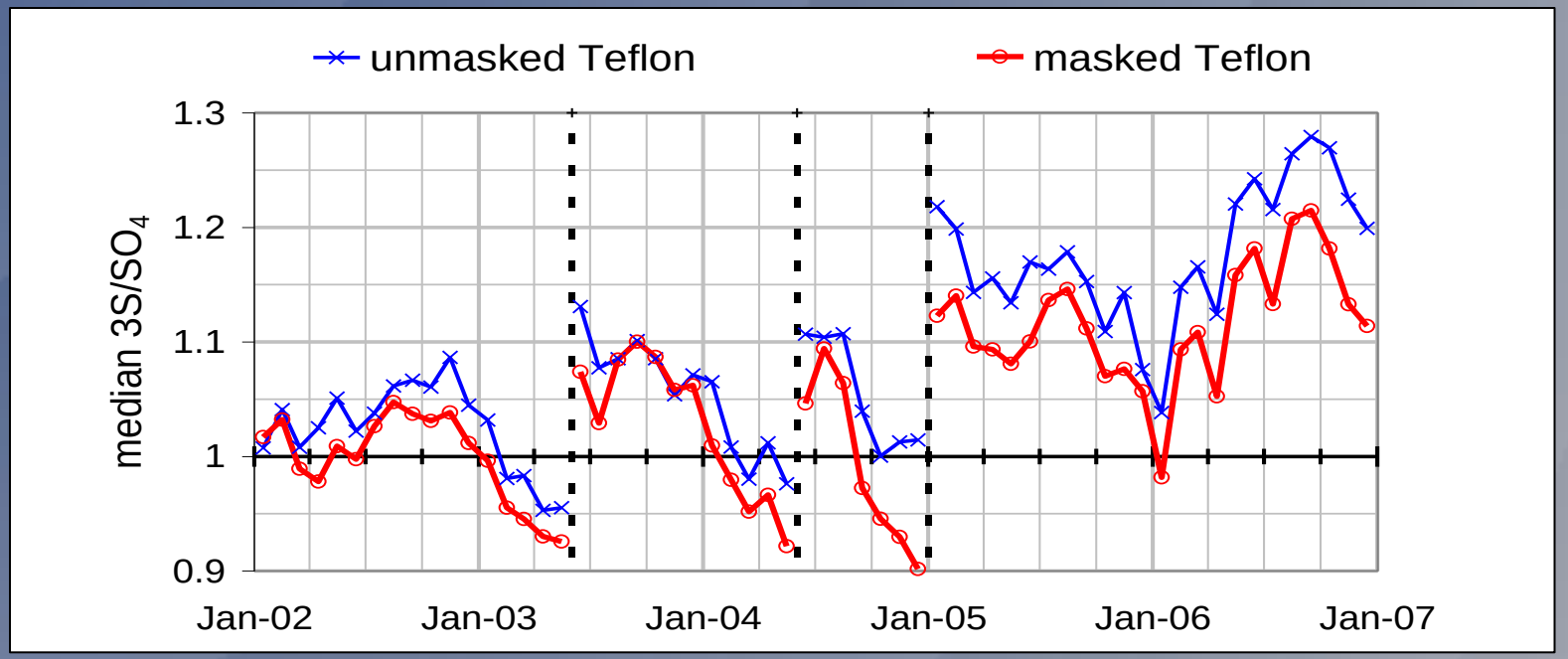
Sample Area
Used to multiply XRF masses in ng/cm2 to obtain ng/filter



Unmasked cassette
Area measured to be 3.53 cm2

Masked cassette
Area measured to be 2.20 cm2
2001 ~50% sites, 2008 zero sites

Motivation to evaluate area of sample



- ~5% bias in sulfur/sulfate ratios between unmasked and masked samples
- Sulfate ion concentrations have been measured by the same protocol at all sites since 2001.

