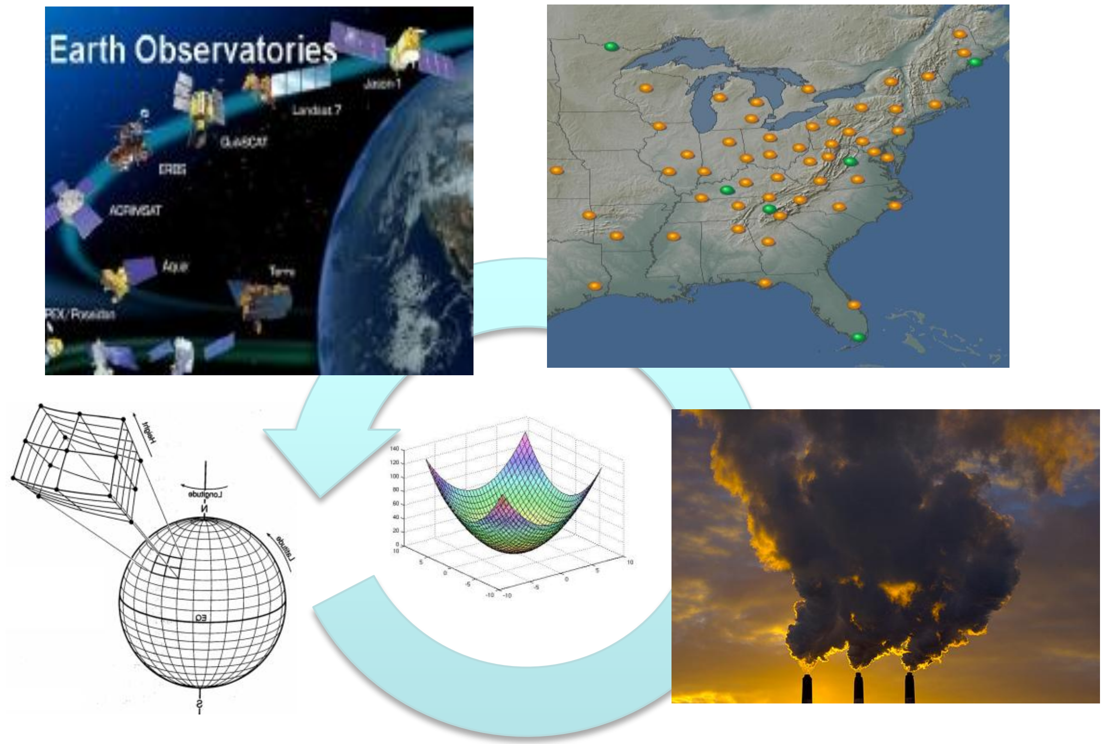
Modeling and Observational Constraints of NH_3 Emissions and Sources of Nitrogen Deposition

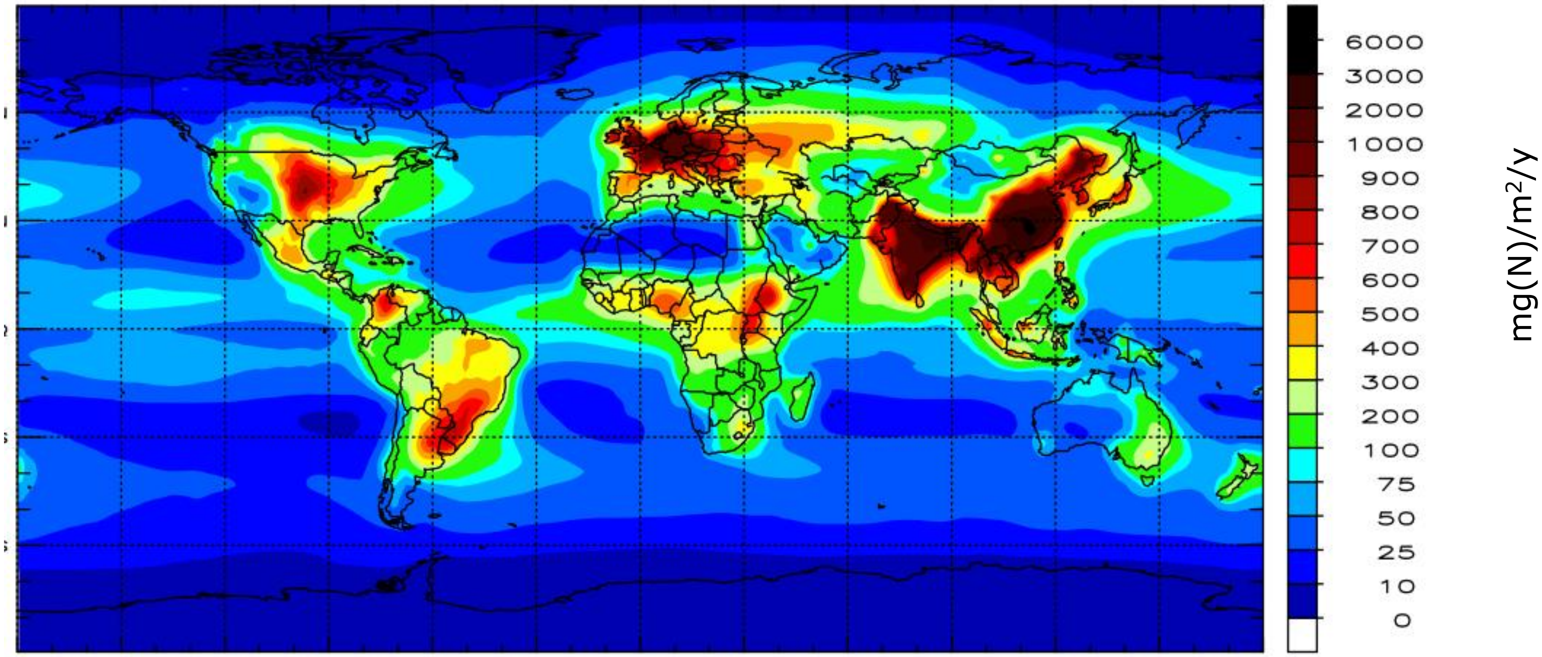


Daven K. Henze
University of Colorado, Boulder

Hyungmin Lee, Juliet Zhu, Jana Milford (CU Boulder)
Aika Davis, Ted Russell (GIT), Gill-Ran Jeong (KIAPS)
Fabien Paulot, Daniel Jacob, Katie Travis (Harvard)
Jesse Bash, Robert Pinder, Riche Scheffe, James Kelly (US EPA)
Bret Schichtel, John Vimont (NPS), Linda Pardo (USFS)

Environmental impacts of NH_3

Estimated N deposition from NH_x, Dentener et al. (2006)



Areas where color approaches dark red --> deposited levels are hazardous to ecosystem.

NH_3 emissions:

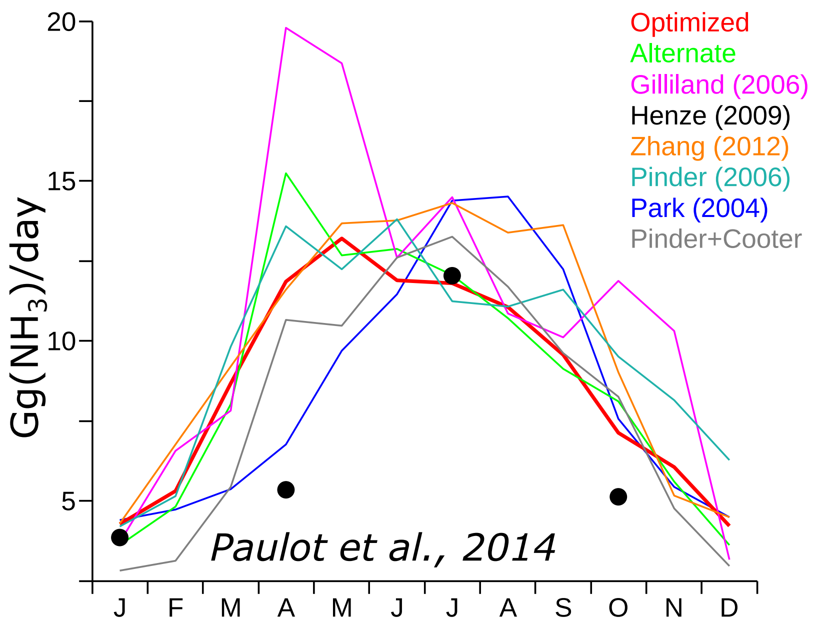
- increased by factor of 2 – 5 since preindustrial era.
- to double by 2050 (*IPCC*, Denman et al., 2007; Moss et al., 2010).
- contribute to 46 Tg gap in global N budget (Schlesinger, 2009)?

Uncertainties in NH_3 emissions

- Global inventories also uncertain
(e.g., Beuson et al., 2008)

- Substantial variability in estimates of total US NH_3 emissions.

- Large uncertainties at regional scales
(e.g., Novak et al., 2012; Walker et al., 2012)



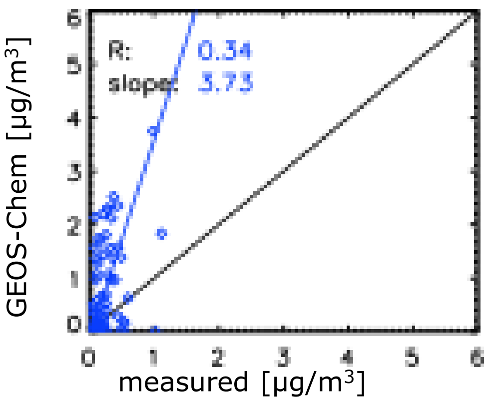
Why so uncertain?
- lack of direct source measurements (hard, expensive)

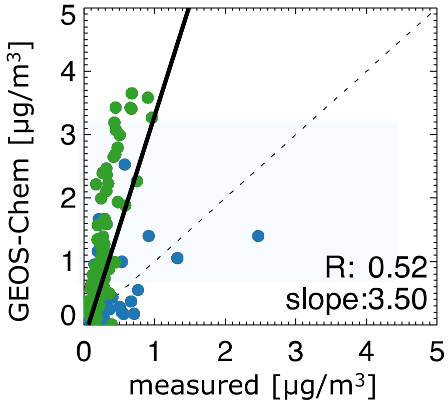
- difficulty in relating associated species to NH_3 sources
    - constraints from observations of [NH_4^+] or [NH_x] complicated by model/measurement error, precipitation
    - observations of [NH_3] less prevalent

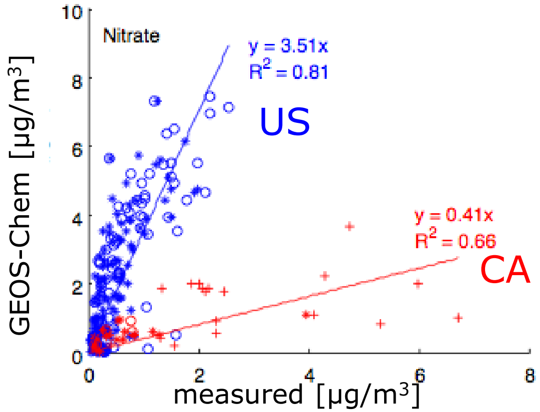
Uncertainties in NH_3 emissions: Implications for air quality and environment

- contribute to errors in assessing $PM_{2.5}$

Ex: GEOS-Chem overestimates nitrate at IMPROVE / CASTNET (July)







Zhu et al., 2013 Heald et al., 2012 Walker et al., 2012

(also Liao et al., 2007; Henze et al., 2009; Zhang et al., 2012)

- undermine regulatory capabilities for secondary standards on SO_x, NO_x to control N_r dep (e.g., Koo et al., 2012)

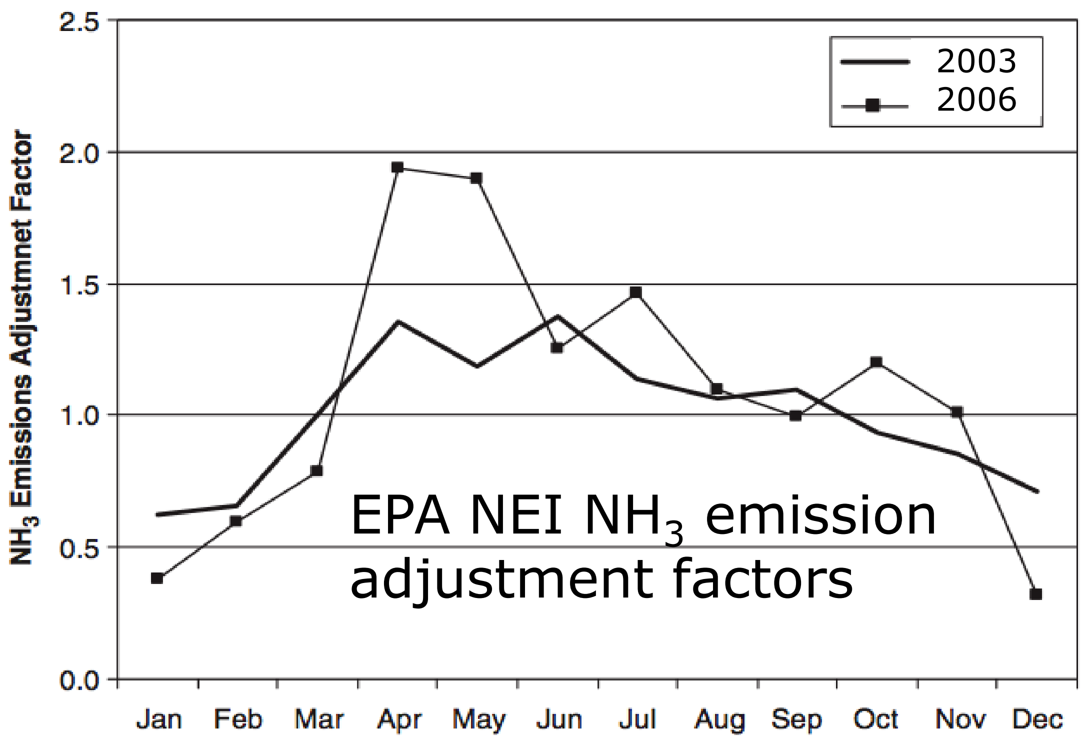
- uncertainties in projections of aerosol direct radiative forcing impacts (Henze et al., 2012)

Constraints on NH_x deposition from inverse modeling

Many US air quality models get NHx deposition correct via assimilation.

