Seasonal Composition of $PM_{2.5}$ and Performance of the Federal Reference Method in Pittsburgh

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$PM_{2.5}$ and Electric Power Generation: Recent Findings and Implications

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Overview

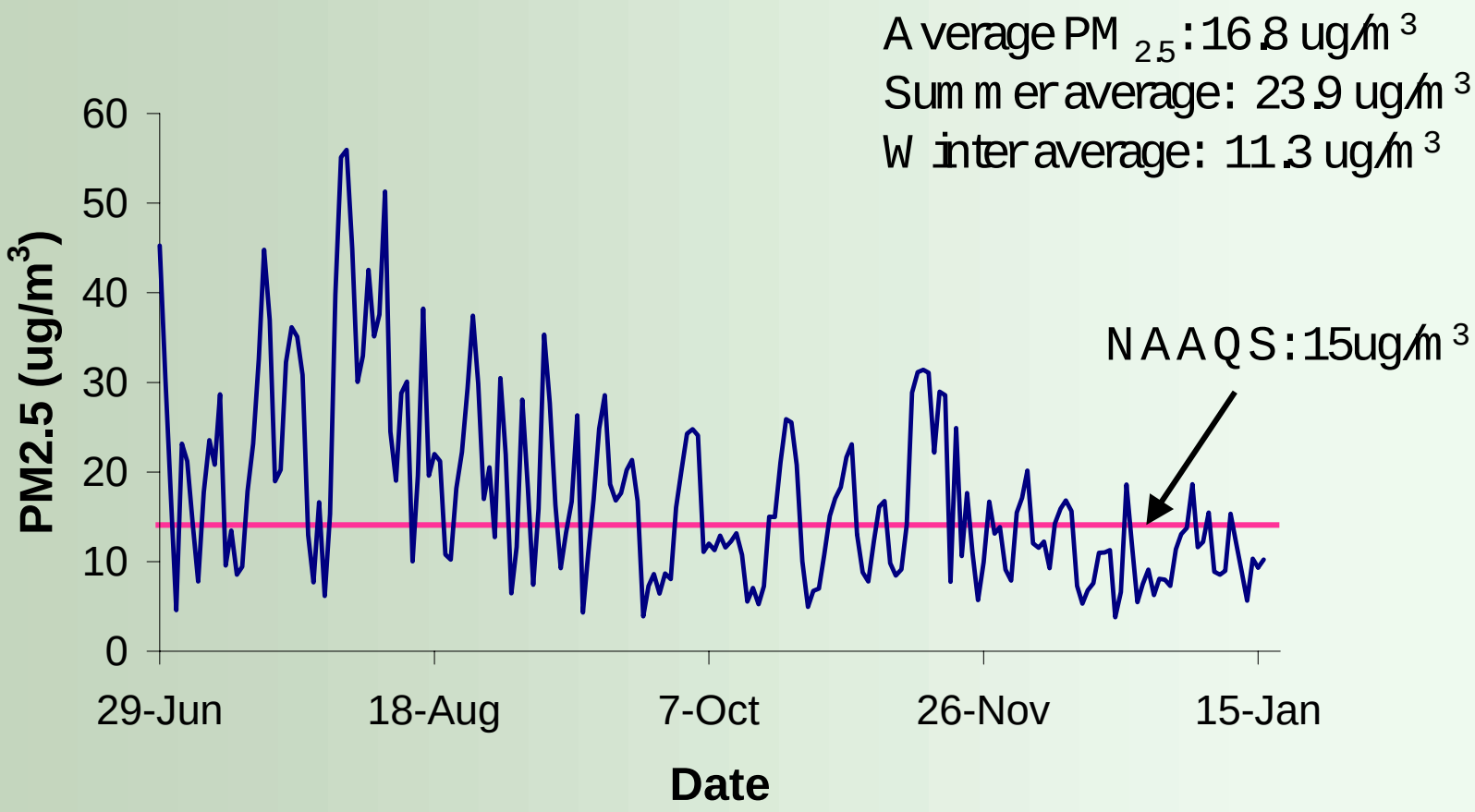
- Evaluate FRM performance
  - Compare FRM $PM_{2.5}$ mass to the sum of aerosol chemical components
- Mass balance discrepancy
  - Positive: FRM > Σ chemical components
  - Negative: FRM < Σ chemical components
- Mass discrepancy ratio

