Analysis of Inorganic Particulate Matter Measurements in the Midwestern United States

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Outline

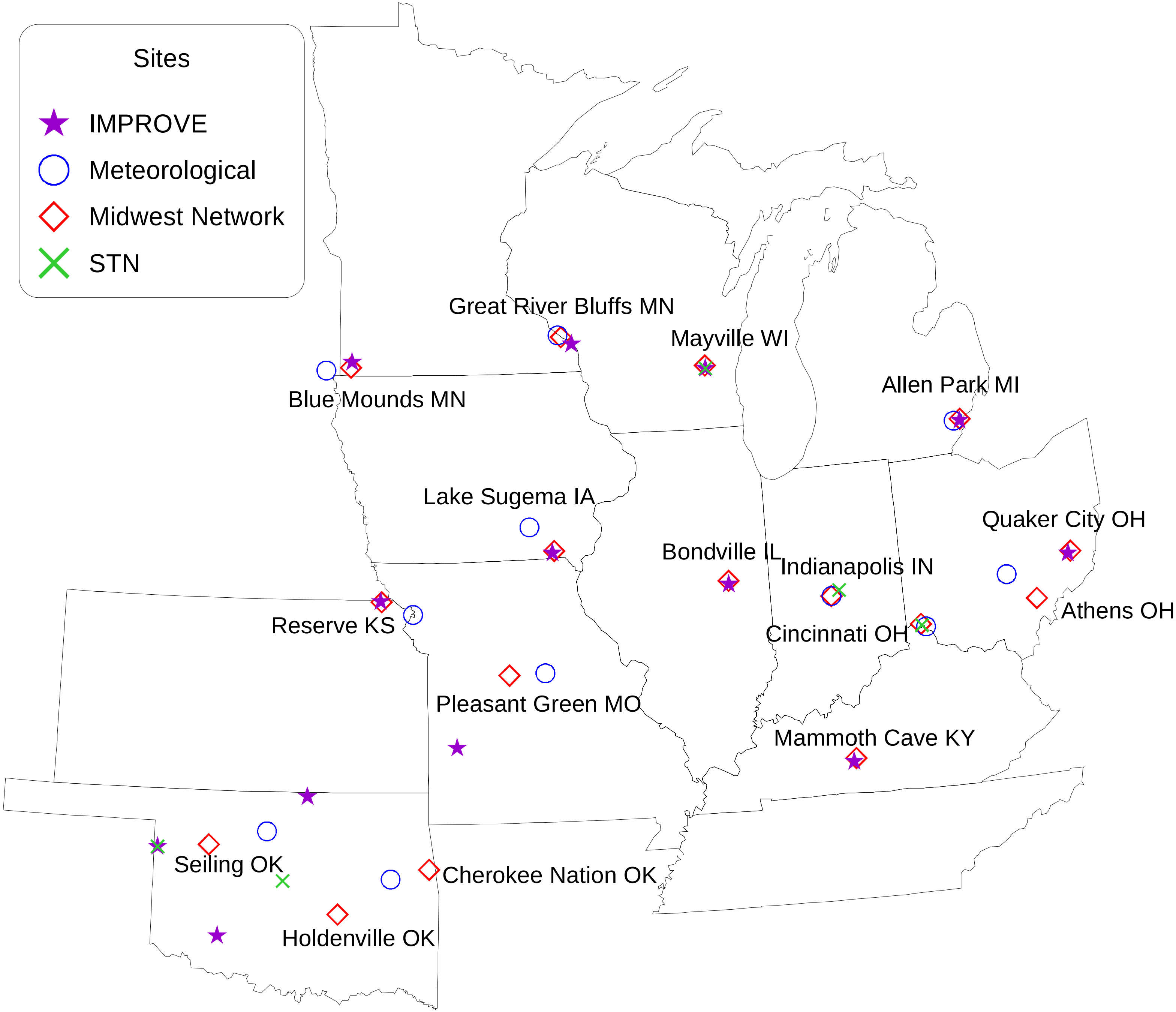
- Objectives
- Data
- Models
- Results – means, winter, episodes
- Limitations and comparisons
- Conclusions

Project Objectives

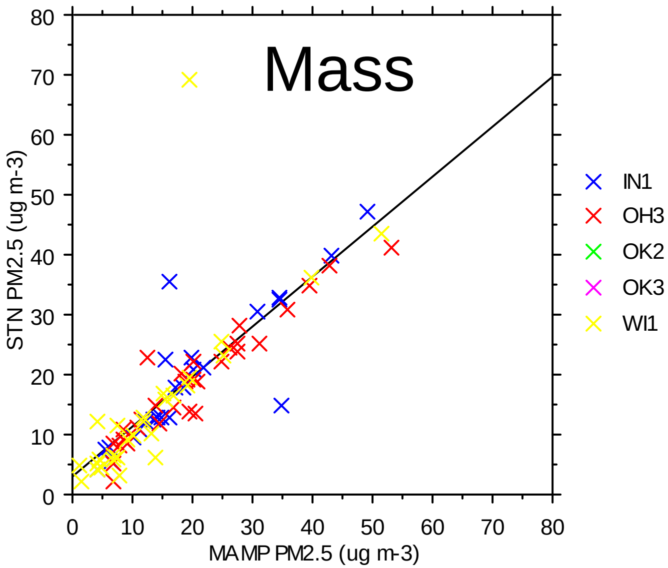
- Primary question: how will $PM_{2.5}$ mass concentrations respond to changes in SO_2, NO_x, and NH_3 emissions?
- Subsidiary questions:
  - Nature of high PM episodes?
  - Seasonal differences?
  - Urban-rural differences?
  - Geographical differences?

Data

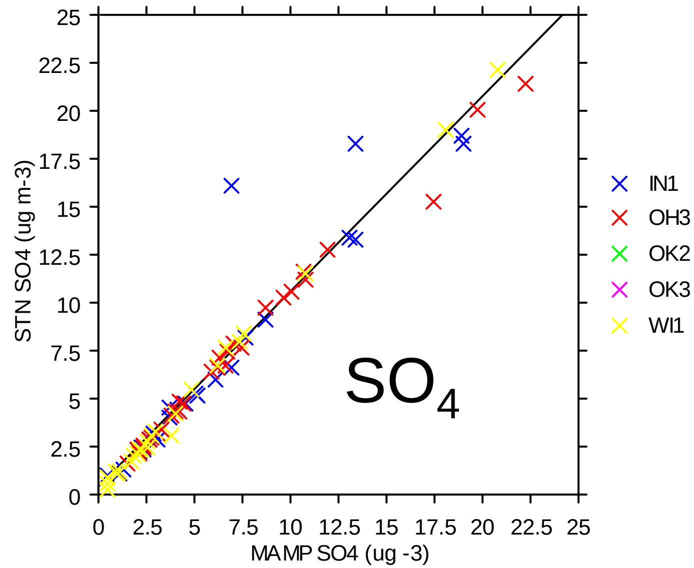
- Midwest Ammonia Monitoring Project measurements of $PM_{2.5}$ mass, sulfate, nitrate, ammonium, SO_2, NH_3, HNO_3: daily 1-in-6, Nov 2003 – June 2006
- 15 sites – most collocated with IMPROVE or STN sites
- Ongoing 2-week resolution passive NH_3


Sites
IMPROVE
Meteorological
Midwest Network
STN
Great River Bluffs MN
Mayville WI
Blue Mounds MN
Allen Park MI
Lake Sugema IA
Quaker City OH
Bondville IL
Indianapolis IN
Reserve KS
Athens OH
Cincinnati OH
Pleasant Green MO
Mammoth Cave KY
Seiling OK
Cherokee Nation OK
Holdenville OK

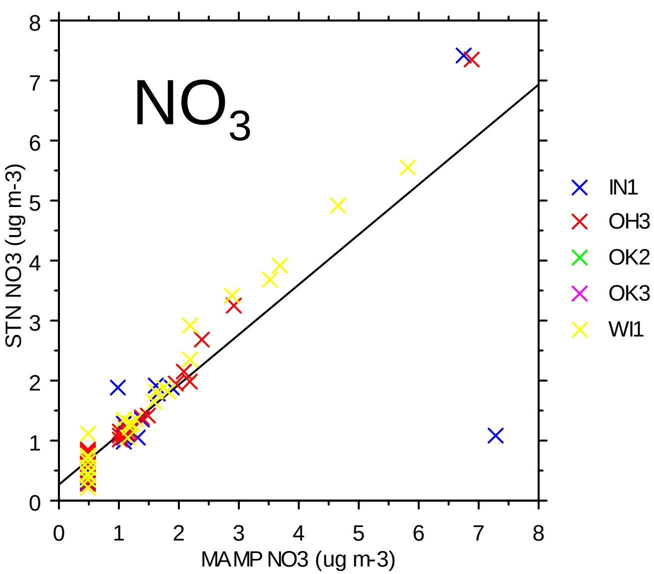
Collocated STN Data Agree Well



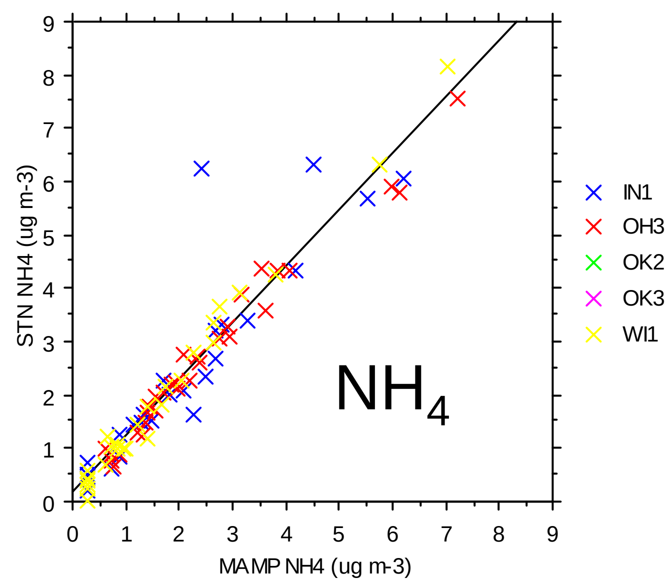
STN PM2.5 (ug m-3) = 3.146 + .83 * MAMP PM2.5 (ug m-3); R^2 = .678