Observations: wet NH_x = aerosol NH_4^+ + gas NH_3

Method: adjust (w/Kalman Filter) monthly nation-wide scale factors



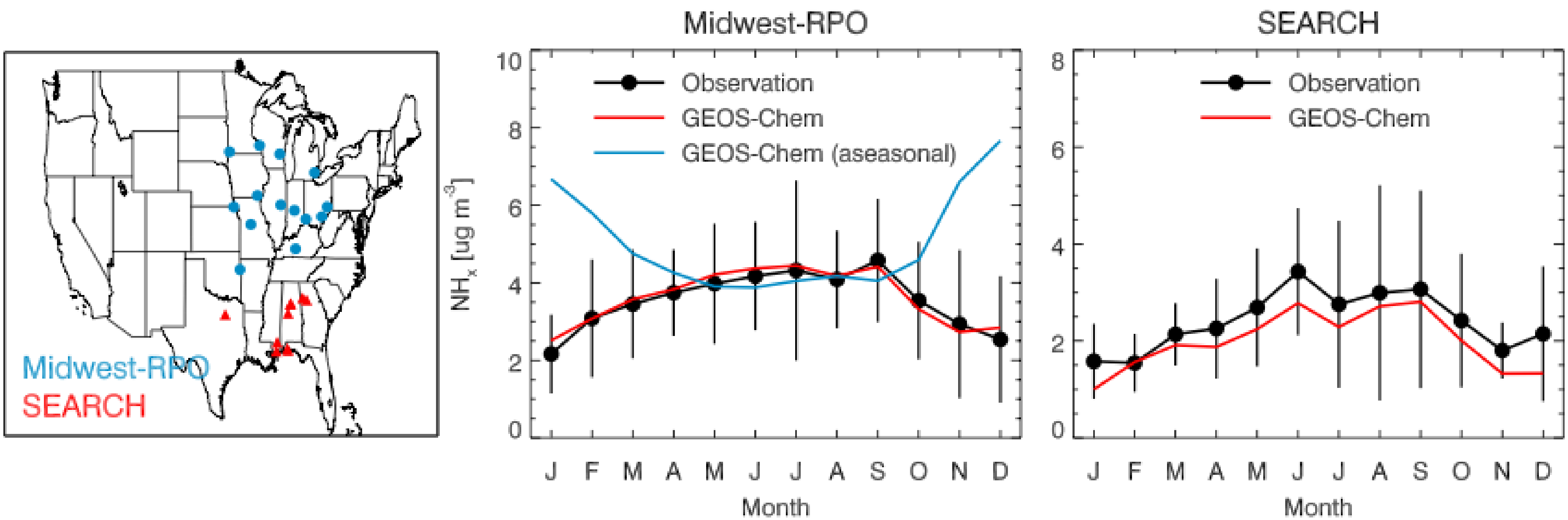
Results:
Gilliland et al., 2003;
Gilliland et al., 2006

Assumptions:
- uniform seasonality throughout broad regions of US

Top-down constraints based on NH_x

Mendoza-Dominguez and Russell, 2001: constraints on NH_3 sources in the SE

Zhang et al., 2012: Seasonality of NH_3 sources adjusted so that Modeled matched RPO and SEARCH NHx measurements

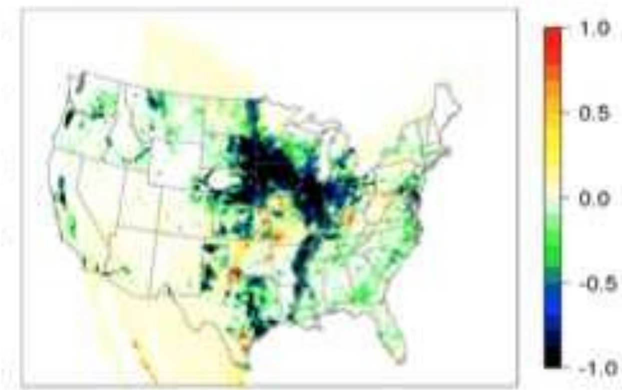


- Resulting annual NHx and NO3 deposition unbiased.
- Enforces a spatially uniform seasonality / correction factor across the US.

Spatial heterogeneity in source-receptor relationships for NH_3

Consider emissions perturbation, Δemiss:

April



July

Kg NH_3/ha/month

Spatial correlations of Δemiss with:

	Δ[NH_3]	Δ wet dep [NH_x]
April	0.83	0.54
July	0.17	-0.06

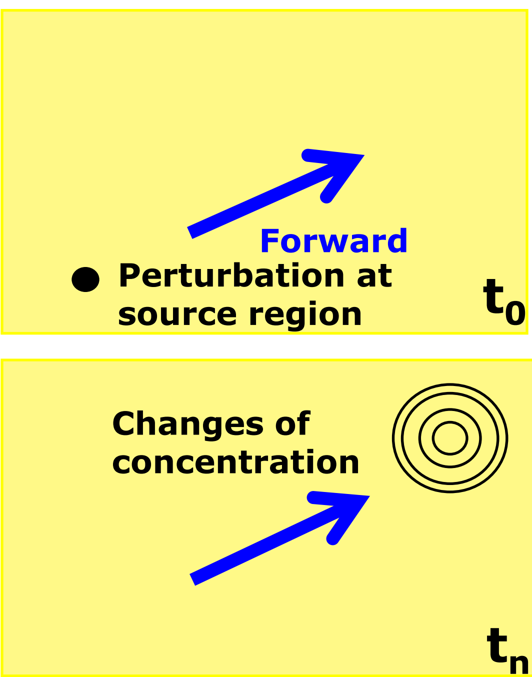
Spatially heterogeneous impacts of NH_3 emissions – can be accounted for using 4D-Var / adjoint inversions

Jeong et al., submitted

Source attribution techniques

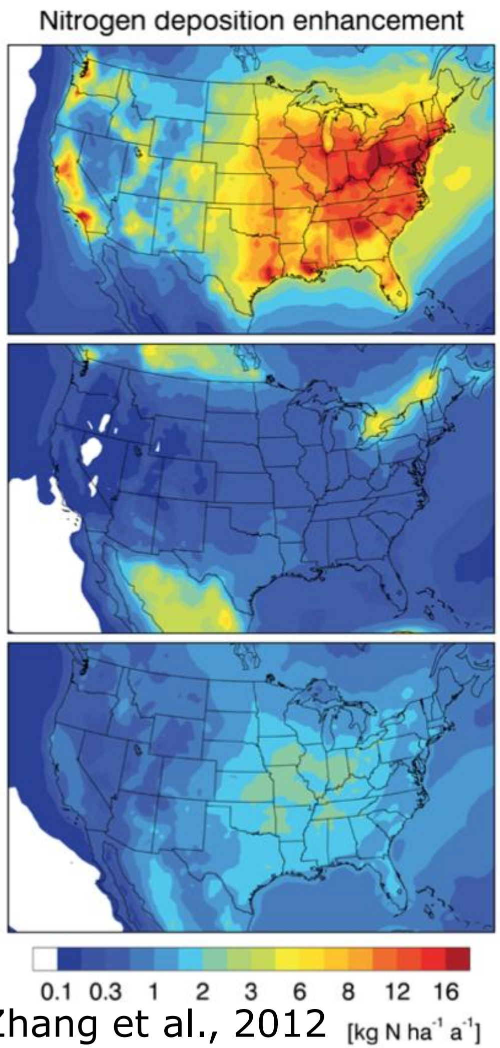
Forward Model (source-oriented)

Sensitivity of all model concentrations to one model source or sector



Source attribution techniques

Forward Model (source-oriented)



US
Anthropogenic
5.0 Tg N / yr

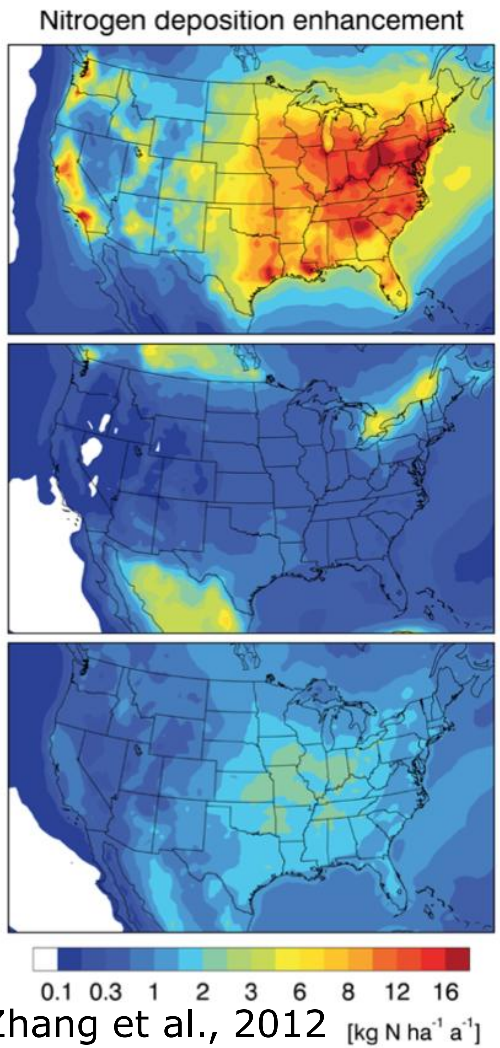
Foreign
Anthropogenic
0.42 Tg N / yr

Natural
1.0 Tg N / yr

Zhang et al., 2012

Source attribution techniques

Forward Model (source-oriented)



US
Anthropogenic
5.0 Tg N / yr

Foreign
Anthropogenic
0.42 Tg N / yr

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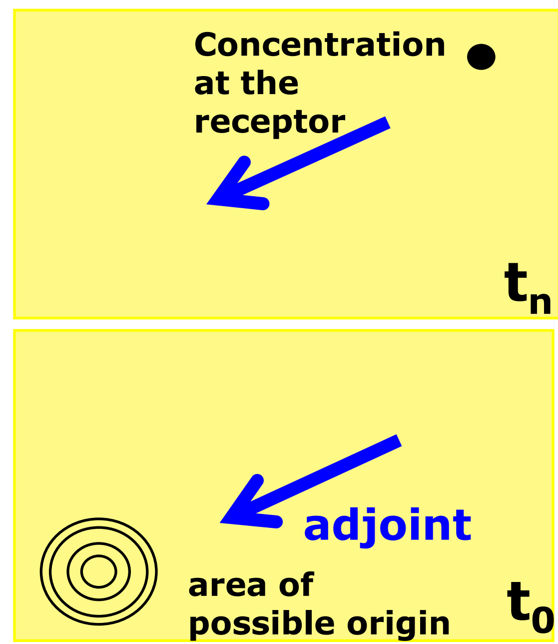
1.0 Tg N / yr

Zhang et al., 2012

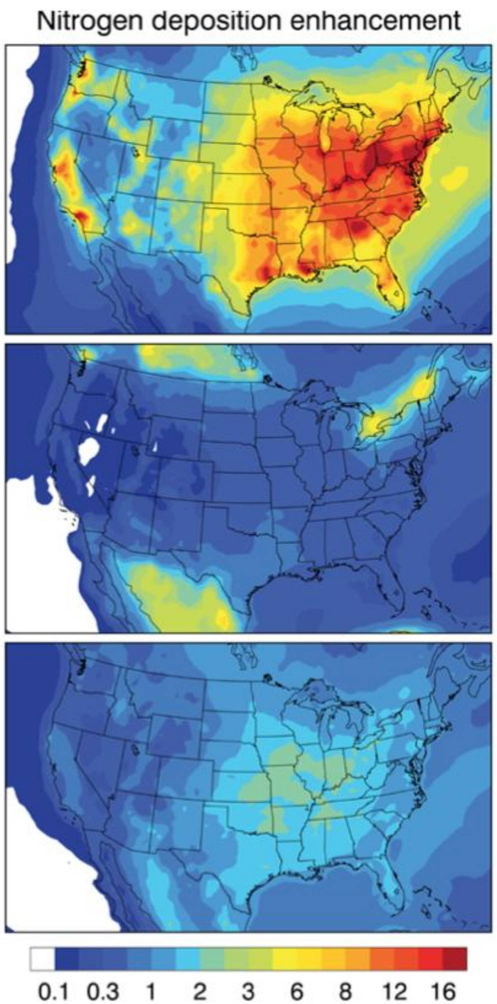
Adjoint Model (receptor-oriented)

Sensitivity of model concentration in specific location to many model sources and sectors



Source attribution techniques

Forward Model (source-oriented)



