



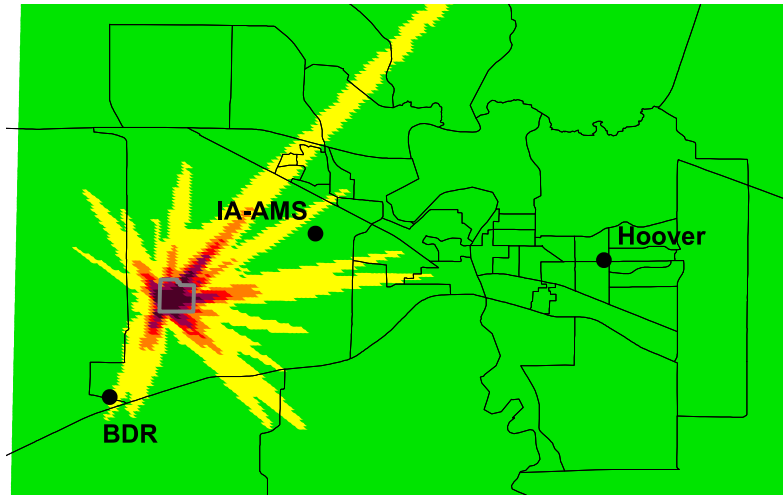
Elevated Winter Nitrate in the Upper Midwest

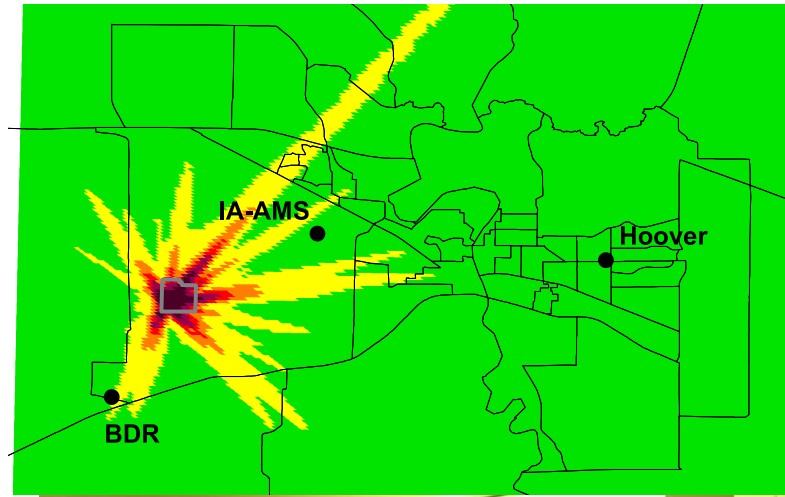
Charles Stanier – University of Iowa

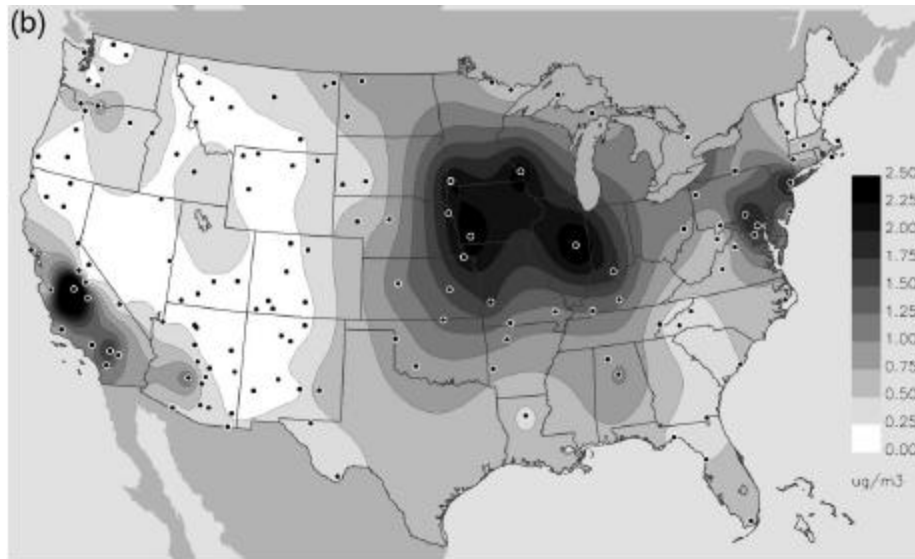
charles-stanier@uiowa.edu

319-335-1399

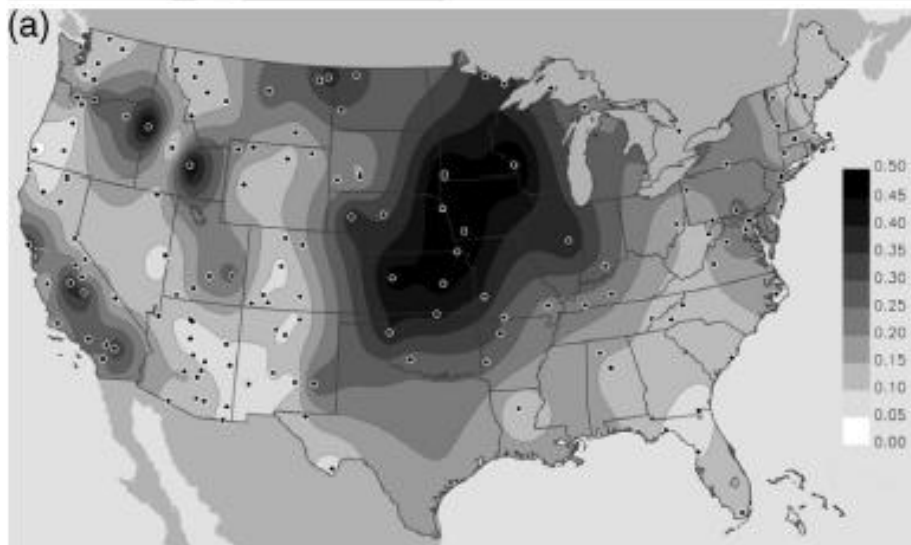






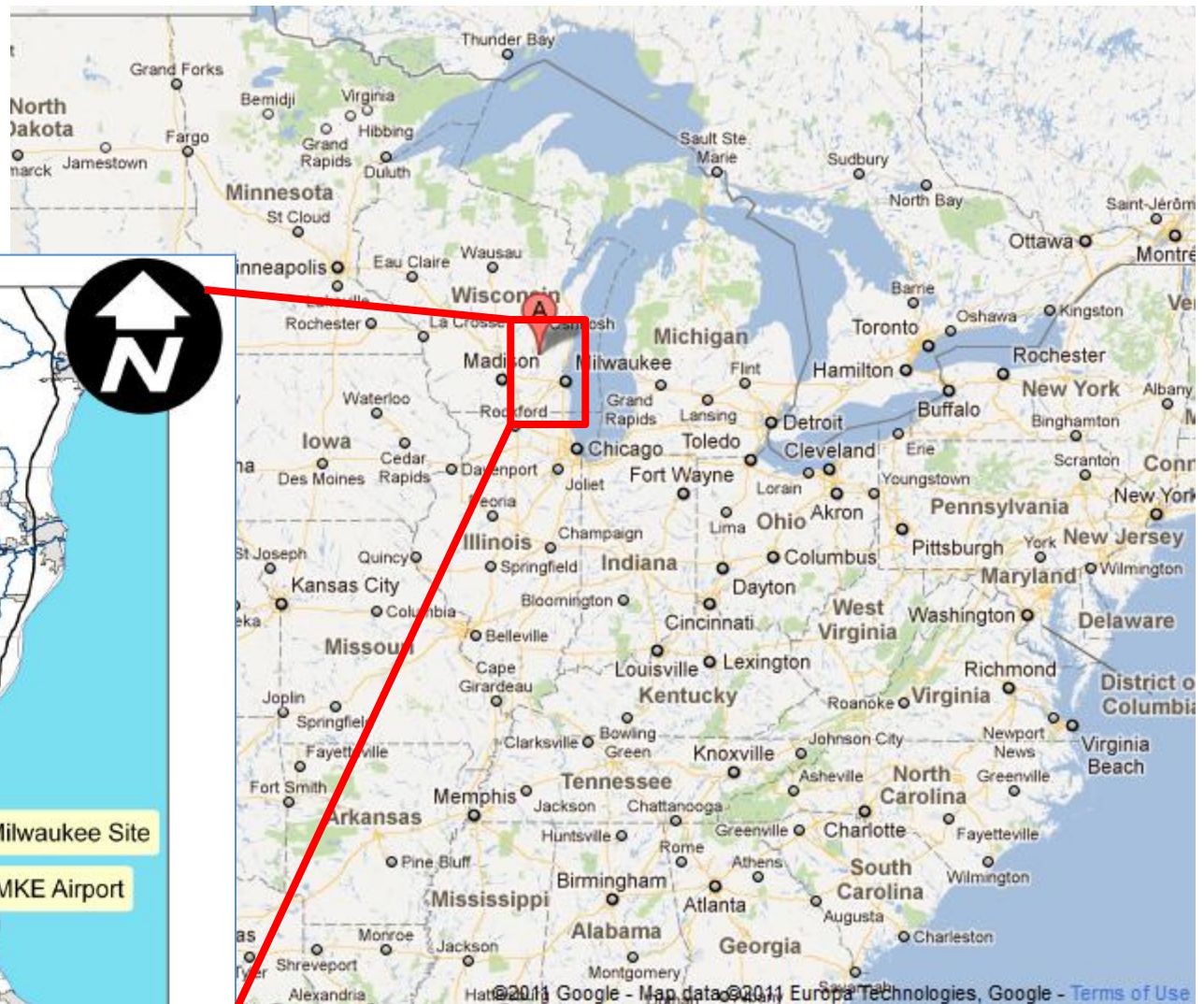
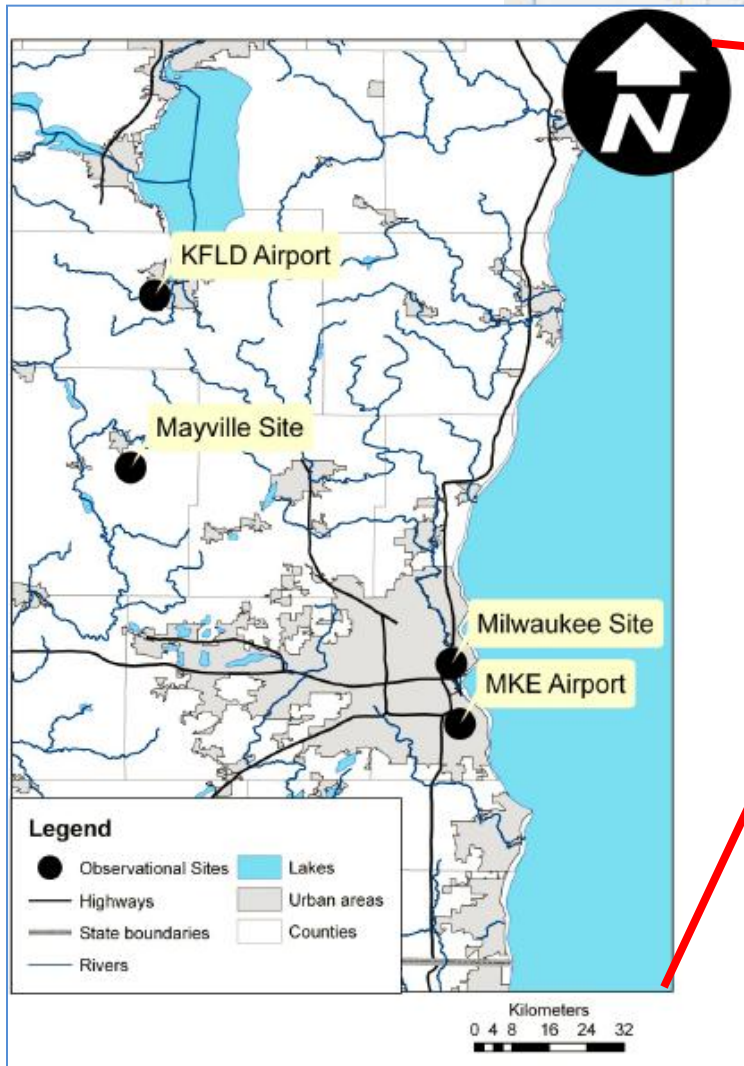


2005-2006 Ammonium
Nitrate from IMPROVE
Network



Jan 2006 Ammonium
Nitrate Fraction of PM_{2.5}

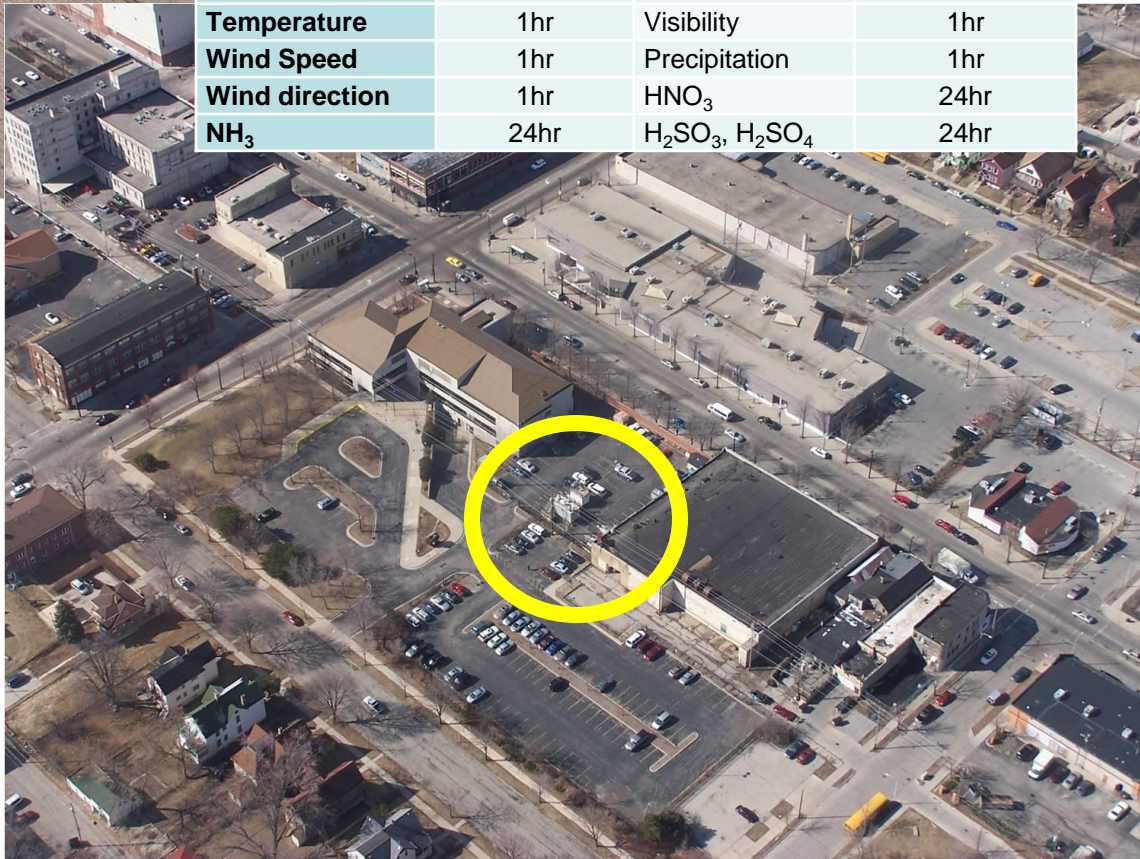
Pitchford et al. JAWMA
(2009)



LADCO Winter Nitrate Study (Jan 1 – Mar 31, 2009)



Species	Averaging time (hr)	Species	Averaging time (hr)
PM _{2.5}	1hr	PM _{2.5}	24hr 1 in 3days
SO ₄	1hr	NH ₄	24hr 1 in 3days
NO ₃	1hr	NO ₃	24hr 1 in 3days
NH ₄	1hr	SO ₄	24hr 1 in 3days
HNO ₃	1hr	OC	24hr 1 in 3days
NH ₃	1hr	EC	24hr 1 in 3days
NO _y	1hr	O ₃	1hr
NOx (note 6)	1hr	Relative Humidity	1hr
SO2 (note 7)	1hr	Surface pressure	1hr
Temperature	1hr	Visibility	1hr
Wind Speed	1hr	Precipitation	1hr
Wind direction	1hr	HNO ₃	24hr
NH ₃	24hr	H ₂ SO ₃ , H ₂ SO ₄	24hr



Science Questions for the Study

Composition: Typical chemical composition during episodes and non-episodes?

Urban-rural contrast: Differences in $PM_{2.5}$ concentrations (frequency and severity), chemical composition, and source regions?

Meteorology: What meteorological conditions favor winter-time episodes? How can we best use this information to improve wintertime episode forecasting?

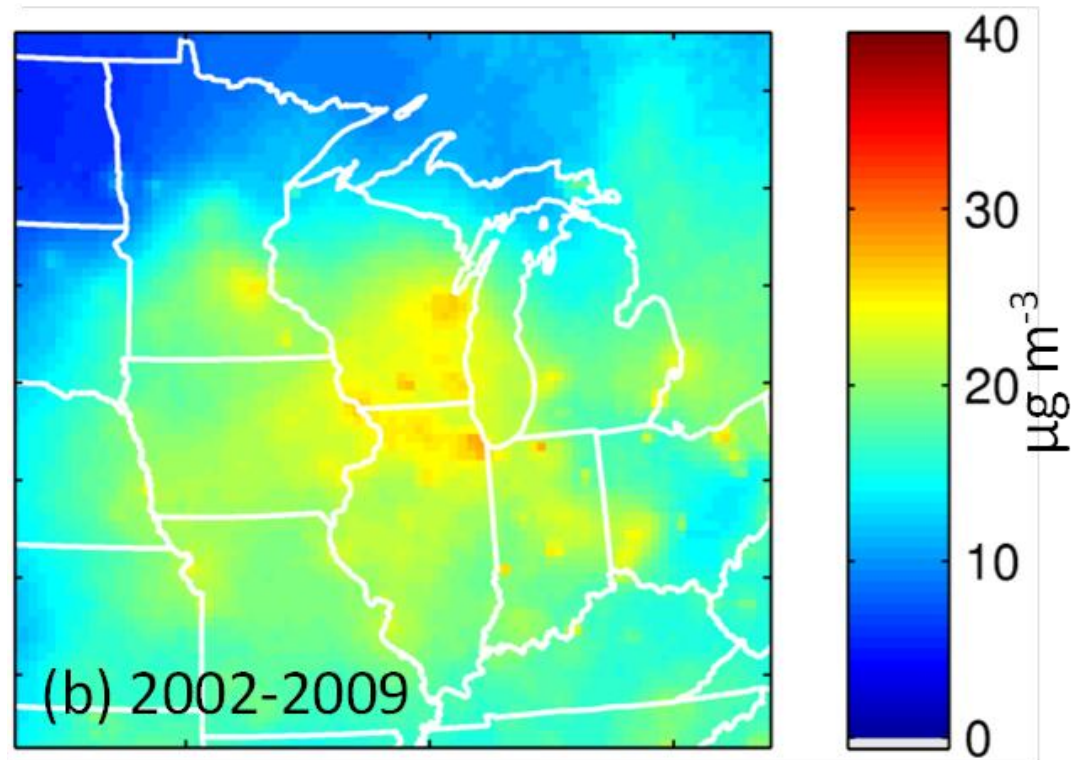
Nitrate formation chemistry: What do the data tell us the nitrate formation chemistry leading to events?

Sensitivity of episodes:

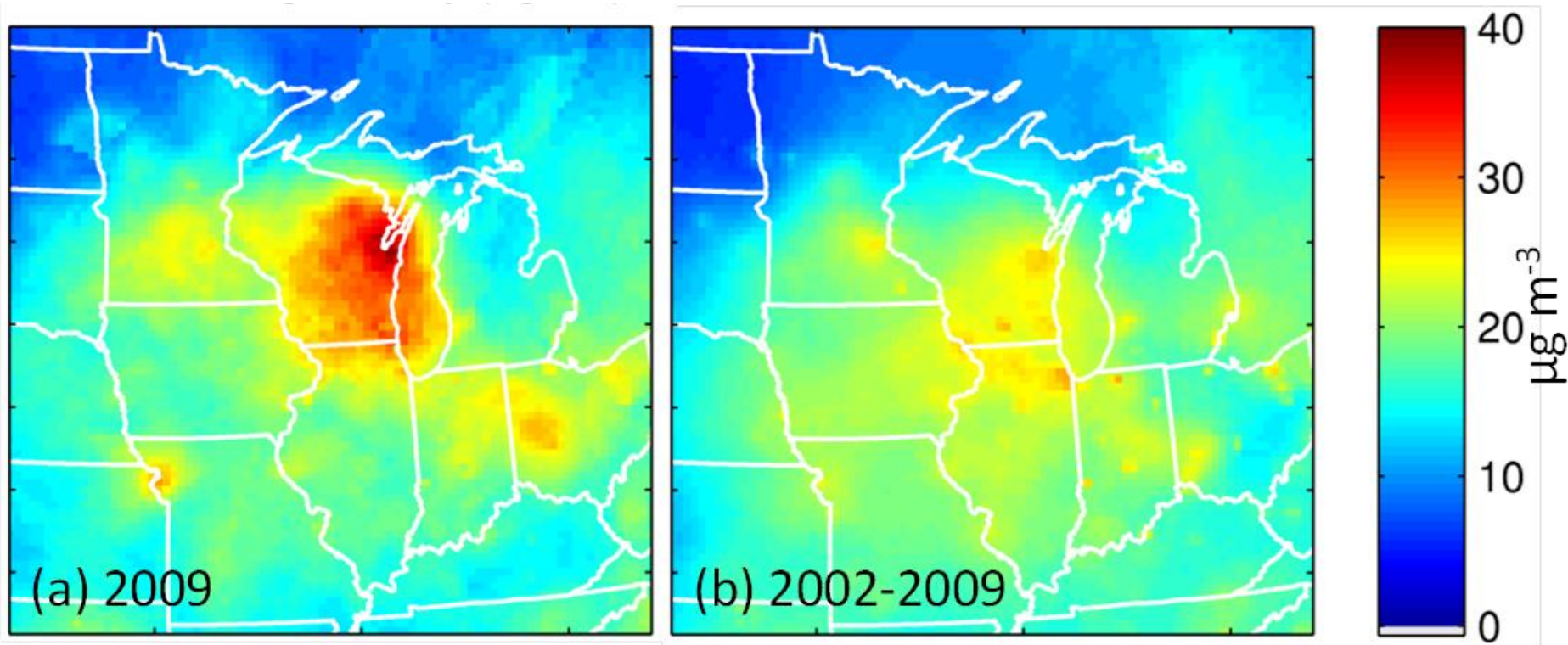
- How sensitive are concentrations to hypothetical changes in total nitrate, total ammonia, and total sulfate?
- What sources categories have leverage on episodes? Do local sources have influence?

3D Model skill: Can photochemical modeling accurately predict $PM_{2.5}$ concentrations during the observed winter-time episodes?