STN SO4 (ug m-3) = .421 + 1.016 * MAMP SO4 (ug -3); R^2 = .954

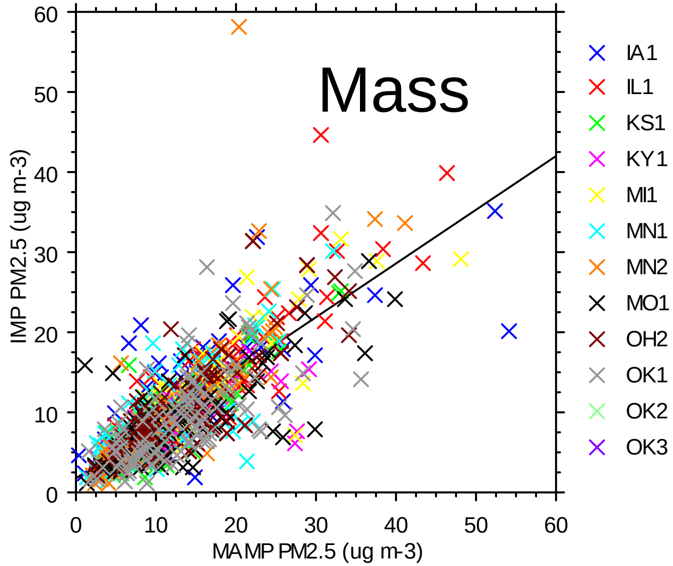


STN NO3 (ug m-3) = .282 + .831 * MAMP NO3 (ug m-3); R^2 = .759

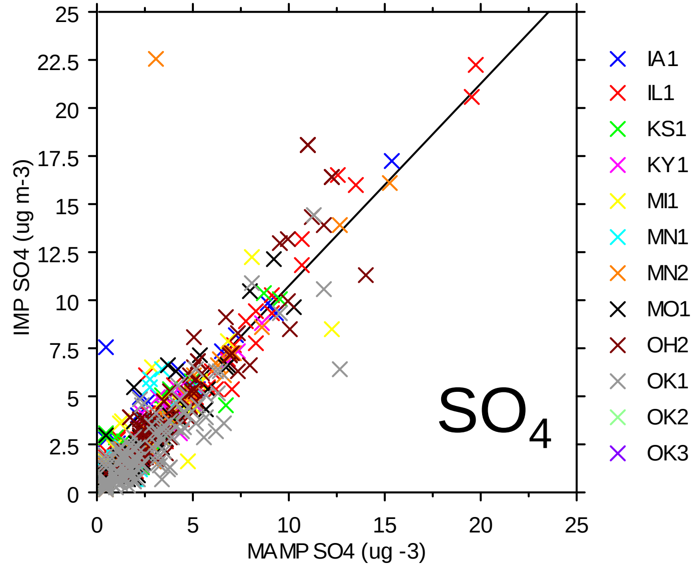


STN NH4 (ug m-3) = .197 + 1.06 * MAMP NH4 (ug m-3); R^2 = .923

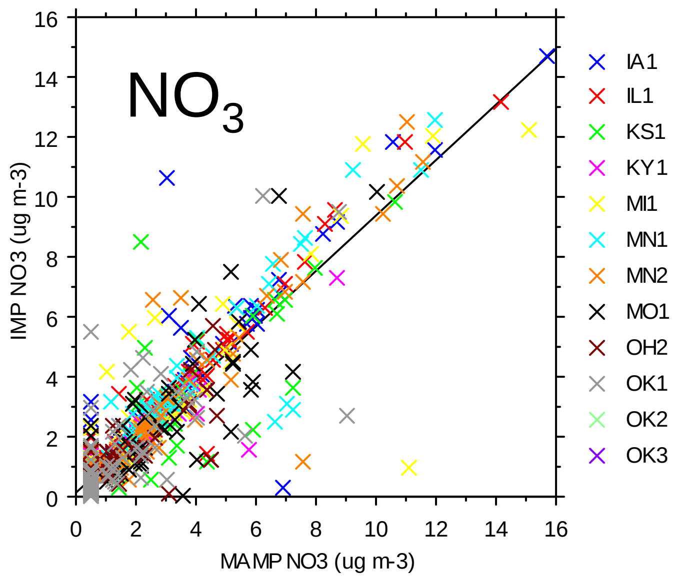
Collocated IMPROVE Species Agree



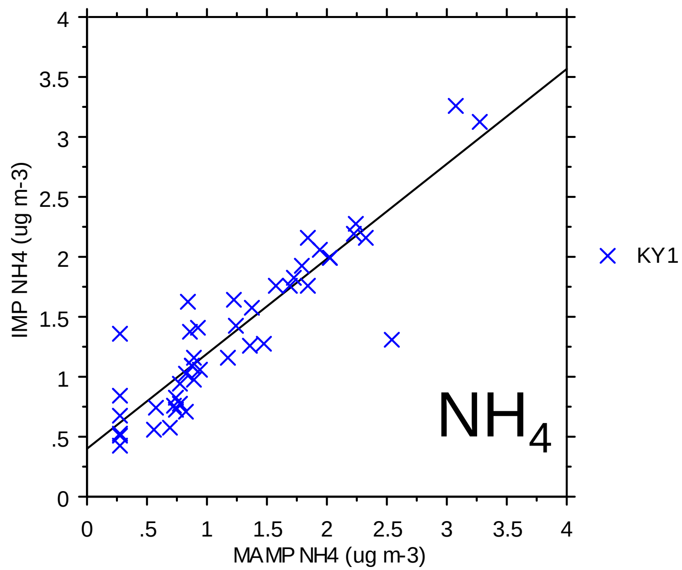
IMP PM2.5 (ug m-3) = 1.776 + .672 * MAMP PM2.5 (ug m-3); R^2 = .63



IMP SO4 (ug m-3) = .209 + 1.051 * MAMP SO4 (ug -3); R^2 = .827



IMP NO3 (ug m-3) = .145 + .926 * MAMP NO3 (ug m-3); R^2 = .813



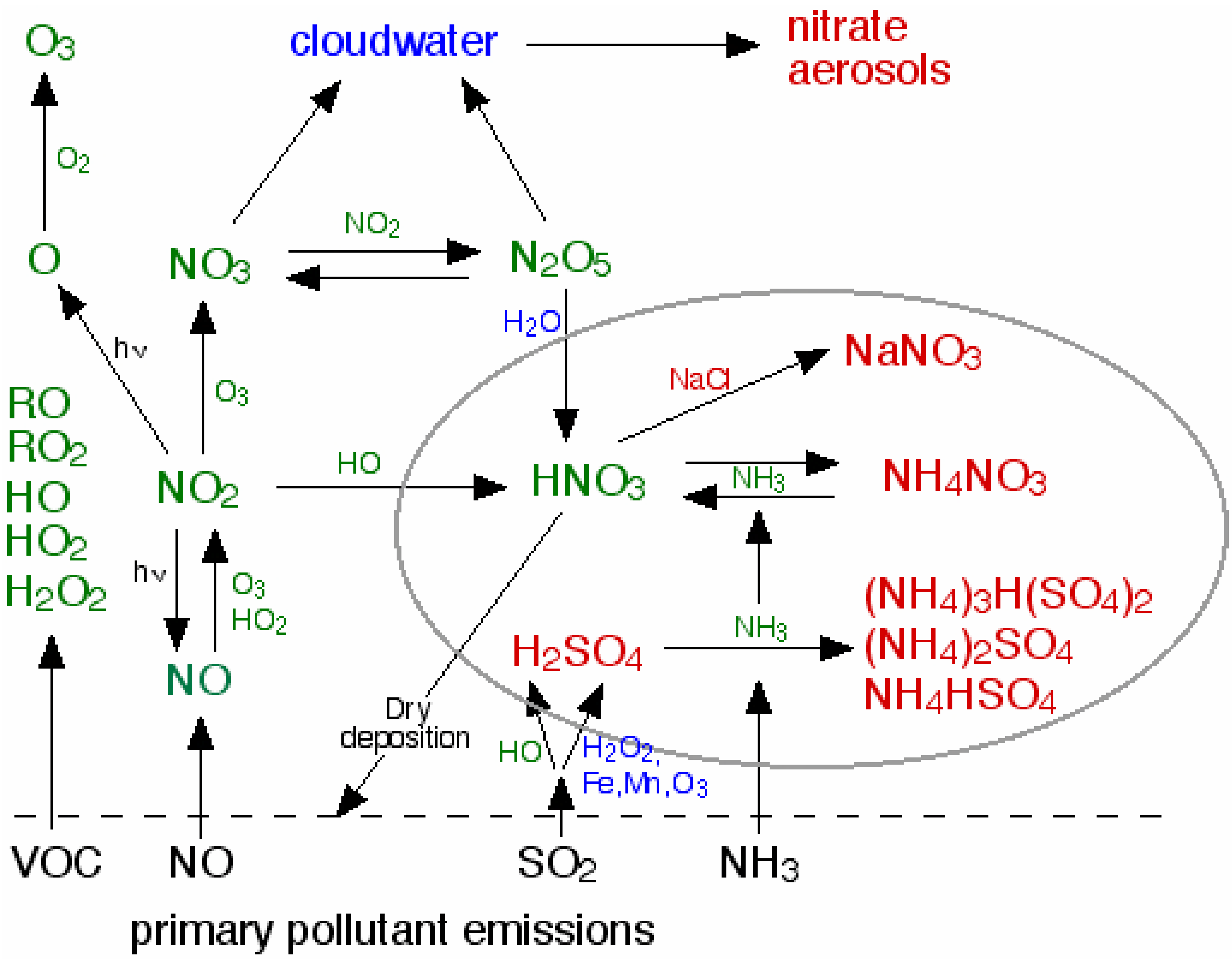
IMP NH4 (ug m-3) = .399 + .792 * MAMP NH4 (ug m-3); R^2 = .816

