Understanding the Components of FRM mass

Part I: Retained Nitrates

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For Presentation to SAMWG

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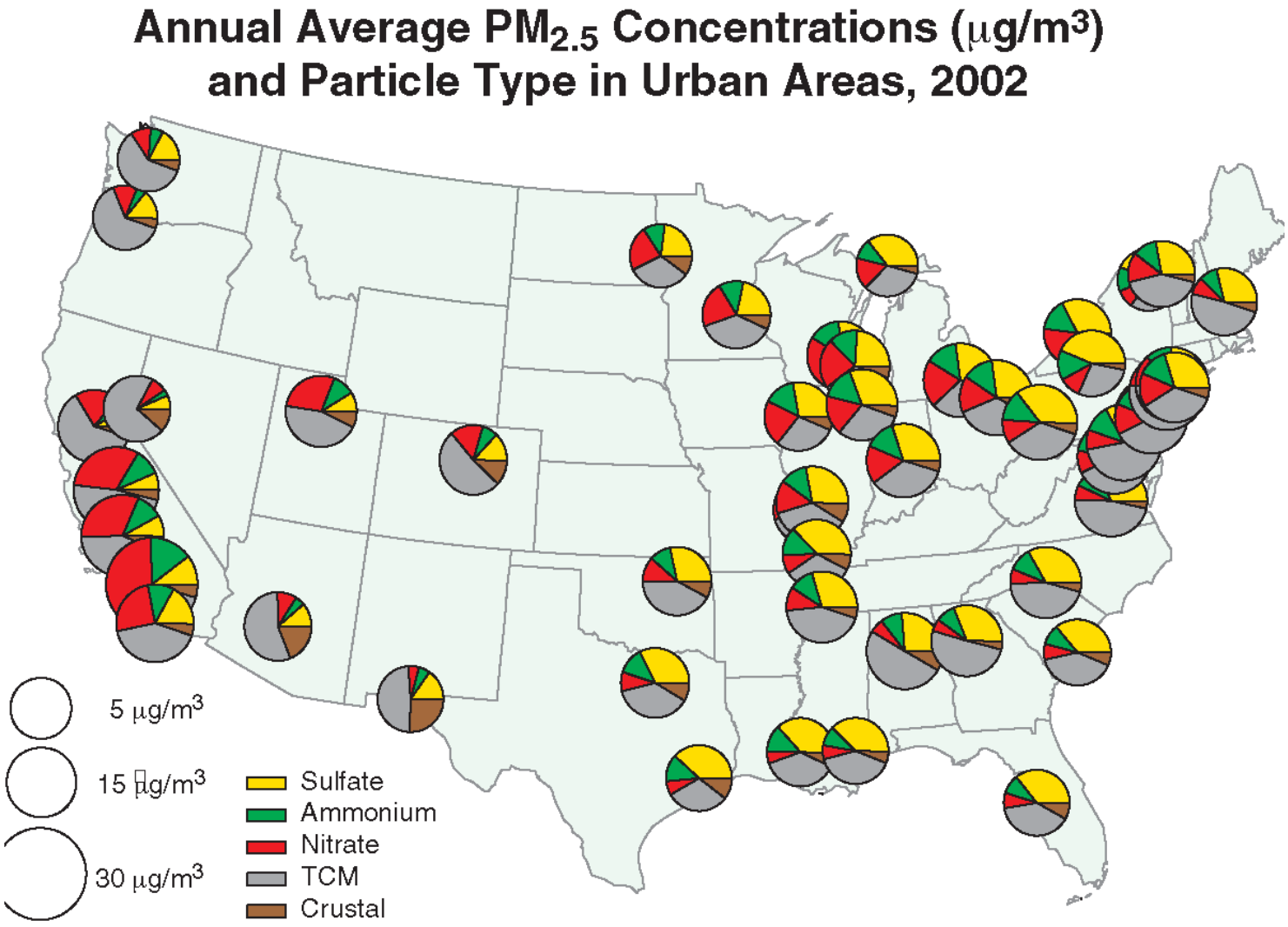
Point Clear, Alabama

Draft Data -- Results are Preliminary

Part 1: Examination of FRM Nitrate

- Background
  - PM2.5 (as measured by FRM)is indicator pollutant
    - teflon filter based FRM not designed to retain all ammonium nitrate and other semi volatile components
    - FRM temperature control intended to reduce losses
  - NO3 measured by STN is reflective of ambient levels
    - uses HNO3 denuder followed by nylon filter (or filter pak)
    - NO3 (as HNO3) binds to nylon filter
  - Generally we present NO3 as ambient fraction of PM2.5 mass

Nitrates (red) are reported to be important component of ambient PM2.5



Source: EPA Speciation Network, 2002.

