Characterization of Coarse Aerosol in St. Louis and Phoenix: Results from EPA's 2010-2011 Pilot Study

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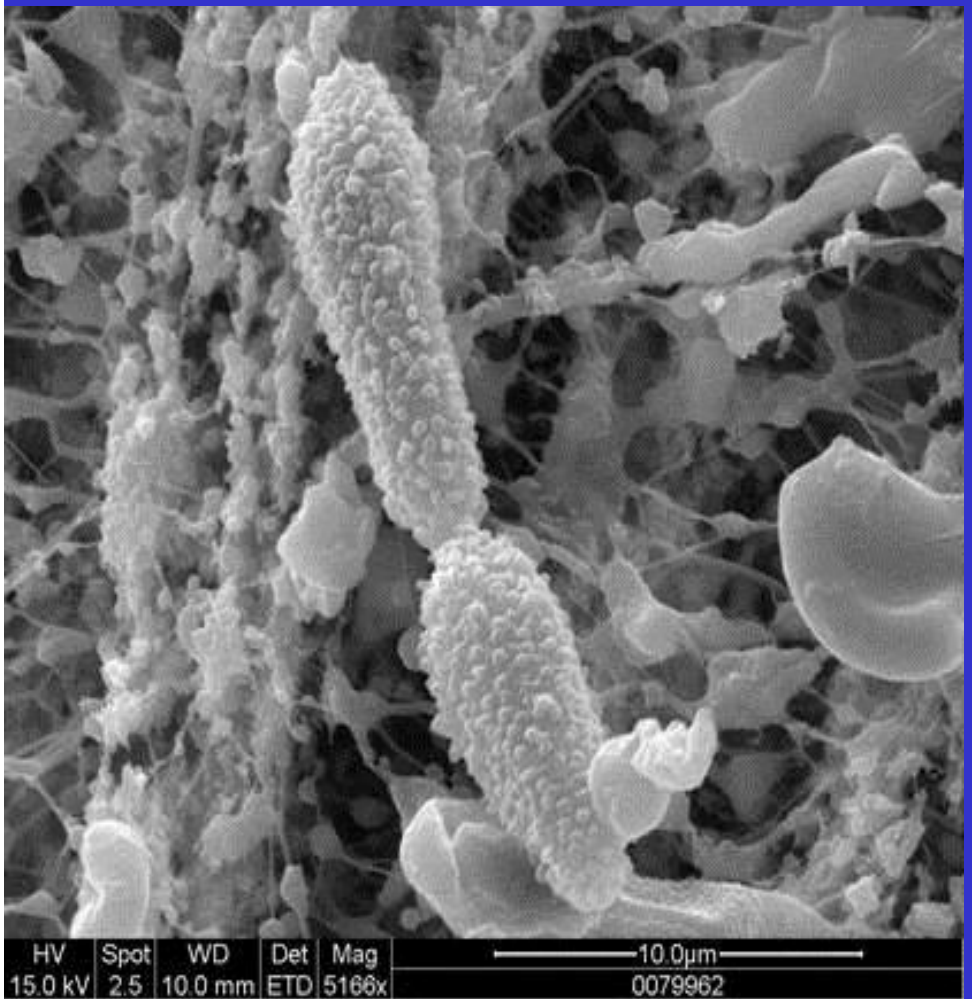

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With Contributions From…

- 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

Study Objectives

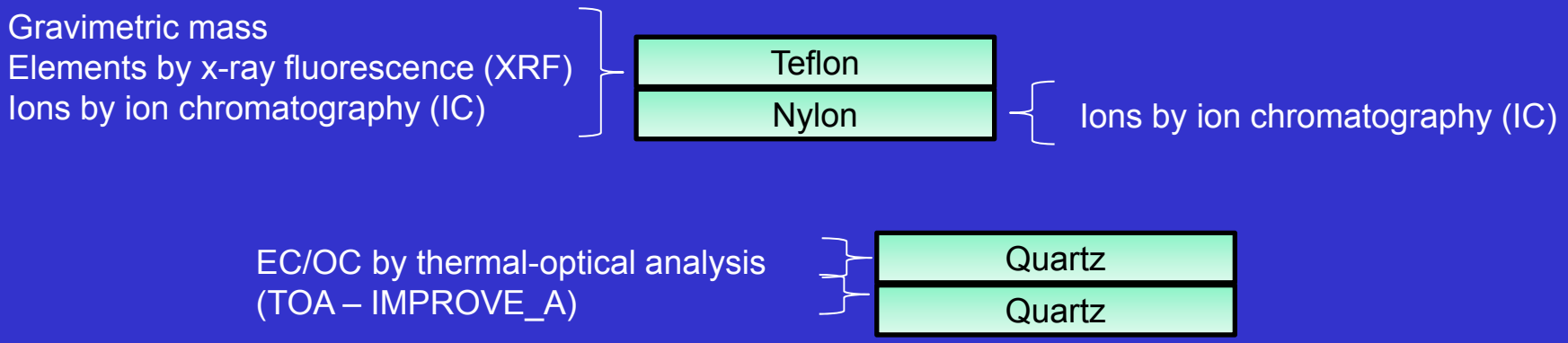
- USEPA conducted a field study in 2010-2011 to evaluate the challenges in sampling and analyzing coarse aerosol
- Study objectives included:
  - Evaluation of analysis methods
    - $PM_{2.5}$ Chemical Speciation Network protocols, perhaps with modifications
  - Development of a target analyte list
  - Comparison of sampling methods
    - FRM by difference (PM_{10} FRM minus $PM_{2.5}$ FRM)
    - Dichotomous sampler (dichot)
  - Field operations experience

