# The EPA Coarse PM Speciation Pilot Study

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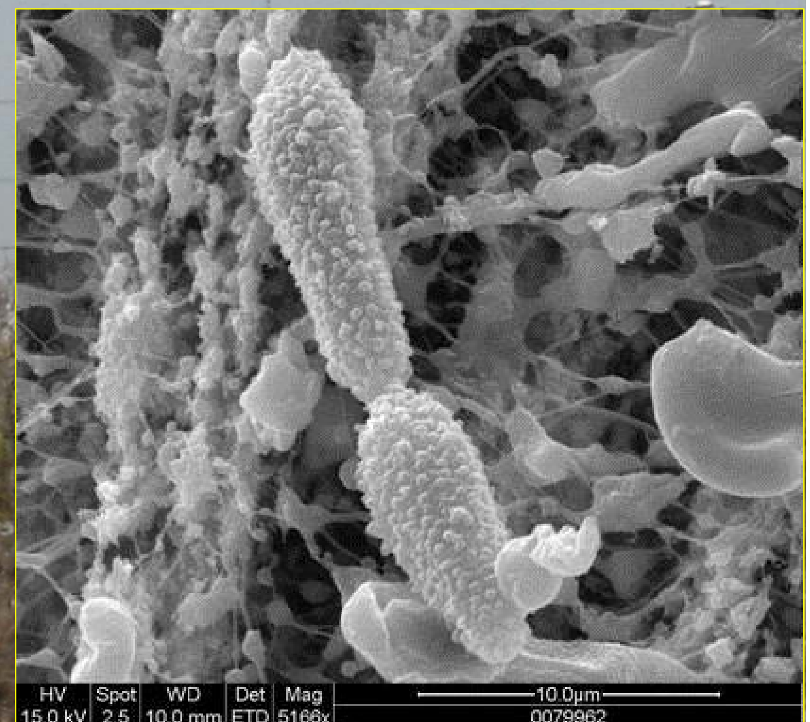



**EPA STAR Coarse PM Final Progress Review** **March 18, 2013**

# With Contributions From…

- Sonoma Technology, Inc.
  - **Hilary Minor, Adam Pasch**
- RTI International
  - **Jeffrey Nichol, James Flanagan**, Frank Weber, Karin Ford
- Maricopa County Health Department
  - **Ben Davis** and colleagues
- Washington University in St. Louis
  - **Varun Yadav**, Li Du and Neil Feinberg

# This Project in Context

- Not an EPA STAR project
- Funded by USEPA Office of Air Quality Planning and Standards (OAQPS)
- Focus on chemical analysis and sampling methods for a coarse PM speciation network

# Motivation

- USEPA monitoring rule for thoracic coarse particles (2006)
  - Rule called for PM coarse (PMc, or $PM_{10\text{-}2.5}$) speciation monitors at NCore sites by January 2011
- USEPA monitoring rule in 2012 revoked PM coarse requirement pending results/recommendations from this pilot study
- Before deploying the PMc speciation network, must assess:
  - Sample collection methods
  - Speciation analysis methods

# Study Objectives

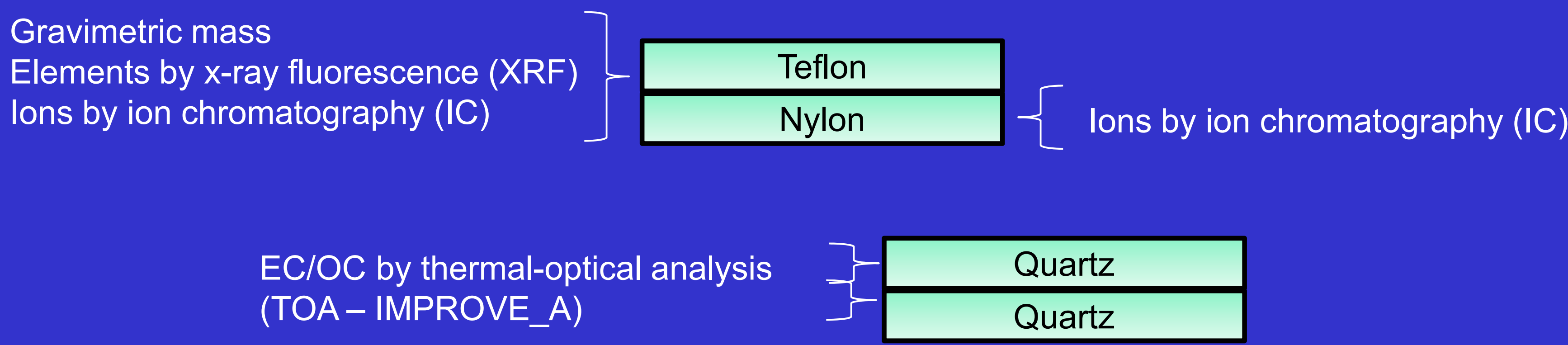
- Analysis methods
  - $PM_{2.5}$ Chemical Speciation Network protocols, perhaps with modifications
- Target analyte list
- Sampling methods
  - FRM by difference ($PM_{10}$ FRM minus $PM_{2.5}$ FRM)
  - Dichotomous sampler (dichot)
- Field operations experience
- Other insights from data analysis
  - e.g. mass reconstruction, climatology

# Pilot Study Design

- May 2010 – May 2011
- Phoenix and St. Louis
- Filter-based sampling with laboratory chemical analysis
  - 1-in-3 day sampling, ~50% of samples archived
    - Operationally a 1-in-6 day data set
  - Filter sandwiches
    - Quartz-Quartz
    - Teflon-Nylon

# Pilot Study Design (con't)

- Speciation generally following the $PM_{2.5}$ Chemical Speciation Network (CSN) protocols

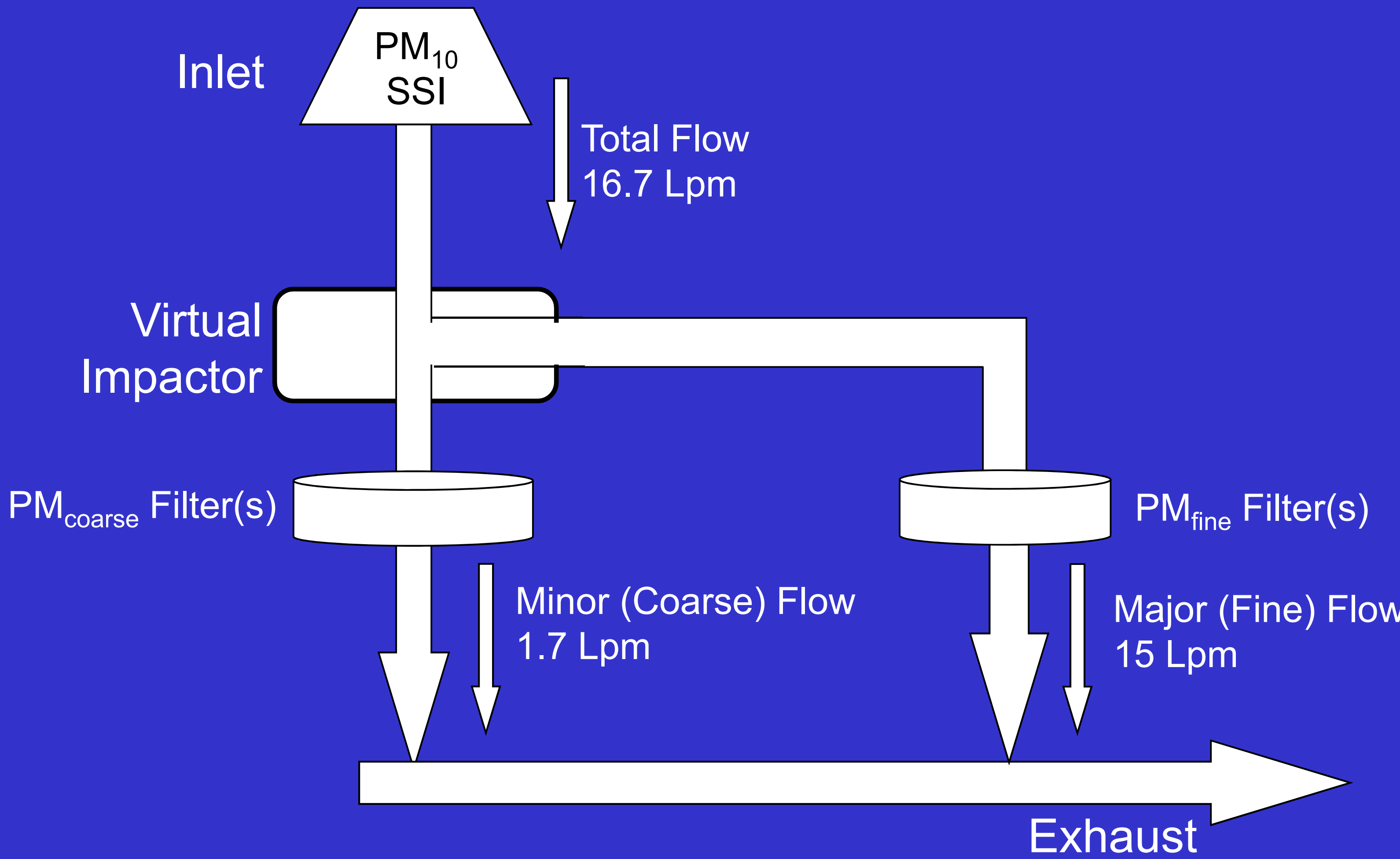



- Subset of samples analyzed for:
  - Carbonate by TOA with acidification
  - Elements by ICP-MS
- Modest additional analyses for:
  - Biomarkers (proteins, (1,3)-β-D-glucans, endotoxins)
  - Organic speciation by GC/MS