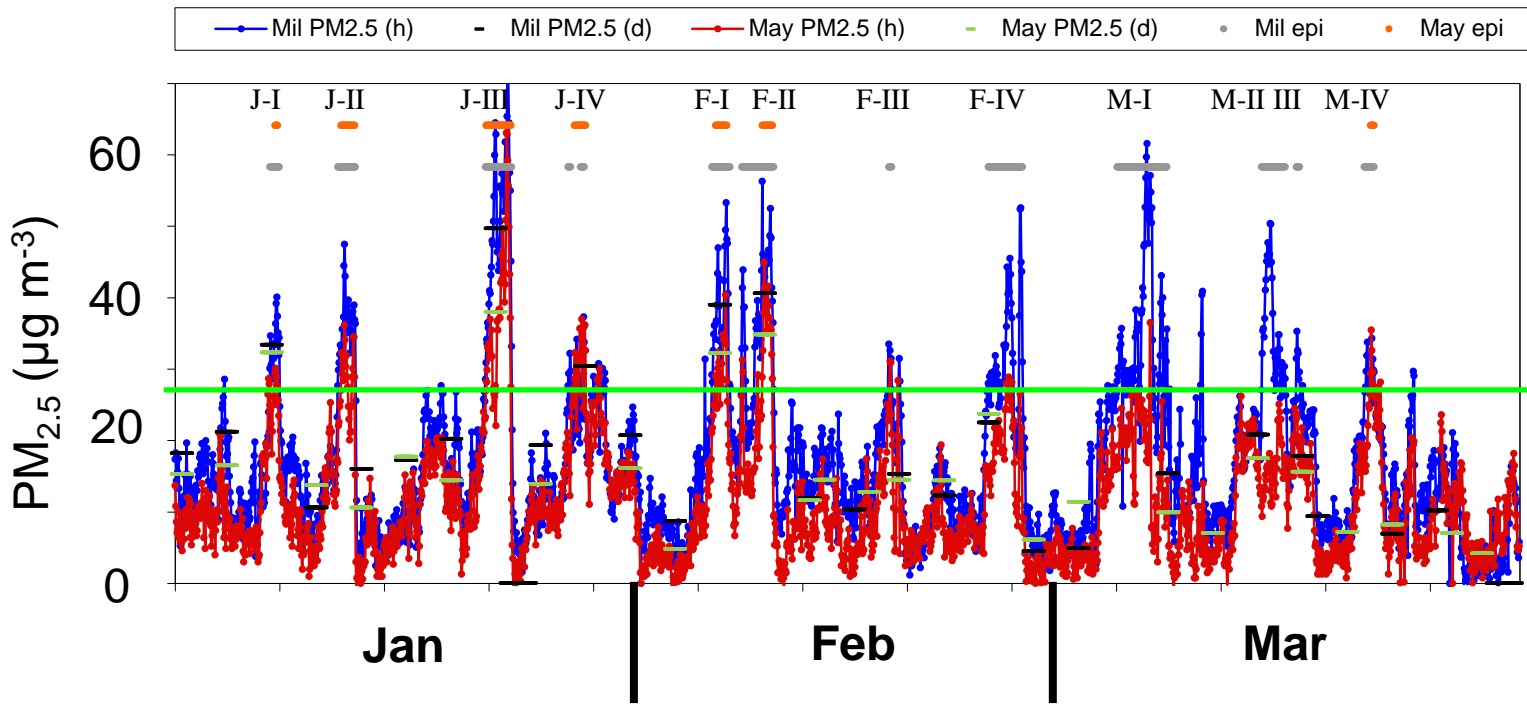
OBSERVATIONAL HIGHLIGHTS



5th Highest Jan-Mar PM_{2.5} Concentration

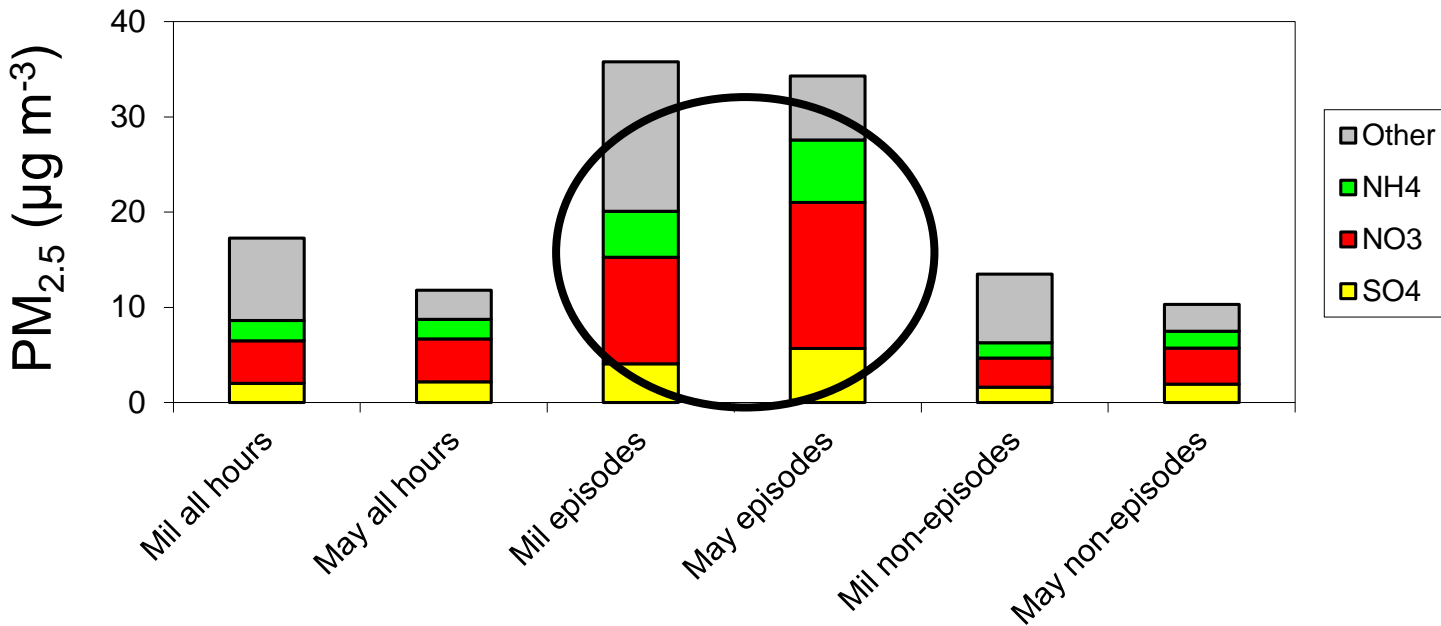


5th Highest Jan-Mar $\text{PM}_{2.5}$ Concentration



Parameter	Milwaukee (Urban)	Mayville (Rural)
PM _{2.5} (µg m ⁻³)	17.1	11.7
Total nitrate (µg m ⁻³)	5.6	4.8
Total ammonia (µg m ⁻³)	3.8	4.0
Gas ammonia (ppb)	2.3	2.4
Nitrate aerosol / total nitrate	78%	69%
NO _y (ppb)	27	6.3
Temperature (°C)	-3	-5
Ozone (ppb)	22	31
OC (µg m ⁻³)	3.6	3.2
EC (µg m ⁻³)	0.5	0.3

Composition and Urban-Regional Differences

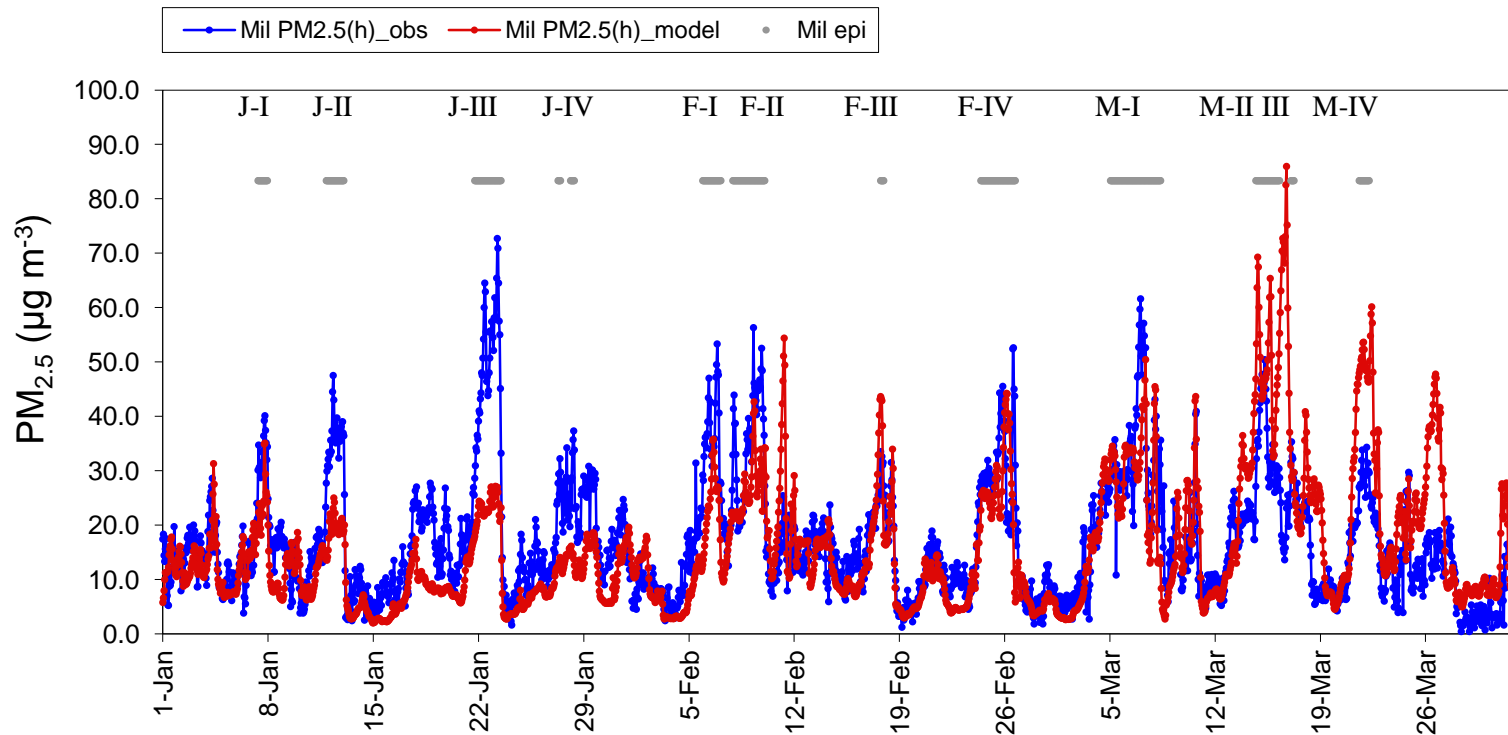


- Gas ratios (ammonia availability) ranged from 1.2-3.1. Lowest at the rural site during episodes.
- Evidence of gas ratio ↓ during episodes at multiple sites in the region.
- Secondary species mainly regional (small urban excess)
- OC, EC, and NO_y have strong urban excess

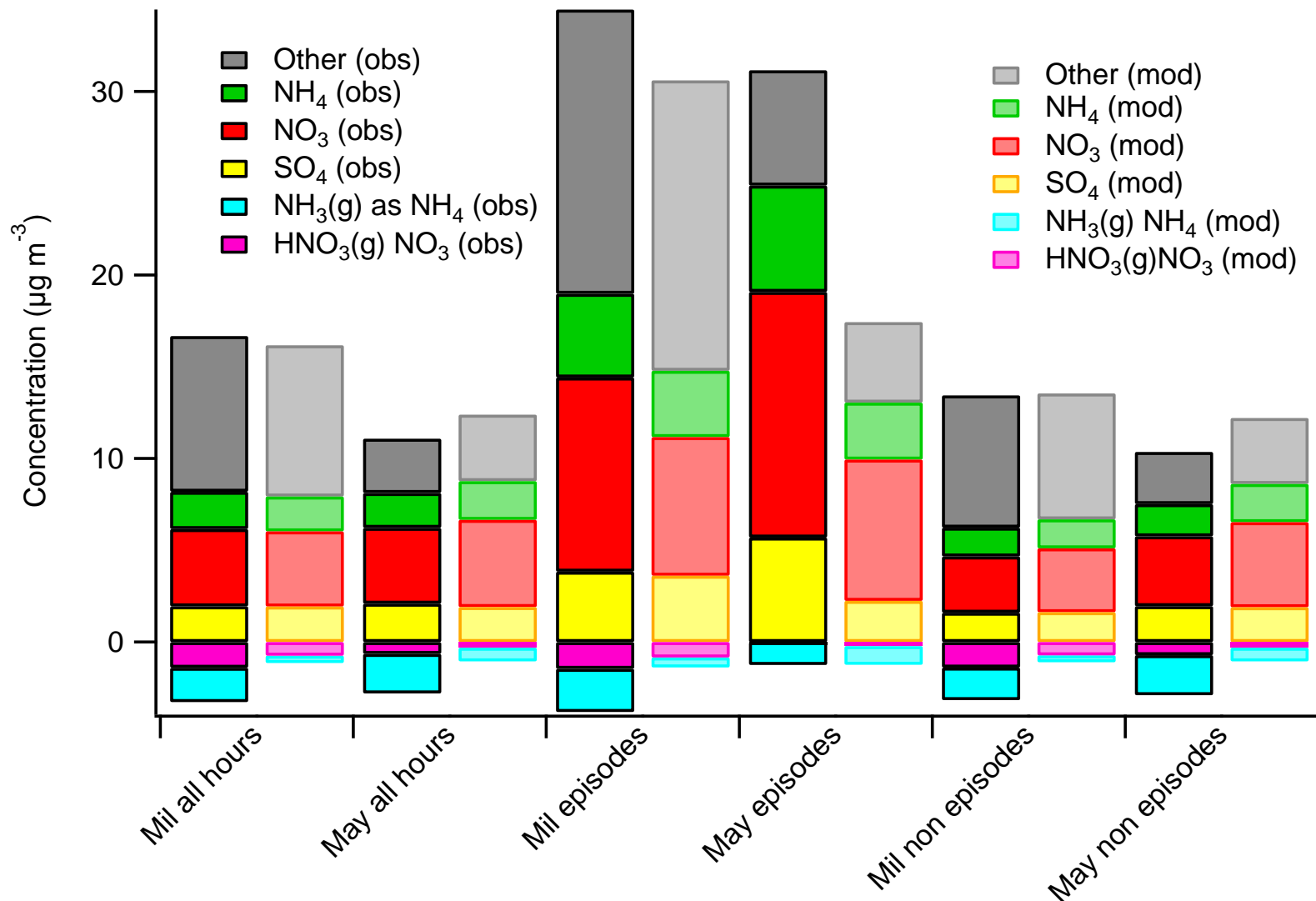
INSIGHTS FROM MODELING

U of I *Model Skill*

Network	Species	Observed	Model
AQS	Ozone	29.8	35.0
Improve	PM _{2.5}	7.0	8.6
	SO ₄	1.8	2.6
STN	PM _{2.5}	12.1	15.4
	NO ₃	3.0	3.0
	NH ₄	1.7	2.0
	SO ₄	2.4	3.6



Model Skill



- Total ammonia underprediction during almost all periods and sites.
- Shows as deficit in gas phase ammonia.
- Nitrate underprediction during episodes.
- Systematic OC underprediction (not shown) but offset by CMAQ other inorganics

Model Skill

Table 3.8.2. Performance analyses of simulated PM_{2.5} in the 12km domain at STN sites.

		No.	CMAQ	OBS	MB	ME	NB	NE	FB(%)	FE(%)	R
Base case	Jan	548	11.97	12.87	-0.90	6.49	0.06	0.53	-13	52	0.30
	Feb	384	15.05	12.71	2.34	6.77	0.72	0.99	11	47	0.37
	Mar	453	19.79	10.73	9.06	10.58	1.02	1.18	39	60	0.57

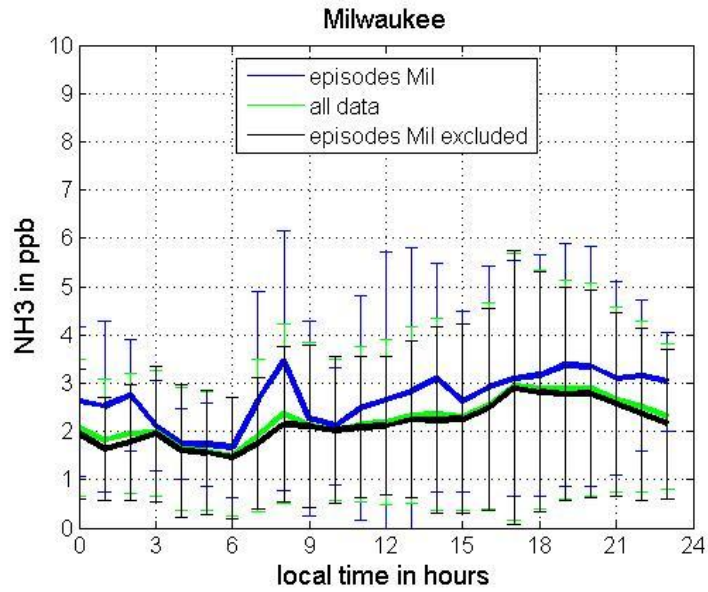
Table 3.8.3. Performance analyses of simulated PM_{2.5} in the 12km domain at IMPROVE sites

		No.	CMAQ	OBS	MB	ME	NB	NE	FB(%)	FE(%)	R
Base case	Jan	311	6.49	6.64	-0.15	2.96	0.15	0.53	-4	46	0.52
	Feb	253	8.45	6.96	1.50	2.95	0.34	0.53	15	38	0.62
	Mar	289	11.00	7.31	3.69	5.14	0.62	0.81	28	52	0.57

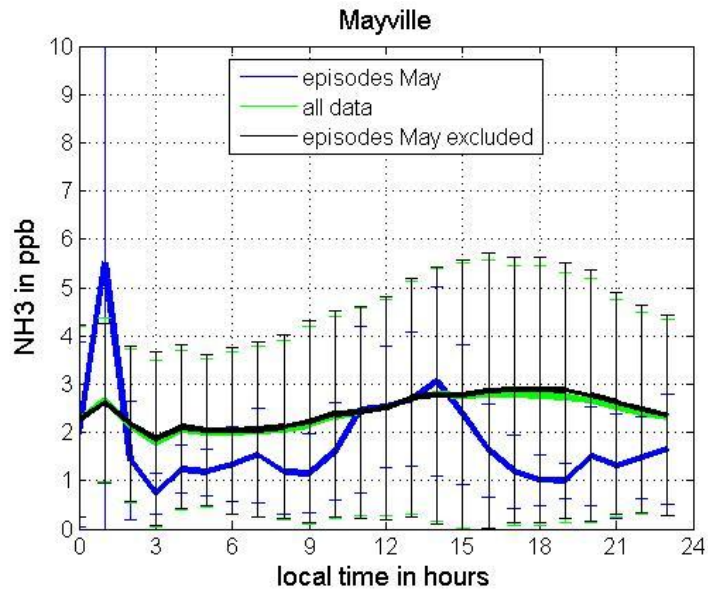
Diurnal Patterns – NH₃(g)

Observations

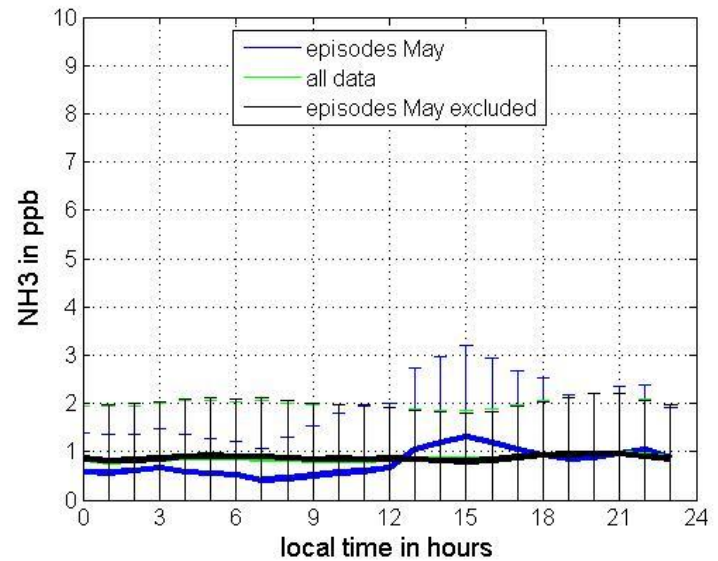
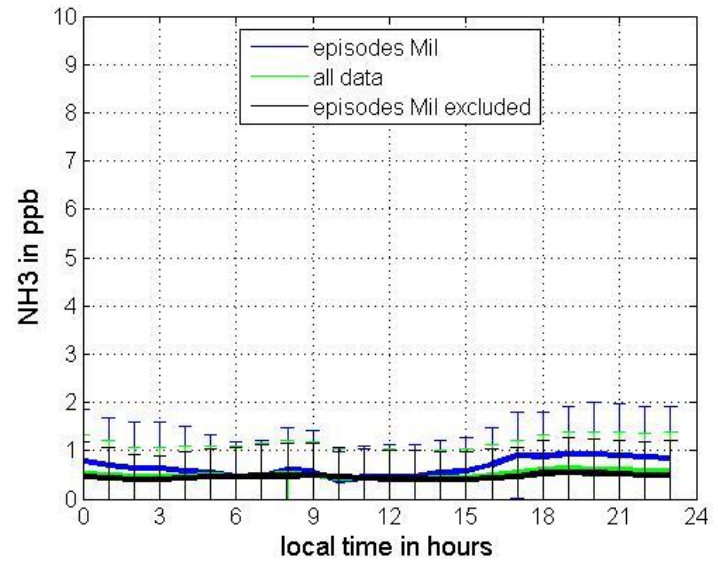
Urban



Rural



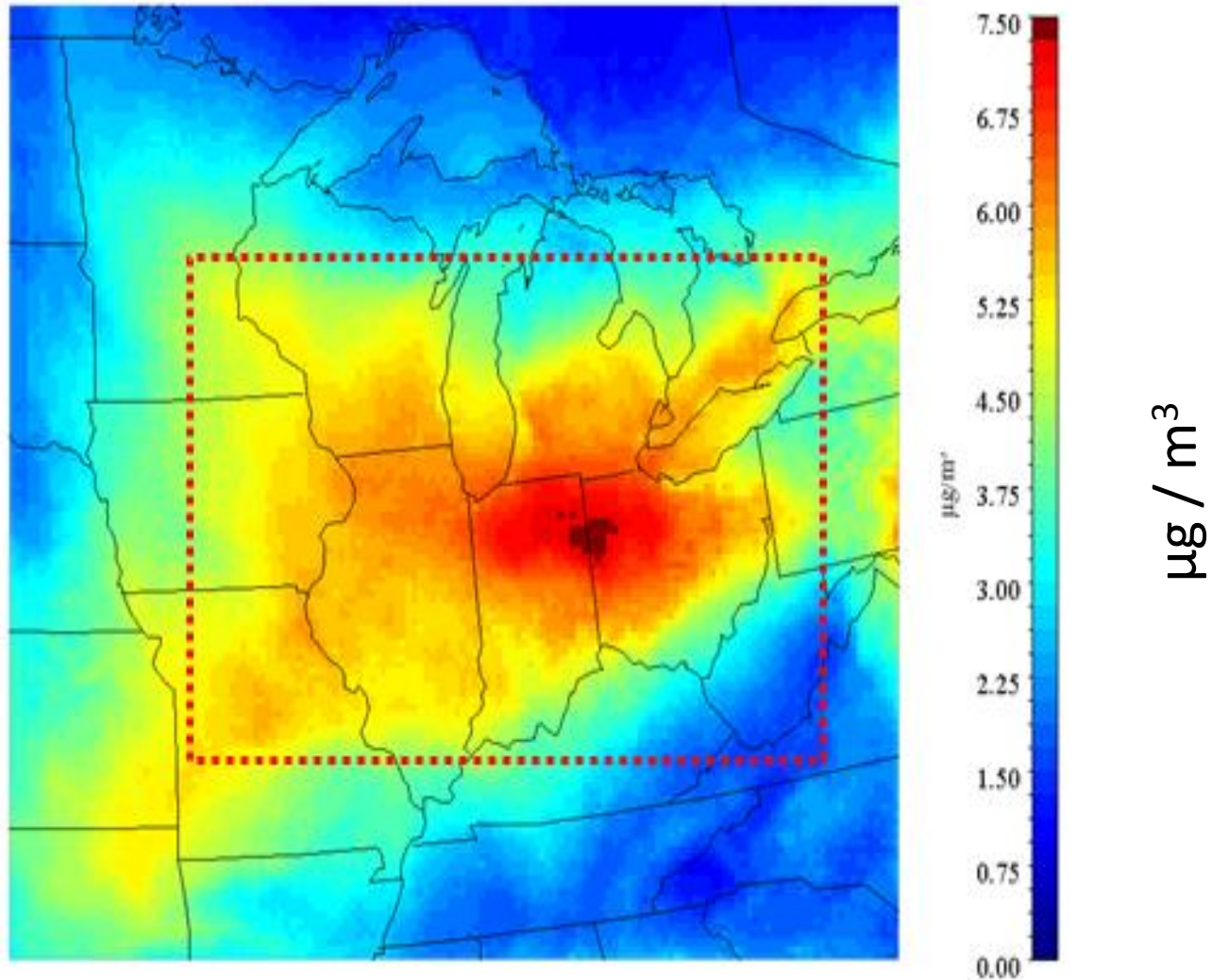
Model



Predictability of PM2.5 Episodes

	Number of Observed Episodes	Number of Observed Episodes with Modeled Episode	Number of Modeled False Positive Episodes
Milwaukee	13	10	2
Mayville	7	4	4

PROCESS ANALYSIS

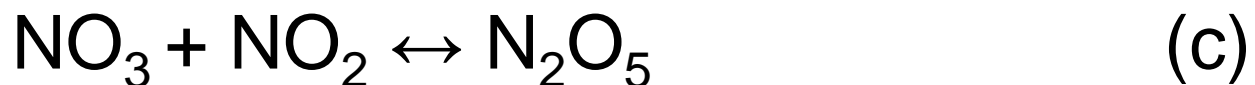
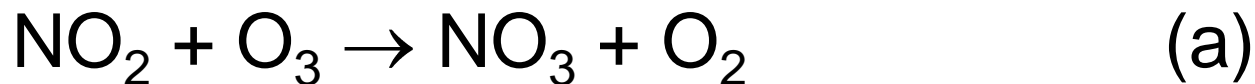


Mean total nitrate Jan – Mar 2009. CMAQ.

