

Analysis of Inorganic Particulate Matter Measurements in the Midwestern United States

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Outline

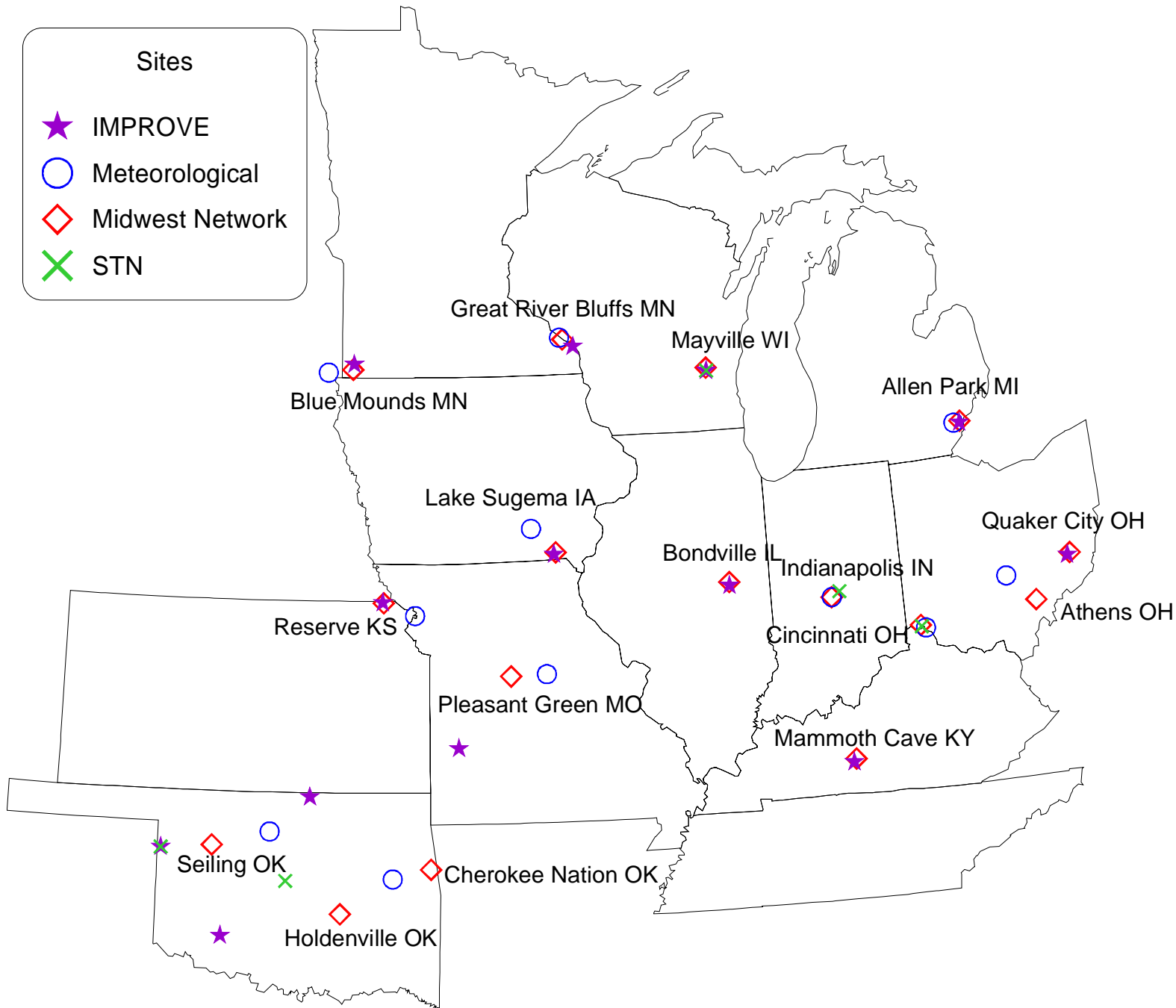
- Objectives
- Data
- Models
- Results – means, winter, episodes
- Limitations and comparisons
- Conclusions

Project Objectives

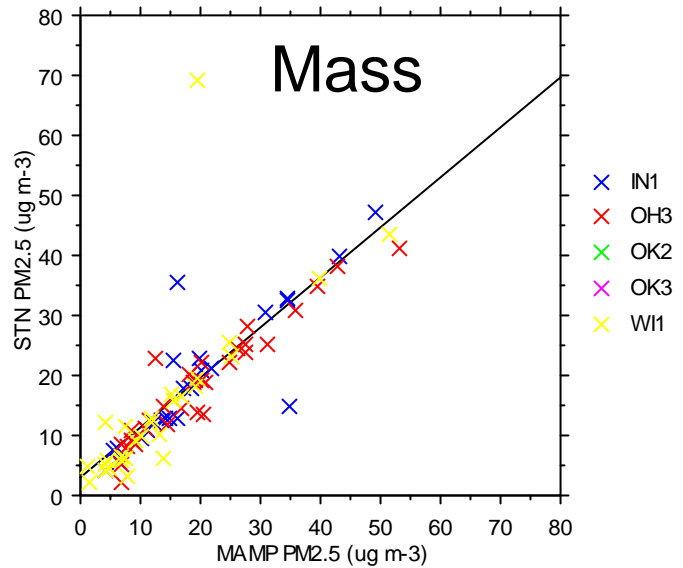
- Primary question: how will $\text{PM}_{2.5}$ mass concentrations respond to changes in SO_2 , NO_x , and NH_3 emissions?
- Subsidiary questions:
 - Nature of high PM episodes?
 - Seasonal differences?
 - Urban-rural differences?
 - Geographical differences?

Data

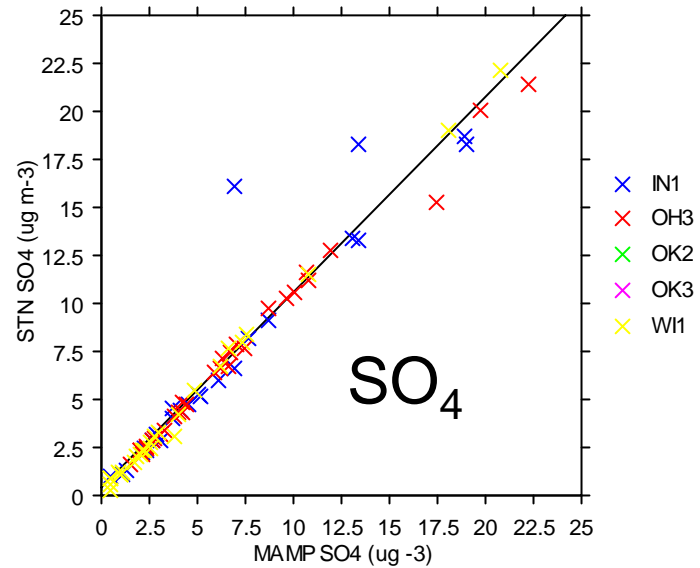
- Midwest Ammonia Monitoring Project measurements of PM_{2.5} mass, sulfate, nitrate, ammonium, SO₂, NH₃, HNO₃: daily 1-in-6, Nov 2003 – June 2006
- 15 sites – most collocated with IMPROVE or STN sites
- Ongoing 2-week resolution passive NH₃



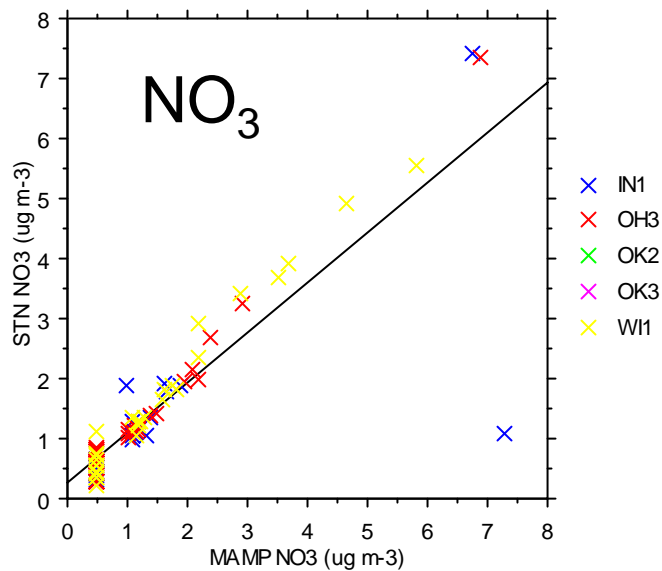
Collocated STN Data Agree Well



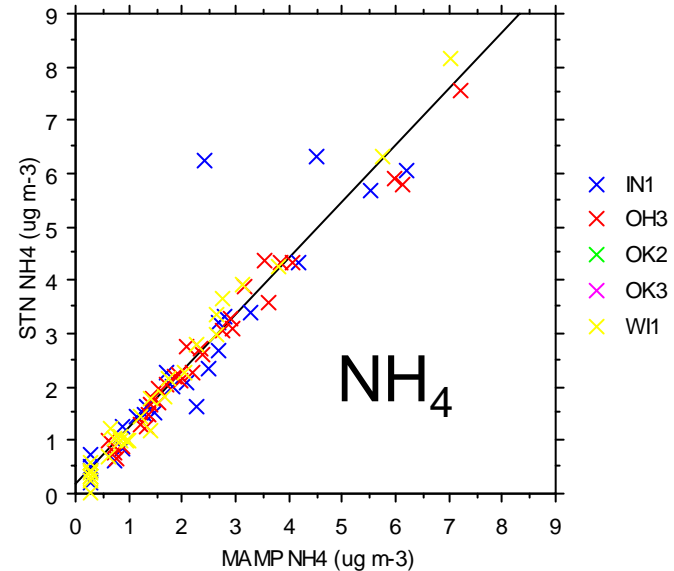
STN PM_{2.5} (ug m⁻³) = 3.146 + .83 * MAMP PM_{2.5} (ug m⁻³); R² = .678