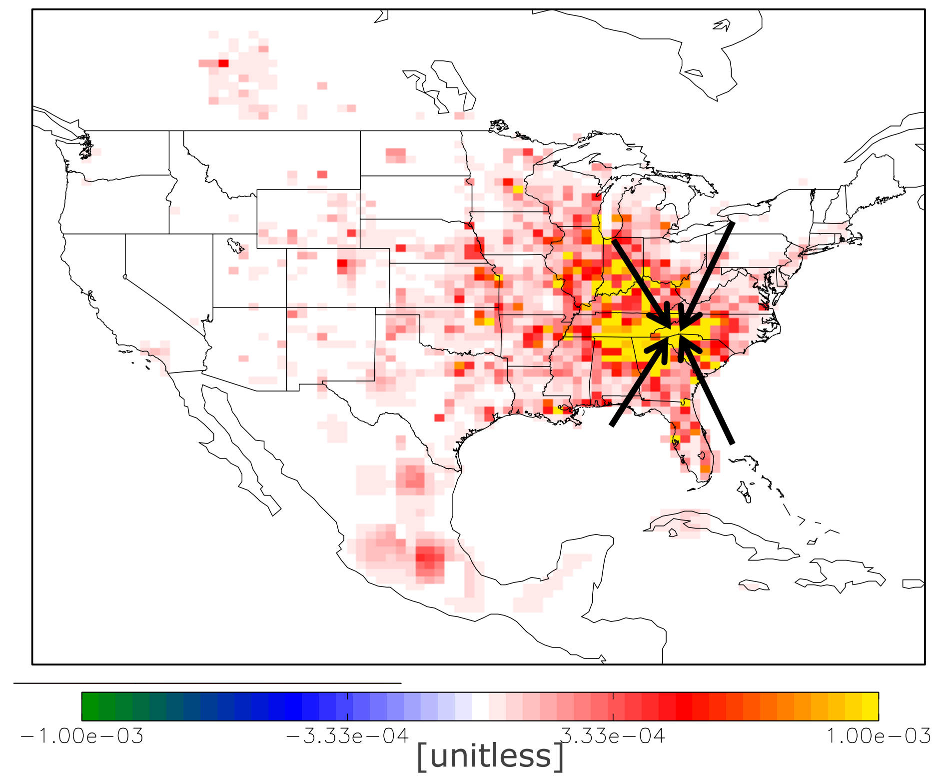
US Anthropogenic 5.0 Tg N / yr

Foreign Anthropogenic 0.42 Tg N / yr

Natural 1.0 Tg N / yr

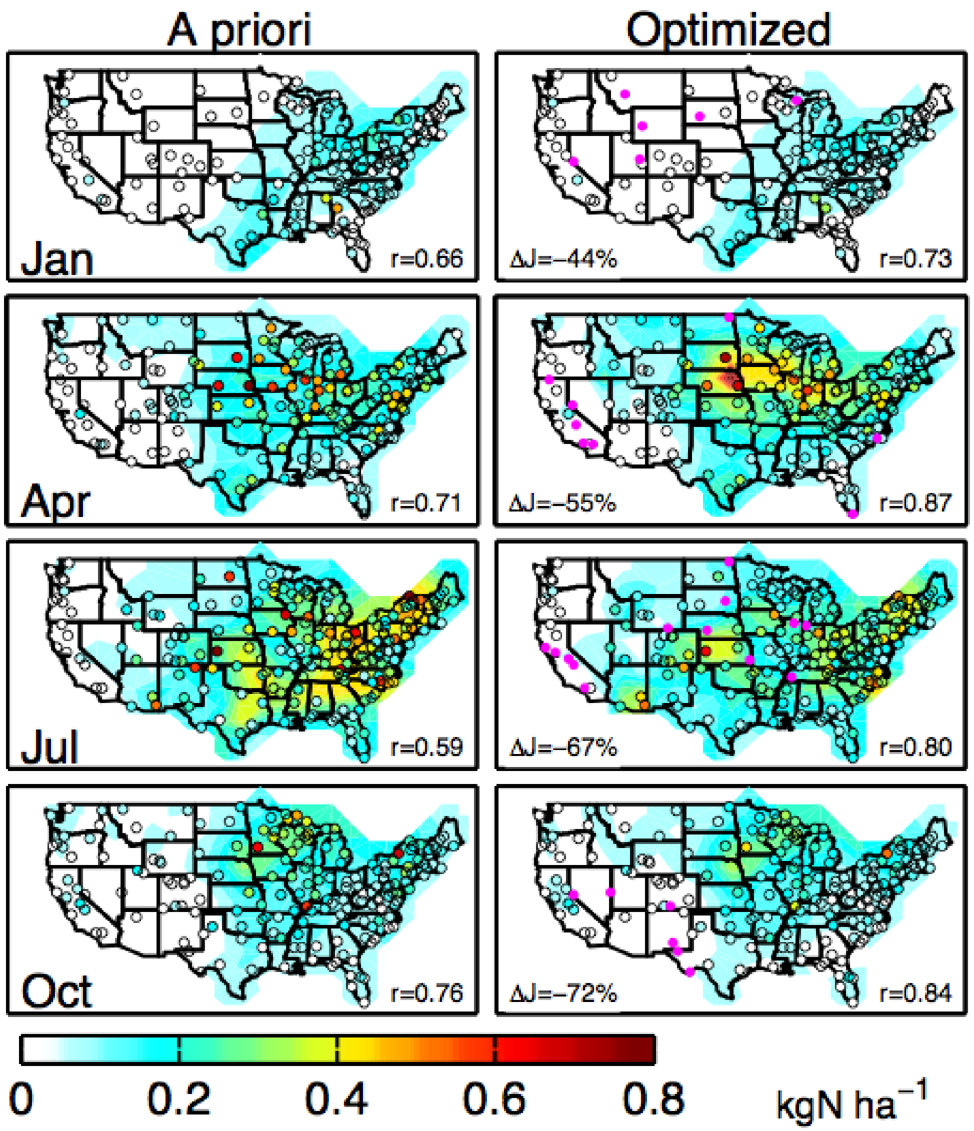
Zhang et al., 2012 [kg N ha^{-1} a^{-1}]

Adjoint Model (receptor-oriented)



Using receptor = sum of squared model error, these relationships can be used for high resolution inverse modeling

Constraints from NH_x deposition, and an alternate bottom up inventory

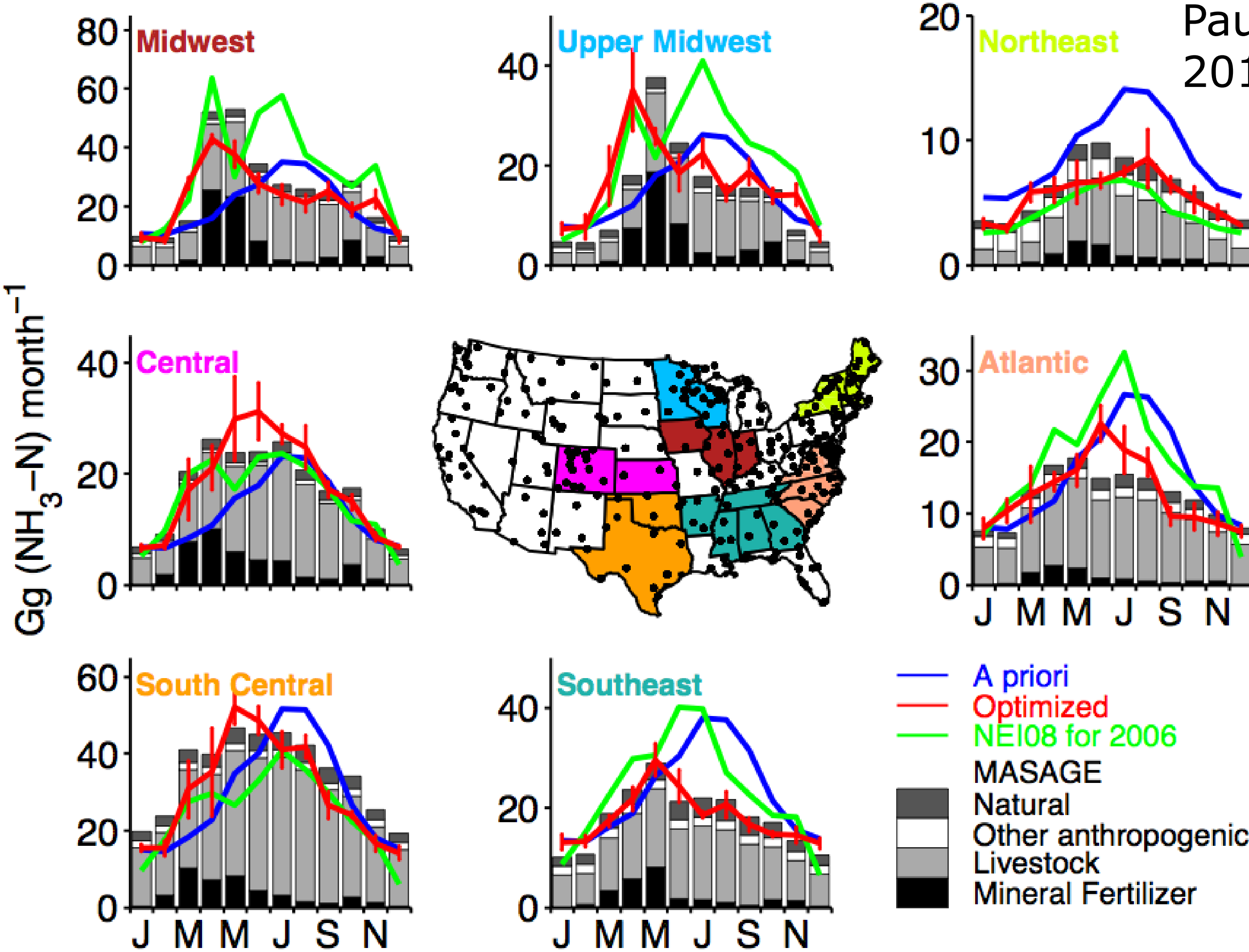


Paulot et al., 2014

- GEOS-Chem 4D-Var (Henze et al., 2007)
- Global 2x2.5
- Assimilate NTN, EMEP, …

Constraints from NH_x deposition, and an alternate bottom up inventory

Paulot et al., 2014

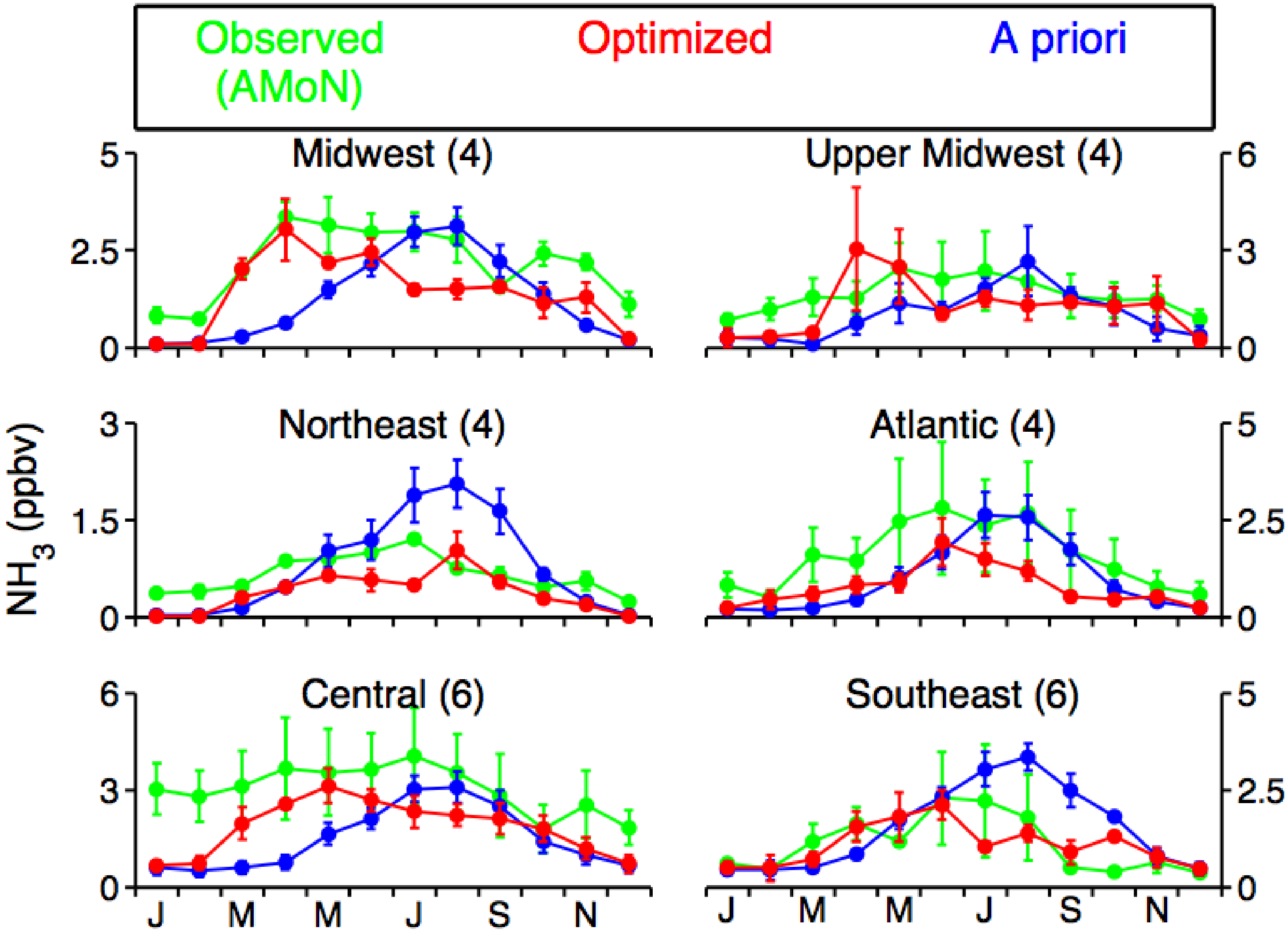


New bottom-up inventory

No support for homogeneous seasonality in the US.
New bottom-up inventory (MASSAGE) can reproduce optimized emissions in some areas.