Thermodynamic Equilibrium Models

- ISORROPIA and SCAPE2
- Model inputs: T, RH, total sulfate, total nitrate (= PM nitrate + HNO_3), total ammonia (= PM ammonium + NH_3), other species
- Model outputs: $PM_{2.5}$ mass, amount of nitrate and ammonium in the gas phase and in particles, particle composition

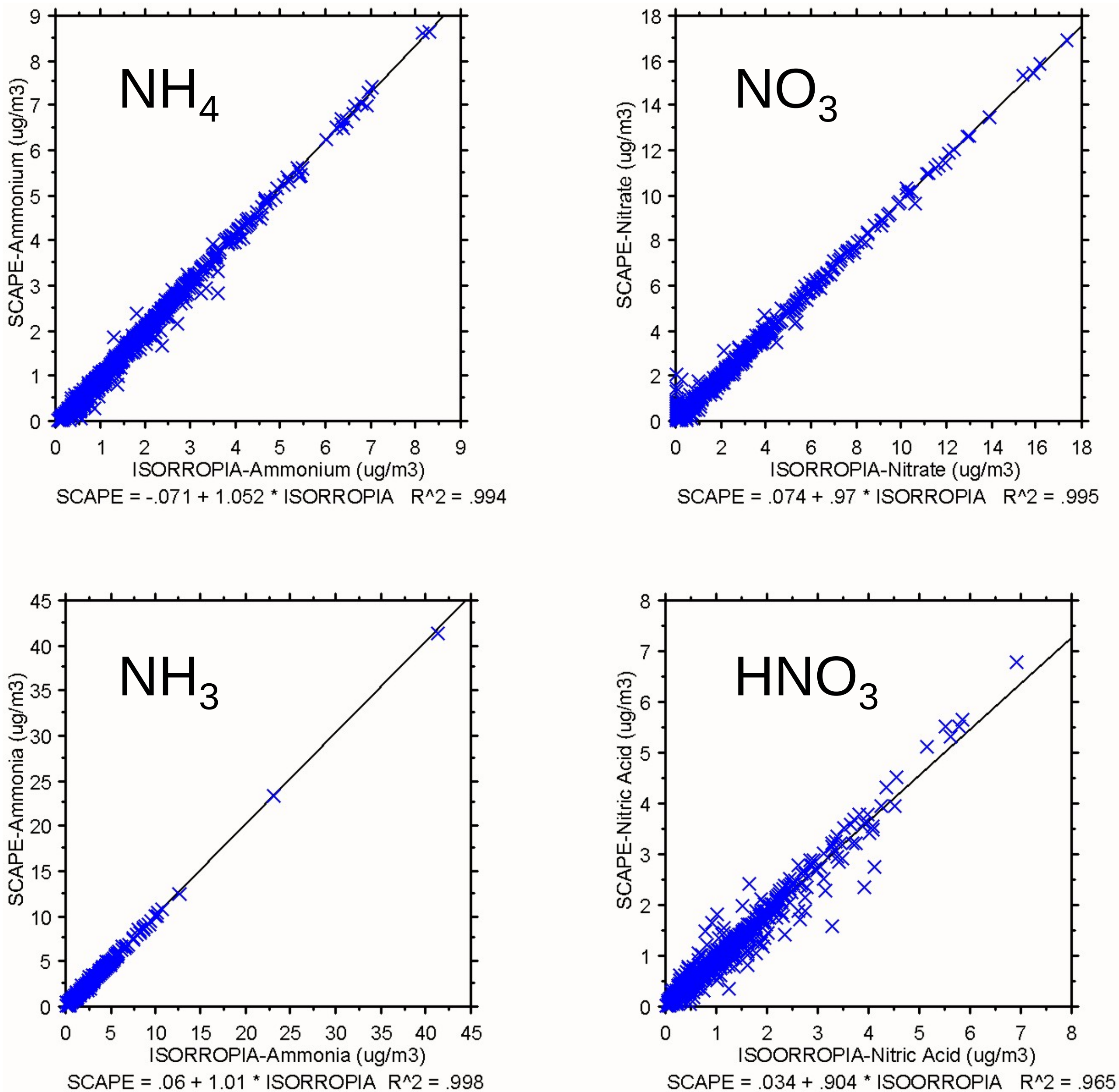
Thermo Eq'bm Models (cont'd)

- Vary amounts of total sulfate, nitrate, and ammonium (25 to 150% of actuals)
- Calculate changes in $PM_{2.5}$ mass
- Advantages: tied directly to ambient data, no emissions estimates required
- Disadvantages: does not simulate some processes – must assume that lower SO_2 & NO_x results in lower sulfate & HNO_3

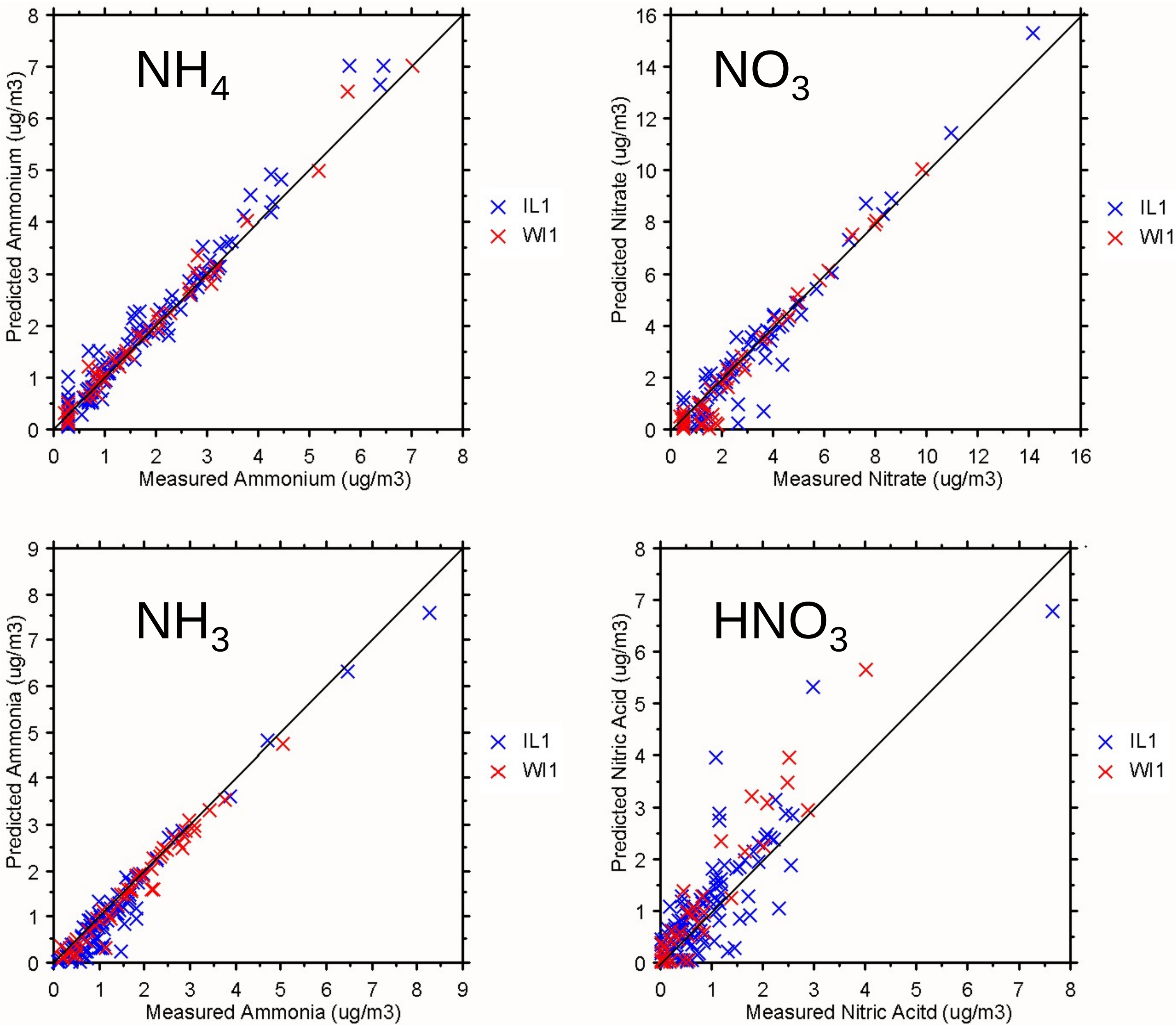


O3
cloudwater
nitrate aerosols
O2
NO2
O
NO3
N2O5
H2O
NaNO3
NaCl
hν
O3
RO
RO2
HO
HO2
H2O2
NO2
HO
HNO3
NH4NO3
NH3
hν
O3
HO2
(NH4)3H(SO4)2
NH3
H2SO4
(NH4)2SO4
NH4HSO4
NO
Dry deposition
HO
H2O2,
Fe,Mn,O3
VOC
NO
SO2
NH3
primary pollutant emissions