Nitrate formation analysis by process analysis



Daytime



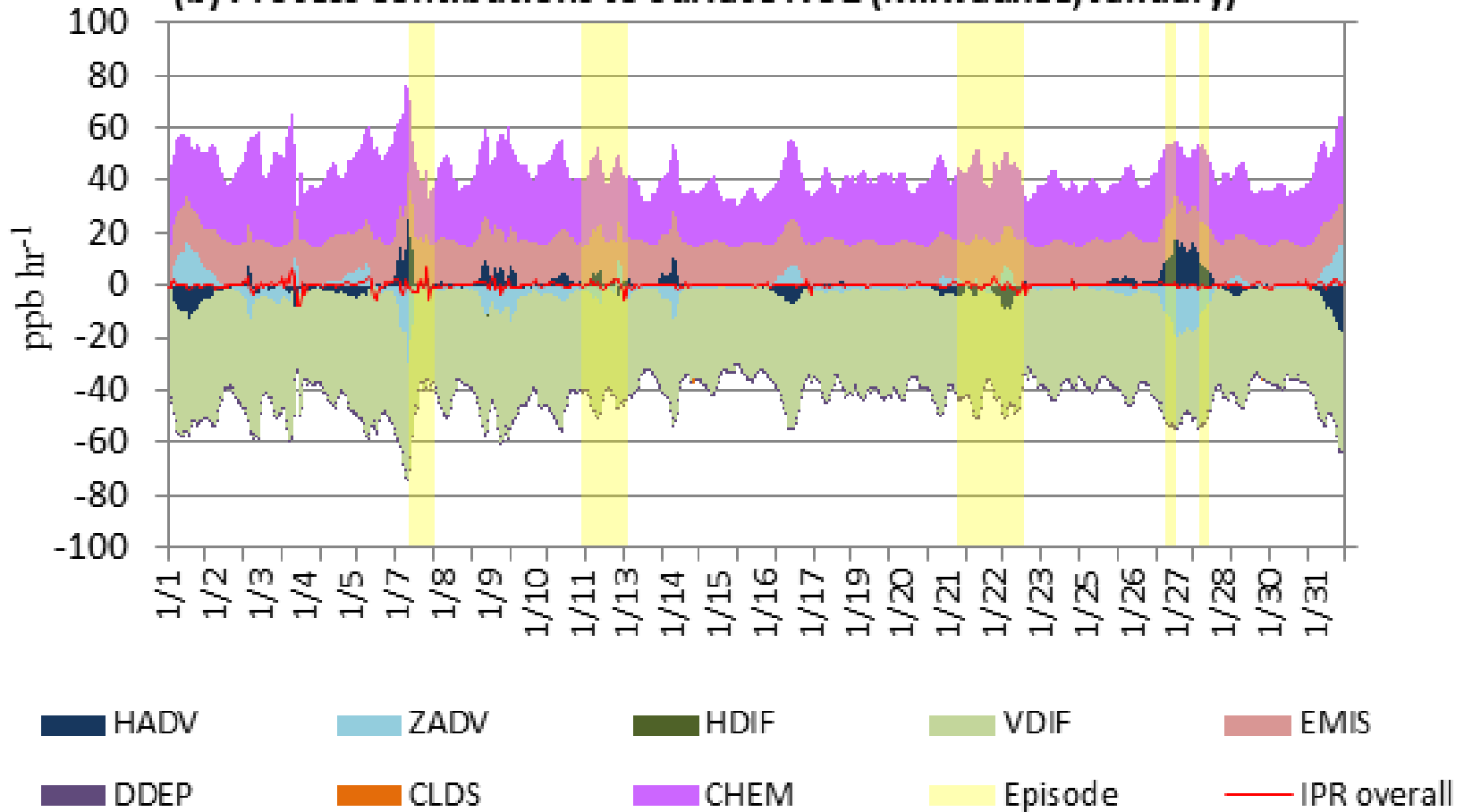
Nighttime

RH and composition dependent accommodation coefficient, uncertain

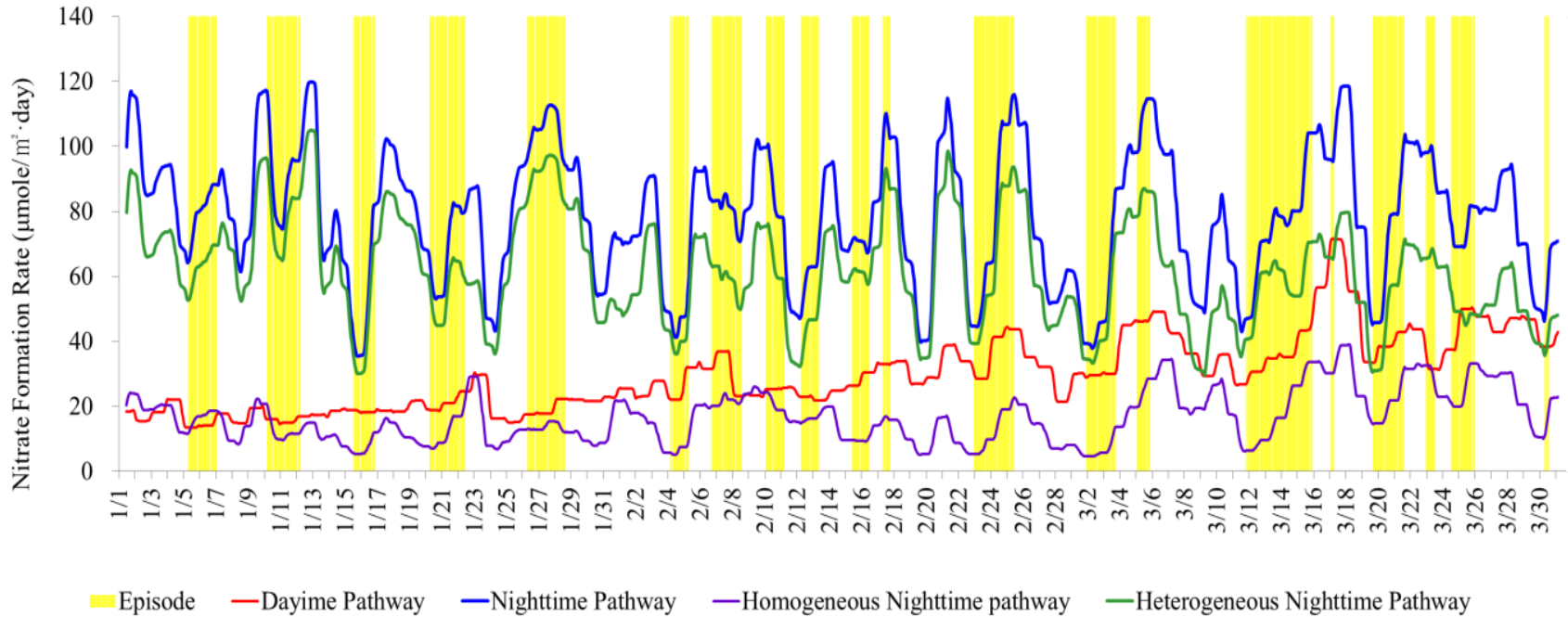
Integrated Reaction Rate Analysis

Reaction	Reactants	Products
R1	$\text{NO}_2 + h\nu$	$\text{NO} + \text{O}$
R3	$\text{O}_3 + \text{NO}$	NO_2
R4	$\text{O} + \text{NO}_2$	NO
R5	$\text{O} + \text{NO}_2$	NO_3
R6	$\text{O} + \text{NO}$	NO_2
R7	$\text{NO}_2 + \text{O}_3$	NO_3
R14	NO_3	$\text{NO}_2 + \text{O}$
R15	NO_3	NO
R16	$\text{NO}_2 + \text{NO}$	2NO_2
R17	$\text{NO}_3 + \text{NO}_2$	$\text{NO} + \text{NO}_2$
R18	$\text{NO}_3 + \text{NO}_2$	N_2O_5
R19	$\text{N}_2\text{O}_5 + \text{H}_2\text{O}$	2HNO_3
R20	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} + \text{H}_2\text{O}$	2HNO_3
R21	N_2O_5	$\text{NO}_3 + \text{NO}_2$
R22	$\text{NO} + \text{NO} + \text{O}_2$	2NO_2
R23	$\text{NO} + \text{NO}_2 + \text{H}_2\text{O}$	HONO
R24	$\text{NO} + \text{OH}$	HONO
R25	HONO	$\text{NO} + \text{OH}$
R26	$\text{OH} + \text{HONO}$	NO_2
R27	$\text{HONO} + \text{HONO}$	$\text{NO} + \text{NO}_2$
R28	$\text{NO}_2 + \text{OH}$	HNO_3
R29	$\text{OH} + \text{HNO}_3$	NO_3
R30	$\text{HO}_2 + \text{NO}$	$\text{OH} + \text{NO}_2$
R31	$\text{HO}_2 + \text{NO}_2$	PNA
R32	PNA	$\text{HO}_2 + \text{NO}_2$
R33	$\text{OH} + \text{PNA}$	NO_2
R46	$\text{NO}_3 + \text{O}$	NO_2
R47	$\text{NO}_3 + \text{OH}$	$\text{HO}_2 + \text{NO}_2$
R48	$\text{NO}_3 + \text{HO}_2$	HNO_3
R49	$\text{NO}_3 + \text{O}_3$	NO_2
R50	$\text{NO}_3 + \text{NO}_3$	2NO_2
R51	PNA	$0.61\text{HO}_2 + 0.61\text{NO}_2 + 0.39\text{OH} + 0.39\text{NO}_3$
R52	HNO_3	$\text{OH} + \text{NO}_2$
R53	N_2O_5	$\text{NO}_2 + \text{NO}_3$
R89	PAN	$\text{C}_2\text{O}_3 + \text{NO}_2$
R90	PAN	$\text{C}_2\text{O}_3 + \text{NO}_2$

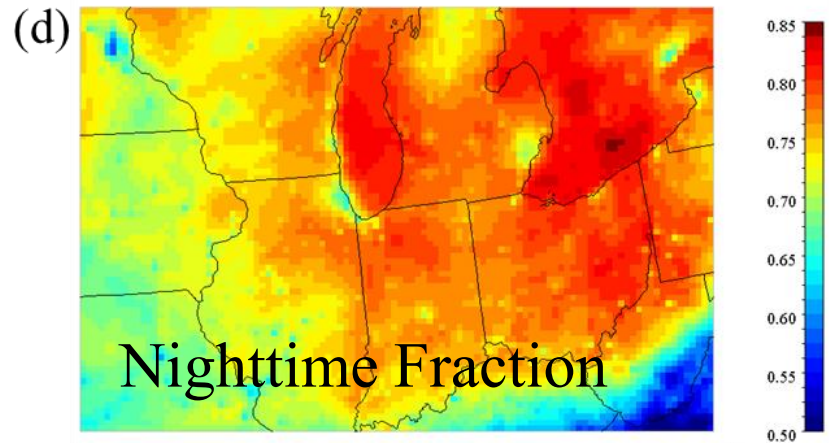
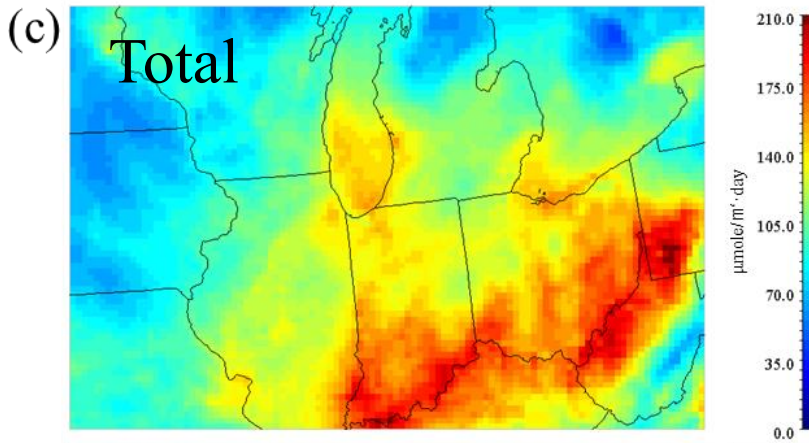
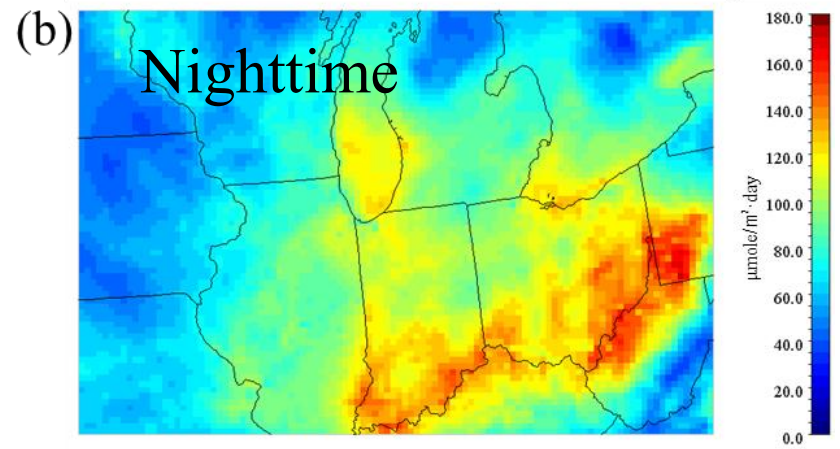
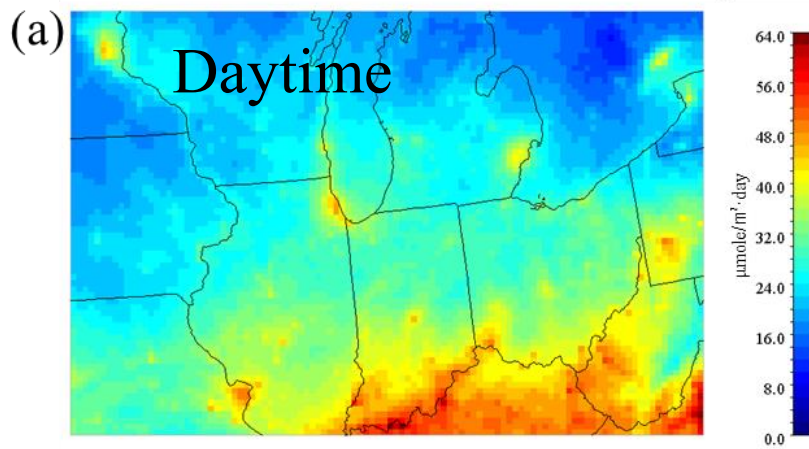
(b) Process Contributions to Surface NO₂ (Milwaukee, January)

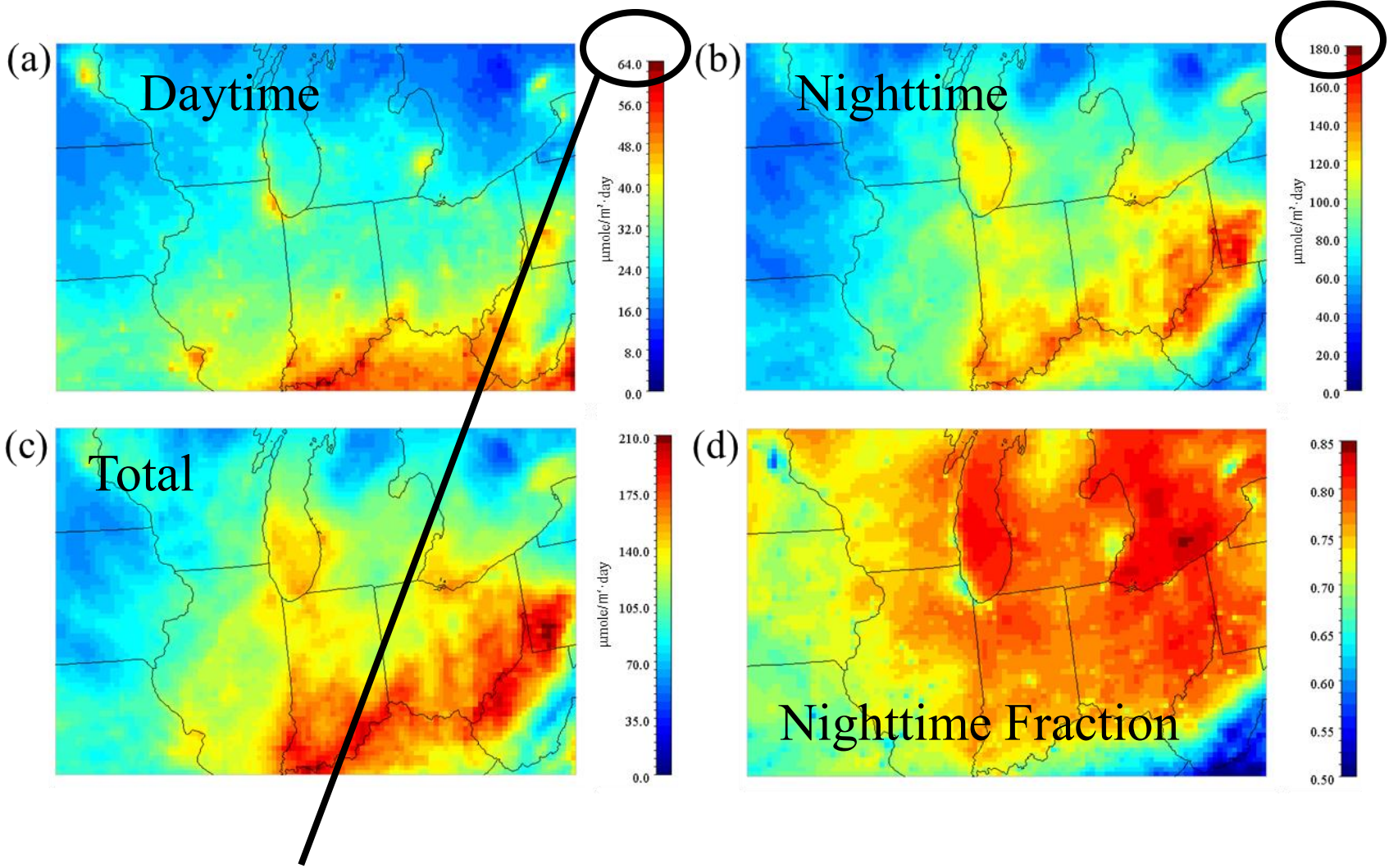


Through model layer 20 (~3.15 km)

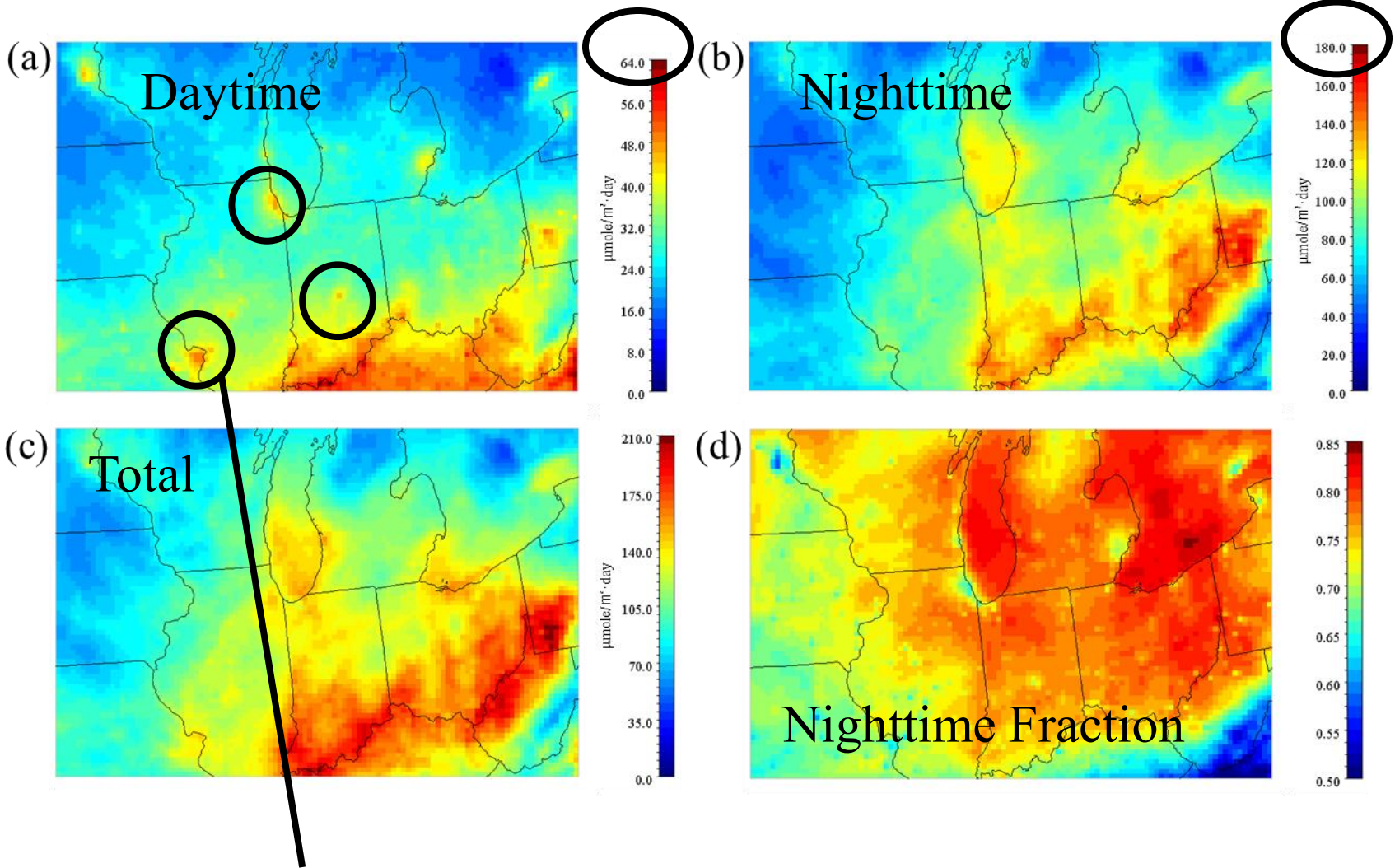


Daytime pathway ($\mu\text{mole}/\text{m}^2\text{-day}$)	Nighttime pathway ($\mu\text{mole}/\text{m}^2\text{-day}$)	Homogeneous nighttime pathway ($\mu\text{mole}/\text{m}^2\text{-day}$)	Heterogeneous nighttime pathway ($\mu\text{mole}/\text{m}^2\text{-day}$)
29.8	78.3	16.7	61.6

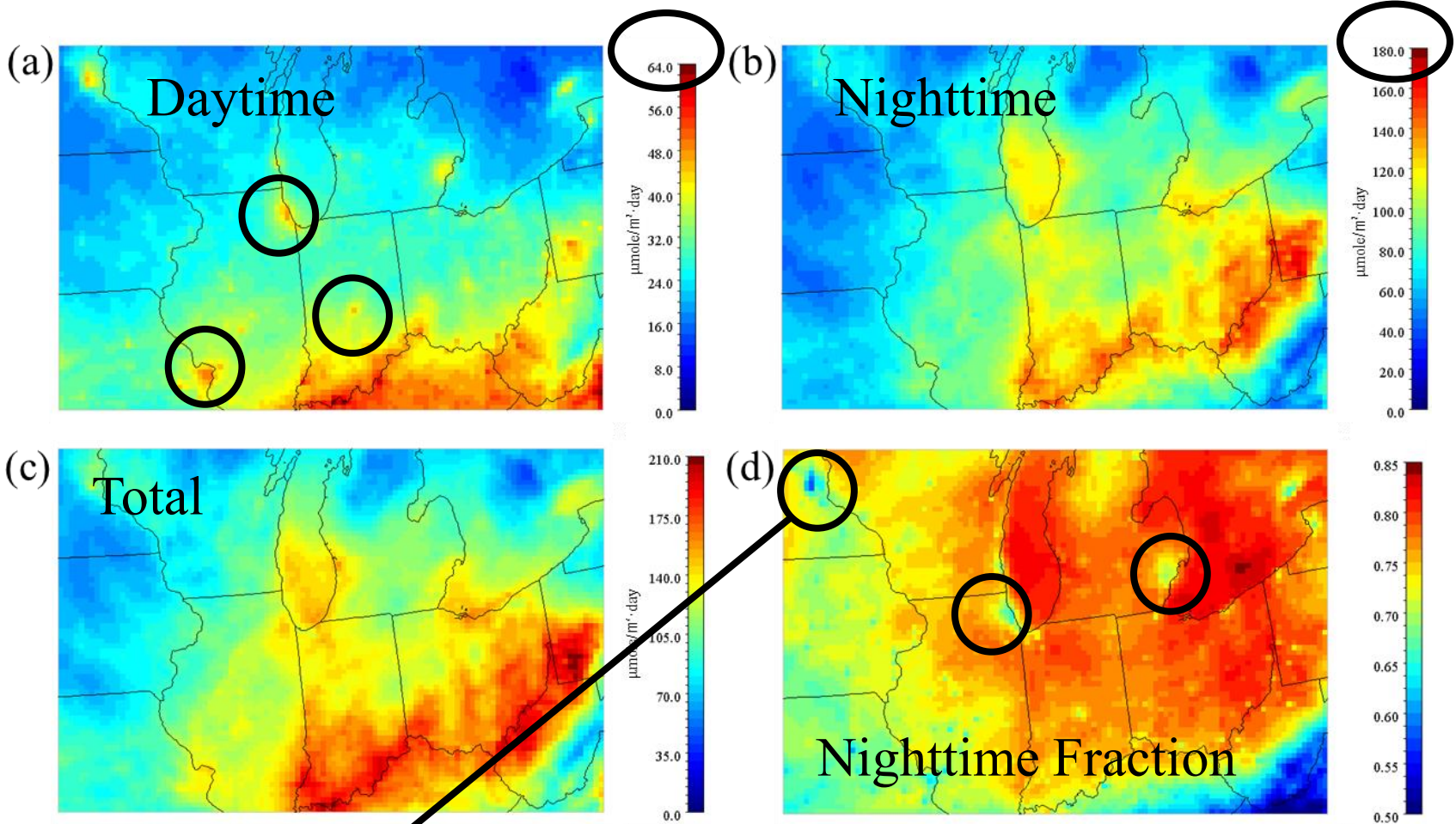




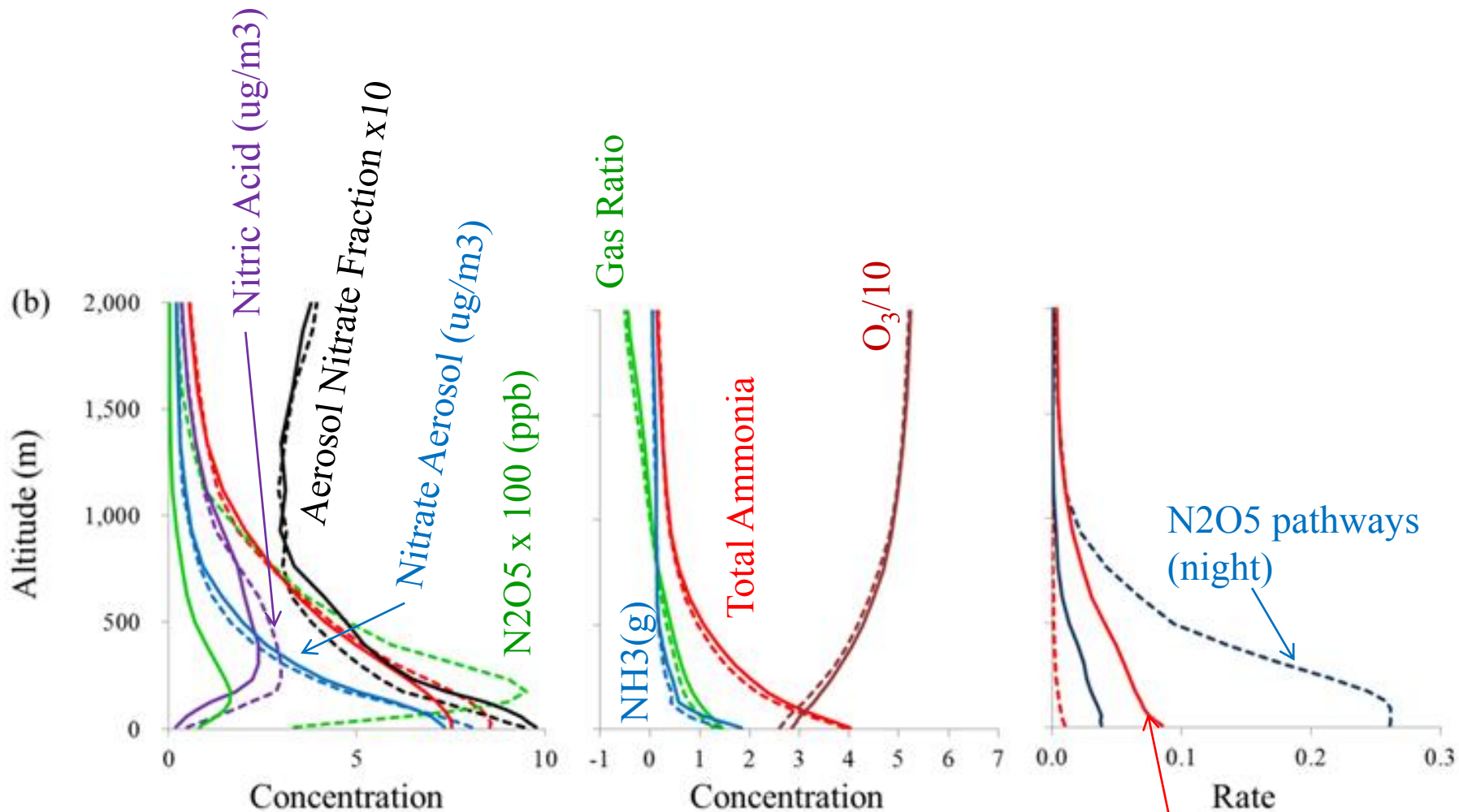
Notice the different scales



Elevated daytime production, mainly at the surface, in high NO_x locations



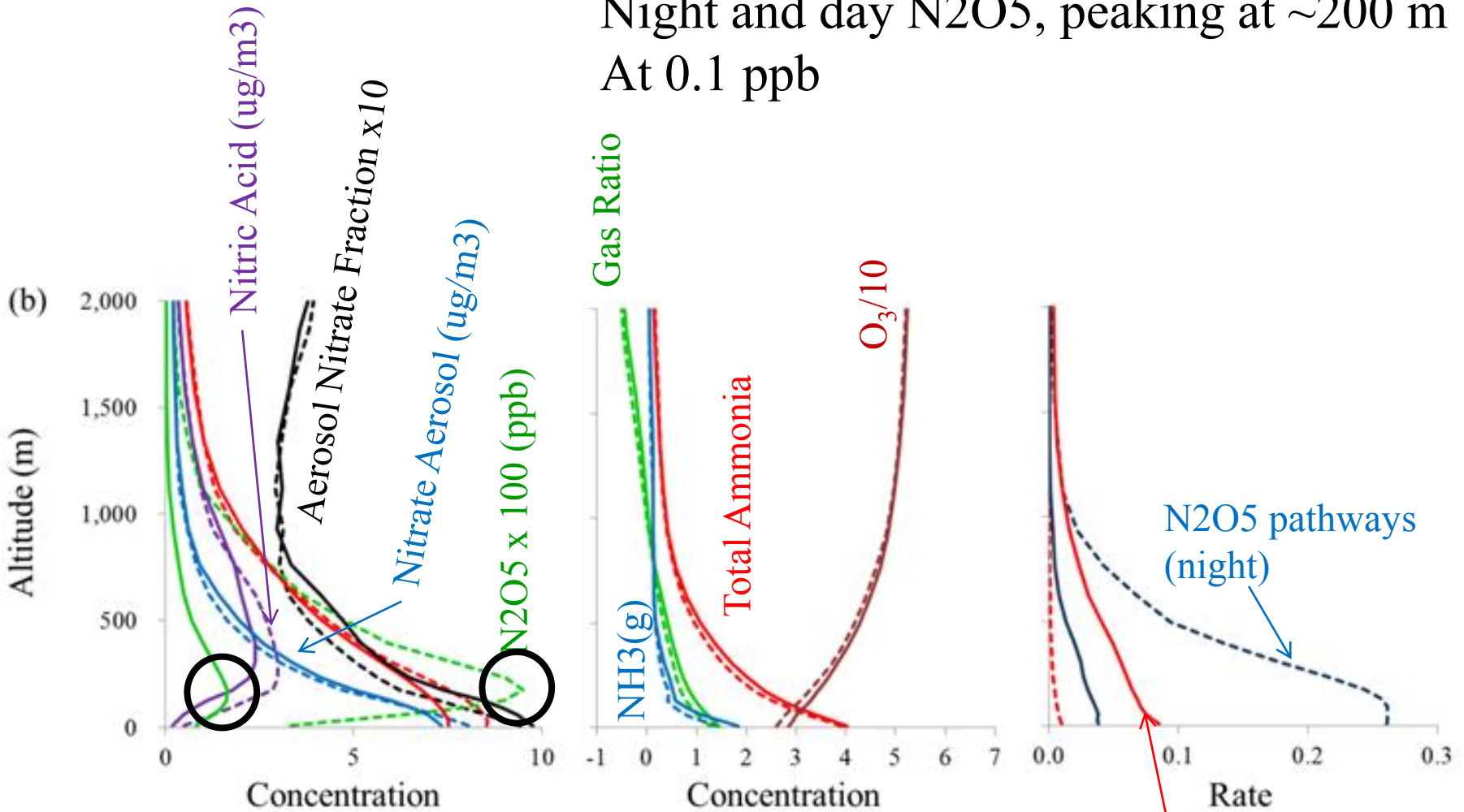
Decrease in the nighttime fraction in some (but not all) cities