Constraints from NH_x deposition, and an alternate bottom up inventory

Comparison to surface NH3 measurements (Puchalski et al., 2011) before and after assimilation:



Paulot et al., 2014

Constraints from NH_x deposition, and an alternate bottom up inventory

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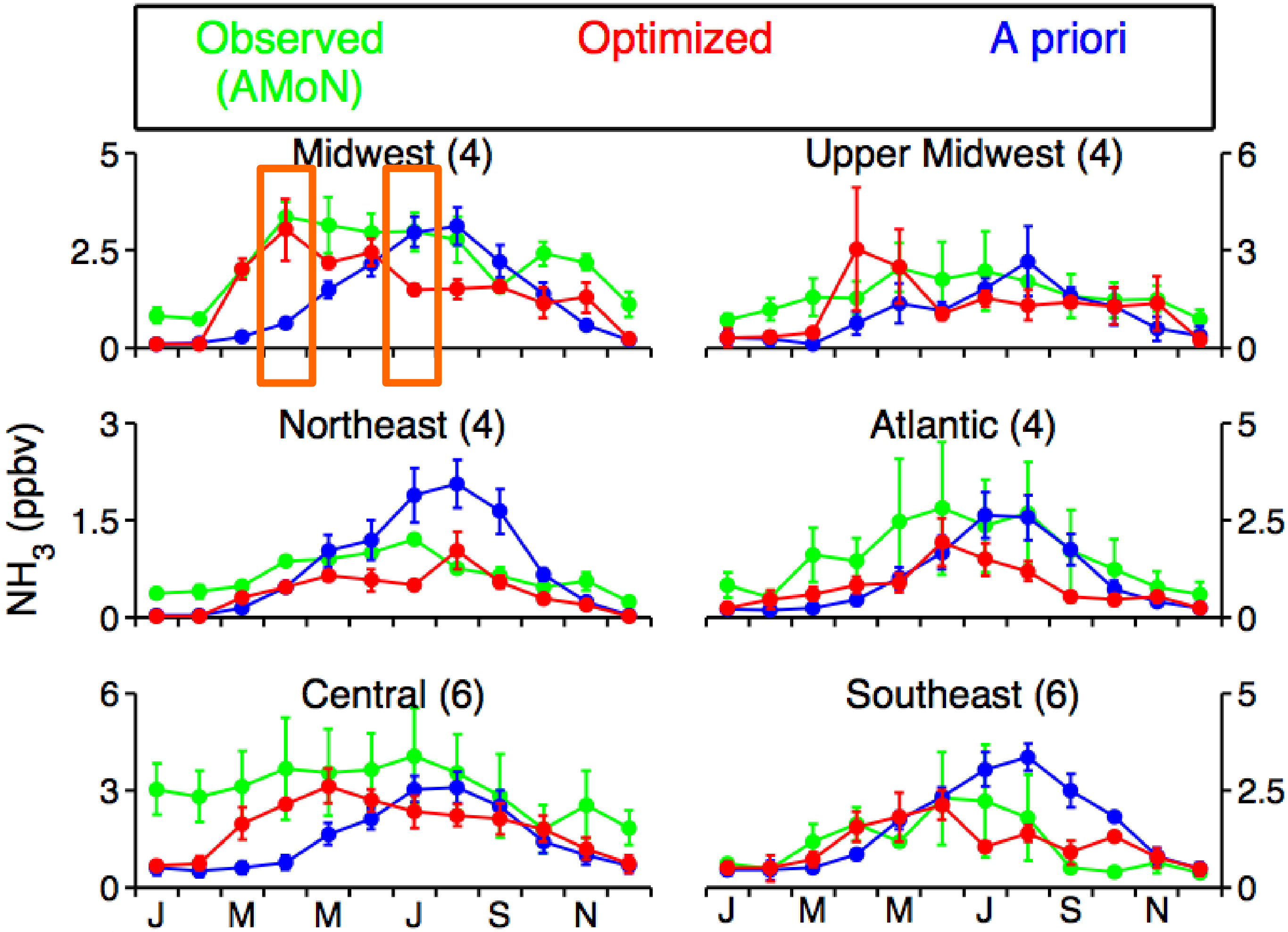
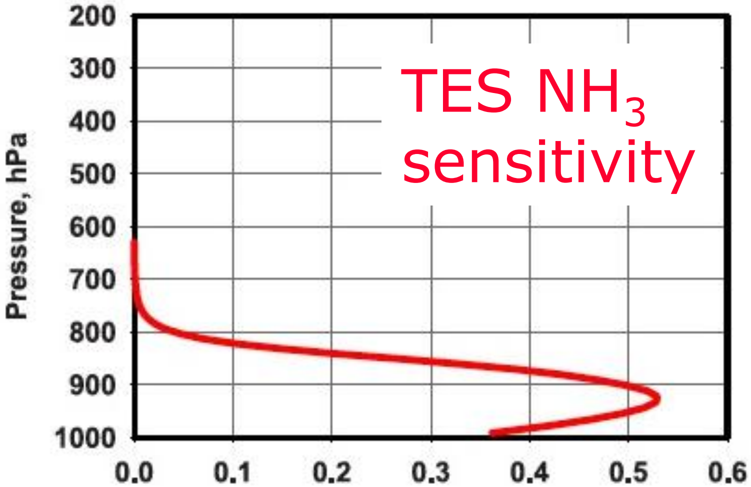


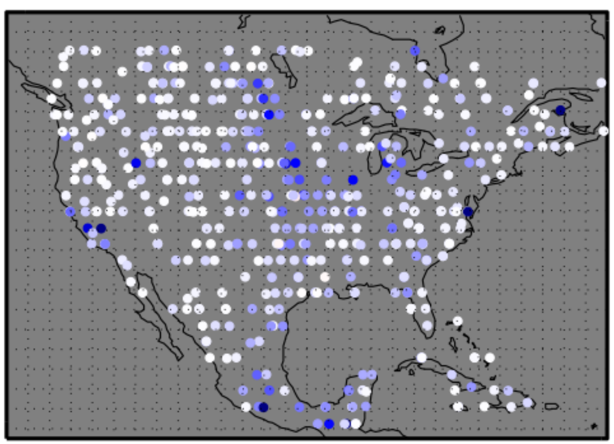
Paulot et al., 2014

Closure for NH_x deposition does not necessarily imply better model NH_3

Potential for making new inroads on this problem: ambient measurements of NH_3

Remote sensing with TES and IASI:





TES:
- 5 km x 8 km footprint
- sensitive to BL
- detection limit of ~ 1 ppb
- bias of +0.5 ppb

more precise & sparse than IASI

(Beer et al., 2008; Clarisse et al., 2009; Clarisse et al., 2010; Mark Shephard et al., 2011)

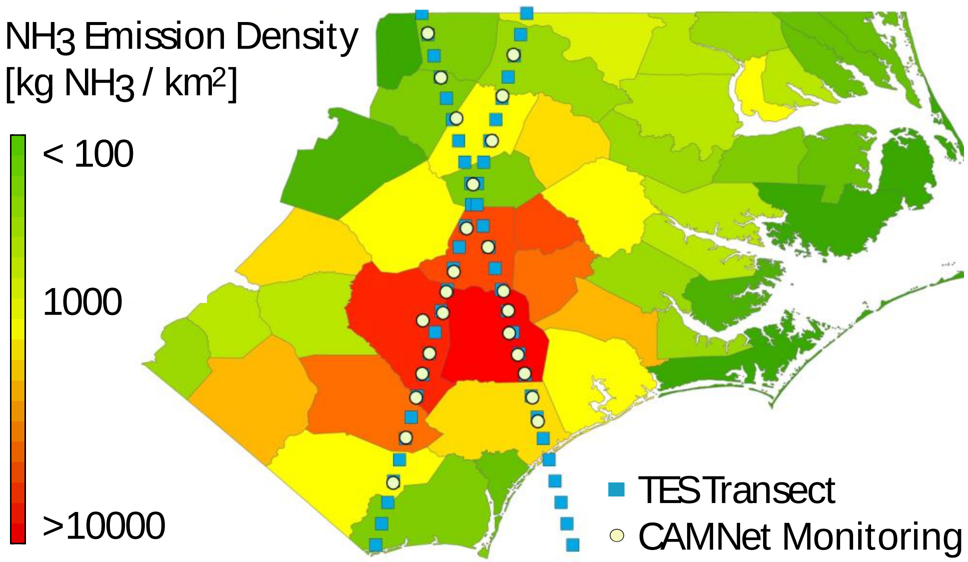
Passive surface measurements:

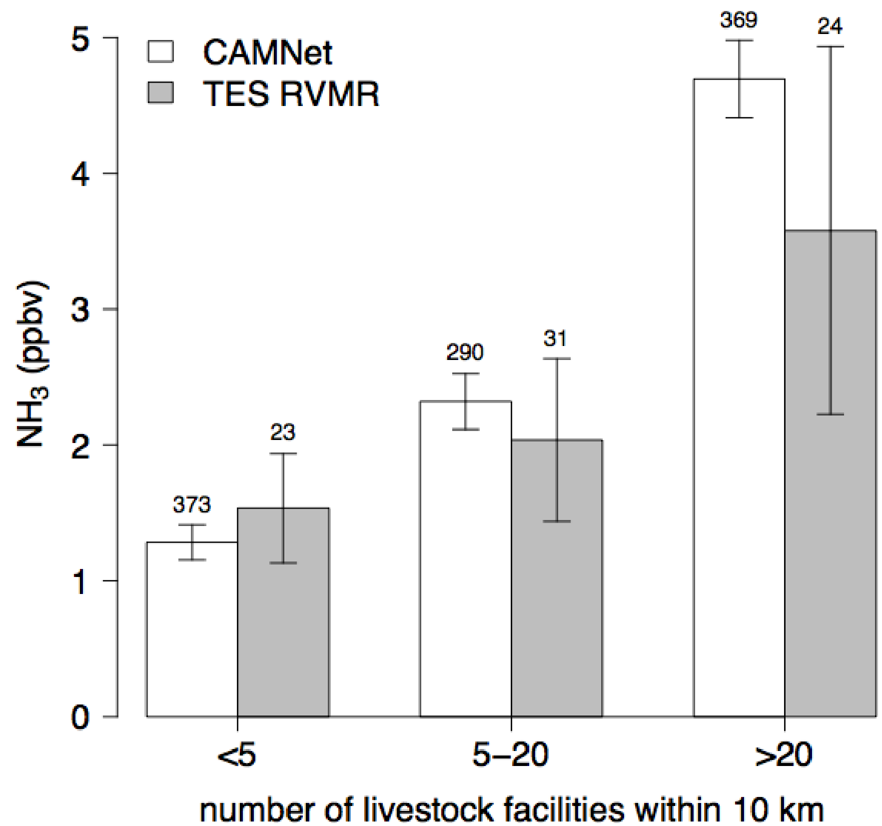
EPA's AMoN sites (>2007)
(Puchalski et al., 2011)

Also LADCO, SEARCH, CSU, ANARChE

Validating TES NH_3 with surface observations

Overlap surface obs with TES Transects for 2009:



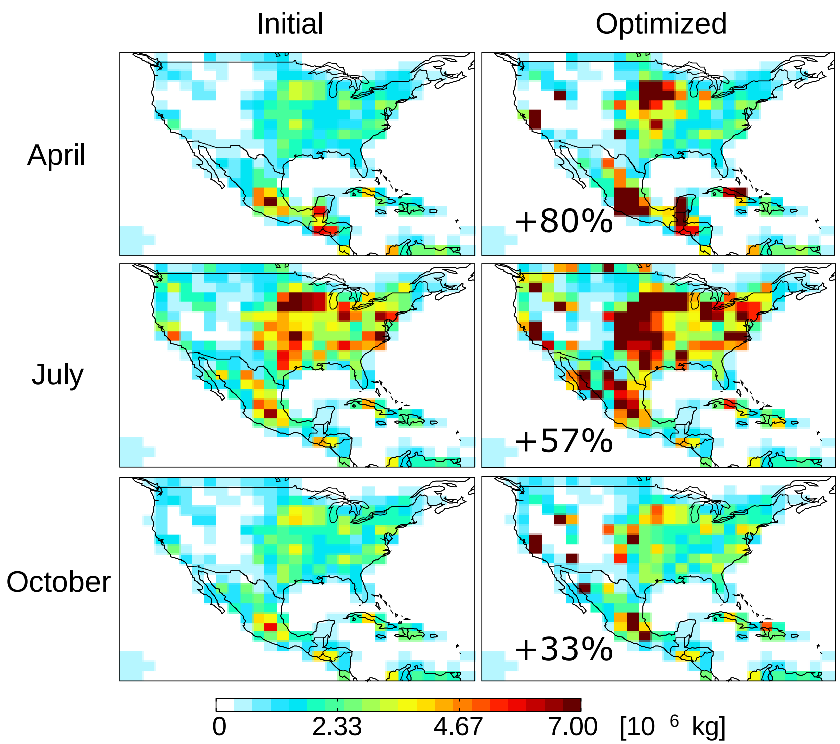


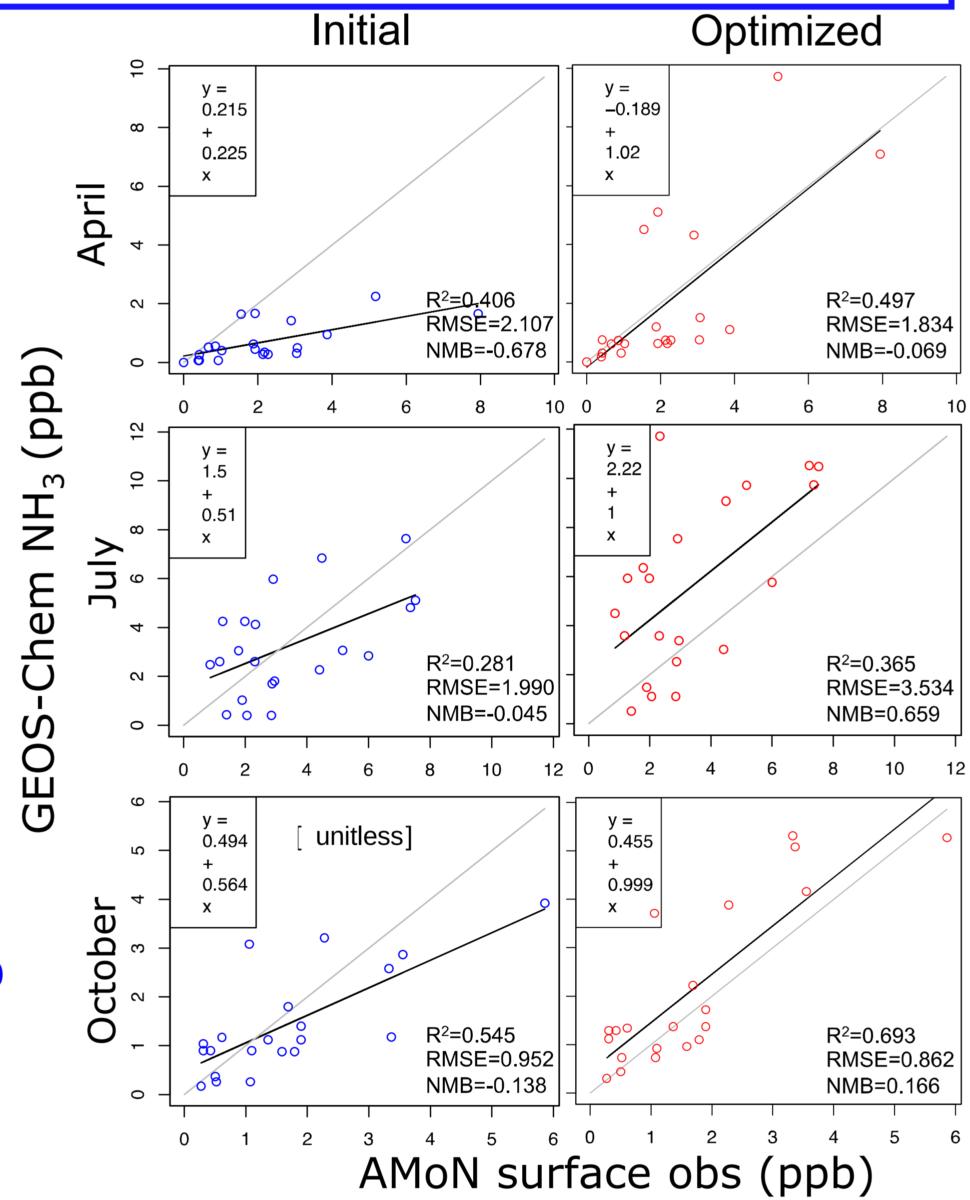
TES reflects real-world spatial gradients and seasonal trends