# Measurements Platform

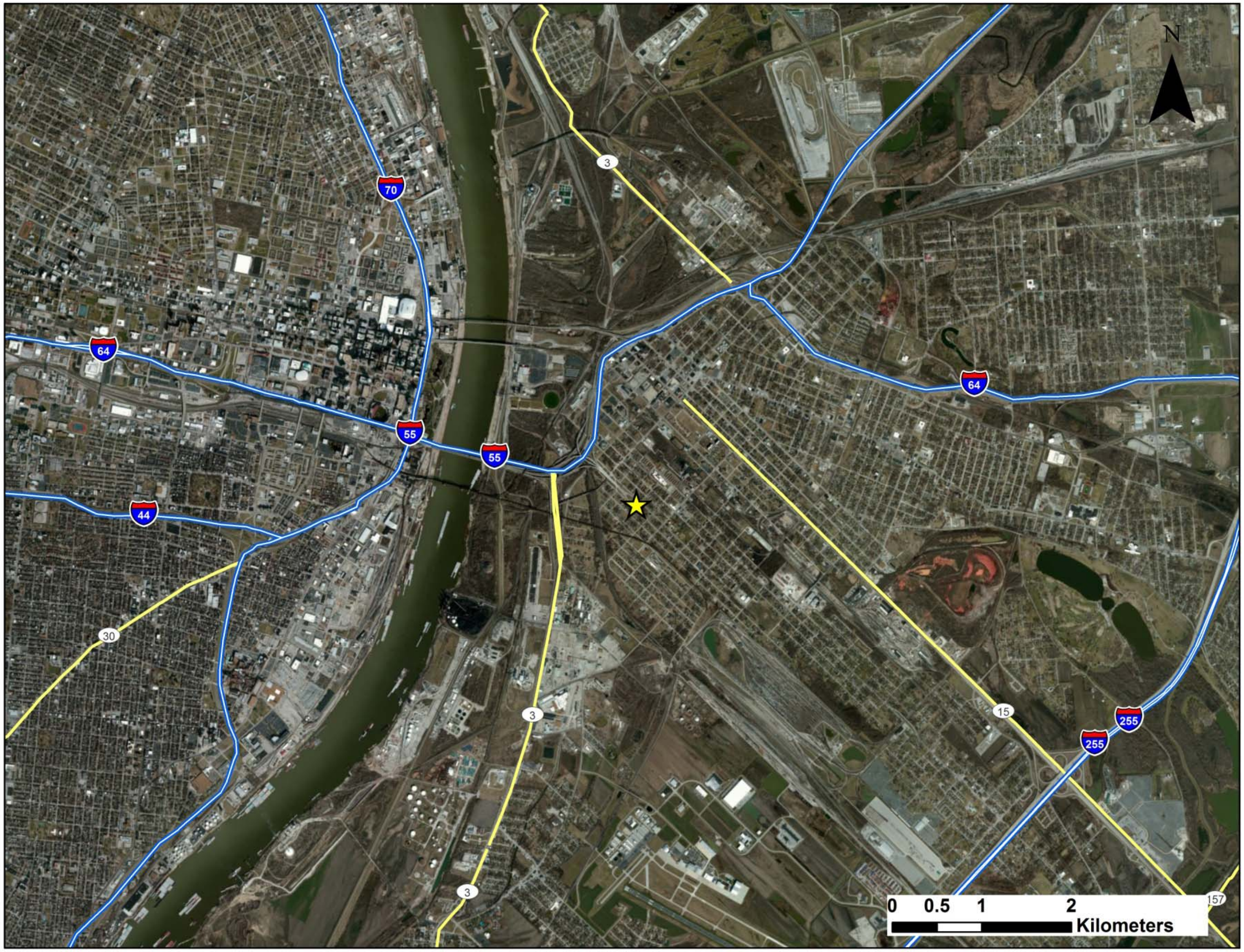
- Hardware at each site
  - Two sequential dichotomous samplers (Thermo 2025D)
  - One sequential $PM_{2.5}$ FRM (Thermo 2025)
  - One sequential $PM_{10}$ FRM (Thermo 2025)
  - One MOUDI cascade impactor (MSP)
  - One dichotomous FDMS-TEOM (Thermo 1405-DF)
- Different filter combinations placed in samplers to address specific questions, e.g.
  - Dichot with Teflon/Nylon, dichot with Quartz/Quartz
    - Mass balance closure
  - Both dichots with Teflon/Nylon or Quartz/Quartz
    - Collocated precision

# Dichotomous Sampler (slide courtesy RTI)




10% of fine particles are in the minor (coarse particle) flow stream; must correct for fine particle intrusion

# East St. Louis



# East St. Louis

# Phoenix

# Phoenix

# Presentation Roadmap*

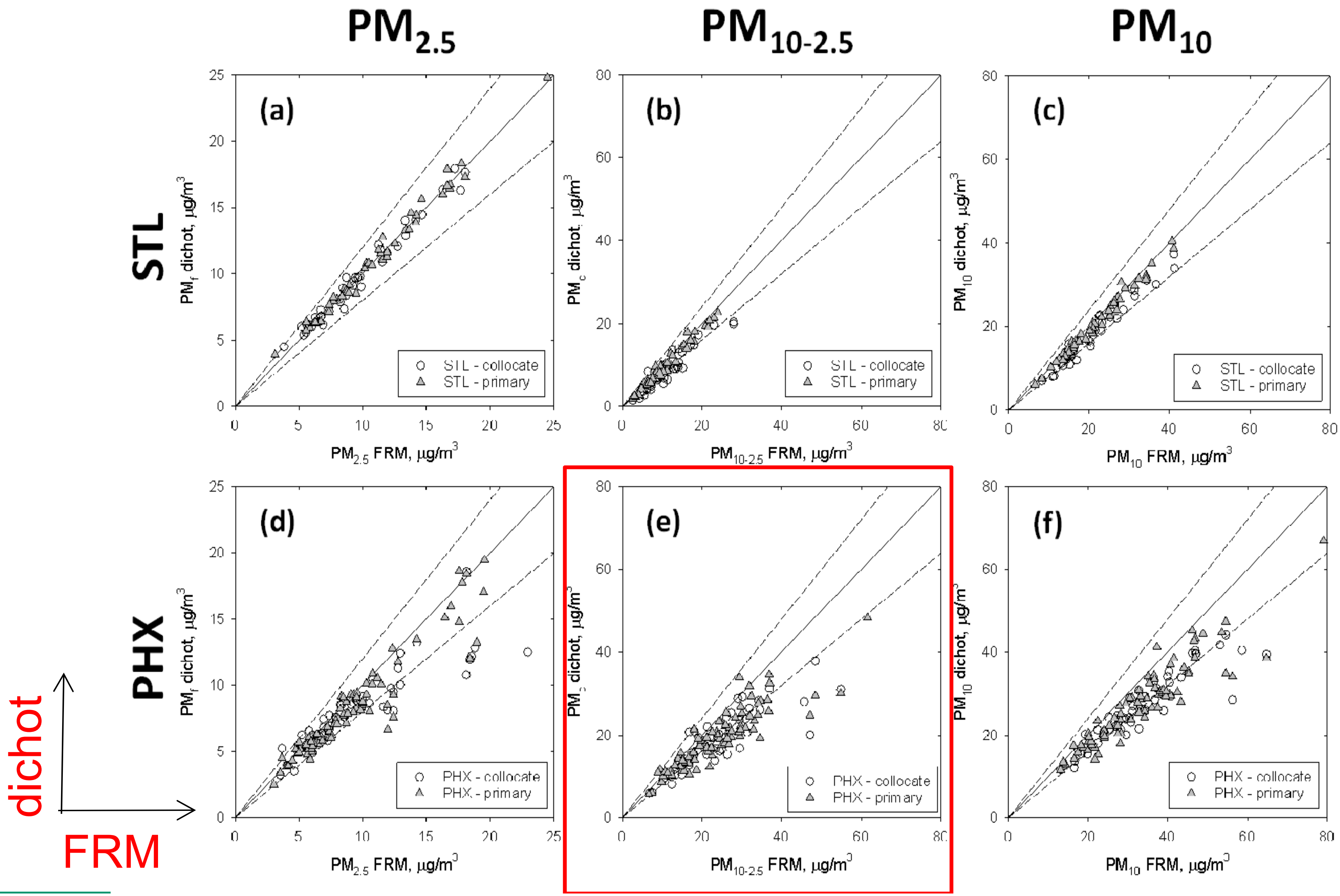
- Field operations summary
- Filter dichot PMc…
  - gravimetric mass and species versus paired FRM
  - collocated precision
  - mass closure
  - XRF attenuation corrections
  - biomarkers
  - carbonate
- PMc mass climatology from TEOM data
- Draft recommendations

* This presentation does not include all of the data analyses conducted; final project report to be submitted April 2013.