$$\frac{[\text{FRM}]}{[\text{Sum of Components}]}$$

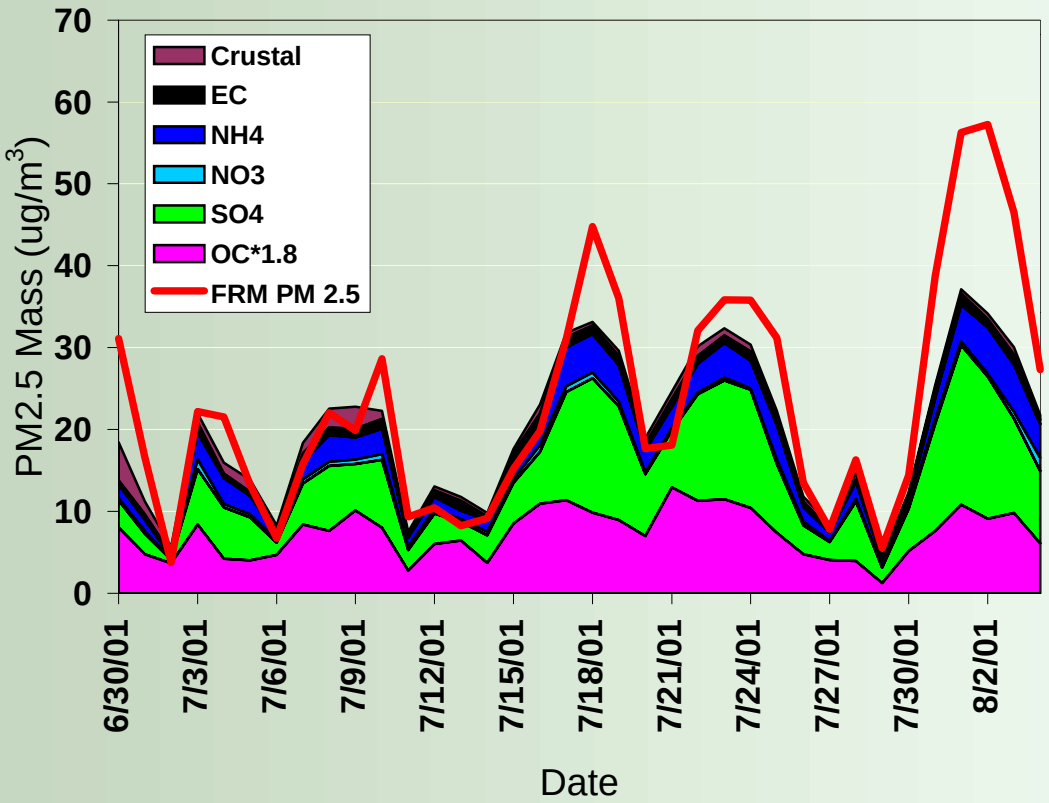
>1, FRM overestimates actual mass

<1, FRM underestimates actual mass

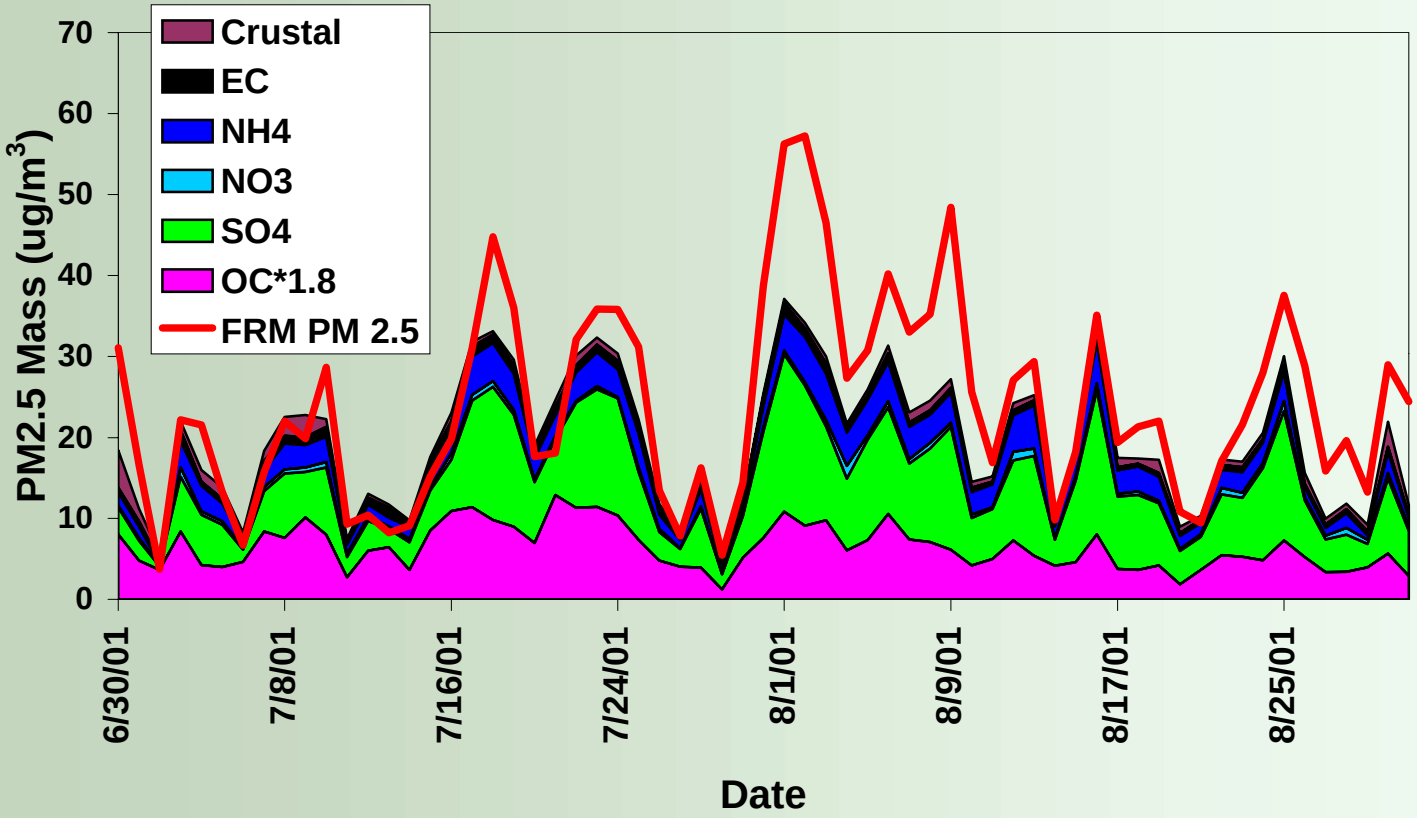
FRM Mass July 01 – Jan 02



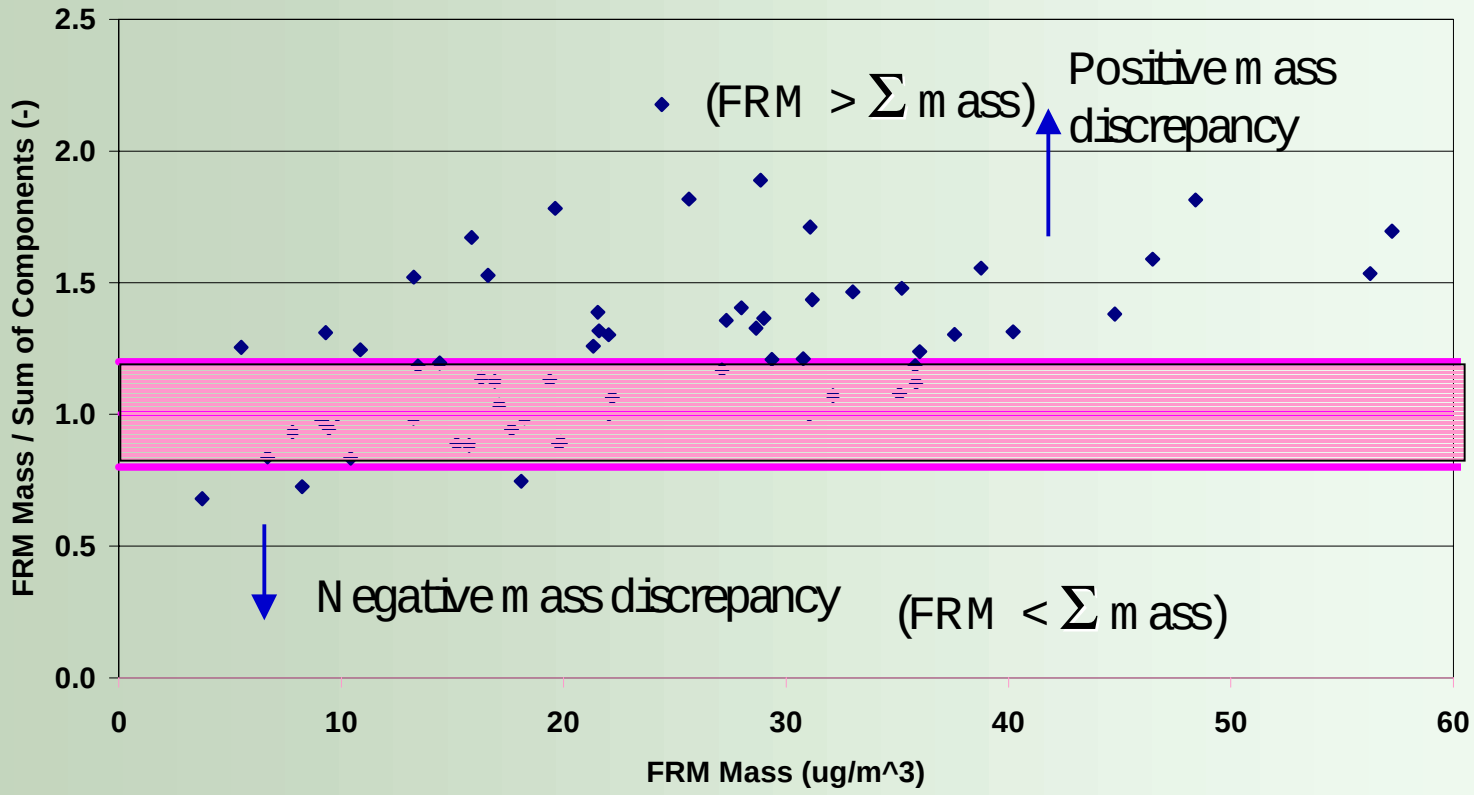
$PM_{2.5}$ Mass Balance July 01



$PM_{2.5}$ Mass Balance July 01 – Aug 01



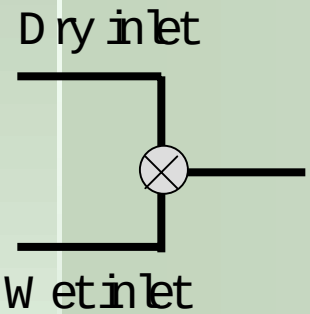
Mass Discrepancy Ratio
July 01 – August



Hypotheses to Explain Mass Discrepancy

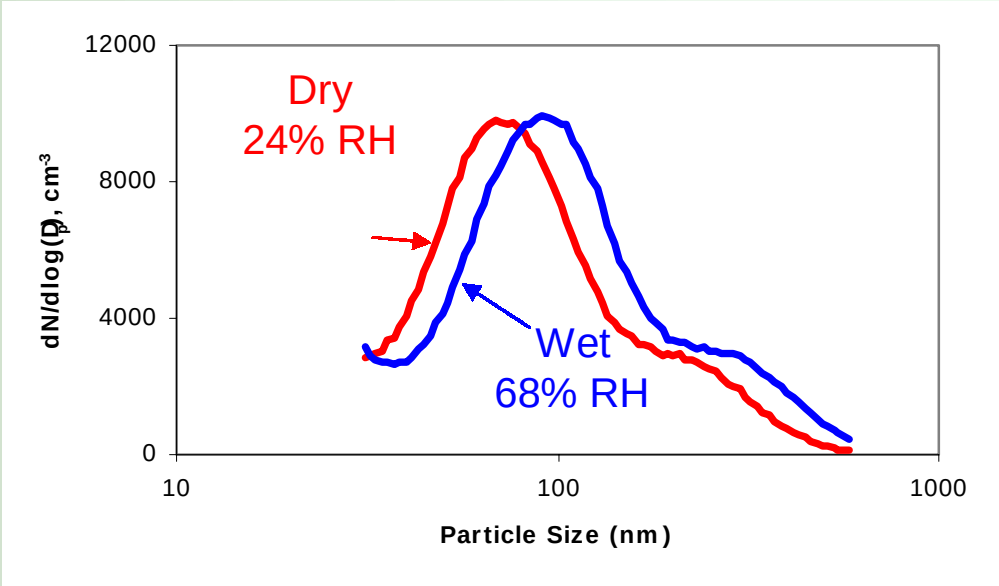
- Water: Positive mass discrepancy (FRM > components)
- Organic Volatilization: Negative mass discrepancy (FRM < sum of components)
- Other factors
  - OC multiplication factor
  - Volatilization of nitrate

Measurements of aerosol water content



Particle Sizers
Nano-SMPS
SMPS
APS

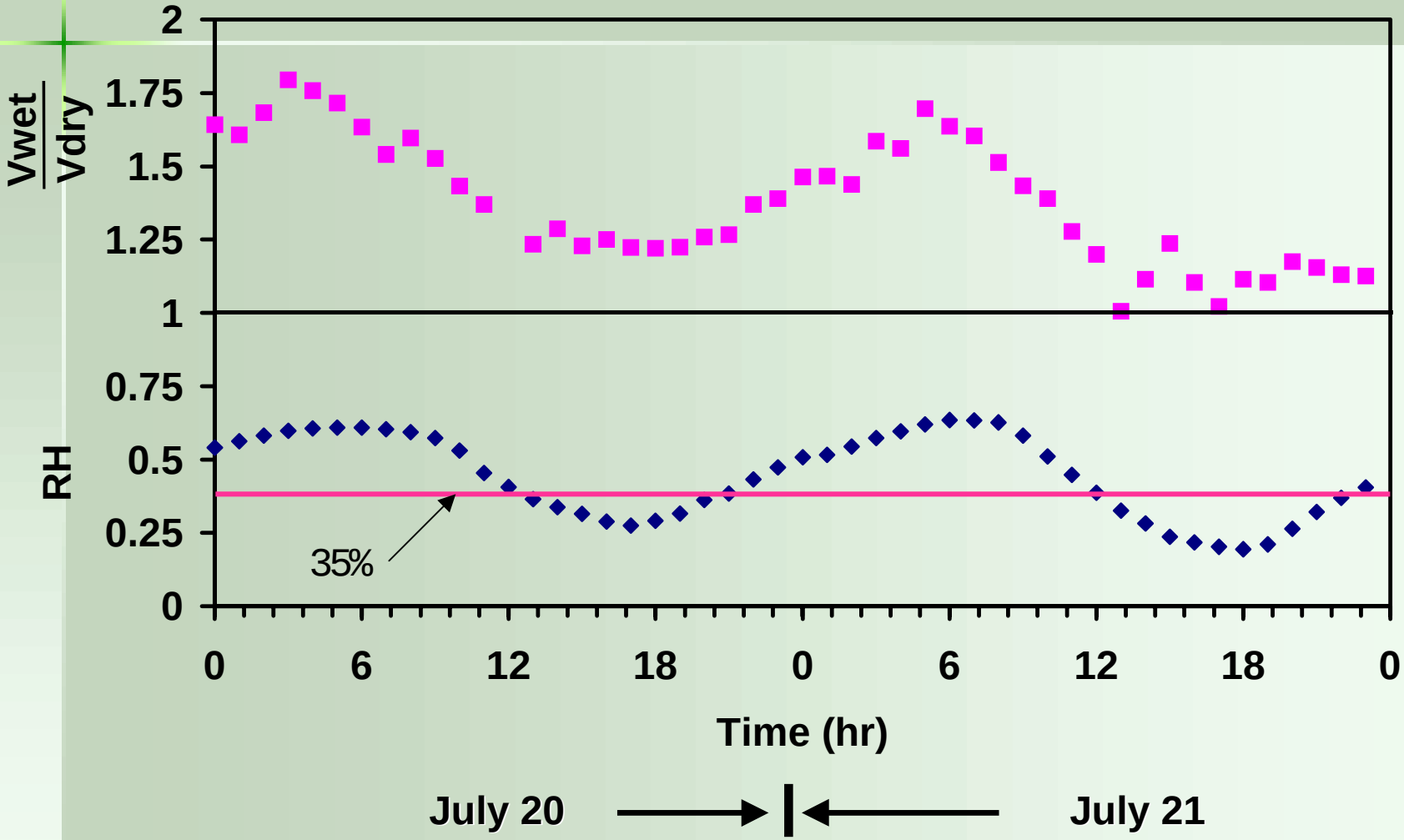
DAASS: Dry/Ambient Aerosol Size Spectrometer