STN SO₄ (ug m⁻³) = .421 + 1.016 * MAMP SO₄ (ug m⁻³); R² = .954

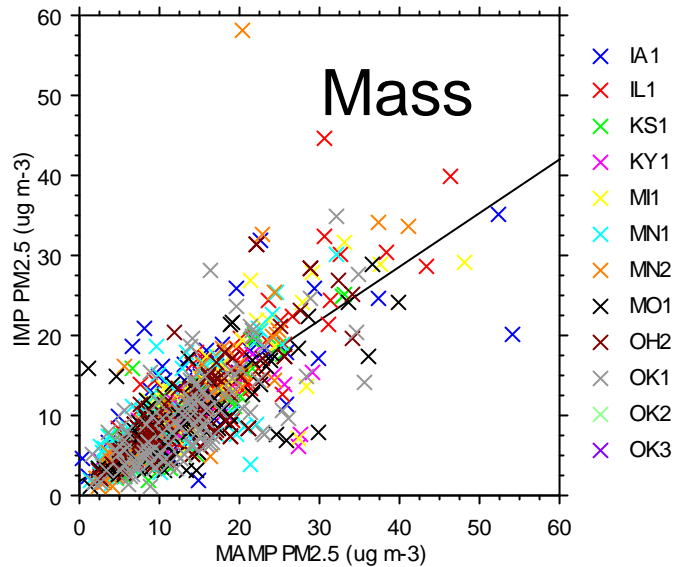


STN NO₃ (ug m⁻³) = .282 + .831 * MAMP NO₃ (ug m⁻³); R² = .759

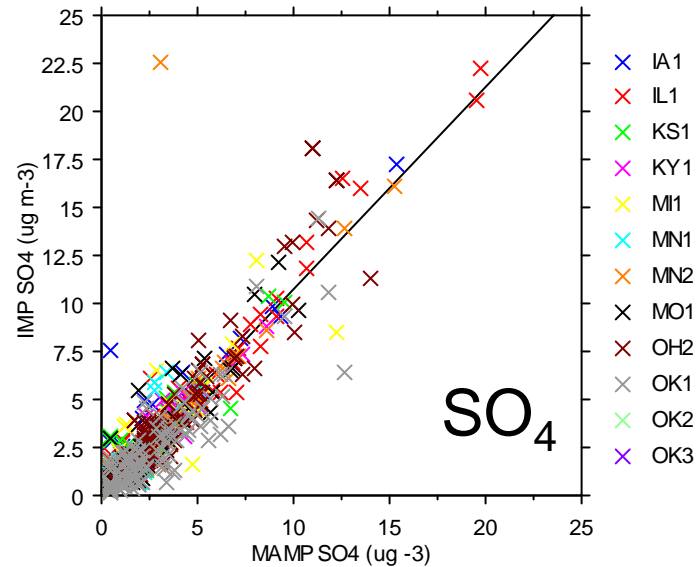


STN NH₄ (ug m⁻³) = .197 + 1.06 * MAMP NH₄ (ug m⁻³); R² = .923

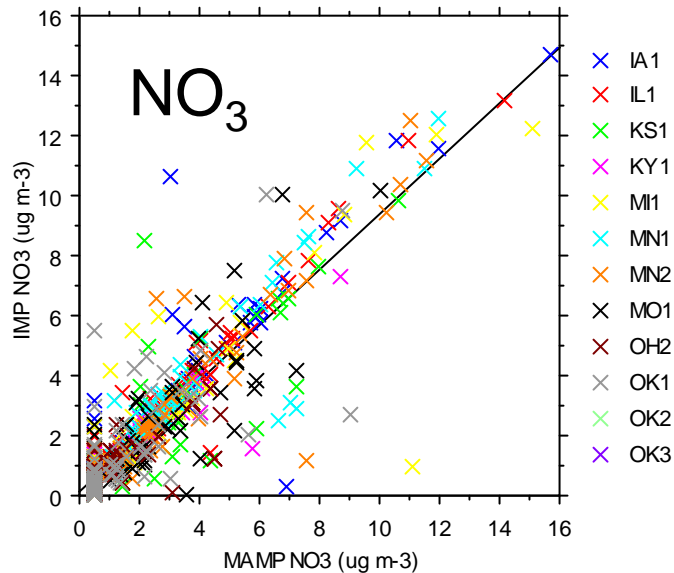
Collocated IMPROVE Species Agree



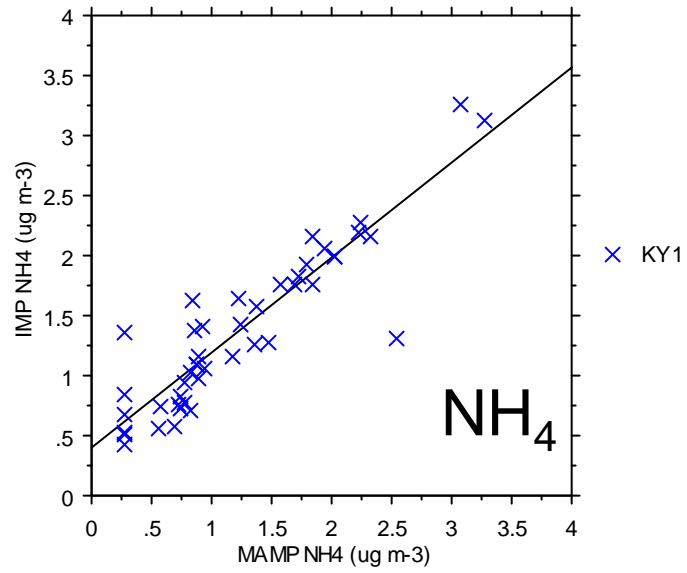
$IMP\ PM_{2.5}\ (ug\ m^{-3}) = 1.776 + .672 * MAMP\ PM_{2.5}\ (ug\ m^{-3}); R^2 = .63$



$IMP\ SO_4\ (ug\ m^{-3}) = .209 + 1.051 * MAMP\ SO_4\ (ug\ -3); R^2 = .827$



$IMP\ NO_3\ (ug\ m^{-3}) = .145 + .926 * MAMP\ NO_3\ (ug\ m^{-3}); R^2 = .813$



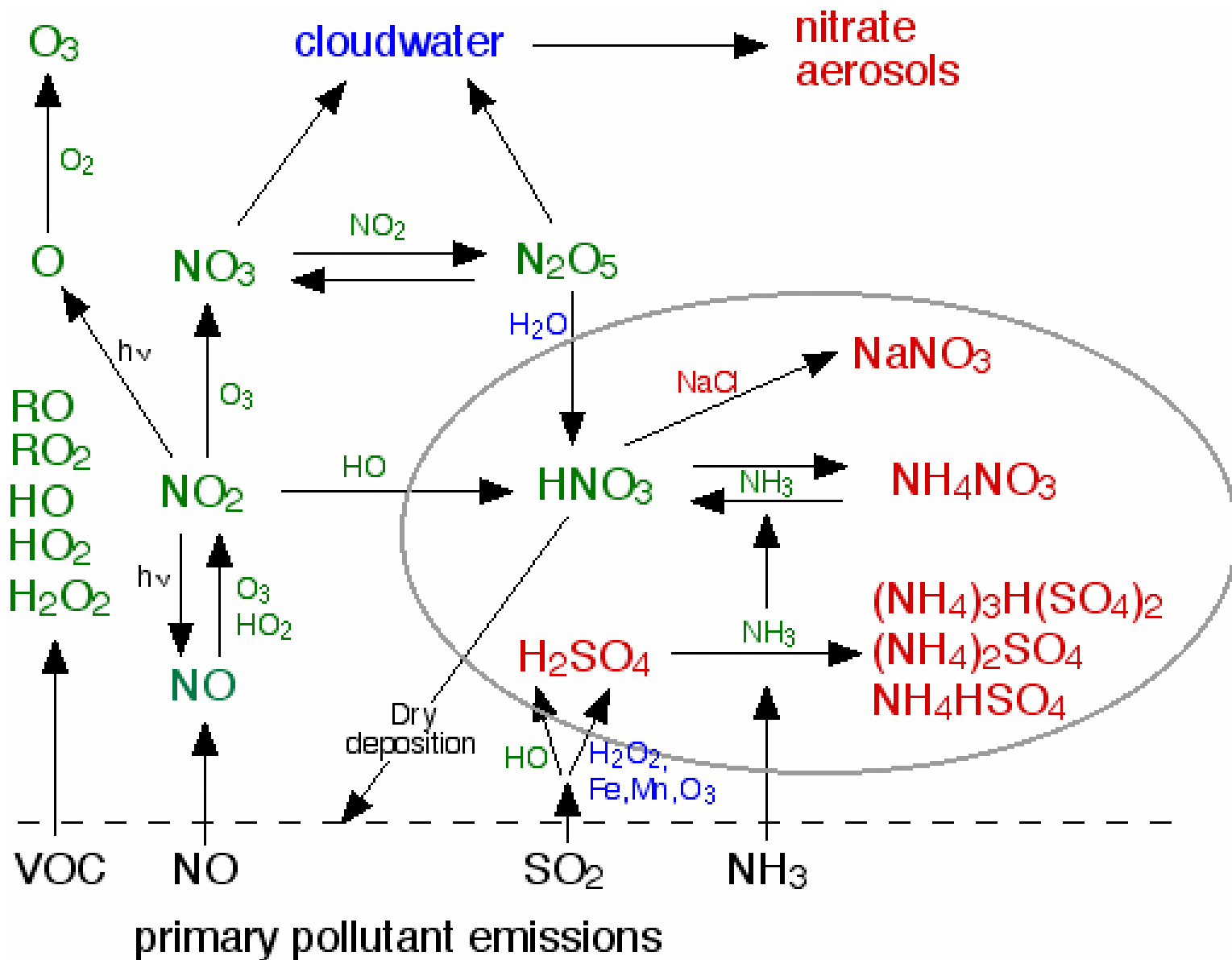
$IMP\ NH_4\ (ug\ m^{-3}) = .399 + .792 * MAMP\ NH_4\ (ug\ m^{-3}); R^2 = .816$