# Field Operations

- Sample Completeness
  - PHX: >90% for all samplers
    - Shaken down at RTI prior to deployment
    - Had backup hardware
  - STL: >80%  for three samplers
    - Not shaken down prior to deployment
    - One dichot returned for repair (large data gap), resulting in 66% completeness
- Most common problem – filter advance error
- For speciation by paired samplers, need simultaneous valid samples

# Gravimetric Mass



# Gravimetric Mass

Possible explanations for dichots biased low

- $PM_{10}$ inlet bias (dichot versus FRM)
- Dichot virtual impactor performance
- Particle losses
  - Shipping and handling
  - Filter exchanges in the sequential dichot sampler

- Sequential dichot samplers deployed in PHX and STL were not Federal Equivalent Method (FEM) designated
  - FEMs not available from vendor in time for study
  - Subsequently modified to be FEM compliant
  - Modest follow-up pilot study at RTP to evaluate performance

# Dichot Collocated Precision

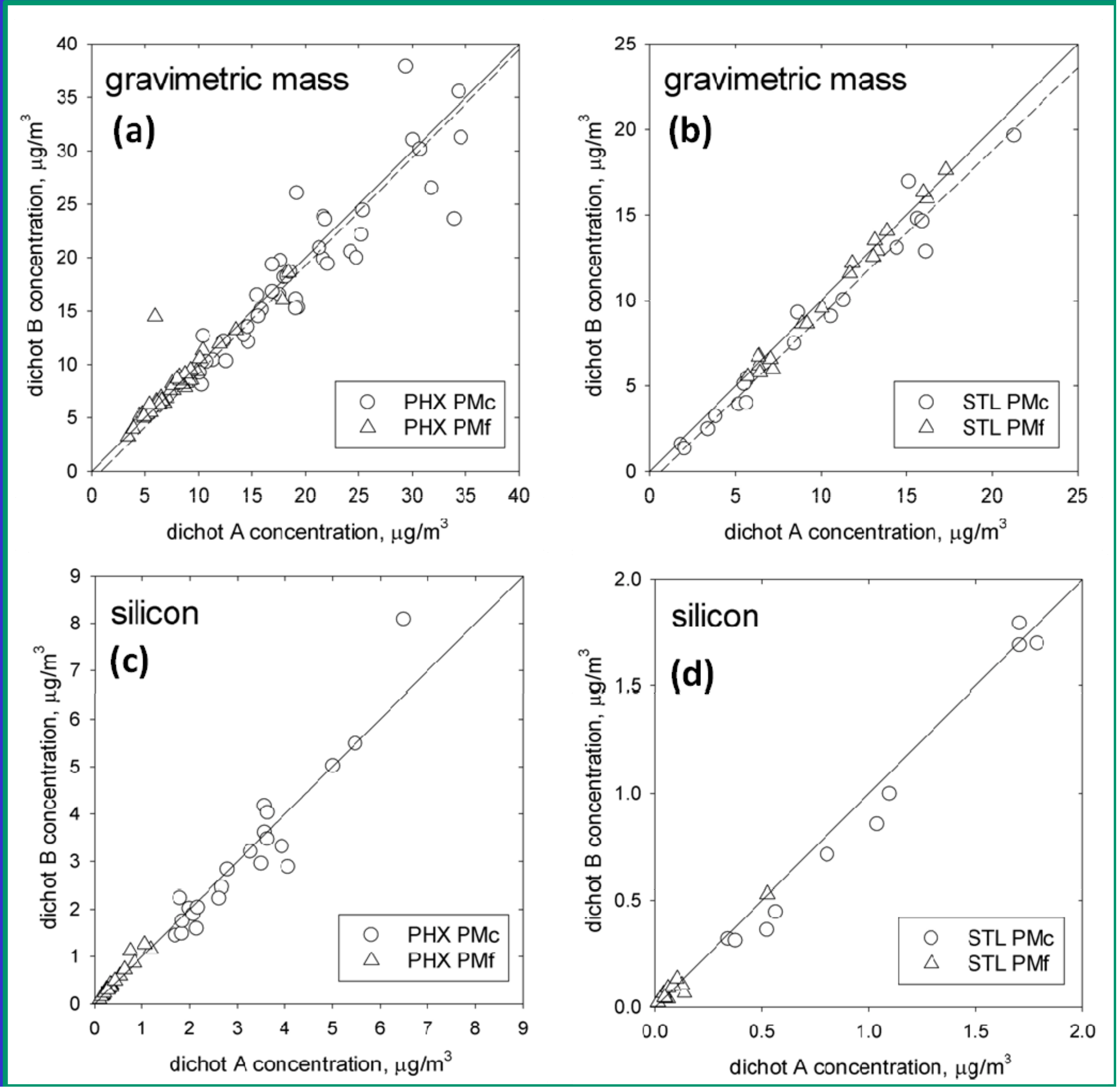
PHX PMc…

gravimetric mass 12%

silicon 12%

STL PMc…

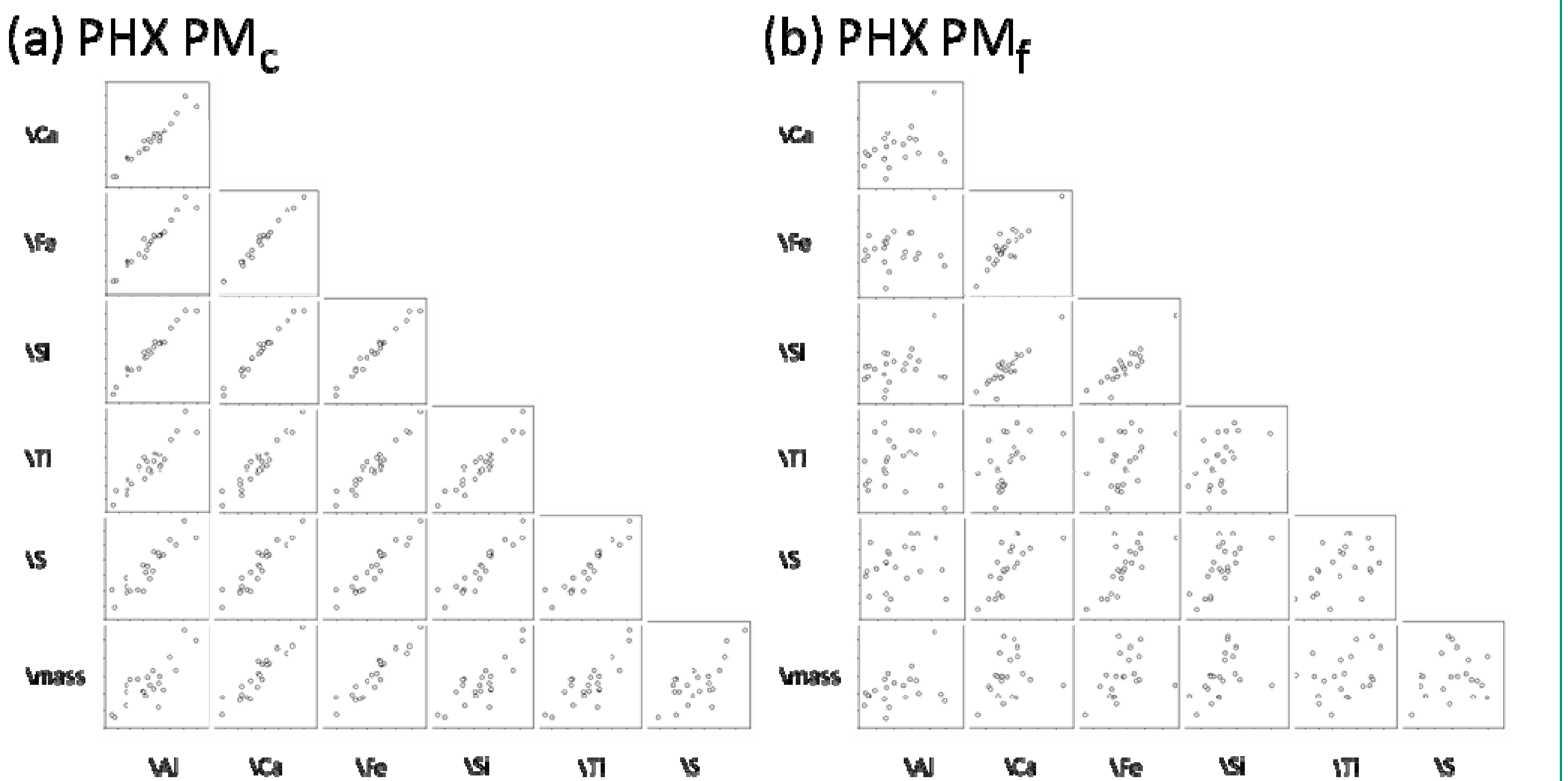
Similar collocated precision as PHX, but more influenced by bias