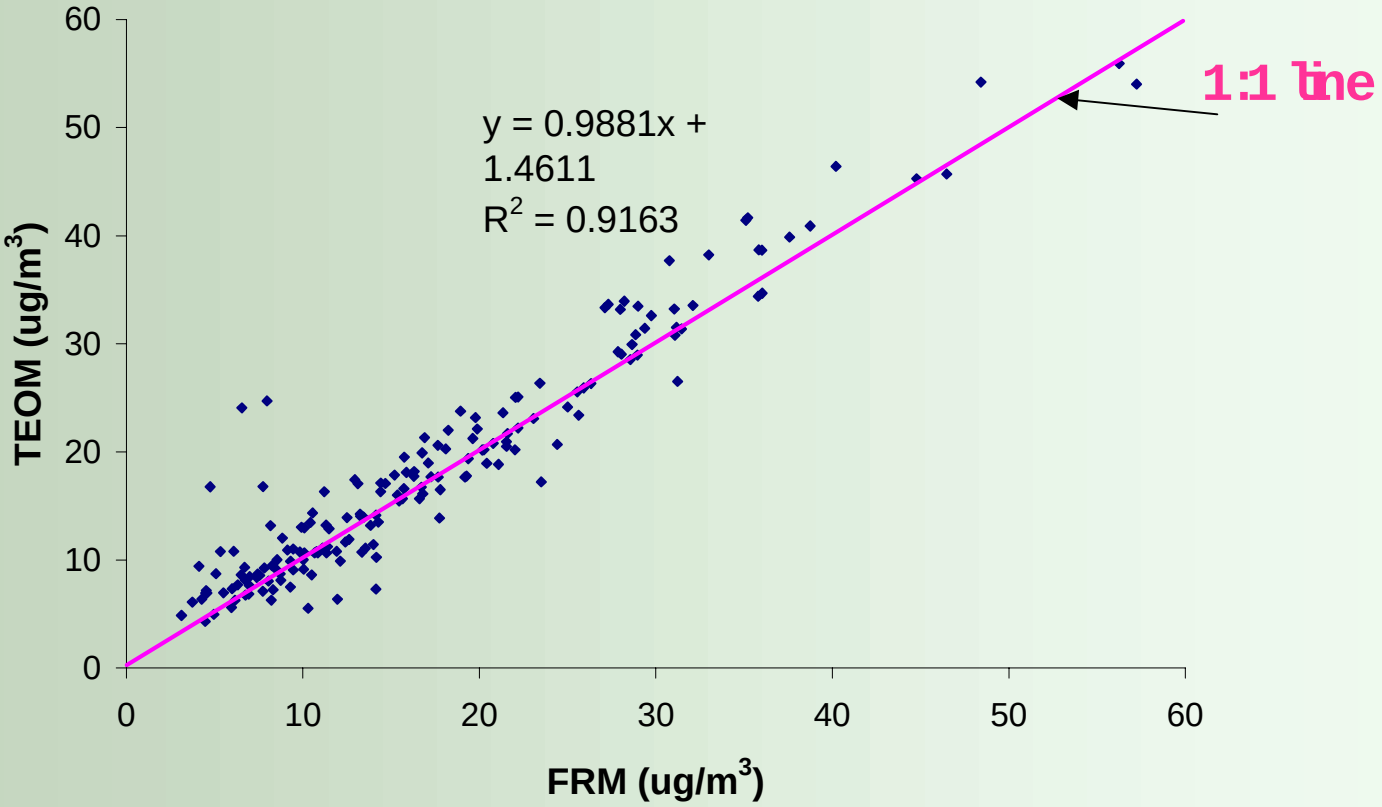
Estimating aerosol water at 35% RH

- Measured $\frac{\text{VolumeWet}}{\text{VolumeDry}}$
  - Extrapolate measured volume ratio to volume ratio at 35% RH
  - Convert to mass basis at 35% RH to estimate amount of water present
- Predictions
  - Aerosol composition and thermodynamic model