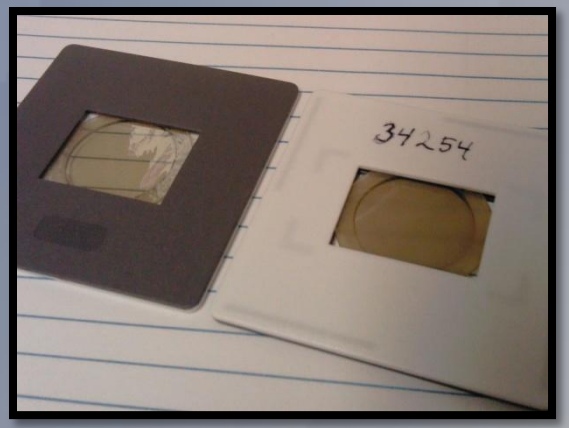
Figure from data advisory by Warren White in 2008
http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0019/da0019_masks.pdf

Effective Area - methodology

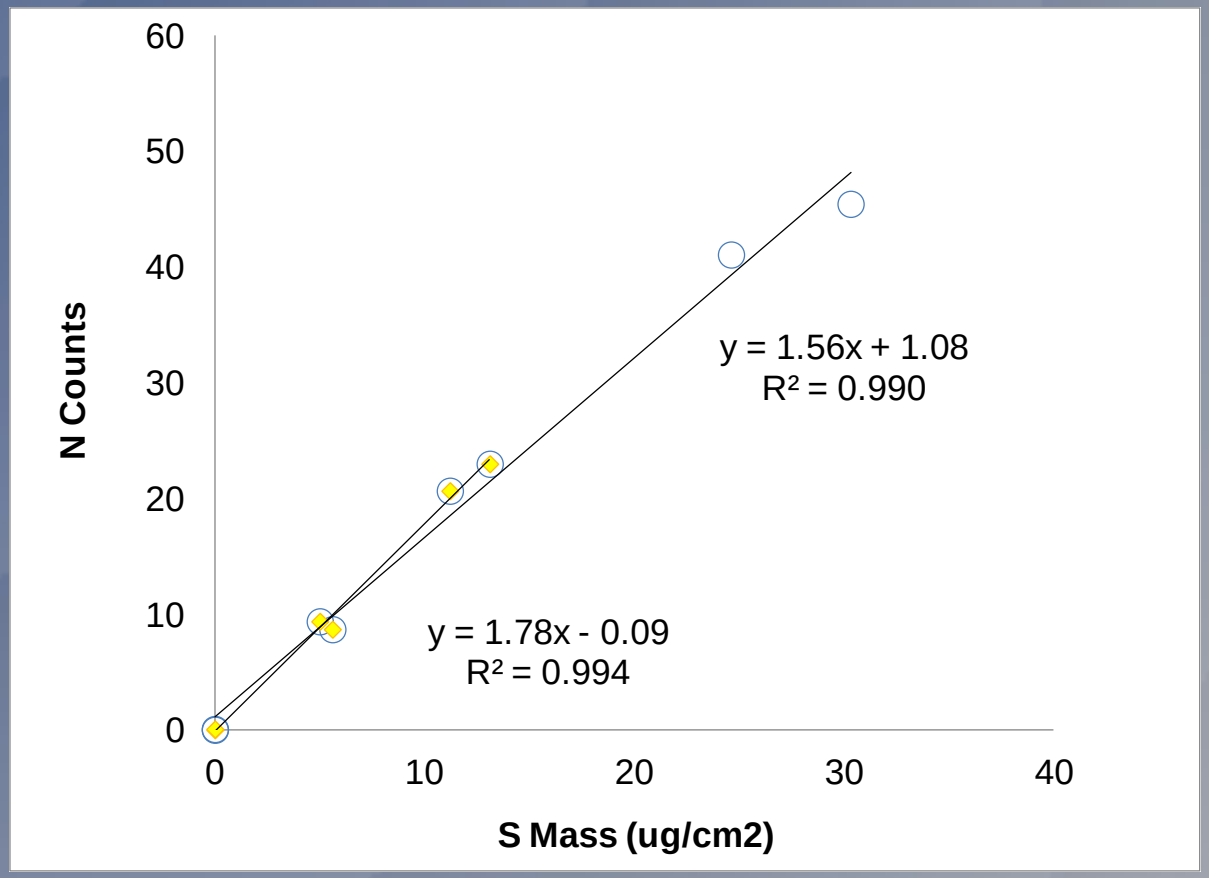
- Deposited ammonium sulfate on Teflon using
  - Unmasked cassettes
  - Masked cassettes (two types)
- Pre and post weighed filters three times (µg/filter)
- Measure S by Cu-vacuum XRF system used by IMPROVE prior to 2011 data
  - Calibrated with new set of standards
  - gives S mass (µg/cm^2)
  - measured 3 times
- Regress two data sets to get effective area (cm^2)