# Dichot: Covariance of Measurement Error (PHX)

For dichots *A* and *B*…

$$\Delta(\text{species } k) = \ln(C_{k,A}/C_{k,B})$$



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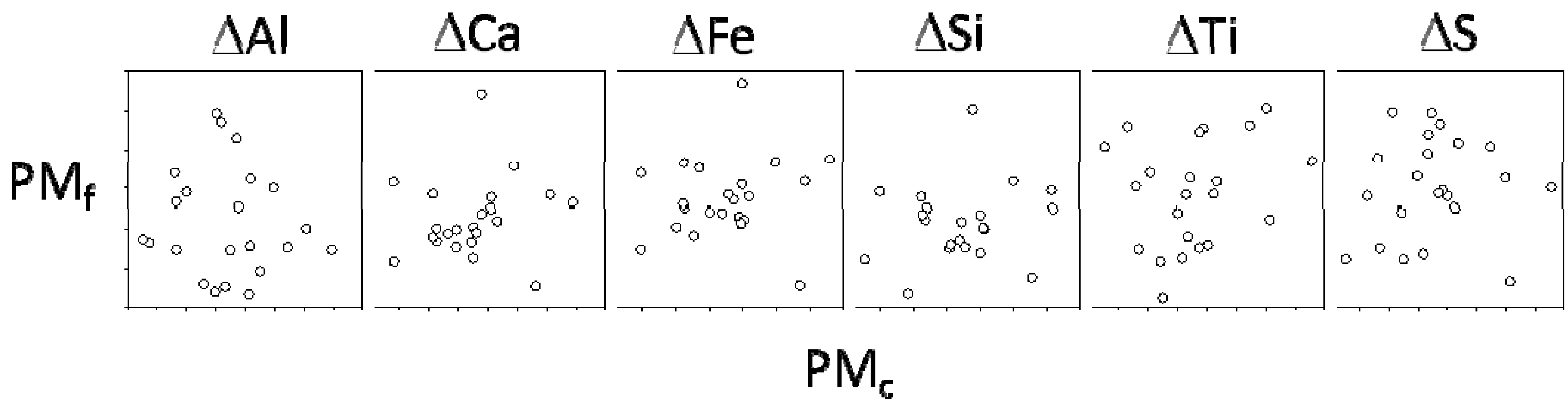
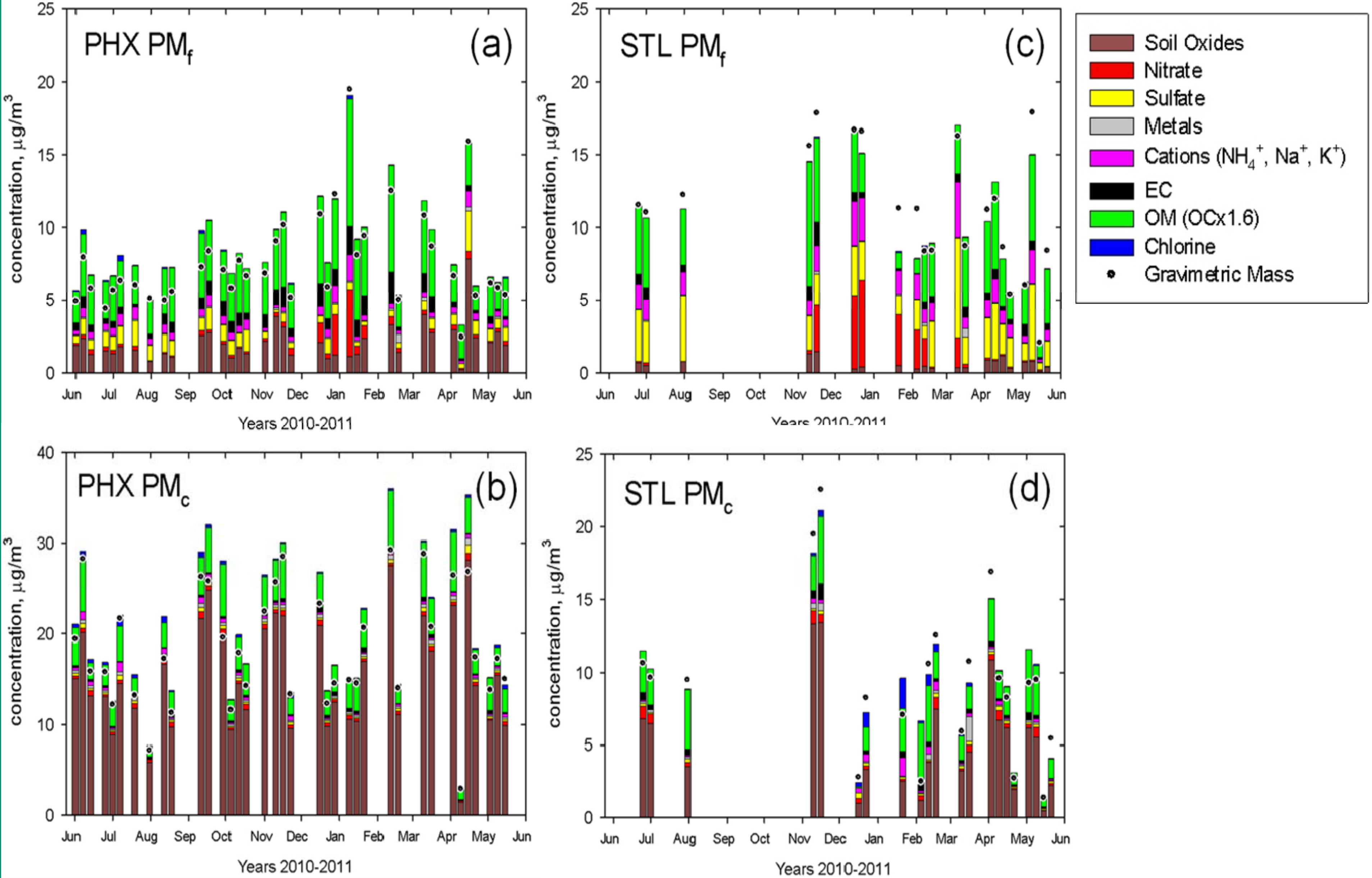



- At most weak correlation between measurement errors for fine and coarse fractions
  - PMc covariance of measurement error likely not driven by virtual impactor performance

# Dichot Mass Balance Closure

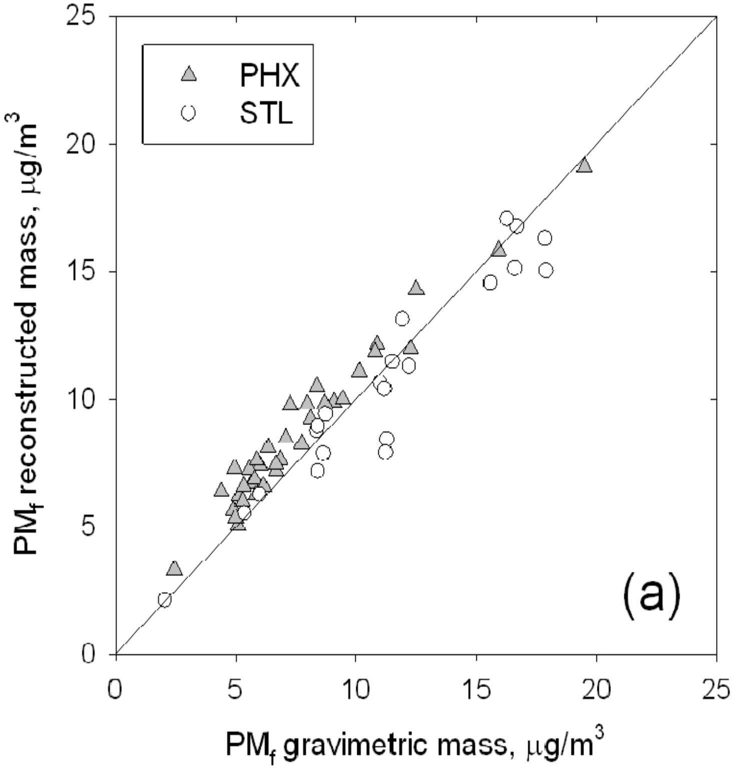
- Measurements
  - Teflon filter
    - Gravimetry → Elements (XRF) → Ions (IC)
  - Quartz filter
    - Elemental carbon [EC] and organic carbon [OC] (TOA)
- Mass reconstruction for <u>Teflon filter</u>
  - Soil oxides ("IMPROVE" equation)
  - Anions – nitrate; sulfate; chlorine (not chloride)
  - Lumped Cations – ammonium; potassium; sodium
  - Carbon – EC; OM = OC×1.6
    - Carbon from front quartz filter only
    - Initial estimate of the OC multiplier
  - PMc adjustments for fine PM intrusion using front filters only