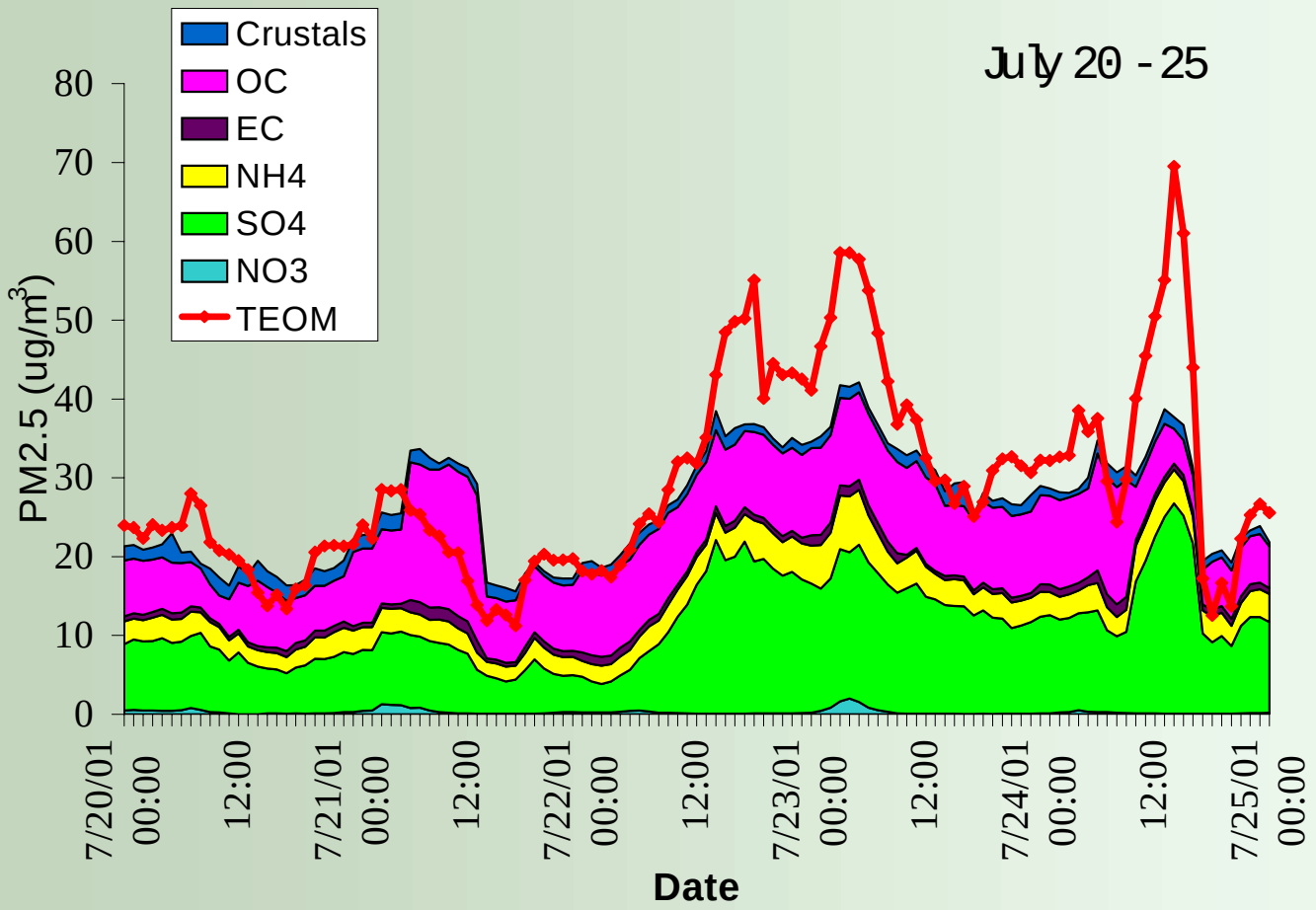
Particle Growth and Ambient RH



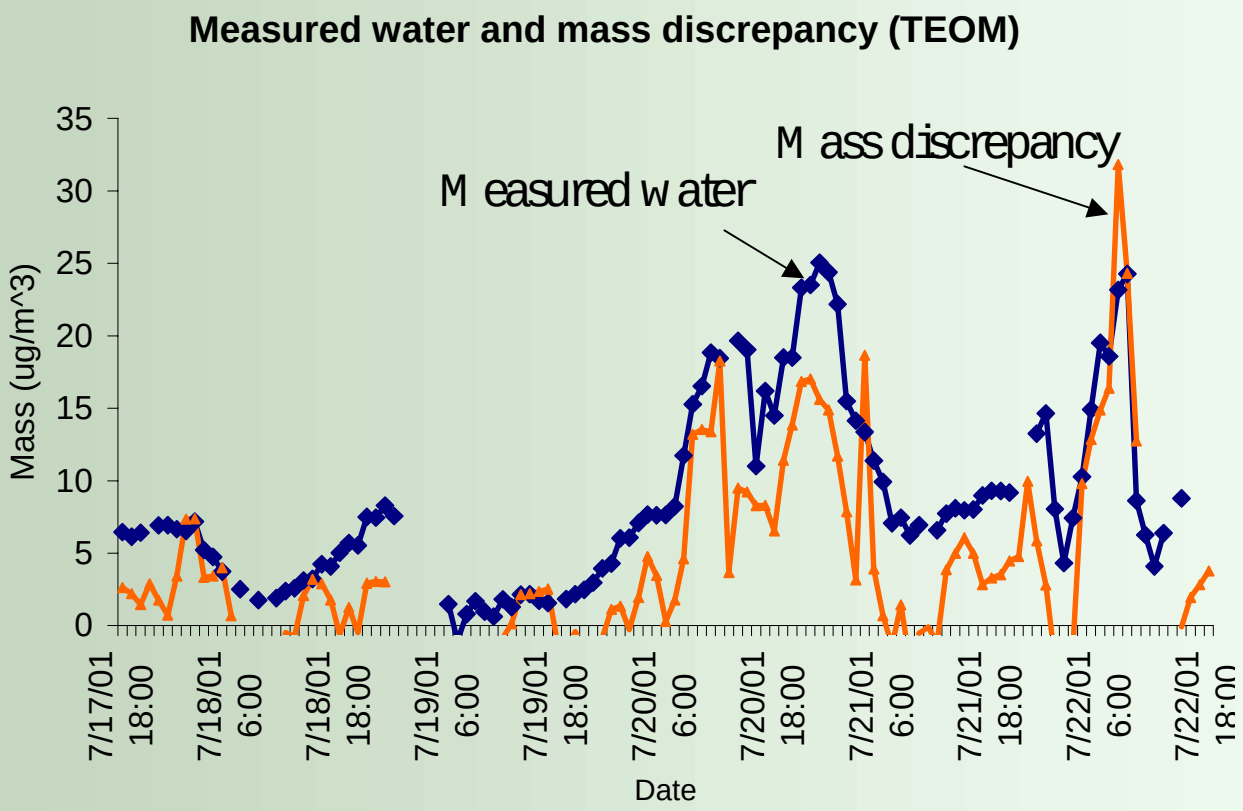
FRM v.TEOM Comparison



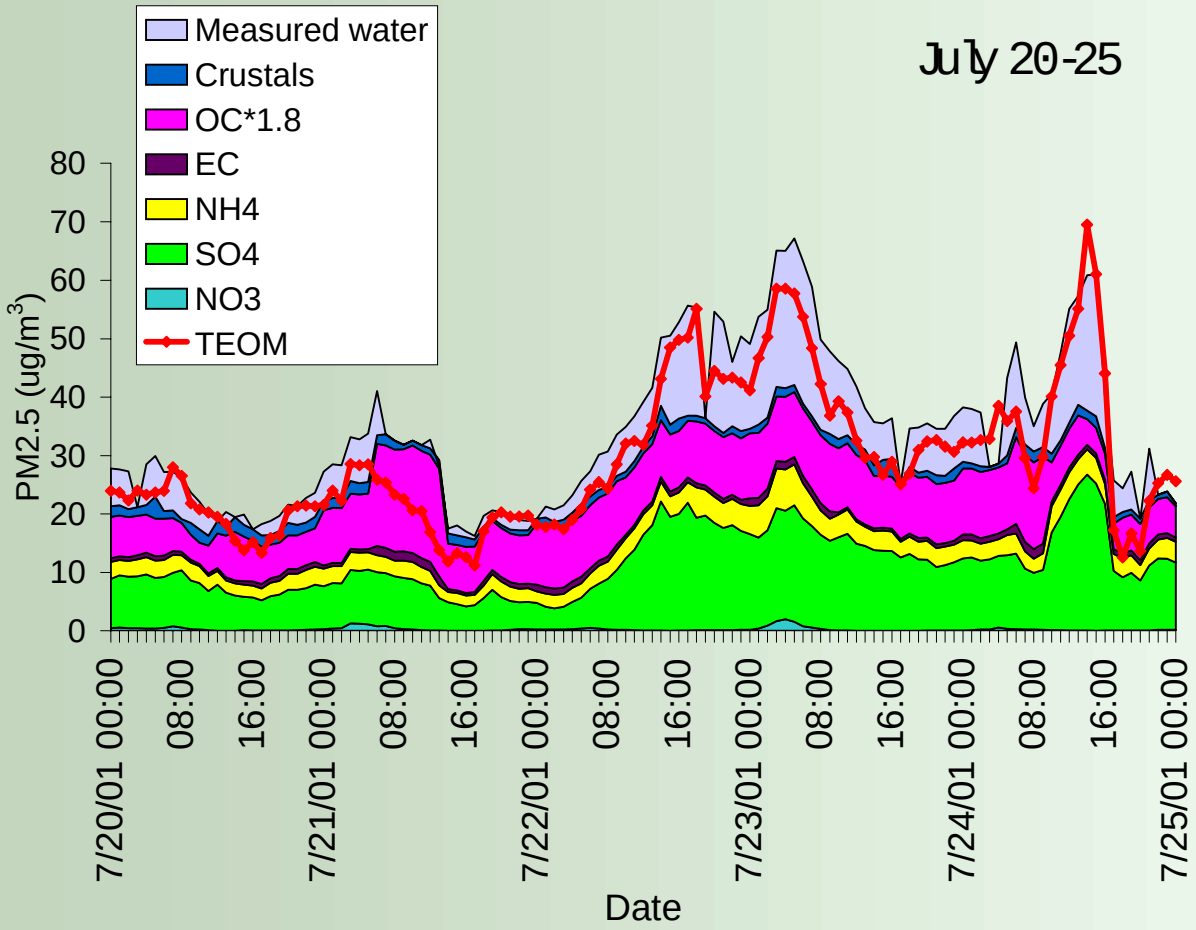
Hourly Mass Balance