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

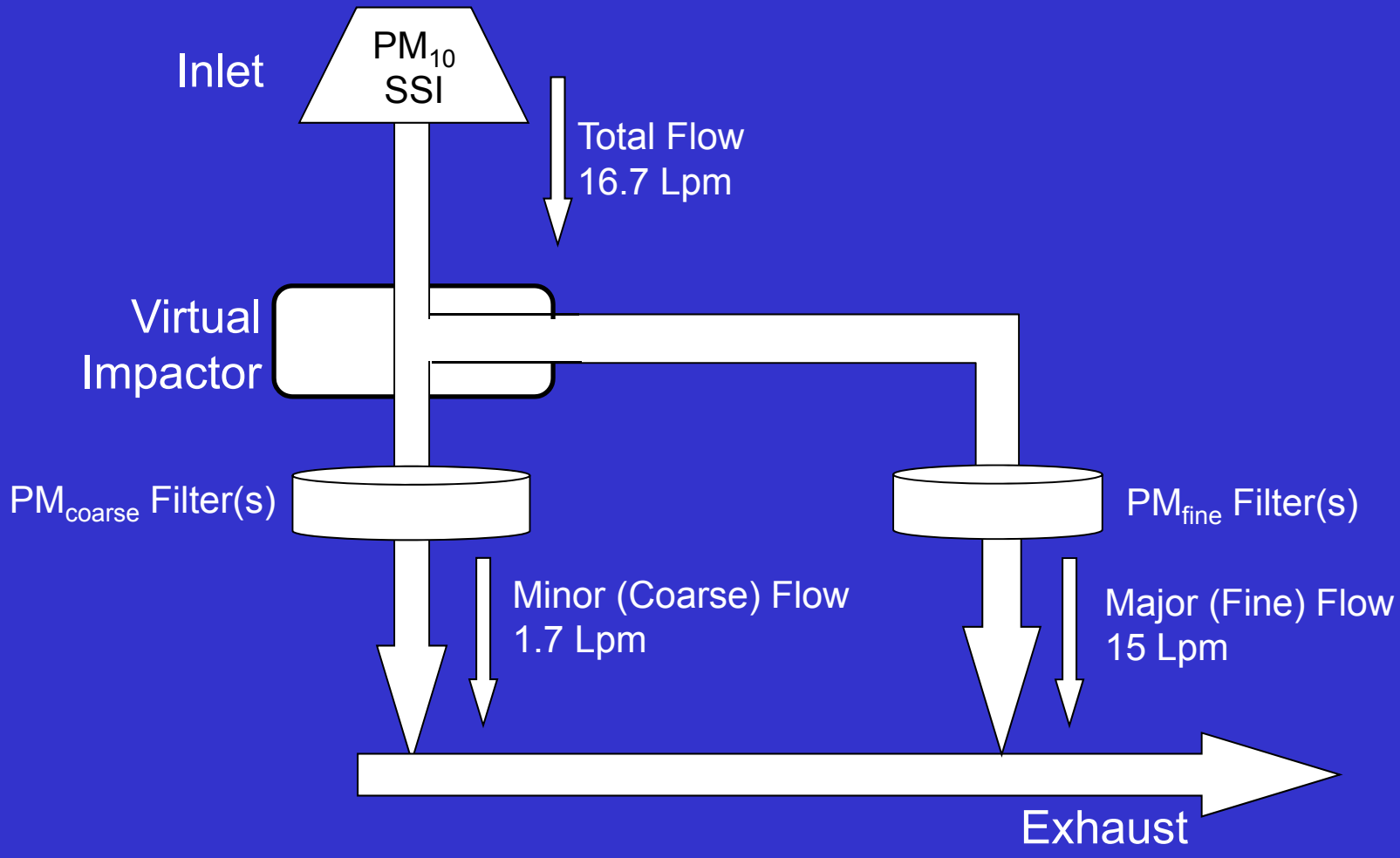


- Subset of samples analyzed for:
  - Carbonate by TOA with acidification
  - Elements by ICP-MS
- Modest additional analyses for:
  - Biomarkers (proteins, (1,3)-β-D-glucans, endotoxins)
  - Organic speciation by GC/MS

Measurements Platform

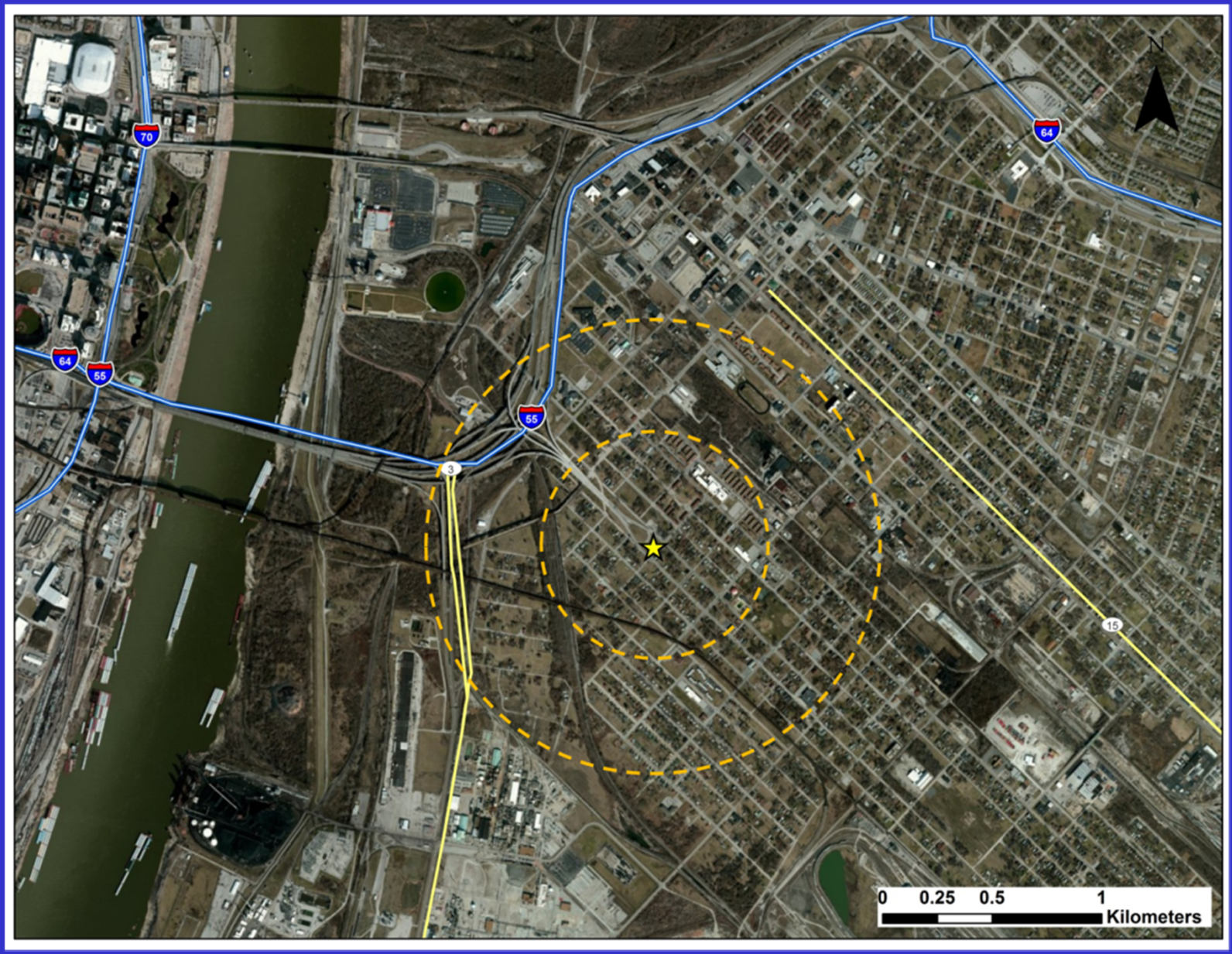
- Hardware at each site
  - Two sequential dichotomous samplers (Thermo 2025D)
  - One sequential $PM_{2.5}$ FRM (Thermo 2025)
  - One sequential PM_{10} FRM (Thermo 2025)
  - One MOUDI cascade impactor (MSP)
  - One dichotomous FDMS-TEOM (Thermo 1405-DF)
- Different filter combinations placed in samplers 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)