2003 STN-FRM Study

- Goal: Characterize relationship between ambient NO3 as measured by speciation samplers and retained NO3 in PM2.5 mass
  - to estimate retained nitrates at FRM sites
  - focus on Eastern US
- Specific Questions
  - How much NO3 is retained on FRM filters
    - 0n average (as % and by ug/m3)
    - how does it vary seasonally, with temperature/RH
    - by location/region
  - Can we predict the loss based on existing measurement data *e.g. STN NO3 and/or temp/RH
- Why?
  - For better NAAQS implementation
  - To understand relationship to continuous PM2.5

NO3 Site Selection and Protocols

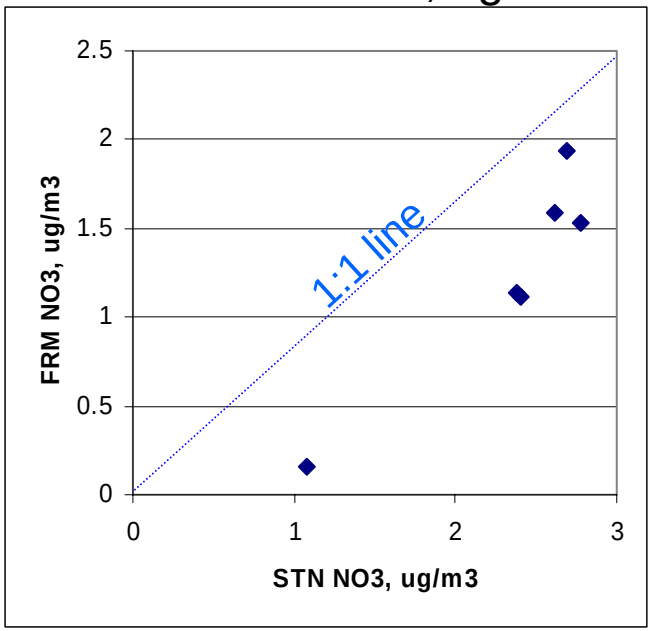
- 6 Sites with High NO3, Geographic Coverage and Different Speciation Samplers
  - Mayville, WI (Met One) - rural
  - Chicago, IL (URG)
  - Indianapolis, IN (Met One)
  - Cleveland, OH (Met One)
  - Bronx, NY (R&P)
  - Birmingham, AL (Met One)
- Mayville and Indianapolis have on-going Continuous PM2.5 studies

Sampling and Data Protocols

- FRM filters shipped cold within weeks of sampling
- RTI confirmation of FRM mass after shipping
  - NYS uses RTI for its gravimetric analysis
- NO3 off teflon filter by RTI on every filter
- Std STN suite at each site collocated with FRM
- FRM and STN samplers provided 1 in 3 day measurements for calendar year 2003
- Data were blank corrected for all analytes
- Hourly temp and humidity from nearby met station, obtained from NCDC

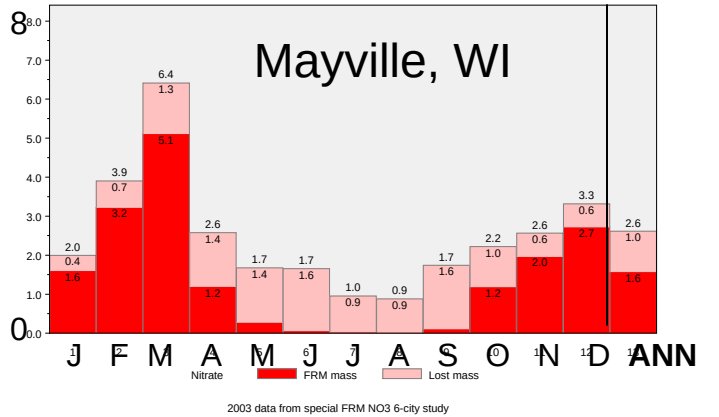
Ammonium Nitrate are not fully retained in PM2.5 FRM mass

