

Issues in Ammonia and Nitric Acid Measurements: Experiences in the Midwest

Donna Kenski

Lake Michigan Air Directors Consortium, Des Plaines, IL

David Gay

Illinois State Water Survey, Champaign, IL

Overview

- Why ammonia?
- Network sites and equipment
- What have we done with the data?
 - How good is it?
 - What does it tell us about PM?

Why ammonia (and nitric acid)?

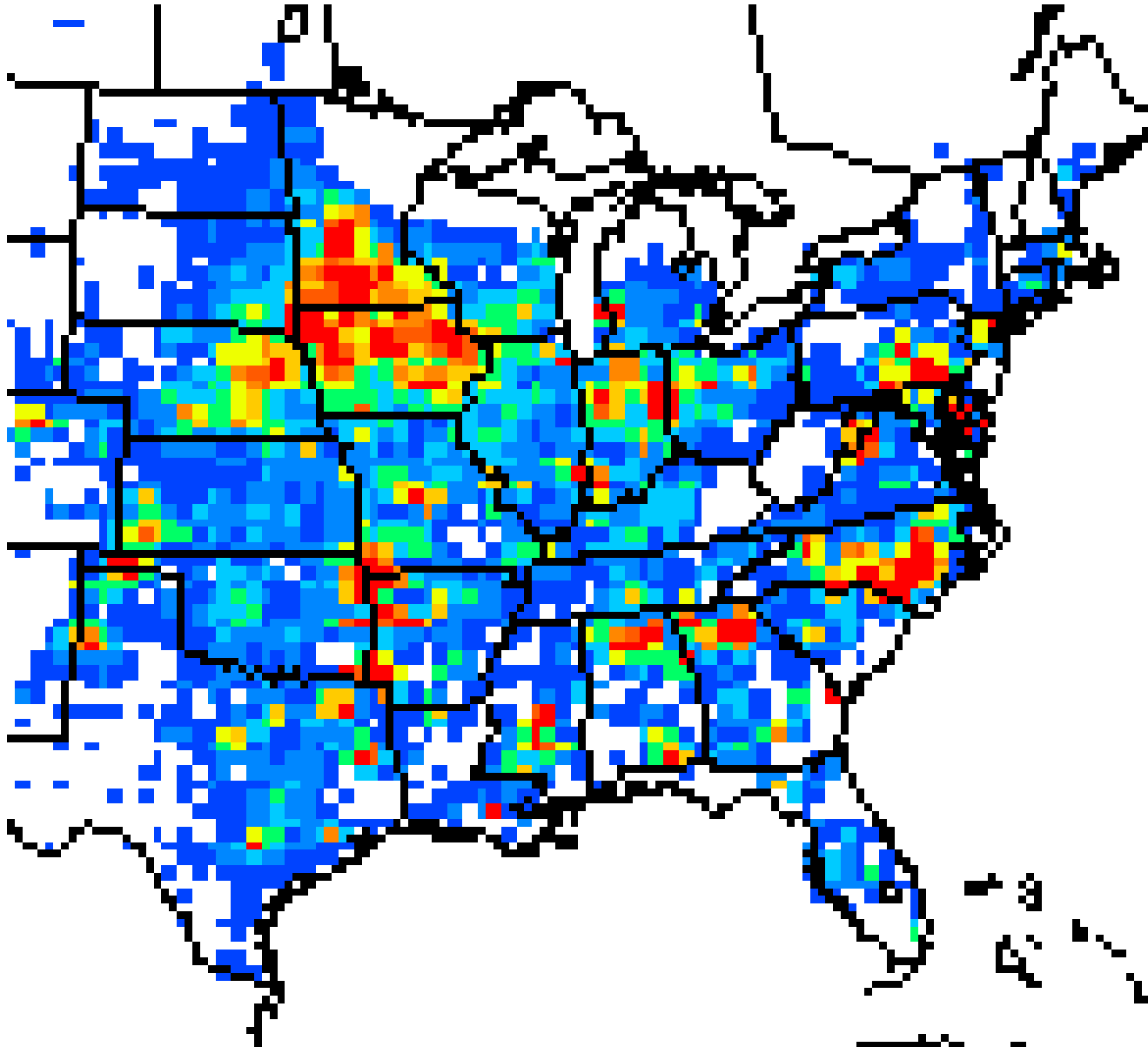
- NAAQS? **No**
- Toxic? **Not at ambient concns.**
 - TLV=50 ppm, typical ambient = <1-3 ppb
- Nuisance? **Yes, at sources (animal feeding, manure spreading)**
- Urban pollutant? **Don't really know**
- Direct environmental effects? **Principal basic gas in atmosphere; deposition results in acidification**
- Chemically reactive? **Yes**

Reactions of ammonia

- $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$ (ammonium nitrate)
- $\text{H}_2\text{SO}_4 + 2 \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4$ (ammonium sulfate)
- Ammonium nitrate and sulfate are two of the top three constituents of PM_{2.5}
- Ammonia reacts preferentially with sulfate so ammonium nitrate is formed only after all sulfate is fully neutralized
- Ammonium nitrate is formed preferentially at low temperatures and high humidity (winter, nighttime)
- Decreasing sulfate can theoretically cause ammonium nitrate concentrations to increase

Why focus on the Midwest?

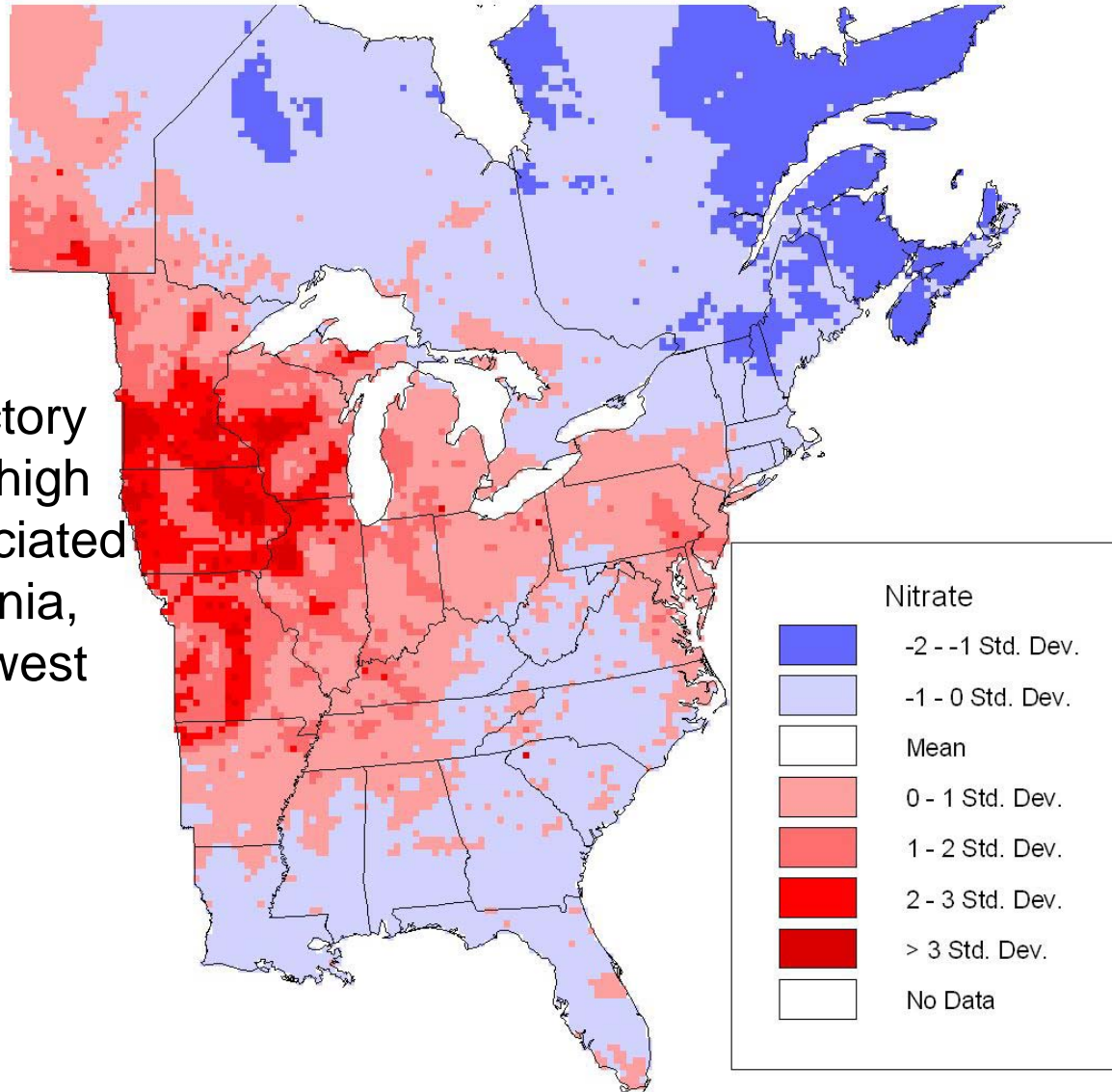
1. Ammonia Emissions Density



Why focus on the Midwest?

2. Ammonia/Nitrate link

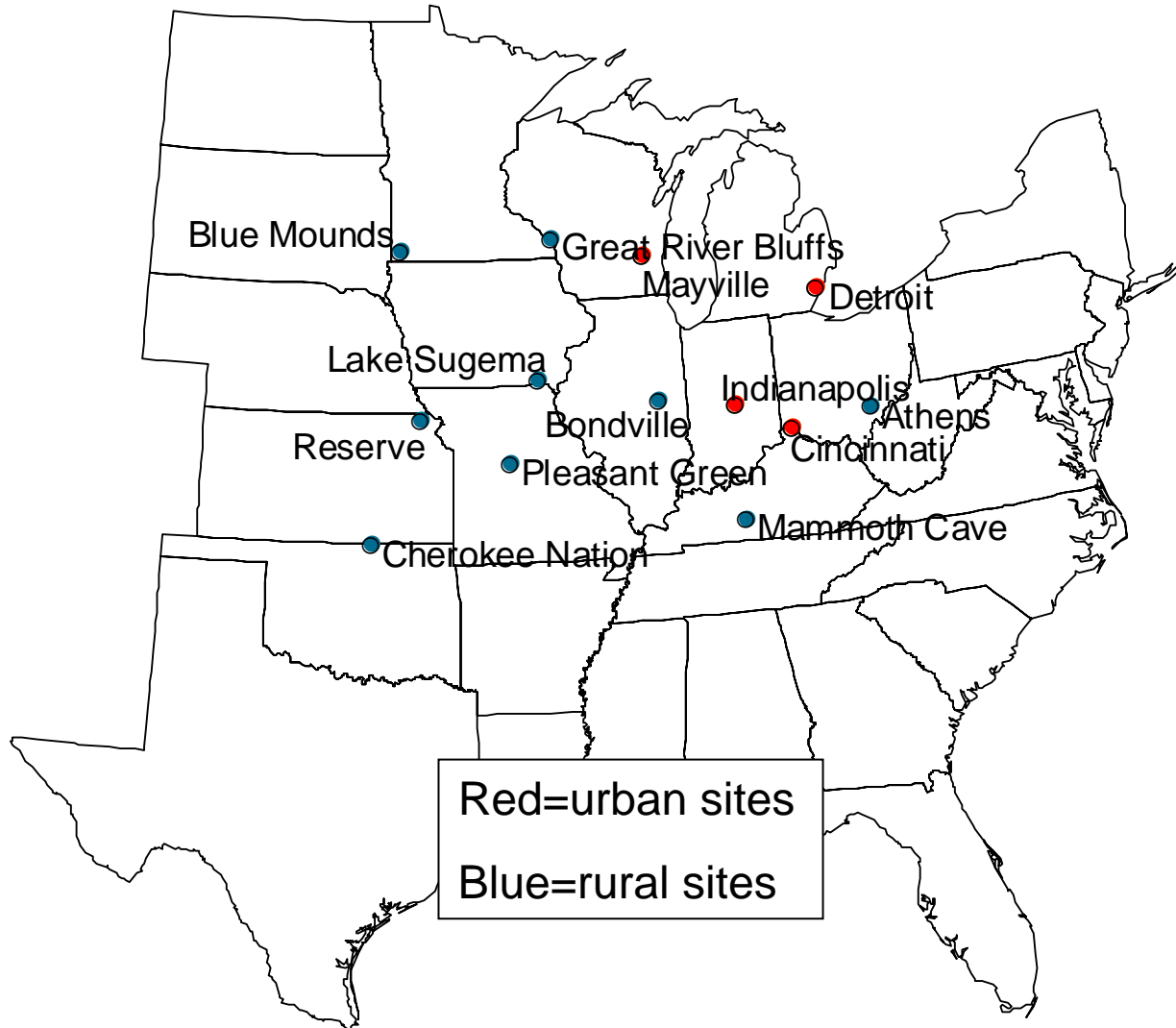
Ensemble trajectory analysis shows high PM nitrate associated with high-ammonia, agricultural Midwest



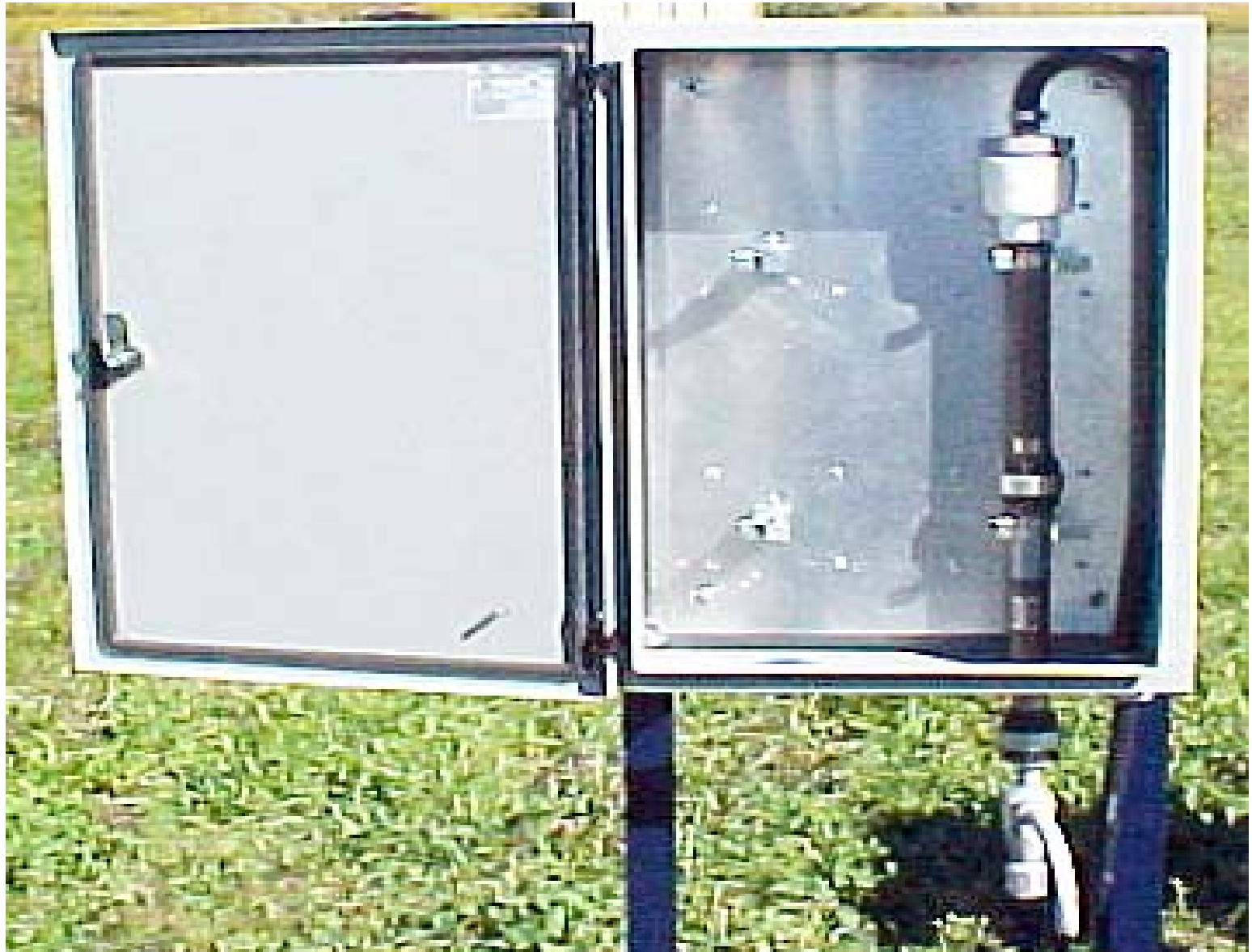
Overview

- Despite importance of ammonia in atmospheric chemistry, no national studies or routine monitoring of ambient (**non-source-influenced**) concentrations has been done
- To fill data gap, MRPO and CENRAP began rural monitoring in Oct. 2003
- Beginning network--10 sites: 9 rural, 1 urban
- Current network – 12 sites, 8 rural, 3 urban
- All rural sites are IMPROVE sites except Pleasant Green, MO
- Denuder/filterpack sampling
 - Phosphoric acid coated denuder for NH₃
 - Sodium carbonate coated denuder for HNO₃ and SO₂
 - Teflon filter followed by nylon filter (for nitrate dissociation)
 - Two sites (Pleasant Green MO, Lake Sugema IA) use automated R&P samplers (different denuder/inlet configurations)
- 1/6 day sampling
- Two continuous samplers, Pranalytica and IC, at Bondville for QA
- Both NH₃ and HNO₃ very difficult to measure, due to reactivity, 'stickiness', low ambient concentrations, significant inlet losses