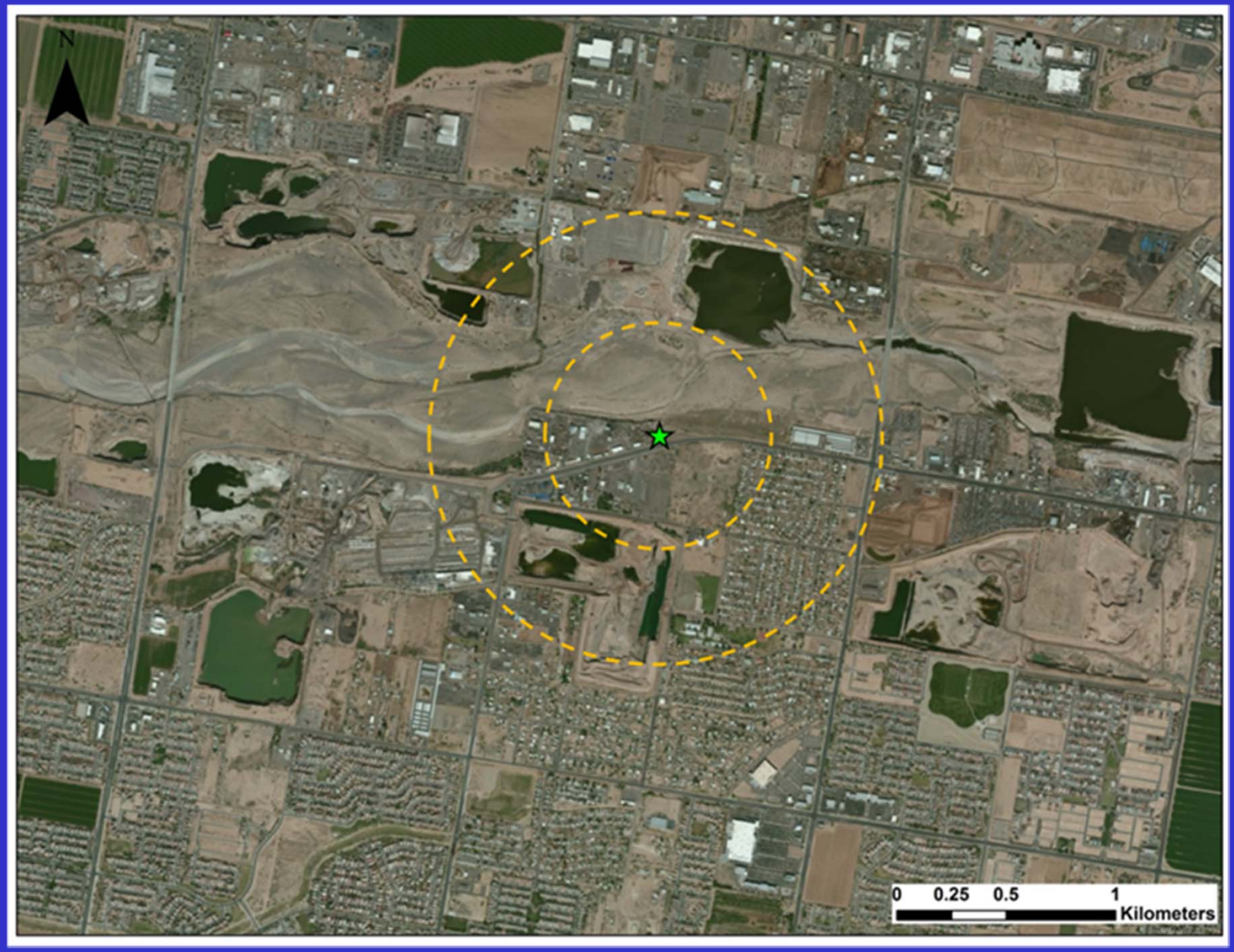


10% of fine particles are in the minor (coarse particle) flow stream; must correct for fine particle intrusion

East St. Louis



Phoenix



Presentation Roadmap*

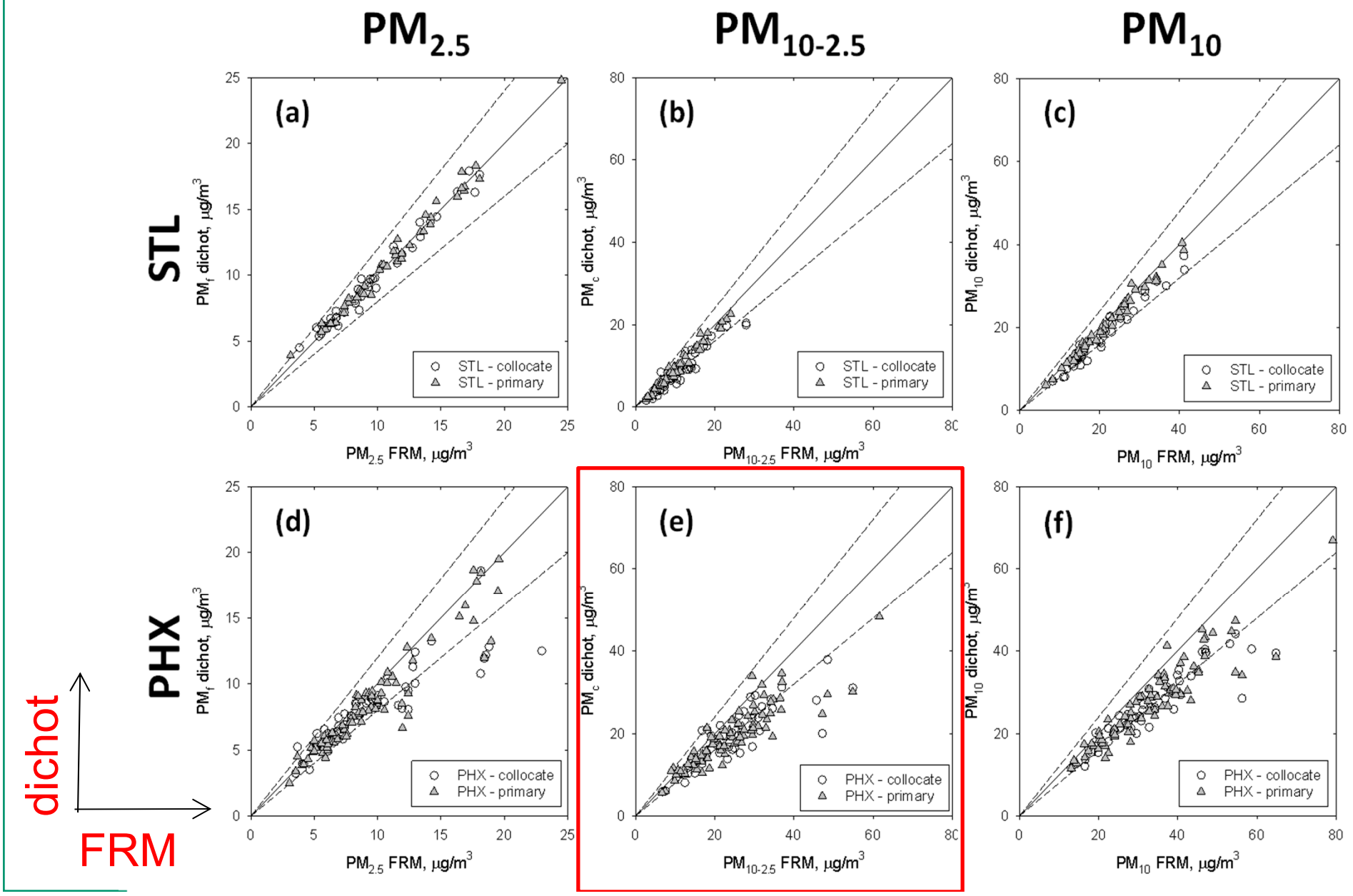
- Field operations summary
- Filter dichot PMc…
  - gravimetric mass and species versus paired FRM
  - collocated precision
  - mass closure
  - XRF attenuation corrections
  - carbonate
- PMc mass climatology from TEOM data
- Draft recommendations