Thermodynamic Equilibrium Models

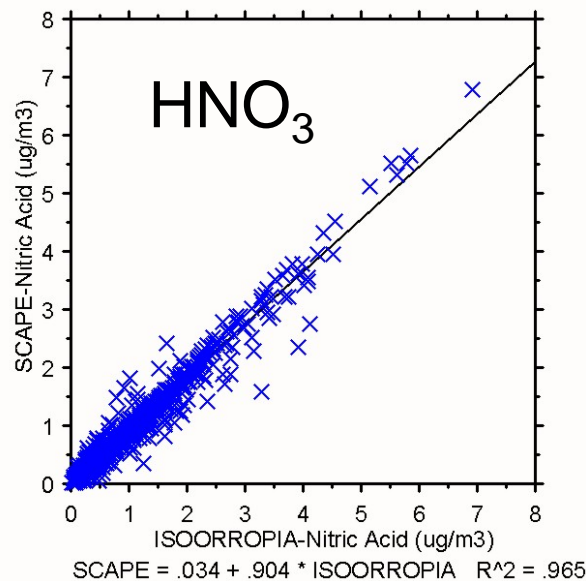
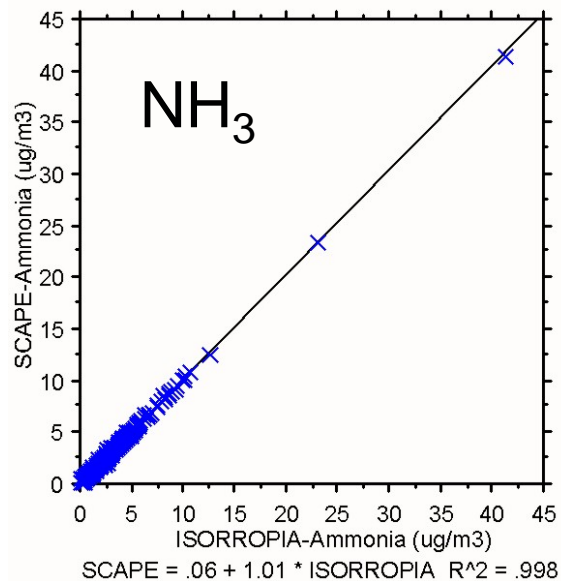
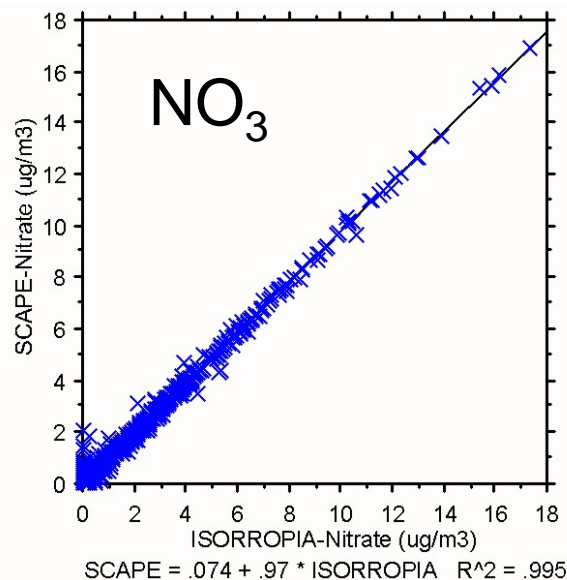
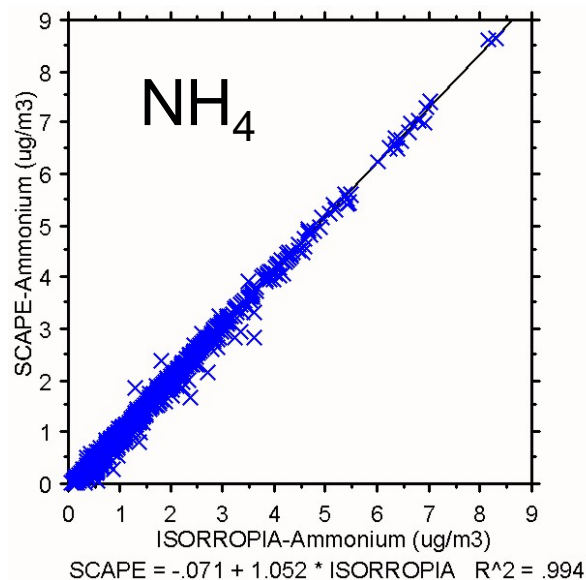
- ISORROPIA and SCAPE2
- Model inputs: T, RH, total sulfate, total nitrate (= PM nitrate + HNO_3), total ammonia (= PM ammonium + NH_3), other species
- Model outputs: $\text{PM}_{2.5}$ mass, amount of nitrate and ammonium in the gas phase and in particles, particle composition

Thermo Eq'bm Models (cont'd)

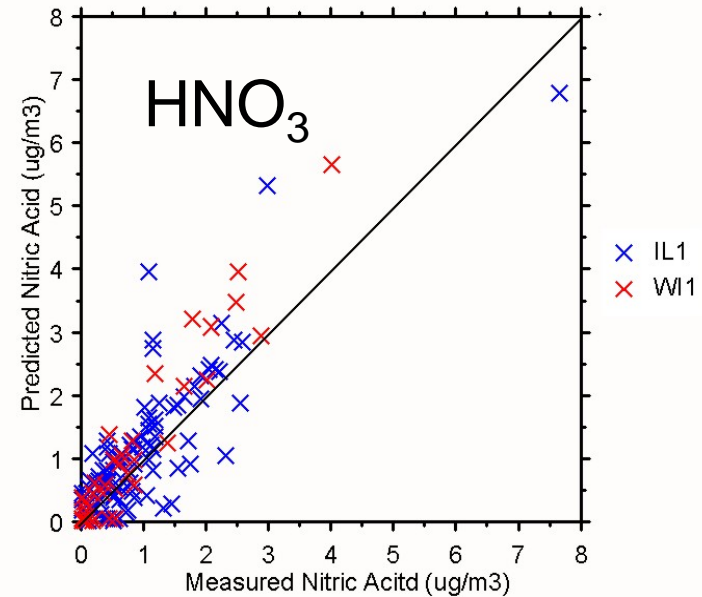
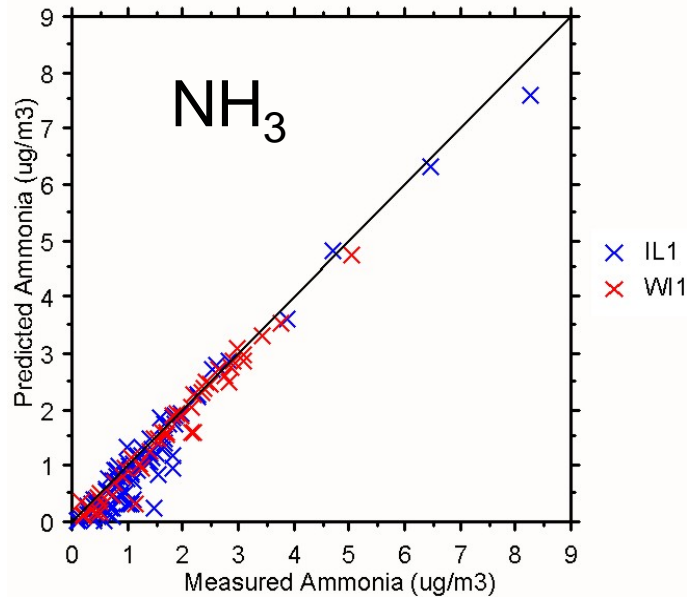
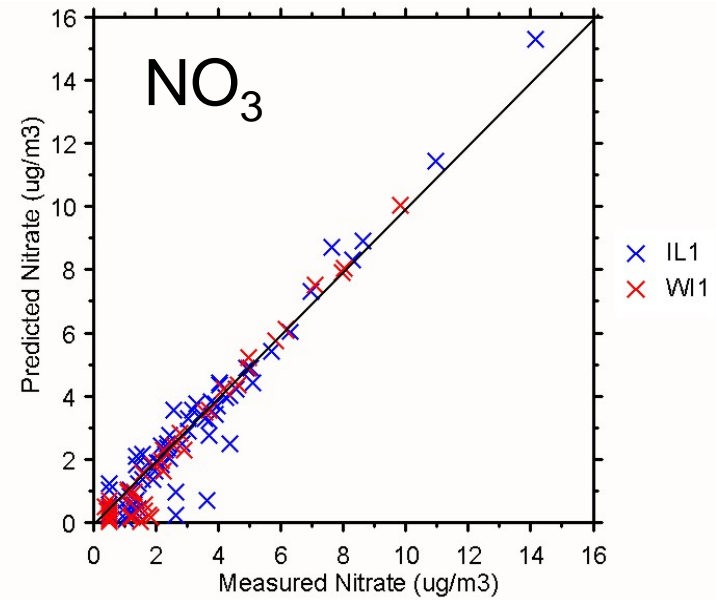
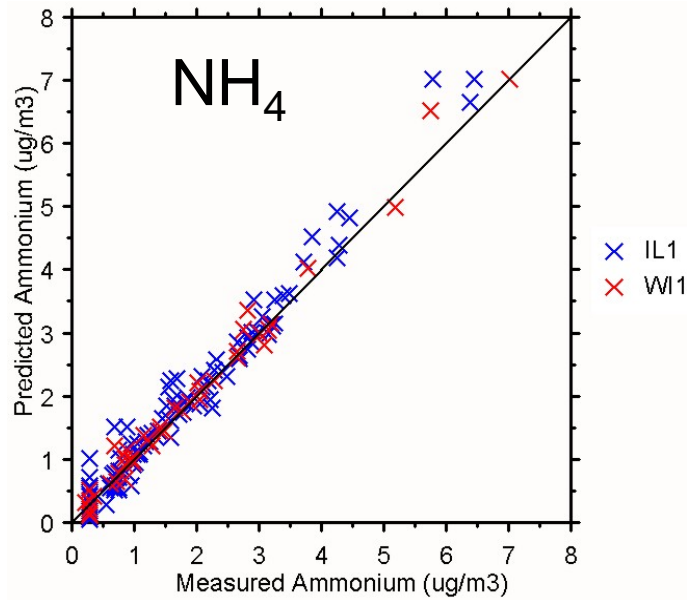
- Vary amounts of total sulfate, nitrate, and ammonium (25 to 150% of actuals)
- Calculate changes in PM_{2.5} mass
- Advantages: tied directly to ambient data, no emissions estimates required
- Disadvantages: does not simulate some processes – must assume that lower SO₂ & NO_x results in lower sulfate & HNO₃