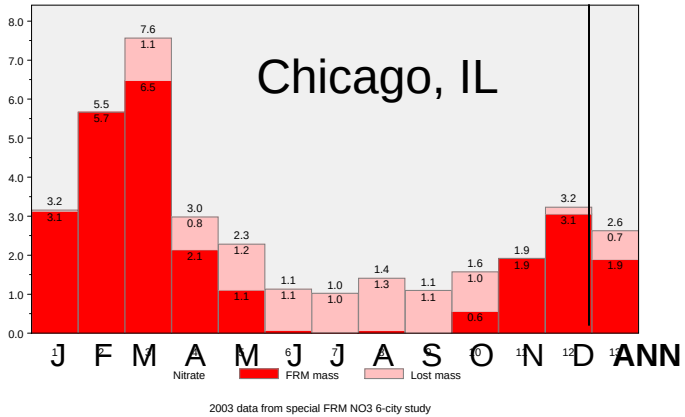
Annual Average Concentrations, ug/m3



cityname	STN NO3	FRM NO3	Diff (ug/m3)	%FRM of STN
Mayville,WI	2.6	1.6	-1.0	61%
Chicago,IL	2.7	1.9	-0.7	72%
Indianap, IN	2.4	1.1	-1.3	47%
Cleveland, OH	2.8	1.5	-1.2	55%
Bronx, NY	2.4	1.1	-1.3	46%
Birmingham	1.1	0.2	-0.9	15%