* This presentation does not include all of the data analyses conducted

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
  - Subsequently modified to be FEM compliant
  - Modest follow-up pilot study at RTP to evaluate performance

Dichot Collocated Precision

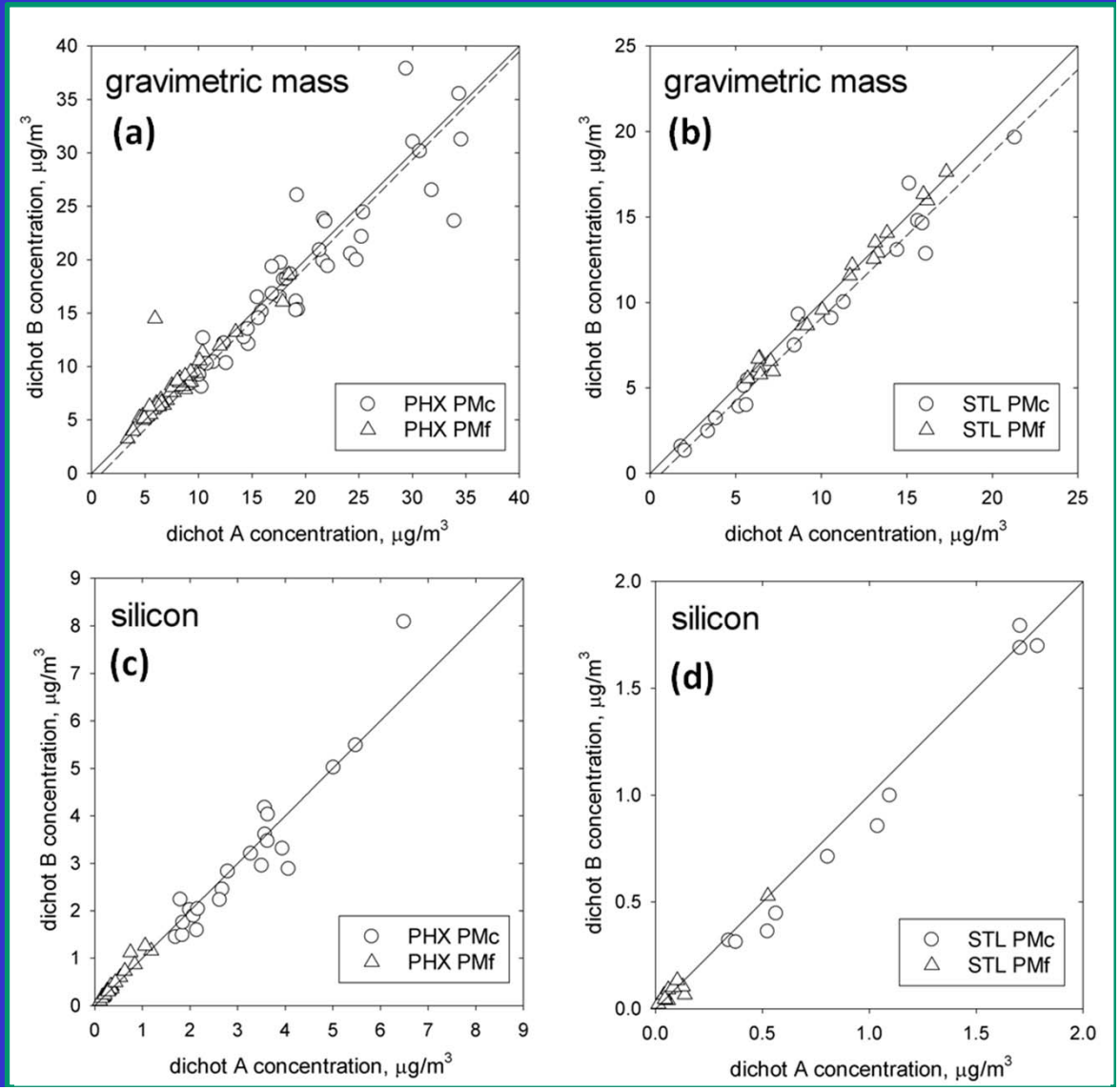
PHX PMc…

gravimetric mass 12%

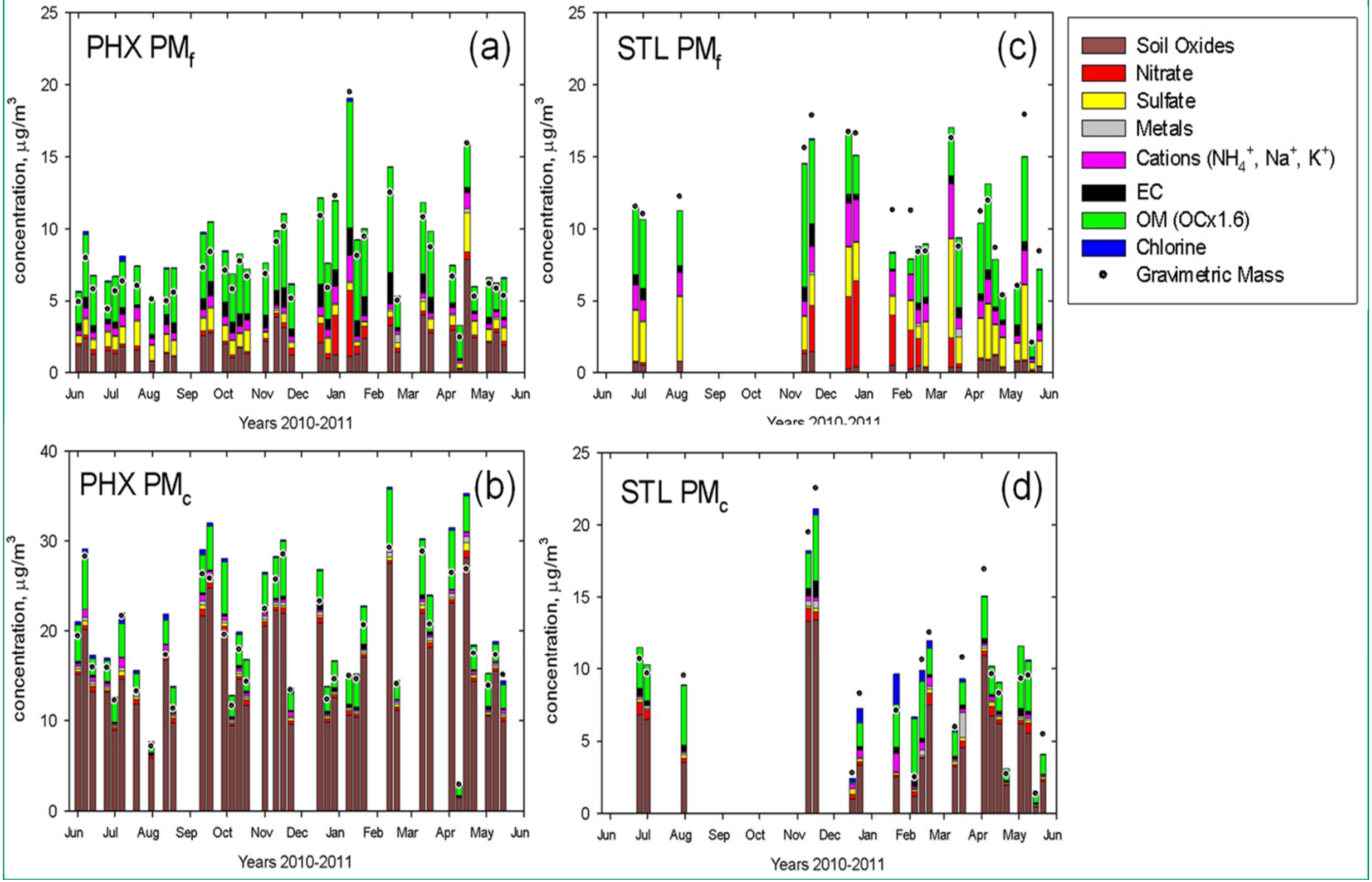
silicon 12%