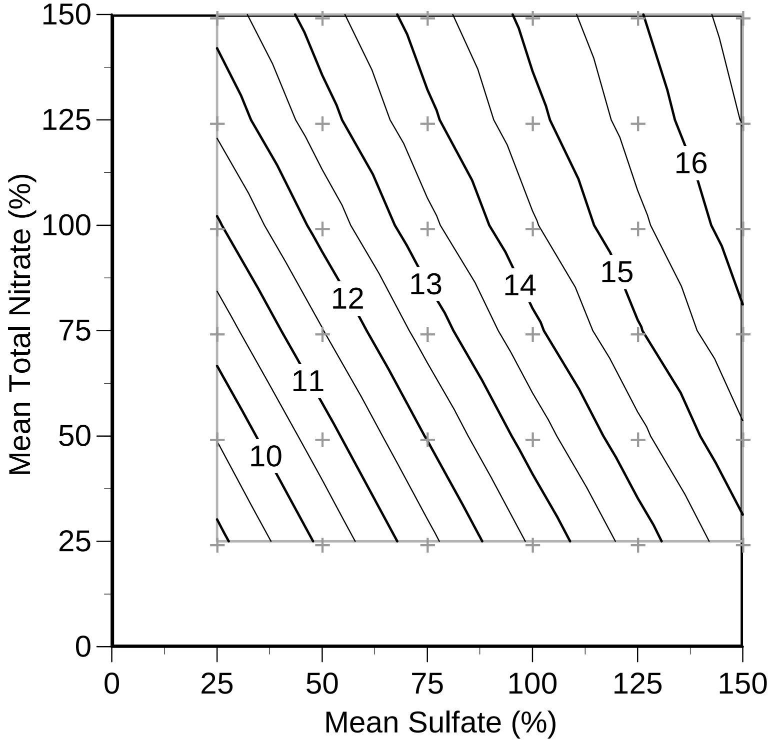
Two Models Produce Comparable Results

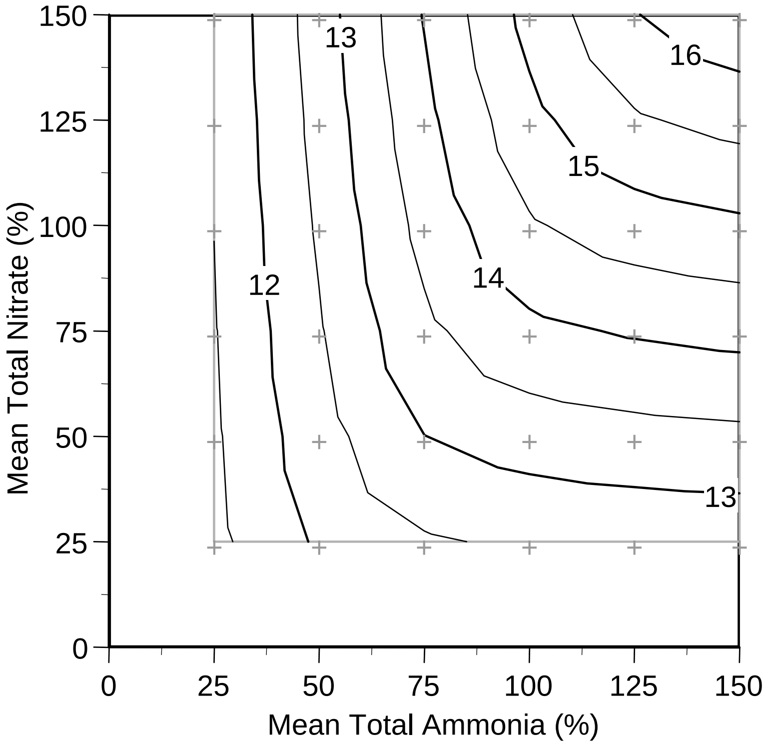


Predictions Agree With Measurements



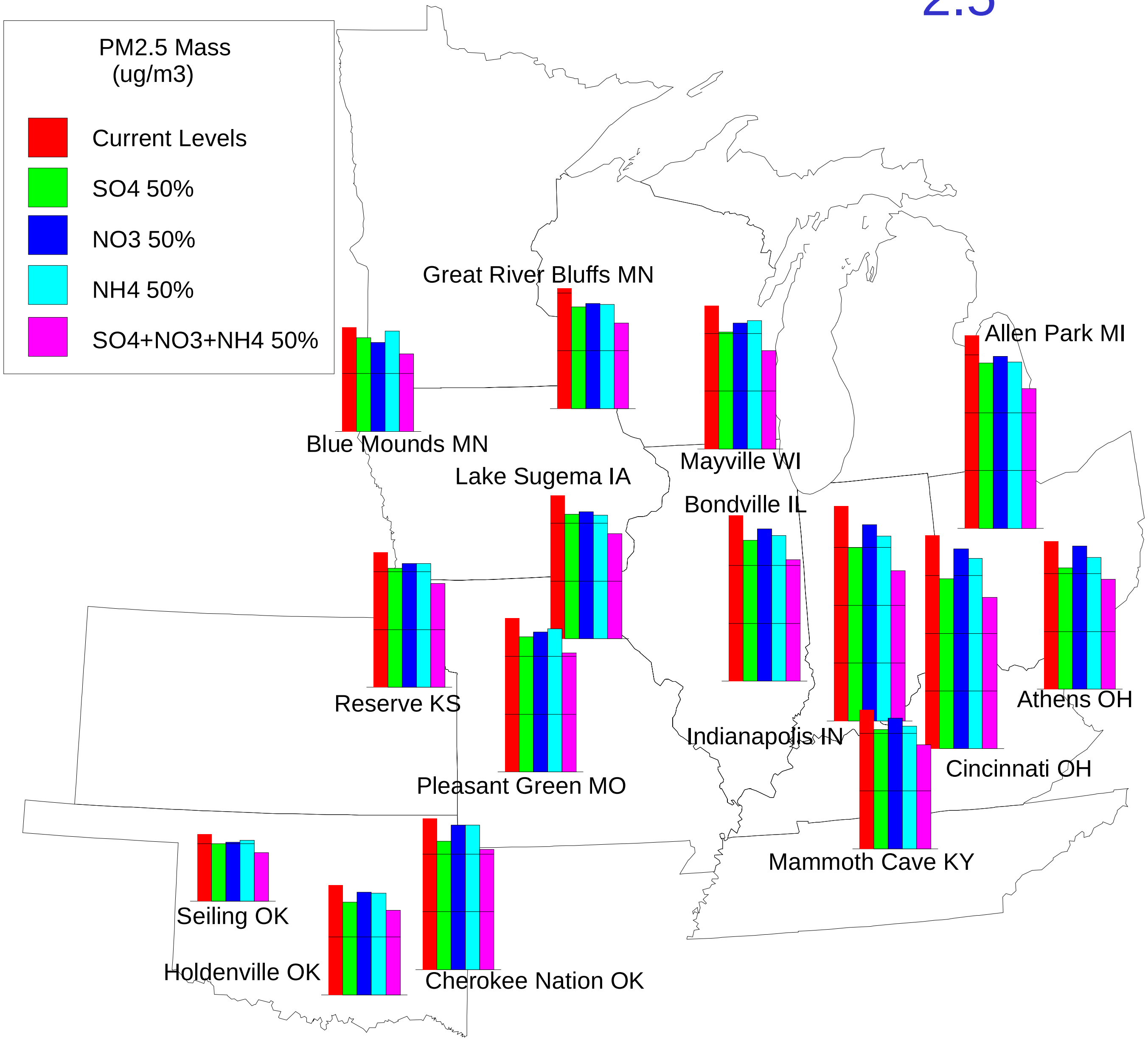
Results for Bondville – Predicted Mean $PM_{2.5}$ Mass (N=111 days)