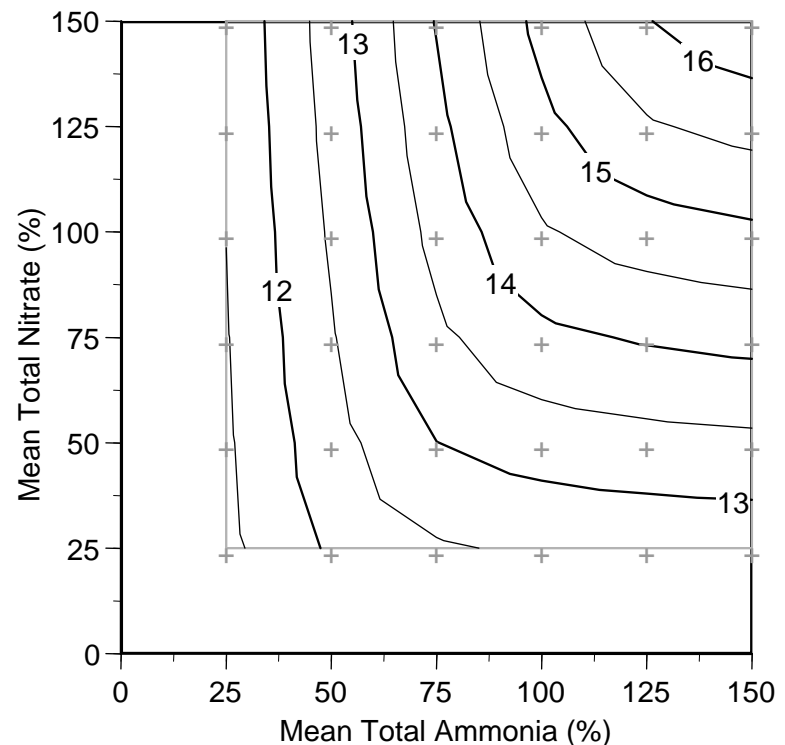
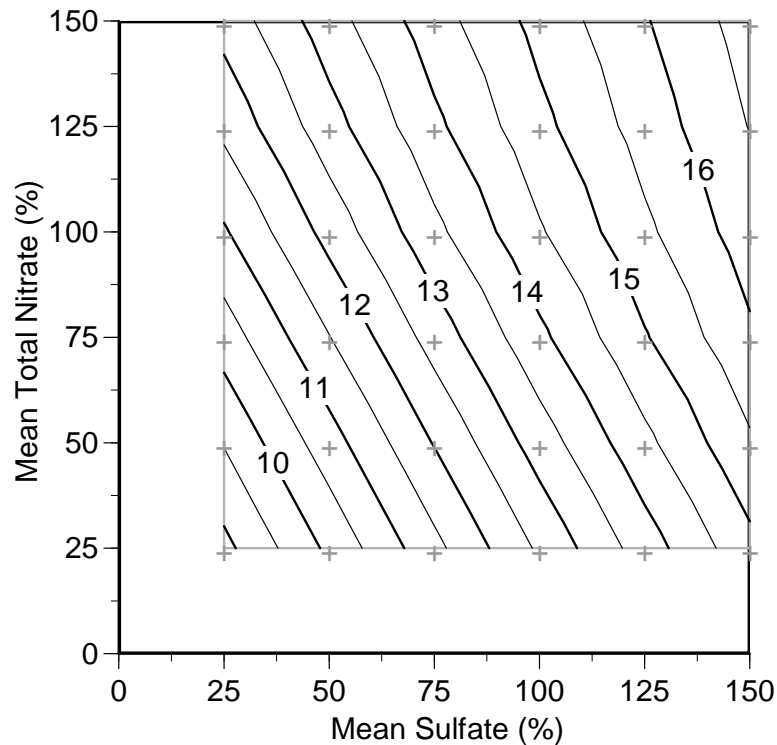
Two Models Produce Comparable Results



Predictions Agree With Measurements

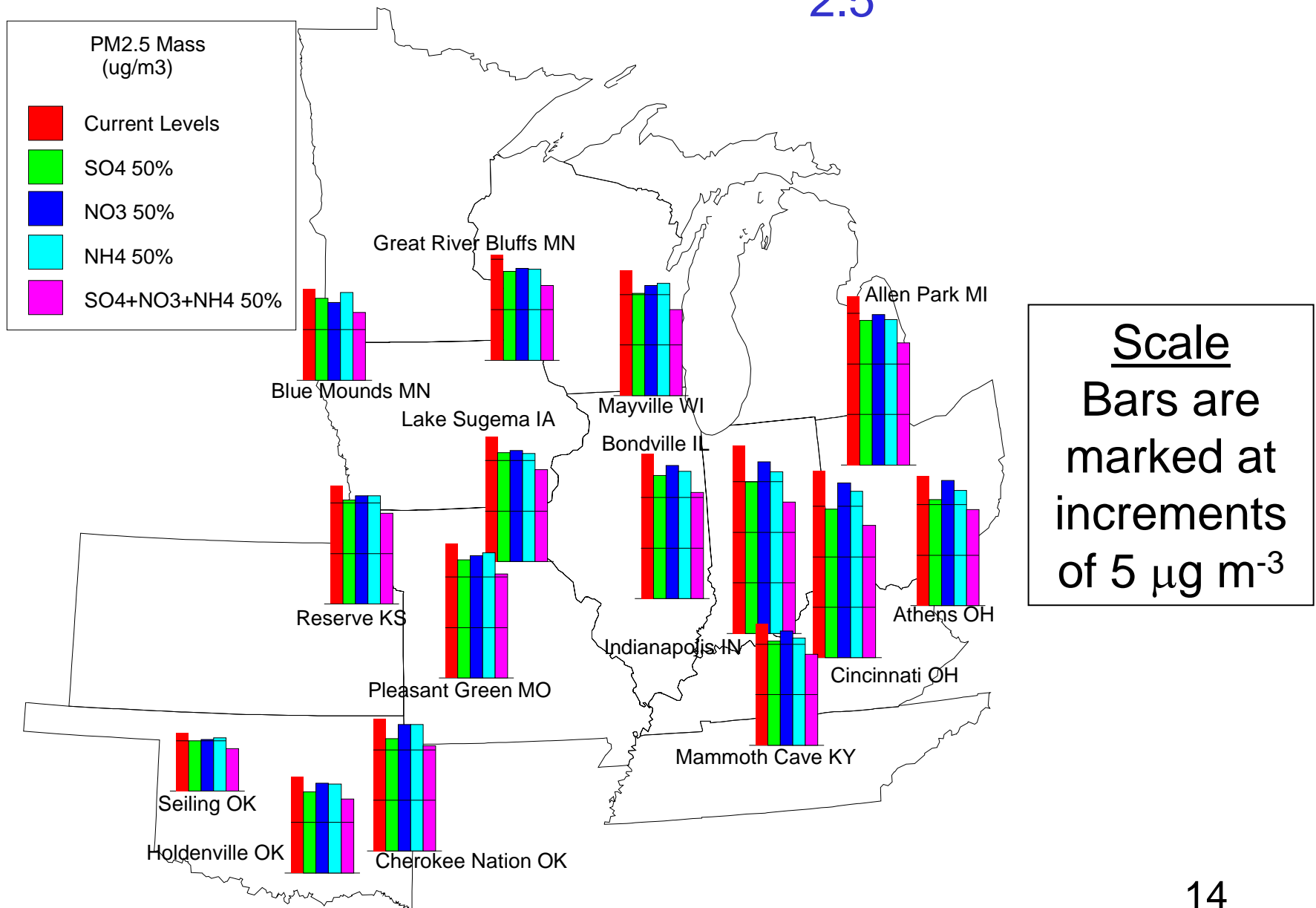


Results for Bondville – Predicted Mean PM_{2.5} Mass (N=111 days)