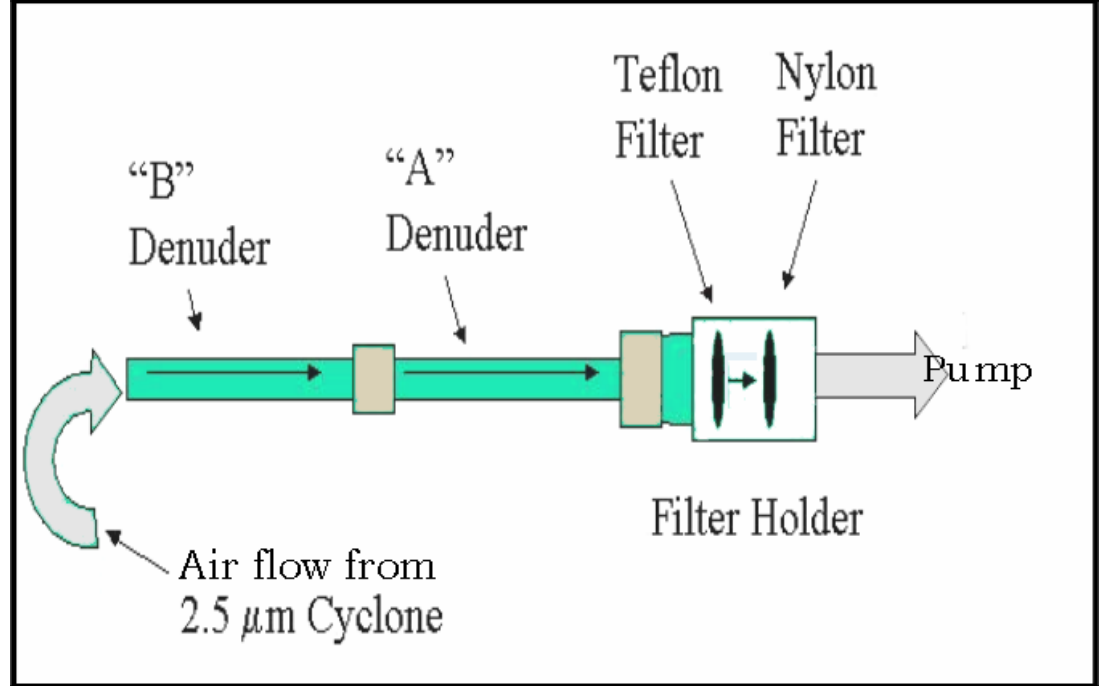
LADCO-CENRAP NH3 Network



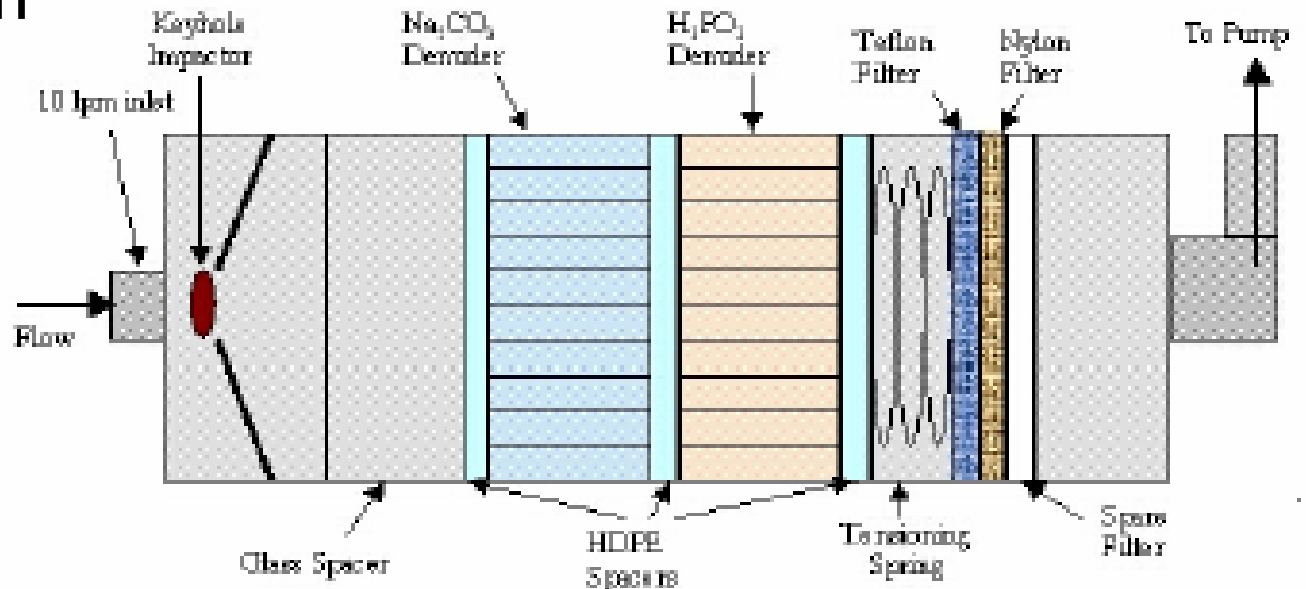
Custom-built URG sampler



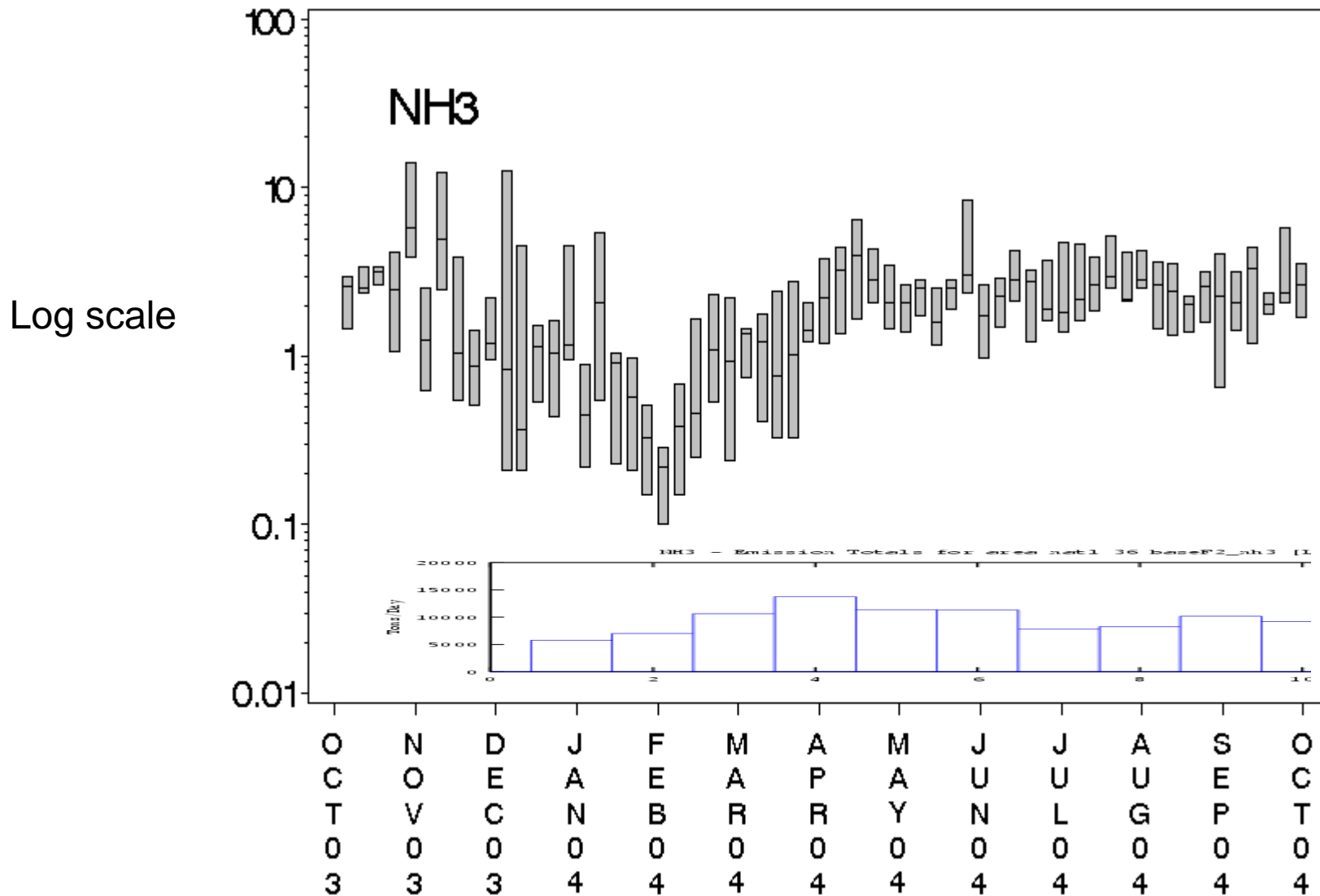
URG System



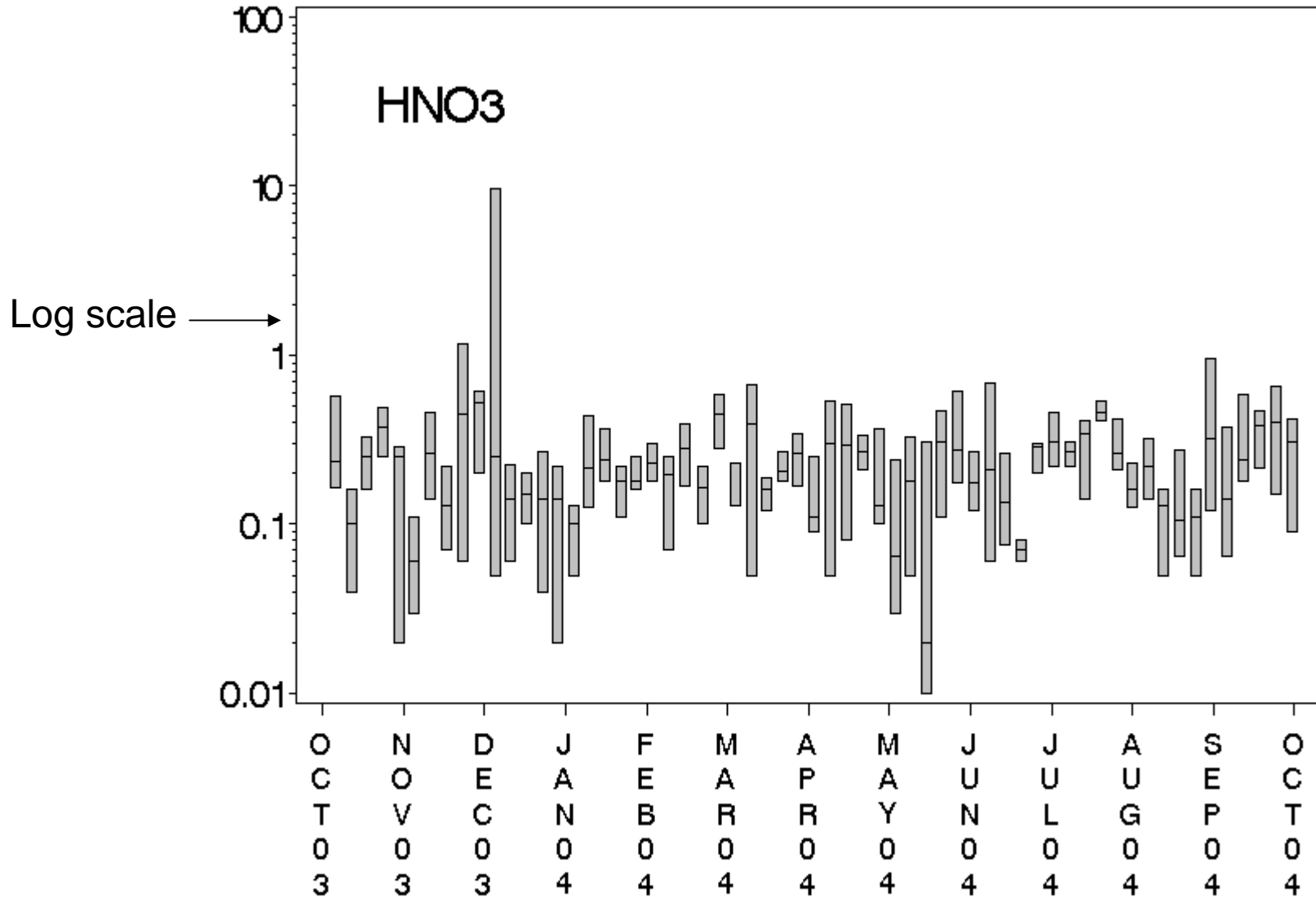
R&P System



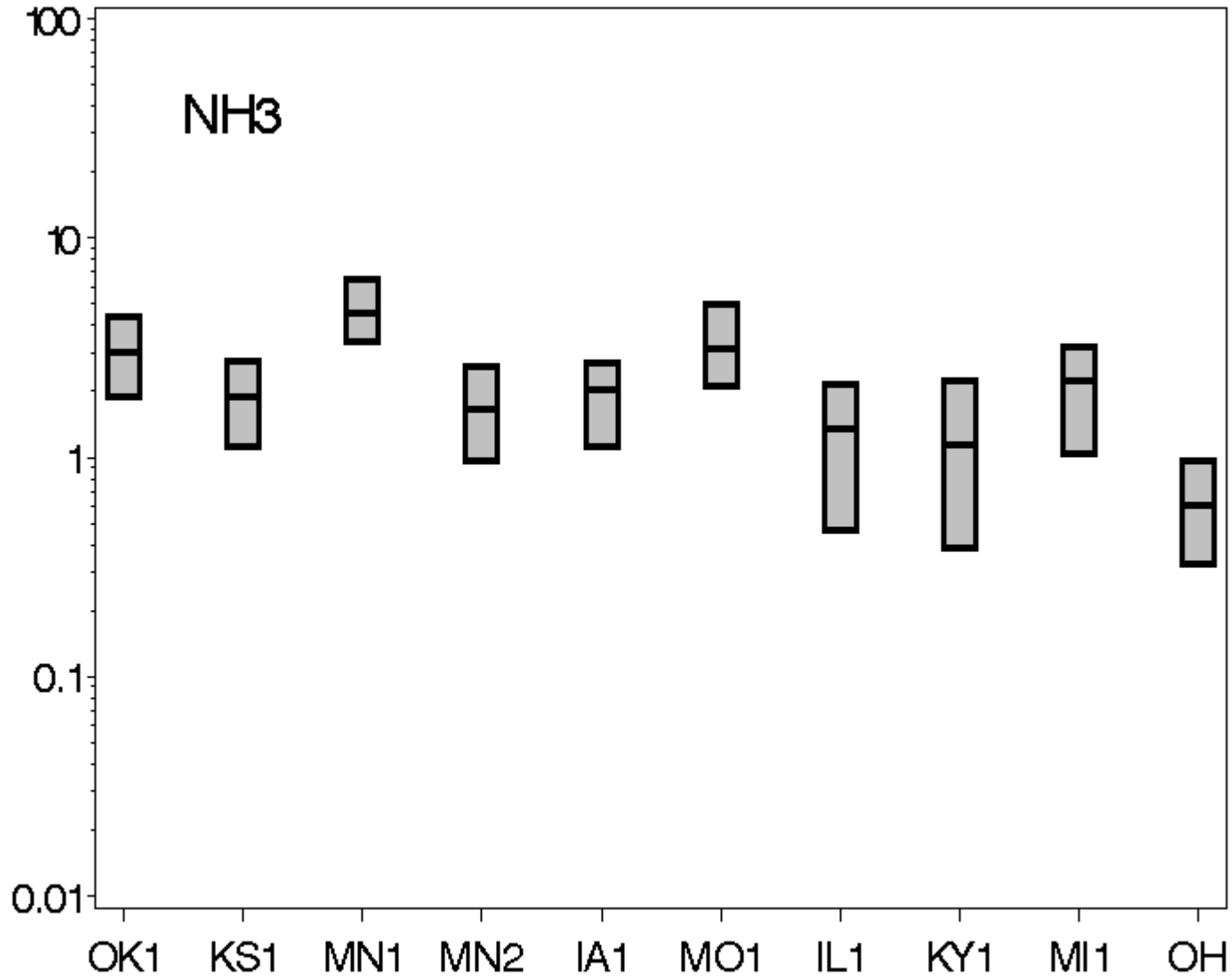
Temporal variation in NH3



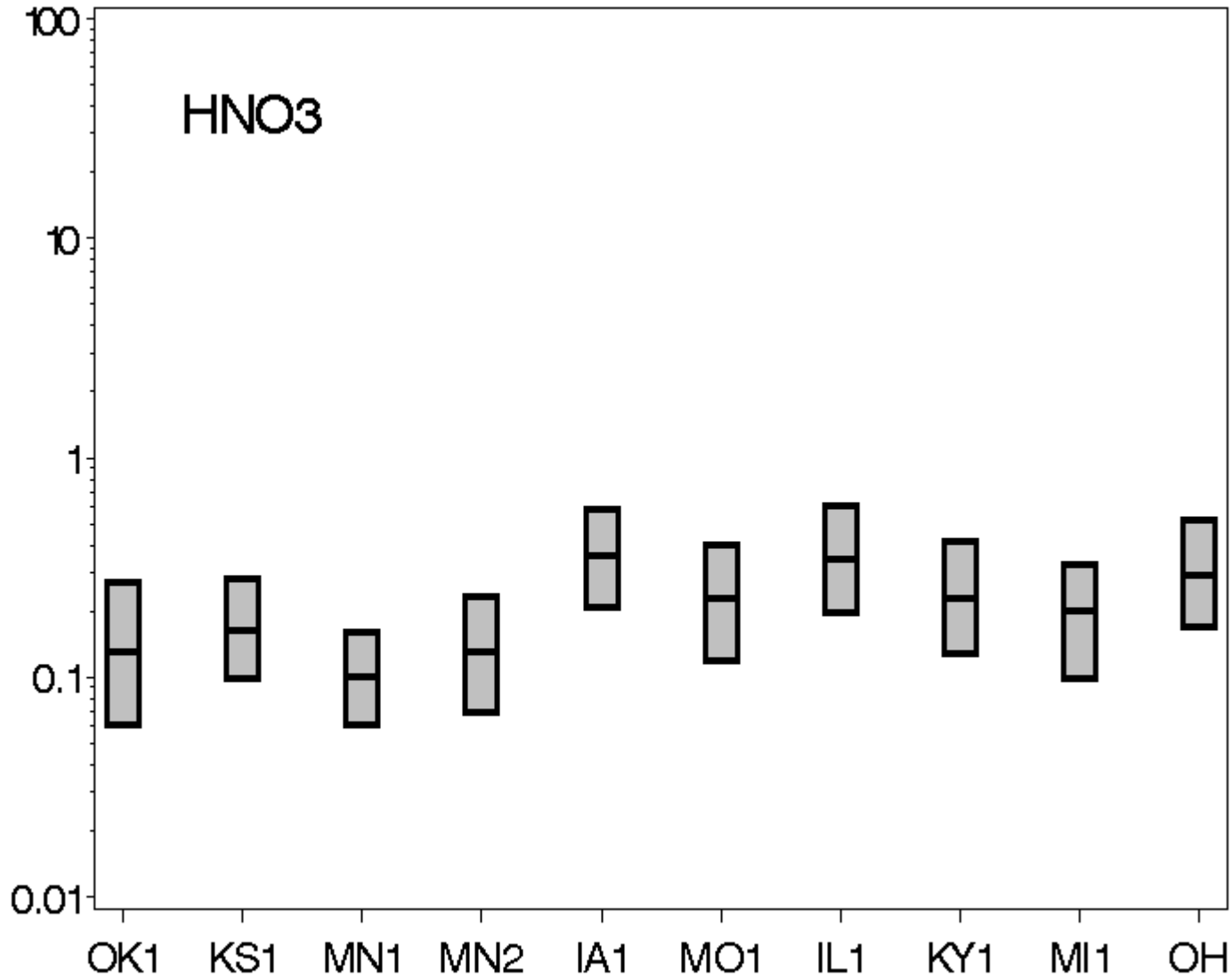
Temporal variation in HNO₃



Spatial variation in NH₃



Spatial variation in HNO₃

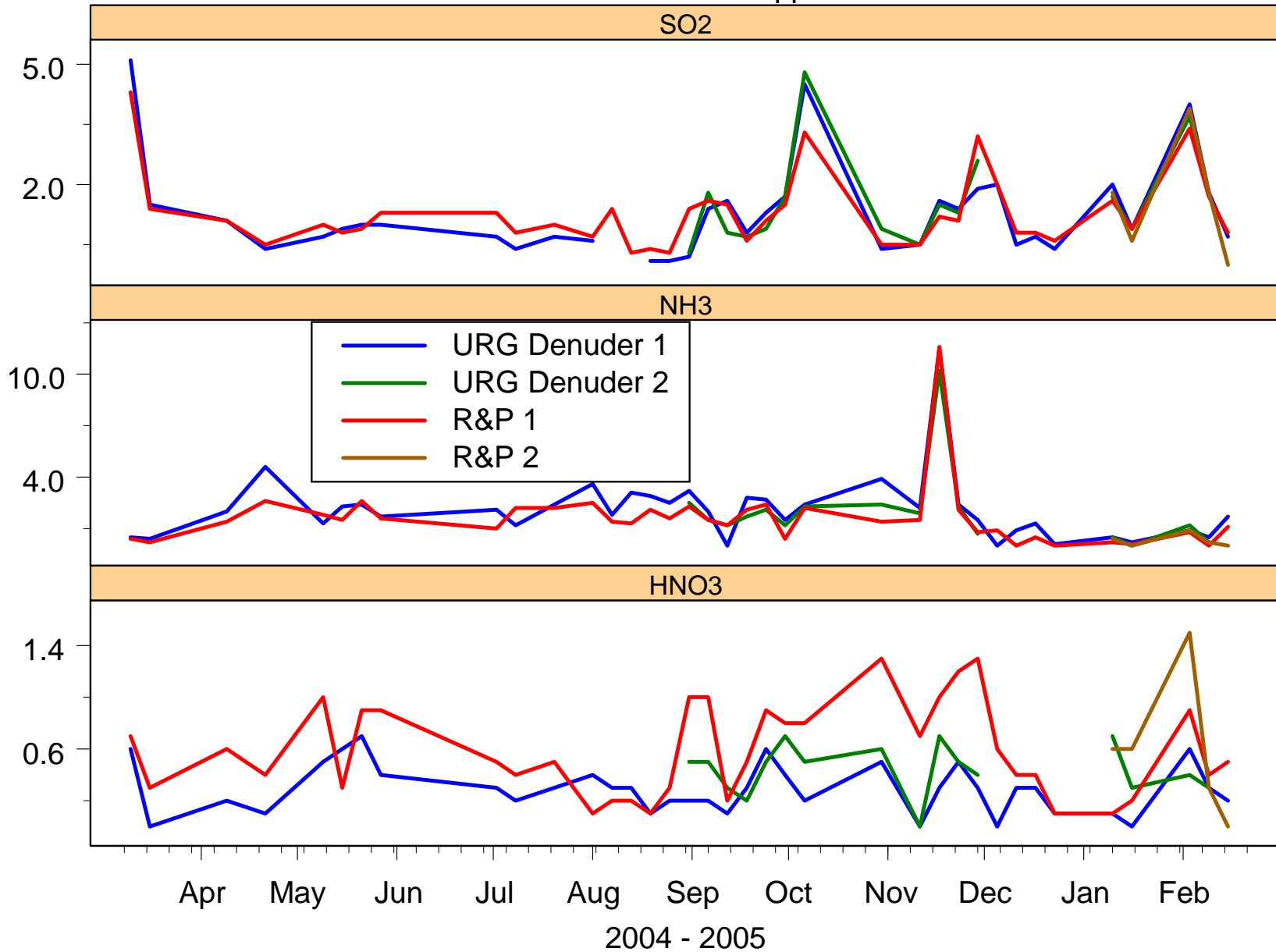


QA Comparisons at Bondville

- Species comparisons
 - Collocated URG and R&P, March 2004-Feb 2005
 - Collocated URGs, Sep. 2004 – Feb. 05