STL PMc…

Similar collocated precision as PHX, but more influenced by bias

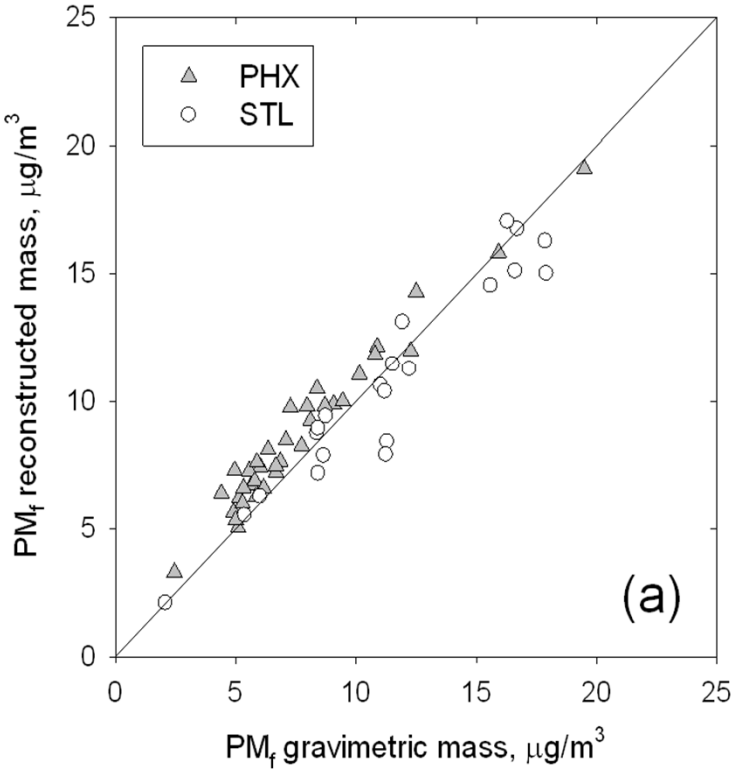


Mass Balance Closure: Dichot Teflon Filters

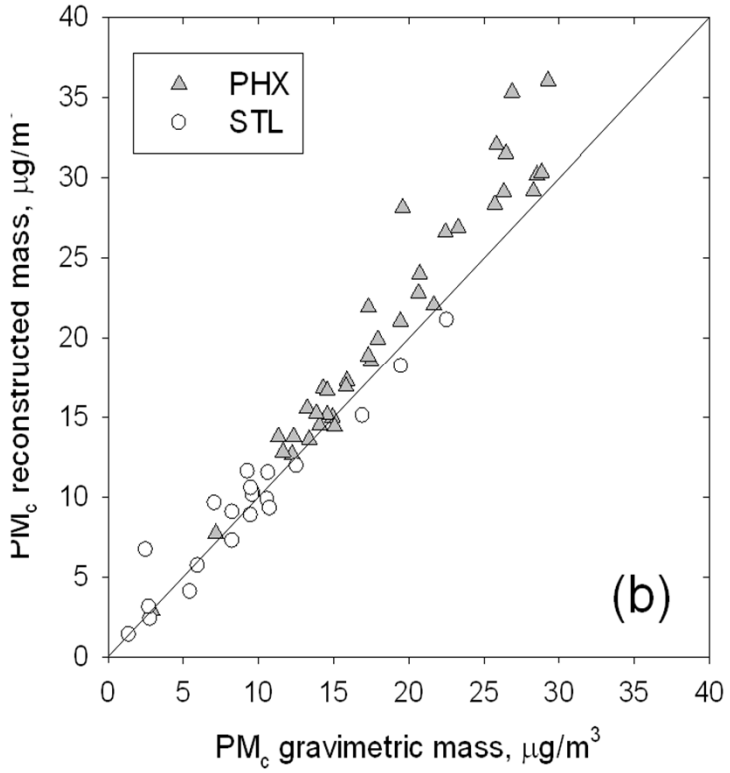


Dichot Mass Balance Closure

Fine PM



Coarse PM



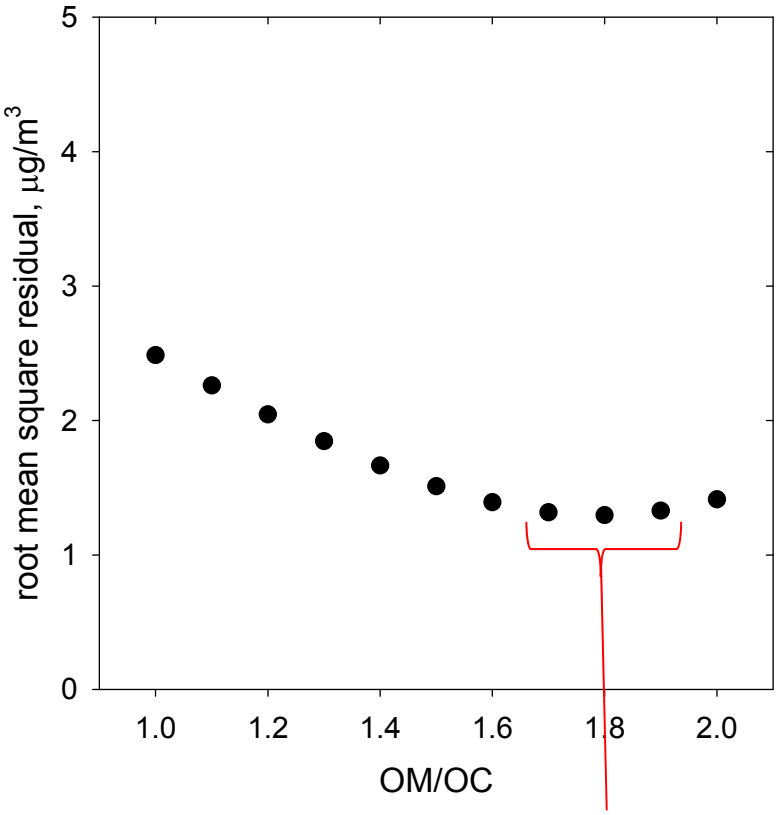
ratio of means (using OM = 1.6×OC):

STL	0.94	1.01
PHX	1.14	1.13

Reconciling Gaps in Mass Balance Closure