Dotted = nighttime period. Solid = daytime.
 Mayville episode buildup periods

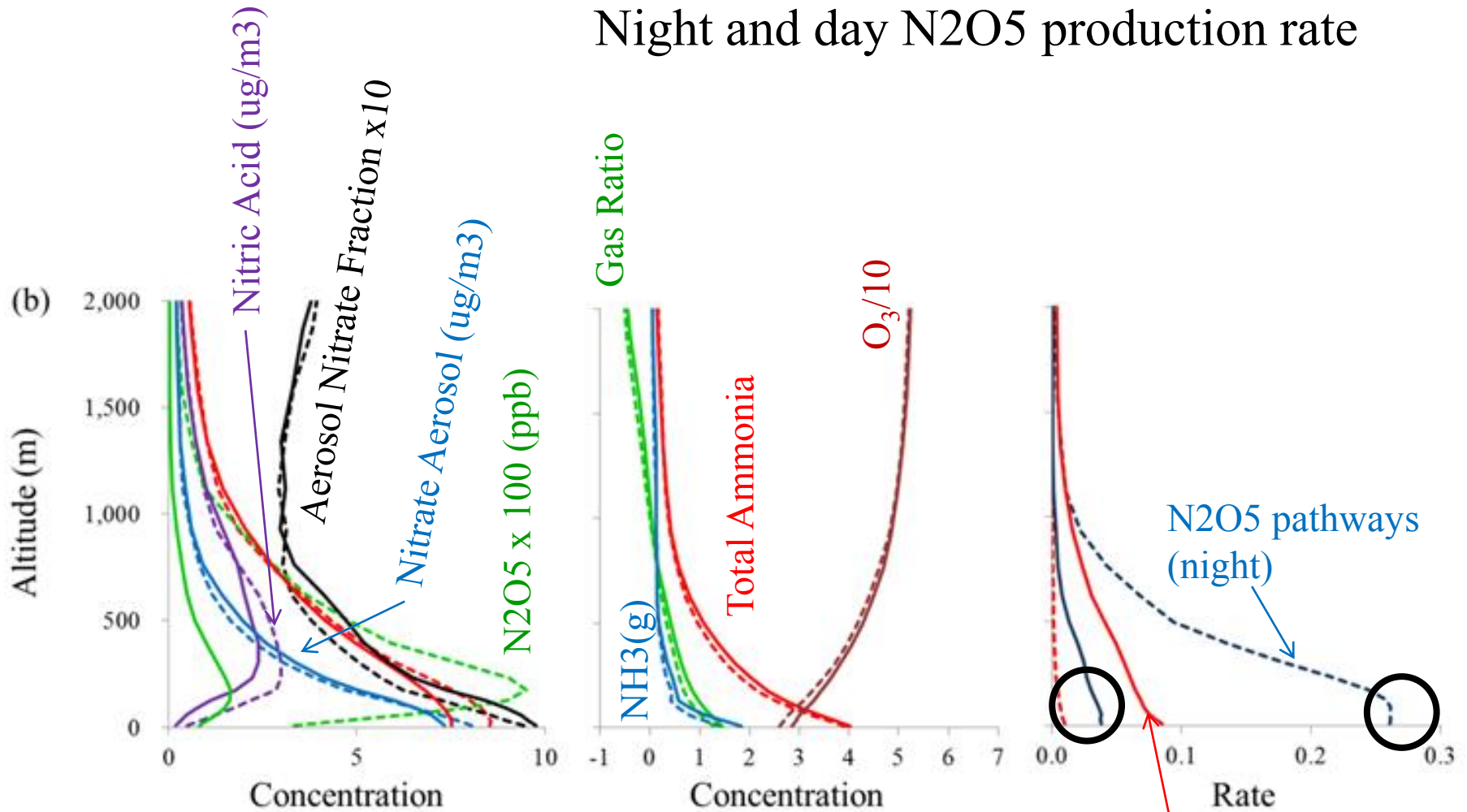
$\text{OH} + \text{NO}_2$ (day)

Night and day N2O5, peaking at ~200 m
 At 0.1 ppb



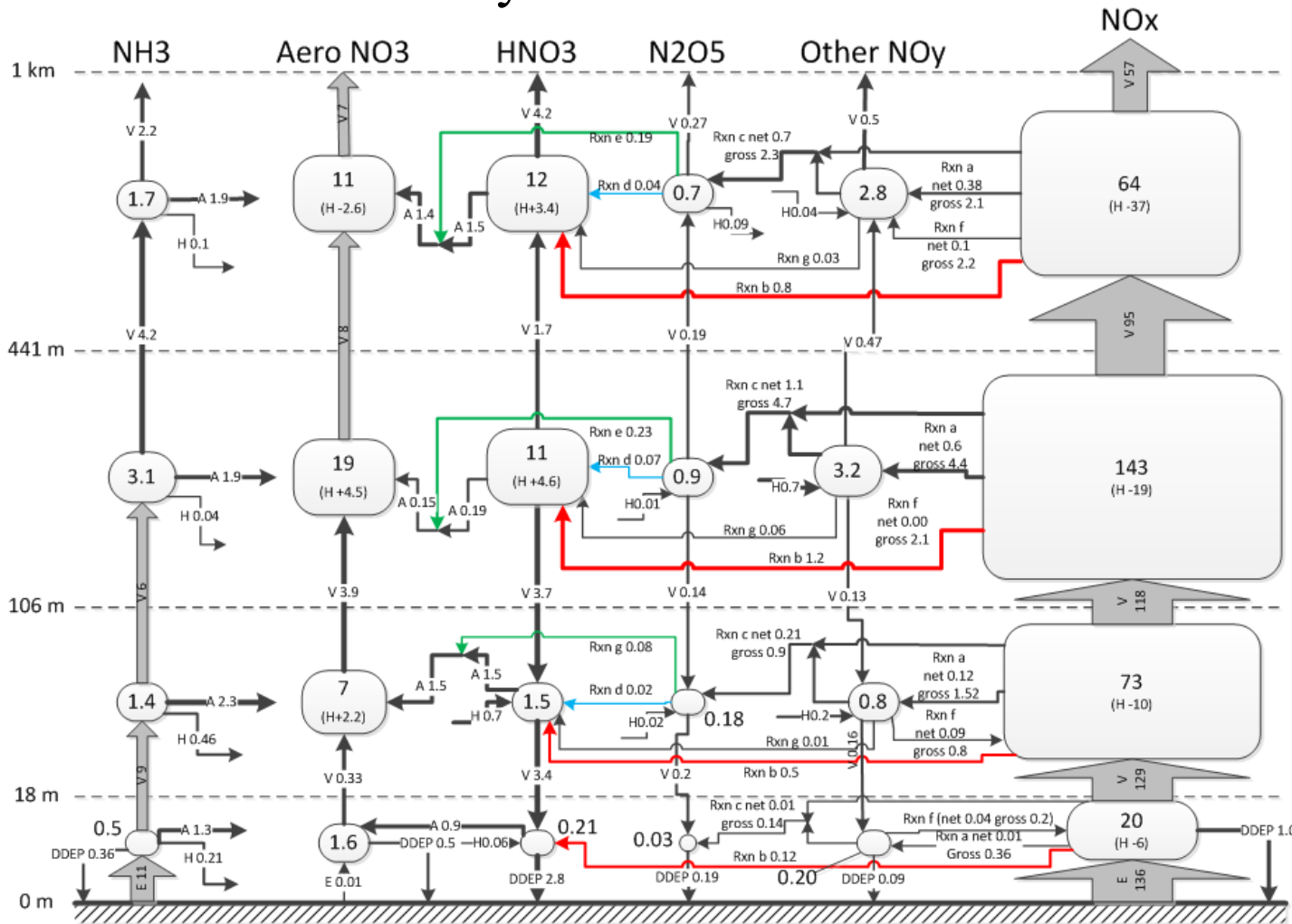
Dotted = nighttime period. Solid = daytime.
 Mayville episode buildup periods