 - Collocated R&Ps, Jan-Feb. 05
- Cyclone Effects
- Denuder Breakthrough
- Ammonium Losses from Filters

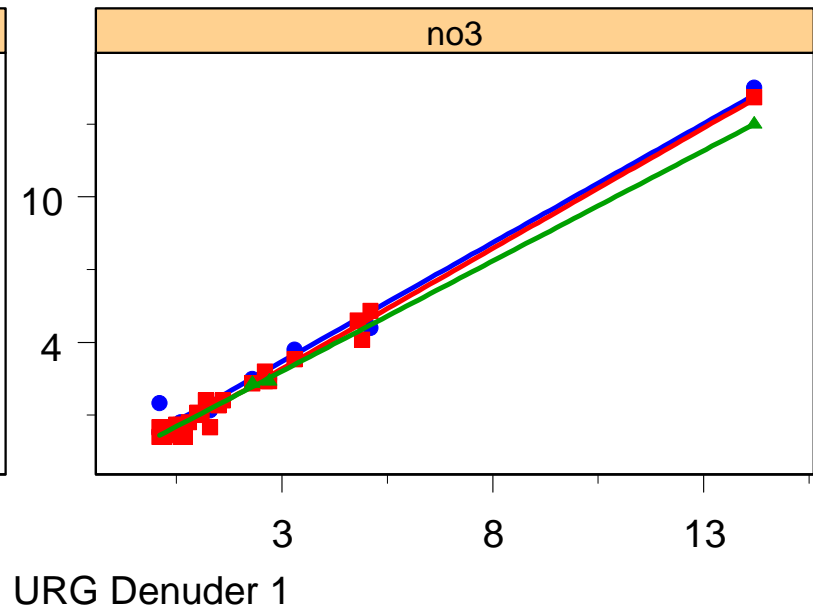
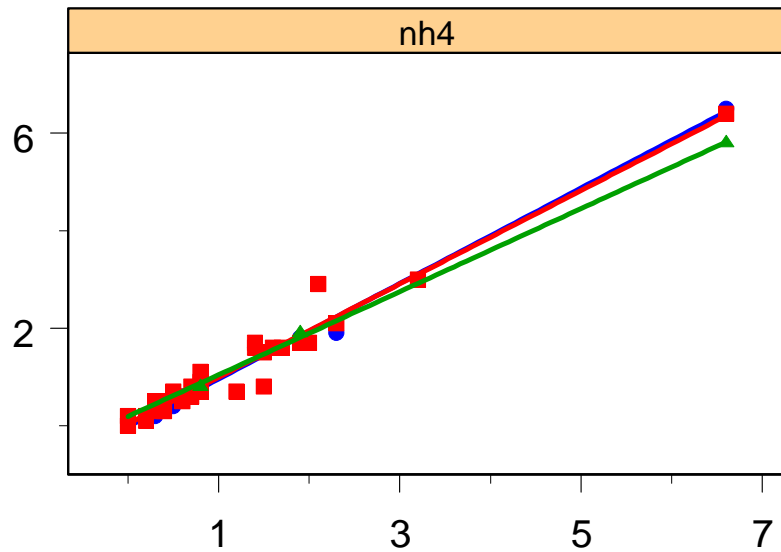
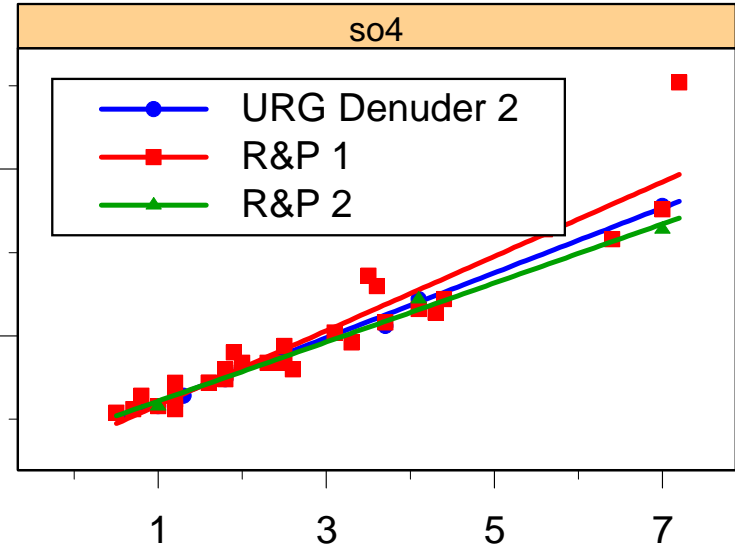
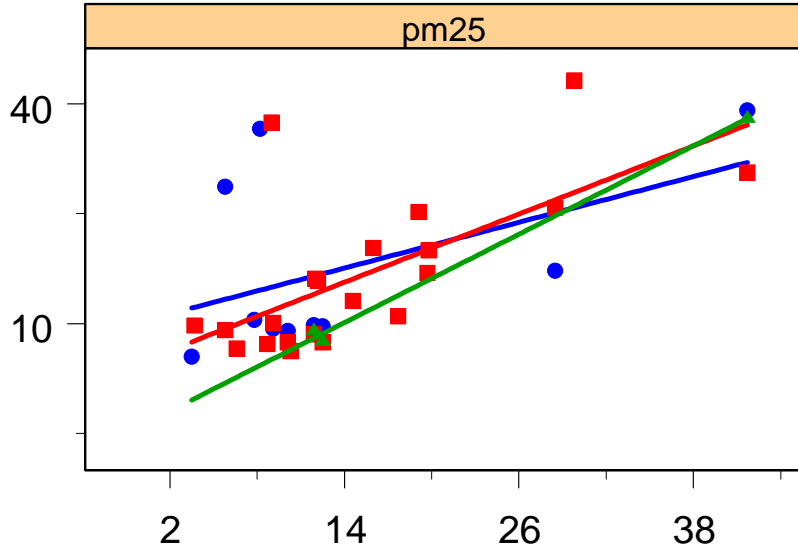
Sampler Intercomparison -- Gases

Concentration in ppb



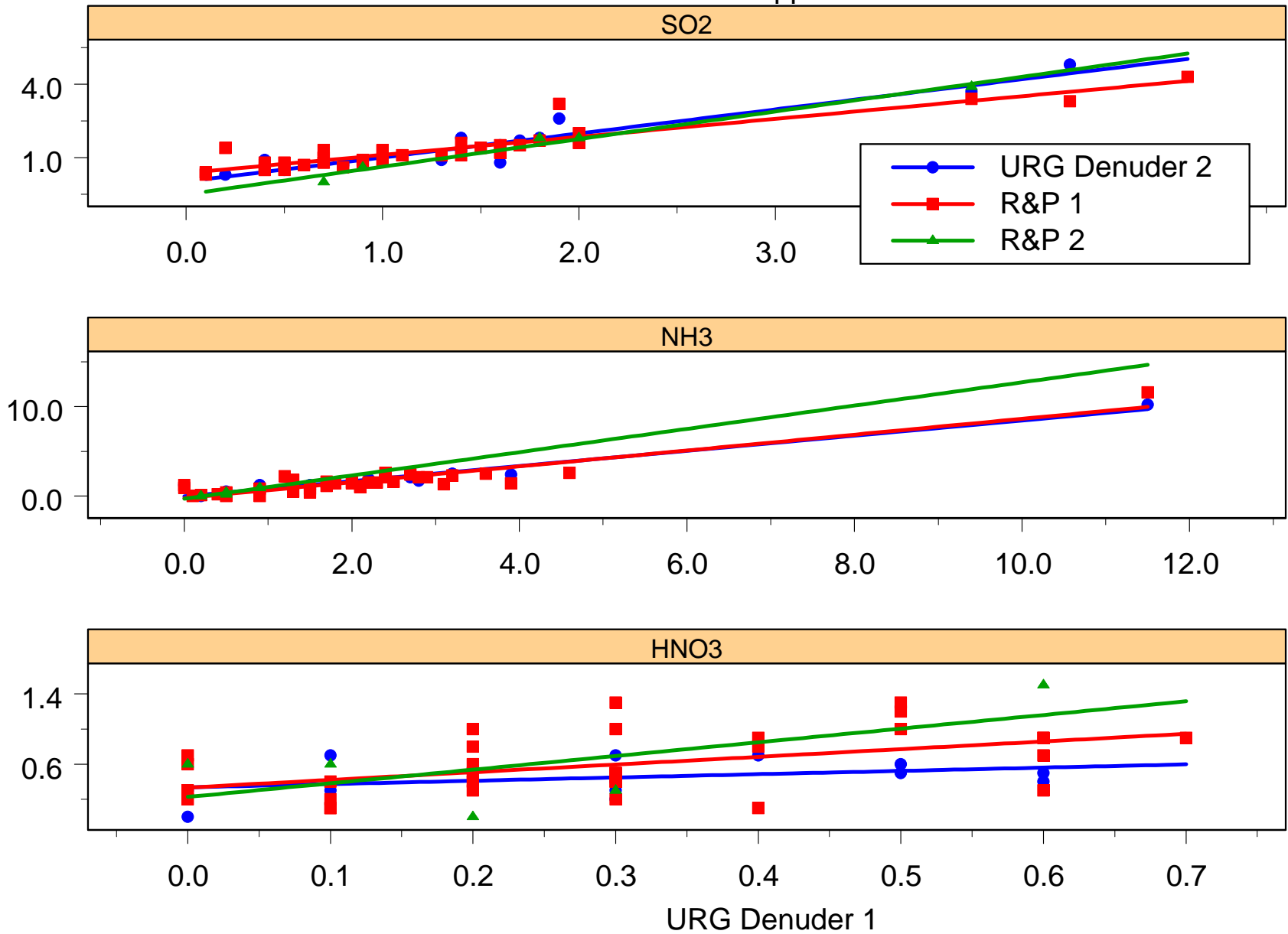
Sampler Intercomparison -- Particles

Concentration in ug/m3



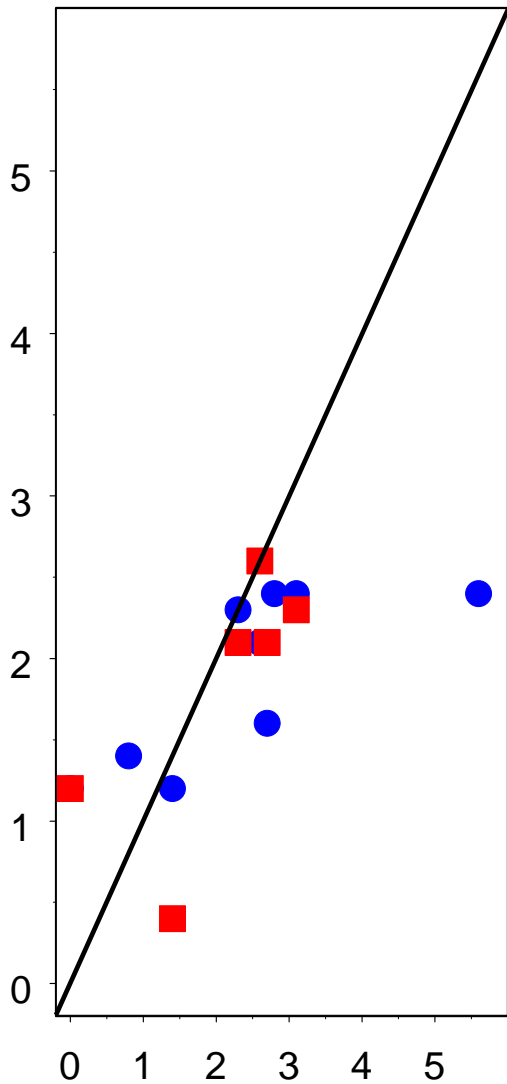
Sampler Intercomparison -- Gases

Concentration in ppb

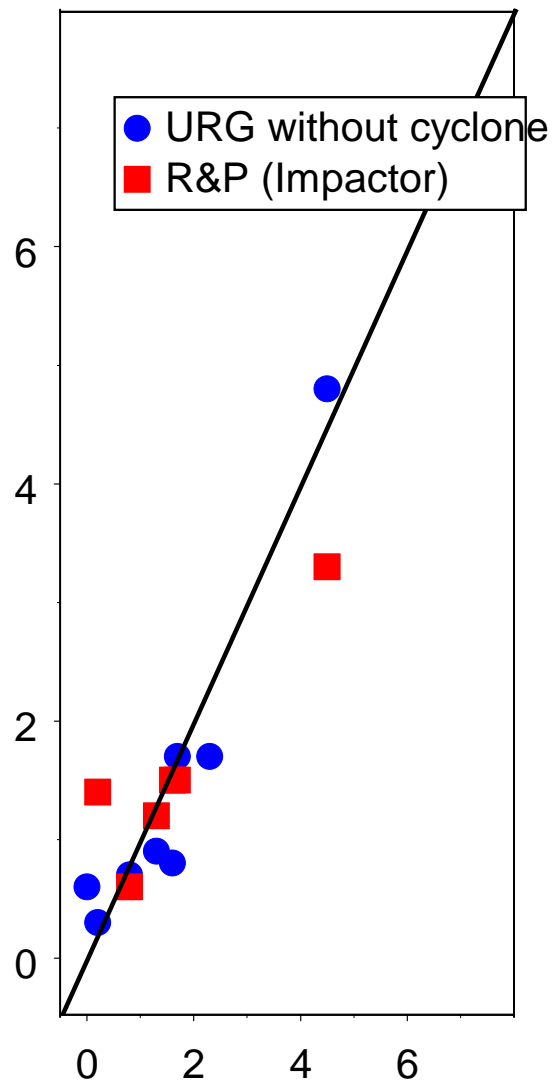


Cyclone Effects

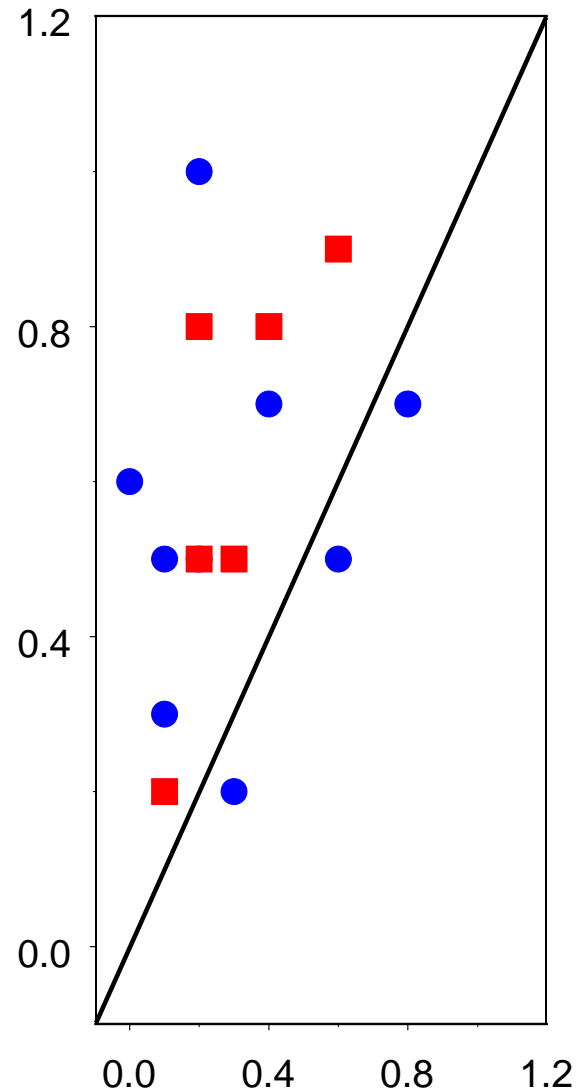
NH₃ (ppb)