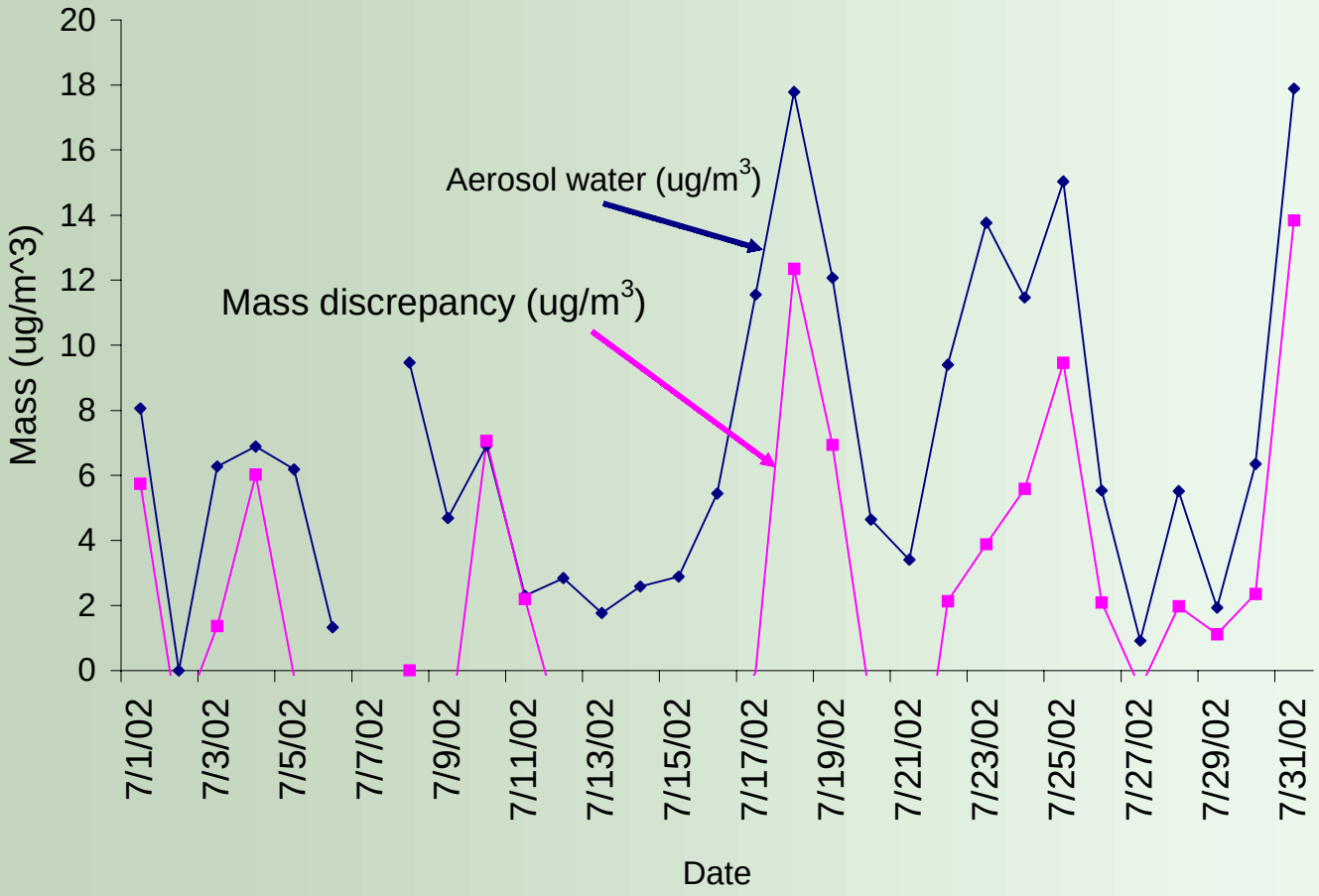
Aerosol Water



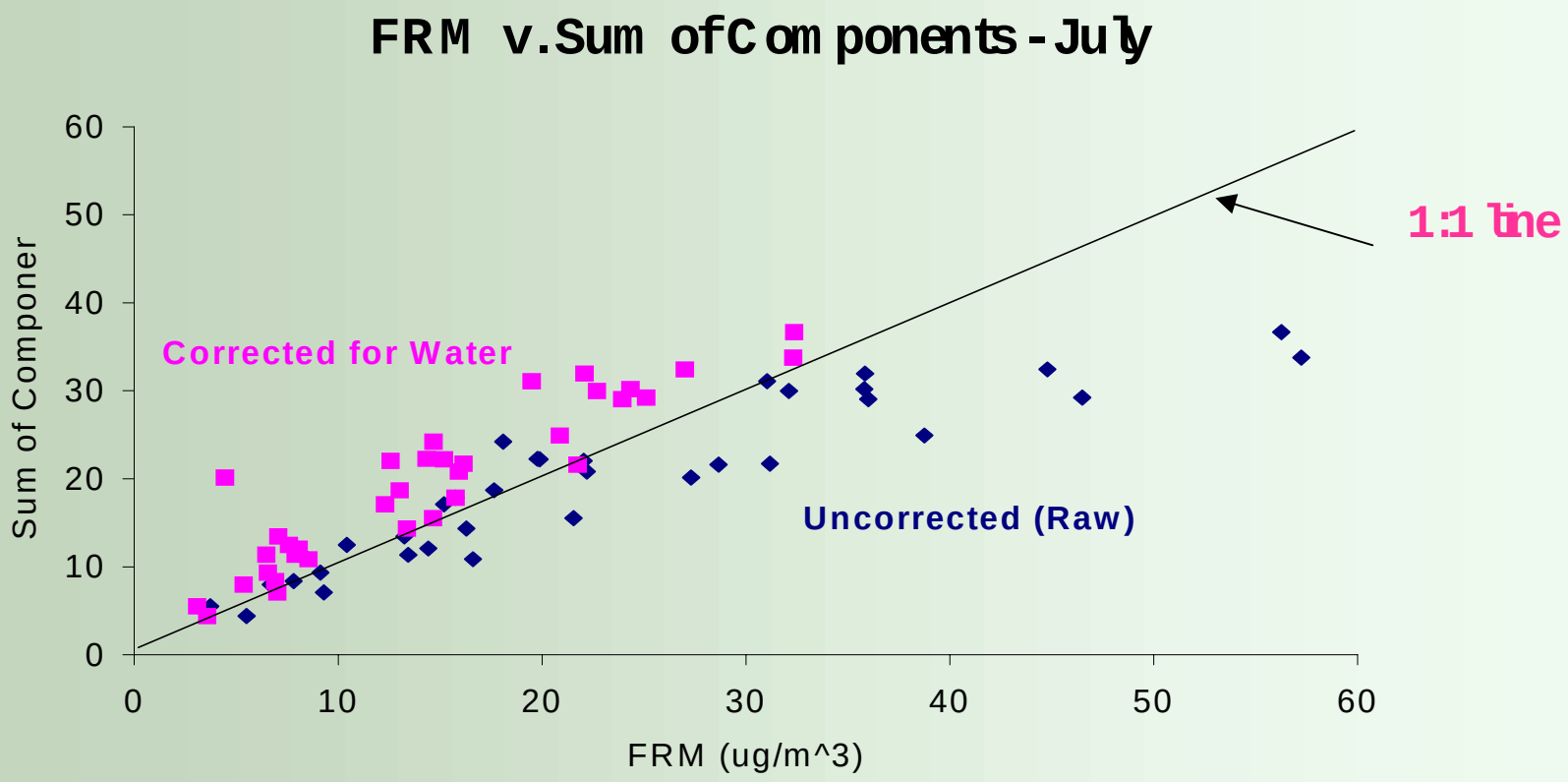
Hourly Mass Balance with Water



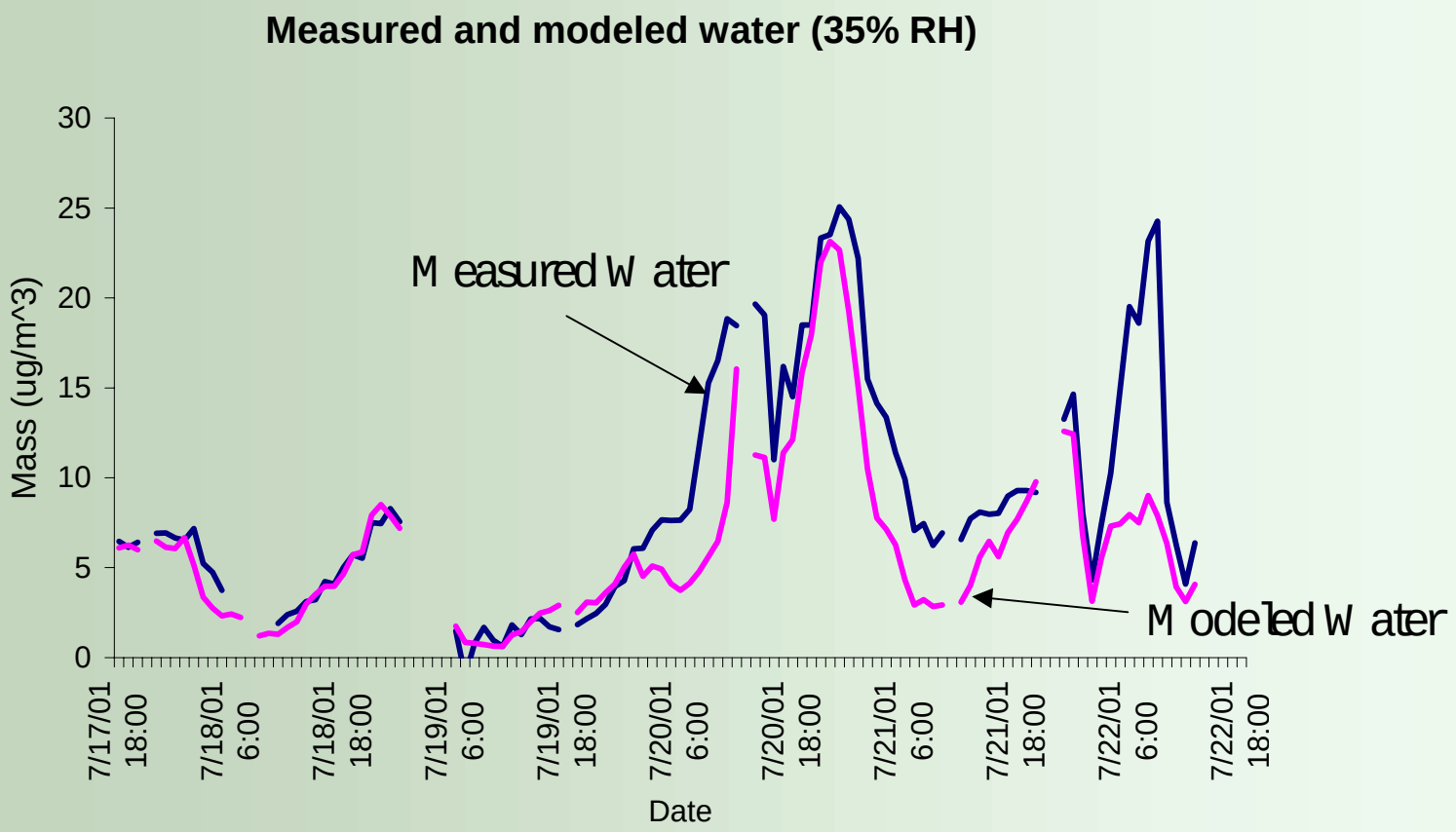
Estimated Aerosol Water Content (Filters, 24 hour basis)



