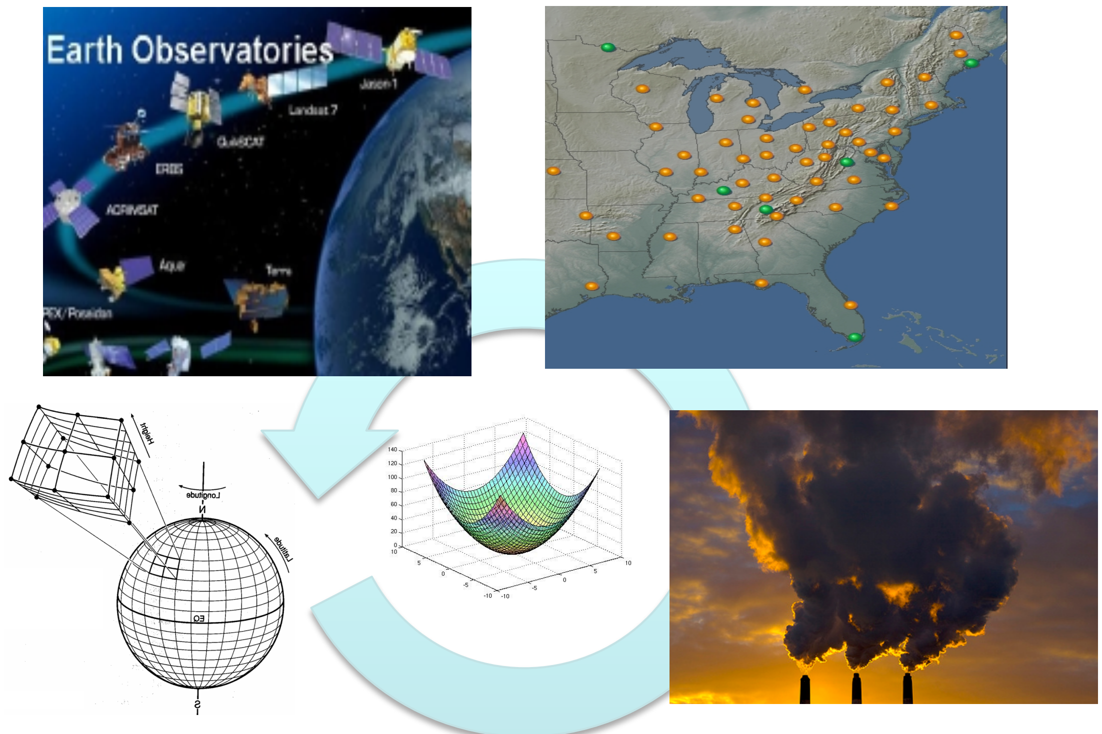
Constraints on air quality budgets of the sources and sinks of reactive nitrogen