SO₂ (ppb)

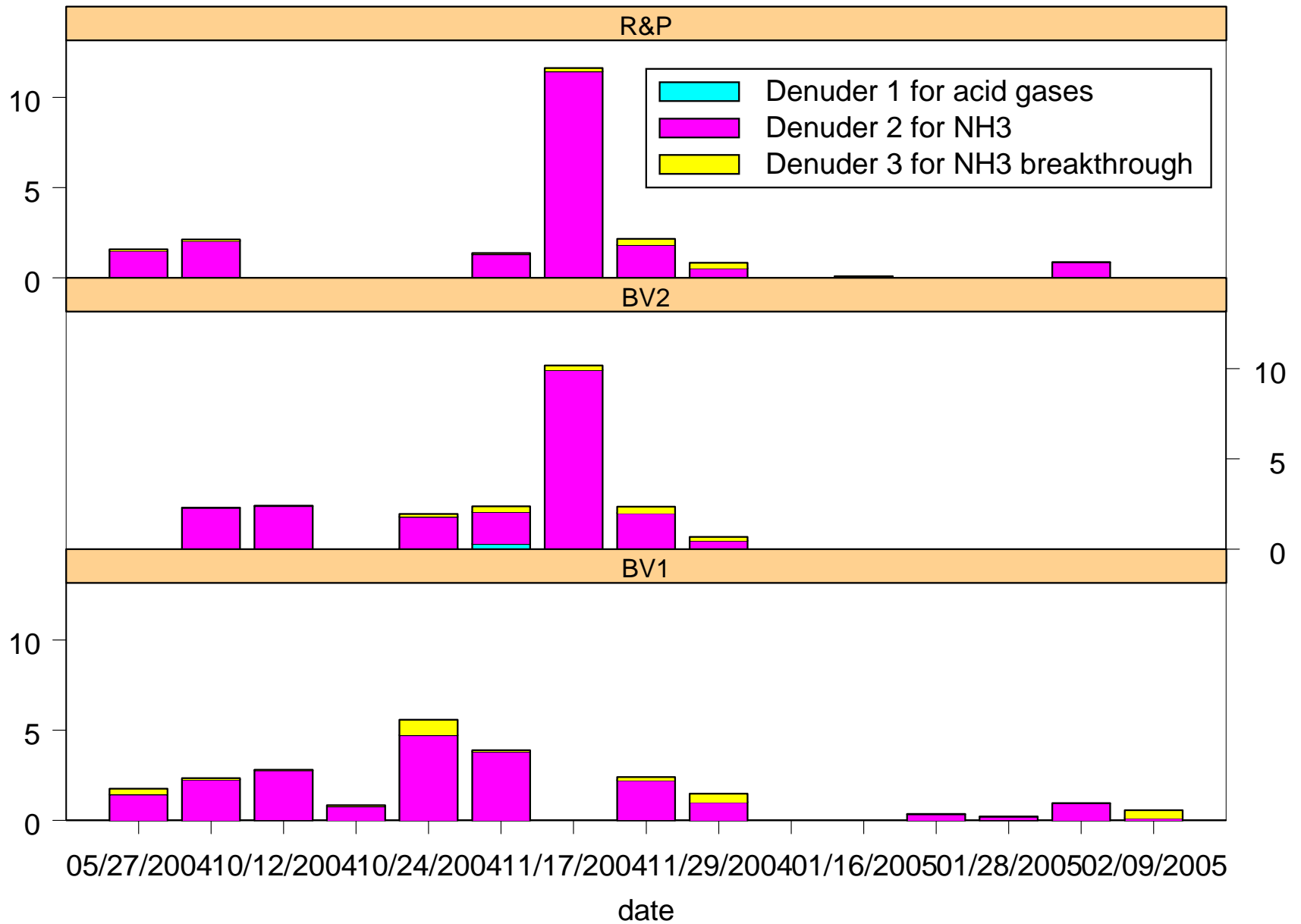


HNO₃ (ppb)