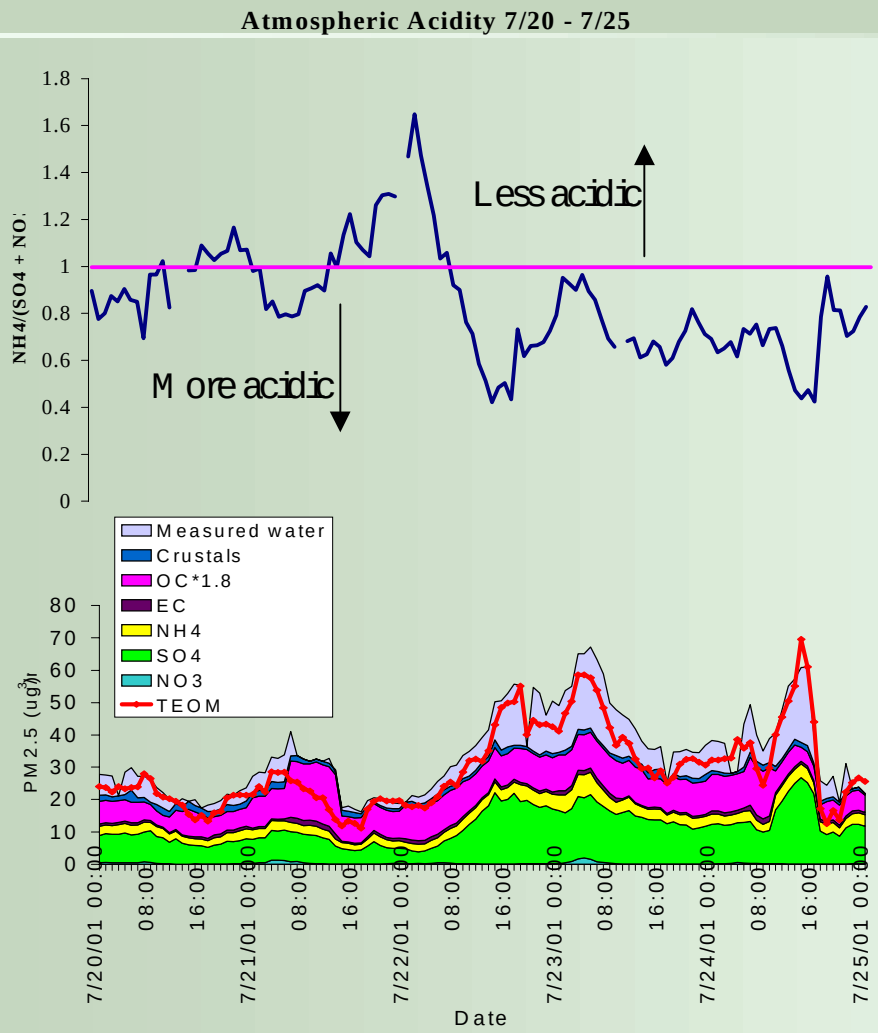
Effect of Water on FRM Measurement



Modeled v. Measured Water



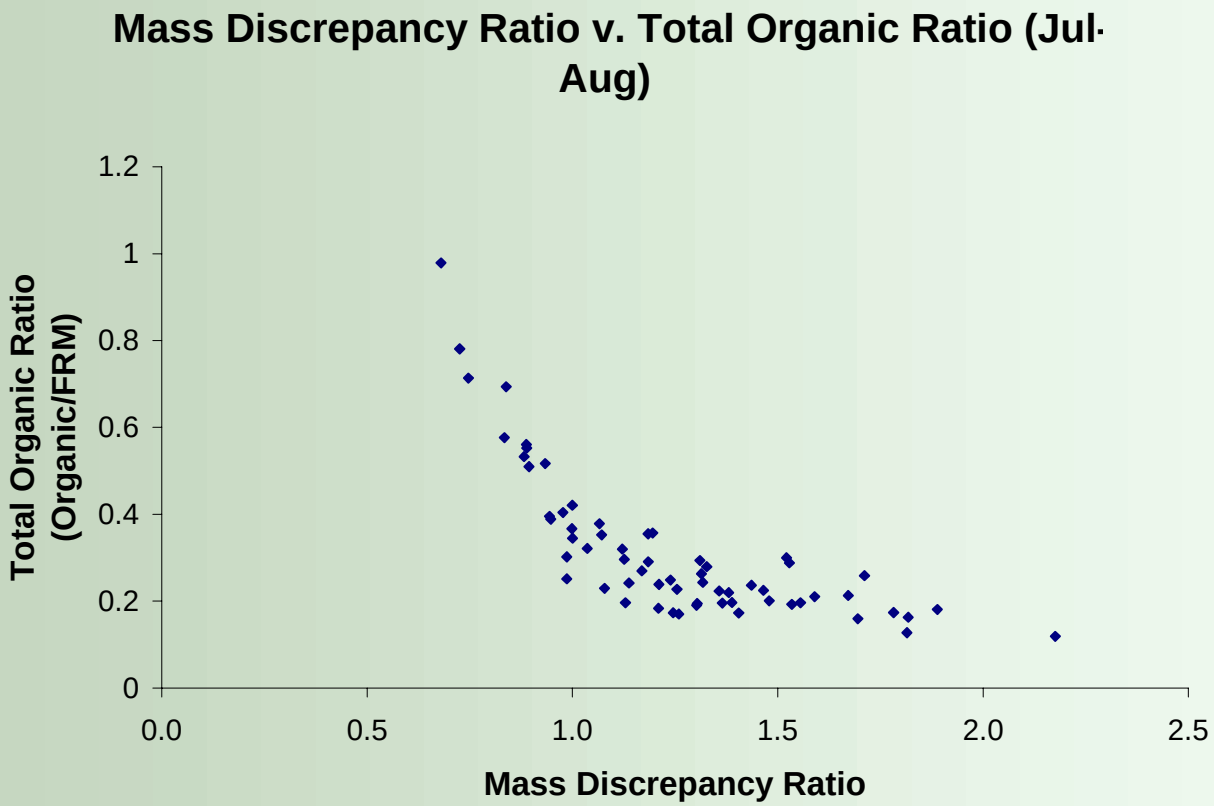
Atmospheric Acidity and Mass Balance



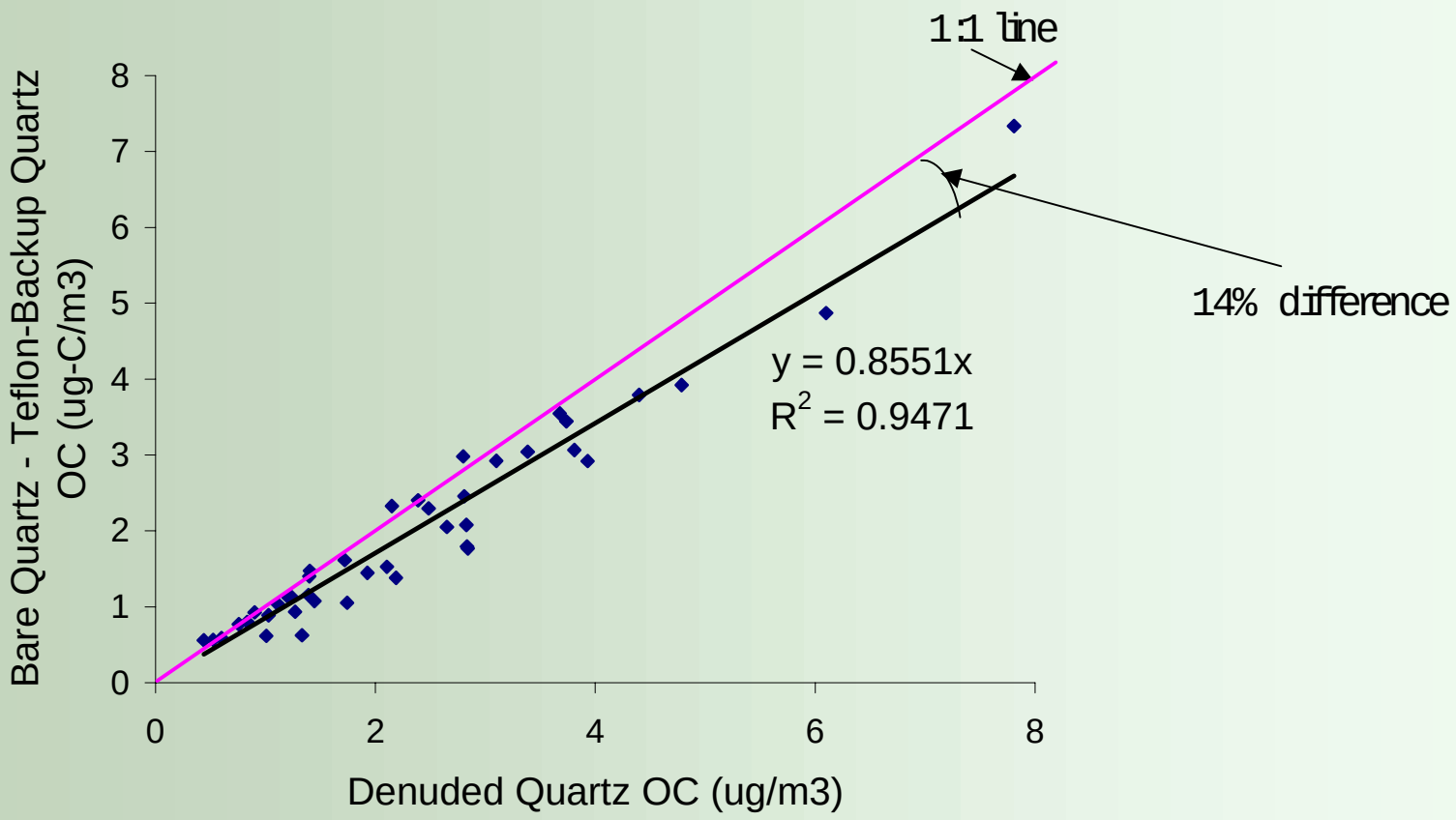
Water content seems impacted by acidity; the more acidic the atmosphere, the greater the aerosol water

Corresponds to presence of NH_4HSO_4, a species with hygroscopic properties

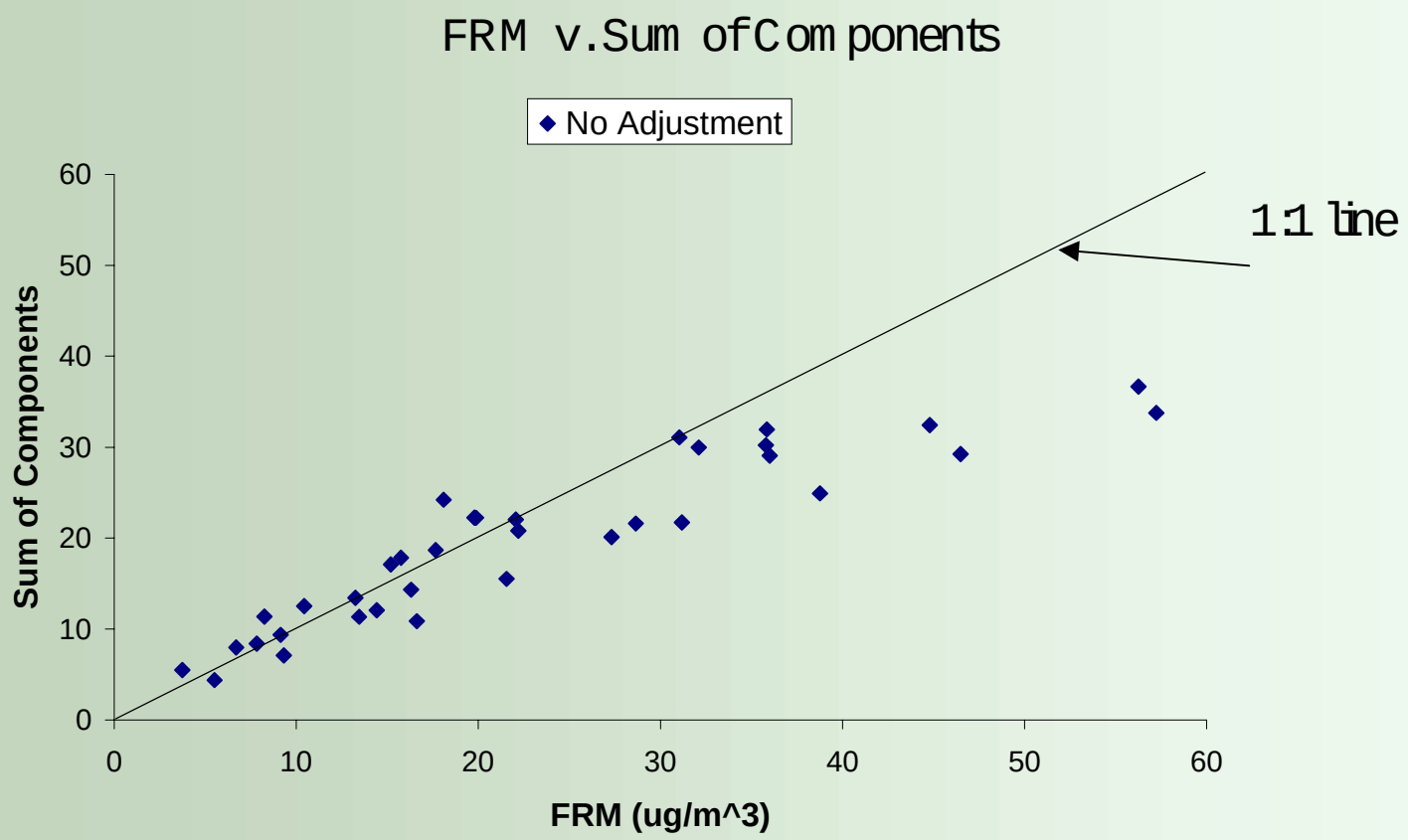
Negative Artifact: Volatilization of Organics



Observed Negative Artifact (Teflon Filter)



Mass Balance Closure?