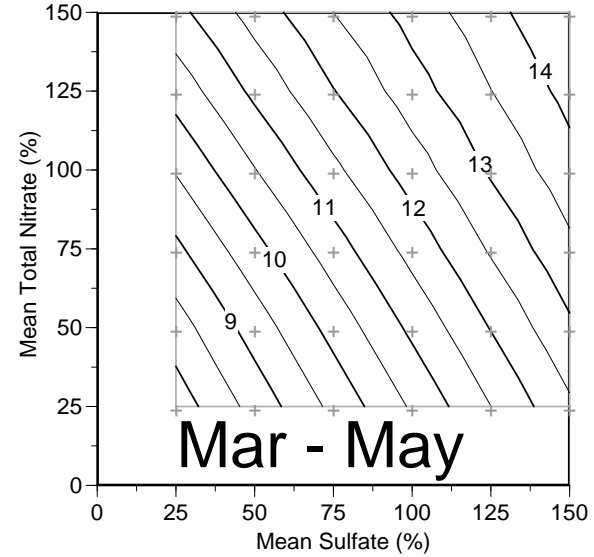
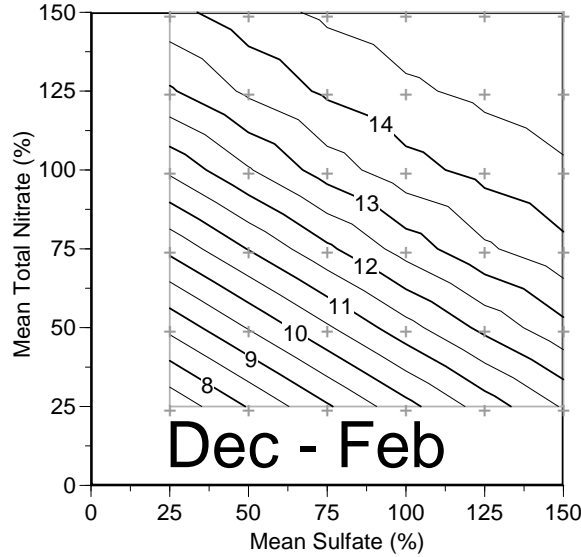
Note: Current concentrations occur at “100%” points

Mean Predicted PM_{2.5} Mass

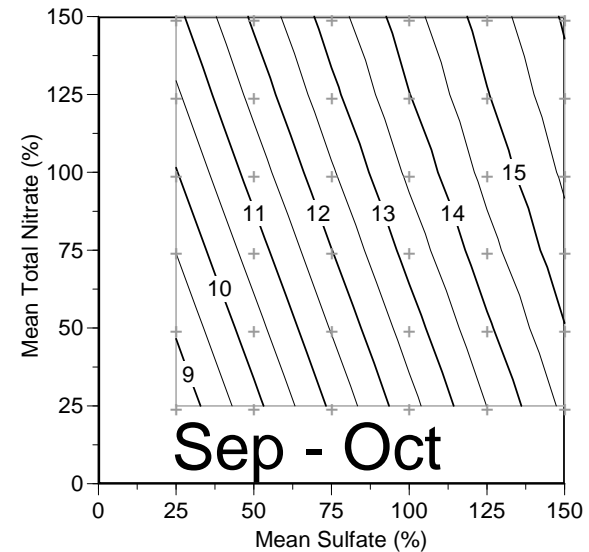
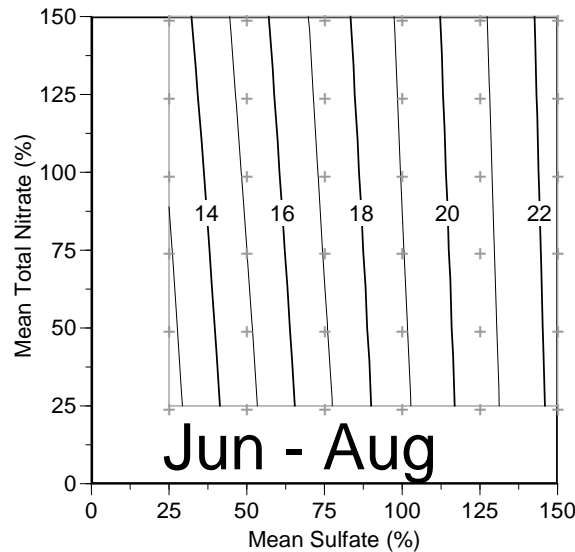


PM_{2.5} Response to SO₄ & NO₃ by Season

Winter
Nitrate
Sensitivity

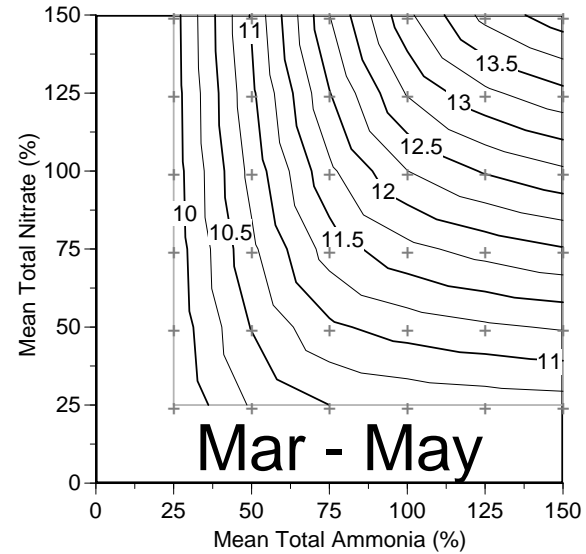
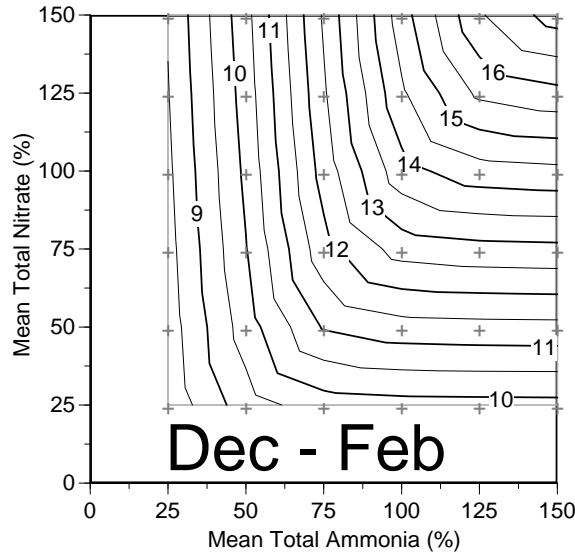


Summer
Sulfate
Sensitivity

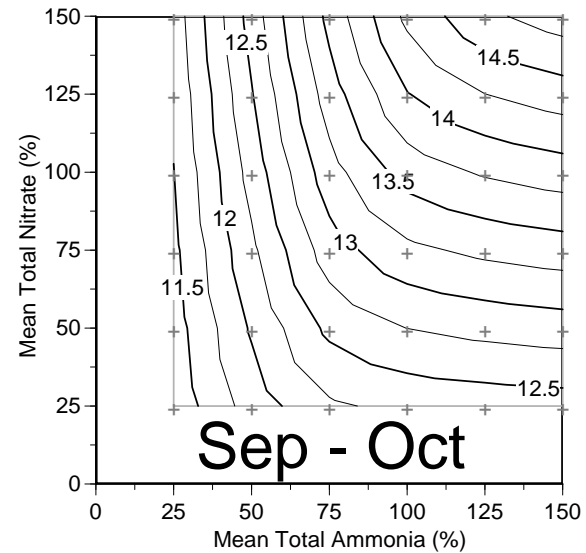
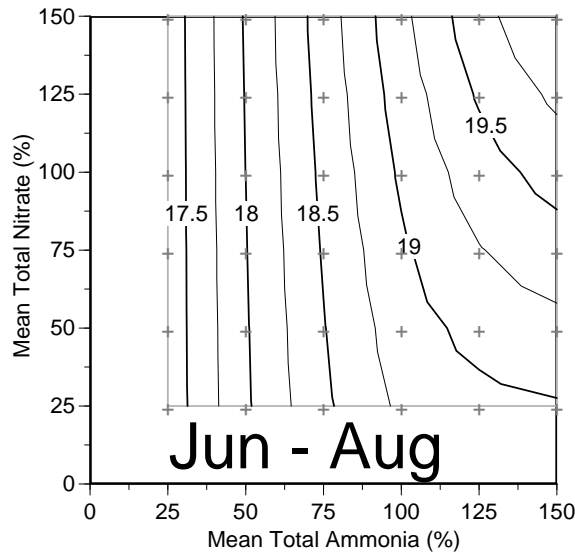