Night and day N2O5 production rate



Dotted = nighttime period. Solid = daytime.
 Mayville episode buildup periods

Milwaukee Day



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO₃ radical formation

c: net N₂O₅ formation

g: HNO₃ formation from the NO₃ radical

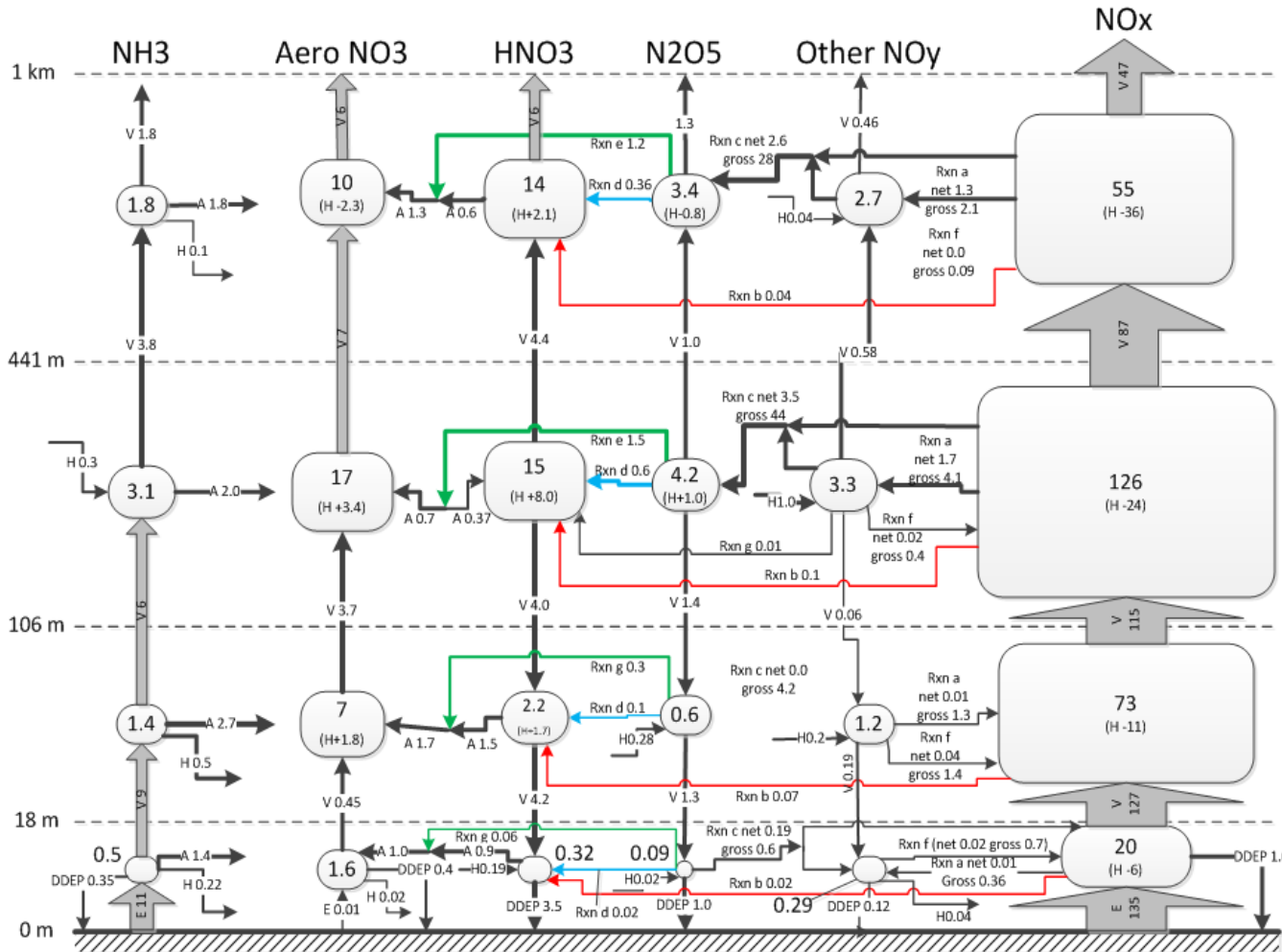
Colored lines

b: NO₂ + OH → HNO₃

d: homogenous formation of HNO₃ from N₂O₅

e: heterogeneous formation of HNO₃ from N₂O₅

Milwaukee Night



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO_3 radical formation

c: net N_2O_5 formation

g: HNO_3 formation from the NO_3 radical

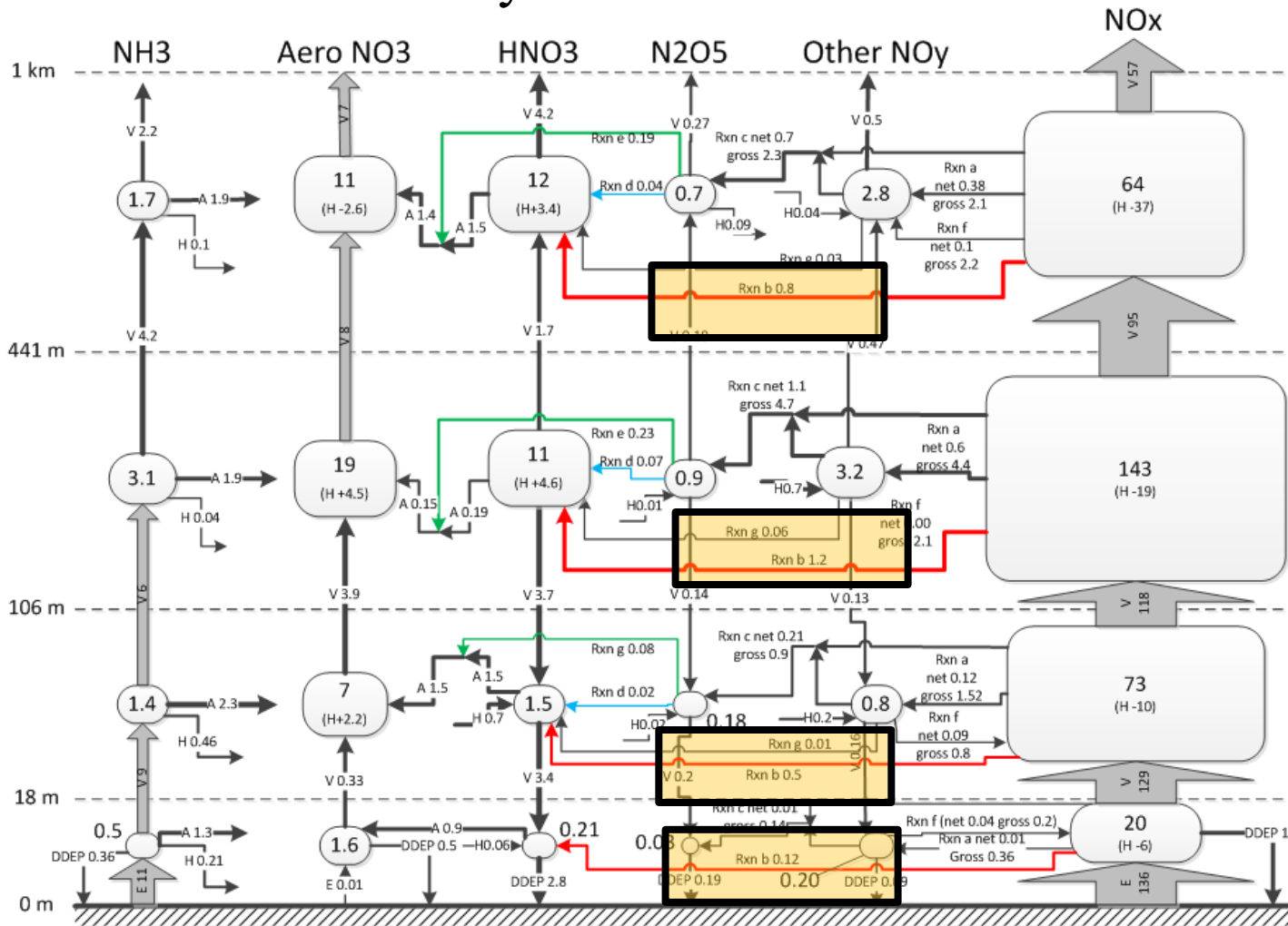
Colored lines

b: $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

d: homogenous formation of HNO_3 from N_2O_5

Flux e: heterogeneous formation of HNO_3 from N_2O_5

Milwaukee Day



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO₃ radical formation

c: net N₂O₅ formation

g: HNO₃ formation from the NO₃ radical

Colored lines

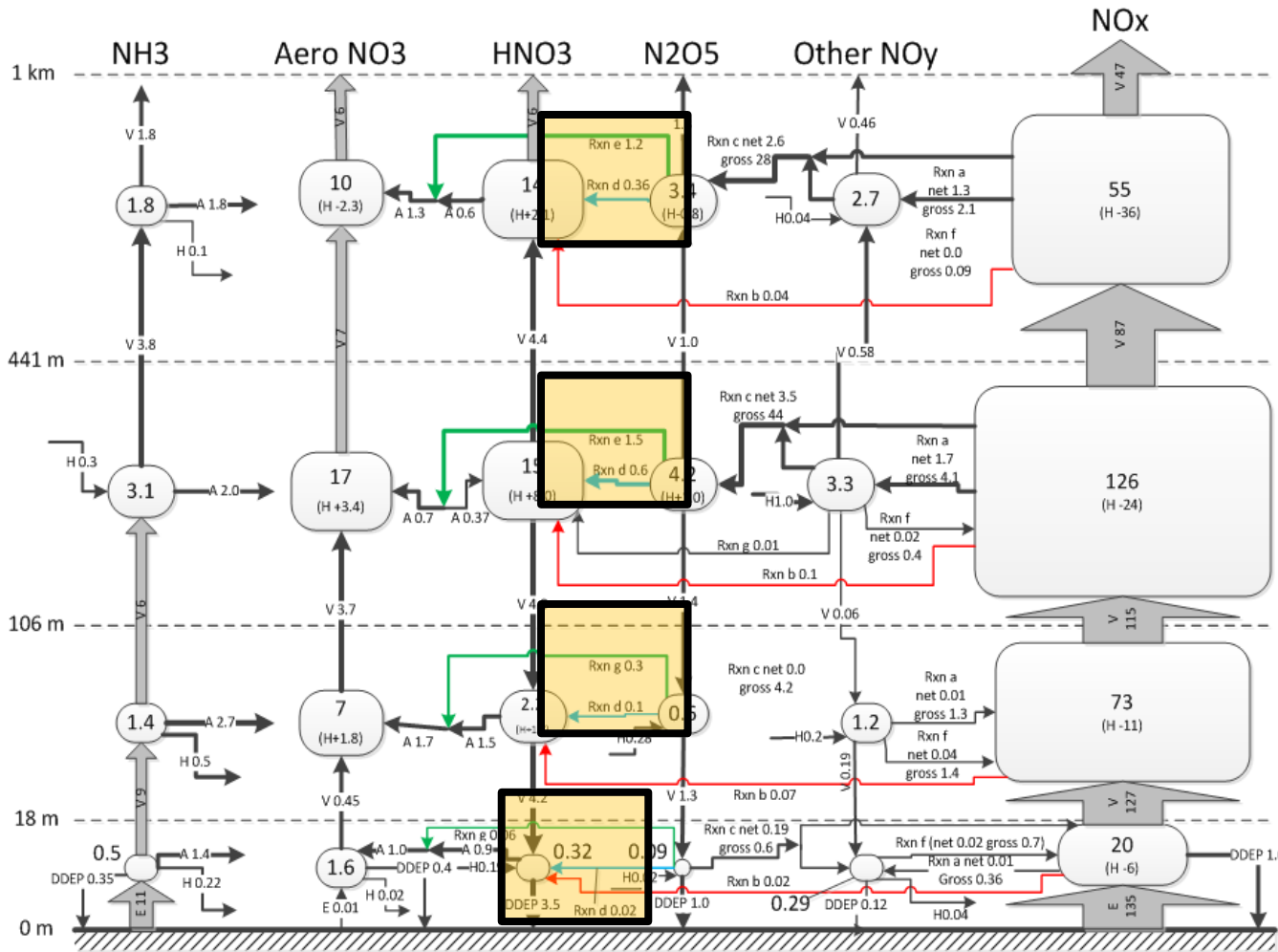
b: NO₂ + OH → HNO₃

d: homogenous formation of HNO₃ from N₂O₅

e: heterogeneous formation of HNO₃ from N₂O₅

2.8 $\mu\text{mole N} / \text{m}^2\text{-hr}$ for the daytime pathway

Milwaukee Night



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO₃ radical formation

c: net N₂O₅ formation

g: HNO₃ formation from the NO₃ radical

Colored lines

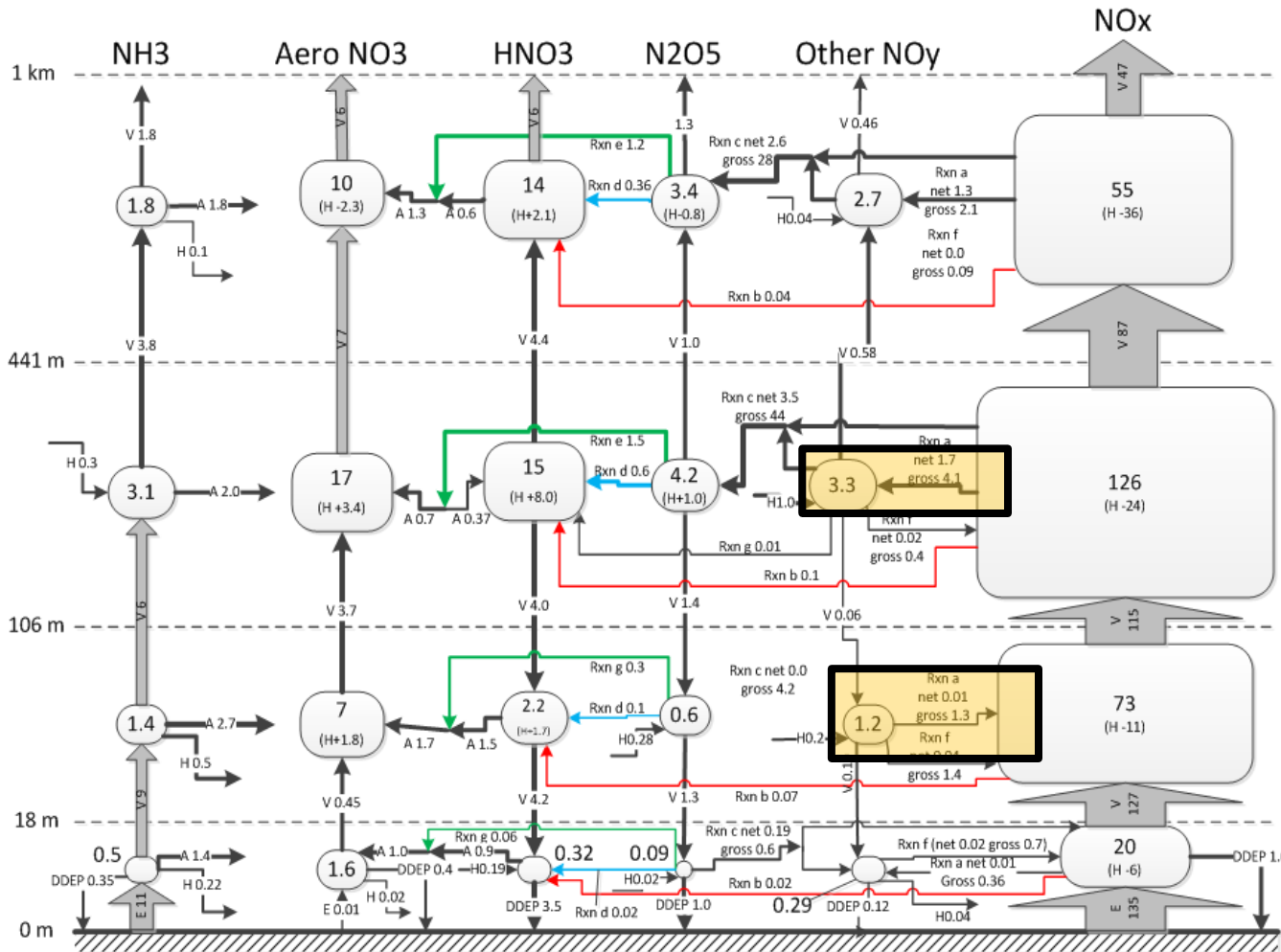
b: NO₂ + OH → HNO₃

d: homogenous formation of HNO₃ from N₂O₅

e: heterogeneous formation of HNO₃ from N₂O₅

4.4 $\mu\text{mole N} / \text{m}^2\text{-hr}$ for the nighttime pathway

Milwaukee Night



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO_3 radical formation

c: net N_2O_5 formation

g: HNO_3 formation from the NO_3 radical

Colored lines

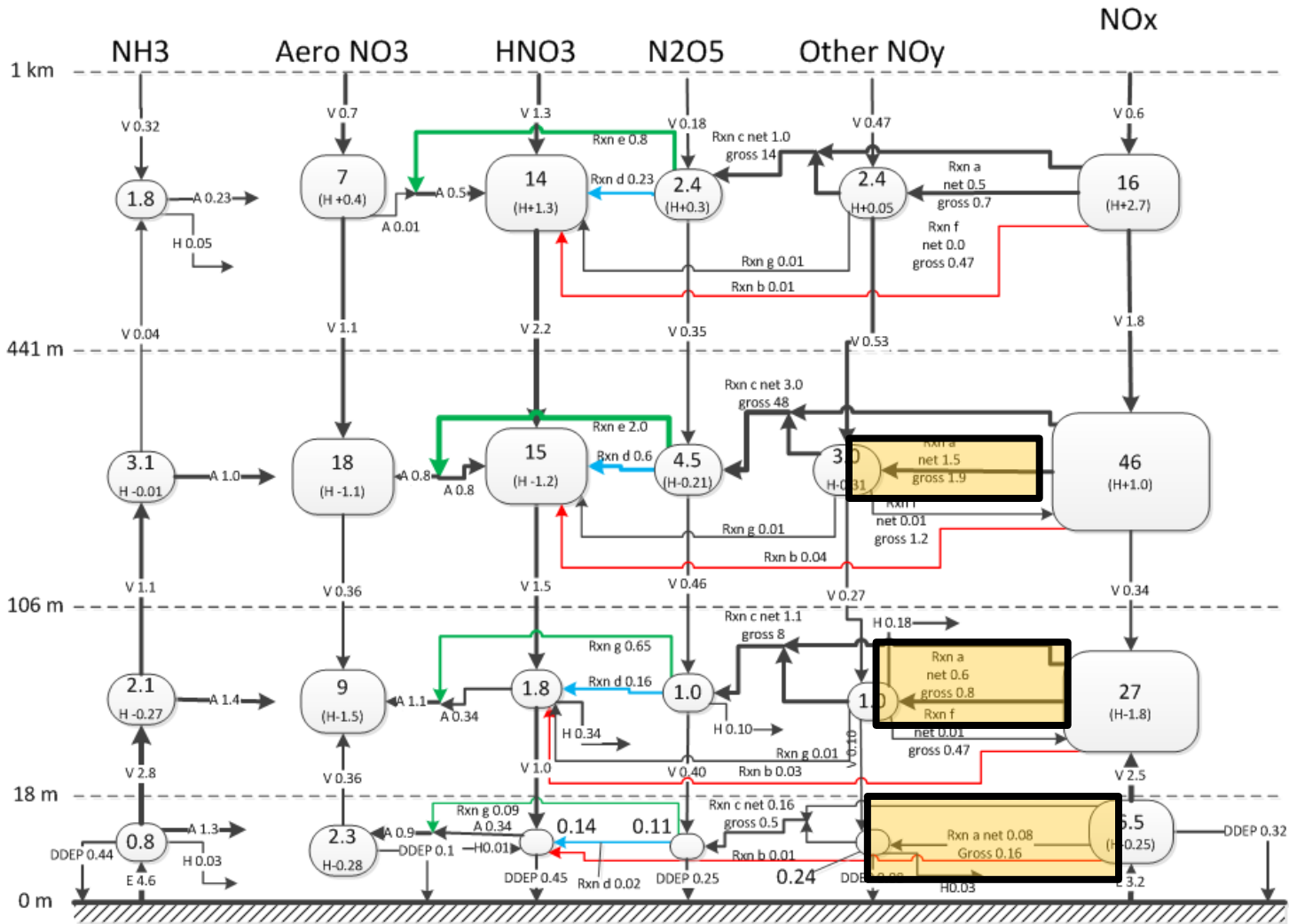
b: $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

d: homogenous formation of HNO_3 from N_2O_5

Flux e: heterogeneous formation of HNO_3 from N_2O_5

Urban nighttime titration of O_3 by high NO_x forces net NO_3 decomposition at surface at night

Mayville Night



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines
Aerosol process
Horizontal advection and diffusion
Vertical advection and diffusion
Emissions
DDEP

a: net NO_3 radical formation
c: net N_2O_5 formation
g: HNO_3 formation from the NO_3 radical

Colored lines
b: $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$
d: homogenous formation of HNO_3 from N_2O_5
Flux e: heterogeneous formation of HNO_3 from N_2O_5

NO_3 formation continues at night at all layers in the rural cell (less NO_x , O_3 remains higher)

Emissions Sensitivity Methods

- Direct Sensitivity

$$\frac{\text{Inorganic } PM_{2.5} \text{ in sensitivity CMAQ run}}{\text{Inorganic } PM_{2.5} \text{ in base CMAQ run}}$$

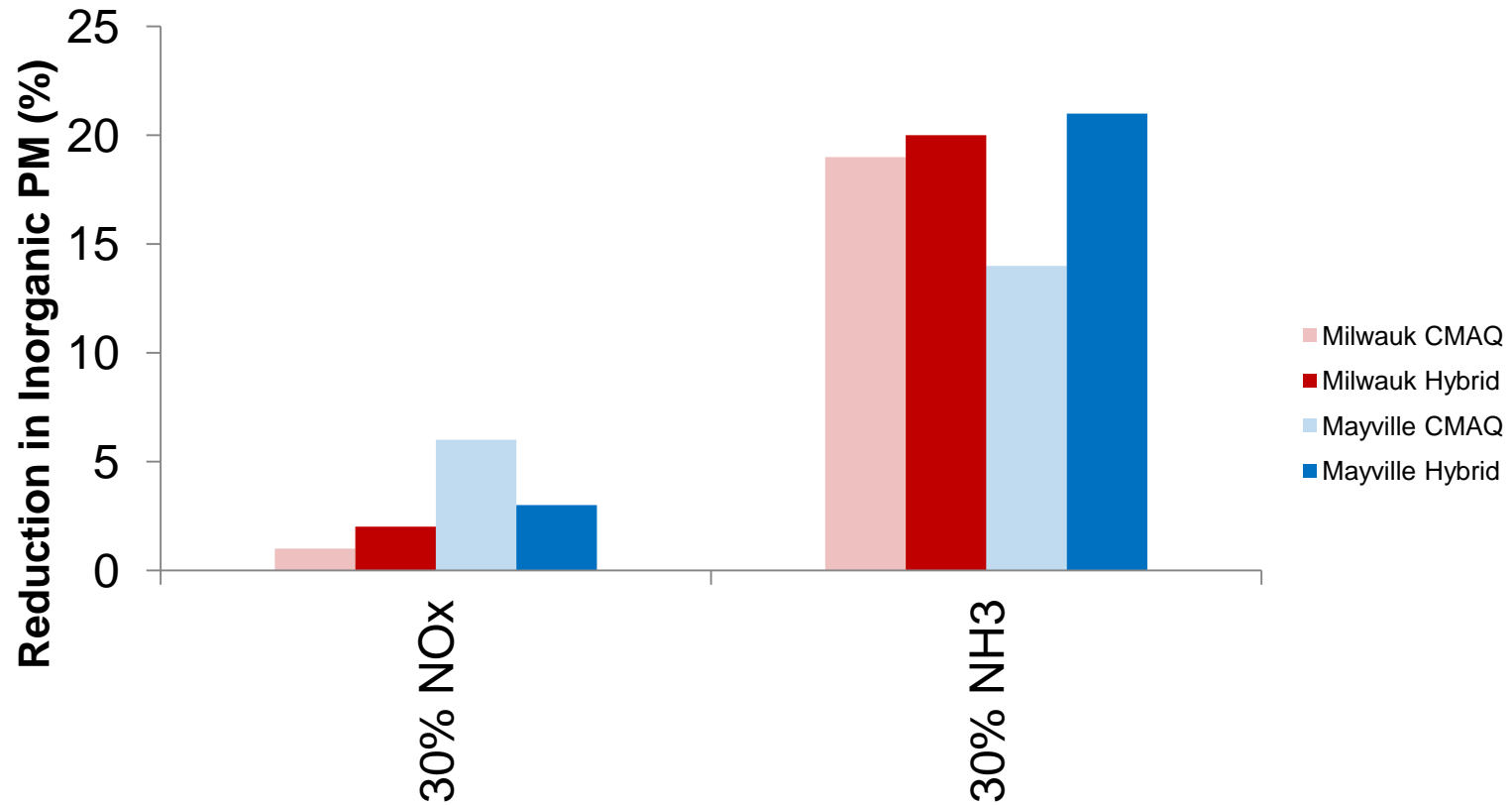
- Hybrid Box Model Sensitivity

$$\frac{\text{Sensitivity case inorganic } PM_{2.5} \text{ in predicted by ISORROPIA}}{\text{Inorganic } PM_{2.5} \text{ from ISORROPIA with all measured inputs}}$$

- Input to sensitivity case box model?
- Measured T and RH
- Measured total sulfate, ammonia, and nitrate x fractional reduction in these species predicted by CMAQ model

Thermodynamic Sensitivity / Model Skill

Direct CMAQ Sensitivities to Emissions versus ISORROPIA Model Hybrid
of Modeled and Measured Values
(During hours with $> 27 \mu\text{g m}^{-3}$ measured PM_{2.5})



Take Home Points

- LADCO Winter Nitrate Study Combined 3 months of observations with CMAQ and CAMx model runs
- Rural / Urban Patterns Identified and Quantified
- Raw Data, 2 Reports, and 2 Pubs Available
- Model Improvements?
 - Urban Locations
 - Boundary layer meteorology > NO_y chemistry, emissions, deposition > Organic aerosols
 - Rural Locations
 - NO_y chemistry, emissions, deposition > Organic aerosols ~ Sulfate aerosols
- Negative model bias for ammonia
- 72% of nitrate formation can be attributed to the nighttime pathway.
- Model treatment of heterogeneous nitrate should be a key factor in model-model differences.

Review of Take Home Points

- The NO_y system: large NO_x reservoir, resistant to depositional removal, that undergoes gradual transformation into nitrate, often (but not always) passing through the reactive intermediate forms of the NO_3 radical, N_2O_5 , and other forms of NO_y such as HONO and PAN.
- Nitrate production is mainly a regional phenomenon, with rates greater than $100 \mu\text{mole}/\text{m}^2\text{-day}$ for most of the domain.
- Urban enhancements in the daytime formation pathway are balanced by urban deficiencies in nighttime pathway leading to minimal urban / rural contrast in nitrate production.
- High concentrations of nitric acid extend spatially over a broad region with a peak near the Ohio River Valley. The southern Great Lakes and the Ohio River Valley have the most intense nitrate formation rates according to the model.
- In Wisconsin, emissions sensitivity to NH_3 is greater than sensitivity to NO_x

Some thoughts on future questions

- Deposition velocities over the Great Lakes are important
- Deposition velocities over open water, ice, and snow-covered ice may need to be considered
- $\text{N}_2\text{O}_5 \rightarrow \text{nitrate}$ rates presented here may be upper limit, as $\text{N}_2\text{O}_5 \rightarrow \text{ClNO}_2$ may consume a fraction of the N_2O_5 , and organic coatings will depress the heterogeneous reaction rate

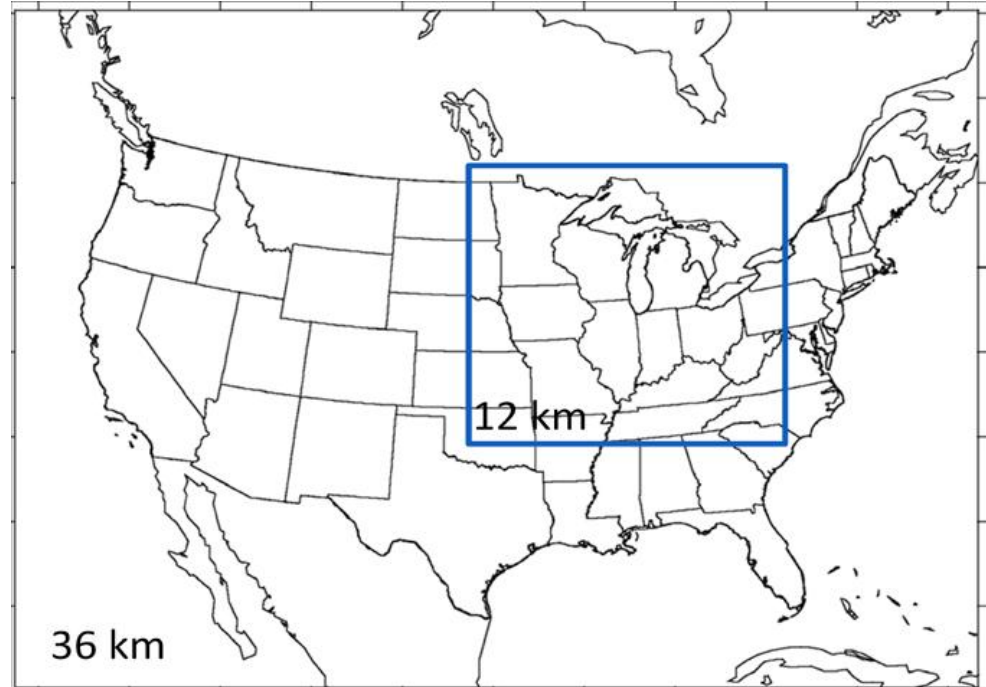
Co-authors and Acknowledgements

- University of Iowa
 - Scott Spak
 - Gregory Carmichael
 - Charles Stanier
 - Jaemeen Baek
 - Sang Rin Lee
 - Yoo Jung Kim
 - Timothy Rohlf
 - Sinan Sousan
 - Ashish Singh
- University of Illinois
 - Nicole Riemer
- EPRI
 - Stephanie Shaw
 - Naresh Kumar
- Measurements
 - Eric Edgerton (ARA Inc)
 - Mike Caughey (ISWS)
 - Wisconsin DNR staff
 - Joe Leair, Jerry Medinger, Dan Nickolie, Mary Mertes, Bruce Rodger, and Bart Sponseller
 - Site operators by John Hillery, Janel Hanrahan, Laura Carnahan
- LADCO (Lake Michigan Air Directors Consortium)
 - Michael Koerber
 - Donna Kenski
 - Mark Janssen
 - Abigail Fontaine
- Wisconsin DNR
 - Michael Majewski
 - Bill Adamski
- Funding
 - LADCO
 - Electric Power Research Institute

Additional slides

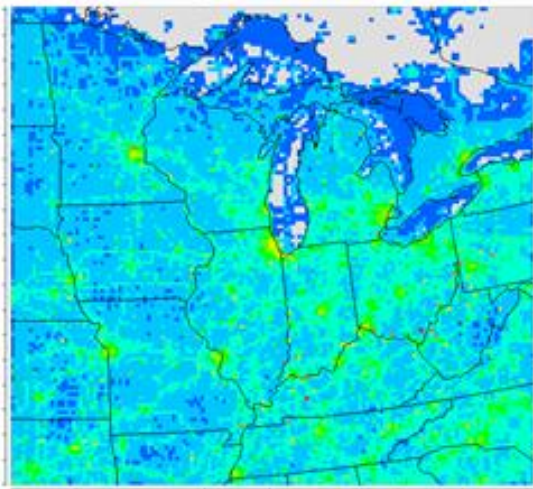
Model Configuration U of Iowa

- **Community Multiscale Air Quality Model (CMAQ) v4.7.1**
 - CB05 gas phase / AERO5 aerosol module
 - ACM2 PBL closure
 - Mass-conserving advection
 - 35 vertical layers
- **LADCO's 12 km regional modeling grid**
 - Hourly boundary conditions from a 36 km simulation (with the same configuration) covering the continental United States.
- **Meteorology**
 - WRF 3.1.1 with the RPO configuration selected by Iowa DNR, SESARM, and LADCO
 - ACM2 PBL closure
 - Pleim-Xu land surface module
 - RRTM radiation
 - Morrison microphysics
 - Kain-Fritsch cumulus
 - NARR 3-hourly met for initial and boundaries
 - Analysis nudging on NARR above the PBL, horizontal winds used for observational nudging in the PBL
- **Emissions**
 - LADCO's 2007 emissions inventory used for 12km domain.
 - Day-specific biomass burning emissions from MODIS fire detection products.

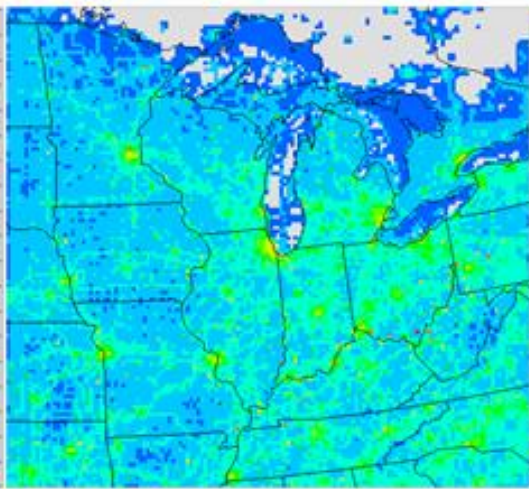


- **Process Analysis**
 - Chemical and process rates stored for all layers up to 550 m, with focus on NO_y processing and N₂O₅ heterogeneous chemistry

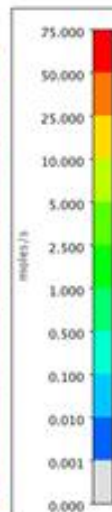
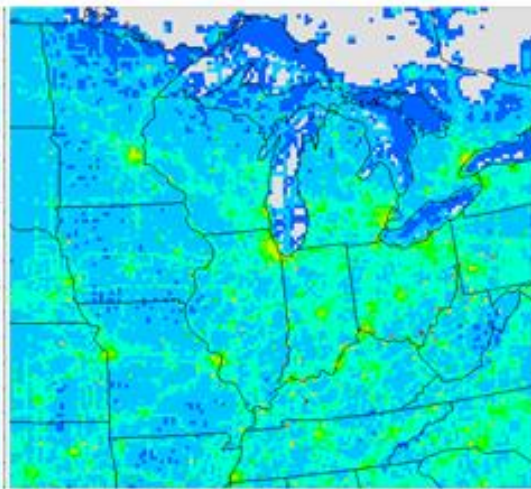
January NOx Emissions



February NOx Emissions

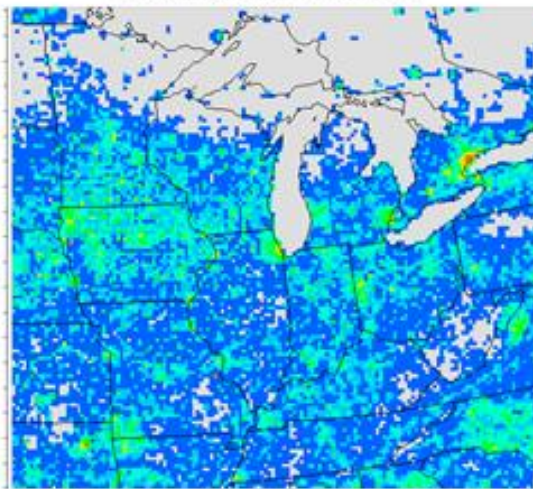


March NOx Emissions



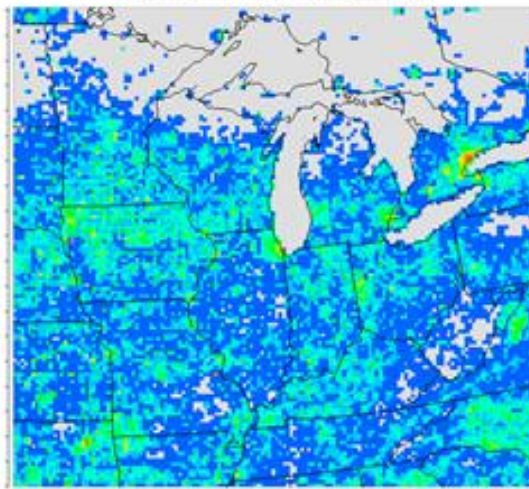
d)

January NH3 Emissions



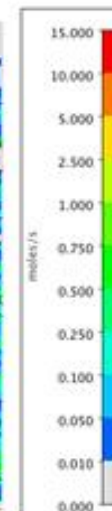
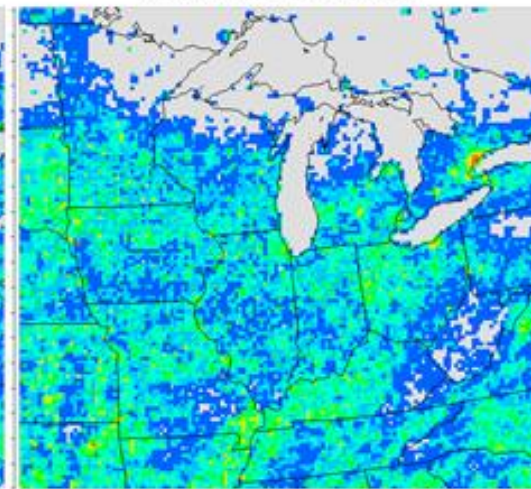
e)

February NH3 Emissions



f)

March NH3 Emissions



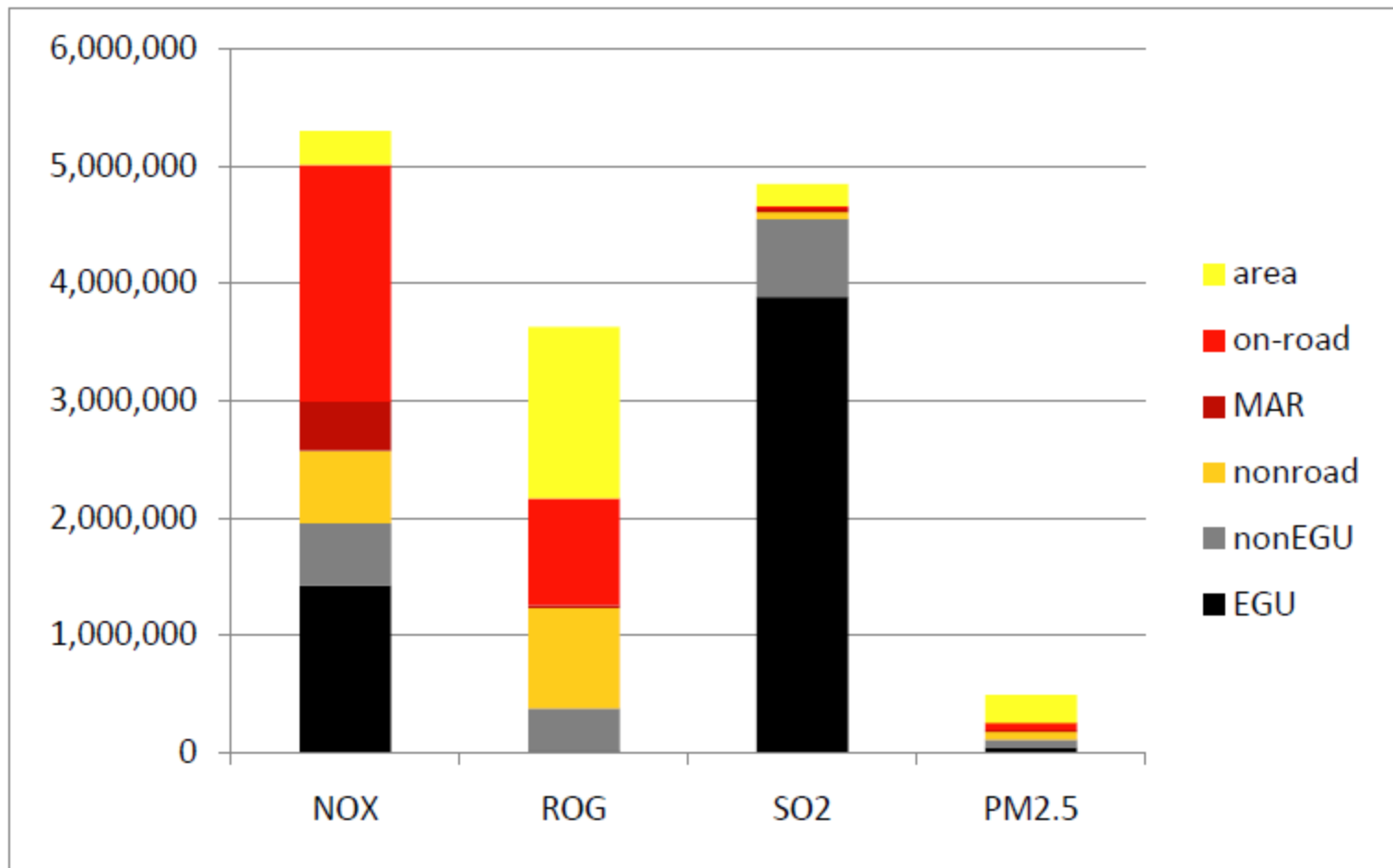


Figure 4. 2007 annual emissions by pollutant and source sector (LADCO States)

Emissions Details

- Emissions represent 2007/2008 conditions, although 2009 was modeled.
- Emissions were based on the May 2011 version of the **LADCO 2007/2008 Base C anthropogenic inventory** (LADCO, 2010), resolving monthly average emissions and their diurnal profiles for each emissions sector.
 - Upper Midwest, which comprise a large part of the 12 km modeling domain, LADCO's 2007 emissions data were used for EGU point, non-road, and on-road sources, and 2008 emissions data were used for non-EGU point and area sources.
 - For other states in the modeling domain, data representing 2005 conditions were provided by RPOs.
- The 2007/2008 inventories for on-road, off-road, and ammonia, emissions were estimated using a range of emission models. EPA's new MOVES2010a model was used with national default inputs to produce on-road emissions for the country.
- EPA's NMIM2008 model was used to produce emissions for most off-road sources. The emissions for three other off-road categories (commercial marine, aircraft, and rail) were developed separately.
- Agricultural ammonia emissions were based on Carnegie Mellon University's Ammonia Emission Inventory for the Continental United States. Specifically, the CMU annual emissions for 2002 were first grown to reflect 2007 conditions.
 - A new process-based ammonia emissions model developed for LADCO (Zhang, *et al.*, 2005; Mansell *et al.*, 2005) was then used to develop monthly and hourly temporal allocation factors.
- The Upper Midwest 2007/2008 inventory for area and point sources was based on data supplied by states. 2007 emissions were supplied for EGU point sources, while 2008 data were supplied for area and non-EGU point sources.
- Emissions for Canada were based on the 2005 Canadian National Pollutant Release Inventory, Version 1.0 (NPRI). A subset of the NPRI data (emissions and stack parameters) relevant to air quality modeling were reformatted and used in the regional modeling. Canadian area sources were allocated from provincial totals to the modeling grid using population as the primary spatial surrogate, which leads to artifacts in agricultural and non-road emissions
- Hourly biogenic emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.04 (Guenther *et al.*, 2004), were processed to both grids from 1 km resolution input fields and hourly WRF meteorology, and speciated for CB05 as in Wilkerson (2006).
- Daily gridcell-specific point fire emissions were taken from the 1 km x 1 km resolution Fire INventory from NCAR (FINN; Wiedinmyer *et al.*, 2011), based on MODIS fire detection retrievals. Emissions were processed for CMAQ by estimating hourly rates and vertical plume rise using a local fire size and intensity clustering technique (WRAP, 2005) as applied to a prior version of this inventory by Tai *et al.* (2008). Speciated VOC emissions rates for the CB05 mechanism were allocated from total VOC emissions as in Tai *et al.* (2008).