Note: Current concentrations occur at “100%” points

Mean Predicted $PM_{2.5}$ Mass



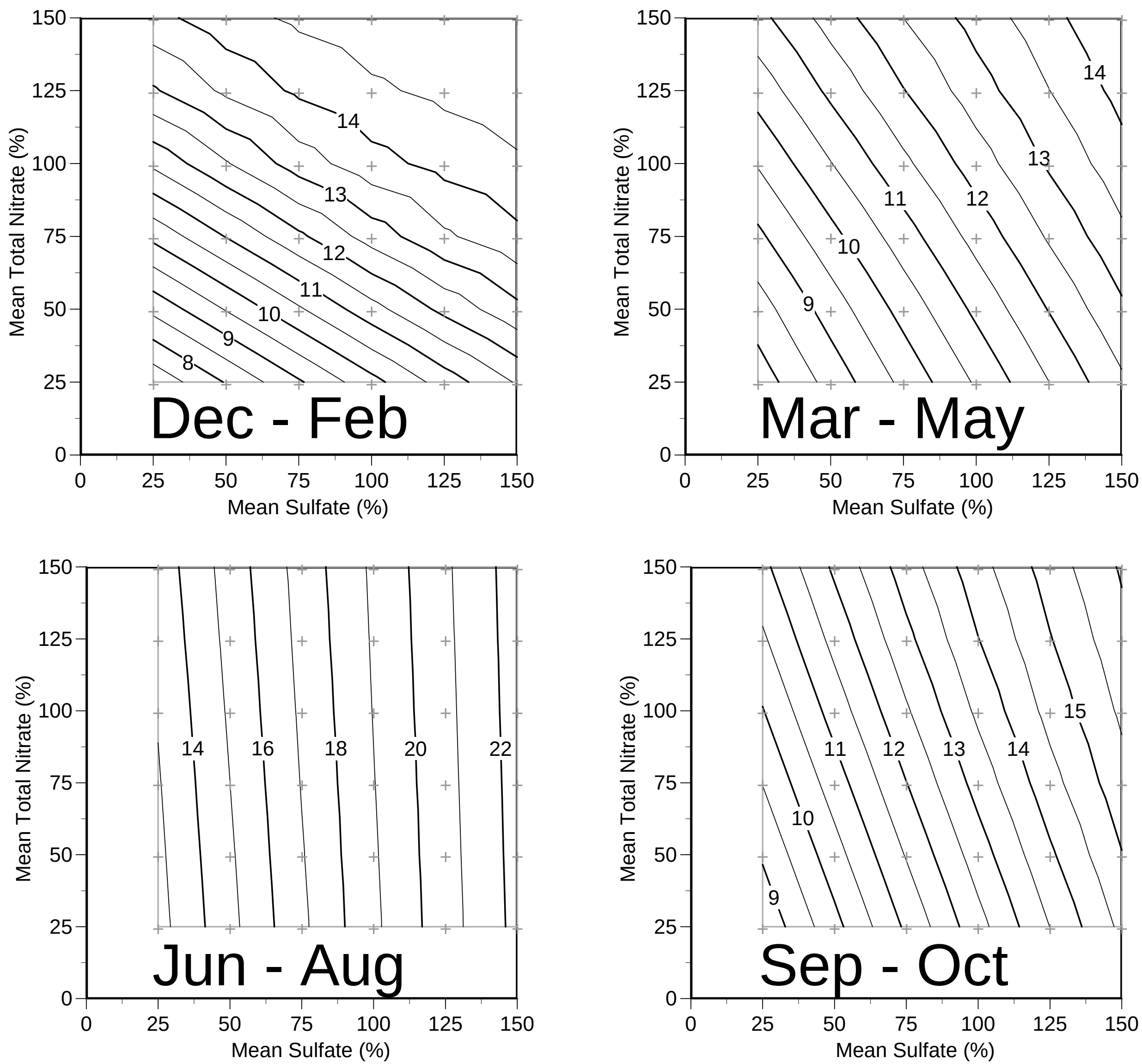
Scale

Bars are marked at increments of 5 $\mu g\ m^{-3}$

$PM_{2.5}$ Response to SO_4 & NO_3 by Season

Winter Nitrate Sensitivity

Summer Sulfate Sensitivity

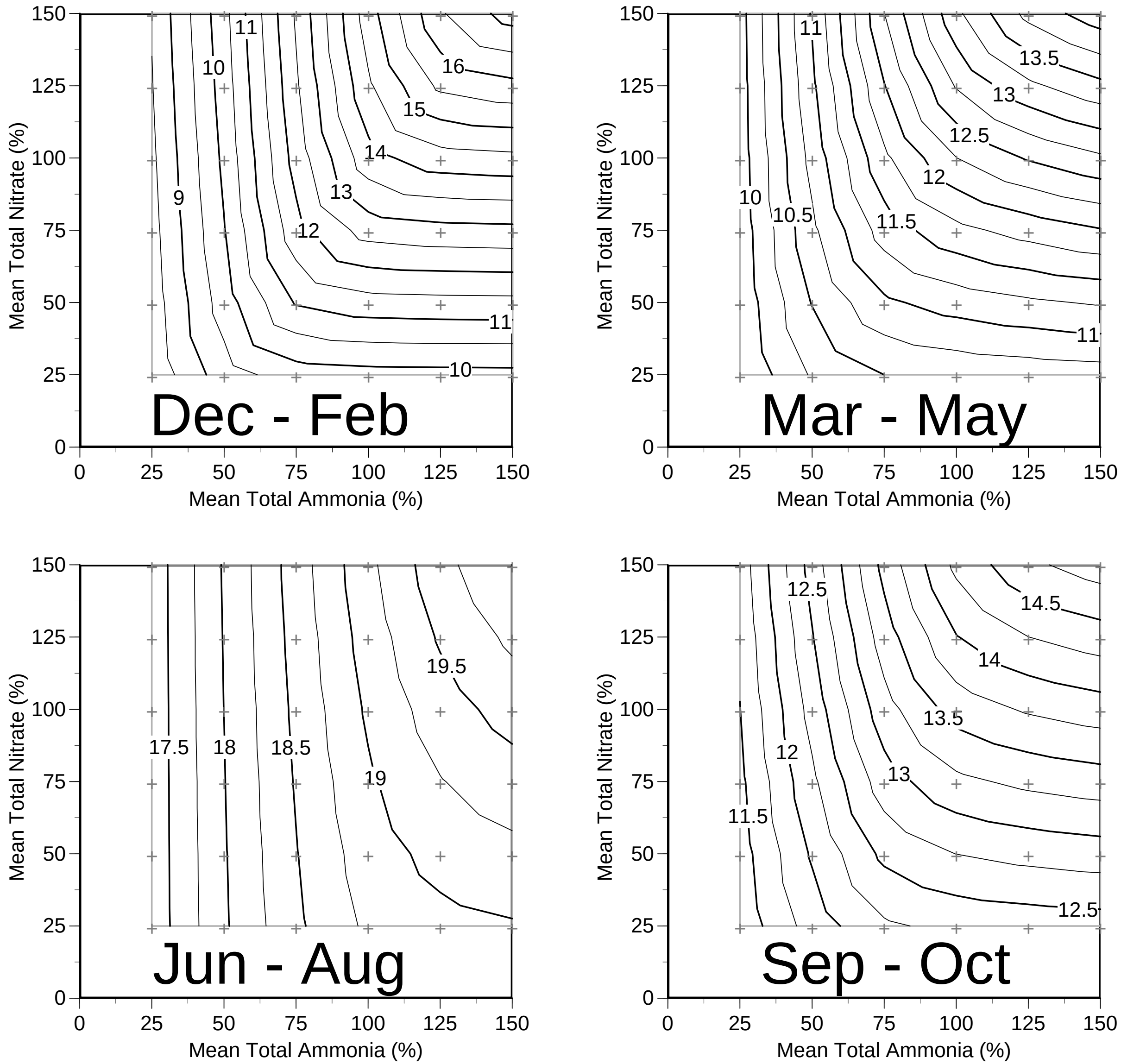


Bondville

$PM_{2.5}$ Response to NH_3 & NO_3 by Season

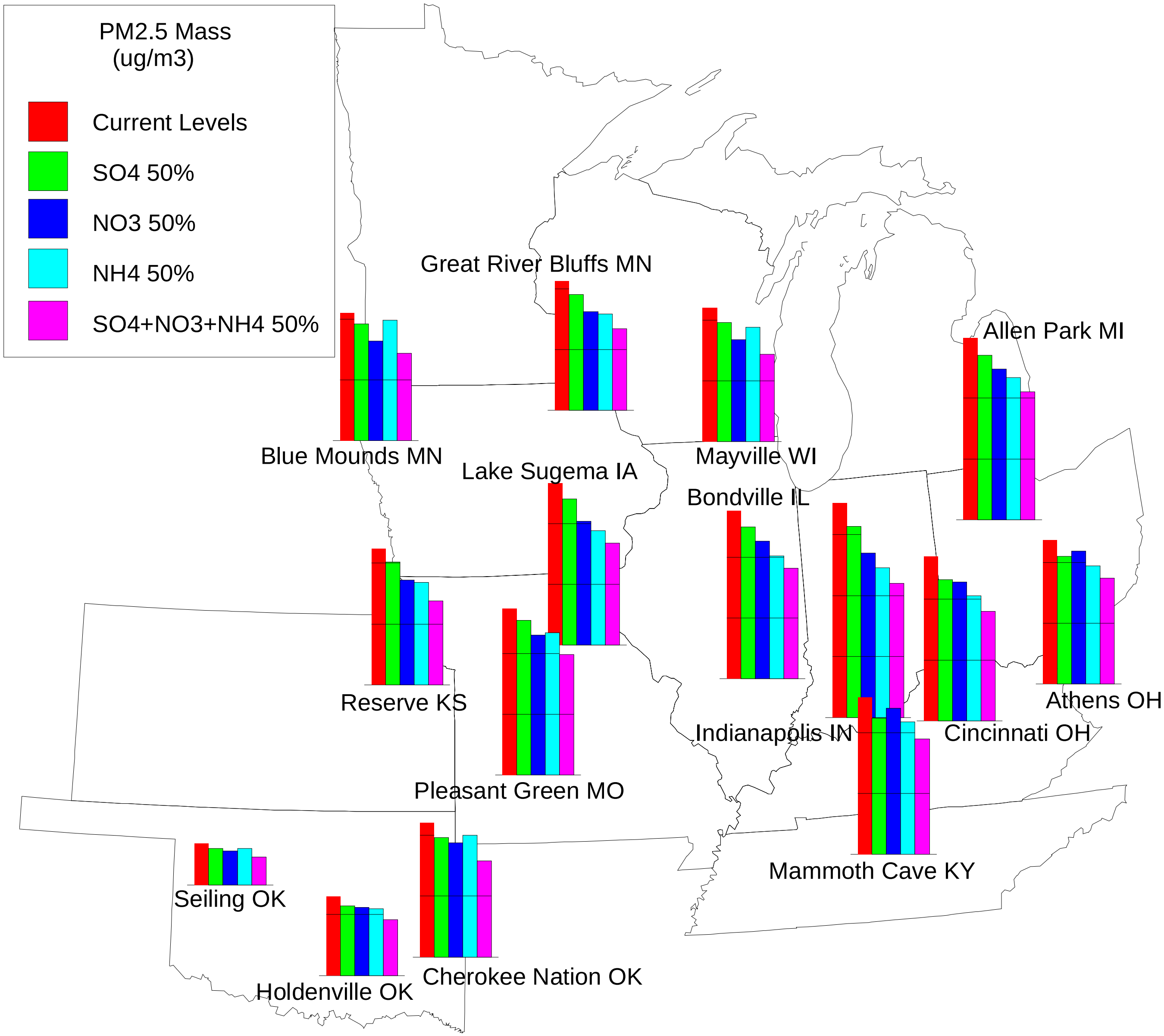