PM_{2.5} Response to NH₃ & NO₃ by Season

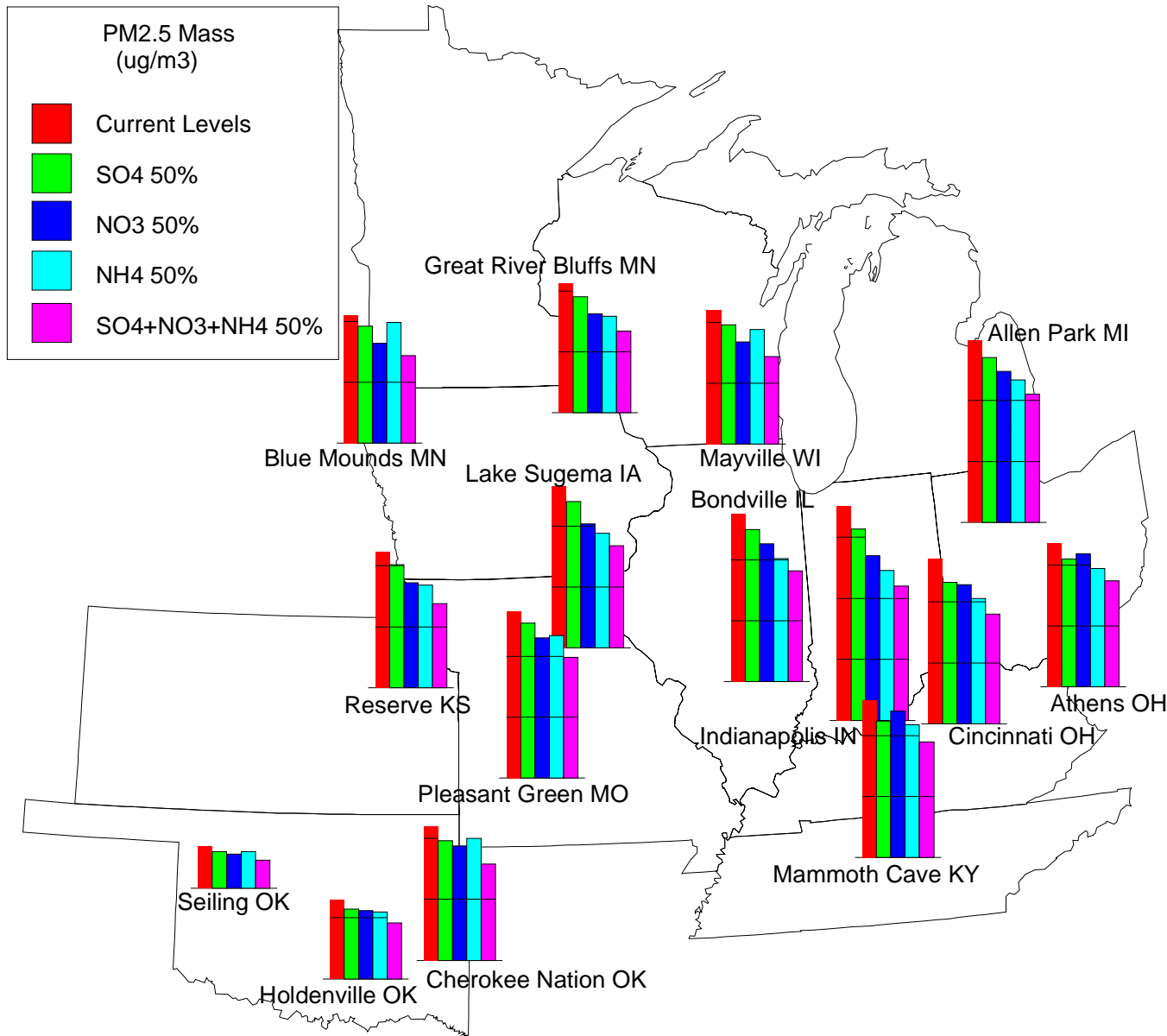
Winter
Ammonia
&
Nitrate
Sensitivity



Summer
Some
Ammonia
Sensitivity



Mean Predicted Winter PM_{2.5} Mass

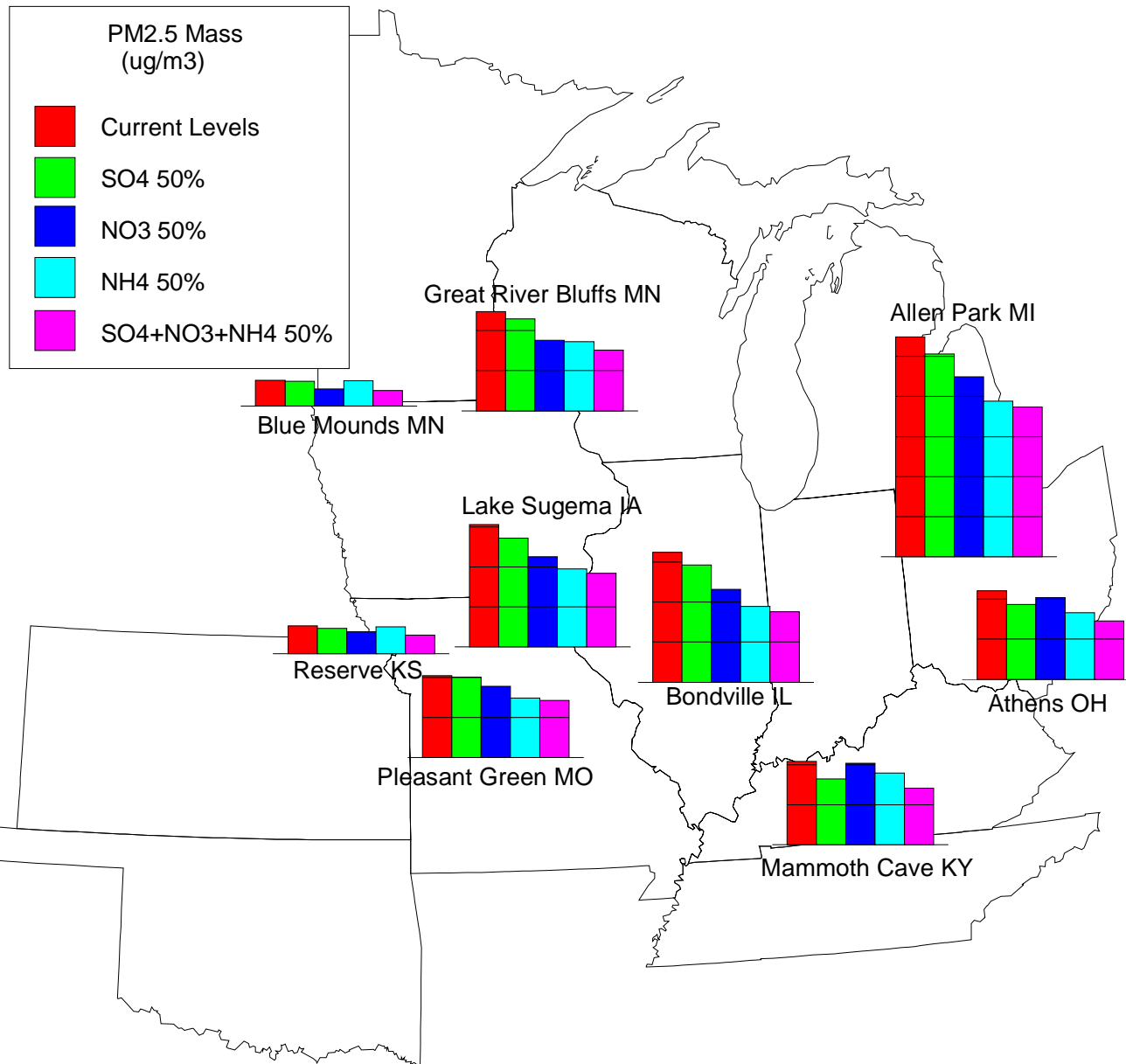


Scale
 Bars are marked at increments of 5 $\mu\text{g m}^{-3}$

Winter PM Episodes

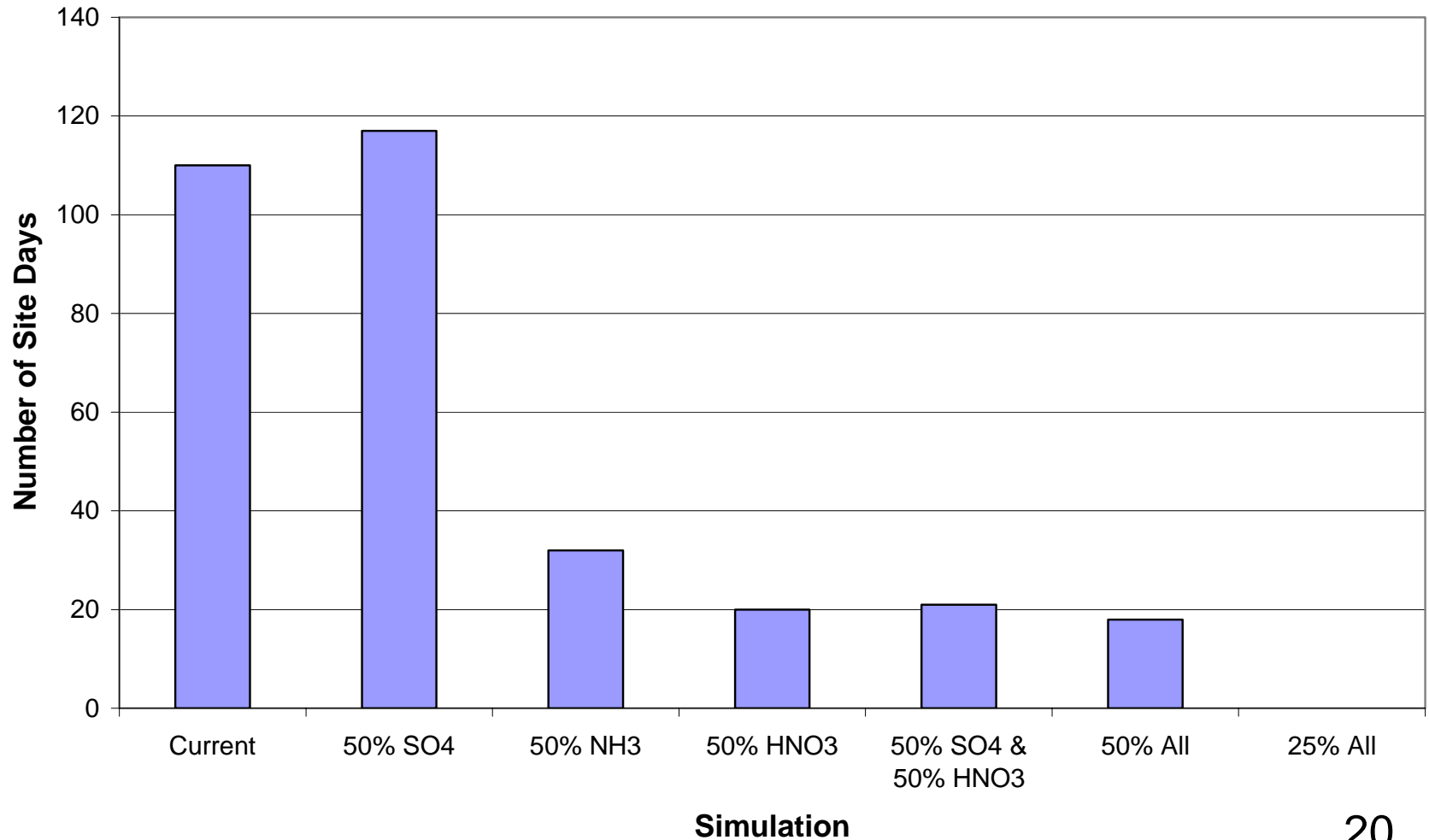
- May have high NH_4NO_3 concentrations
- Equilibrium favors particulate NH_4NO_3