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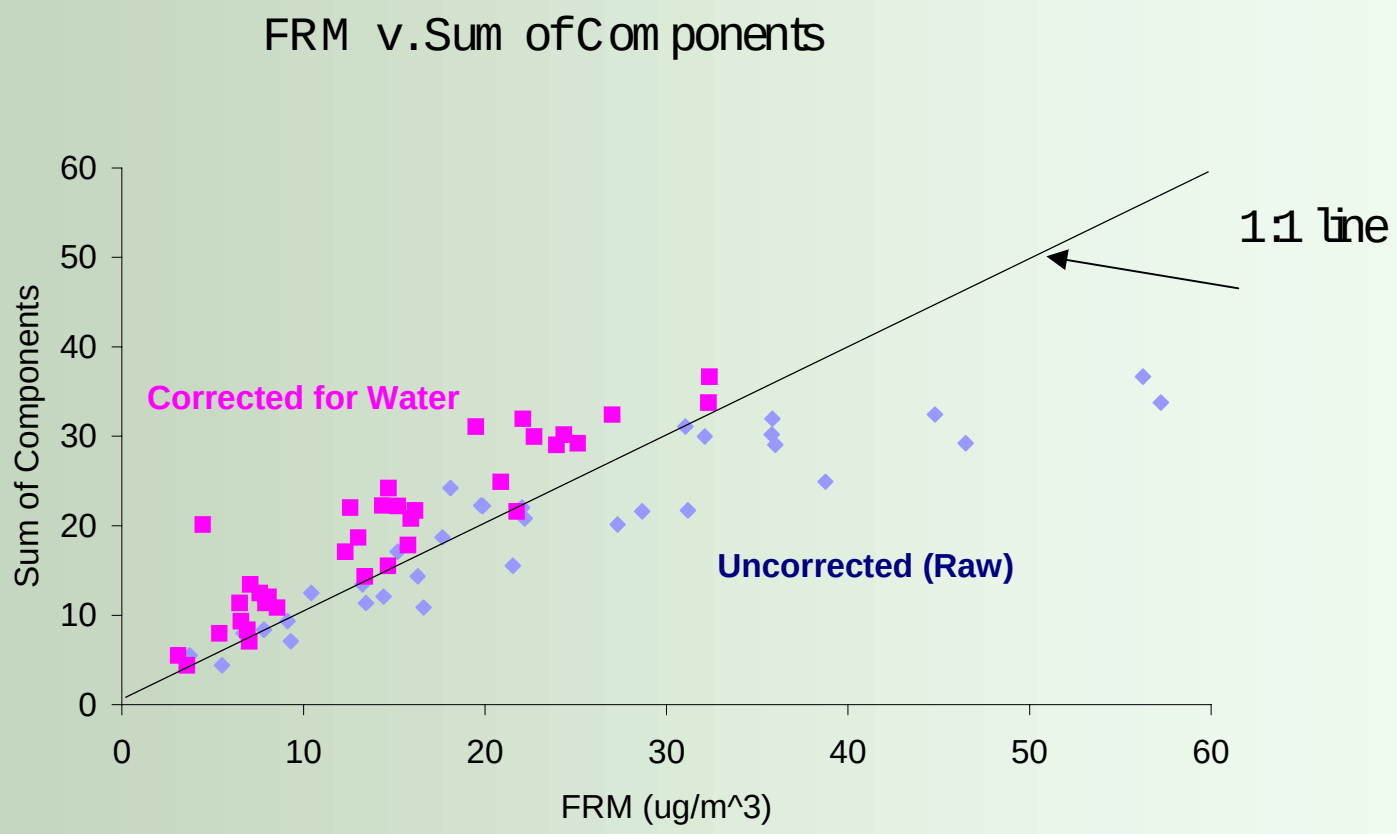

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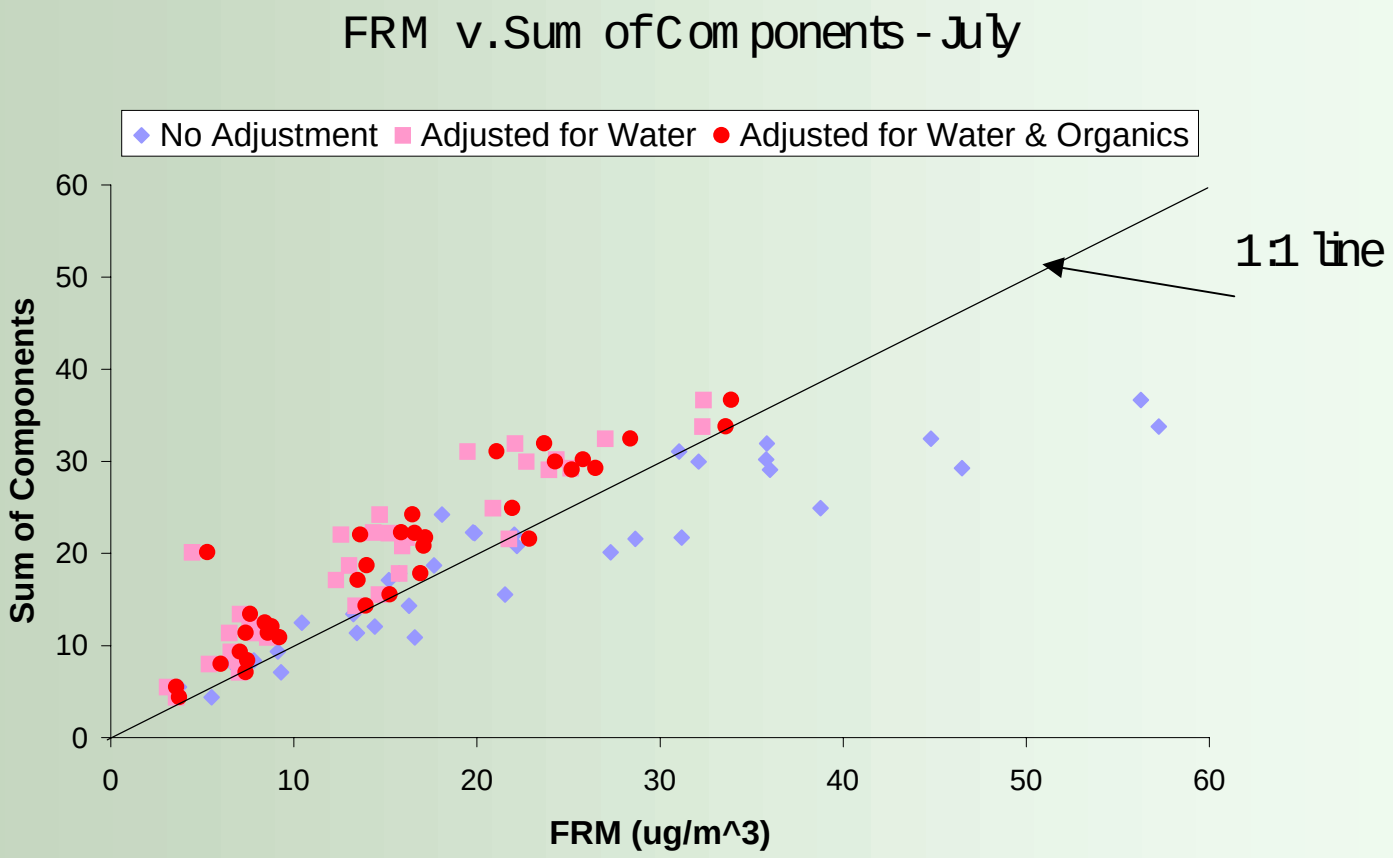
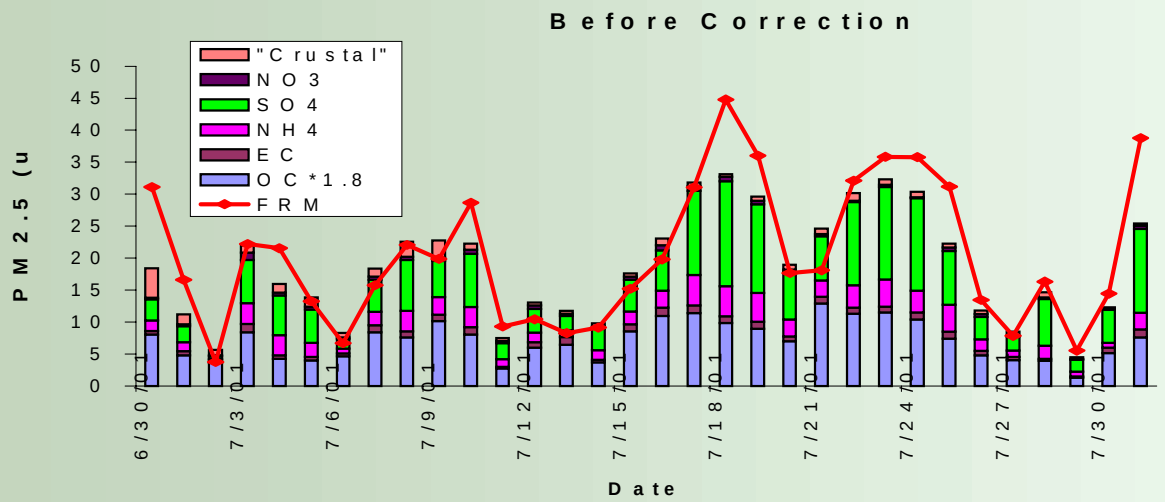
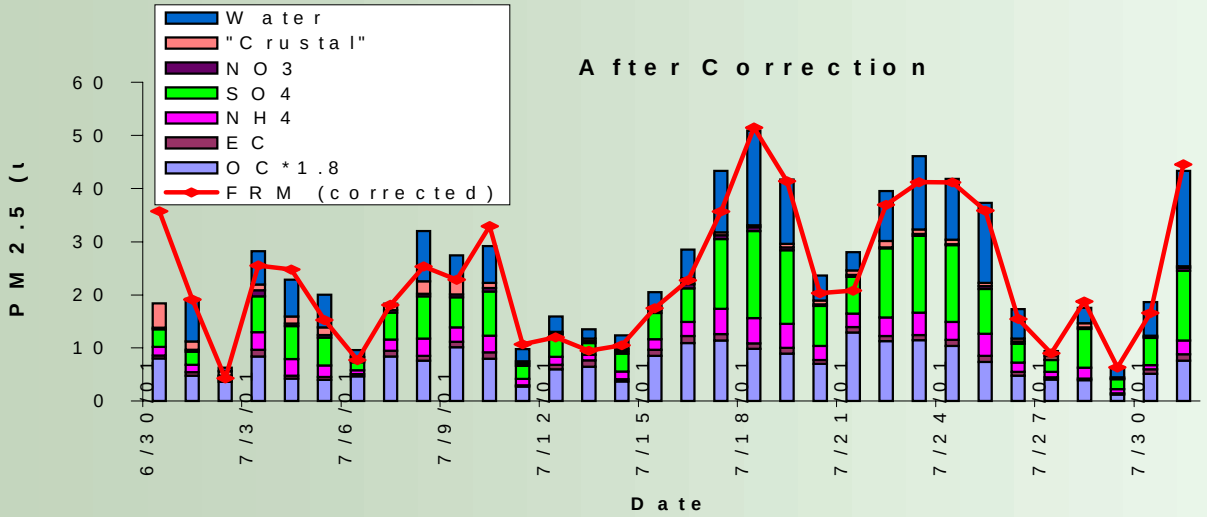