Winter
Ammonia
&
Nitrate
Sensitivity

Summer
Some
Ammonia
Sensitivity



Bondville

Mean Predicted Winter $PM_{2.5}$ Mass



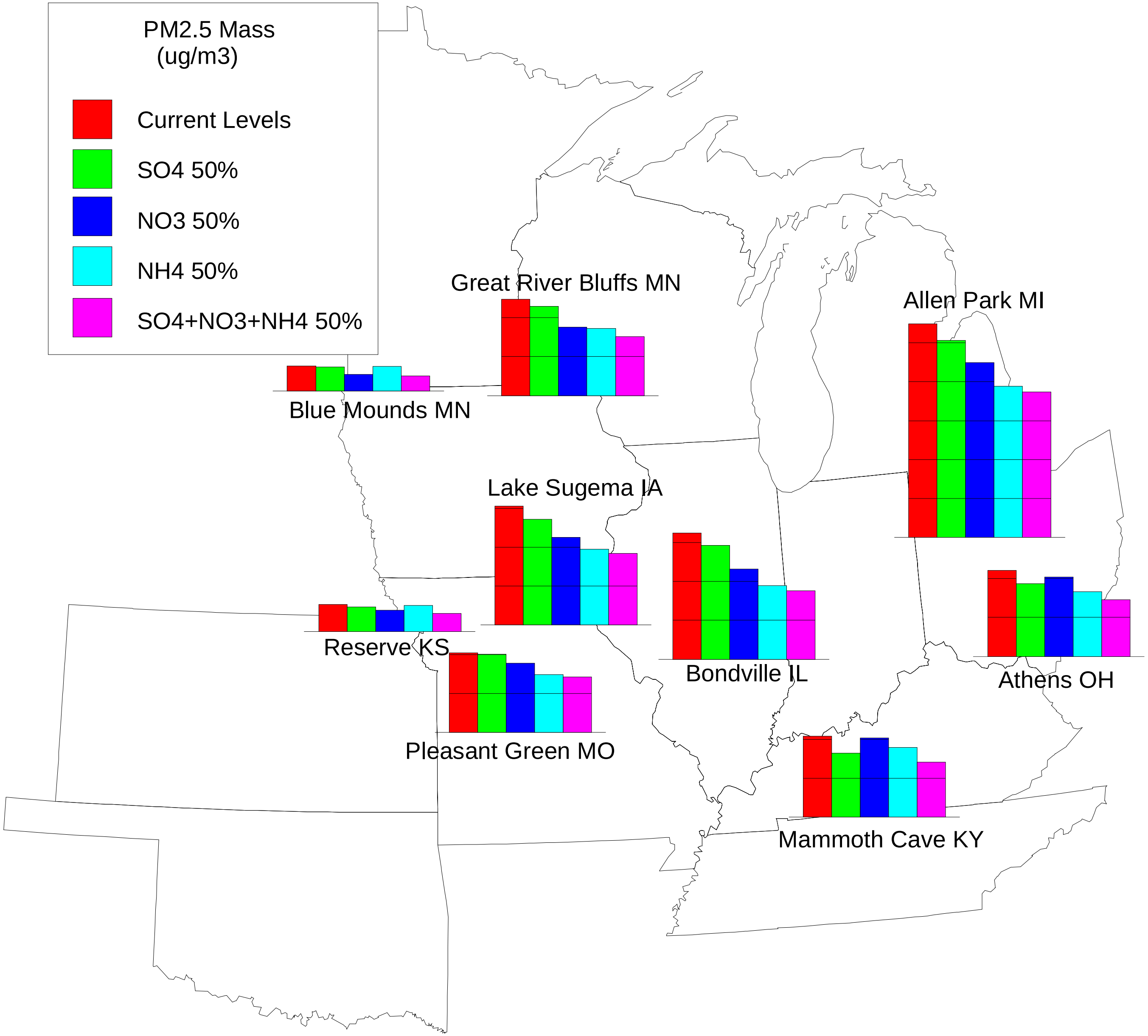
Scale

Bars are marked at increments of 5 $\mu g\ m^{-3}$

Winter PM Episodes

- May have high NH_4NO_3 concentrations
- Equilibrium favors particulate NH_4NO_3
- $PM_{2.5}$ mass may respond to reductions of either or both ammonia or total nitrate