- $\text{PM}_{2.5}$ mass may respond to reductions of either or both ammonia or total nitrate

Predicted PM_{2.5} Mass Feb 3, 2005



How to Reduce High Nitrate?

Number of Site Days With Nitrate Concentrations At Least $5 \mu\text{g m}^{-3}$

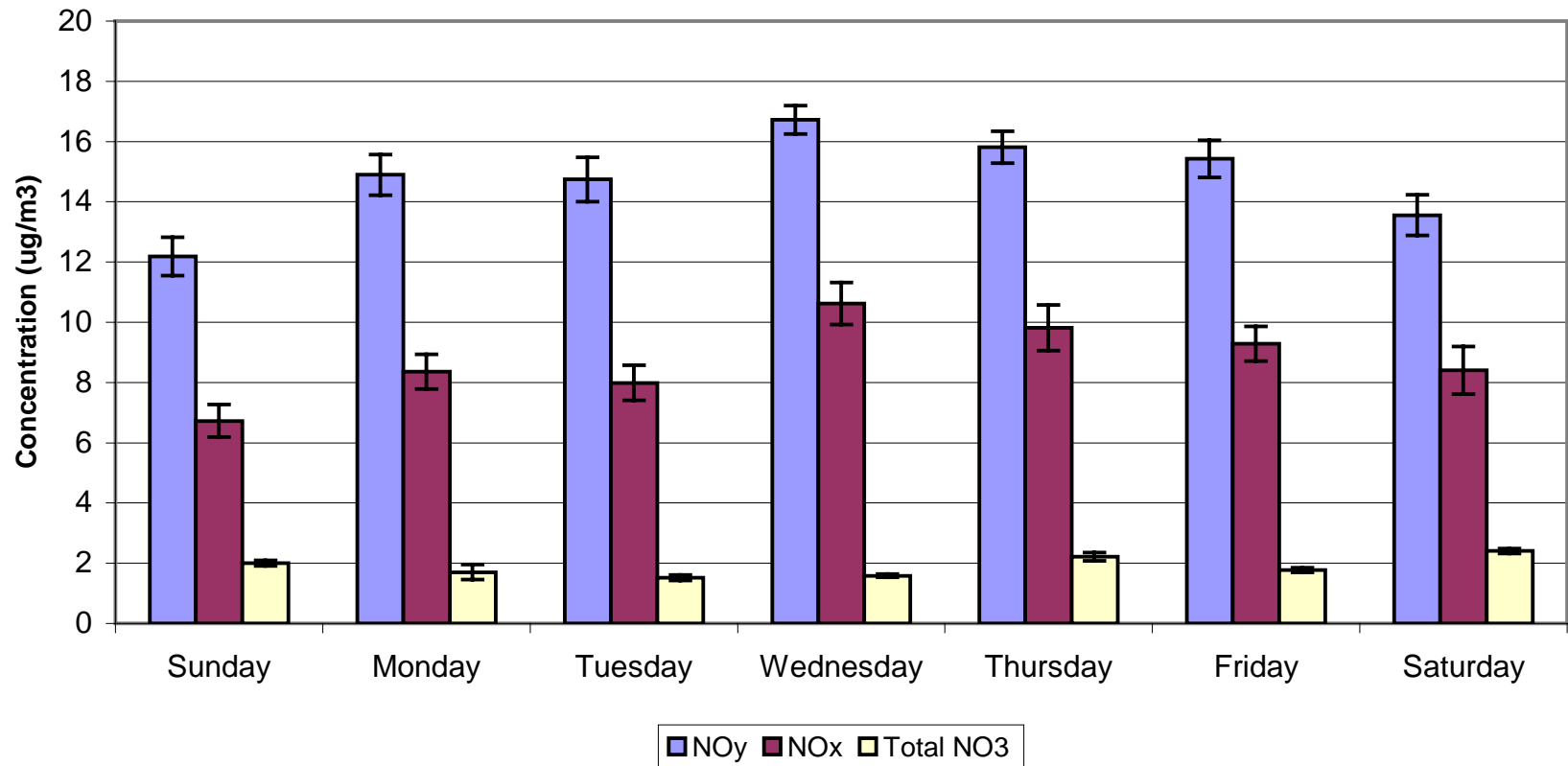


Study Limitations

- 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 NO_x and NO_y

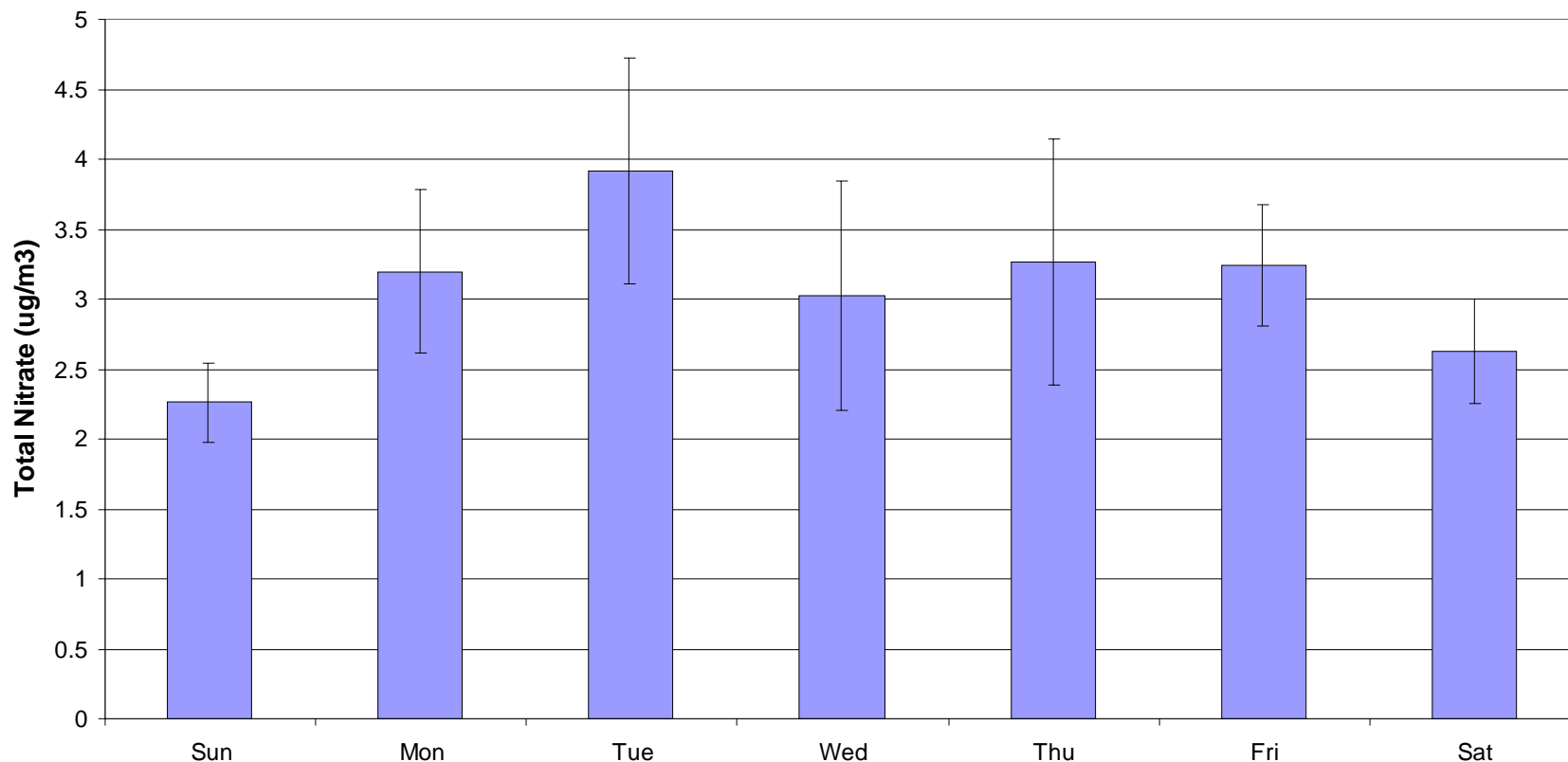
Comparison of Day of Week Averages at Bondville