# Mass Balance Closure

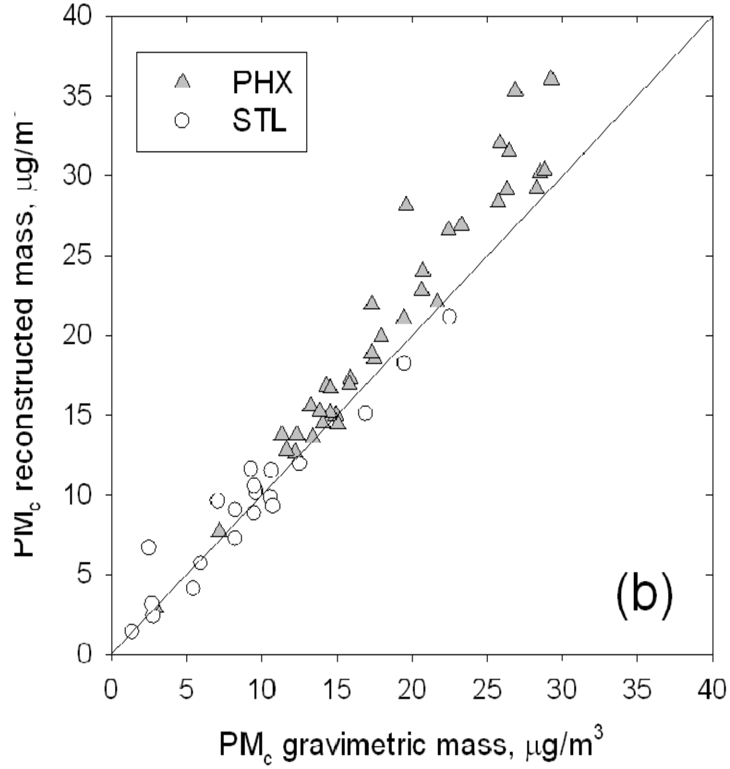


# Dichot Mass Balance Closure

## Fine PM




## Coarse PM

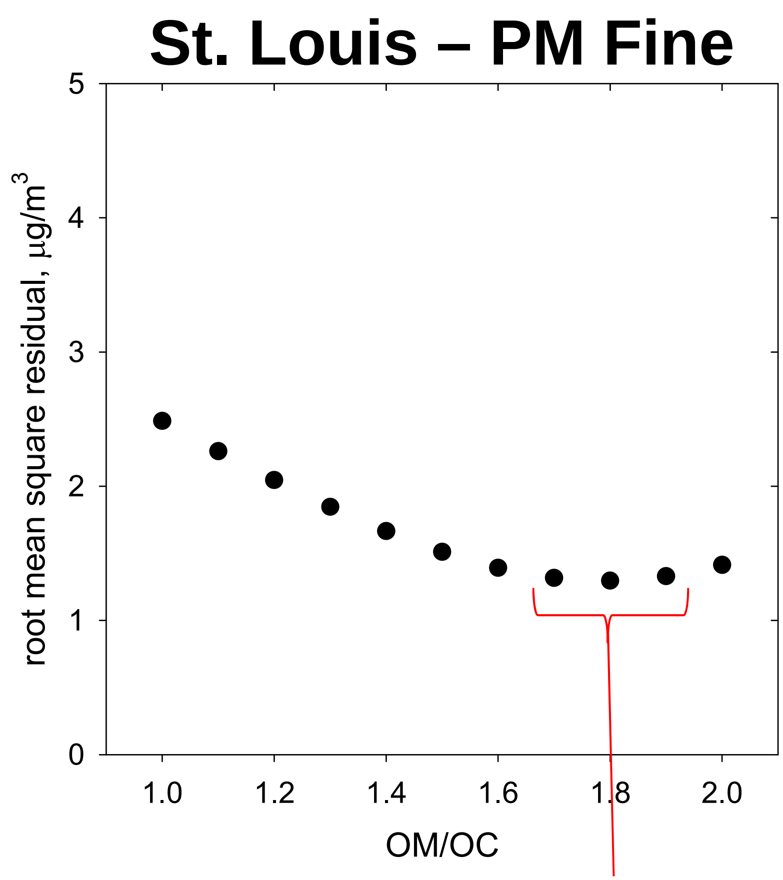


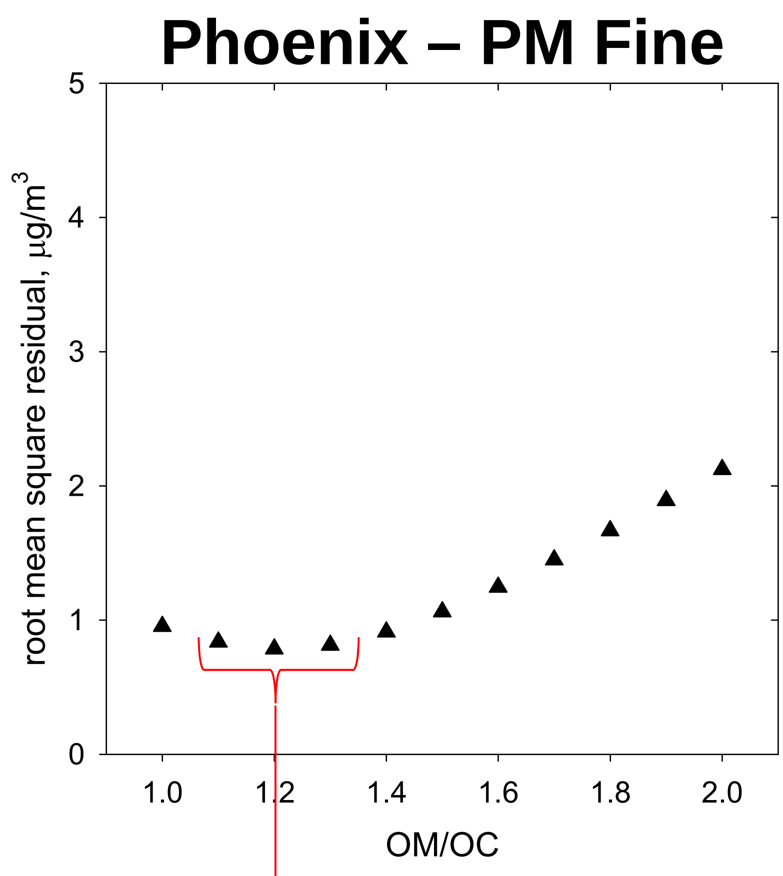

ratio of means (using OM = 1.6×OC):

| | | |
|---|---|---|
| STL | 0.94 | 1.01 |
| PHX | 1.14 | 1.13 |

# Reconciling Gaps in Mass Balance Closure

- Assume all estimates are accurate except OM/OC ratio
- For each site and size range, find best-fit OM/OC ratio *assuming OM/OC ratio is constant*