Draft 2003 Results

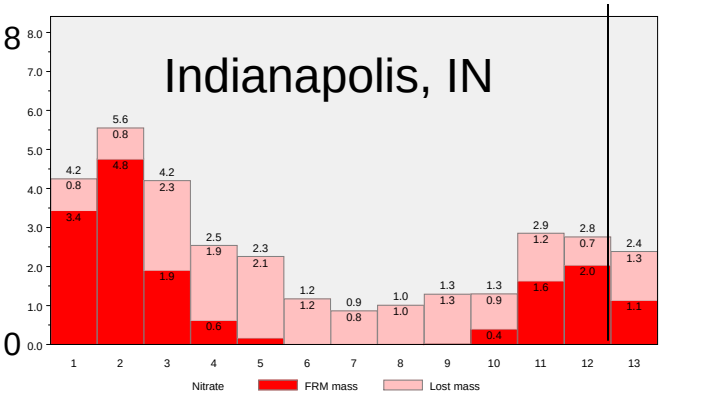


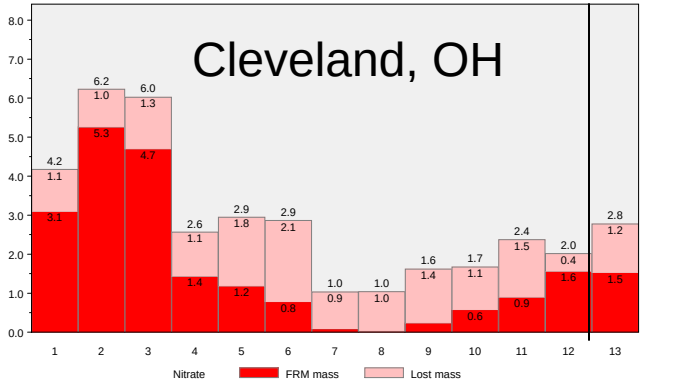


Monthly

&

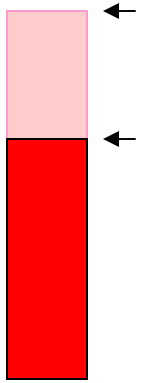
Annual Averages

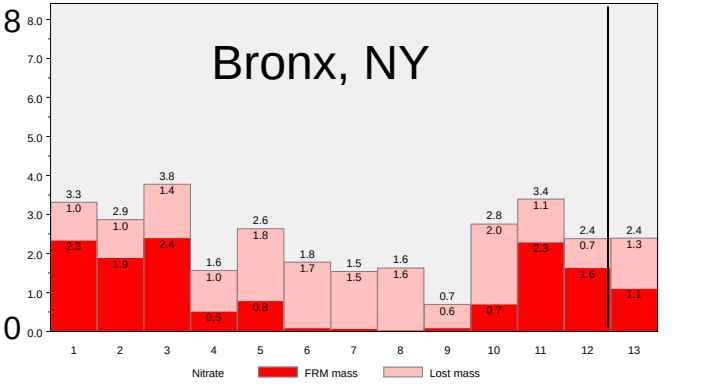


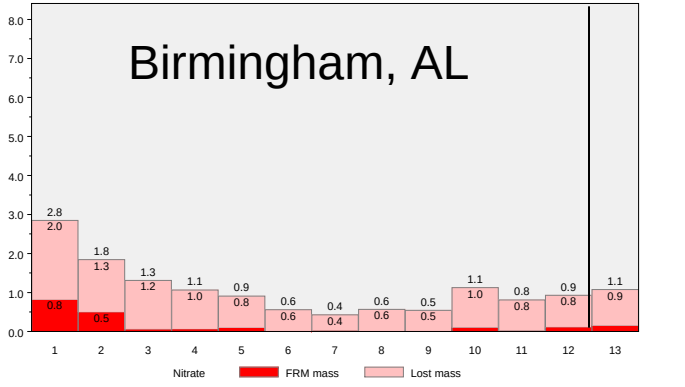


Predicted FRM NO3

Measured NO3







NH_4NO_3 Evaporation Model

- Nitrate loss (from Hering,1999)
  - delta NO3 (ug/m3)= $745.7/T_R$ * 1/24 Sum($\mathbf{K}^{1/2}$)
    - where T_R is the reference sample temperature
    - 745.7 comes from conversion of nitric acid to nitrates

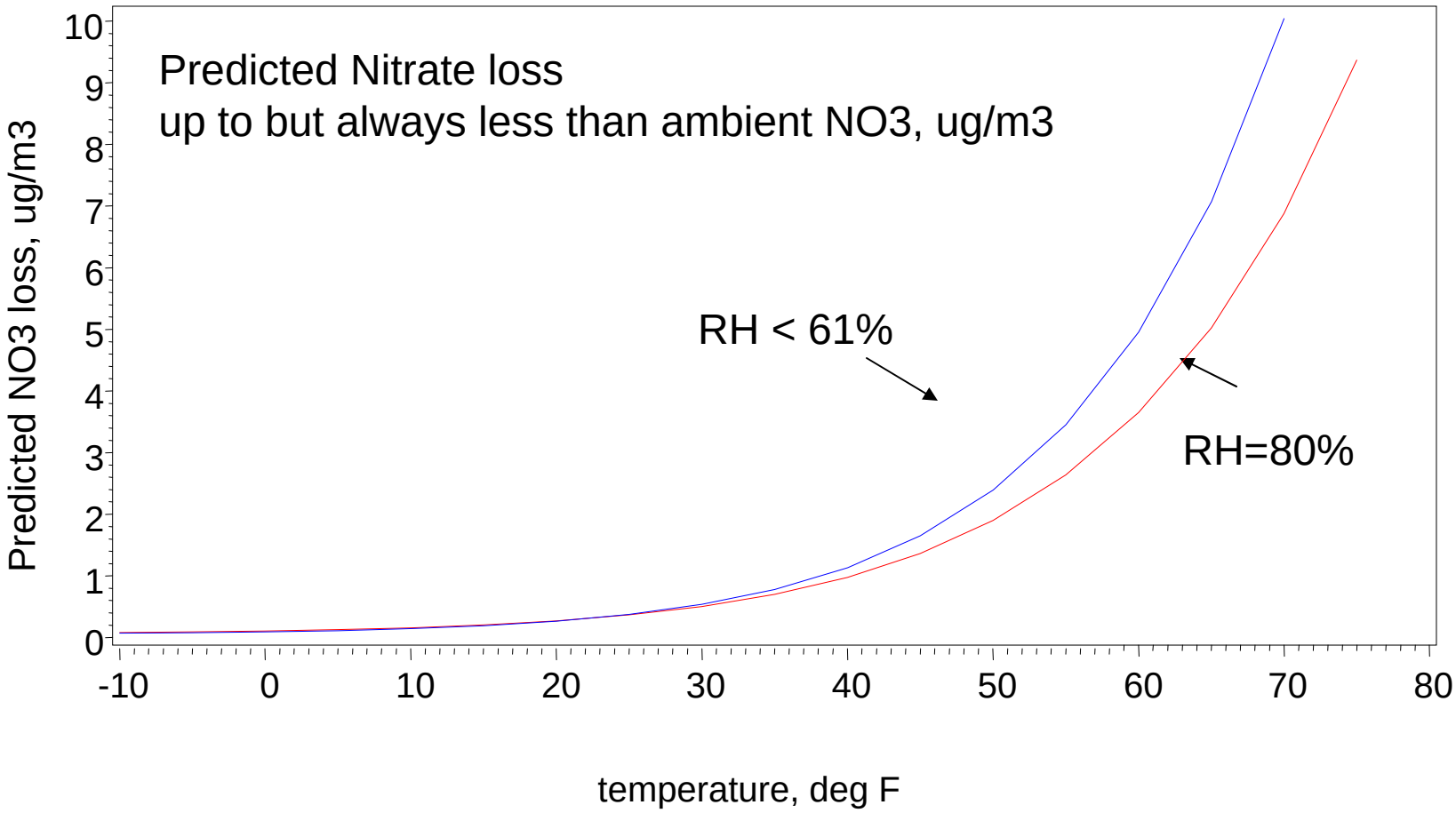
- Equilibrium dissociation constant for ammonium nitrate, K, was calculated from the hourly temperature and Humidity based on Mozurkewich (1993)
  - When RH is less than deliquescence point of ammonium nitrate (61%)
    - Ln **K** = 118.87 - (24084/T)-6.025 ln T