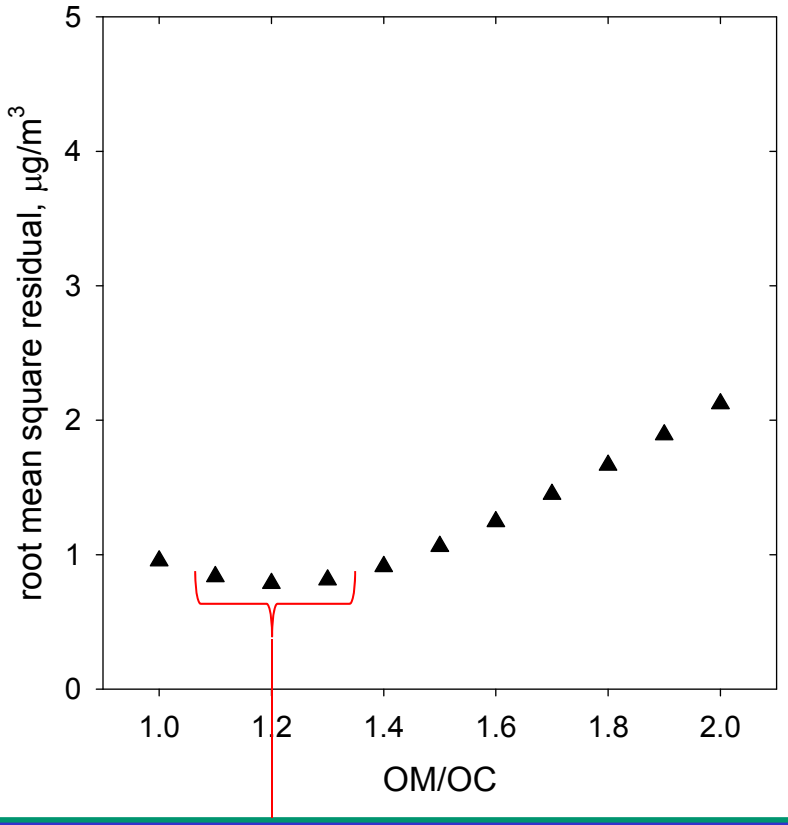
- Assume all estimates are accurate except OM/OC ratio
- For each site and size range, find best-fit OM/OC ratio *assuming OM/OC ratio is constant*

St. Louis – PM Fine



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

Phoenix – PM Fine

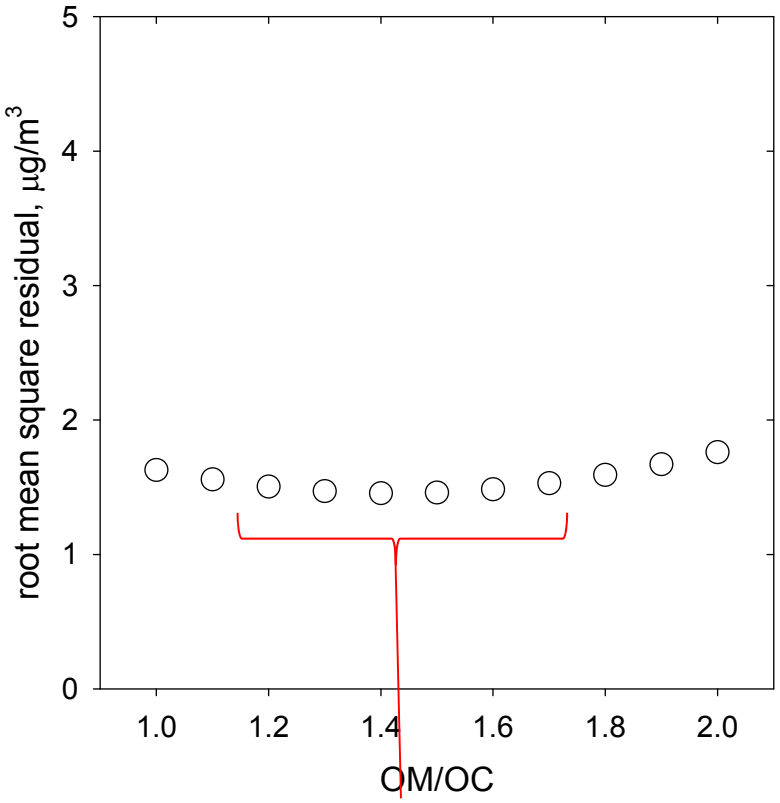


consistent with 1.25 reported by Simon *et al.* (2011)