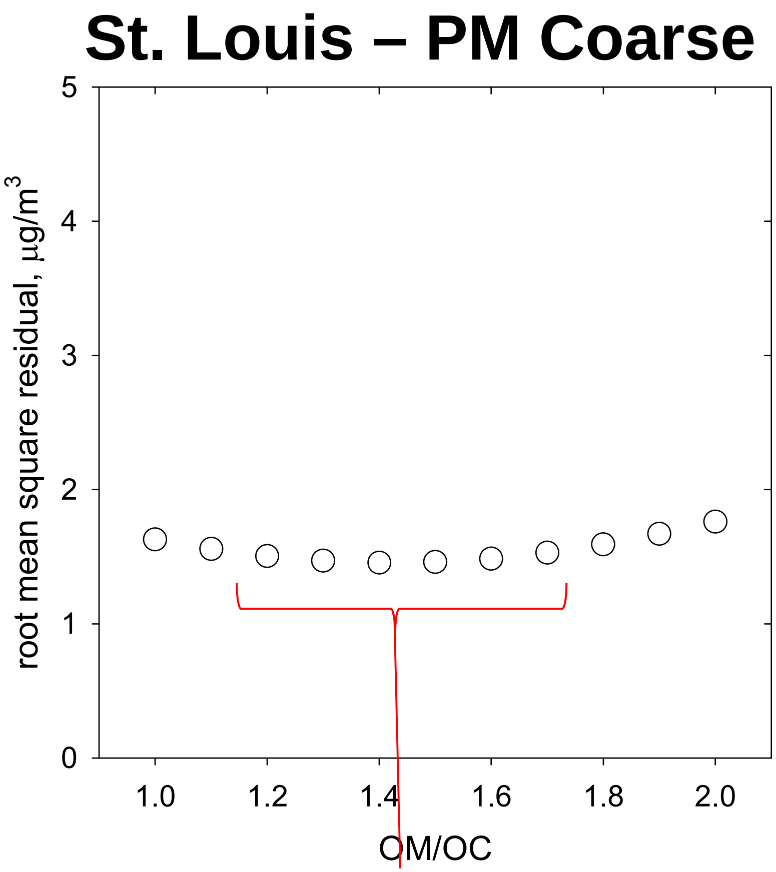



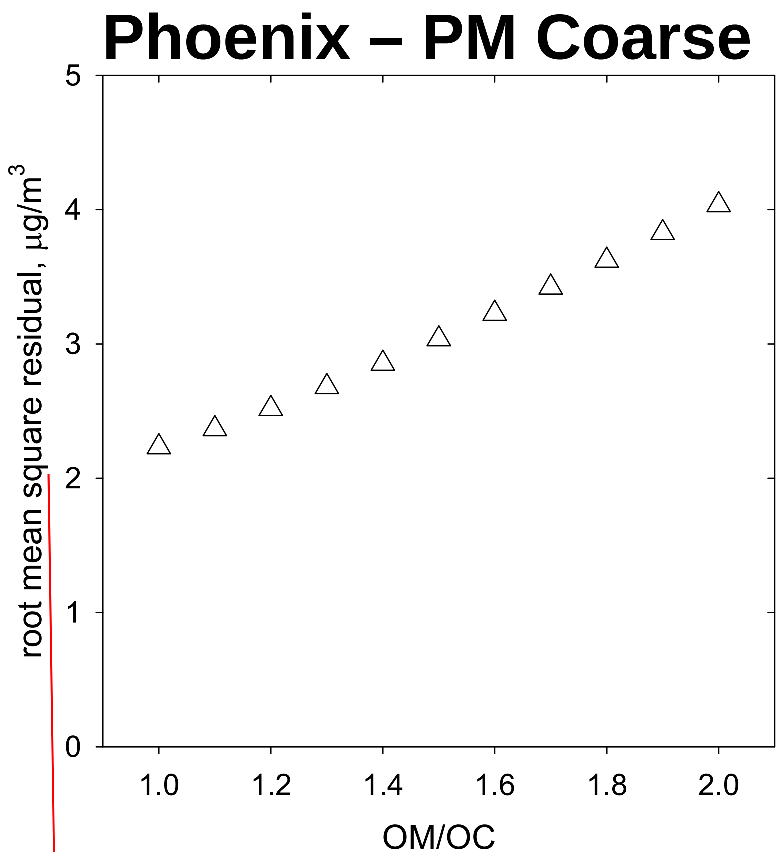

consistent with 1.81 reported by Bae *et al.* (2006)

consistent with 1.25 reported by Simon *et al.* (2011)

# Reconciling Gaps in Mass Balance Closure

- Assume all estimates are accurate except OM/OC ratio
- For each site and size range, find best-fit OM/OC ratio *assuming OM/OC ratio is constant*




wide range of plausible OM/OC

minimum for OM/OC = 0.6, implausible (OM/OC < 1)

# Dichot Mass Balance Closure – PHX PMc

- Reconstructed mass systematically greater than gravimetric mass
- Cannot reconcile by adjusting OM/OC ratio
- Overestimation of crustal contributions?
  - Assumed oxide forms of crustal species?
  - Overcorrecting for XRF self-absorption by light elements (e,g. Al, Ca, Si)?

# XRF Attenuation Corrections

- Self-absorption (attenuation) during XRF analysis
  - Primarily affects light elements ($Z \leq 20$), including Al, Si, Ca
  - Depends on element and size distribution
- Attenuation-corrected mass loadings, $m_i$

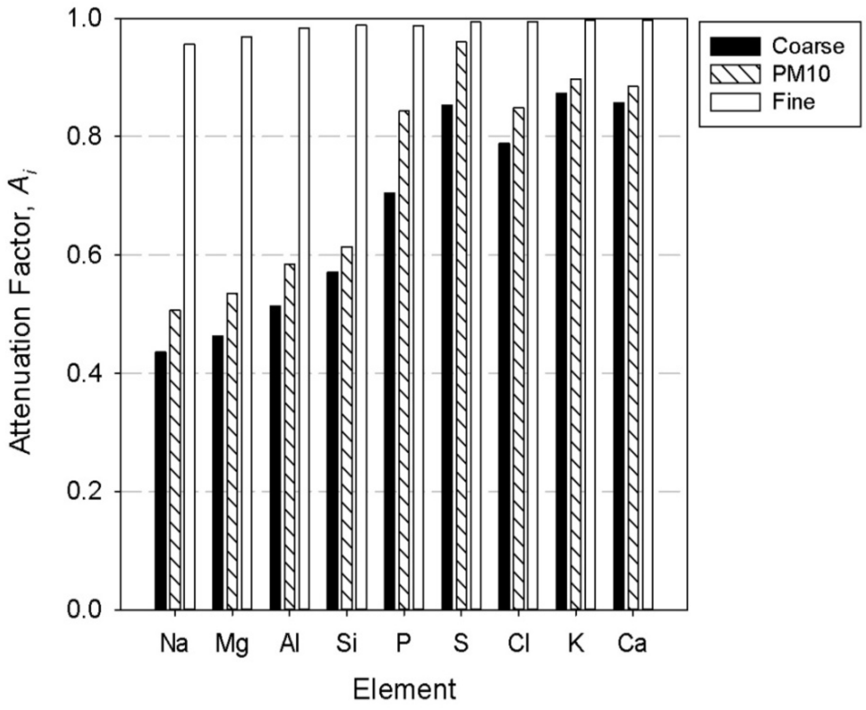
$$m_i = \frac{m_{no\,corr,i}}{A_i}$$

where $m_{no\,corr,i}$ is the XRF instrument-reported mass loading and $A_i$ is the attenuation factor, range $A_i \leq 1$

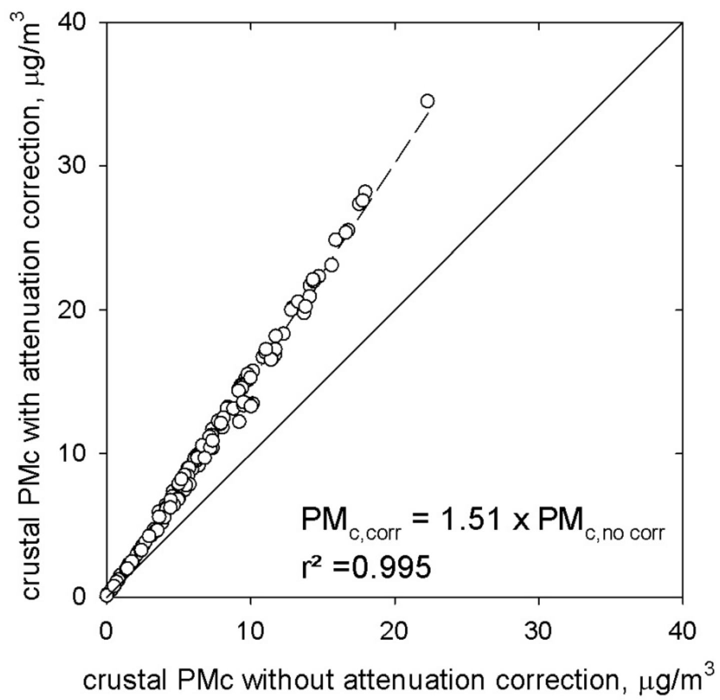
- RTI applied XRF attenuation factors using software developed by Kellogg (2005)

# XRF Attenuation Corrections

## attenuation factors




## impact on crustal PMc

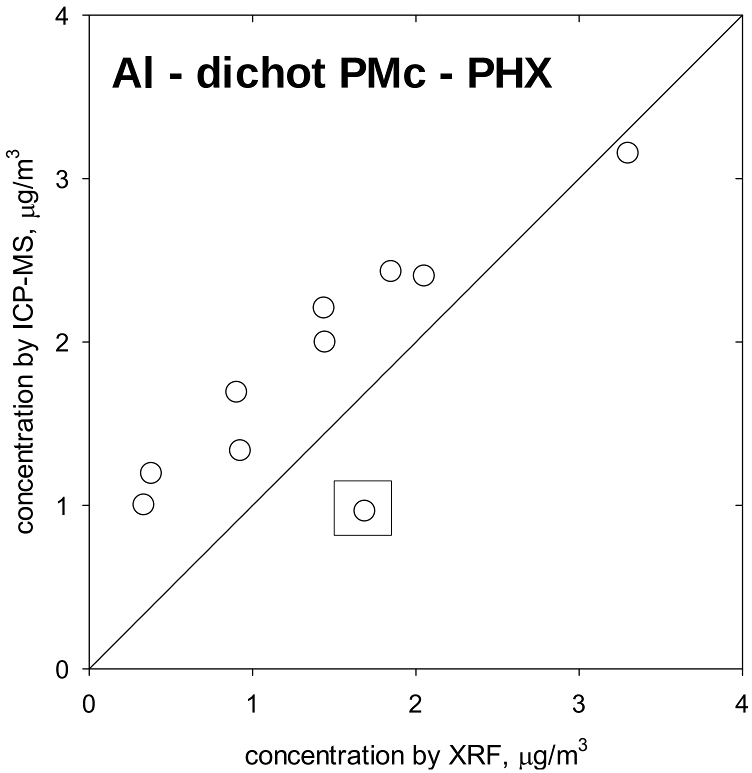



- PMc attenuation correction nearly 100% for Al to 15% for Ca
- Correction increases PMc soil oxides estimate by 50% (IMPROVE equation) compared to uncorrected data