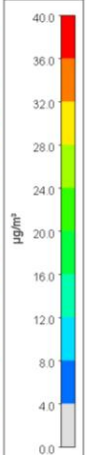
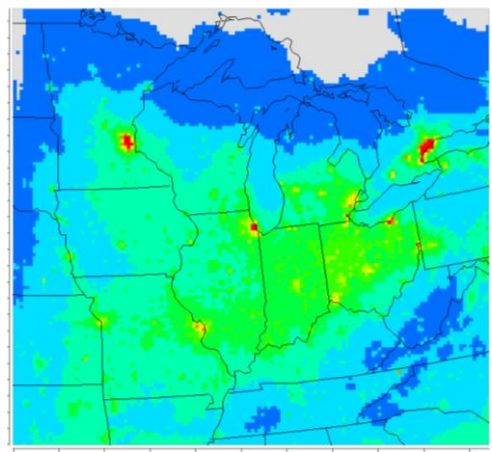
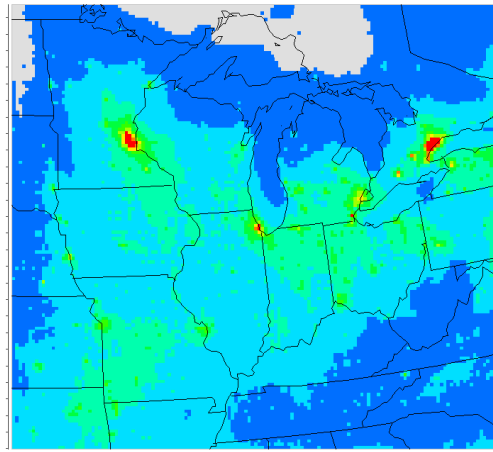
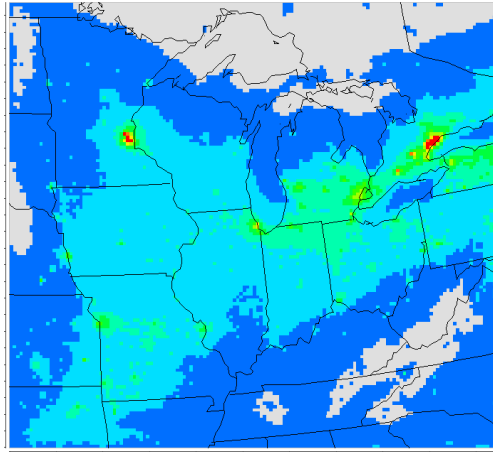
PM2.5

JAN

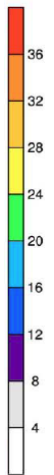
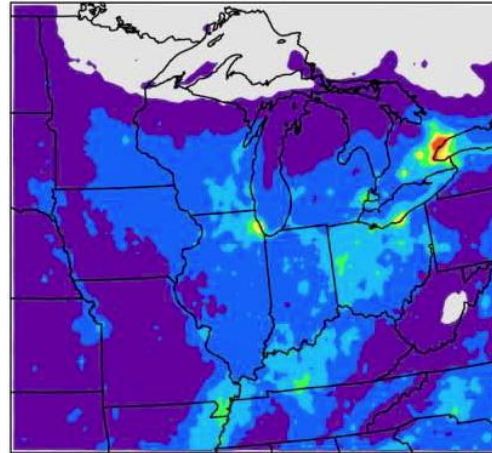
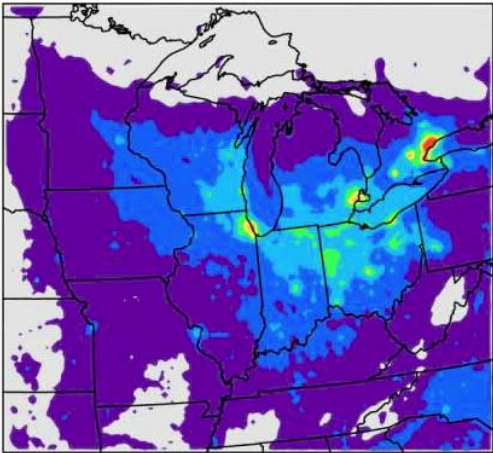
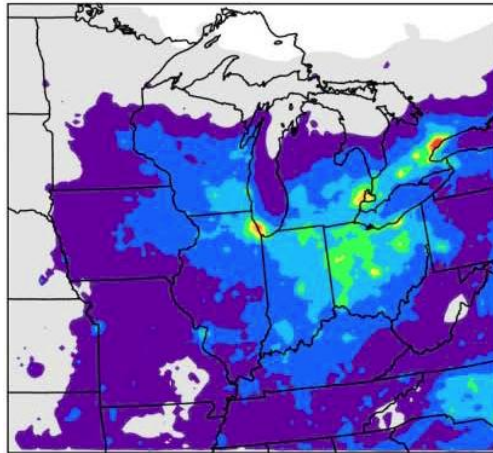
FEB

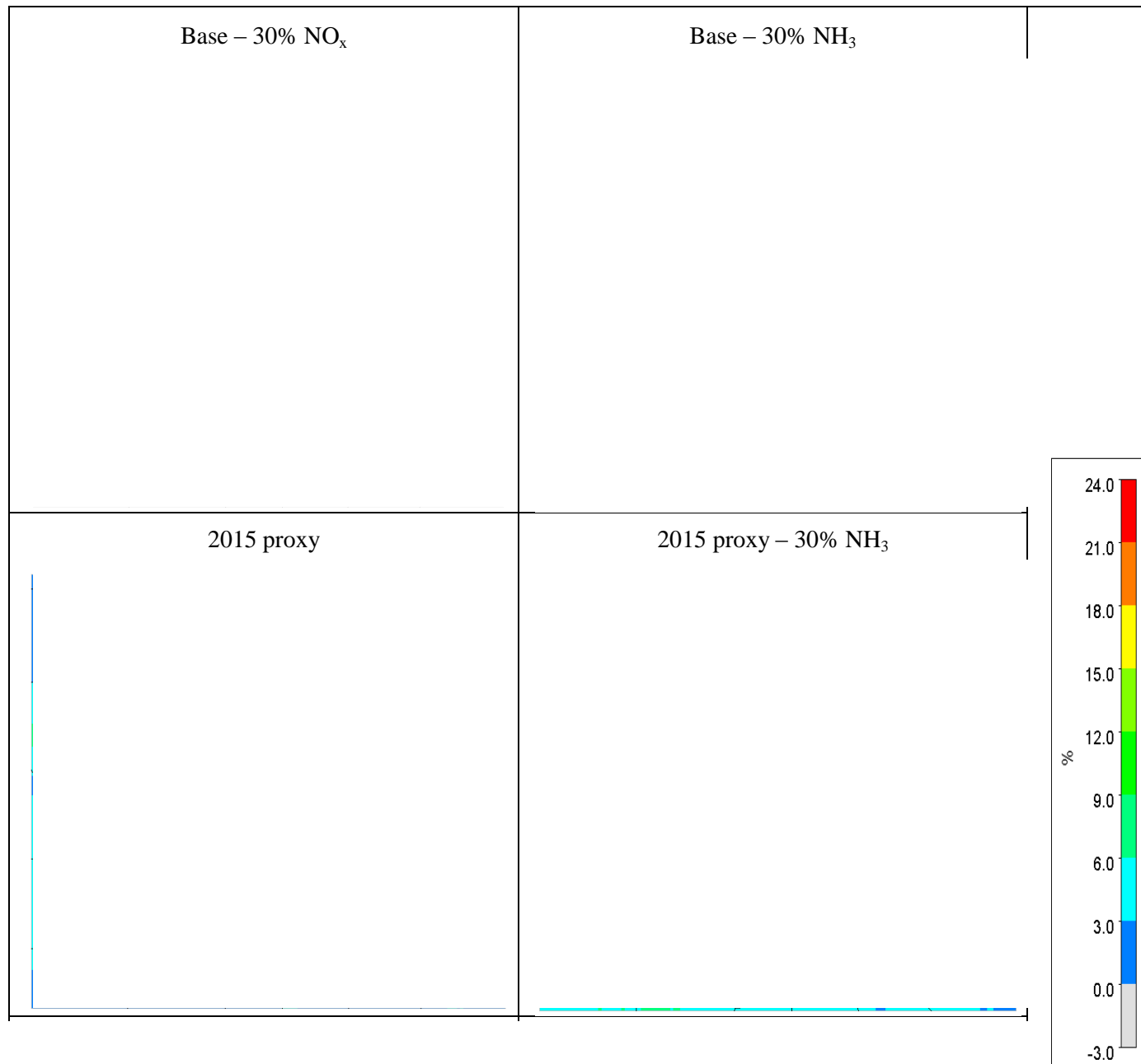
MAR

CMAQ

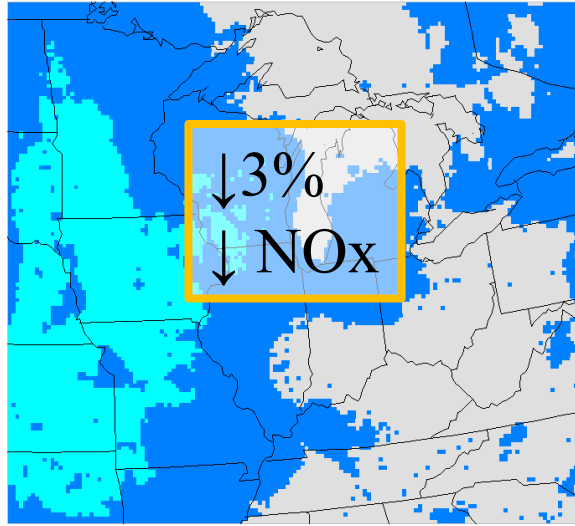


CAMx



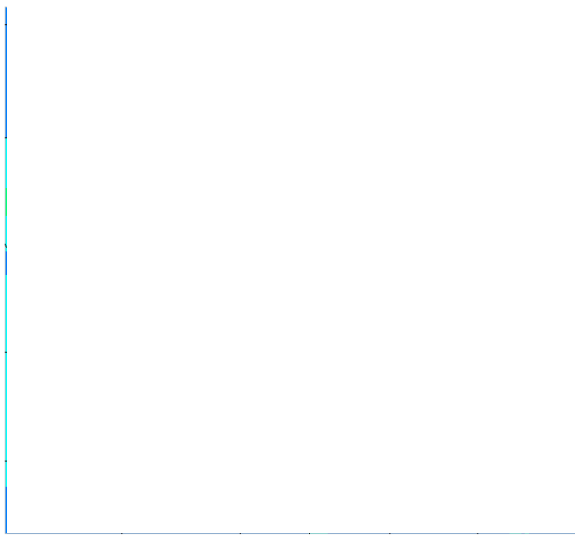


Base – 30% NO_x

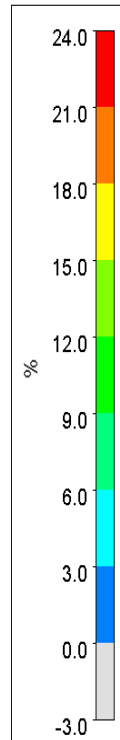
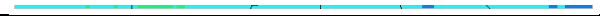


Base – 30% NH₃

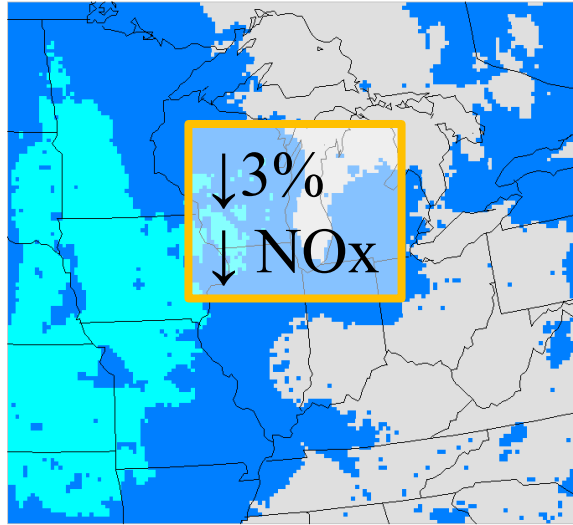
2015 proxy



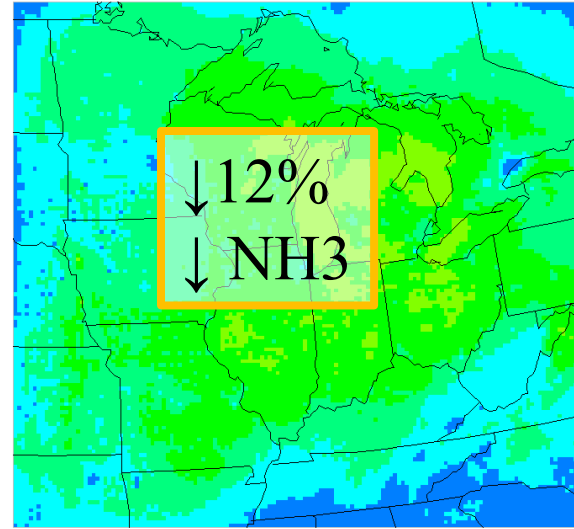
2015 proxy – 30% NH₃



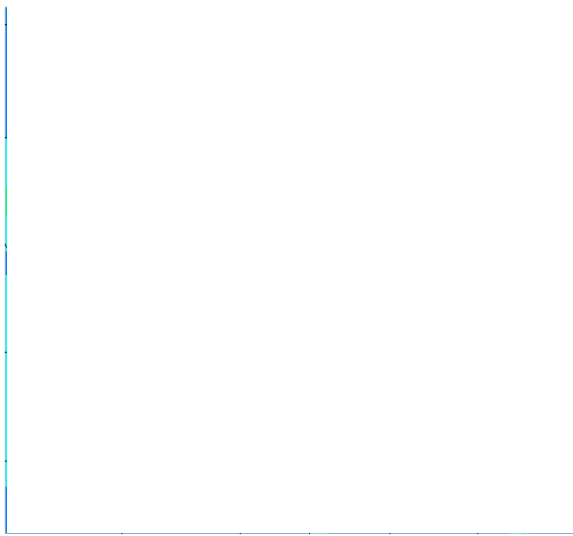
Base – 30% NO_x



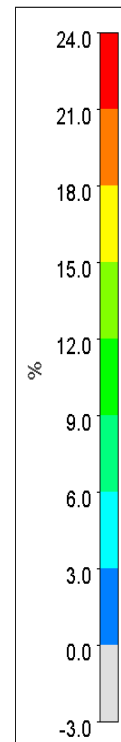
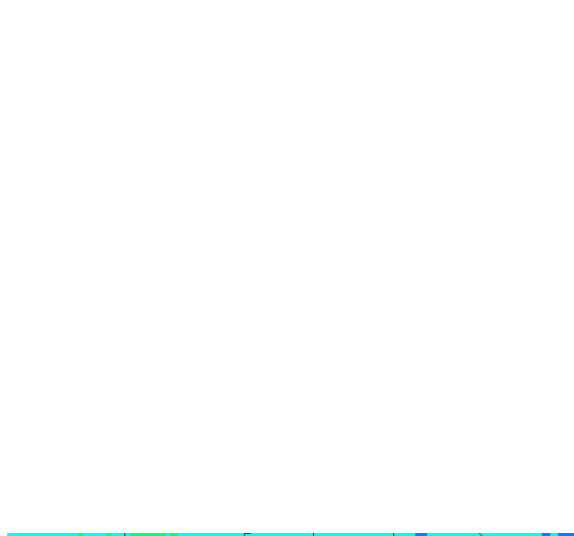
Base – 30% NH₃



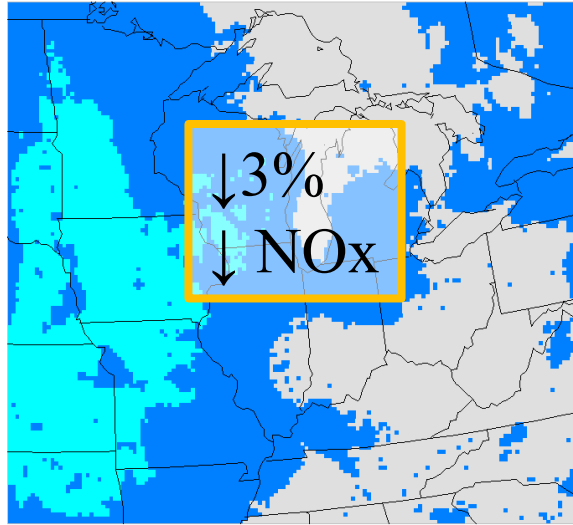
2015 proxy



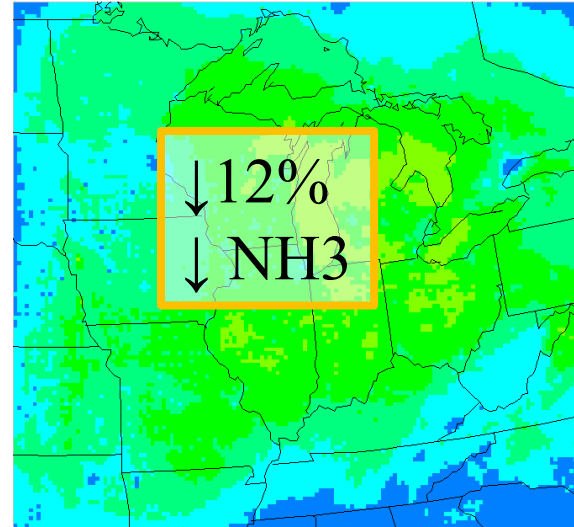
2015 proxy – 30% NH₃



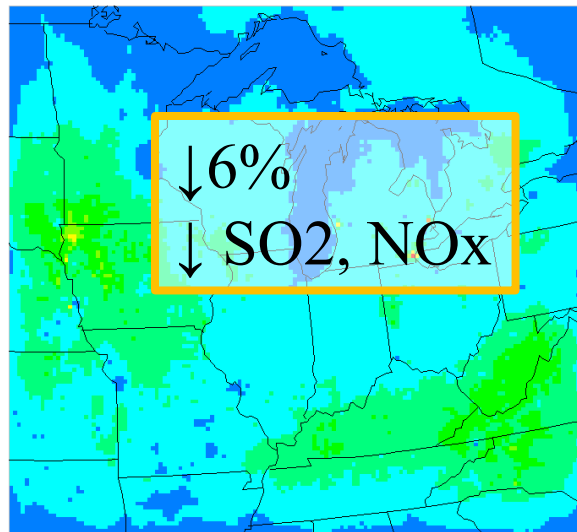
Base – 30% NO_x



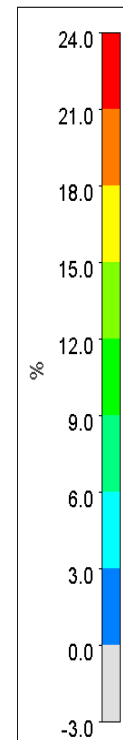
Base – 30% NH₃



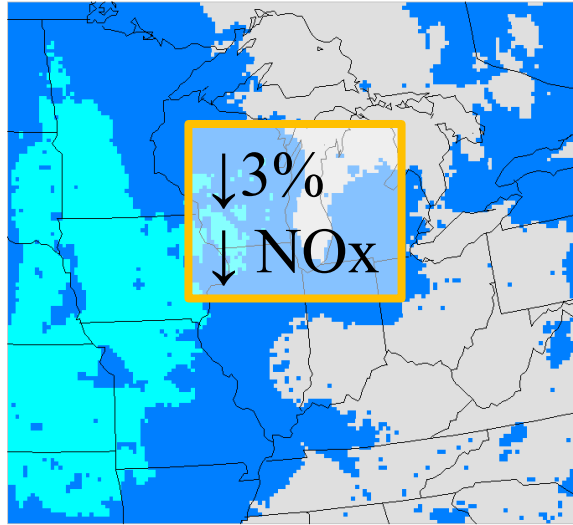
2015 proxy



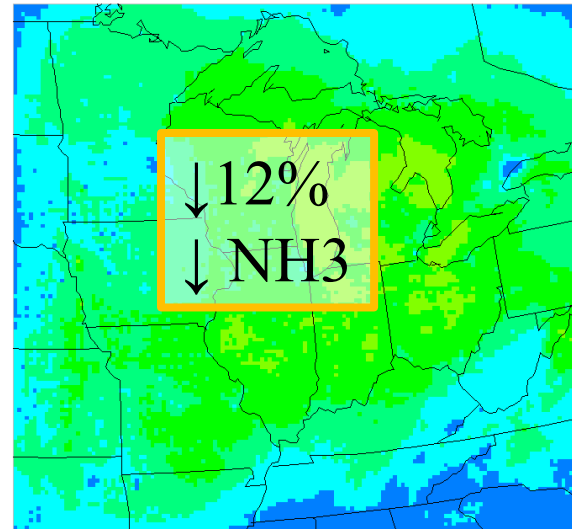
2015 proxy – 30% NH₃



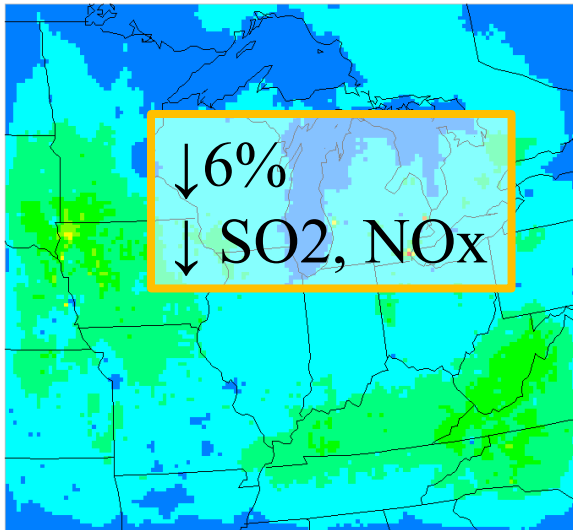
Base – 30% NO_x



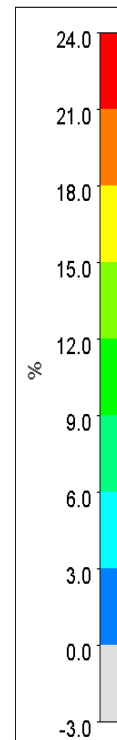
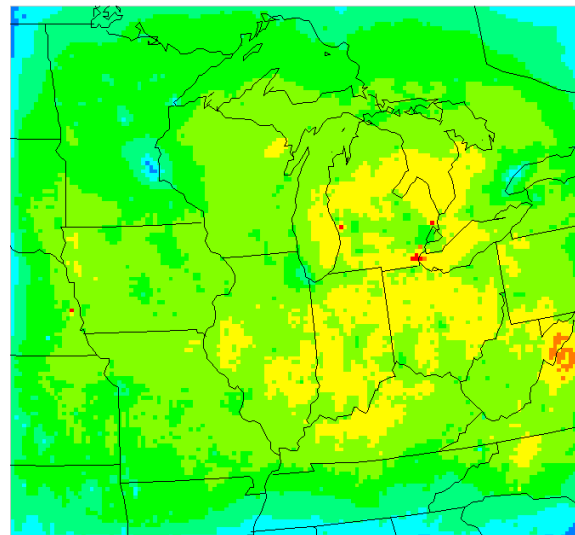
Base – 30% NH₃



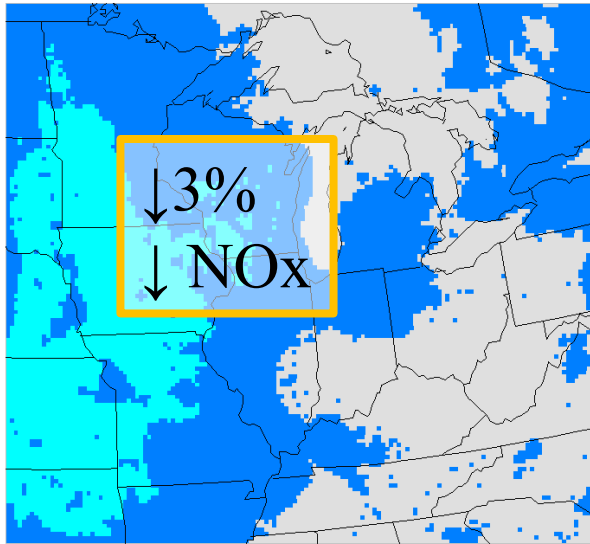
2015 proxy



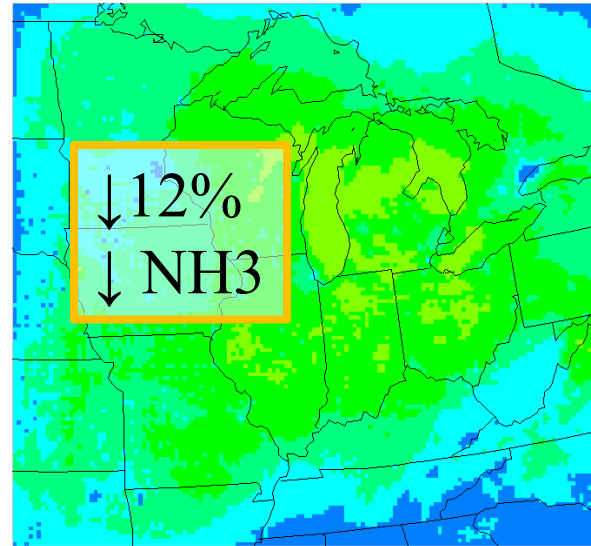
2015 proxy – 30% NH₃



Base – 30% NO_x (domain wide)