Continuous monitoring May 2003 – Dec 2004

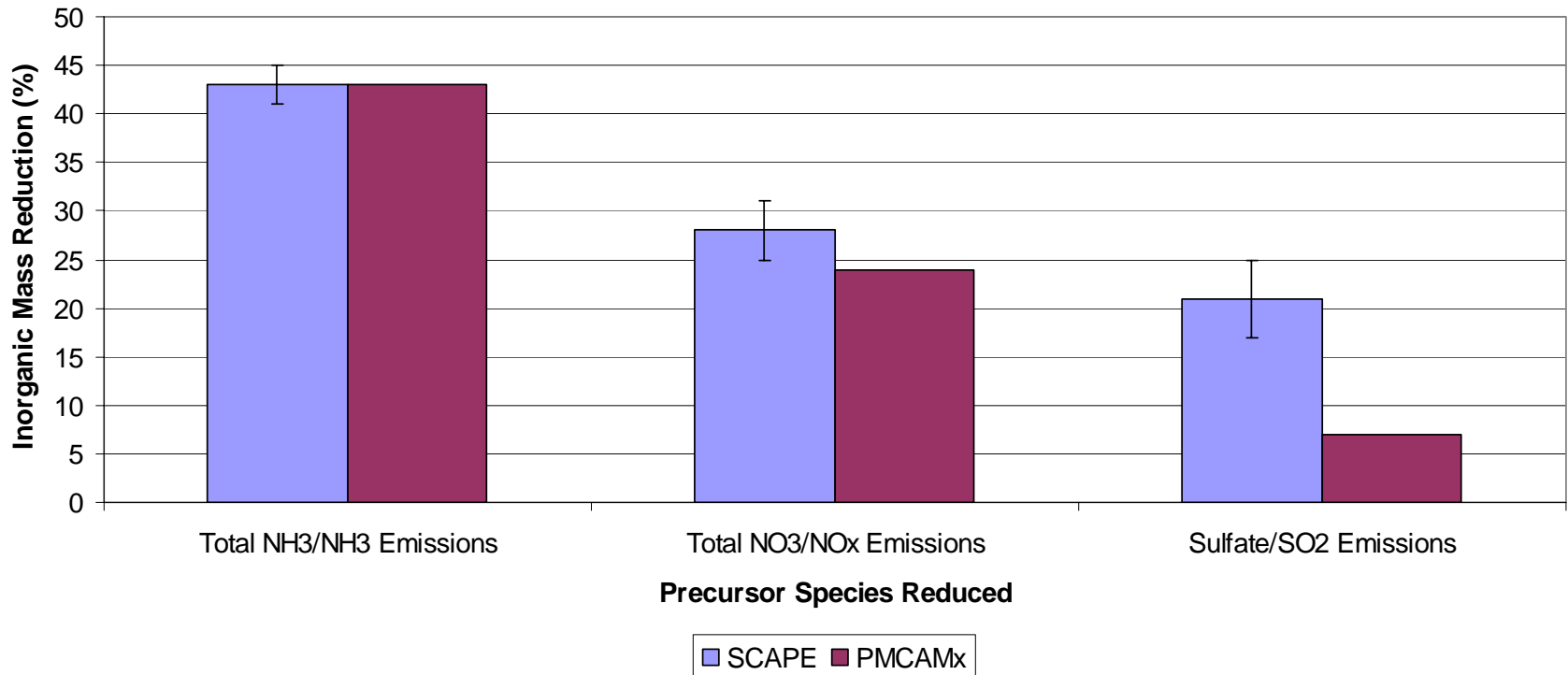
Weekly Cycles Also Occur in Total Nitrate

Day of Week Total Nitrate at Bondville, IL



Comparisons to Complete Model System

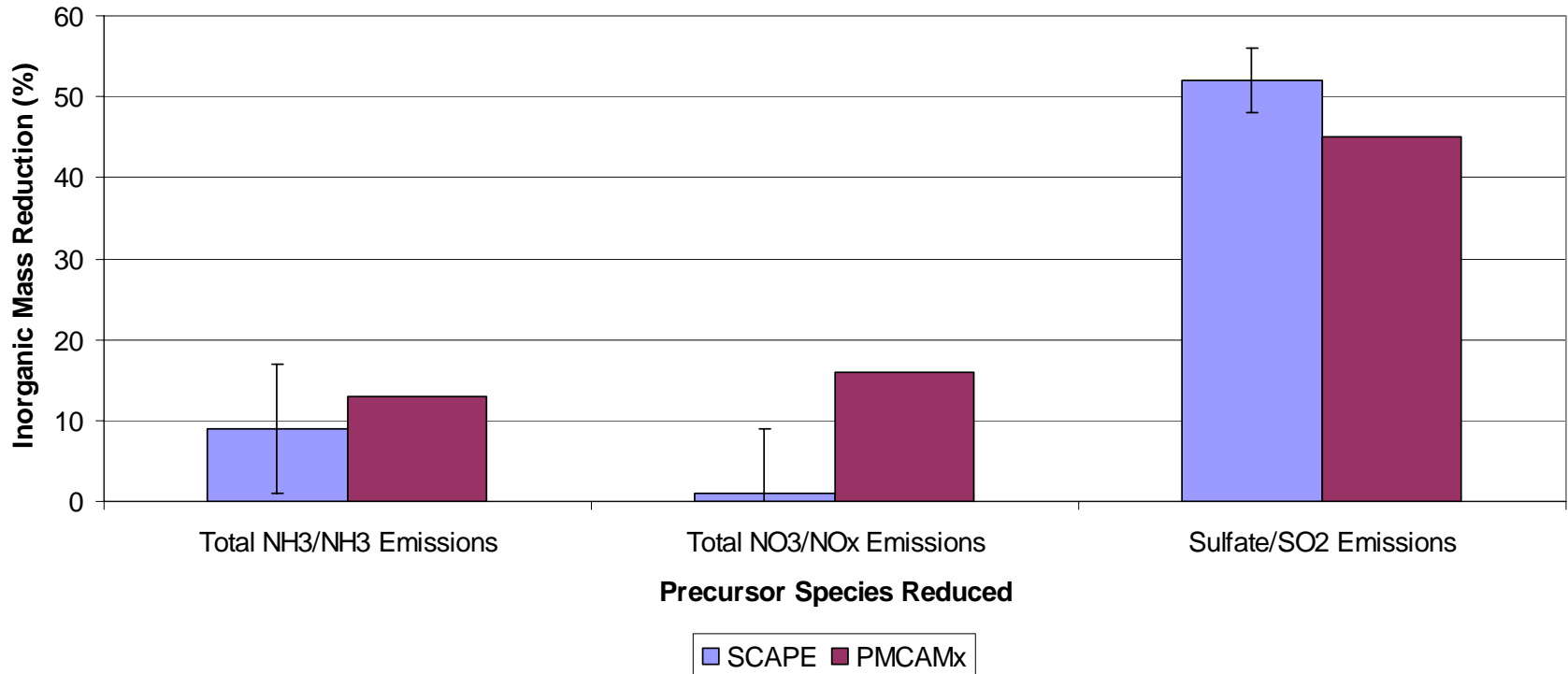
**Mean Reduction of Inorganic PM Mass - January
Indianapolis Monitoring Site Compared to Indiana Modeling Subregion**



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

Comparisons to Complete Model System

Mean Reduction of Inorganic PM Mass - July
Indianapolis Monitoring Site Compared to Indiana Modeling Subregion



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

Summary of Findings (concluded)

- Sulfate (SO_2) reductions yield greatest reductions of PM mass in summer
- Reductions of ammonia and total nitrate (NO_x) 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)