Reconciling Gaps in Mass Balance Closure

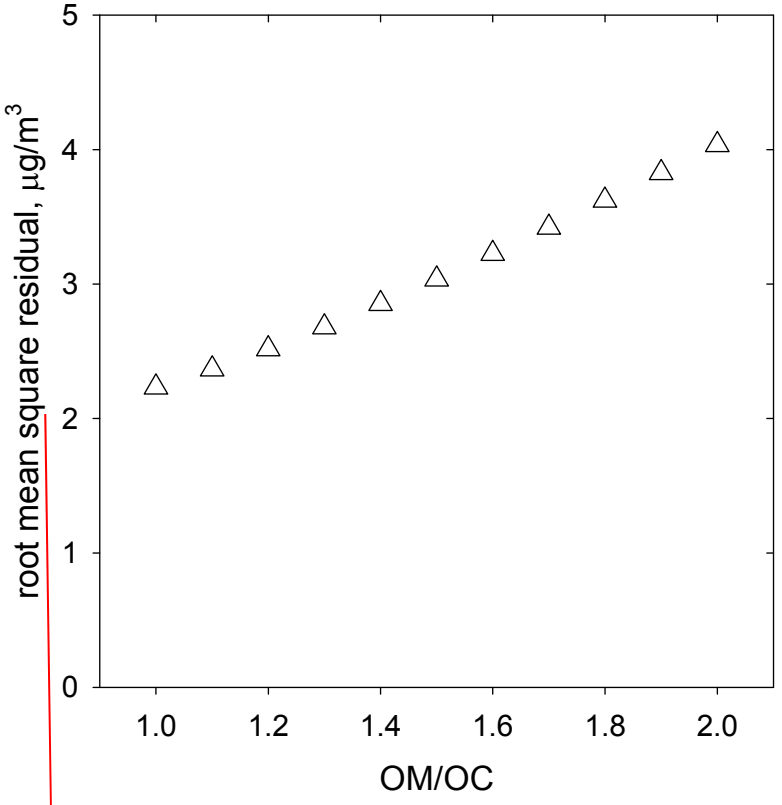
- Assume all estimates are accurate except OM/OC ratio
- For each site and size range, find best-fit OM/OC ratio *assuming OM/OC ratio is constant*

St. Louis – PM Coarse



wide range of plausible OM/OC

Phoenix – PM Coarse



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

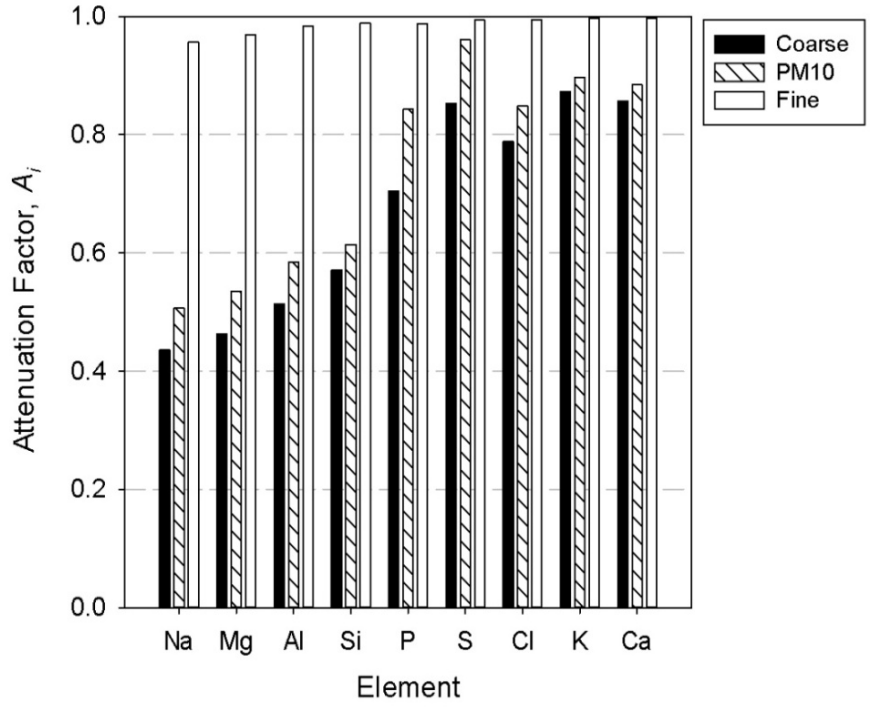
$$m_i = \frac{m_{no\,corr,i}}{A_i}$$

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

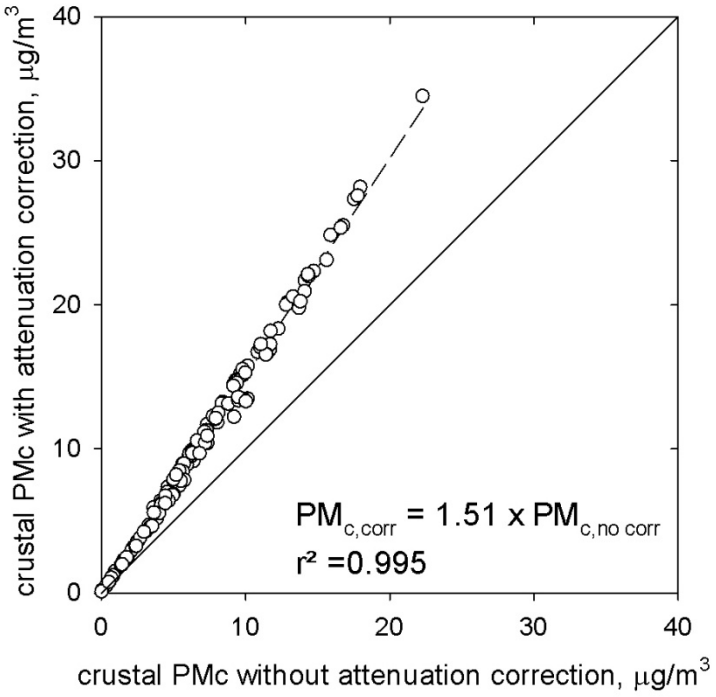
- RTI applied XRF attenuation factors using software developed by Kellogg (2005)