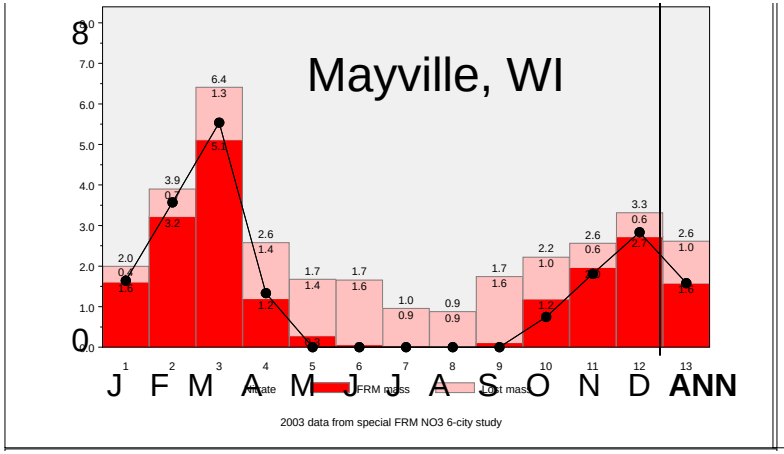
    - When RH (a) is > 61%, use
      $\mathbf{K^*} = [P_1-P_2(1-a)+P_3(1-a)^2] (1-a)^{1.75}\mathbf{K}$

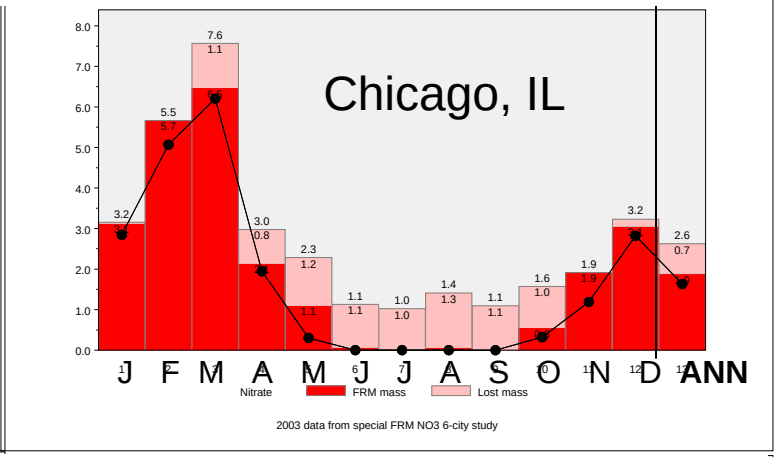
      - where
        - $Ln(P_1)=-135.94+8763/T+19.12ln(T)$
        - $Ln(P_2)=-122.65+9969/T+16.22ln(T)$
        - $Ln(P_3)=-182.61+13875/T+24.46ln(T)$

References: Zhang and McMurray (1992), Mozurkewich (1993), Hering and Cass (1999), Chang et al (2000)