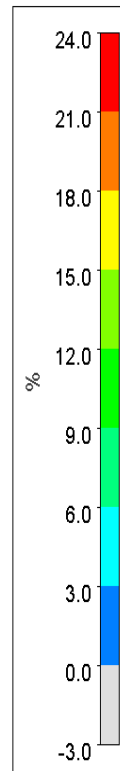


Base – 30% NH₃ (domain wide)

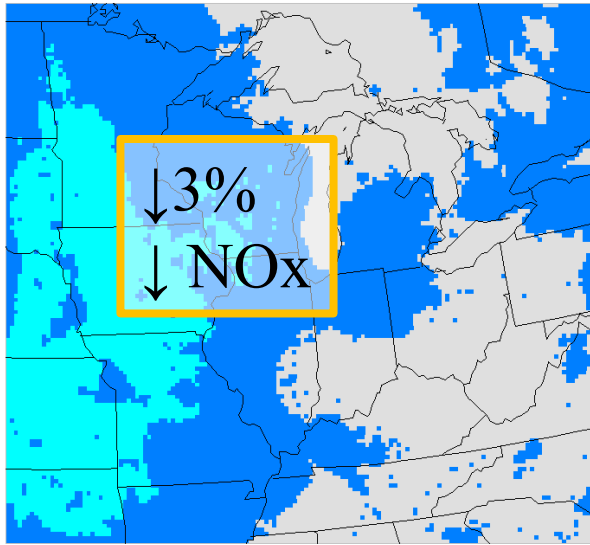


Base – 30% NO_x (250 km)

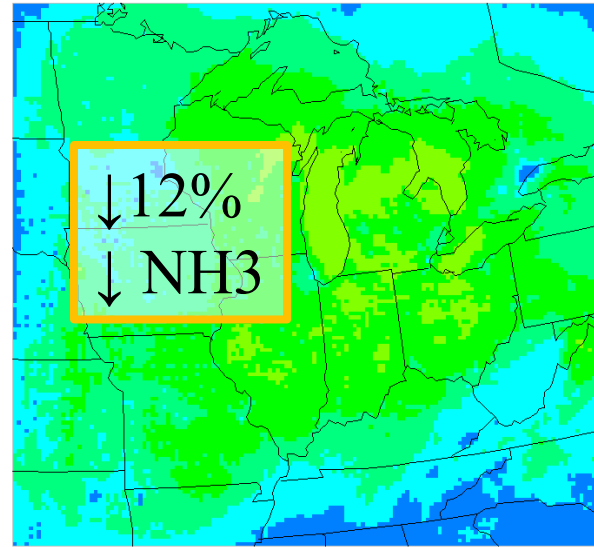
Base – 30% NH₃ (250 km)



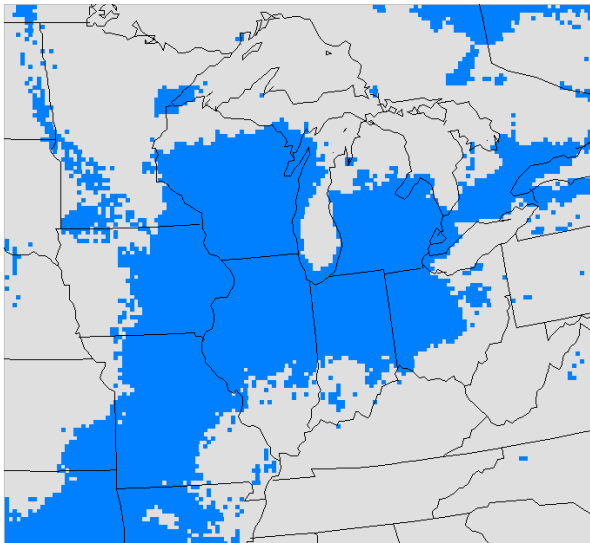
Base – 30% NO_x (domain wide)



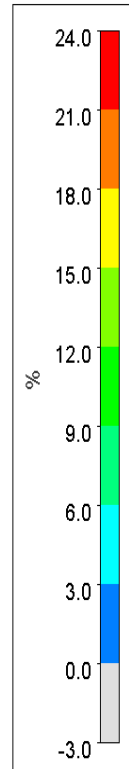
Base – 30% NH₃ (domain wide)



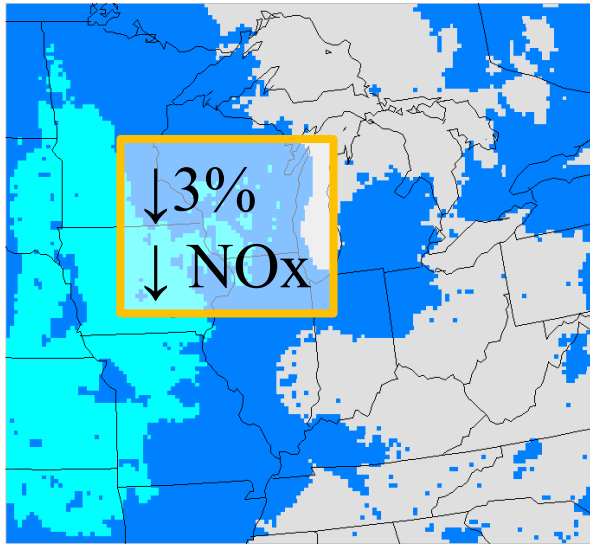
Base – 30% NO_x (250 km)



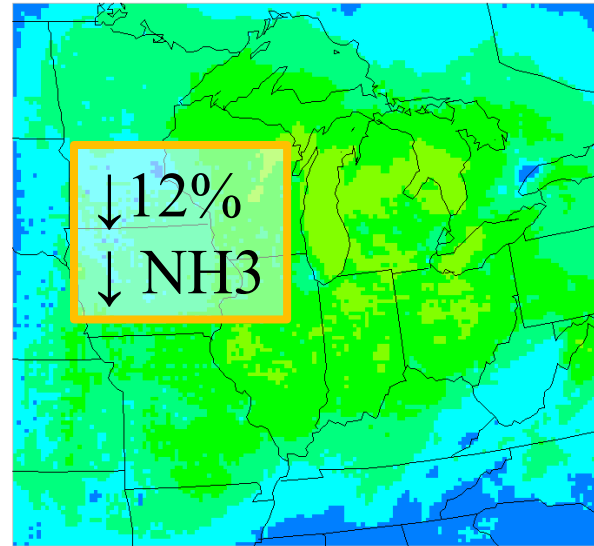
Base – 30% NH₃ (250 km)



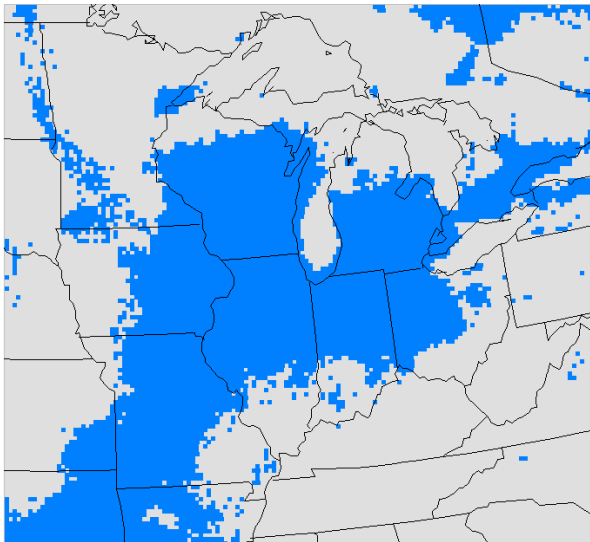
Base – 30% NO_x (domain wide)



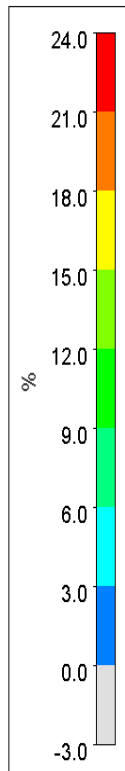
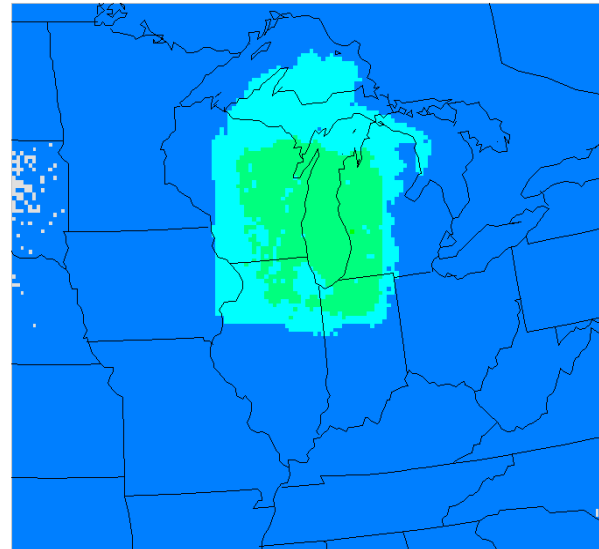
Base – 30% NH₃ (domain wide)

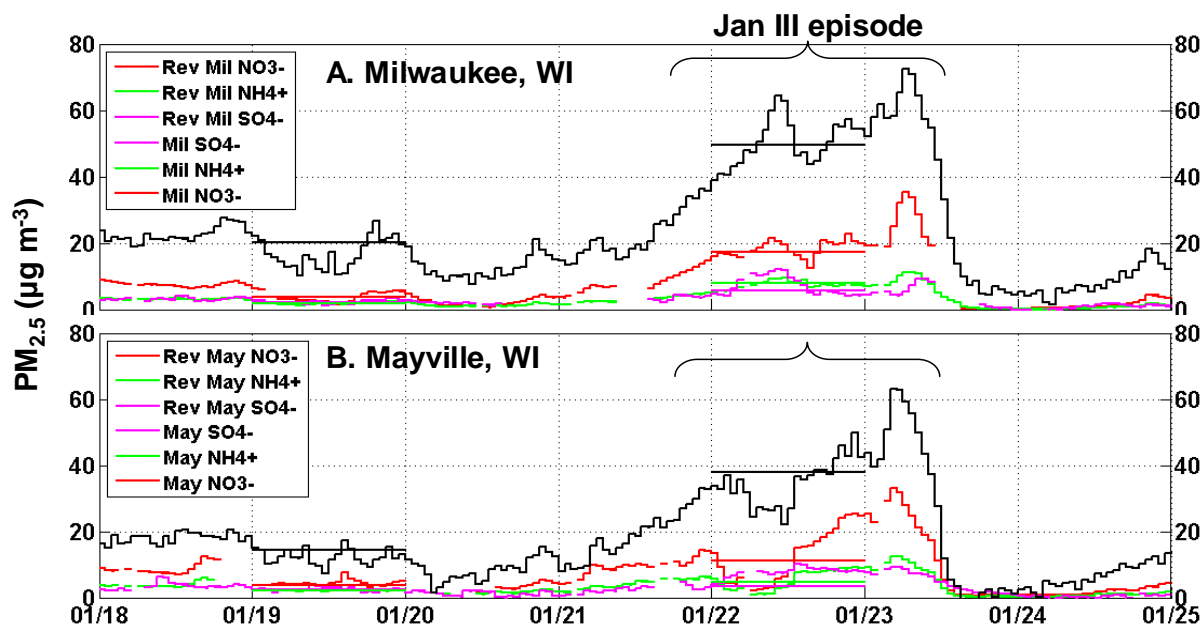


Base – 30% NO_x (250 km)

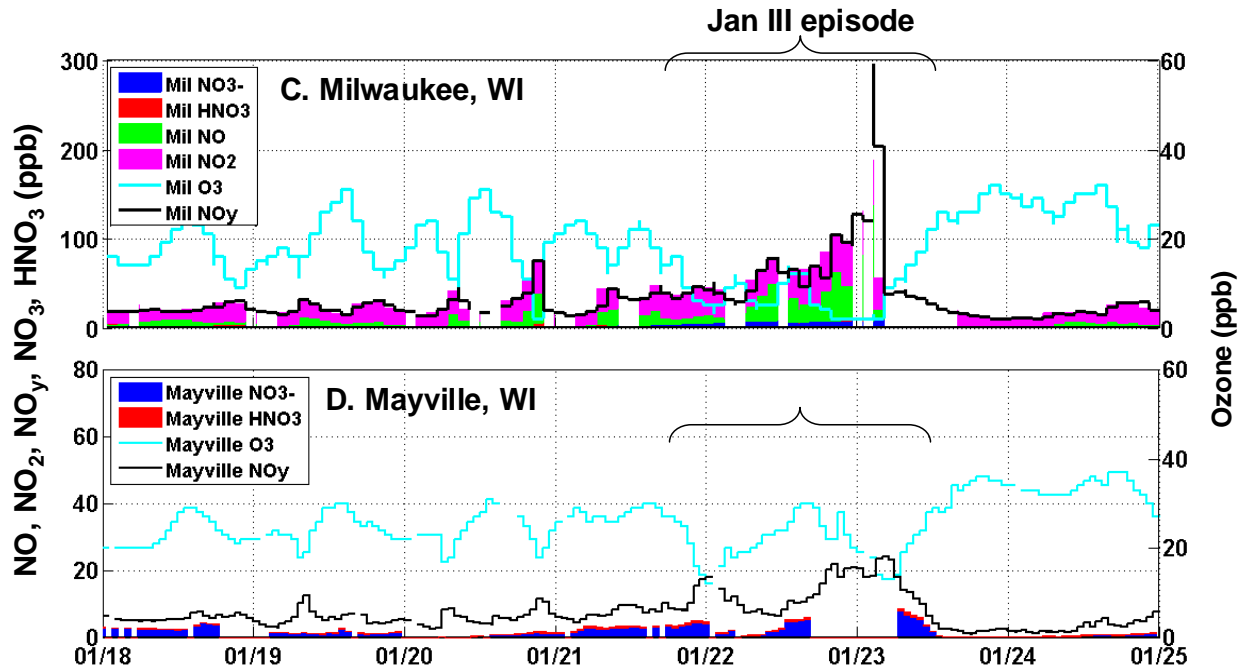


Base – 30% NH₃ (250 km)

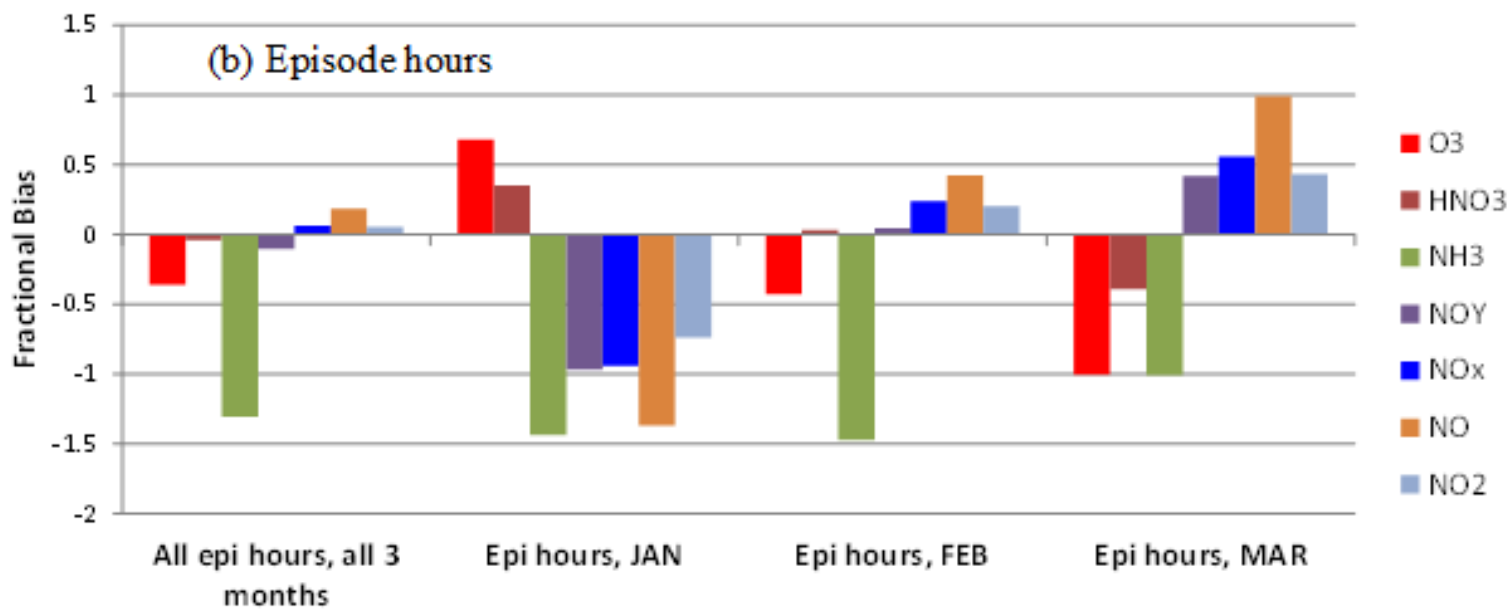
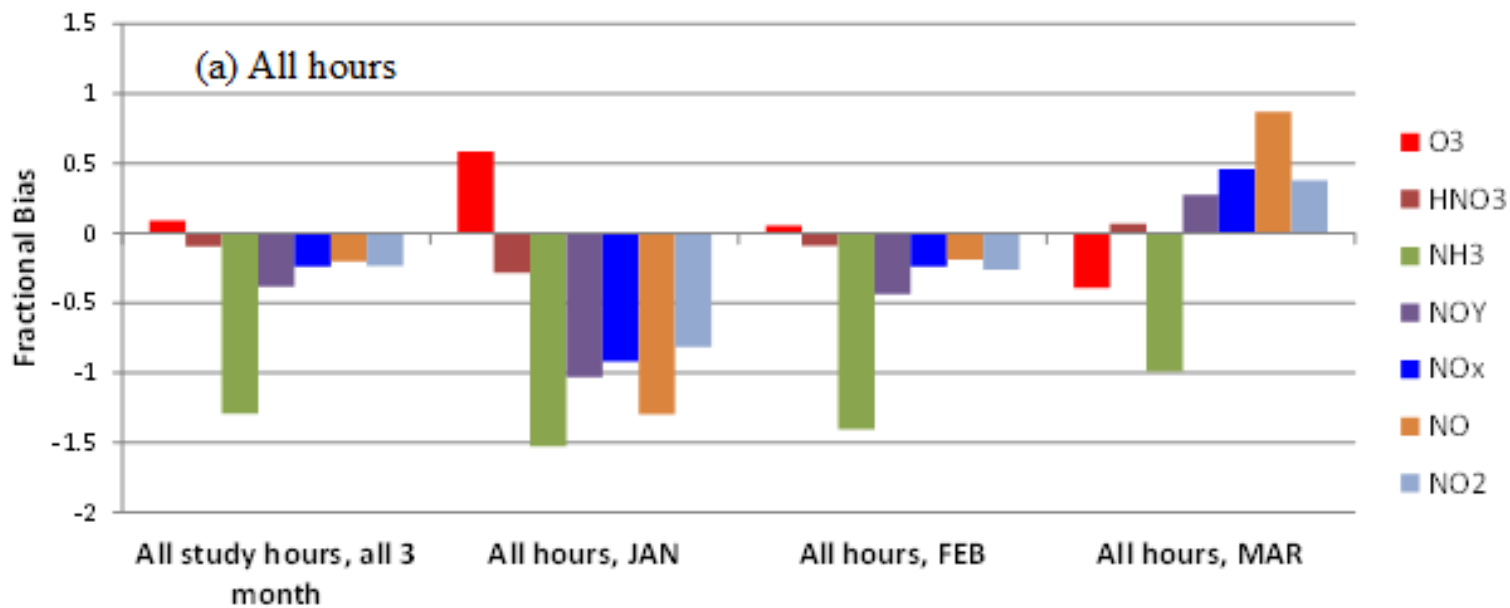


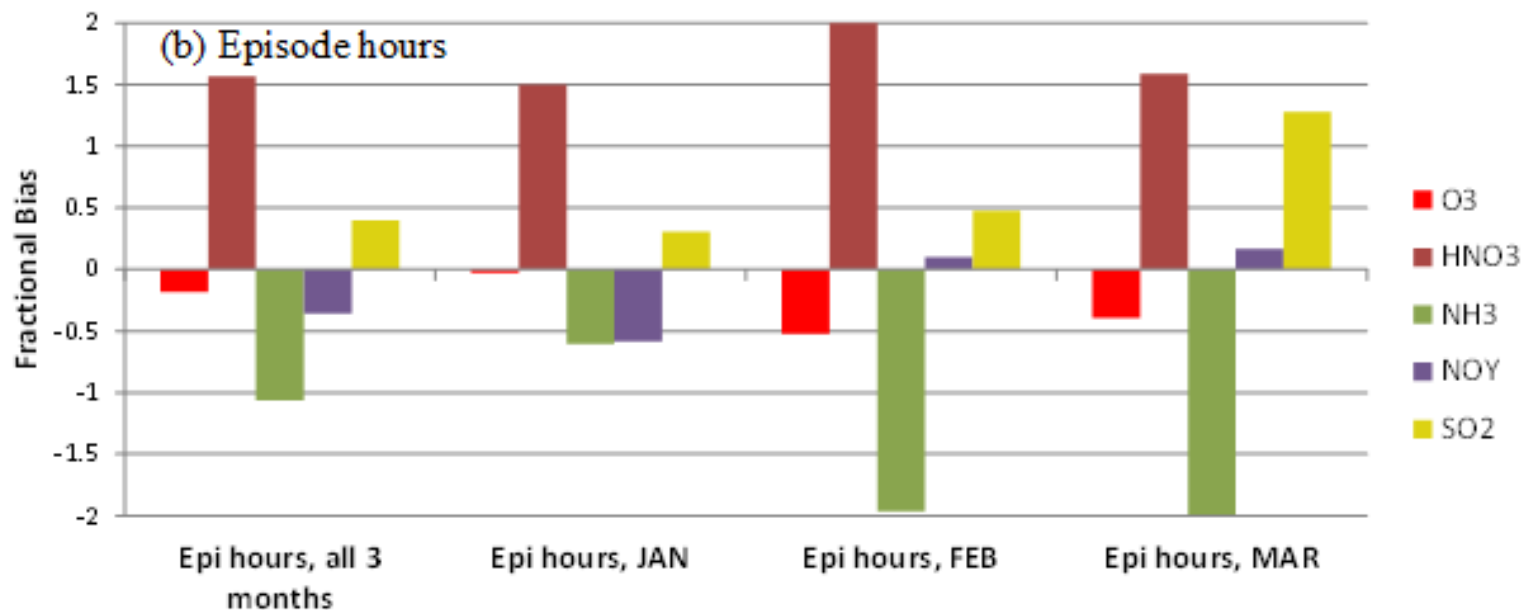
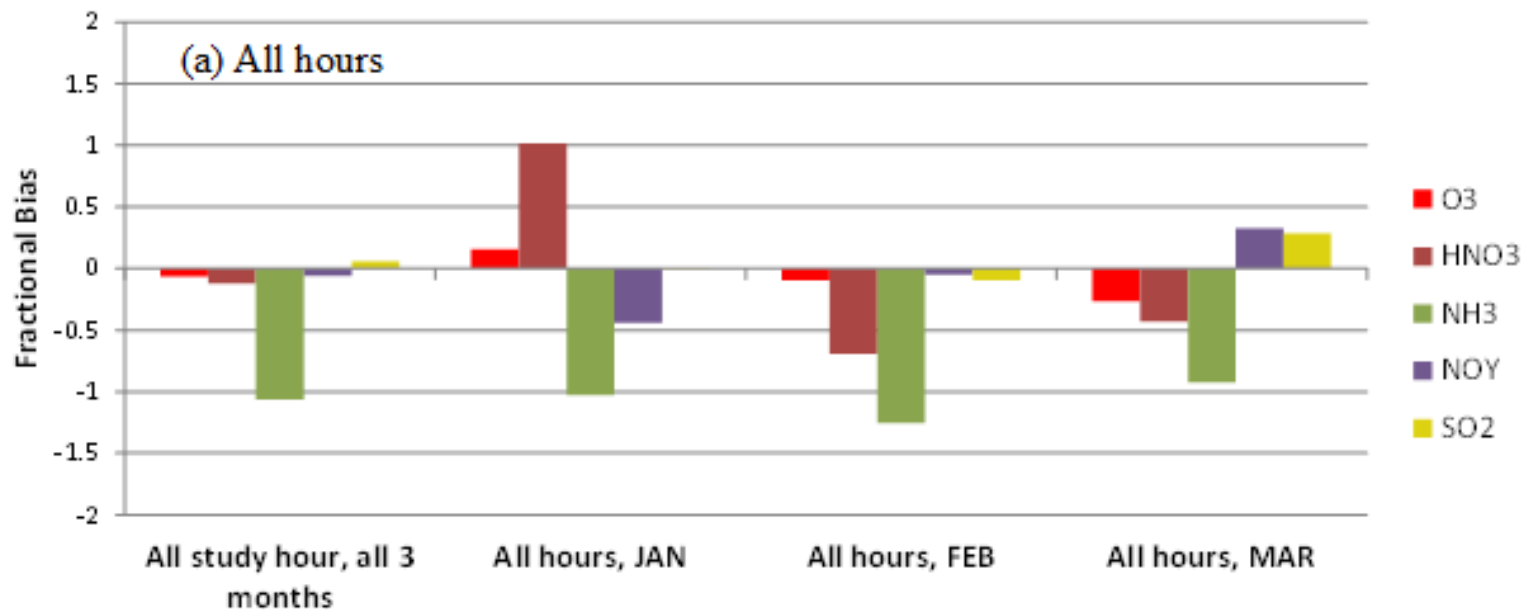