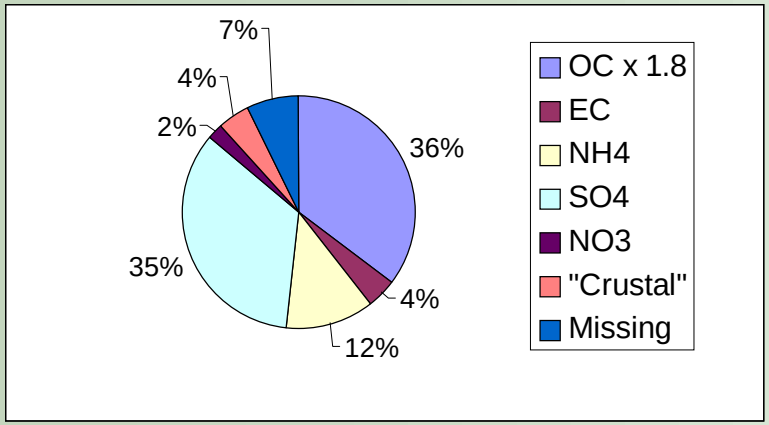
Mass Balance Closure – July 01





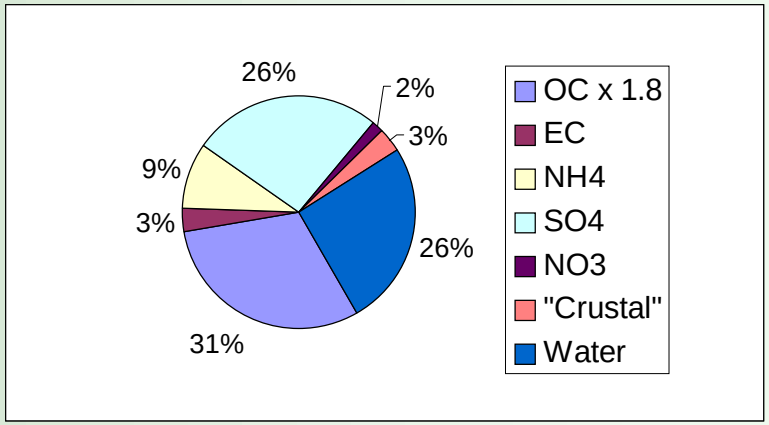
Mass Balance Composition - July

Before Corrections



FRM : 20 ug/m^3

Corrected for Water & Organics



Adjusted FRM : 14.5 ug/m^3

Conclusions

- FRM appears to measure significant water in Pittsburgh
- Organic negative artifact significantly impacts FRM
- Policy implications
  - FRM could control to species that do not address $PM_{2.5}$ concerns
  - Mass balance discrepancy may not manifest uniformly across the country

Future Work

- Continue quantification of mass balance closure
- Review data for seasonal effects
- Address policy implications of observed FRM performance

Acknowledgements

- Dr. Allen L. Robinson
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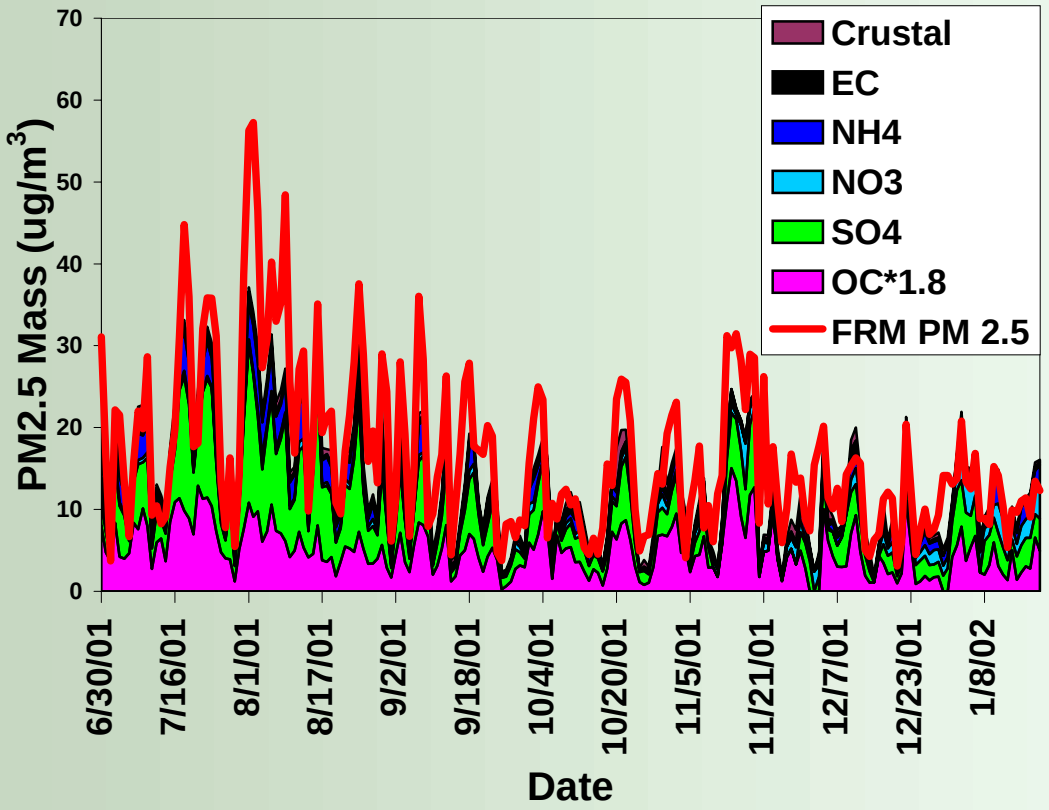
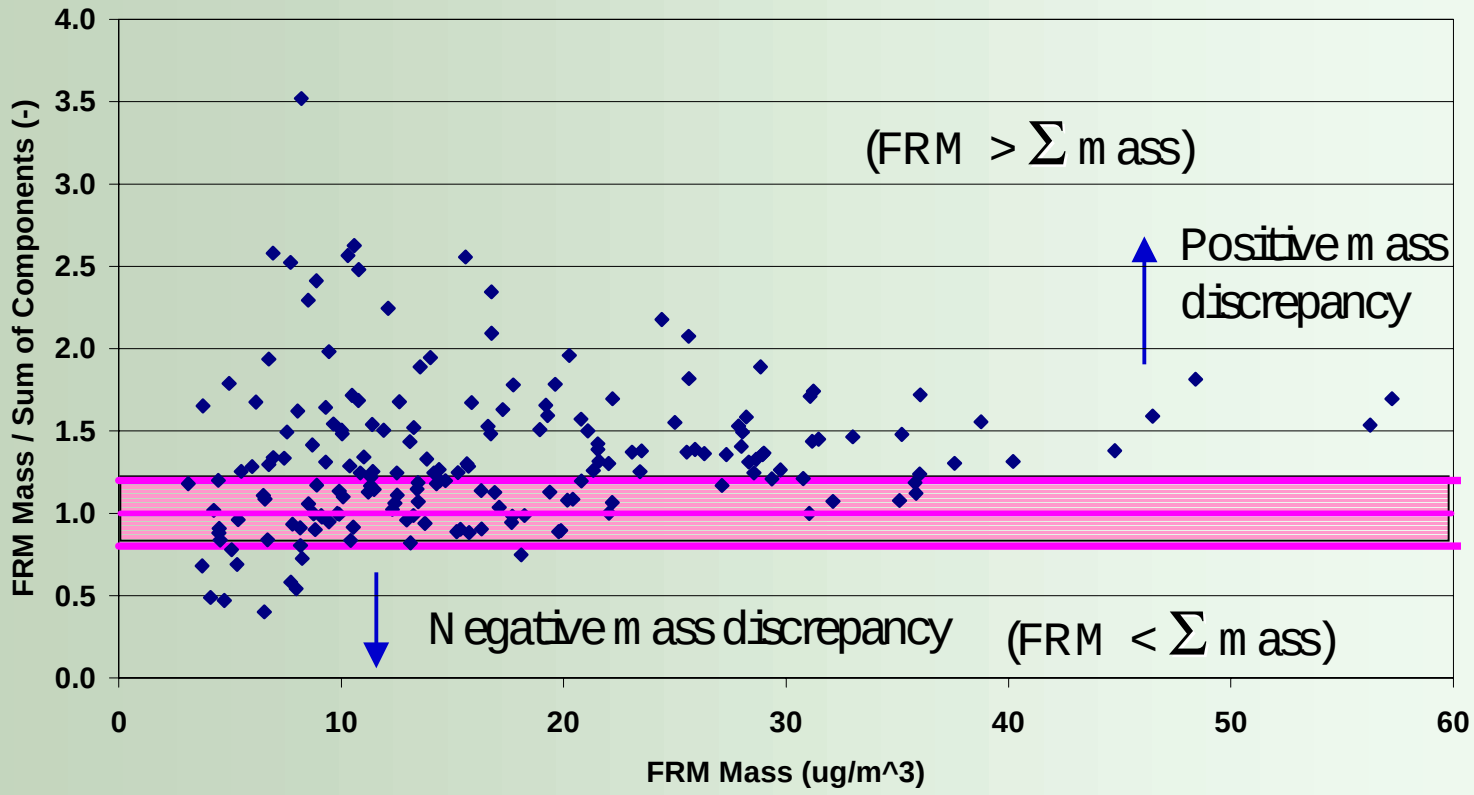
- Dr. Beth Wittig, R. Subramanian, Satoshi Takahama
- US EPA Supersites Program, US DOE/NETL

Questions

$PM_{2.5}$ Mass Balance July - January



Mass Discrepancy Ratio
July - January