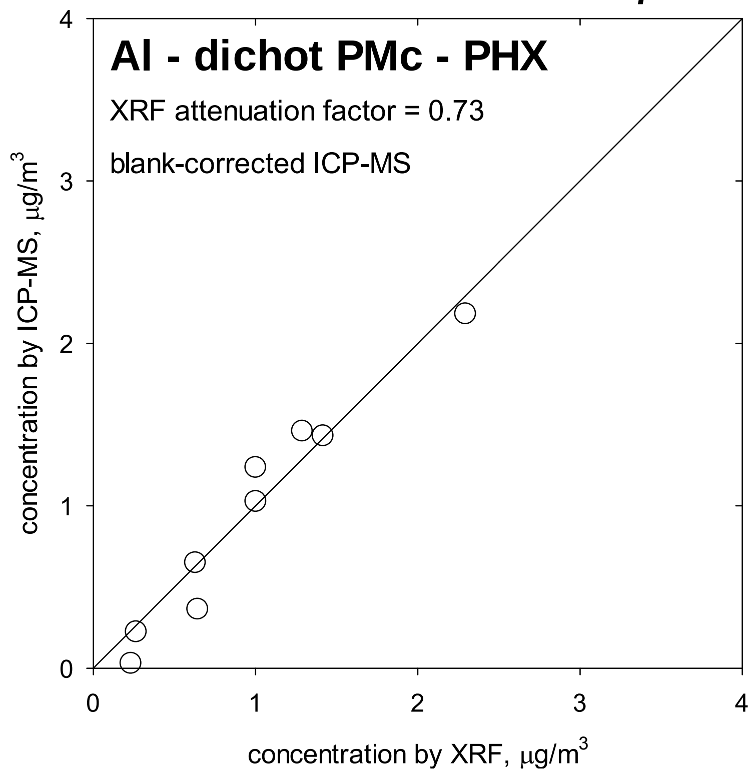
# Preliminary Evaluation of Correction Factors

- Analyze filters from 18 sampling events (10 PHX, 8 STL) by ICP-MS at RTI
- ICP-MS measurements confounded by elements present in filter support ring and adhesive

## uncorrected data




## ICP-MS blank correction and best-fit XRF $A_i$




- Applied $A_i$ = 0.51, best-fit $A_i$ = 0.73… reported [Al] biased high?

# Preliminary Evaluation of Correction Factors

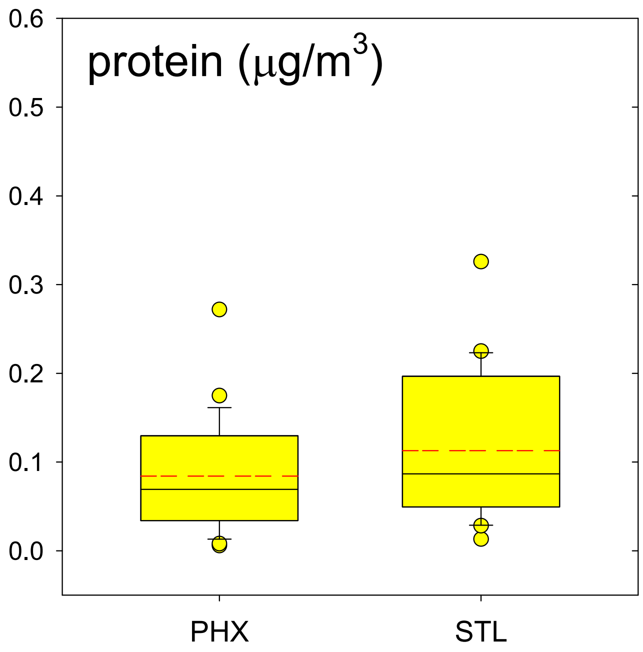
- Several potential confounders
  - Blank correction of ICP-MS data (elements in filter support ring and adhesive)
  - Recovery correction of ICP-MS data
  - Small data set

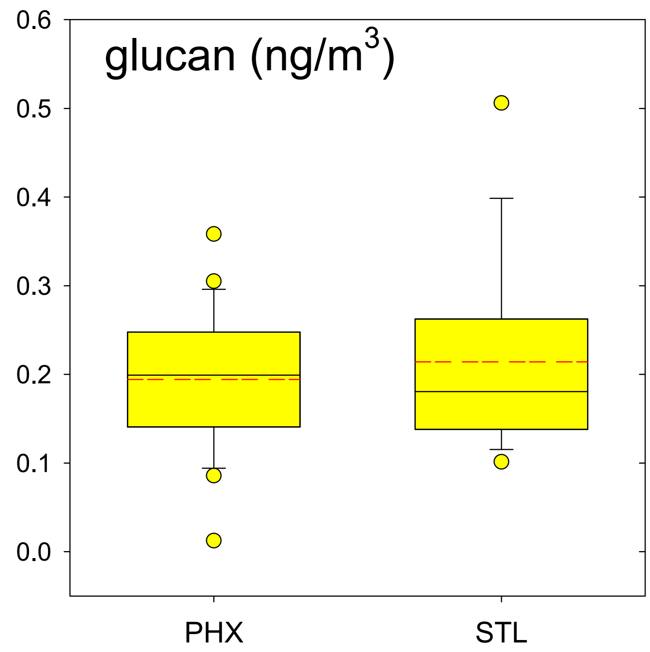
| element | A (RTI) | A (best-fit) | |
|---|---|---|---|
| | | 100% recovery | recovery adjusted |
| Aluminum | 0.51 | 0.73 | 0.63 |
| Sulfur | 0.85 | 0.87 | 0.87 |
| Calcium | 0.86 | 0.91 | 0.91 |

- Comprehensive evaluation is needed

# PMc Biomarkers

- February – May 2011 (N = 28 for PHX, N = 26 for STL)
- Sample analysis by RTI
- Protein by Molecular Probes® NanoOrange® Protein Quantitation Kit
- (1-3)-β-D-glucans by Glucatell® assay



# Carbonate ($CO_3$)

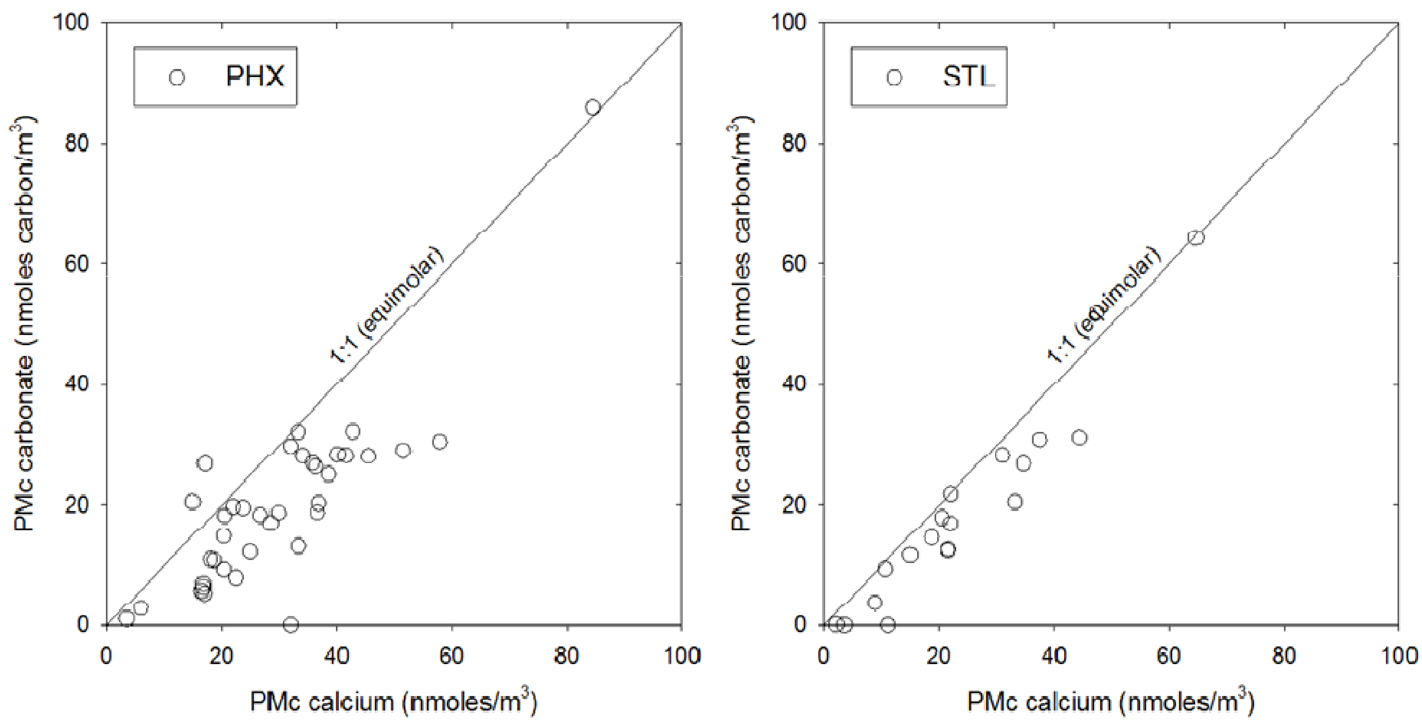
- $PM_{2.5}$ $CO_3$ low at IMPROVE sites (Chow & Watson, 2002)
- Measure $CO_3$ on subset of samples
  - Thermal-optical analysis with acidification (DRI)
  - $CO_3 \leq$ MDL for FRM $PM_{2.5}$ and dichot PMf
  - Dichot PMc carbonate
    - Collocated precision 22% (N = 12)
    - No bias compared to FRM $PM_{10-2.5}$ (N = 6)

| Site | N | Mean, $\mu g/m^3$ (% of PMc mass) | Range, $\mu g/m^3$ (min, max) |
|---|---|---|---|
| PHX | 43 | 1.2 ( 6%) | (0, 5.2) |
| STL | 26 | 1.3 (12%) | (0, 4.0) |