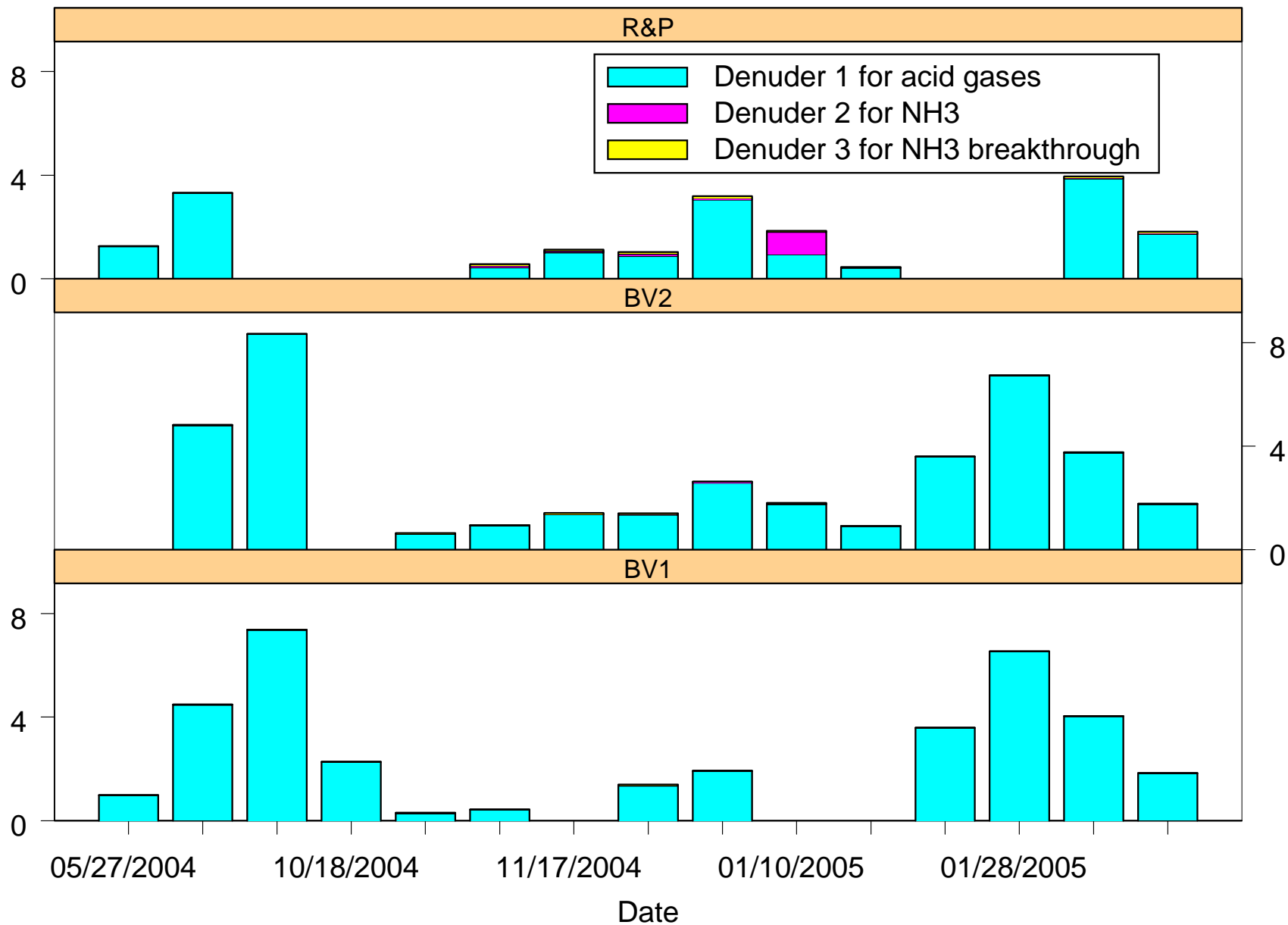


URG with Cyclone

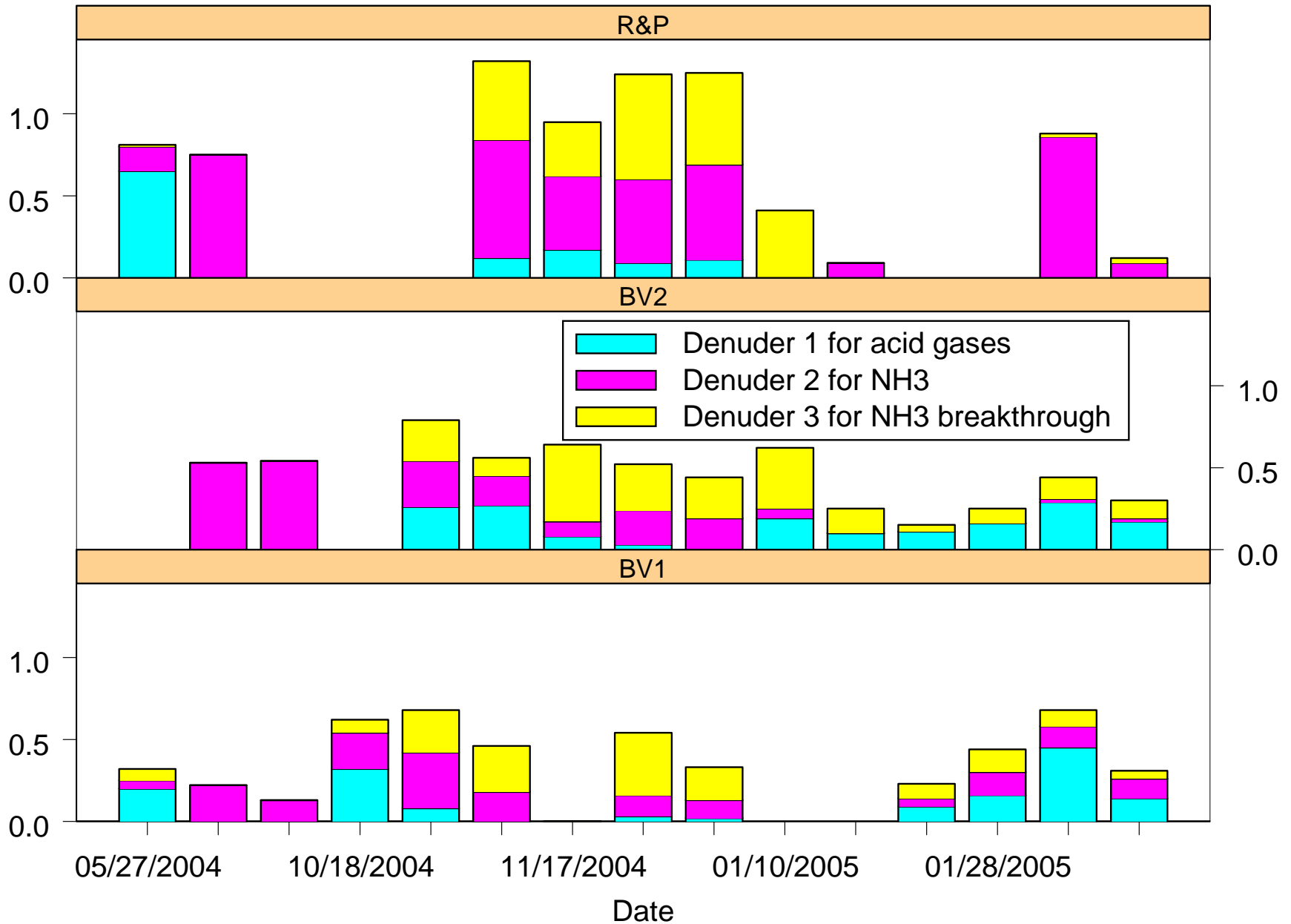
NH3 Breakthrough, ppb



SO2 Breakthrough, ppb

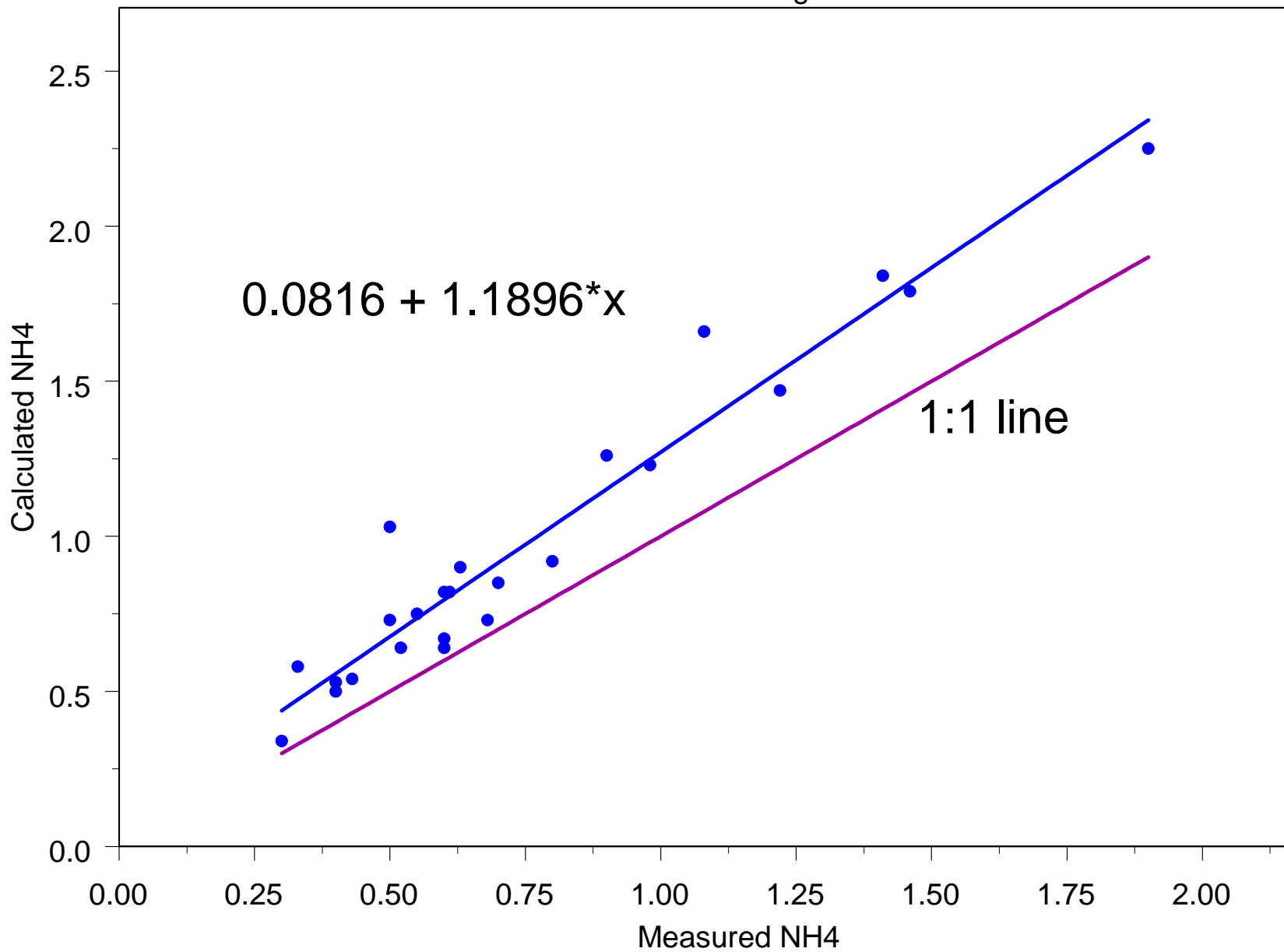


HNO3 Breakthrough, ppb



Ammonium Losses from Filters

Concentration in ug/m3

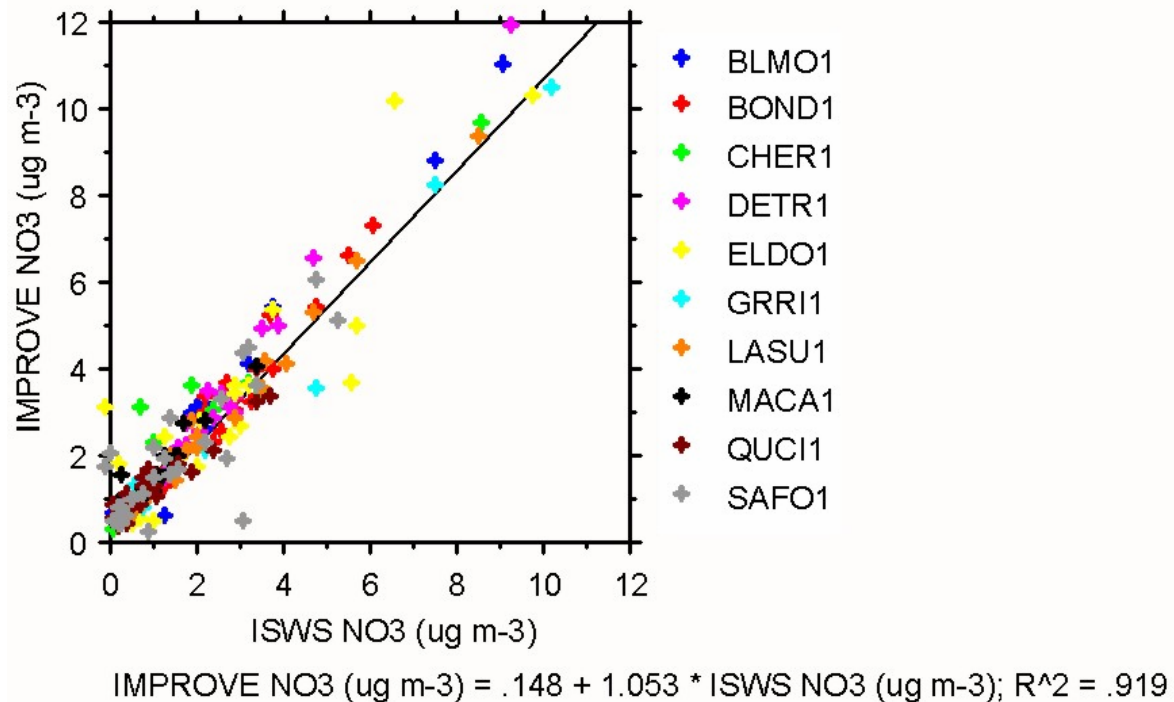
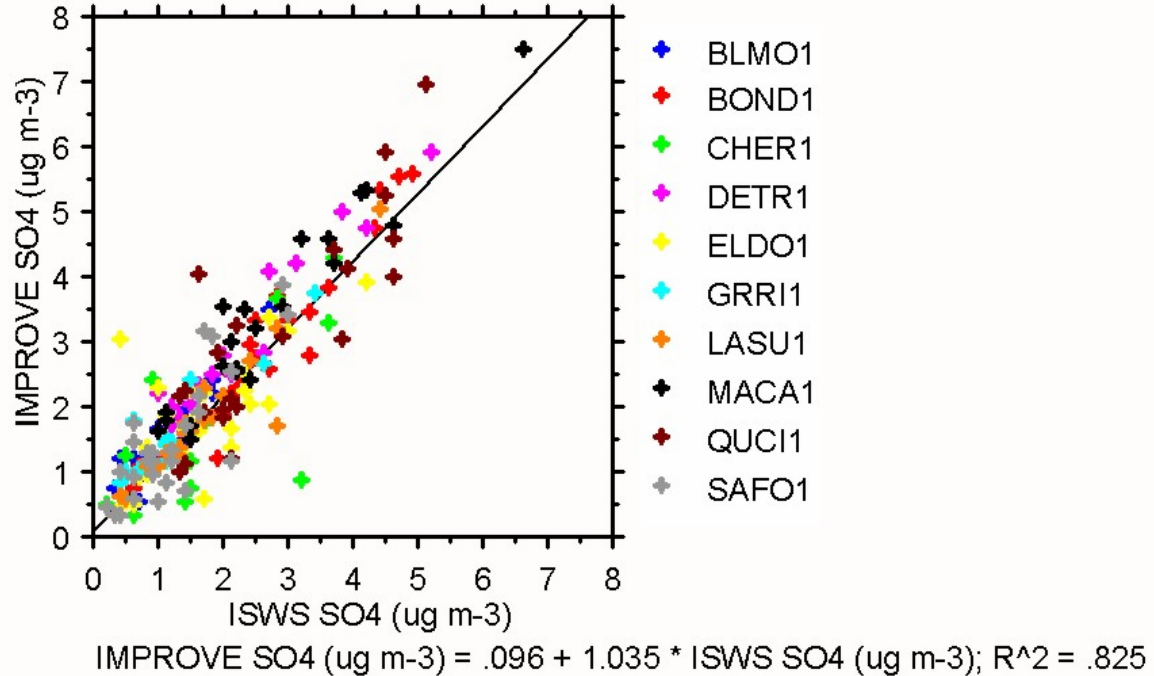


How good are the network data?

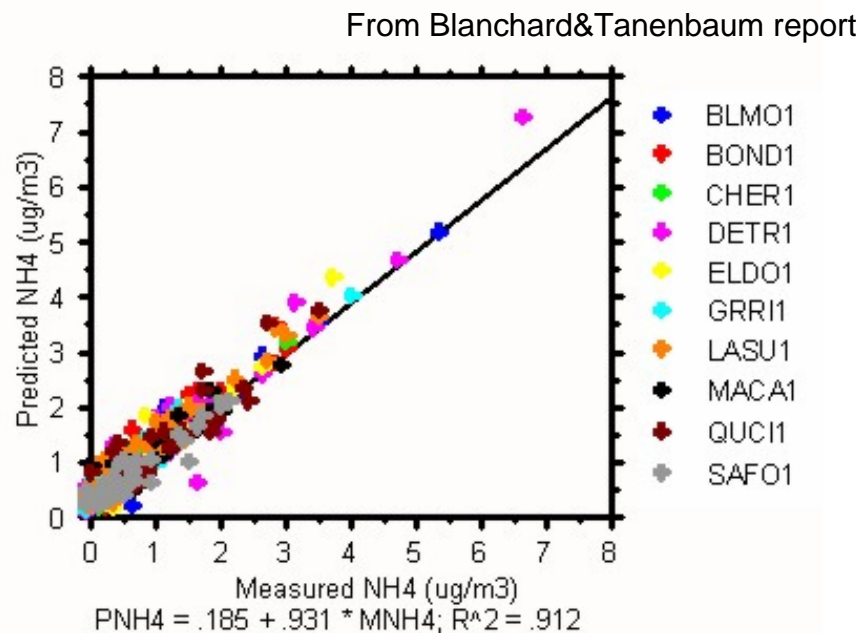
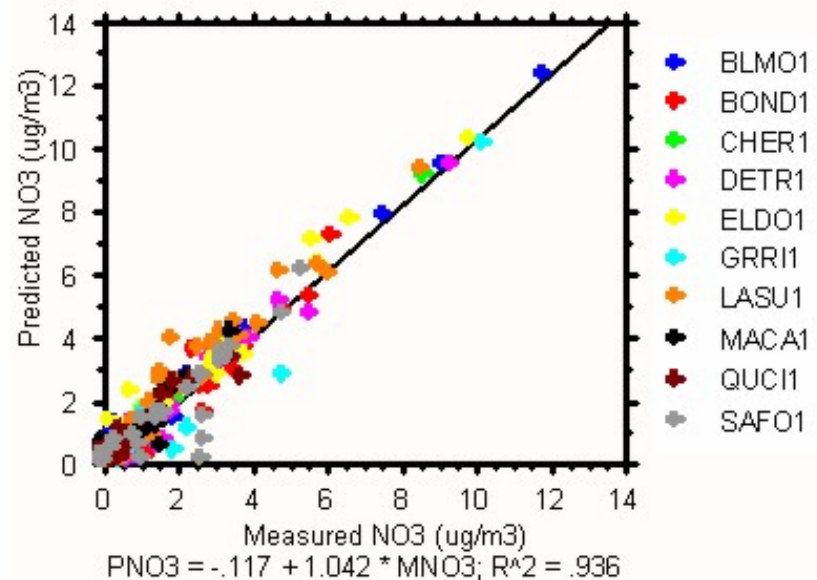
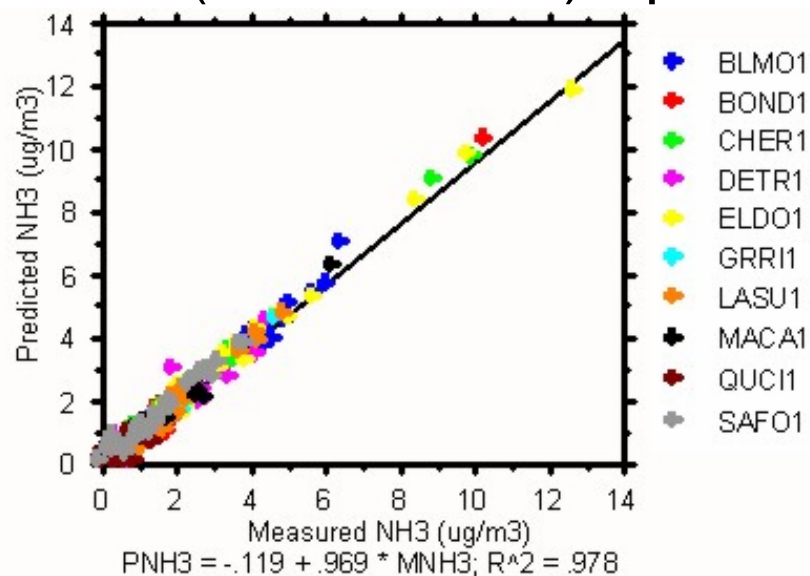
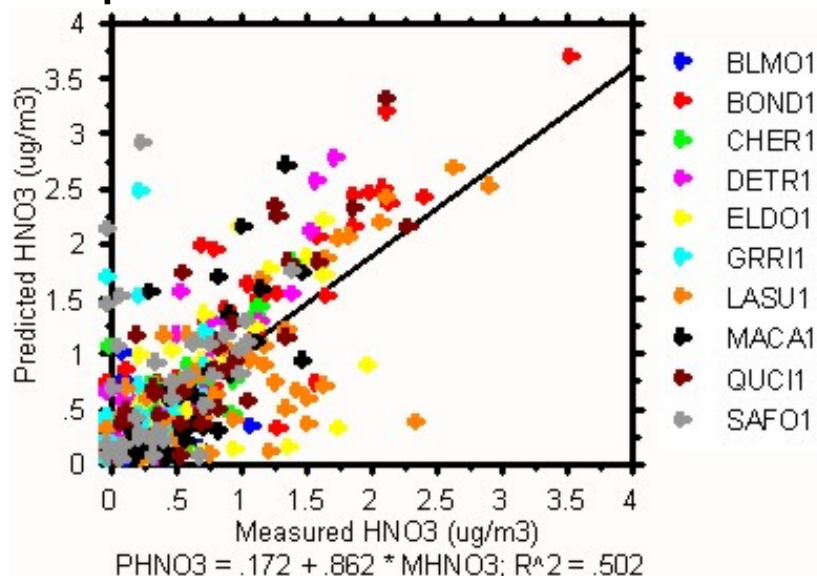
- Comparison of collocated monitors
- Comparison with IMPROVE
- Comparison with modeled data

Comparison of IMPROVE with LADCO data

Work by Blanchard & Tanenbaum



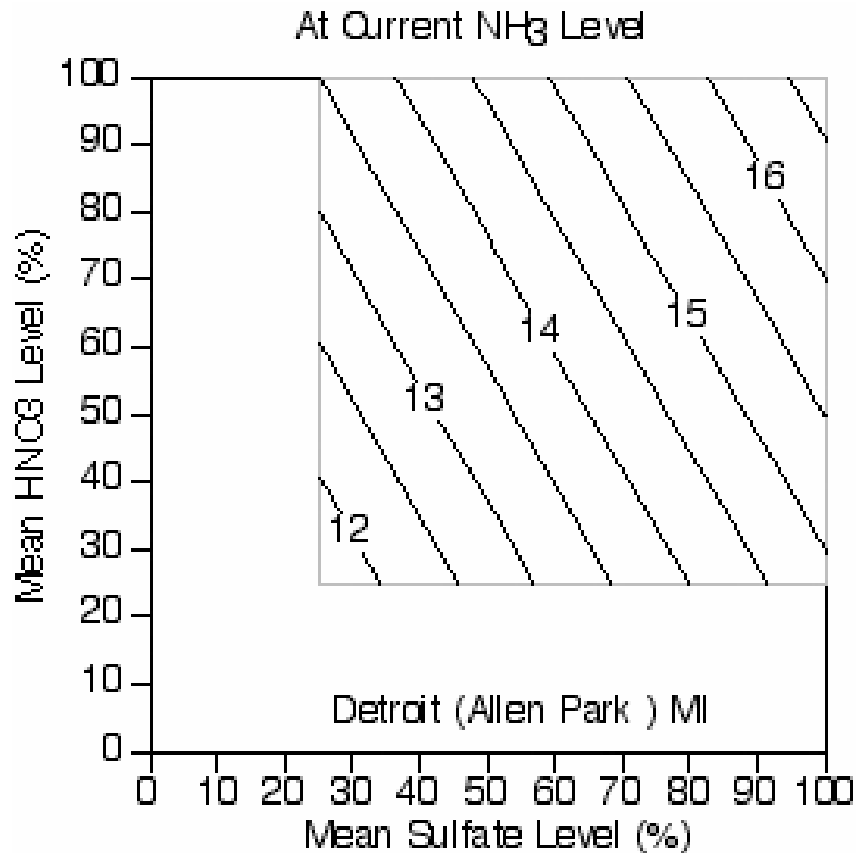
Comparison of Ambient with Modeled (ISORROPIA) Species



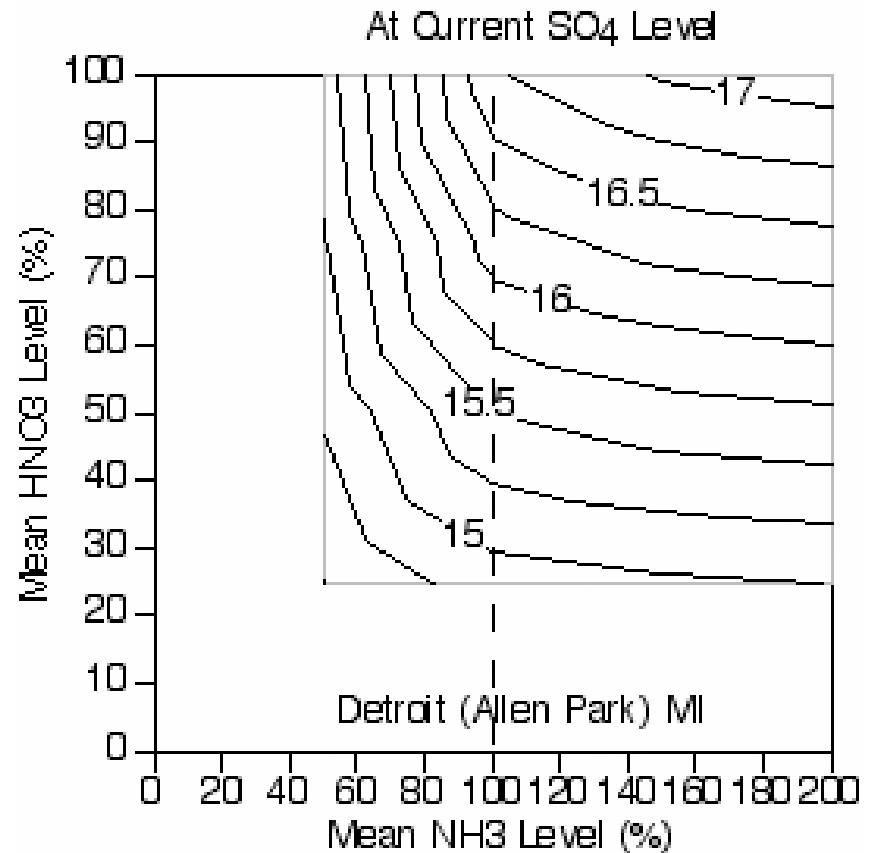
Thermodynamic Models— ISORROPIA and SCAPE2

- Thermodynamic models predict the partitioning of PM species between gas and particle phases, based on concentration, temperature, and RH
- Using measured NH_3 , HNO_3 , NH_4 , NO_3 , and SO_4 , systematically vary concentrations from starting (ambient) conditions and calculate new equilibrium concentrations
- Resulting isopleths tell us how sensitive PM is to changes in precursors
- SO_4 and NO_3 – 25, 50, 75, 100% of current
- NH_4 – 50, 100, 150, 200% of current