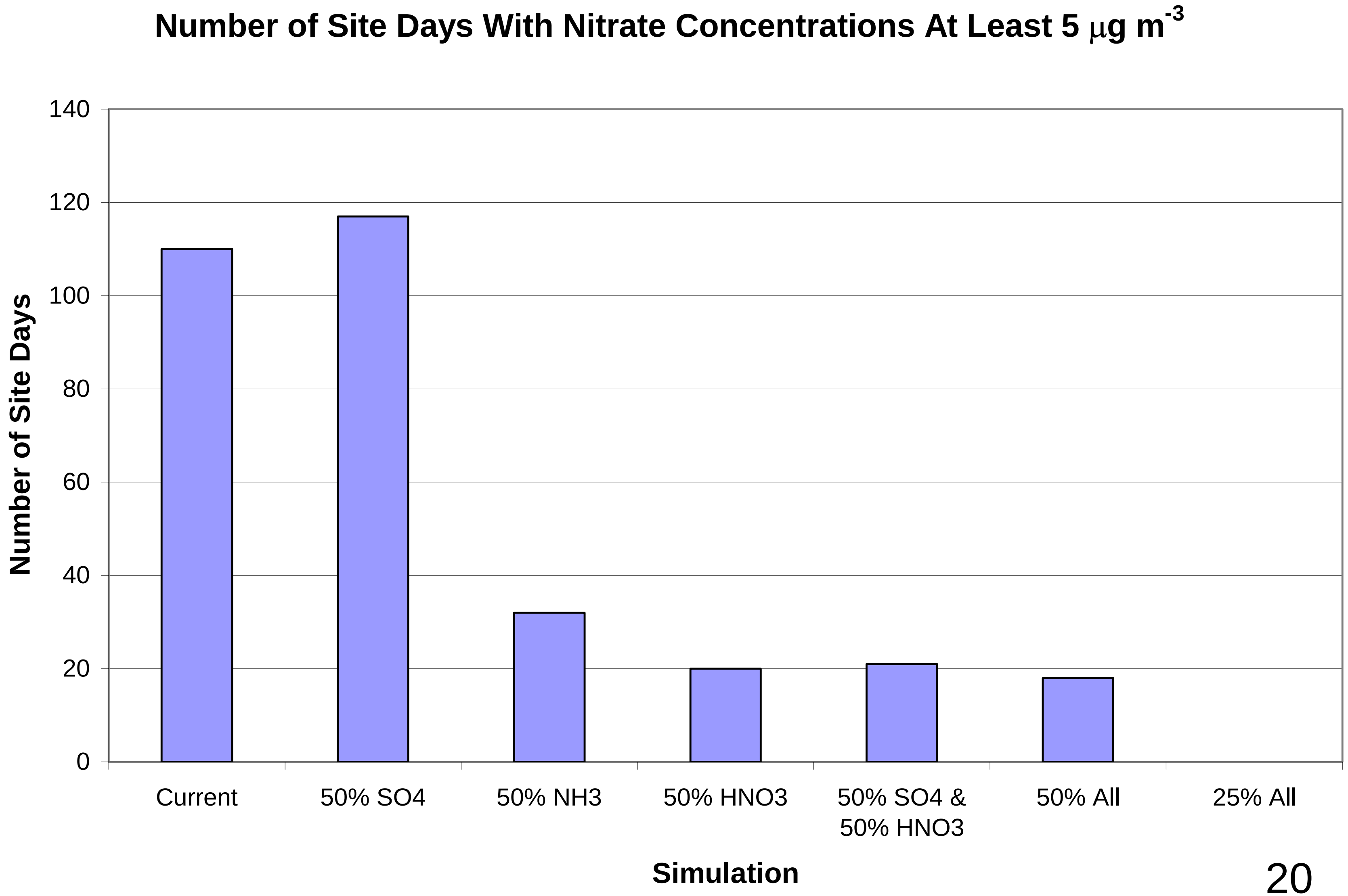
Predicted $PM_{2.5}$ Mass Feb 3, 2005



<u>Scale</u>

Bars are marked at increments of 10 $\mu g\ m^{-3}$

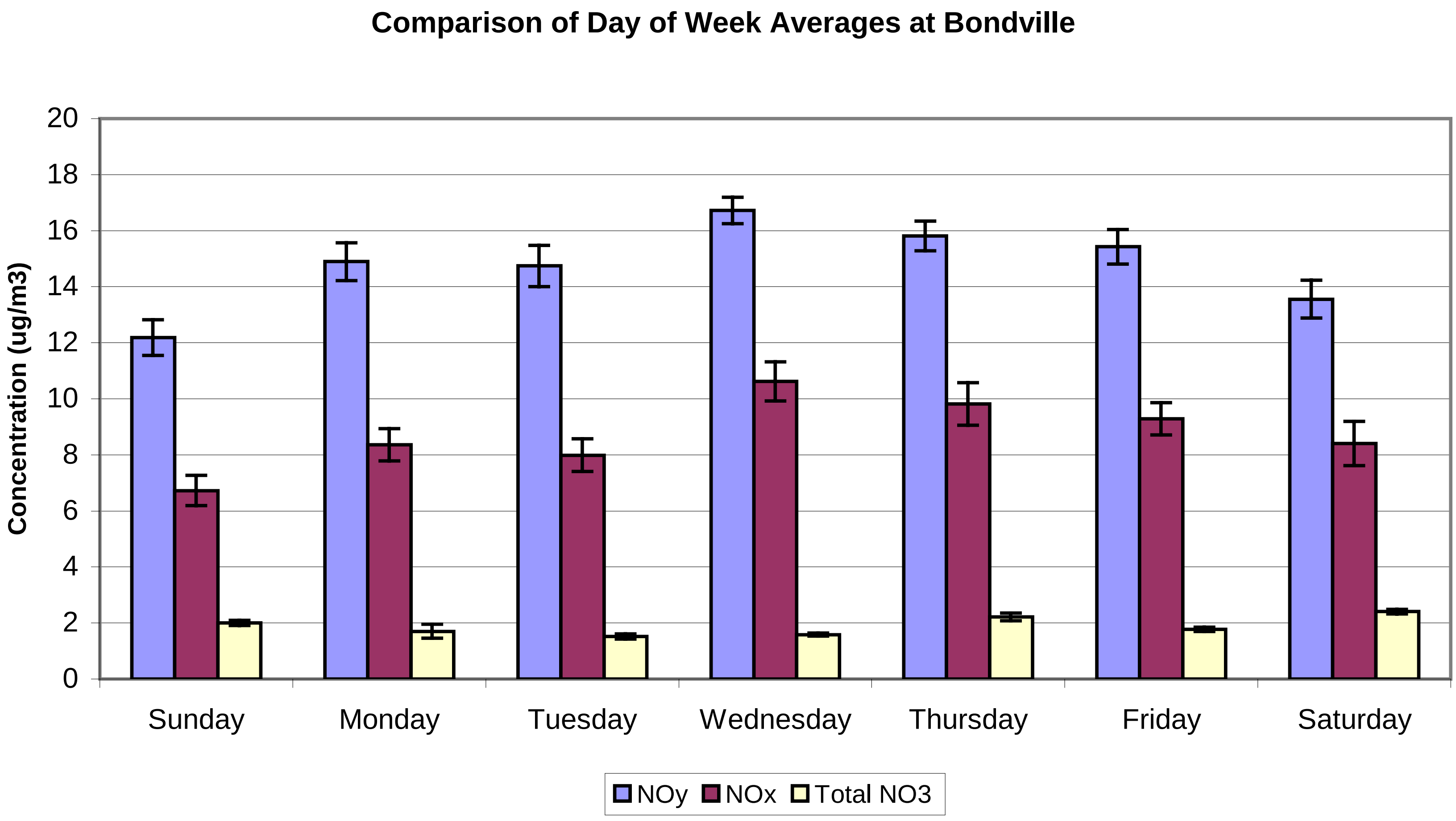
How to Reduce High Nitrate?



Study Limitations

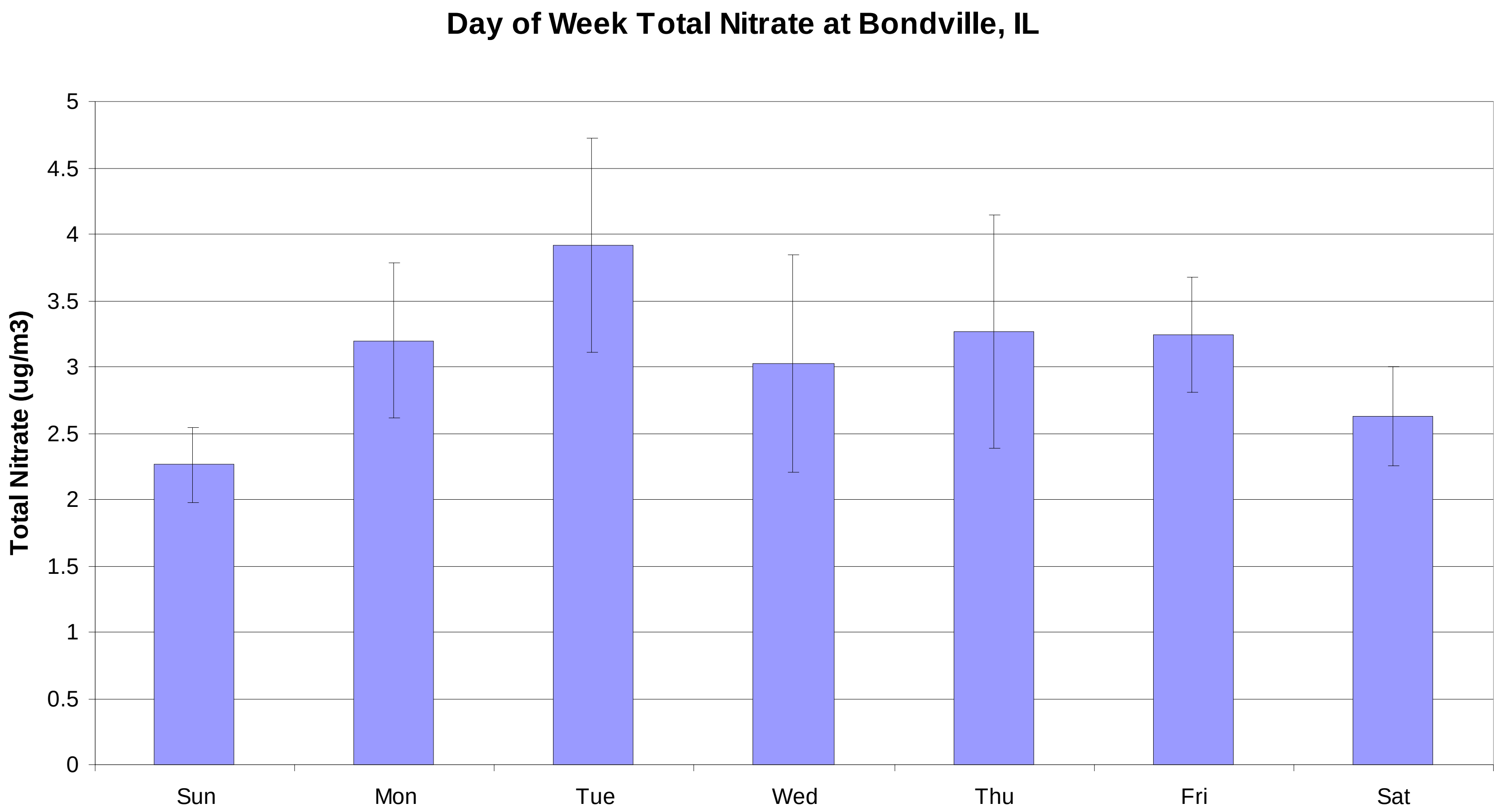
- Not a complete modeling system
- How do we know that reductions of SO_2, NH_3, and NO_x emissions will reduce ambient concentrations of sulfate, HNO_3, and NH_3?
- Cross-checks?
  - Ambient measurements
  - Emissions-driven modeling