# PMc Carbonate

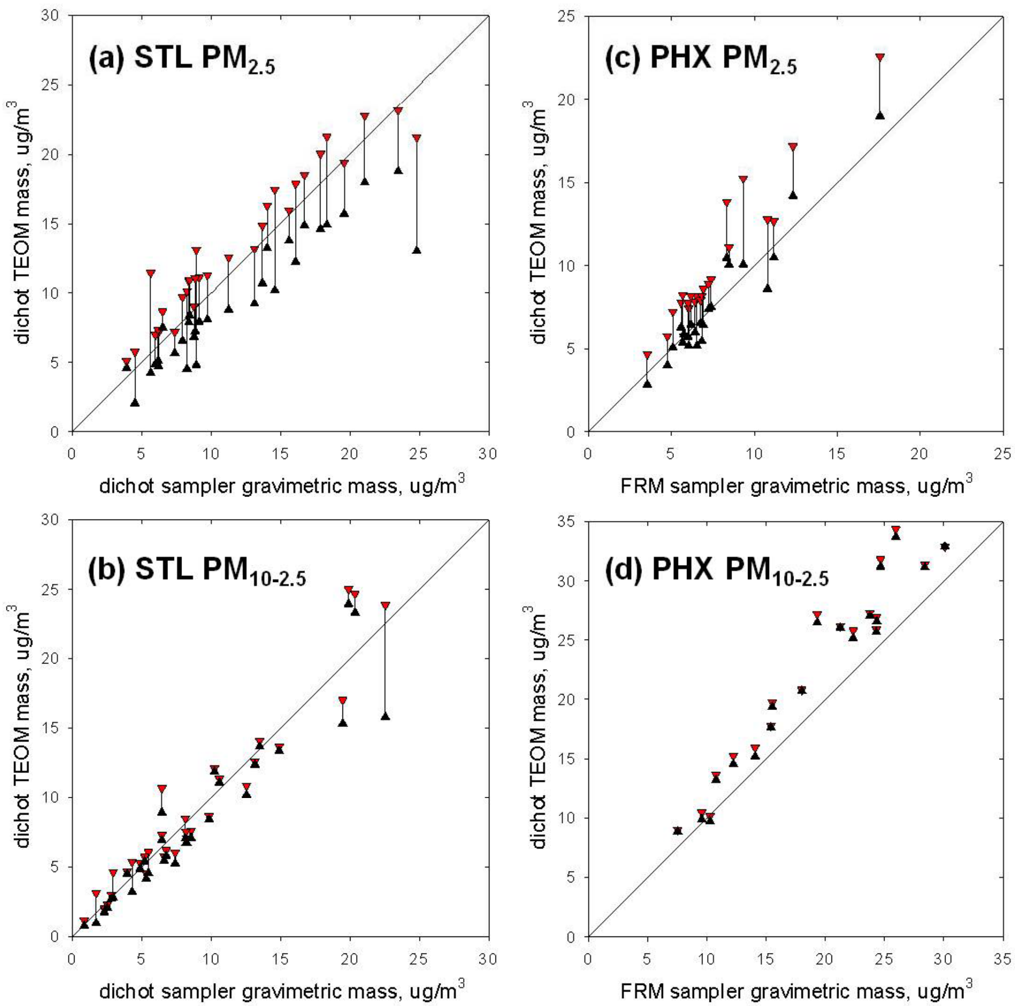
- PHX – correlated with most species, best with Ca ($r$ = 0.85)
- STL – uncorrelated with Total Carbon, best with Ca ($r$ = 0.97)

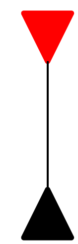
## dichot PMc carbonate versus dichot PMc calcium




Carbonate can explain ~2/3 (~1/2) of the calcium in PHX, ~2/3 (~2/3) of the calcium in STL

# FDMS TEOM vs. Filter-Based PM Mass



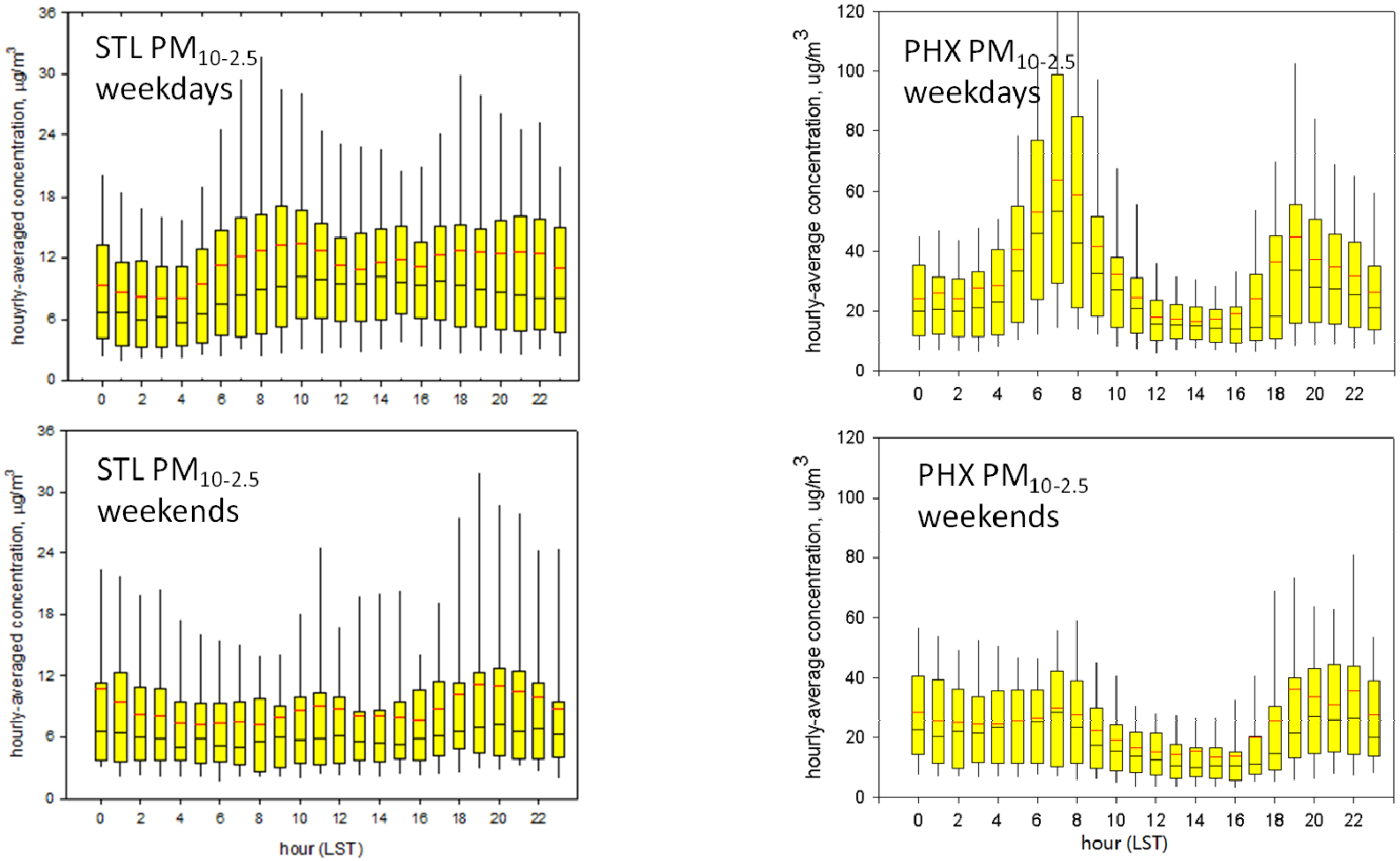




Filter $PM_{2.5}$ bracketed by TEOM nonvolatile PM and total PM

Filter PMc vs. TEOM PMc
- good agreement in STL
- TEOM biased high in PHX

PMc is largely nonvolatile

# PMc Diurnal Profiles from FDMS TEOM




Anthropogenic influences at both sites, especially strong at PHX

# Draft Recommendations

- The dichot is attractive compared to paired FRM samplers
  - Further evaluation of Thermo 2025D sequential dichot
    - Performance of FEM model
    - Field operations experience from other users
  - Paired dichots - one with Teflon, one with quartz
- Sample analyses
  - Gravimetric mass
  - Elements by XRF but need to evaluate attenuation factors for key crustal species (Al, Ca)
  - EC/OC and carbonate by thermal-optical analysis
  - Ions only in cases where PMc nitrate is expected

# Disclaimer

This analysis has not been subjected to review and approval by the United States Environmental Protection Agency. No endorsement should be inferred.