Predicted PM_{2.5} Concentrations



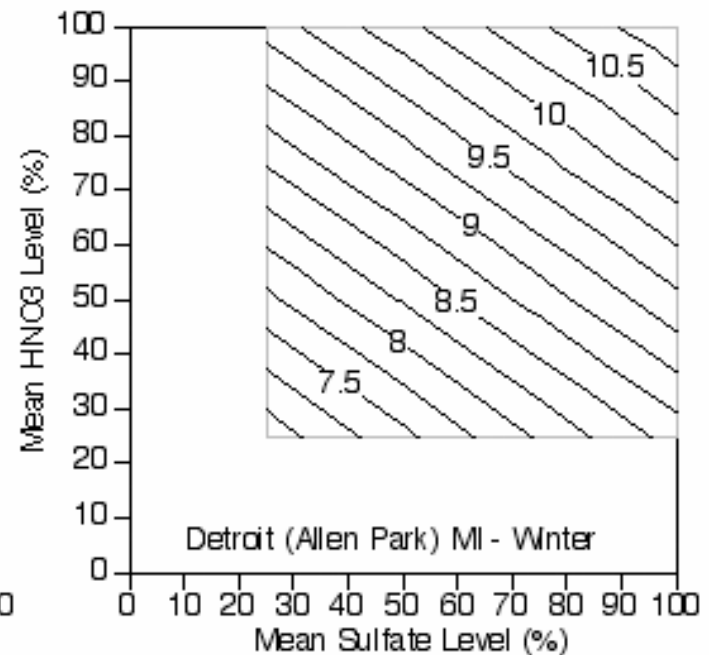
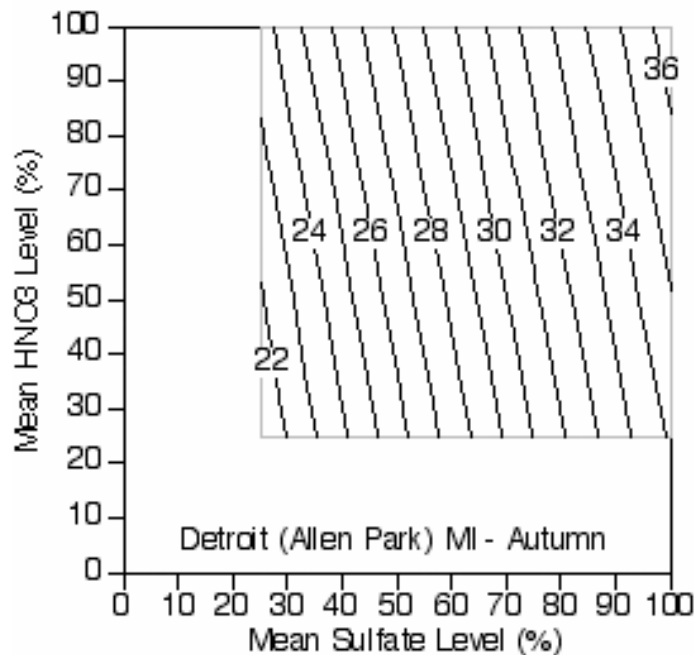
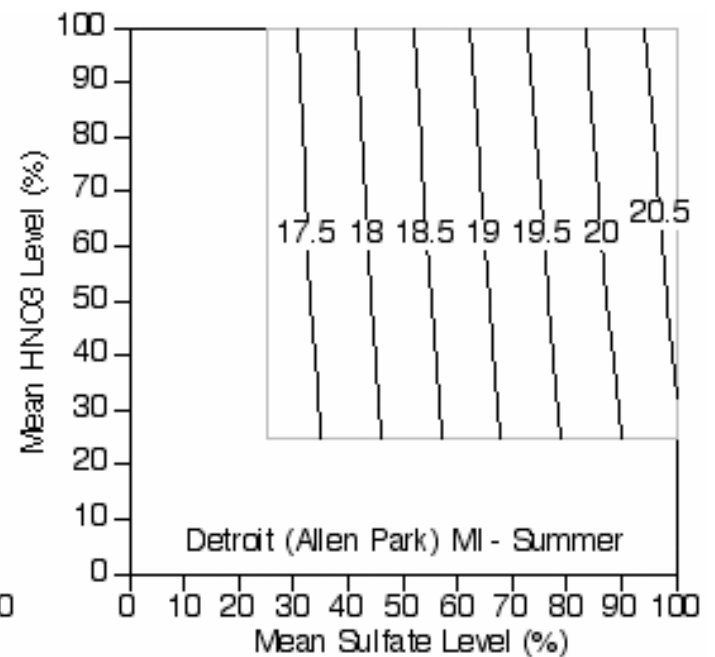
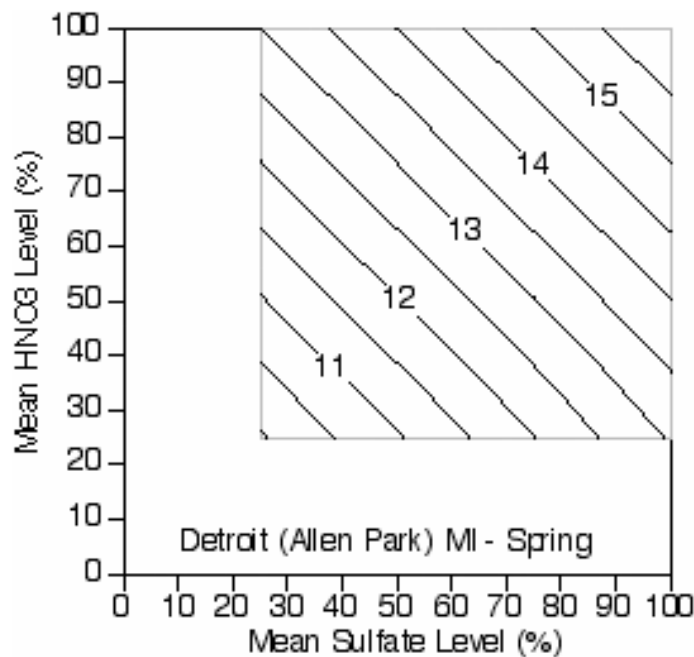
PM is about equally sensitive to reductions in SO₄ and NO₃



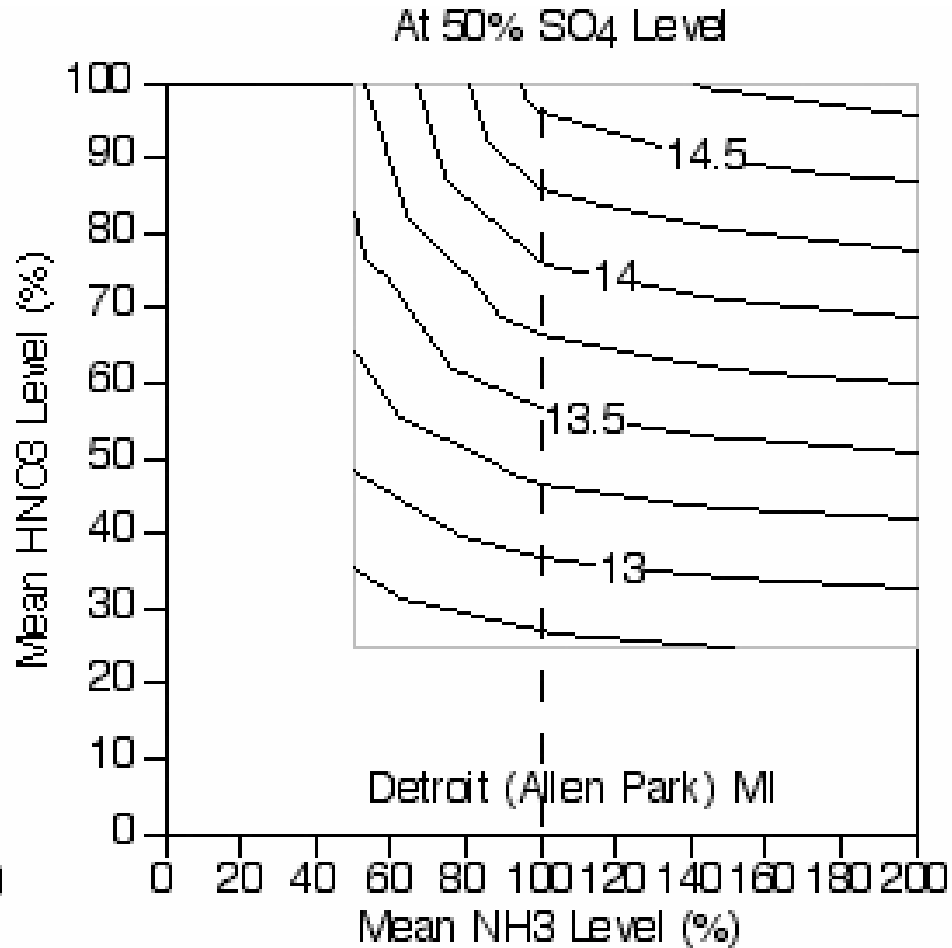
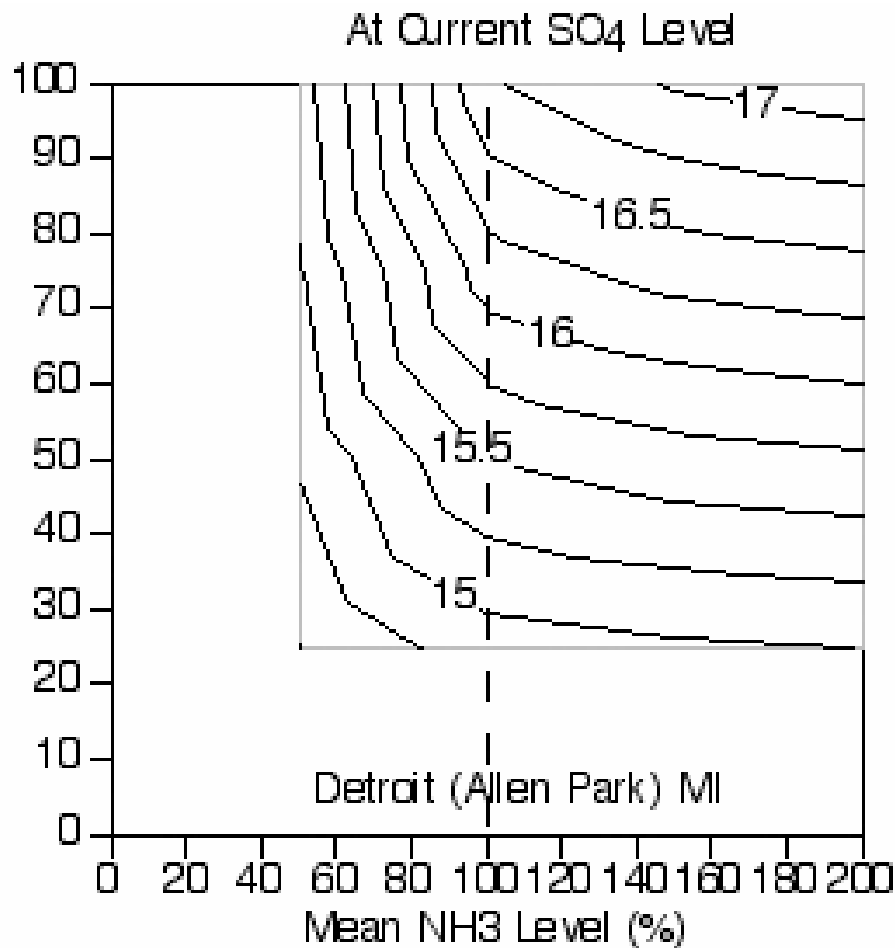
PM is slightly more sensitive to NH₃ reductions than to HNO₃

Seasonal PM_{2.5} Concentrations

PM is most responsive to NO₃ in the winter; response to sulfate is similar year-round.



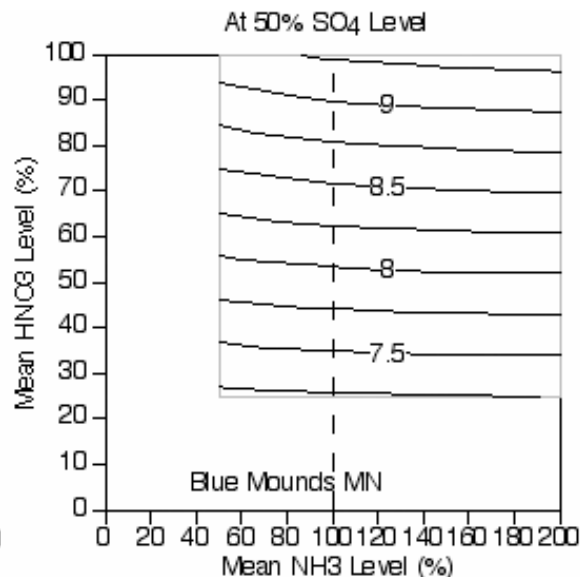
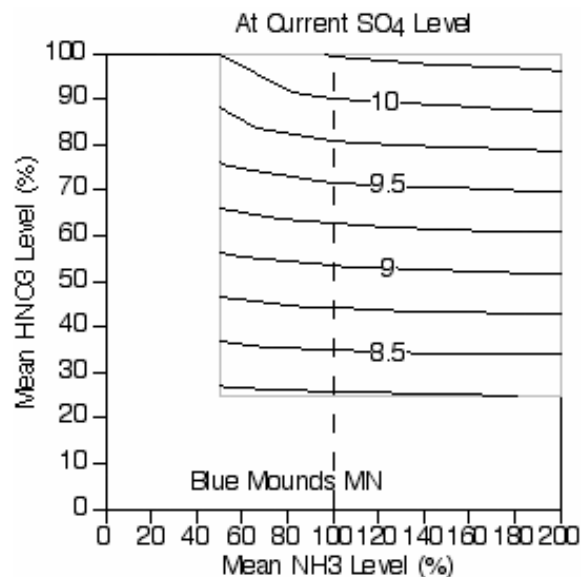
Predicted PM_{2.5} Concentrations



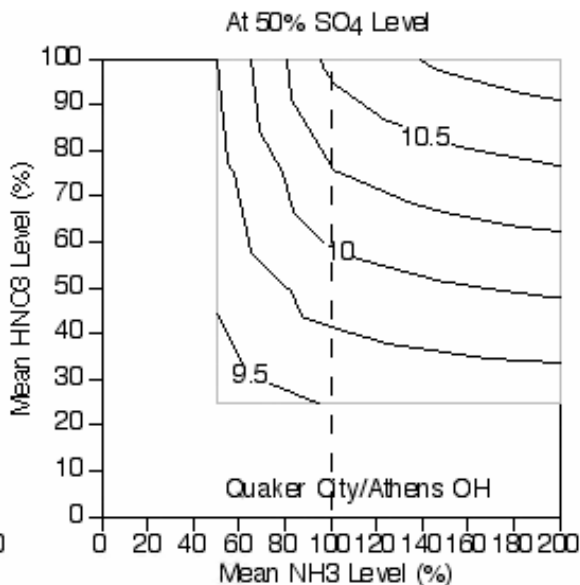
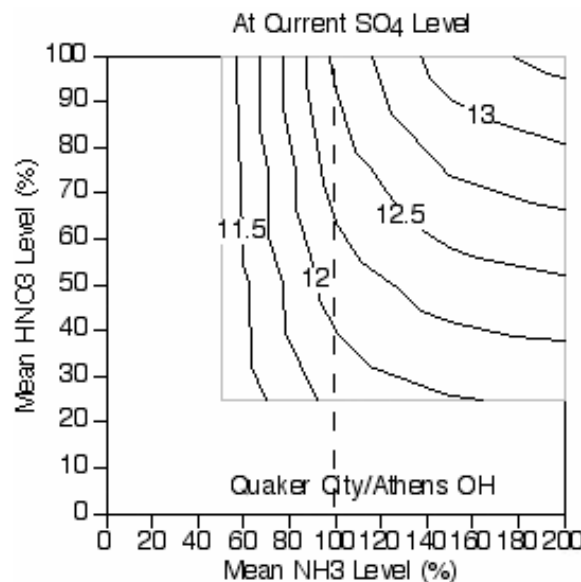
Expected reductions in SO₄ may lead to PM being less responsive to reductions in ammonia

Geographic extremes

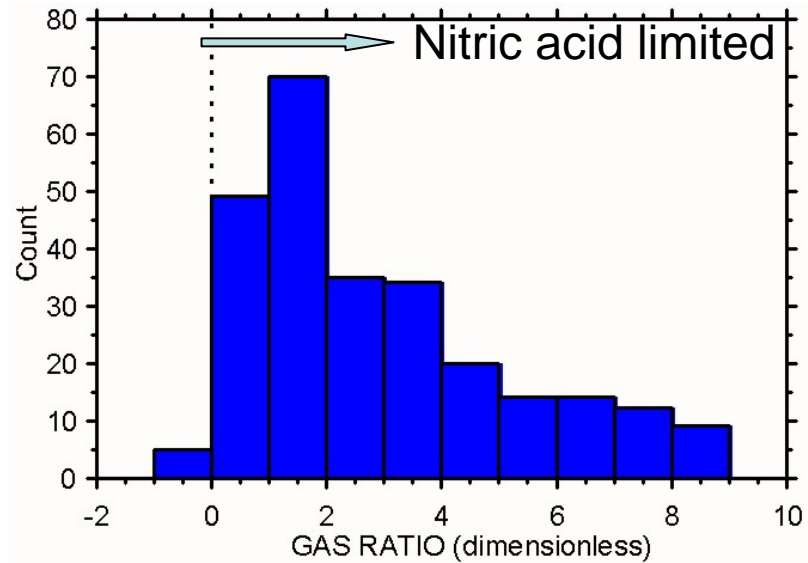
Blue Mounds, MN:
Least sensitive to
NH₃; farthest north,
and highest NH₃ site



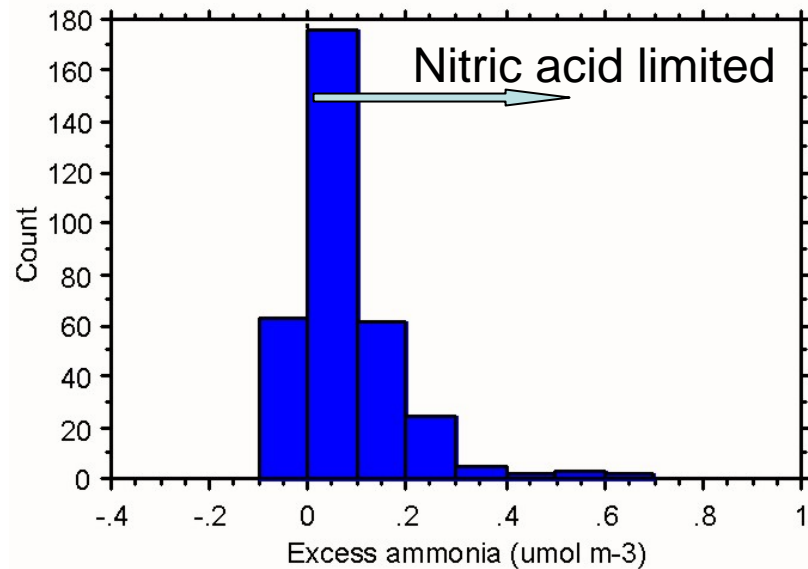
Athens, OH:
Most sensitive to
NH₃; farthest east,
lowest NH₃ site



Sample-by-sample evaluation of gas ratio and excess ammonia



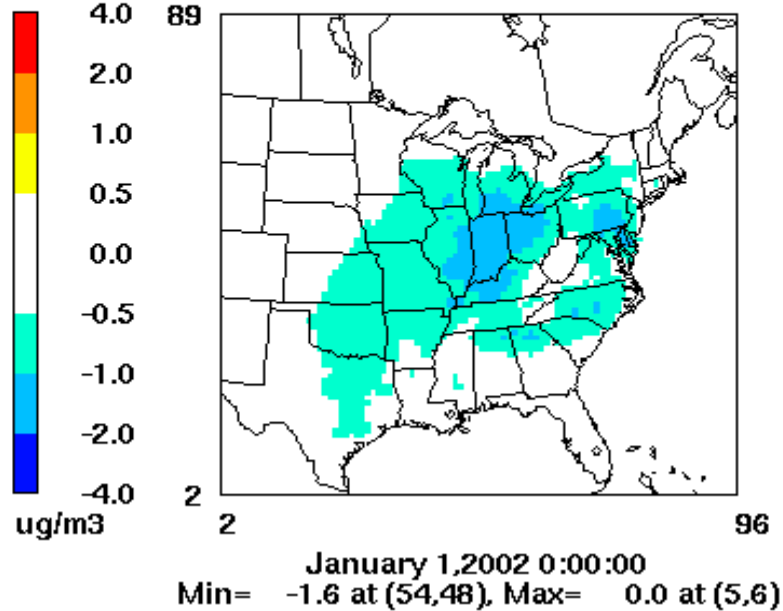
The intervals specified do not contain the entire range of the data.