Calibration of XRF to obtain accurate µg/cm^2 response

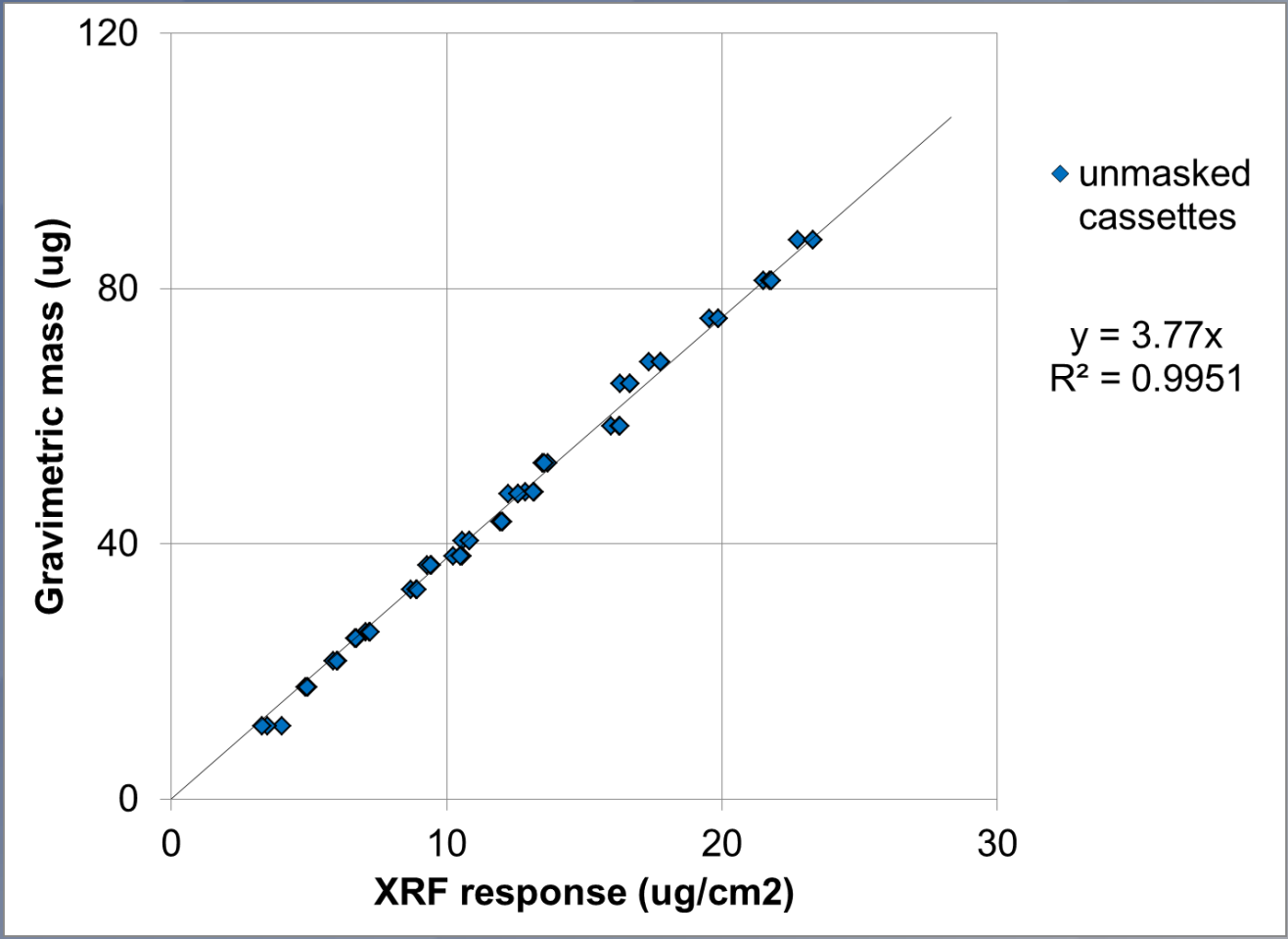
- 3 Mylar and 3 Nuclepore plus blank of each substrate in IMPROVE sulfur range
- Custom mounting with <1.0 mm thick ring, similar to Teflon filters
- Fit into sample slides frames used for sample analysis
- Analyzed 3 times, before each analysis of effective area study filters