Predicted Nitrate Loss by Temp and Humidity







Monthly

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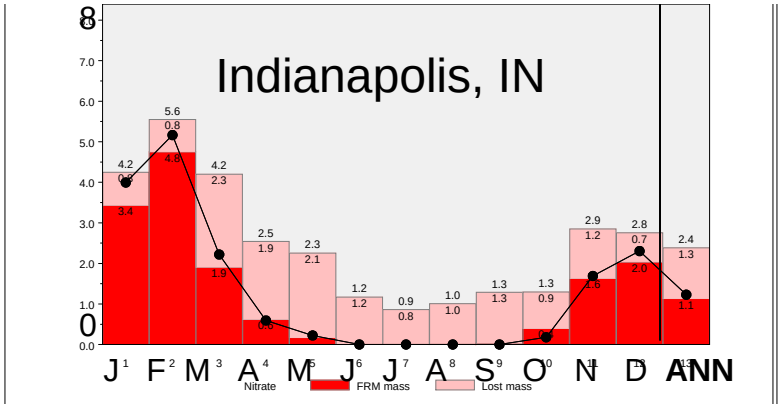
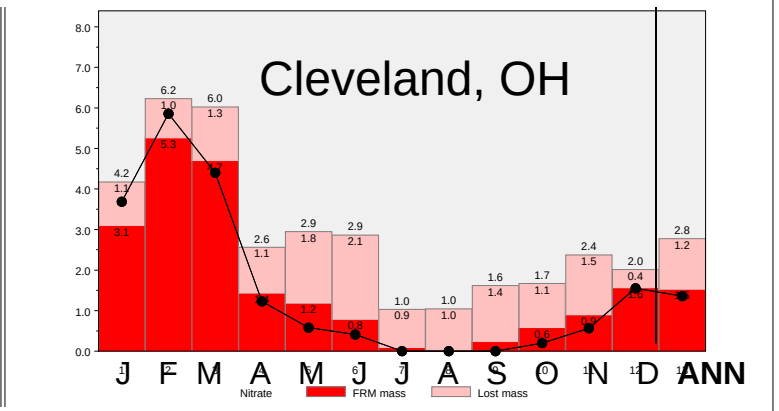
Annual