How do ambient results compare with modeling?

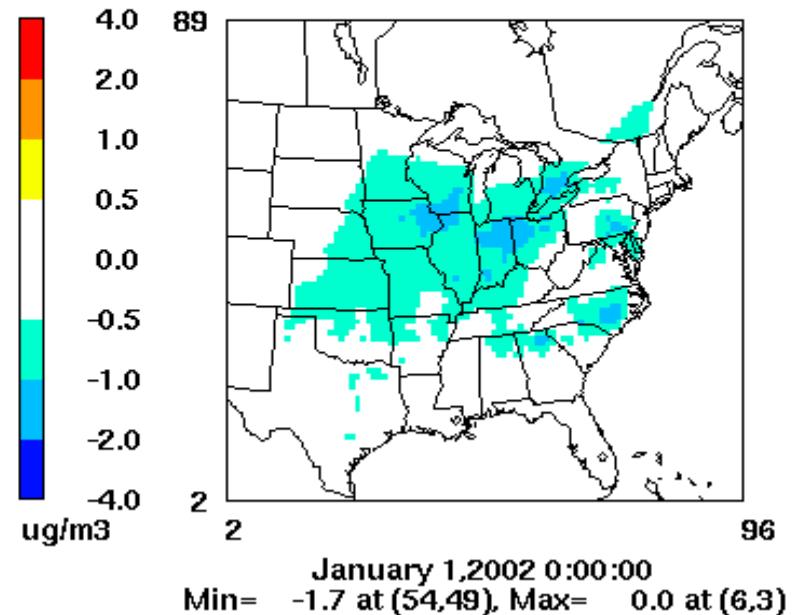
baseG - nh3-30

Episode Average PNO3 Difference
36km grid



pr2009G - nox30

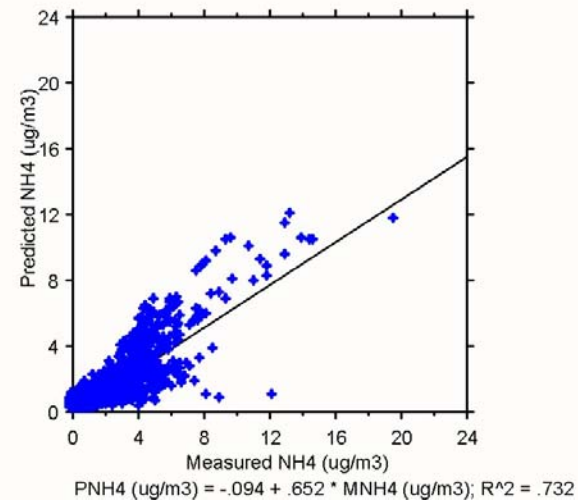
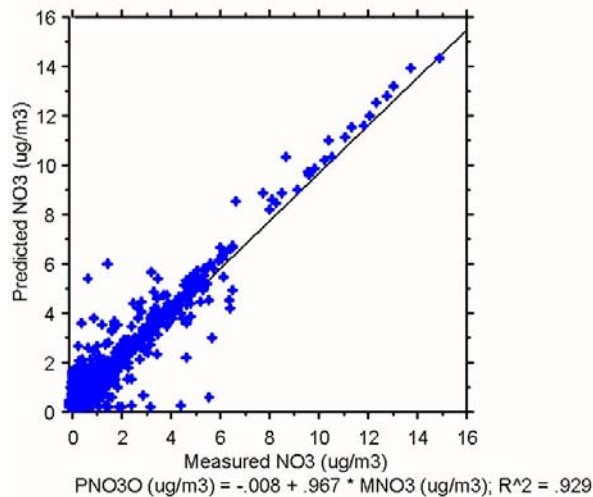
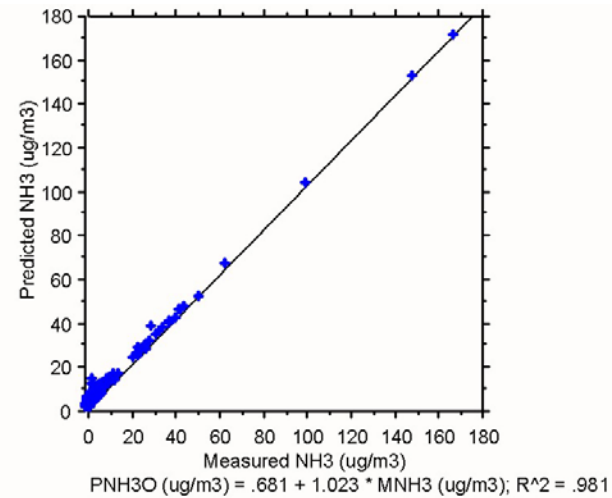
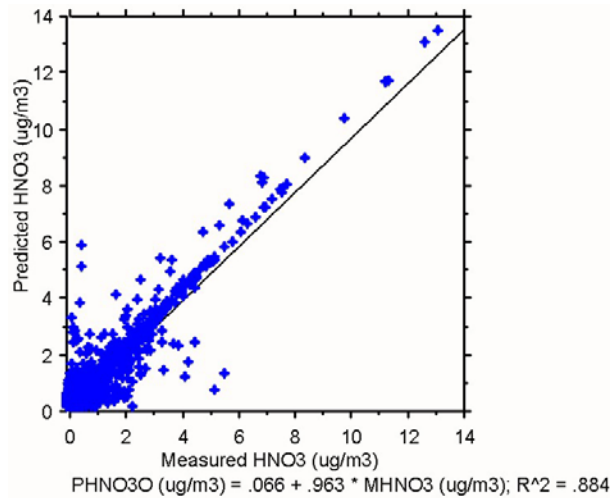
Episode Average PNO3 Difference
36km grid



**Agricultural (CMU Model) NH3 30%
Reduction Annual Average Difference**

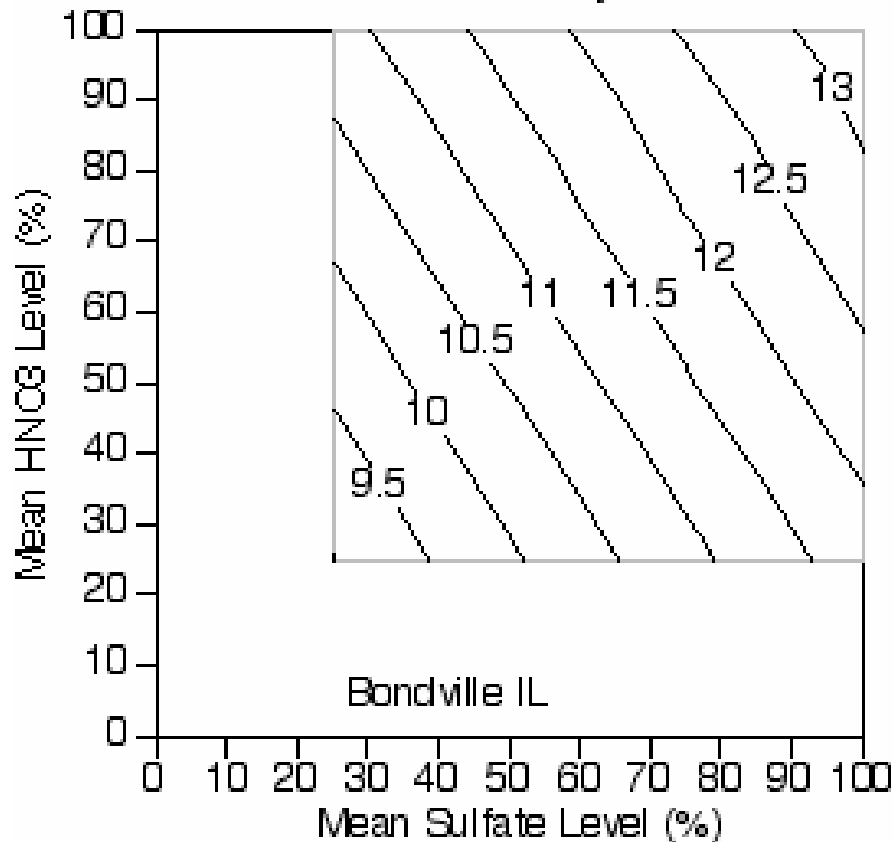
**Entire Domain Anthropogenic
NOX 30% Reduction
Annual Average Difference**

Analysis of hourly data from IC

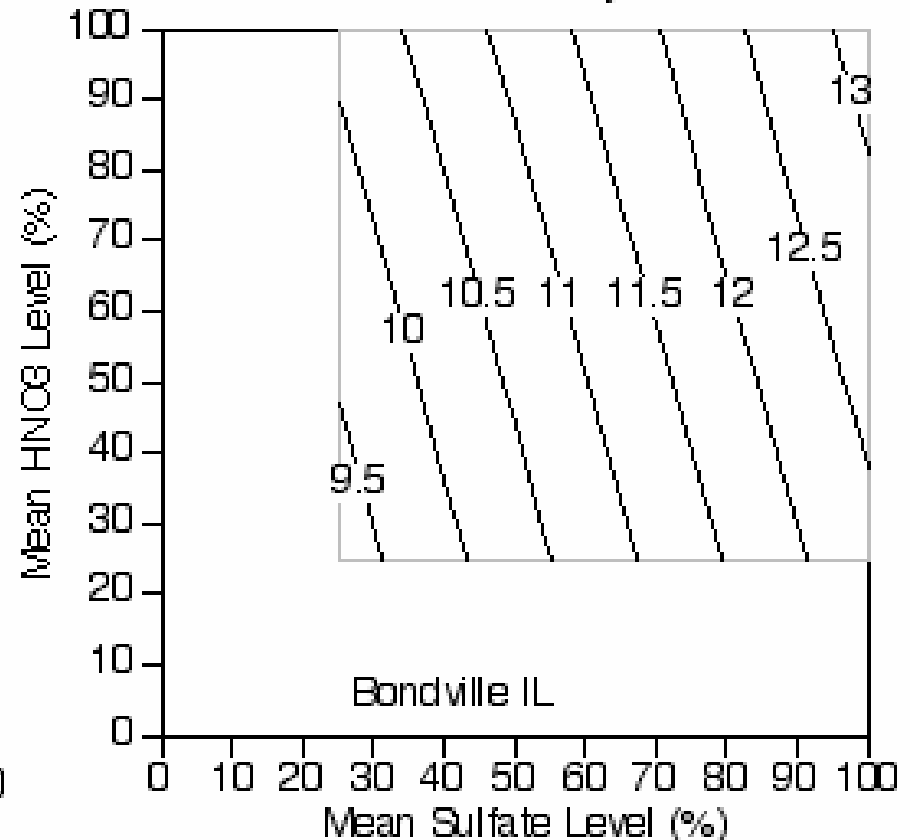


24-hr vs. hourly model results at current NH3

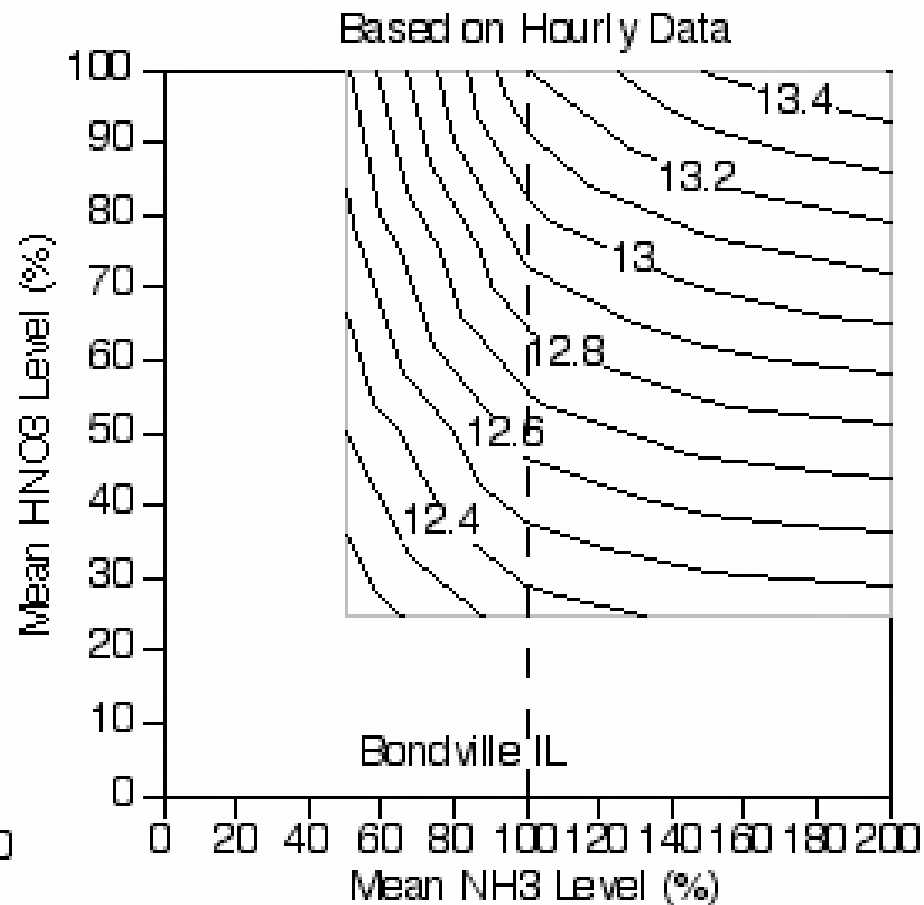
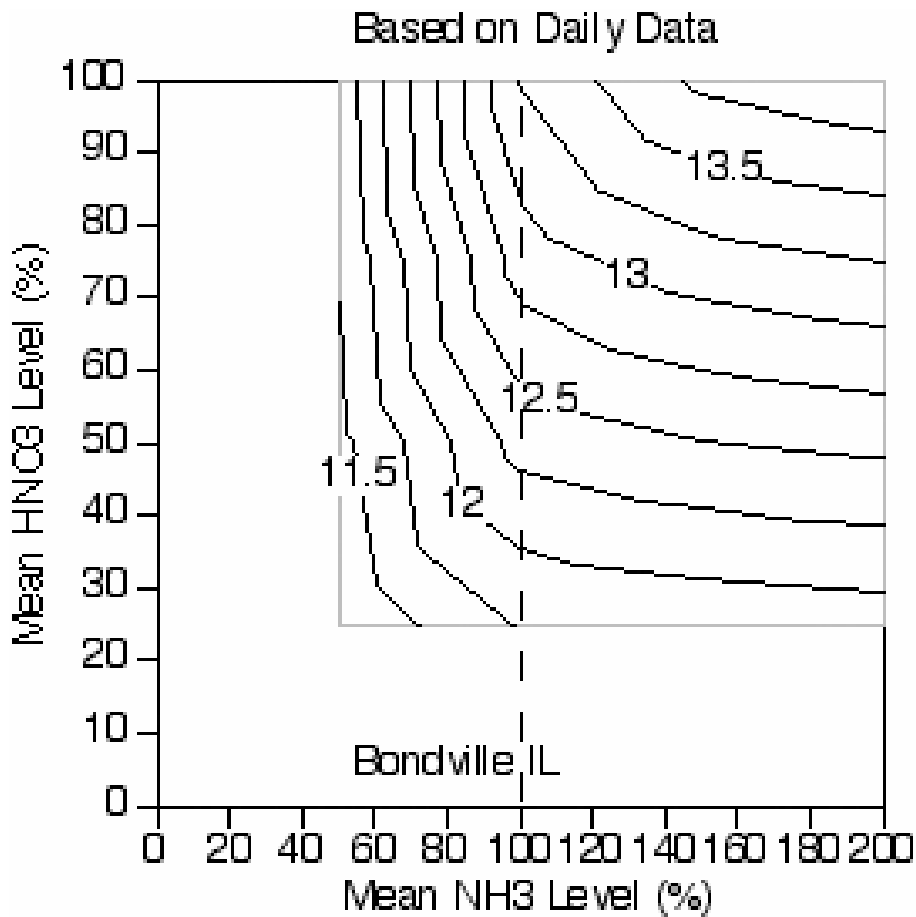
Based on Daily Data



Based on Hourly Data



24-hr vs. hourly model results at current SO4



Preliminary Conclusions

- At current conditions, PM mass decreases in response to reductions in sulfate, nitric acid, and ammonia
- At current conditions, particulate nitrate formation limited generally by nitric acid
- At expected future conditions (i.e., lower sulfate), PM mass is more responsive to nitric acid reductions
- Daily and hourly data support same conclusions