Effective Area – Calibration and matrix effects in highest mass S standards



Effective Area – Unmasked cassettes

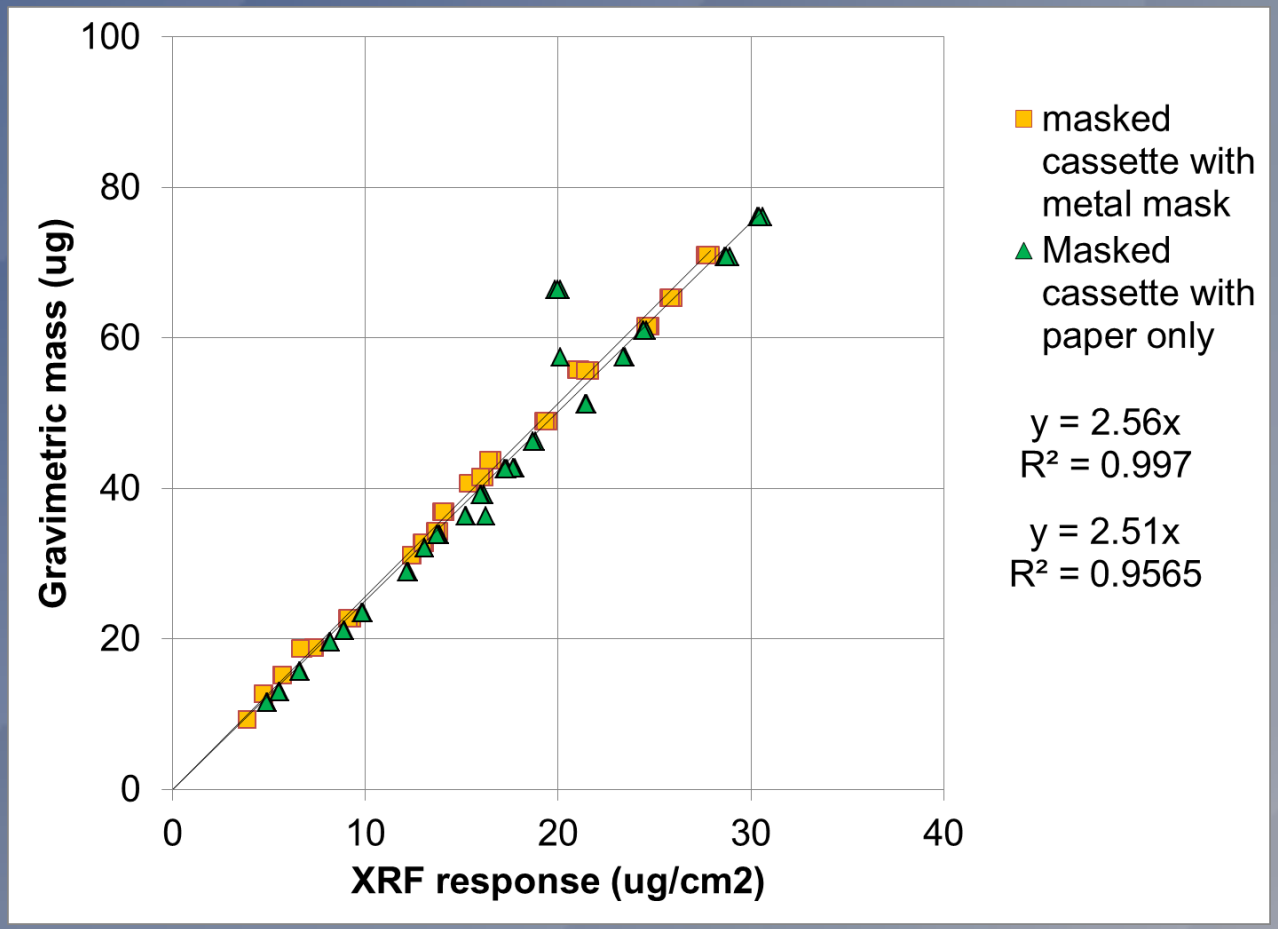


Area historically used = 3.53 cm^2

Unmasked effective area = 3.77±0.04 cm^2

Effective area is 6.7% higher

Effective Area – Masked Cassettes



Historical area used = 2.2 cm^2

Average Masked effective area = 2.54±0.11 cm^2

Effective area is 15% higher

- Average IMPROVE masked to unmasked ratio

$$\frac{\frac{\text{Unmasked S (ug/cm2)} * 3.53}{\text{Sulfate}}}{\frac{\text{Masked S (ug/cm2)} * 2.2}{\text{Sulfate}}} = \sim 1.05$$

- Correct above ratio using measured effective area

$$1.05 * \frac{\frac{3.77}{3.53}}{\frac{2.54}{2.2}} = 0.97$$

- Using effective areas brings the 3S/SO4 ratio between masked and unmasked sites closer to 1, the expected value.