Pinder et al., 2011

Constraining emissions of NH_3 in GEOS-Chem using 4D-Var technique (Zhu et al., 2013)

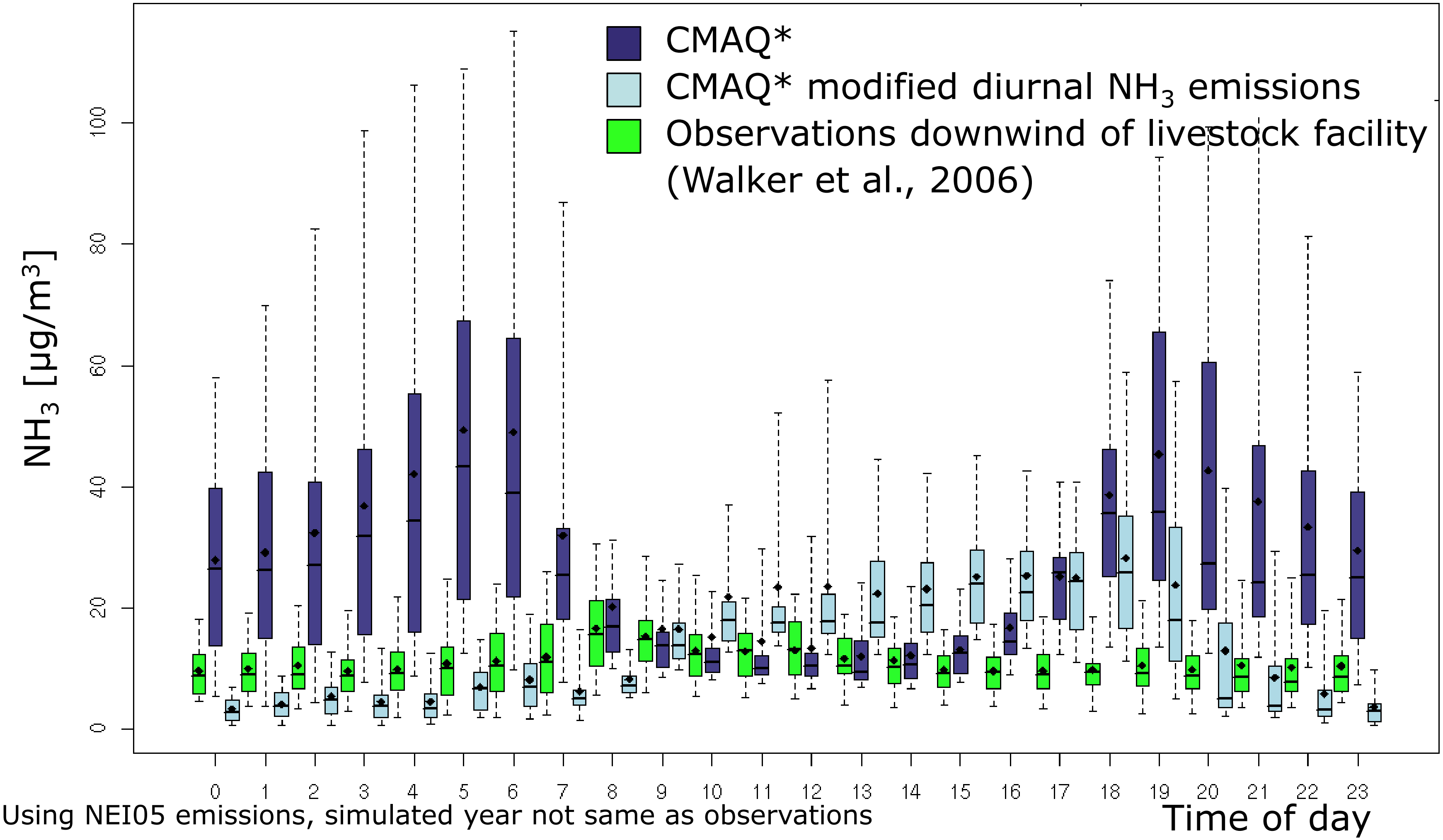
NH_3 emissions in GEOS-Chem





Agrees with constraints using NH_x deposition & new bottom up inventory from Paulot in April (+/- 20%) but not in July

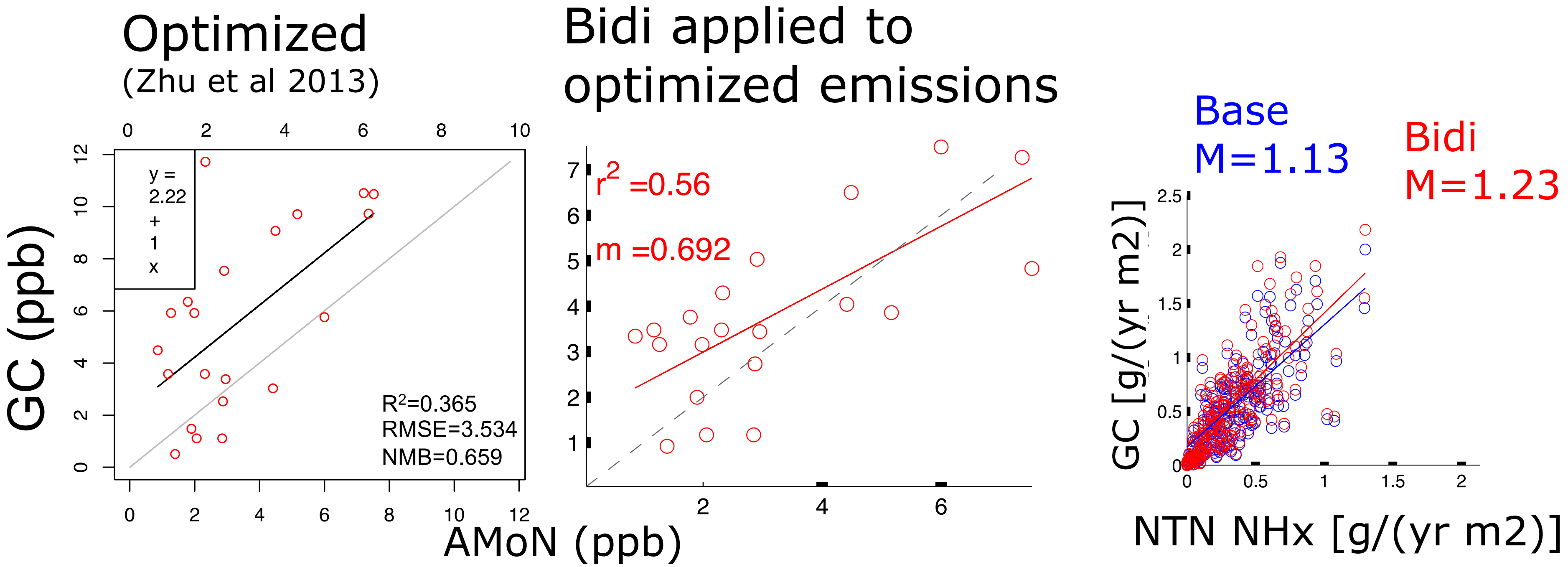
Diurnal variability of NH_3: case study in Warsaw, NC, with CMAQ regional model



* Using NEI05 emissions, simulated year not same as observations

Improved diurnal variability (Bash) can help resolve discrepancies between in situ and satellite obs (Jeong et al., submitted)

Impacts of bidirectional exchange in GEOS-Chem



Improved (mechanistic) representation of NH3 fluxes may help resolve inconsistencies between NH_3 and $[NH_x]_{dep}$ constraints.

Other considerations in remote-sensing constraints:
- temporal sampling bias
- spatial sampling bias

Zhu

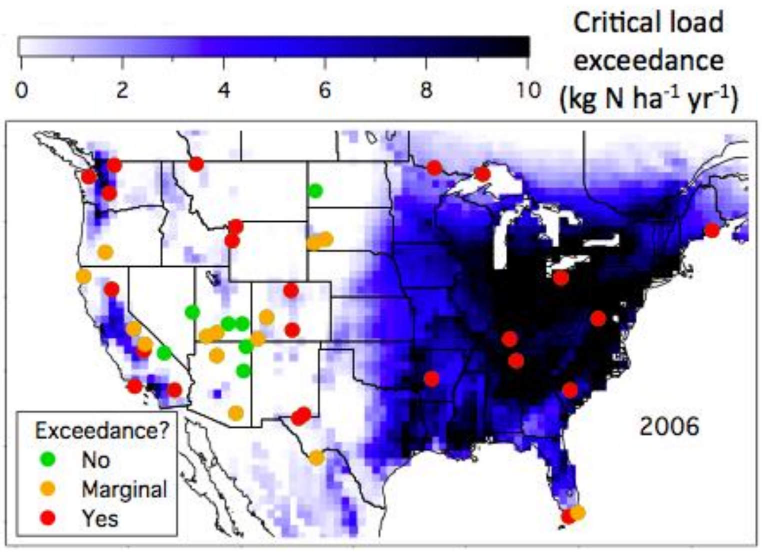
NASA AQAST Tiger Team

Overview:

- multi-model assessment of current and future sources of reactive nitrogen deposition in Class I and at-risk ecosystems in the US

Members:

- Daven Henze, Jana Milford (CUB)
- Fabien Paulot, Daniel Jacob (Harvard)
- Aika Yano,Ted Russell (Georgia Tech)
- Bret Schichtel, John Vimont (NPS)
- Rich Scheffe, James Kelly (US EPA)
- Linda Pardo (USFS)



Ellis et al., 2013)

What are the sources contributing to exceedences in Federal Class I Areas?

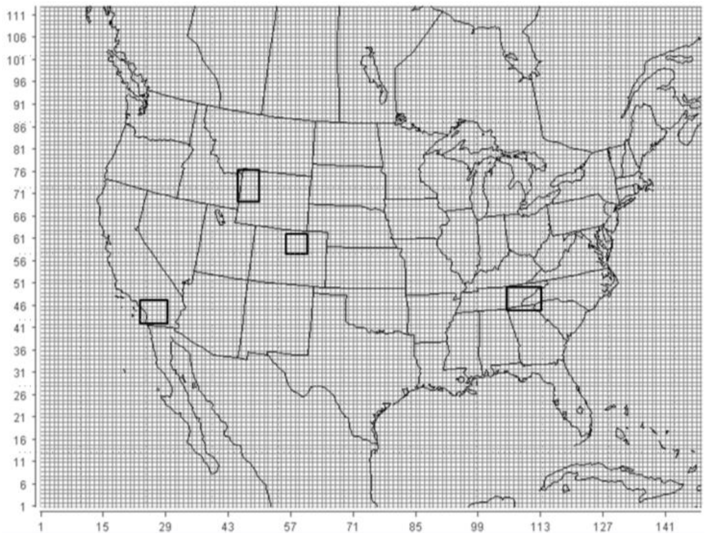
Tools / Observations:

- NH_3 remote sensing, in situ observations (RMNP,…)
- GEOS-Chem and CMAQ models
- Source attribution techniques: sector perturbations, DDM, adjoint

model configurations and domains

CMAQ v5:

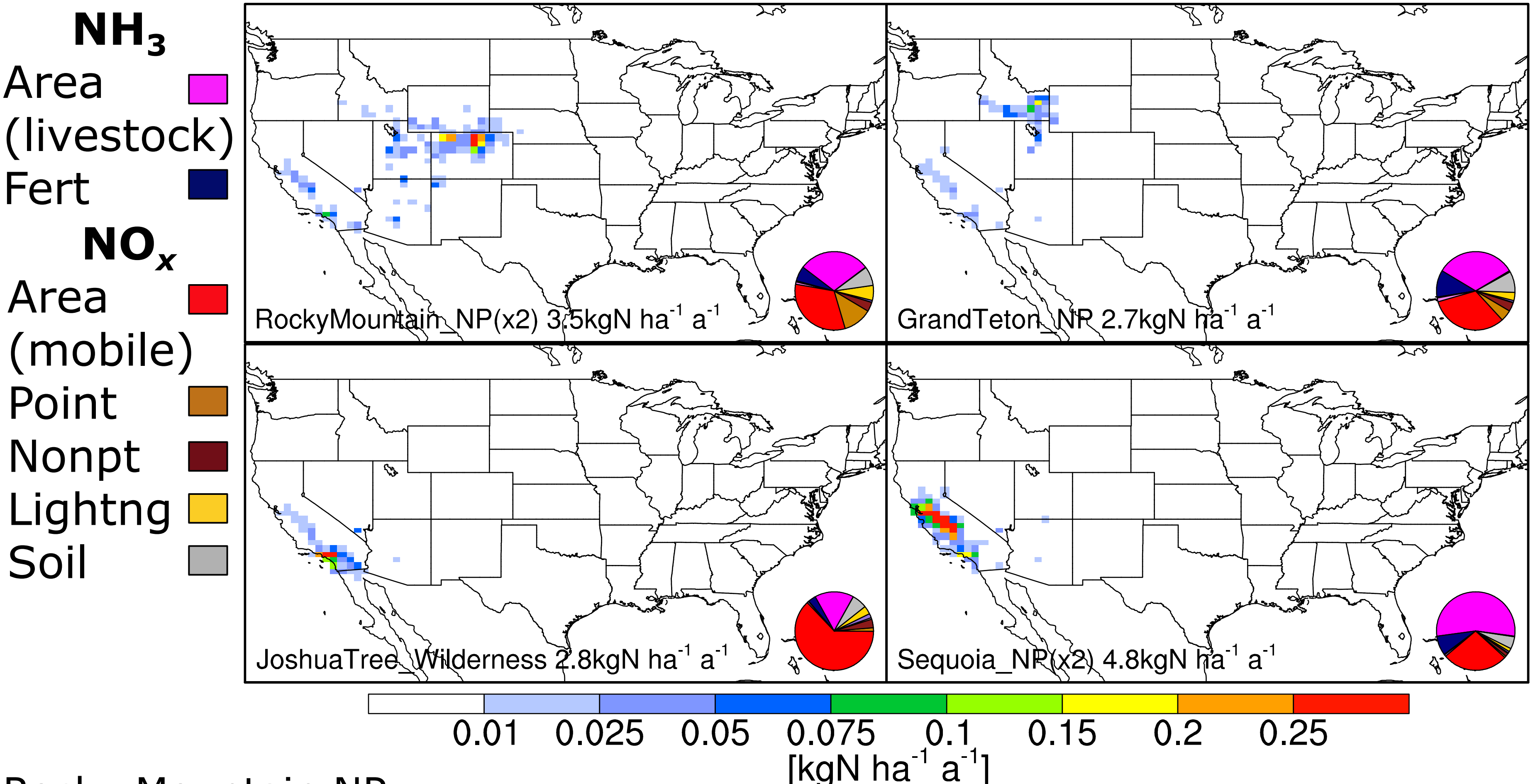
- 36km CONUS
- 4km over NPs
- 2010
- NEI 2005 scaled to 2010
- Bidirectional NH_3 exchange
- CB05 with Pleim-Xiu LSM
- WRF v3



GEOS-Chem:

- 0.5° x 0.667°
- 2010
- NEI 2008
- GFEDv3

Footprints of reactive Nitrogen deposition

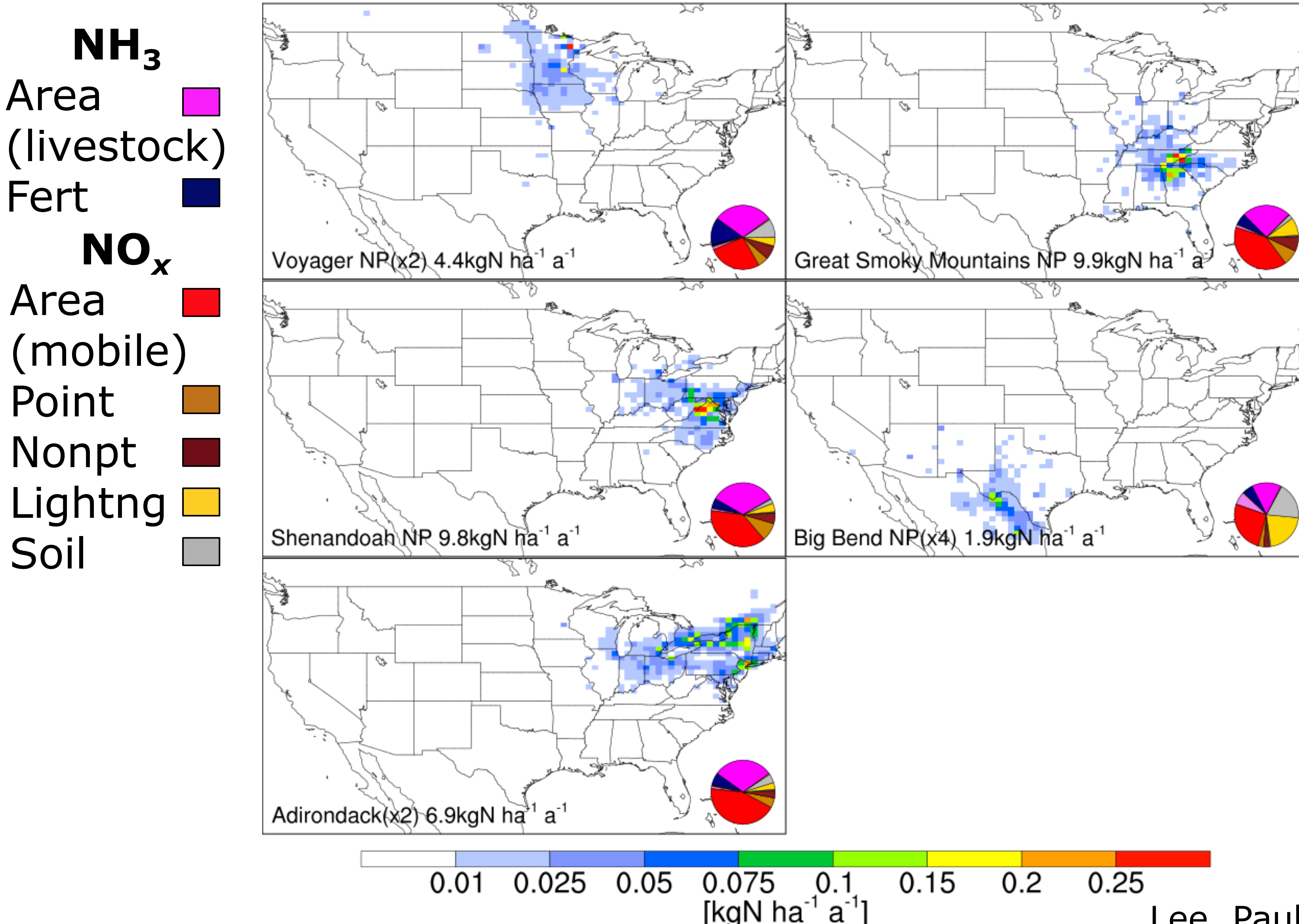


Rocky Mountain NP:

- CMAQ: 0.85 kgN/ha/a from livestock NH3, 1.55 kgN/ha / from mobile NO_x
- Gebhart et al. (2011): 50% of NH3 inputs from out-of-state
- Benedict et al. (2013):

Lee, Paulot, Davis

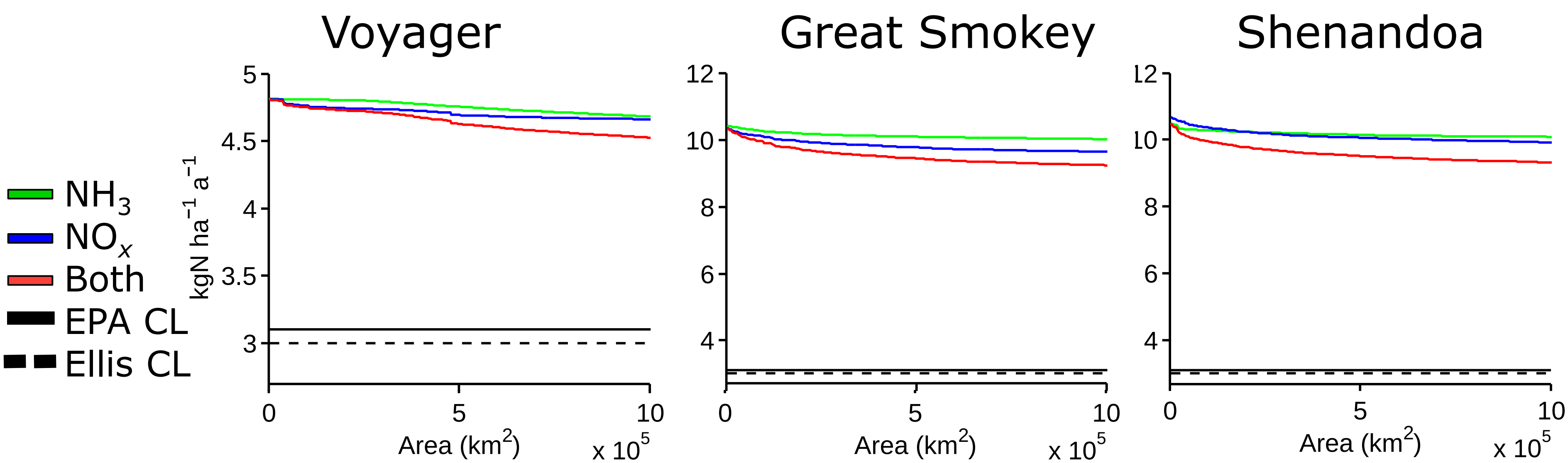
Footprints of reactive Nitrogen deposition



Lee, Paulot

Effectiveness of NH3 vs NOx emission controls for approaching deposition Critical Loads

What is the impact of reducing anthropogenic emissions by 20% as a function of distance (area) away from the park?



-local NOx
-distant NH3

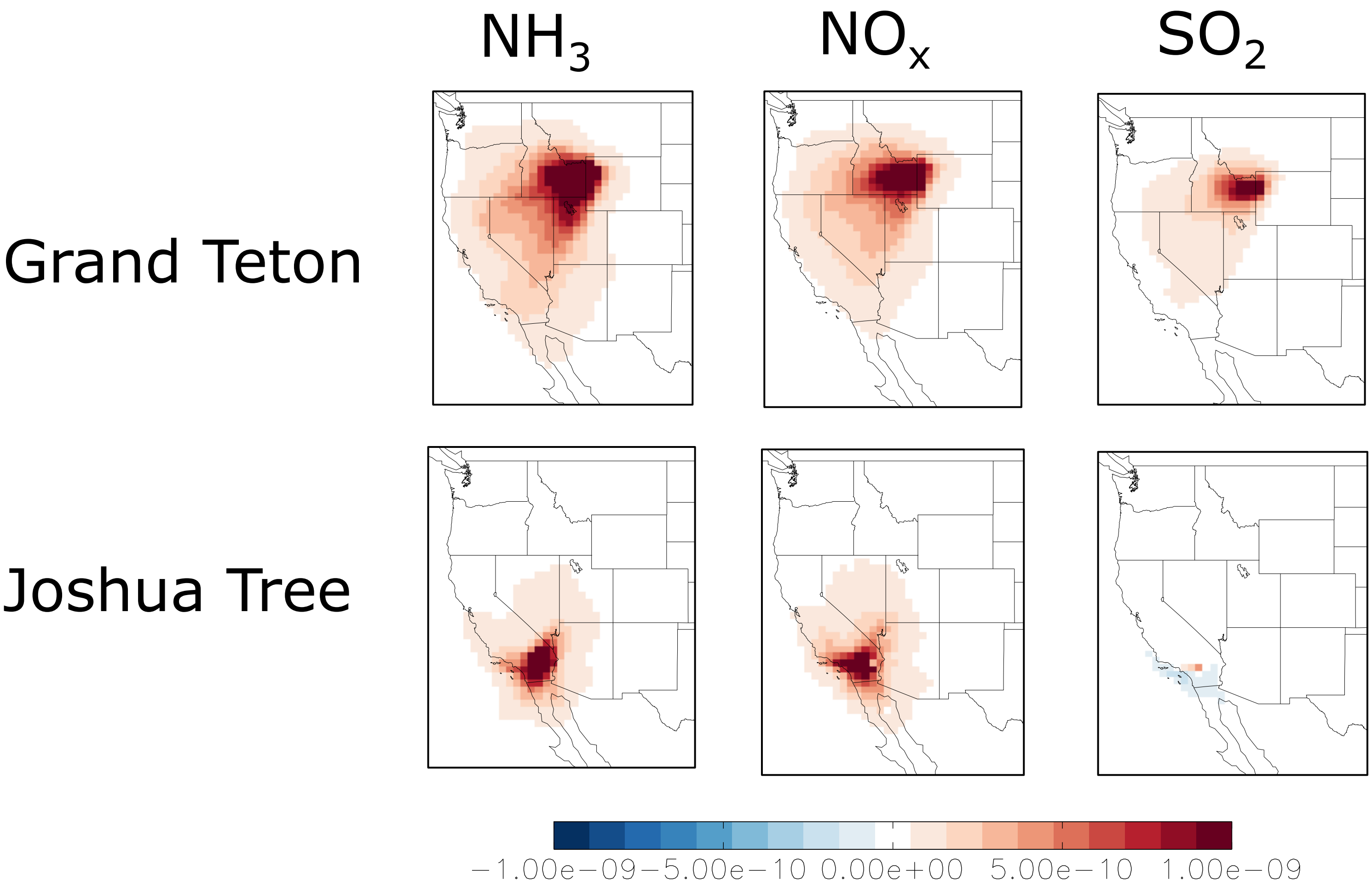
- NOx

- same

All regions are far from attaining CL values with small reductions to emissions over a wide 10^6 km^2 area (size of France!)

Paulot

What is the nitrogen deposition efficiency?