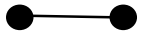
Averages





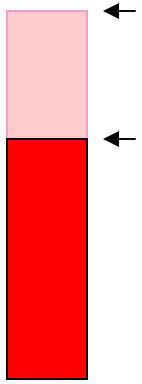
Predicted

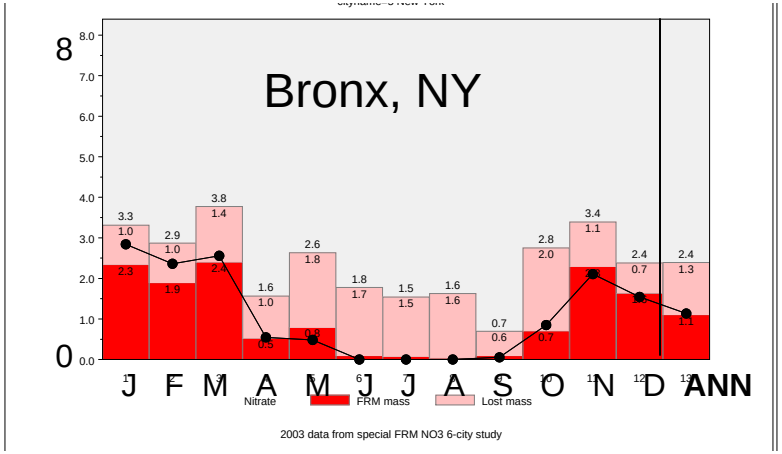
FRM NO3

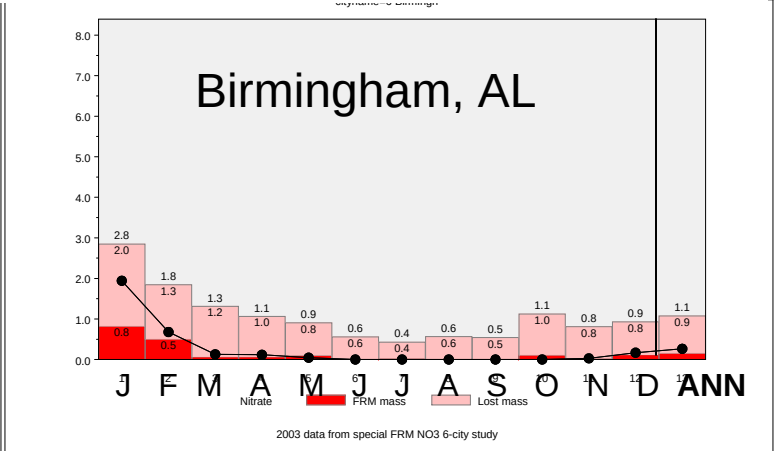


Measured

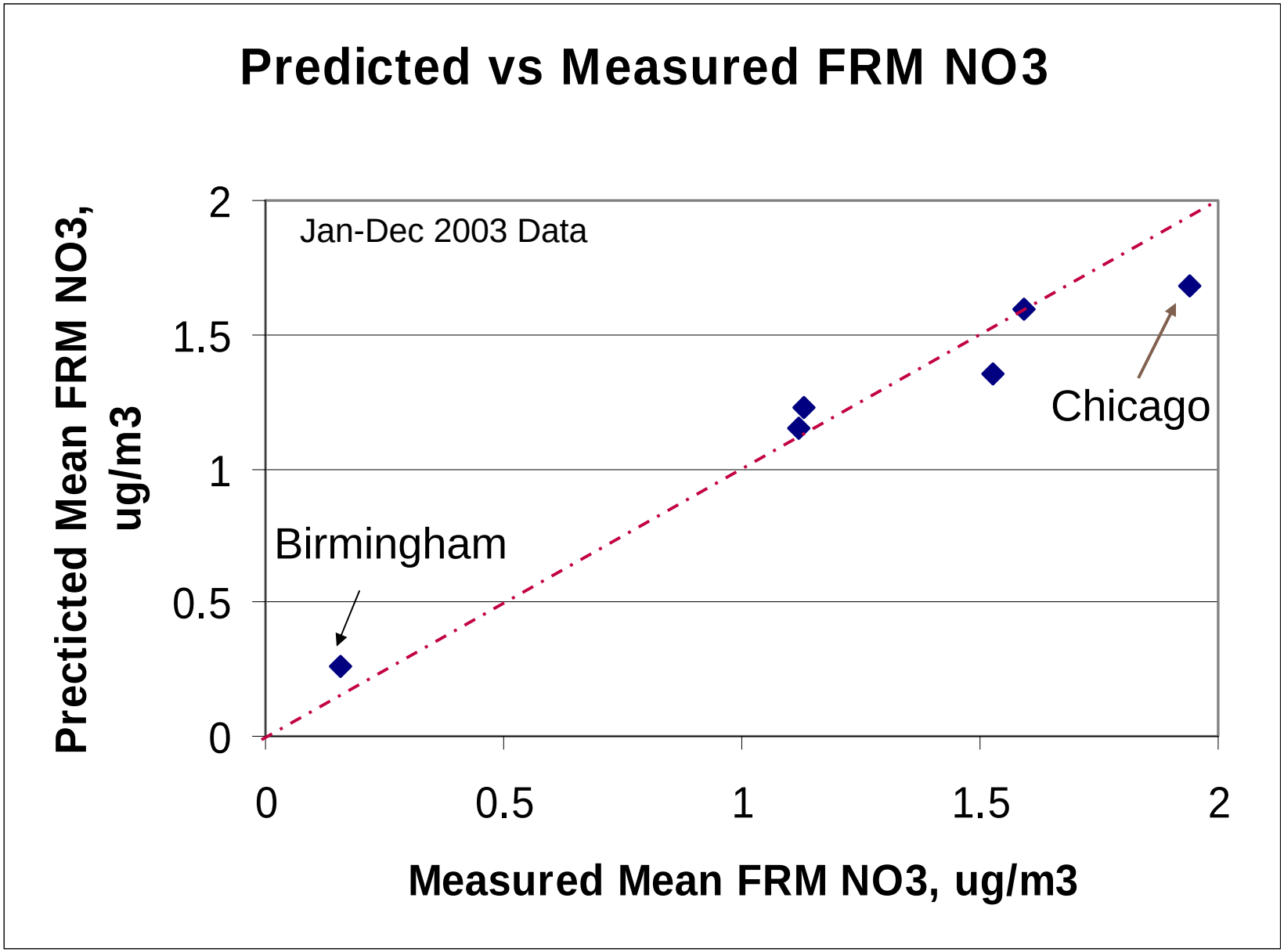
NO3







We can accurately predict FRM NO3 using an evaporation model using STN NO3 and hourly temperature and RH



How can we use knowledge about NO3 retention (Using Predicted FRM NO3)