Weekly Cycles Occur in NOx and NOy



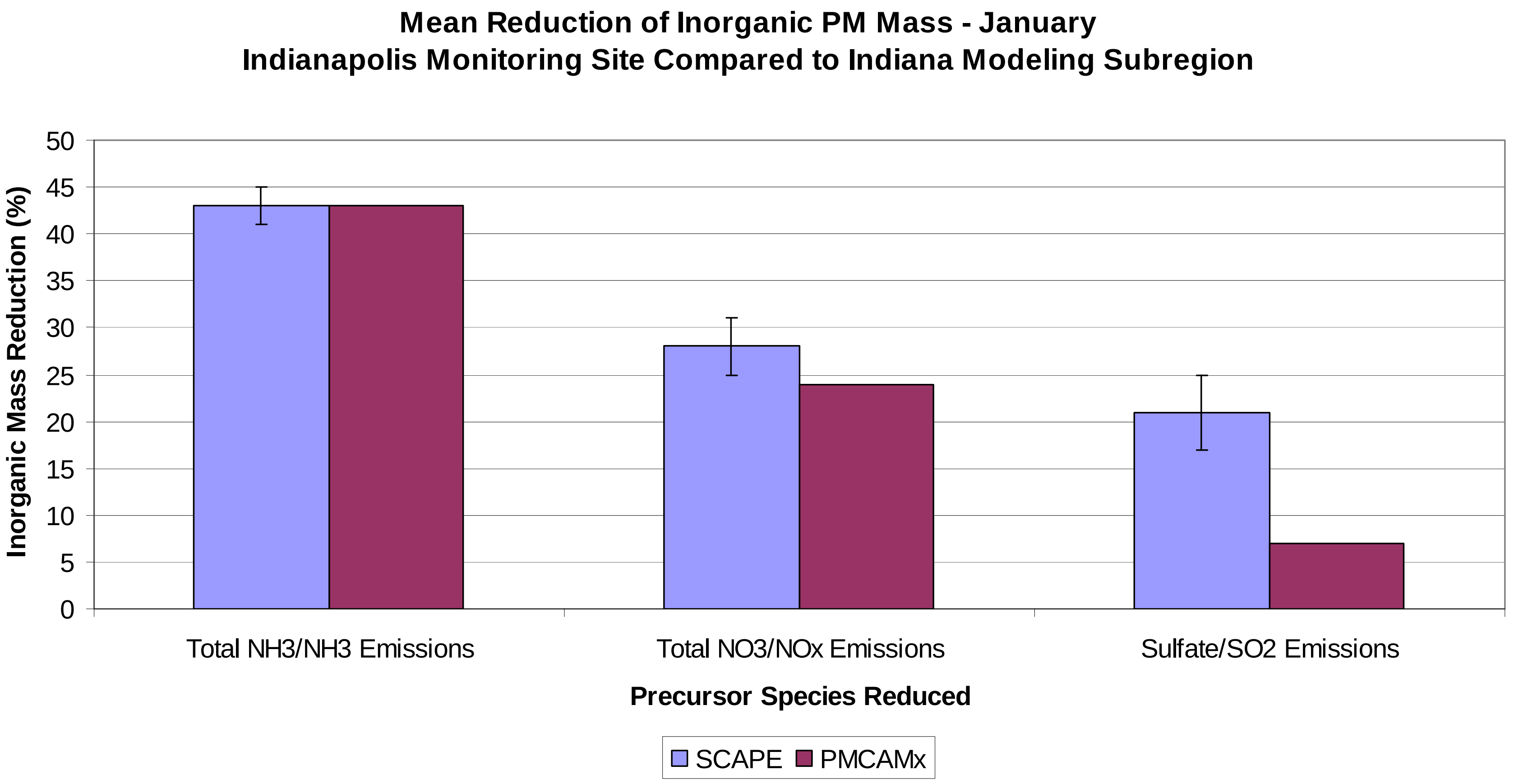
Continuous monitoring May 2003 – Dec 2004

Weekly Cycles Also Occur in Total Nitrate



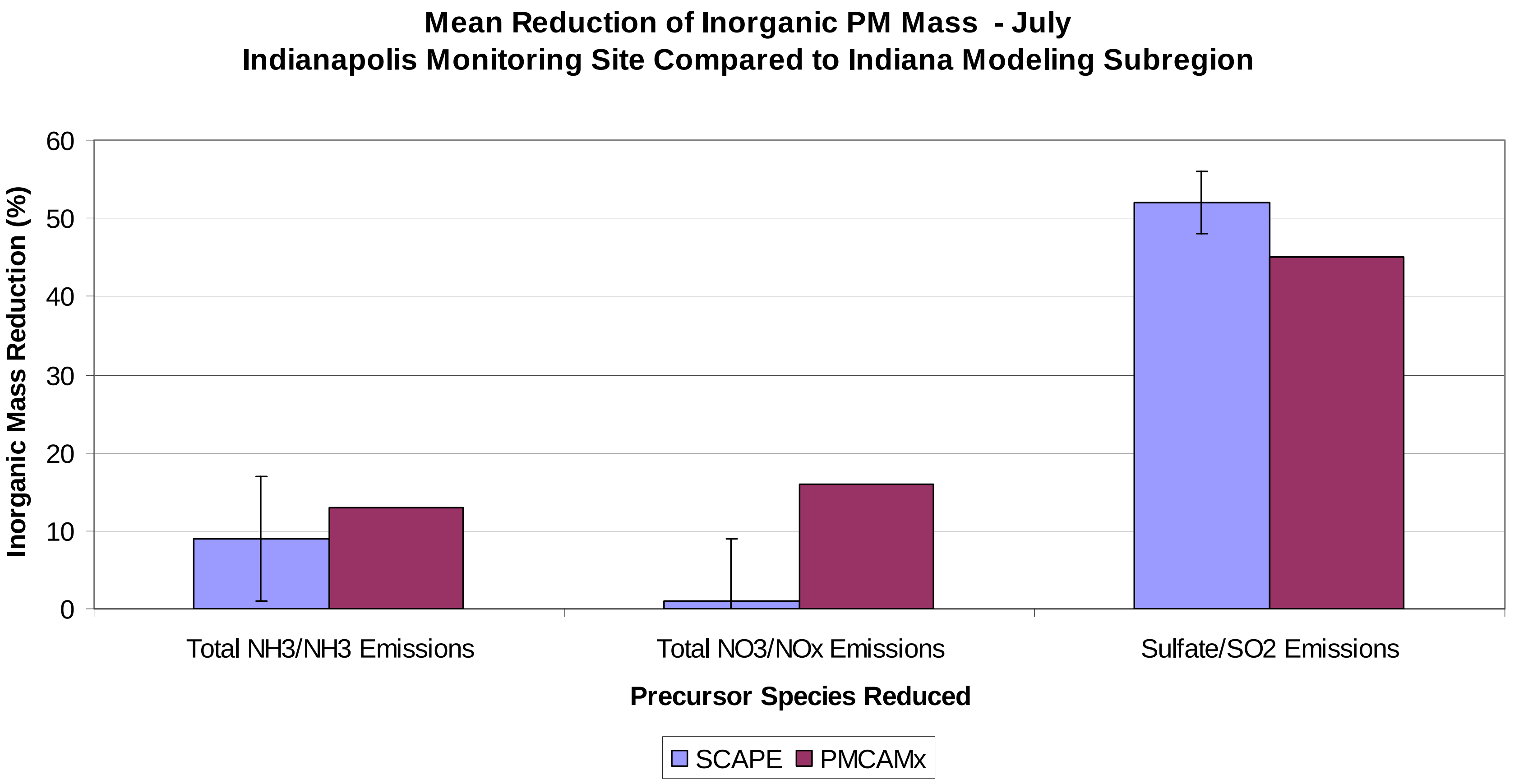
Daily filter-based monitoring Nov 2003 – Jun 2006

Comparisons to Complete Model System



PMCAMx results from Pinder et al. 2007. *ES&T* 41: 380-386.

Comparisons to Complete Model System



PMCAMx results from Pinder et al. 2007. *ES&T* 41: 380-386.

Summary of Findings

- Data and thermodynamic equilibrium models permit useful predictions
- Models predict seasonal and geographic variations in the response of $PM_{2.5}$ mass to changes in inorganic precursor species concentrations
- Study results are consistent with related work

Summary of Findings (continued)

- Mean $PM_{2.5}$ decreases for 50% reductions:
  - Sulfate (SO_2): 0.8 – 3.6 $\mu g\ m^{-3}$
  - Total NH_3 (NH_3): 0.4 – 2.6 $\mu g\ m^{-3}$
  - Total nitrate (NOx): 0.4 – 1.8 $\mu g\ m^{-3}$
- When sulfate is at 50% of current, mean $PM_{2.5}$ decreases for 50% reductions are:
  - Total NH_3 (NH_3): 0.2 – 1.5 $\mu g\ m^{-3}$
  - Total nitrate (NOx): 0.6 – 1.7 $\mu g\ m^{-3}$

Summary of Findings (concluded)

- Sulfate (SO_2) reductions yield greatest reductions of PM mass in summer
- Reductions of ammonia and total nitrate (NOx) yield greatest reductions of PM mass in winter
- Regional variations in PM response: SE (Ohio River Valley), central (Michigan, Indiana, Illinois, Iowa), NW & West (Wisconsin to Oklahoma)