XRF Attenuation Corrections

attenuation factors

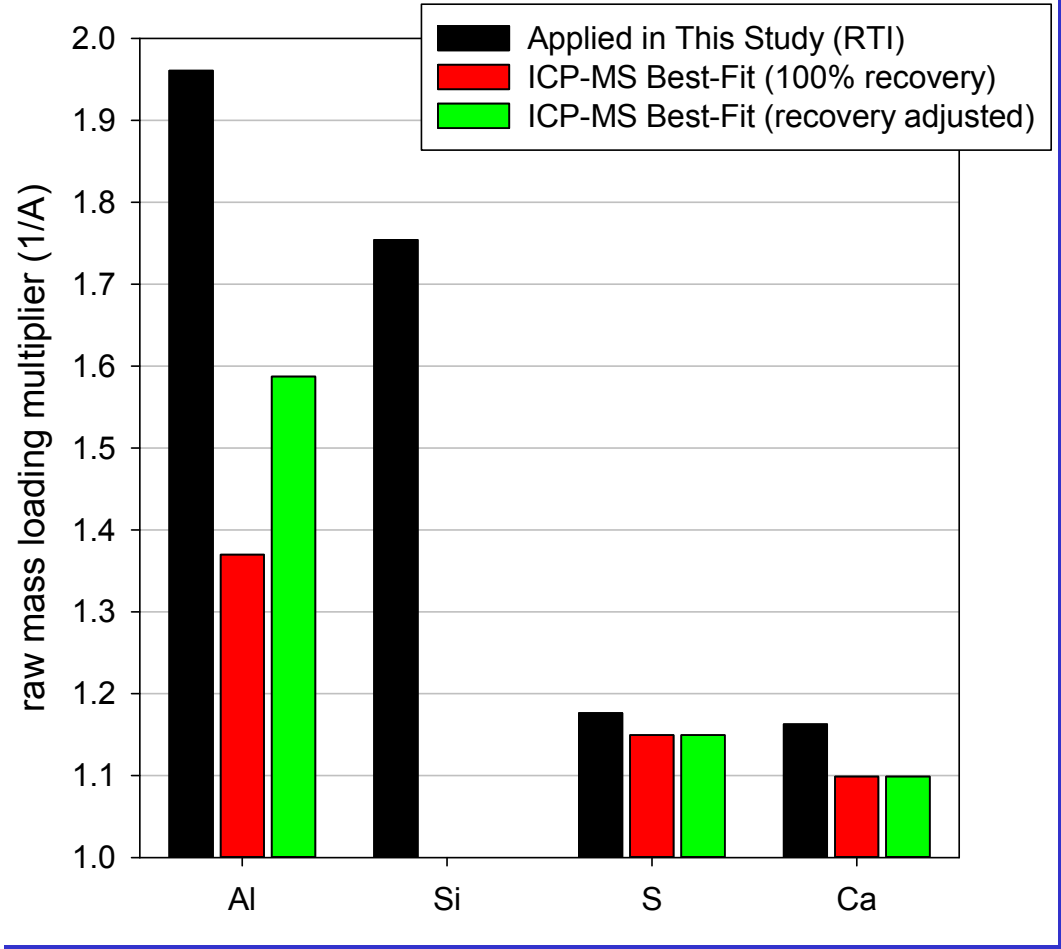


impact on crustal PMc



- 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 PHX Dichot Minor Flow Correction Factors



Several potential confounders

- Assumes XRF calibration is correct
- Blank correction of ICP-MS data (elements in filter support ring and adhesive)
- Recovery correction of ICP-MS data
- Small data set (PHX = 10, STL = 8)

…Comprehensive evaluation is needed

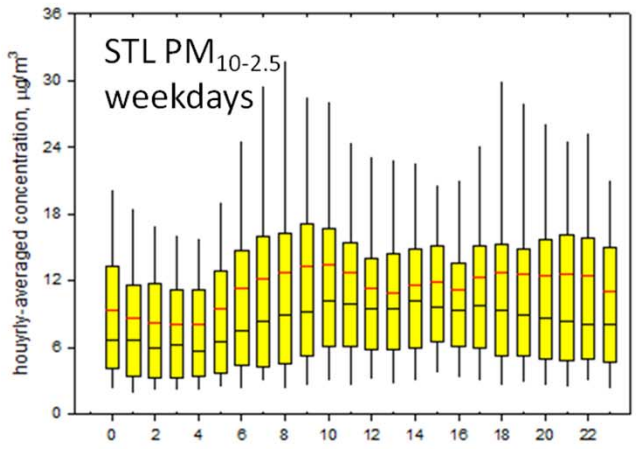
Carbonate (CO_3)

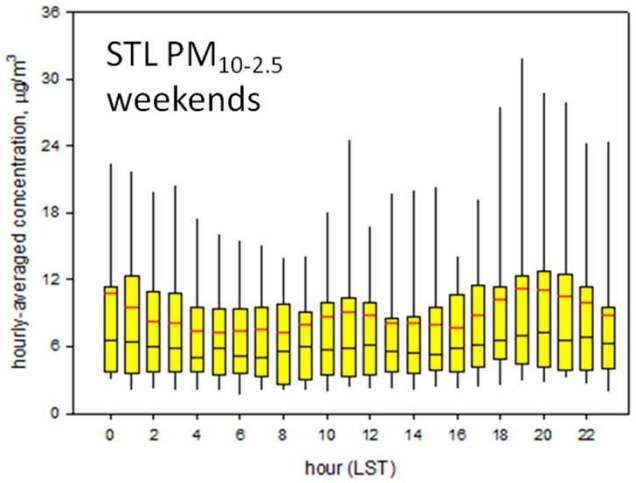
- $PM_{2.5}$ CO_3 low at IMPROVE sites (Chow & Watson, 2002)
- Measure CO_3 on subset of samples
  - Thermal-optical analysis with acidification (DRI)
  - $CO_3 \leq$ MDL for FRM $PM_{2.5}$ and dichot PMf
  - Dichot PMc carbonate
    - Collocated precision 22% (N = 12)
    - No bias compared to FRM $PM_{10-2.5}$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

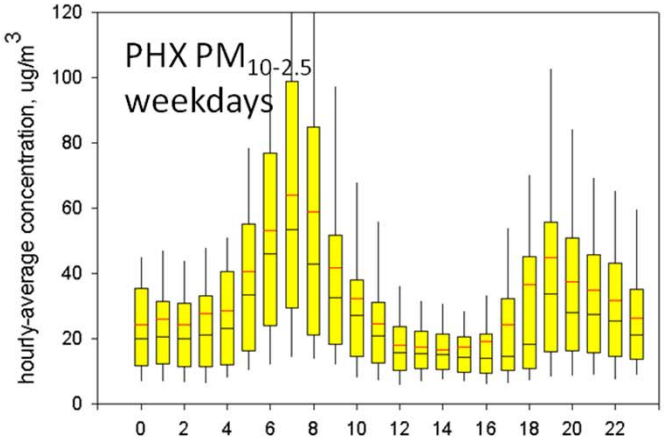
Site	N	Mean, μg/m³ (% of PMc mass)	Range, μg/m³ (min, max)
PHX	43	1.2 (**6%**)	(0, 5.2)
STL	26	1.3 (**12%**)	(0, 4.0)

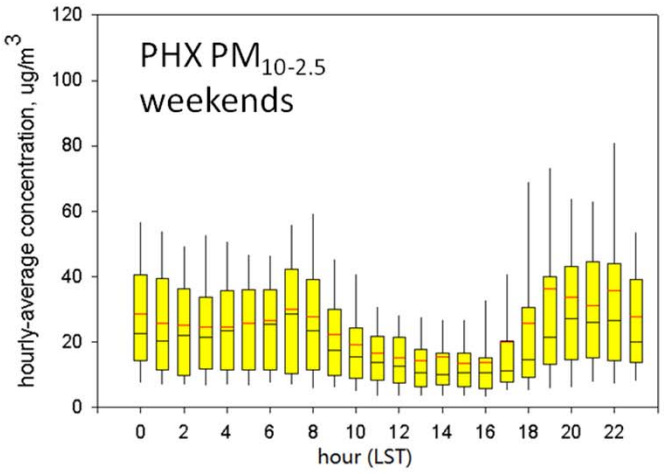
- Can explain ~1/2 to 2/3 of the Ca if present as $CaCO_3$

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