- NAAQS Implementation
  - Provide a better estimate of "nitrate" component of FRM PM2.5 mass (indicator pollutant for PM2.5)
  - to develop more effective control strategies to attain PM2.5 NAAQS
- Monitoring
  - Evaluation of FRM vs TEOMS
    - Help find the missing mass in heated TEOMS
    - Explain why FDMS > FRM
      - Also need estimated water
  - Examination of optimal 24hr FRM sampling (less loss with noon to noon sampling?)
  - Revised data reporting requirements
    - Provide filter temperatures above ambient

End of presentation

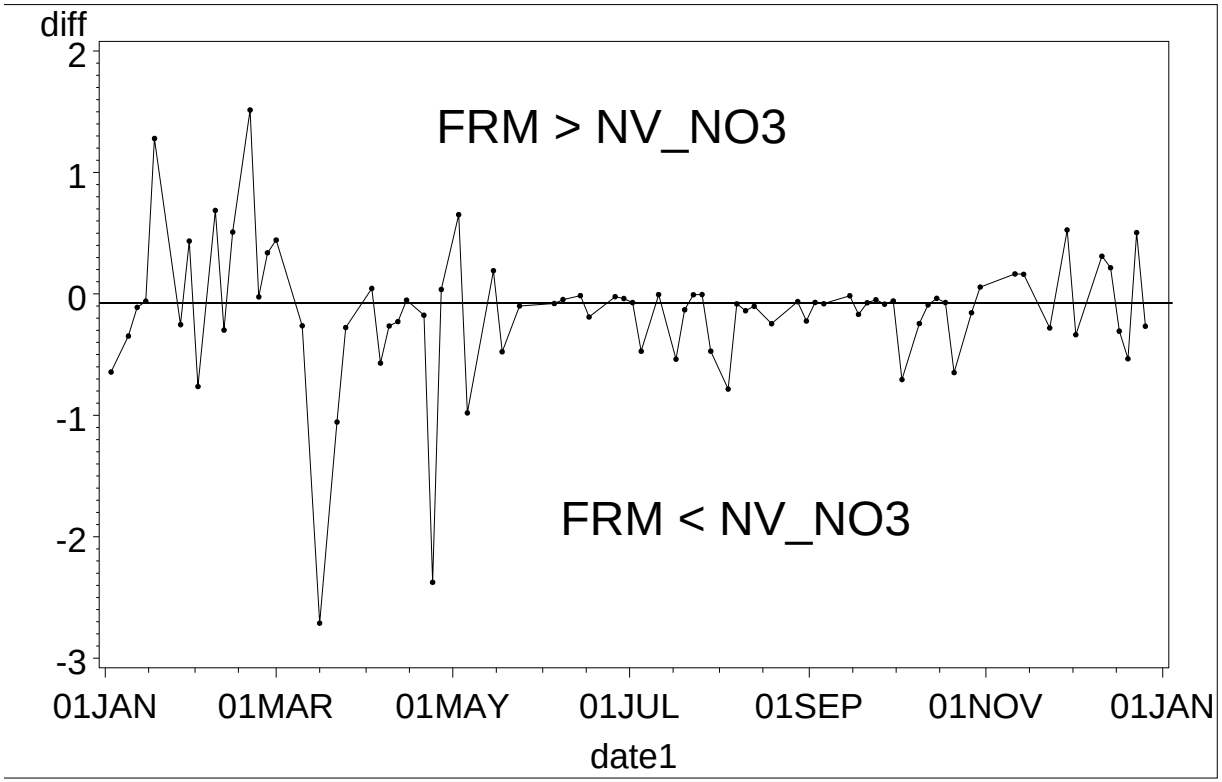
Appendix

FRM and Speciation Samplers among Six Study Cities

site	FRM sampler	Speciation Sampler
Mayville, WI	R & P MODEL 2000 PM2.5 SAMPLER	Met One SASS
Chicago, IL	ANDERSON RAAS2.5-300 PM2.5 SEQ	URG MASS
Indianapolis, IN	R & P MODEL 2025 PM2.5 SEQUNTL	Met One SASS
Cleveland, OH	ANDERSON RAAS2.5-300 PM2.5 SEQ	Met One SASS
Bronx, NY	R & P MODEL 2025 PM2.5 SEQUNTL	R&P MDL2300 PM2.5 SEQ SPEC (check model number)
Birmingham, AL	BGI MODEL PQ200 PM2.5 SAMPLER	Met One SASS

Non Volatile NO3 is often less than FRM NO3 with Chicago's URG (winter-time)

FRM_NO3 – NV_NO3, ug/m3



Lost NO3 is > “Volatile” NO3 with Chicago’s URG (winter-time)