Effective Area - Conclusions

- The historically used areas of 3.53 and 2.20 cm^2 are lower than the effective areas measured
- Correcting the historic data using effective area decreases difference in S/SO4 for masked and unmasked sites
- Results applicable to small particles (~100 nm)

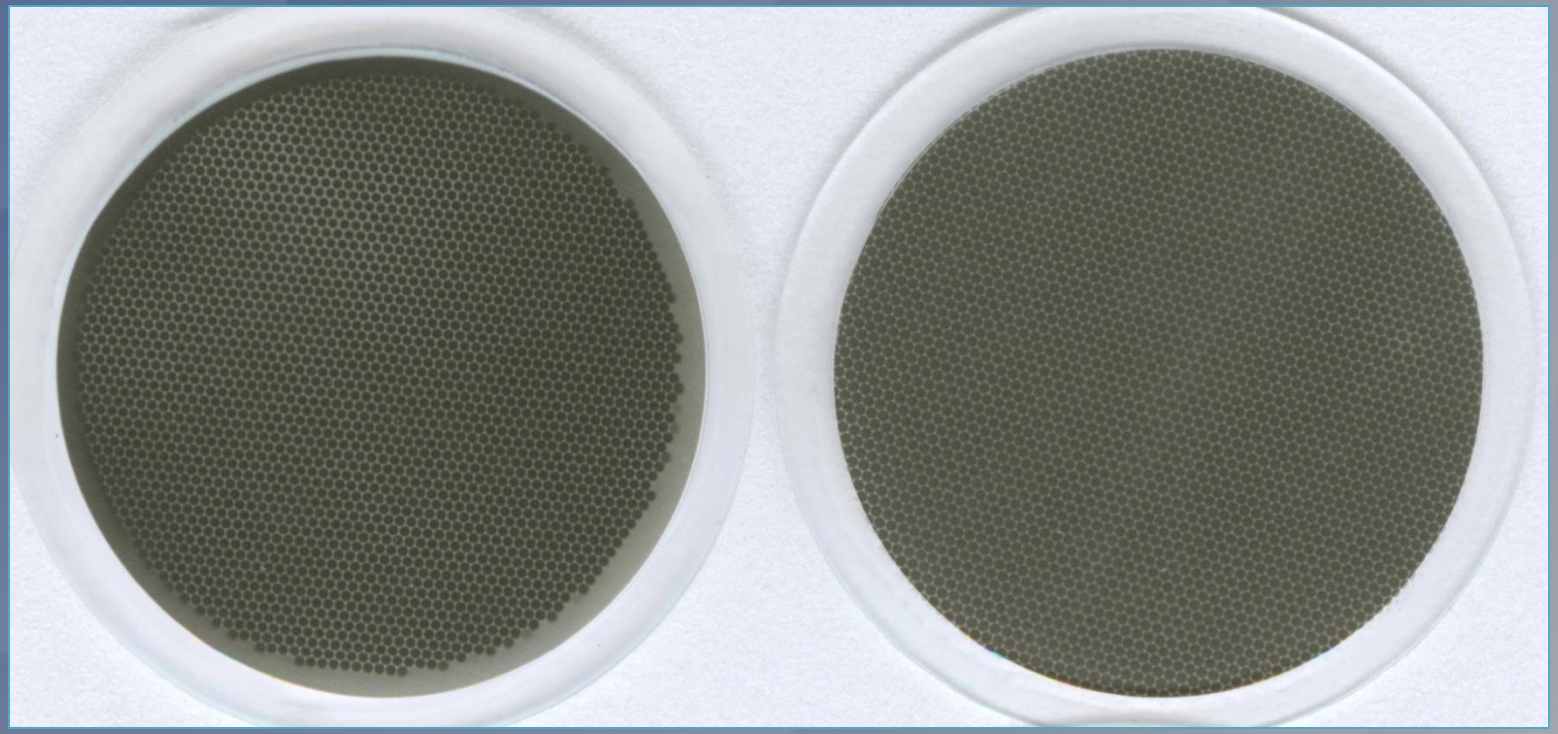
Future Work

- Measure effective area of filters collected using new detached screen cassette using the Epsilon 5 instruments
- Repeat experiments with particles in the upper end of the PM2.5 size range
- Continue to make XRF standards using AWIM which produce output in ng/filter