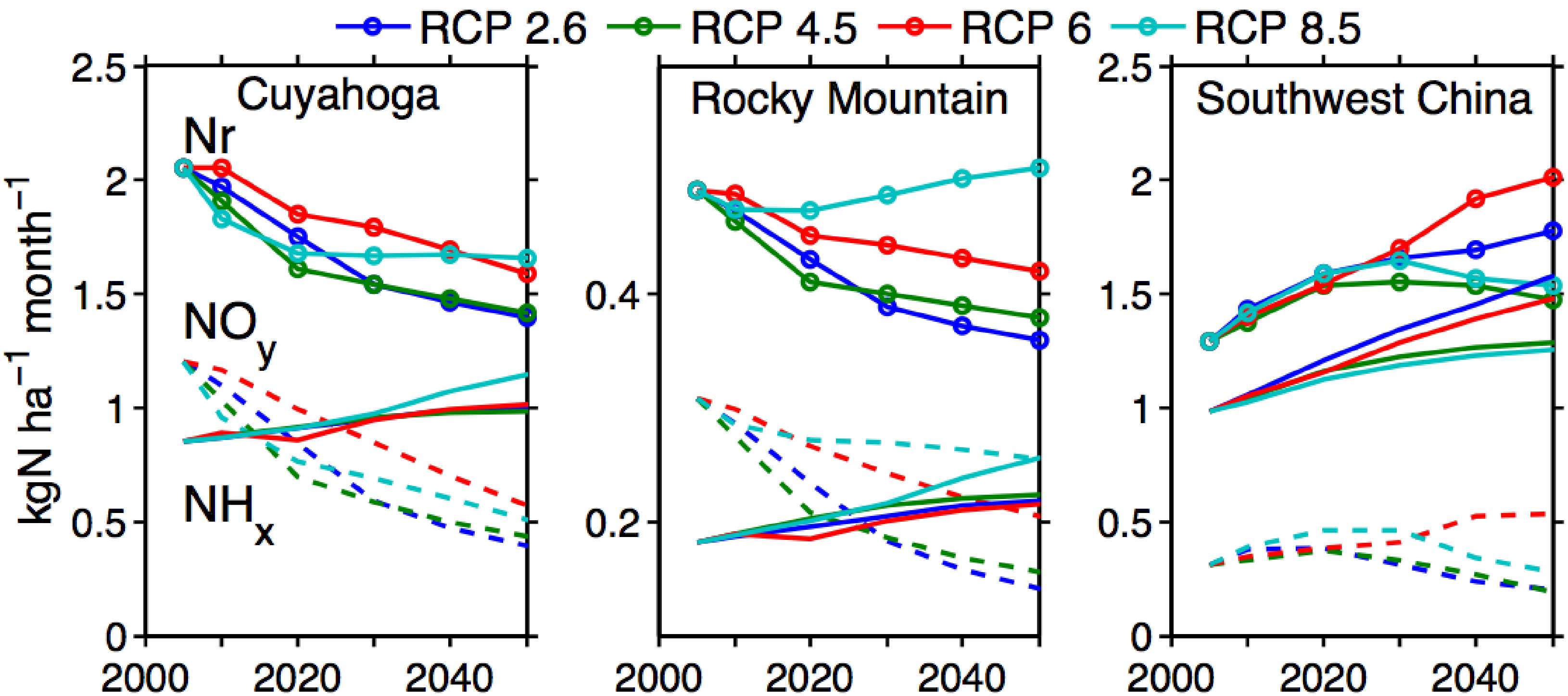
(kg N dep / ha / yr) / (mol emission / yr)

Implications for impacts of new sources

Lee

Projections of Nr deposition

Projections of the evolving roles of NH_3 and NO_x on Nr deposition following emission projections from IPCC AR5 (Moss et al., 2010)



Paulot et al., 2012; also Ellis et al. 2013

While Nr may be decreasing, role of NH_3 increasing

Final comments

- Constraints from multiple sources (remote sensing, deposition, in situ measurements) helping reduce uncertainty in NH_3 emissions.

- 4D-Var techniques allow inversion process to consider spatially heterogeneous biases in emissions inventories.

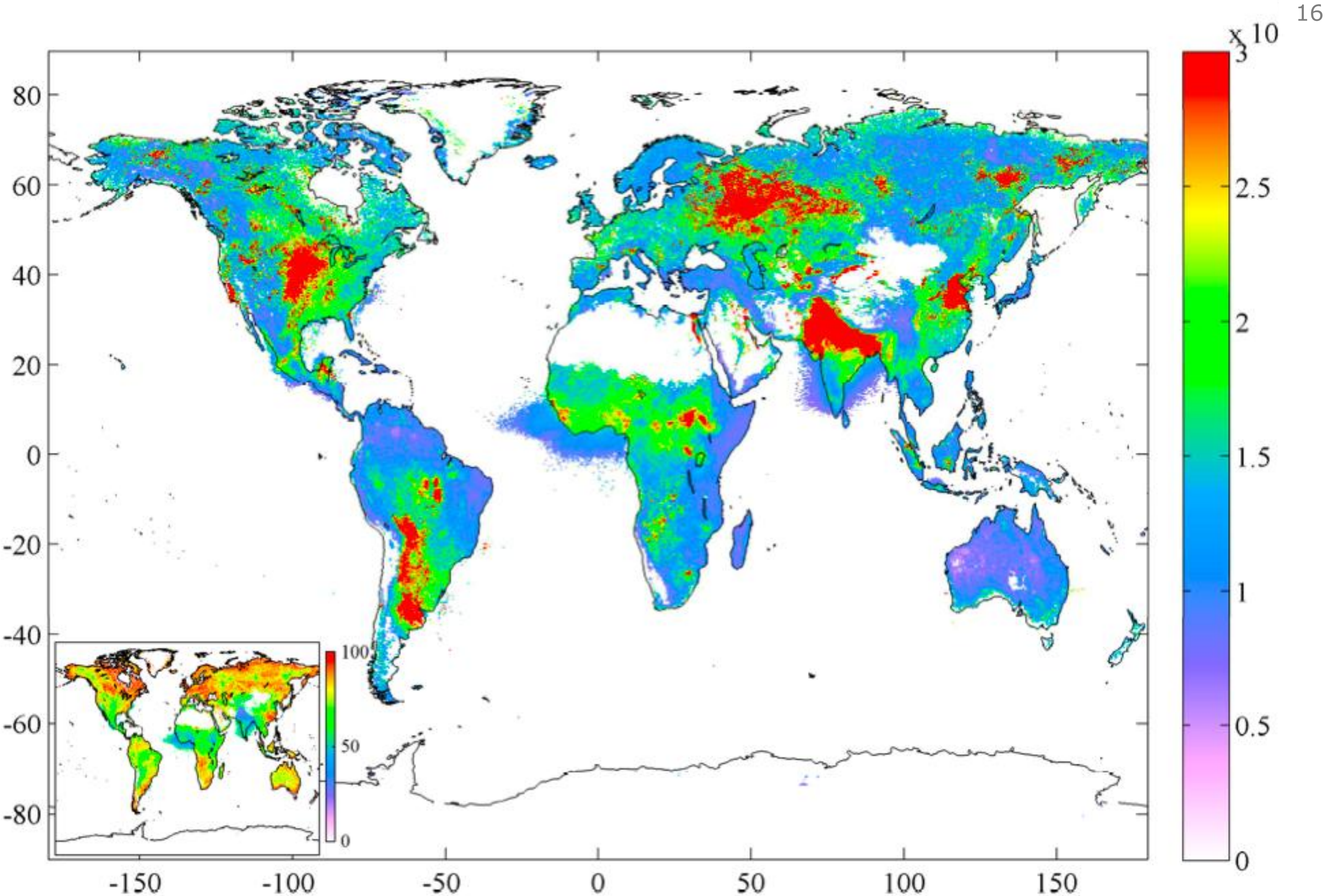
- It's an iterative procedure, and we're learning more about process-level emissions (diurnal variability, bi-directional fluxes).

- NH_3 and NO_x sources can contribute significantly to reactive nitrogen deposition several states away.

- Substantial controls required to approach critical loads, particularly given projected increases in NH_3 emissions.

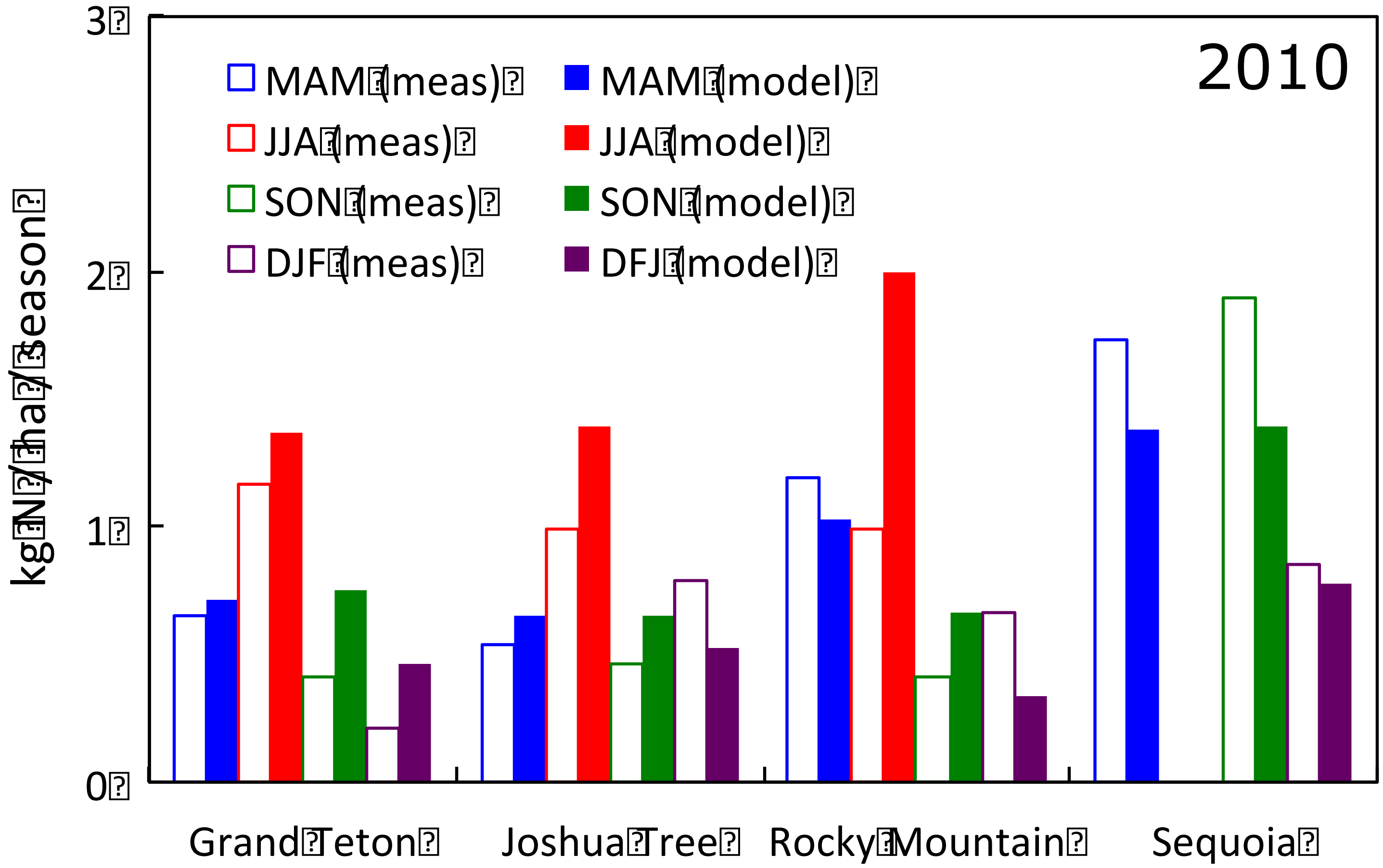
End

Remote sensing of NH_3: IASI



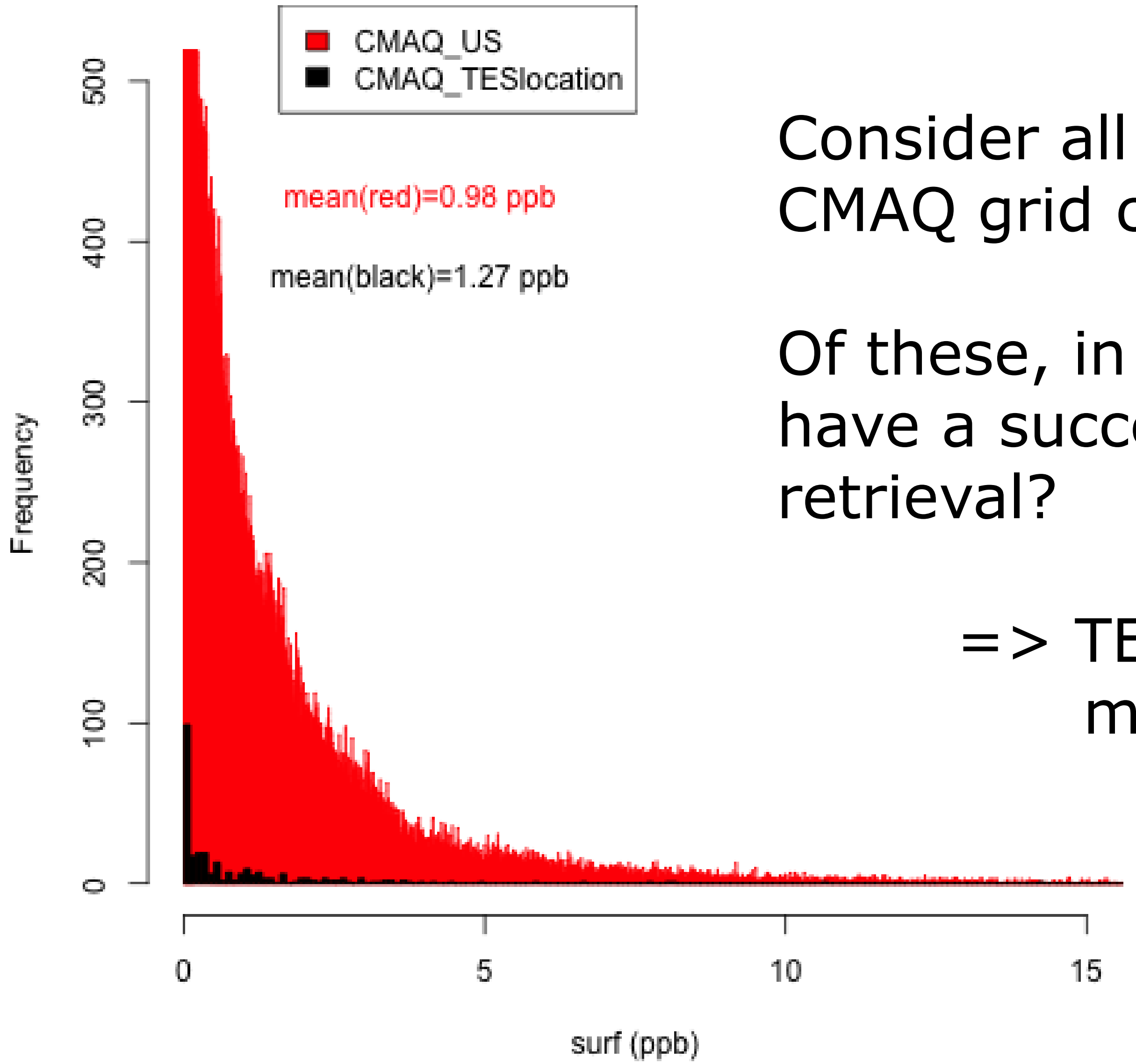
Van Damme et al., ACPD, 2013

Model evaluation:
GEOS-Chem vs observed (NTN) N deposition



TES NH_3 visualization

TES NH3 constraints in GEOS-Chem: spatial sampling / retrieval bias



Consider all 12 x 12 km2 CMAQ grid cells

Of these, in which did we have a successful TES retrieval?