Conclusions

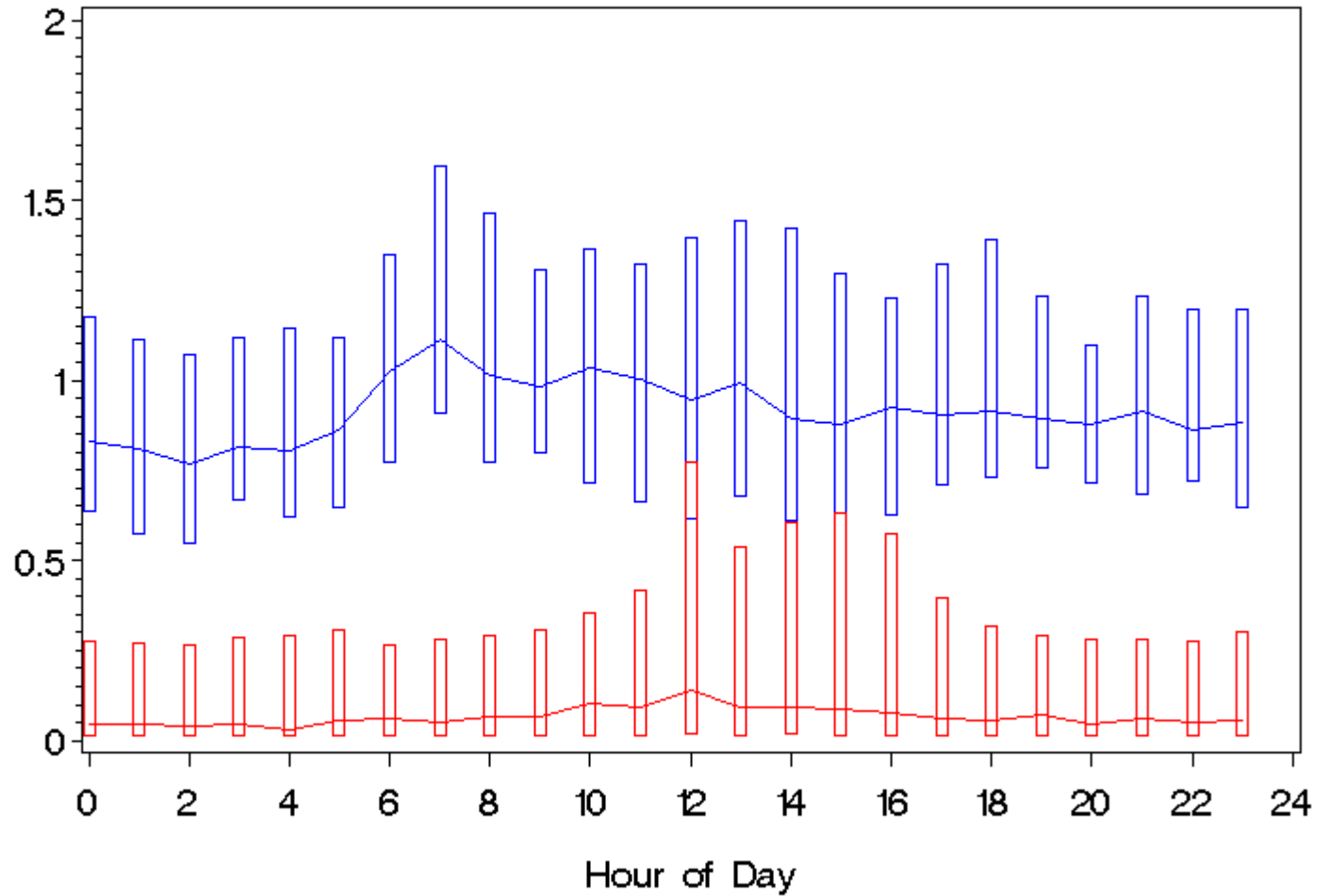
- No significant differences between URG and R&P samplers except in HNO₃ measurements
- Differences in HNO₃ due partly to cyclone losses
- Ammonium losses average 20%
- Denuders highly efficient for SO₂ and NH₃; HNO₃ results were erratic

Applications for NH₃ data

- Thermodynamic evaluation across the region; when and where are conditions limited by nitric acid vs. ammonia (Charlie Blanchard)
- PM episode analysis – Feb. '05 event, role of snow as source/sink
- Model evaluation (Kirk Baker dissertation?)
- Eventually: inventory validation

Seasonal Changes in Diurnal NH3 Variability

NH3 Concentration in ppb



season



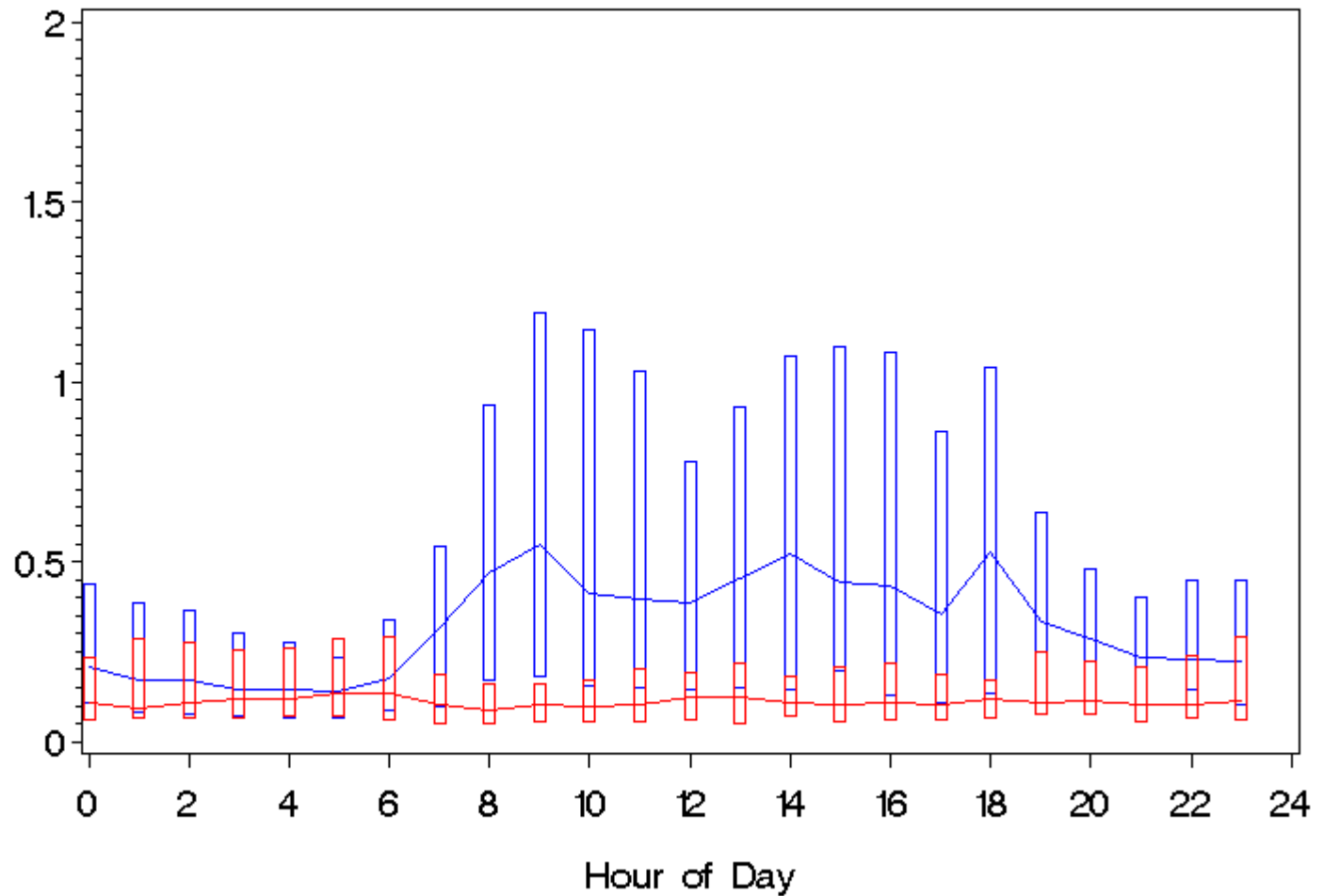
Summer



Winter

Seasonal Changes in Diurnal HNO_3 Variability

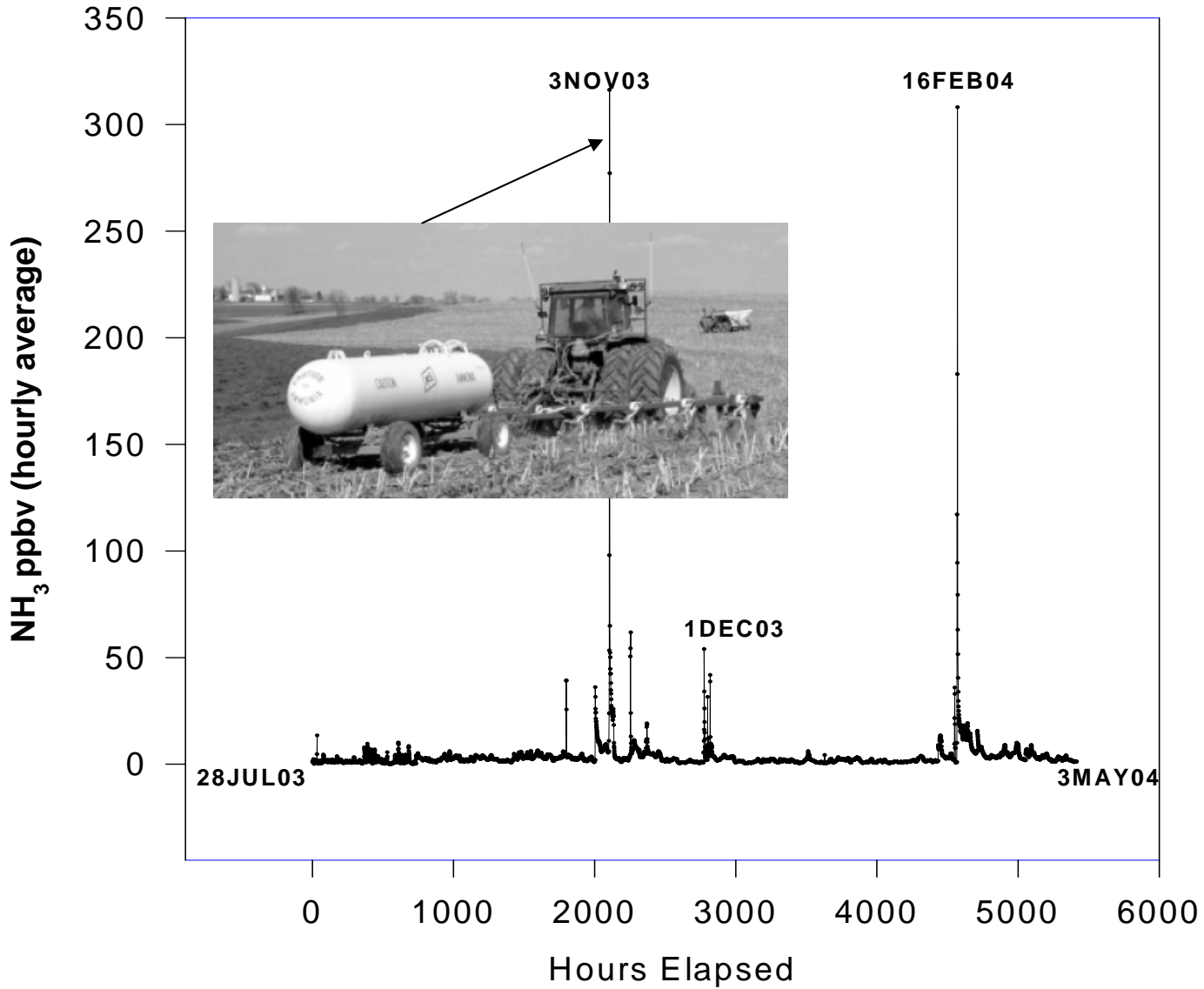
HNO_3 Concentration in ppb



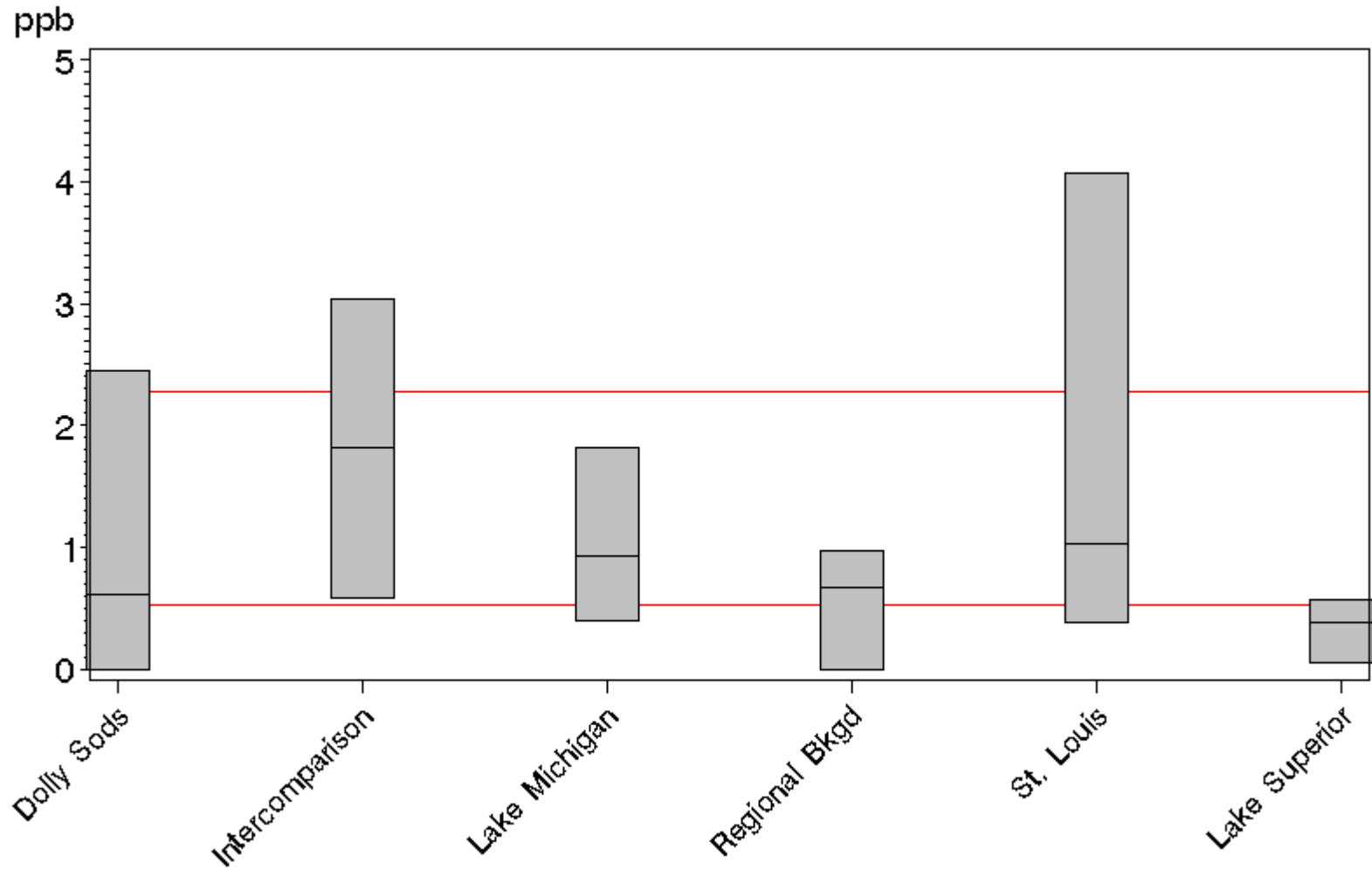
season — Summer — Winter

Hourly NH₃ at Bondville

Extreme Daily Nitrogen Flux Hourly Average

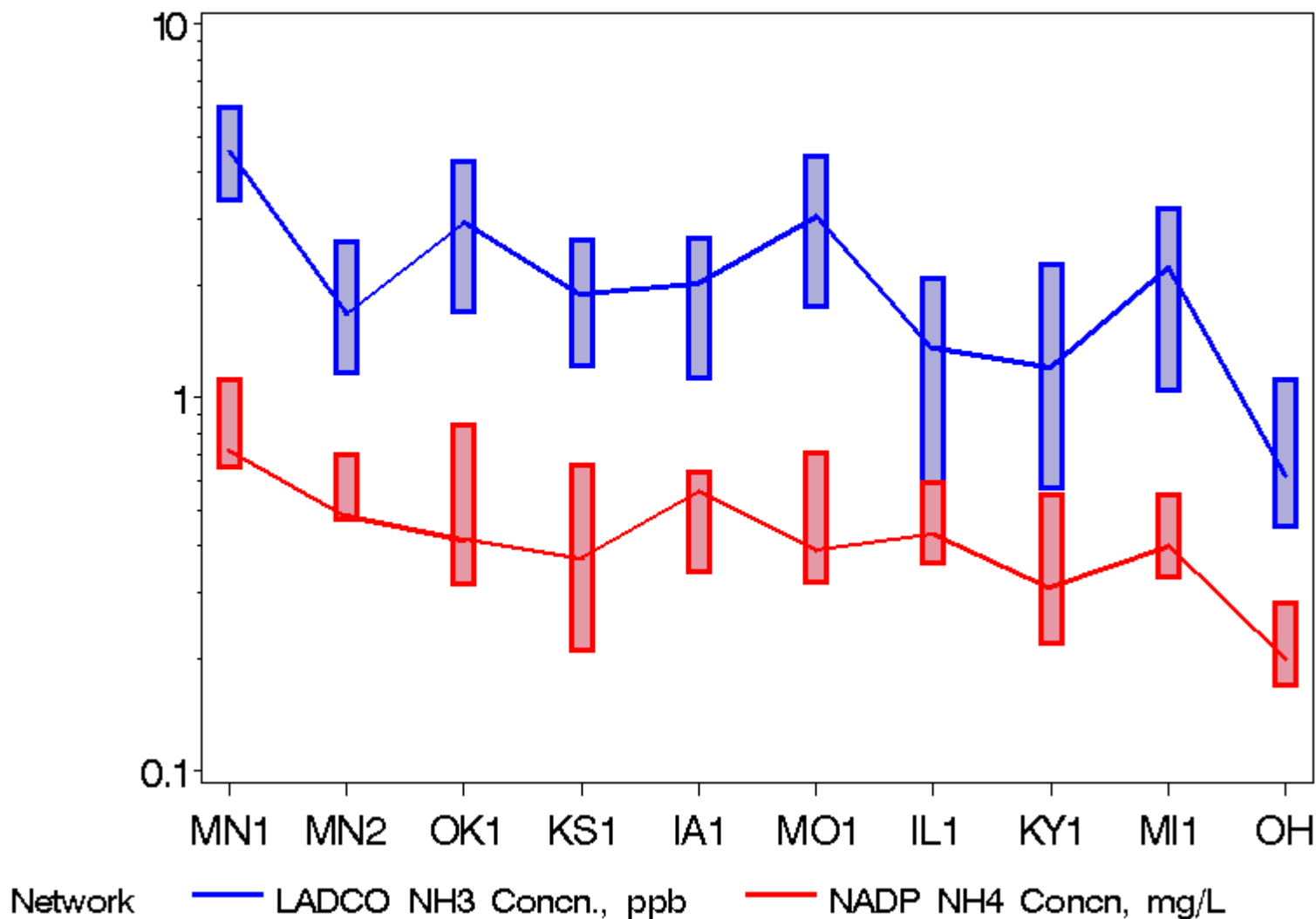


Ammonia Concentrations Aloft, by Route



Red lines = Ground-level median concentrations, summer (top) and winter (bottom)

Spatial Patterns: NADP NH4 and LADCO NH3



Method Intercomparison: IC vs. Denuder

Conc, ppb