Acknowledgements

- CNL colleagues
  - Krystyna Trzepla-Nabaglo and the IMPROVE XRF group
  - Warren White
  - Chuck McDade
  - Nicole Hyslop
  - Chris Wallis
  - Frank Latora
  - Brian Devine

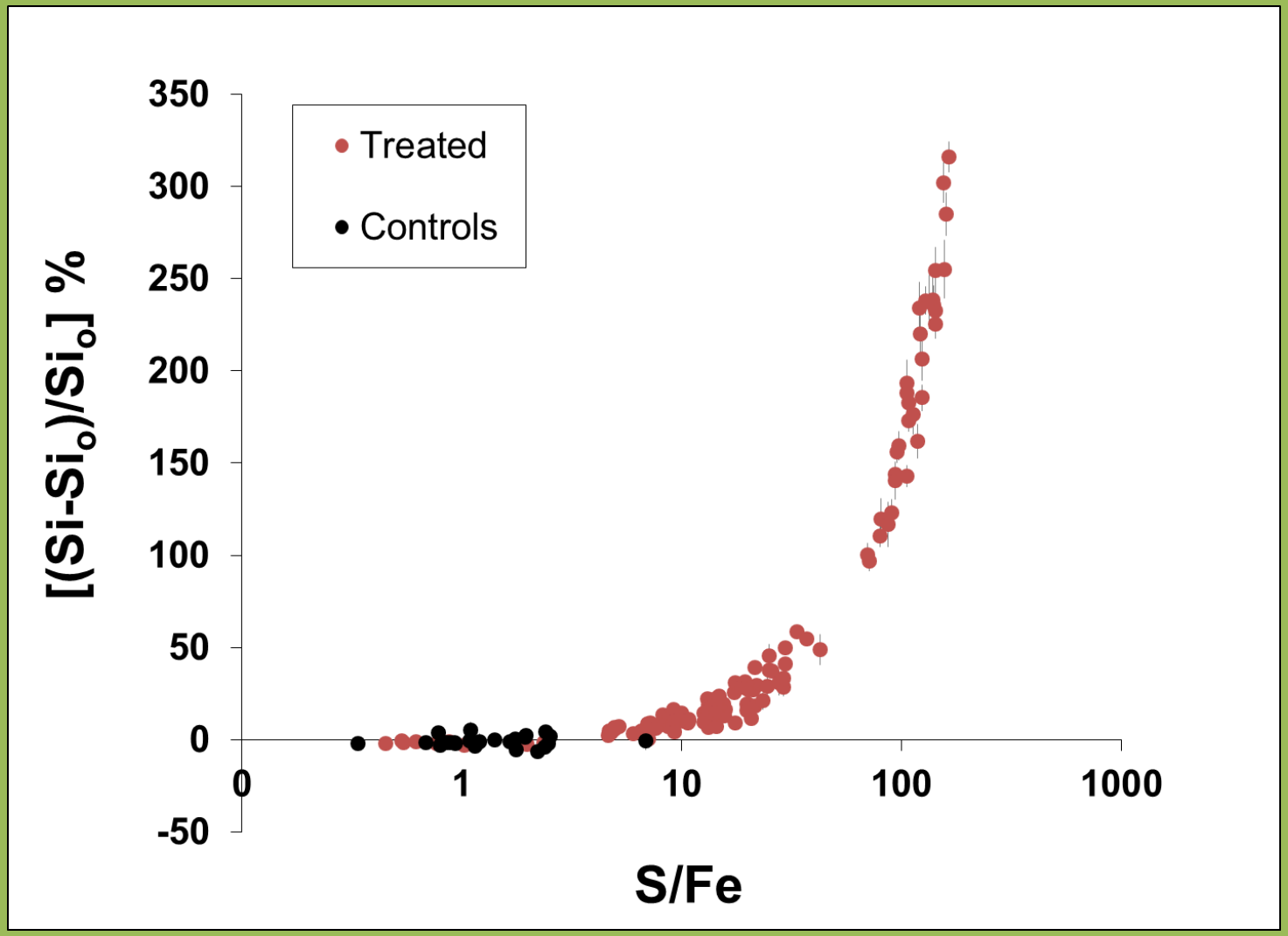
Sample deposits for two unmasked cassettes



Unmasked cassette used prior to October, 2012

Unmasked cassette used as of October, 2012

Si increases with increasing S/Fe



Not a function of Si mass