=> TES constraints may be ~30% high

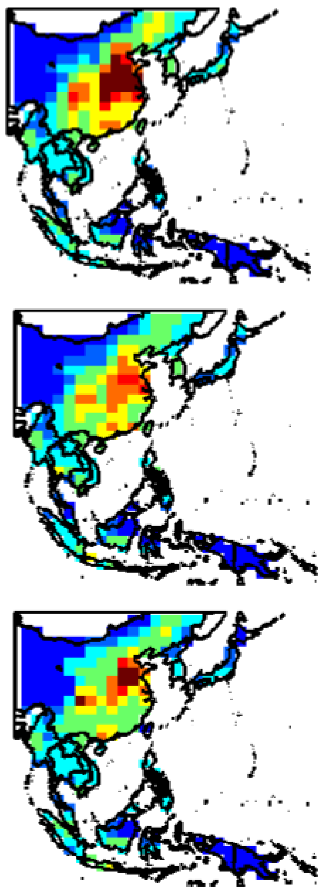
Constraints from NH_x deposition, and an alternate bottom up inventory

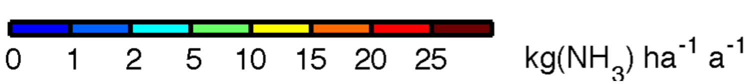
Annual NH_3 emissions in GEOS-Chem

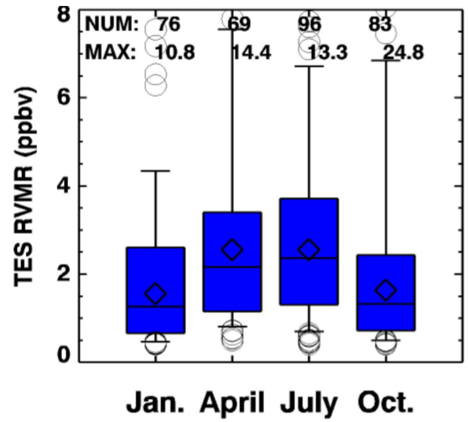
a priori

optimized

Alternative bottom-up

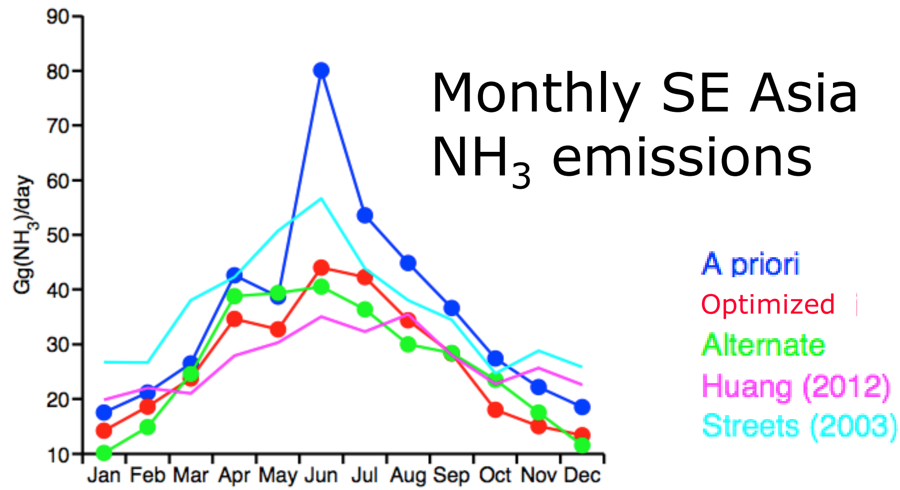






Seasonality in SE China from TES NH_3 observations (Shephard et al., 2011)

Monthly SE Asia NH_3 emissions

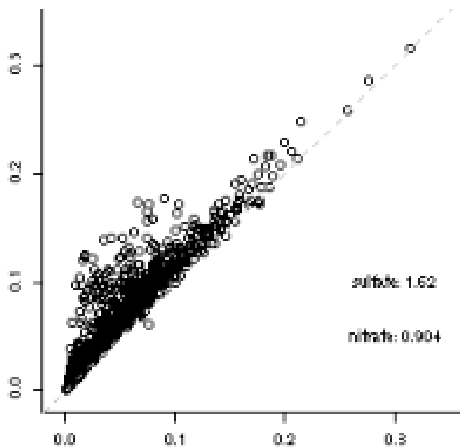


Top-down constraints agree with recent bottom up inventories: Huang (2012) and Alternate.

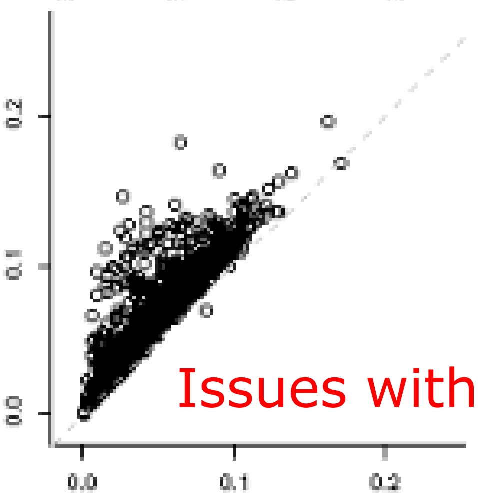
Paulot in prep

Constraints from CASTNet NH_4^+?
$n(NH_4^+) : 2n(SO_4^{2-}) + n(NO_3^-)$

CASTNet, all sites, 2005-2006 (R. Pinder)



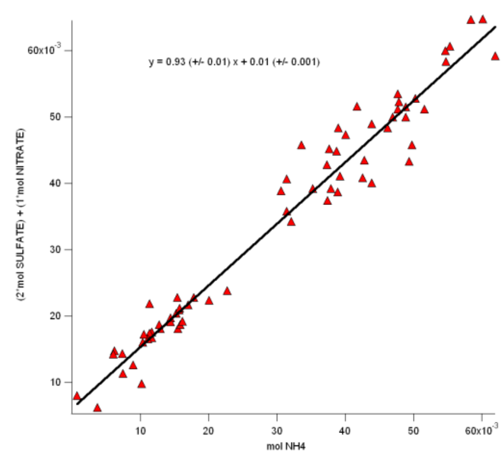
January



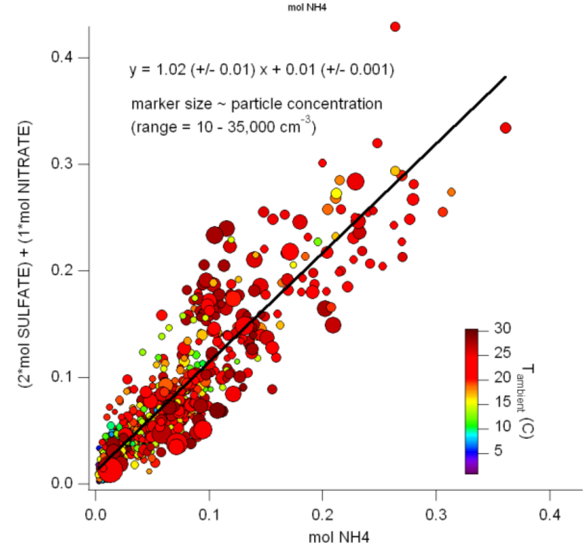
April

Issues with evaporation

Field campaigns (Sorooshian et al.)

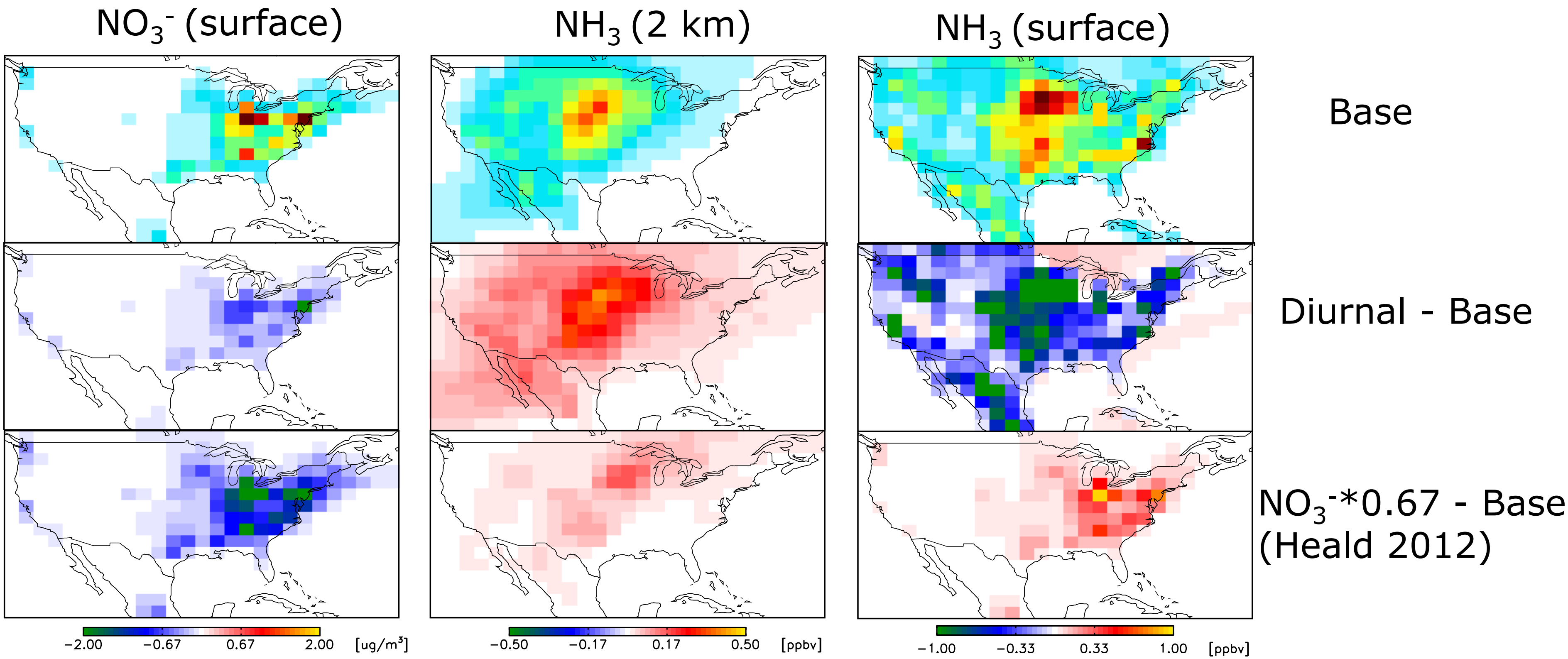


SJ Valley



Houston

Conundrum of nitrate (too high) and ammonia (too high at surface, too low higher up) in July in GEOS-Chem



Mechanistic NH_3 emissions an important future direction for global models.

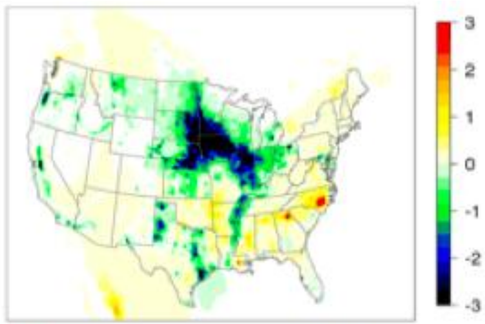
Other factors:

- BL heights (Dalhousie, following Lin and McElroy, 2010)
- excessive N_2O_5 (Zhang et al., 2012; Paulot et al., submitted)

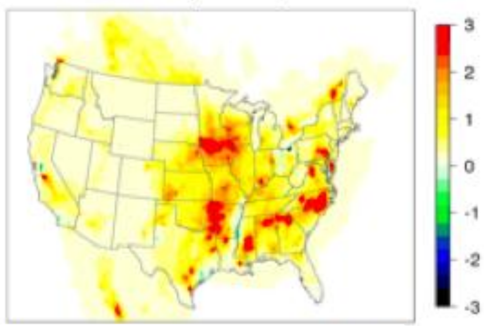
Impacts of bidirectional exchange in GEOS-Chem

NH_3: $CMAQ_{bidi}$ - $CMAQ_{base}$

April

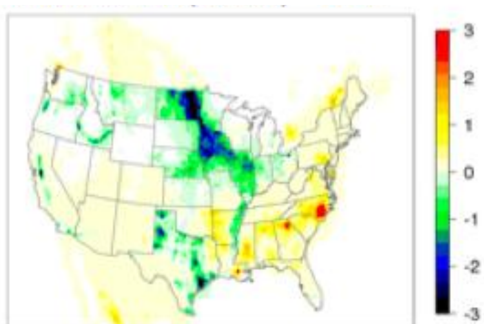


July



Decreased deposition in July leads to enhanced NH3 lifetime throughout the US.

October



Jeong et al., submitted