Detailed view of an episode

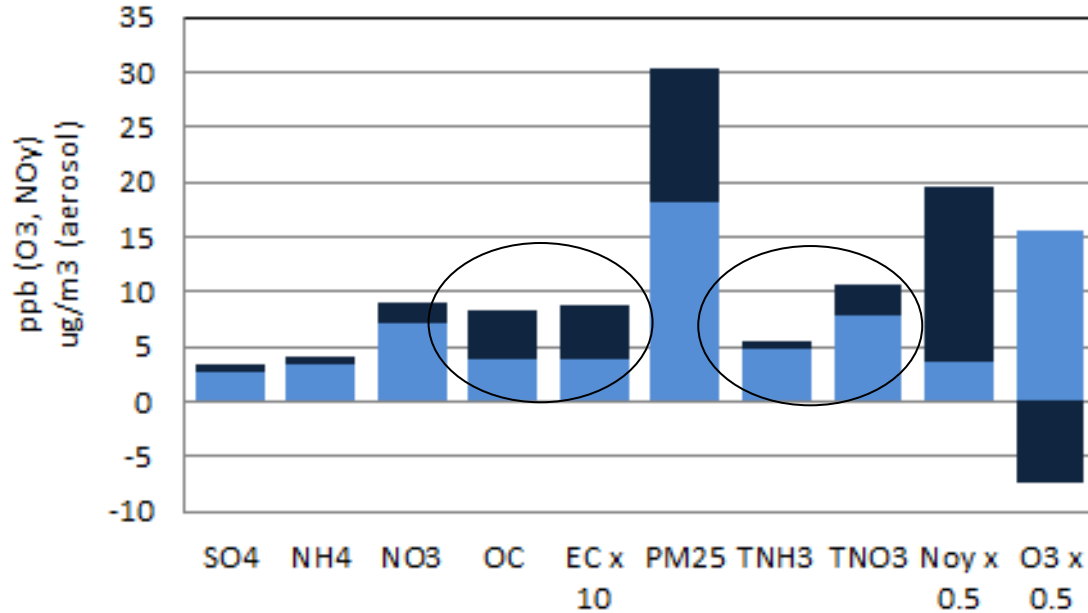


Agreement between multiple independent measurements





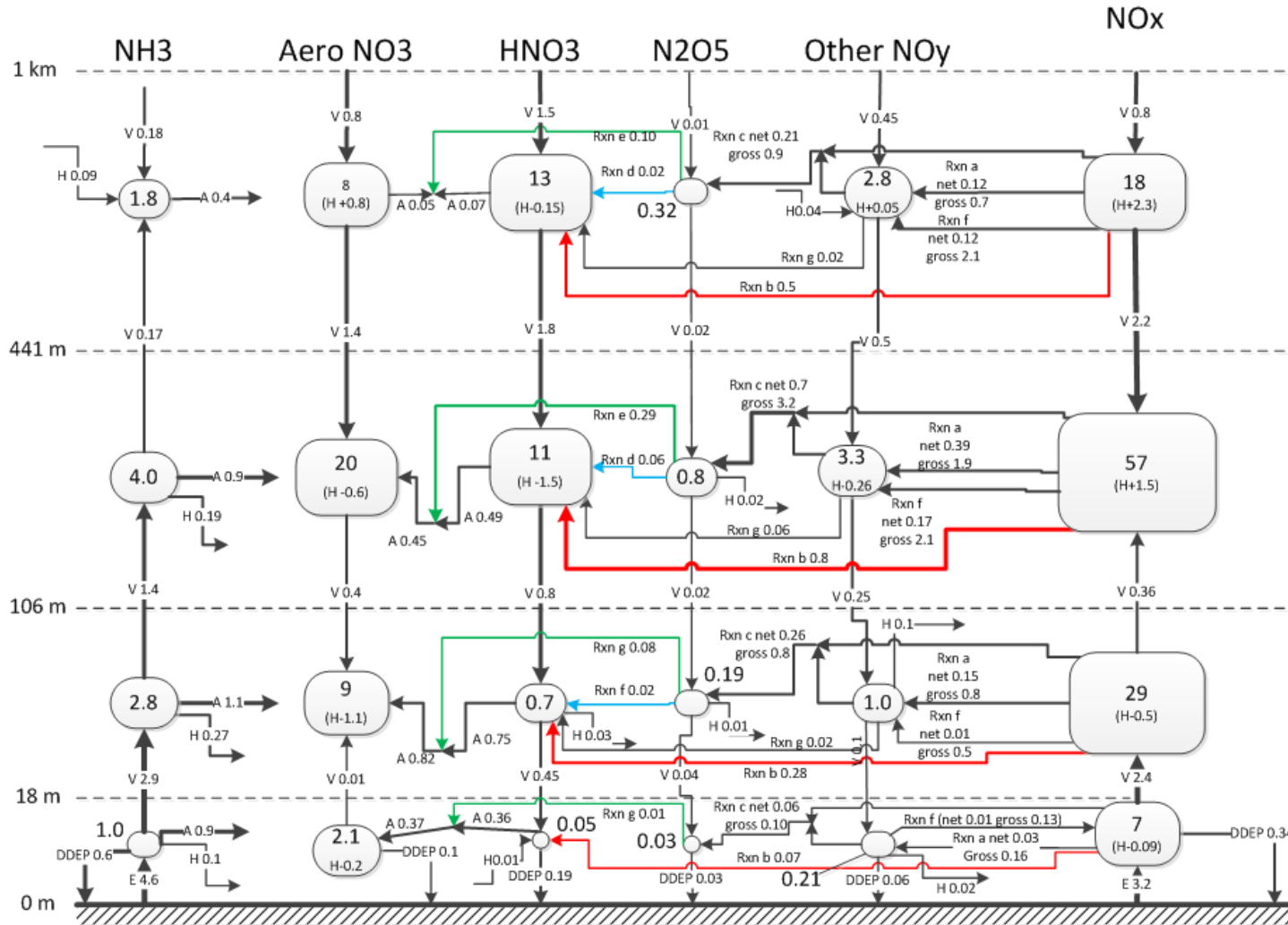
Urban-Rural Contrast During Episodes



Secondary species mainly regional (small urban excess)

OC, EC, and NO_y have strong urban excess.

Mayville Day



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO_3 radical formation

c: net N_2O_5 formation

g: HNO_3 formation from the NO_3 radical

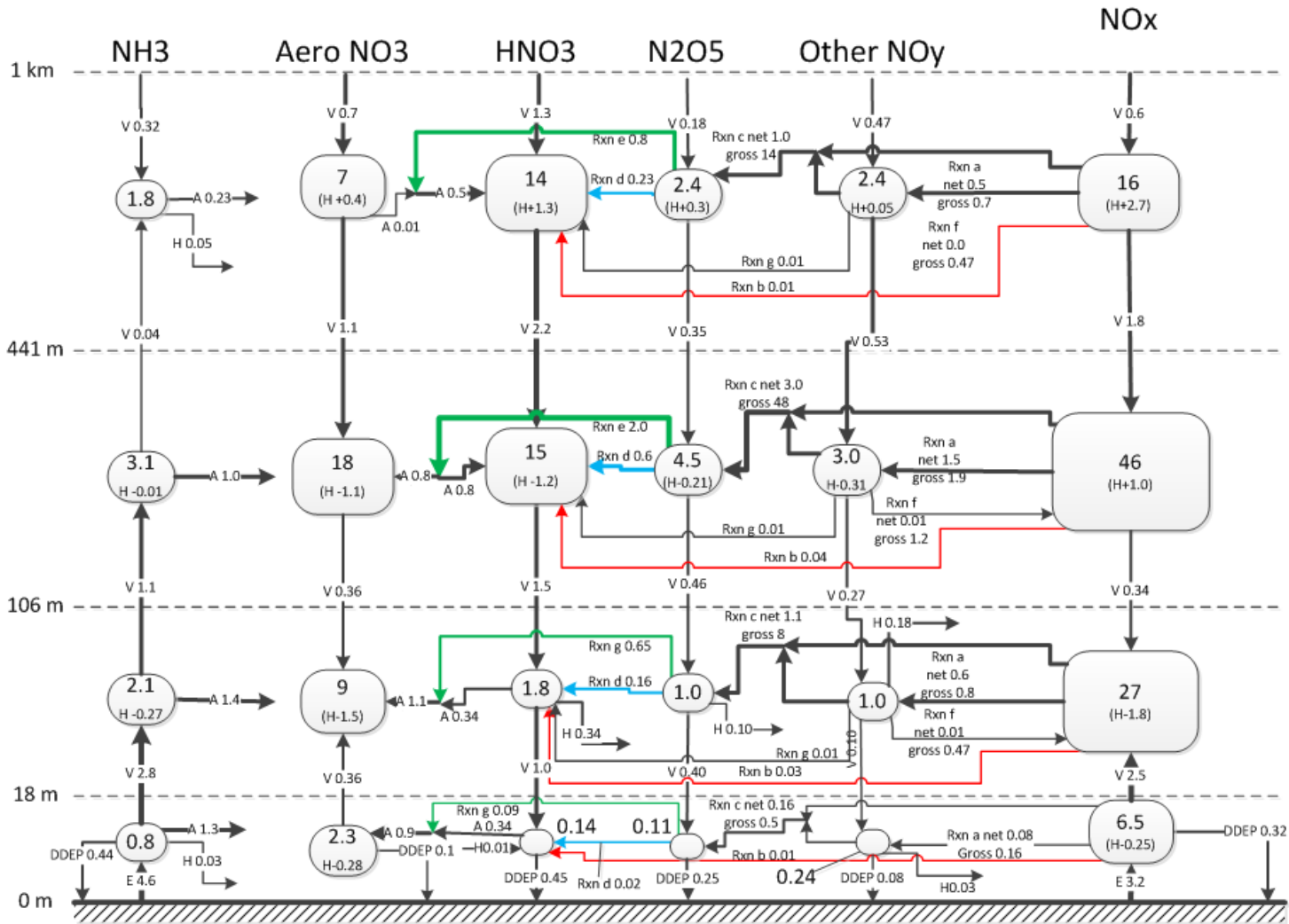
Colored lines

b: $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

d: homogenous formation of HNO_3 from N_2O_5

Flux e: heterogeneous formation of HNO_3 from N_2O_5

Mayville Night



Reservoir in $\mu\text{mole N} / \text{m}^2$.
Fluxes are in $\mu\text{mole N} / \text{m}^2\text{-hr}$.

Black lines

Aerosol process

Horizontal advection and diffusion

Vertical advection and diffusion

Emissions

DDEP

a: net NO₃ radical formation

c: net N₂O₅ formation

g: HNO₃ formation from the NO₃ radical

Colored lines

b: NO₂ + OH → HNO₃

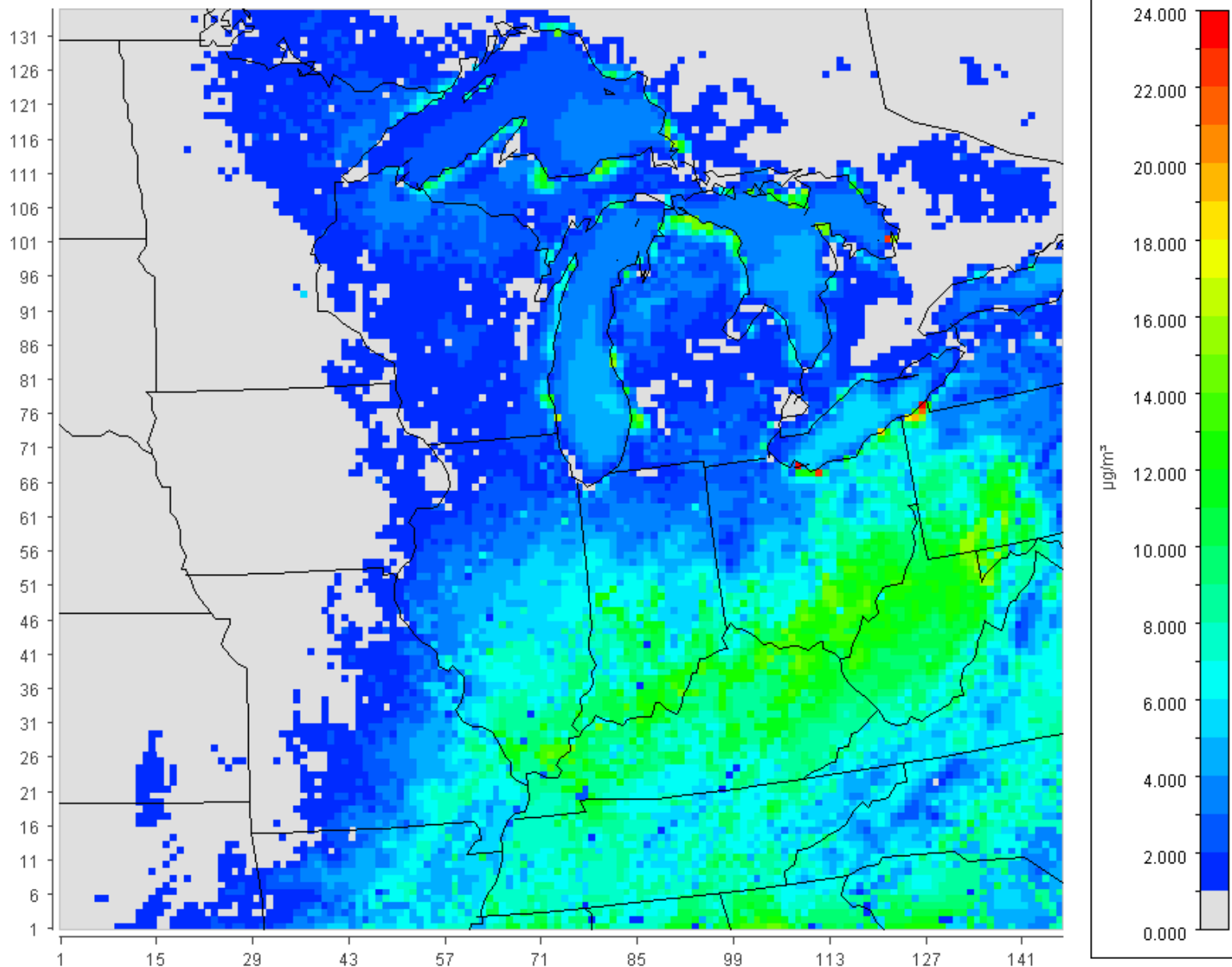
d: homogenous formation of HNO₃ from N₂O₅

Flux e: heterogeneous formation of HNO₃ from N₂O₅

Layer 1 DDEP_ANO3[1]*(-1) + DDEP_HNO3_UGM3[1]*(-1)

[1]=Drydeposition_IPR_AVG.ncf

Dry Deposition Rate, Total Nitrate (ug/m3 per hour)



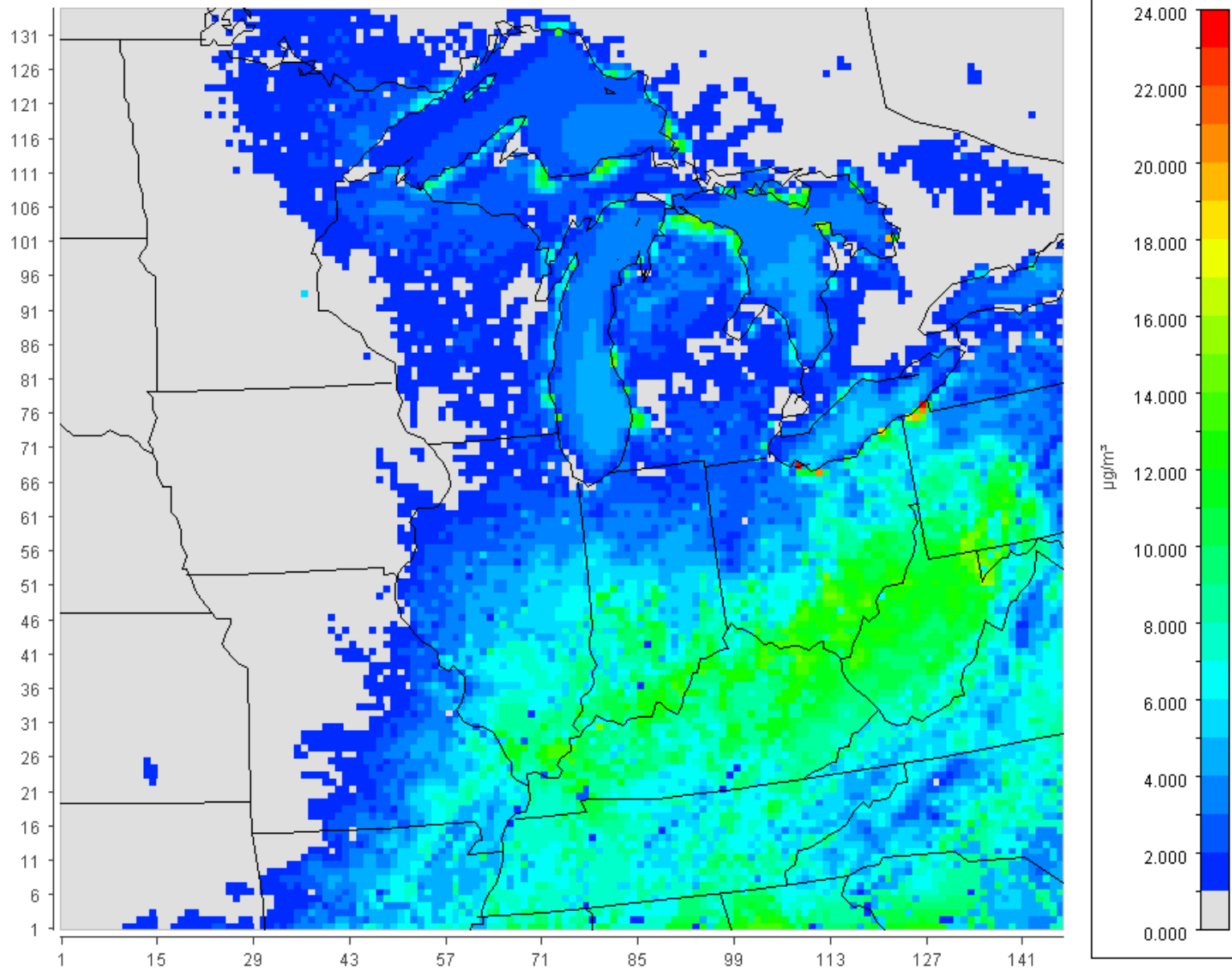
January 1, 2009 01:00:00 UTC

Min (122, 134) = 0.069, Max (108, 68) = 31.531

Dry Deposition Nitric Acid (ug/m3 per hour)

Layer 1 DDEP_HNO3_UGM3[1]*(-1)

[1]=Drydeposition_IPR_AVG.ncf



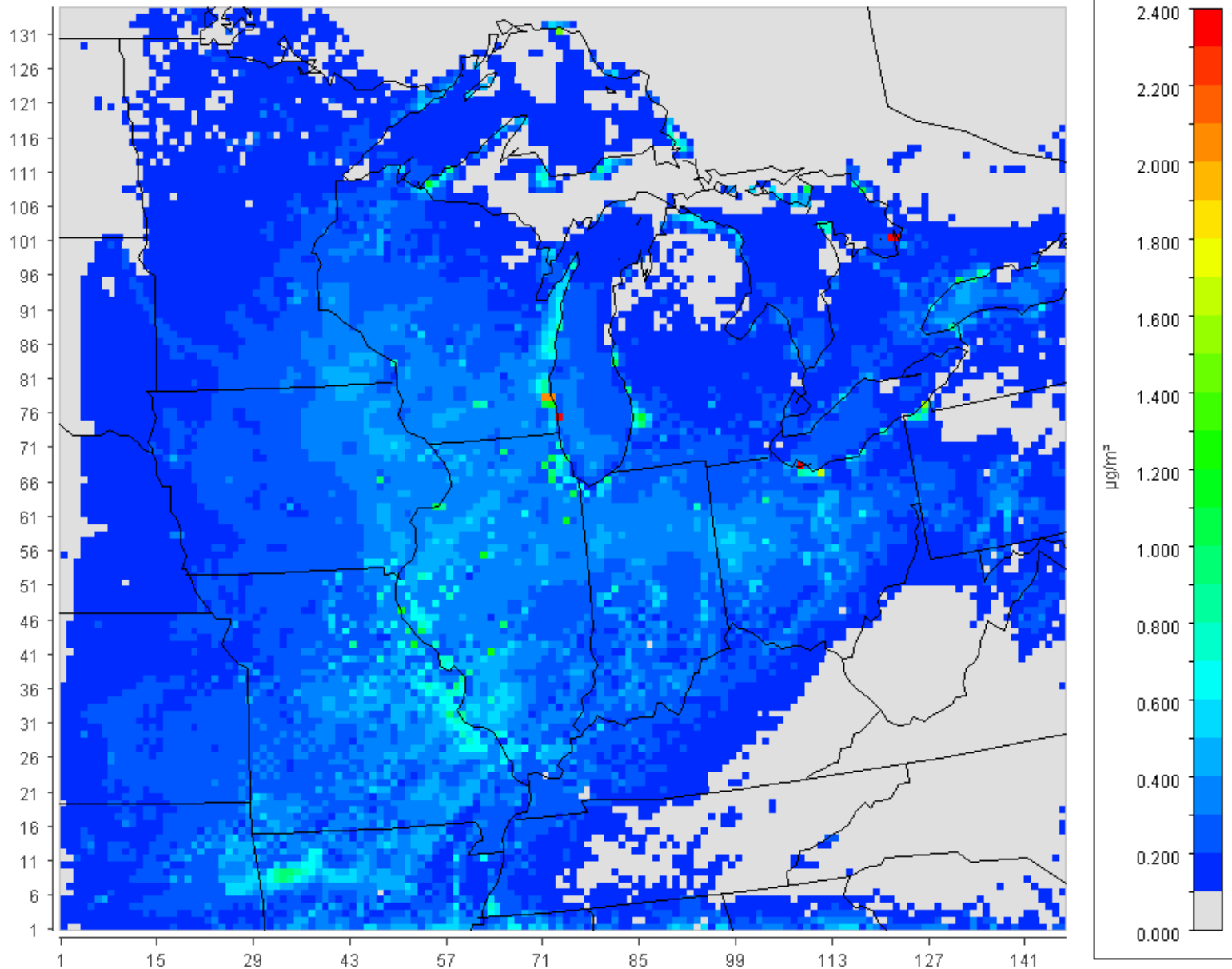
January 1, 2009 01:00:00 UTC

Min (5, 132) = 0.000, Max (108, 68) = 27.806

Layer 1 DDEP_ANO3[1]*(-1)

[1]=Drydeposition_IPR_AVG.ncf

Dry Deposition Nitrate ($\mu\text{g}/\text{m}^3$ per hour)



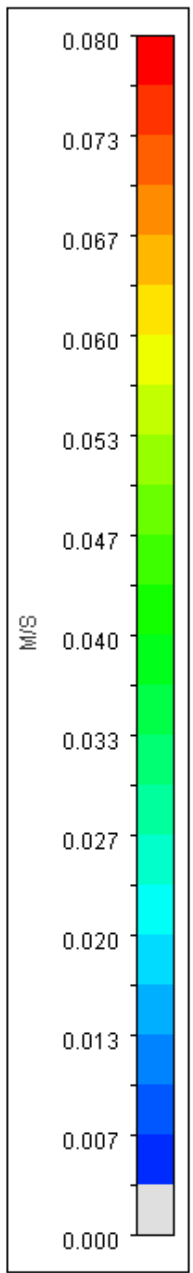
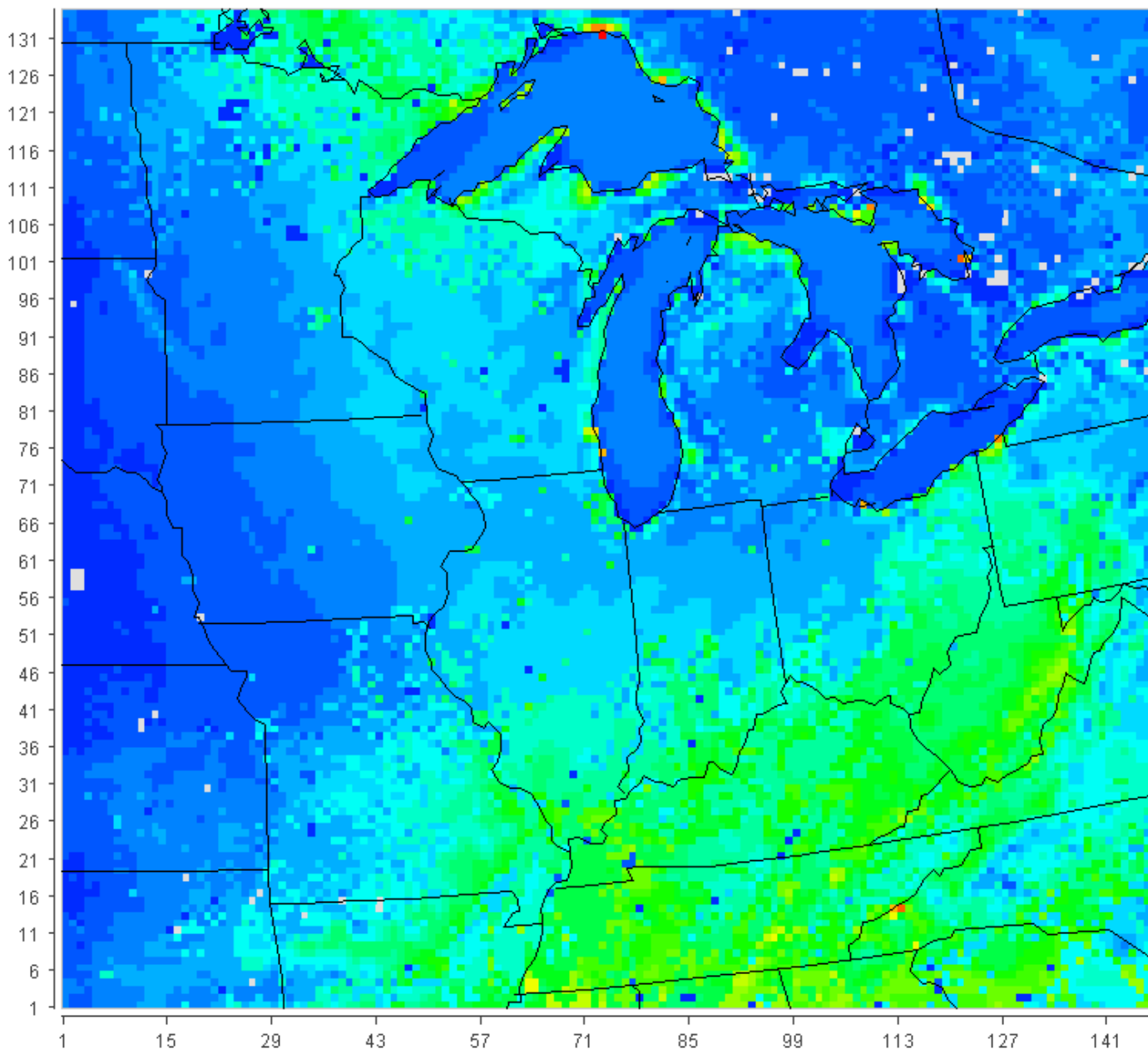
January 1, 2009 01:00:00 UTC

Min (125, 20) = 0.008, Max (108, 68) = 3.725

Layer 1 VD_HNO3[2]

[2]=METCRO2D_LADC012_DD_Vel_AVG.ncf

HNO3 Deposition Velocity



January 1, 2009 00:00:00 UTC

Min (126, 101) = 0.001, Max (73, 121) = 0.082

Emissions Sensitivity: Emissions Scenarios

- 30% NO_x from base case
- 30% NH₃ from base case
- 2015 Proxy Case
 - Simulate near-term changes in mobile NO_x & simulate approximation of implementation of Cross State Air Pollution Rule (CSAPR) effect on coal-fired power plant NO_x & SO_x emissions
 - 70% EGU SO₂
 - 10% EGU NO_x
 - 30% mobile NO_x
- Additional scenarios: add all-sector reductions to the 2015 Proxy Case
 - 30% NH₃
 - 30% NO_x
 - 30% NH₃ & - 30% NO_x