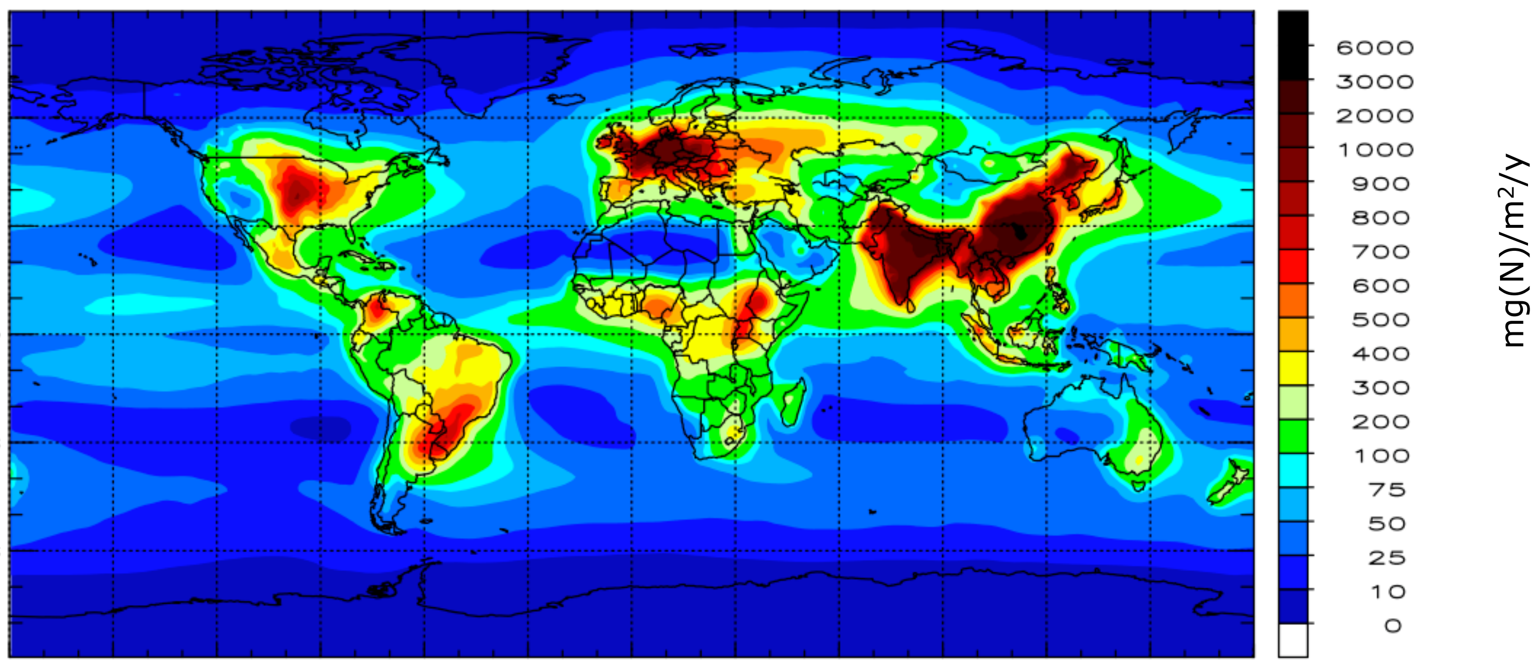


Daven K. Henze
University of Colorado, Boulder

Juliet Zhu, Jana Milford (CU Boulder), 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)
Ted Russell, Aika Yano (Georgia Tech(

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:

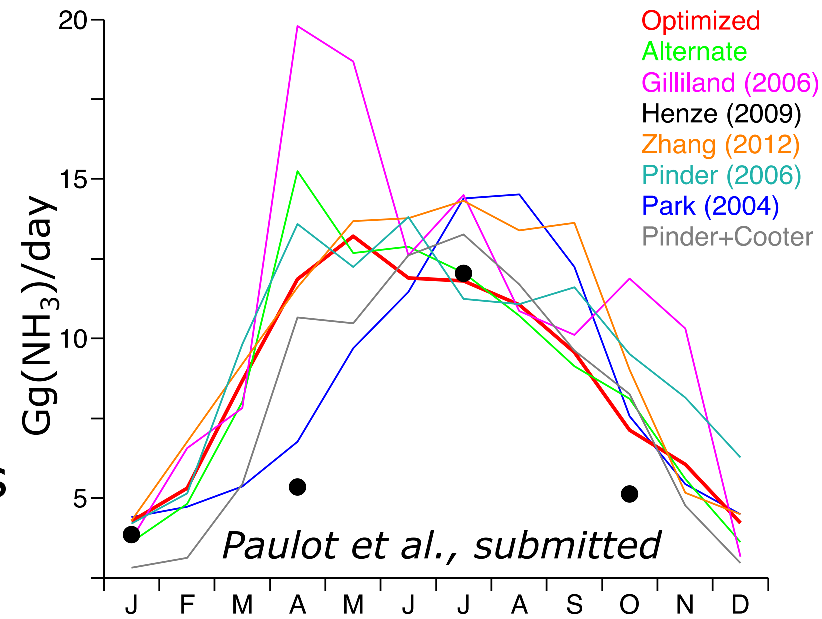
- increased by factor of 2 – 5 since preindustrial era.
- to double by 2050 (*IPCC*, Denman et al., 2007; Moss et al., 2010).
- contribute to 46 Tg gap in global N budget (Schlesinger, 2009)?

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)



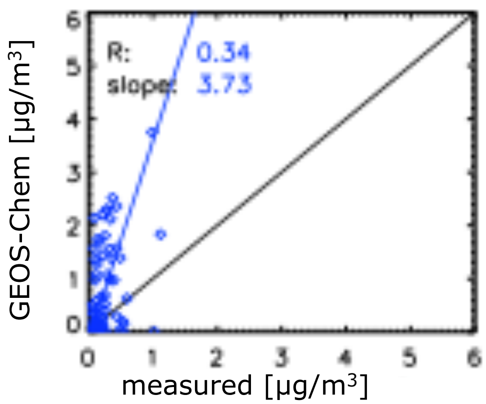
Why so uncertain?
- lack of direct source measurements (hard, expensive)

- 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

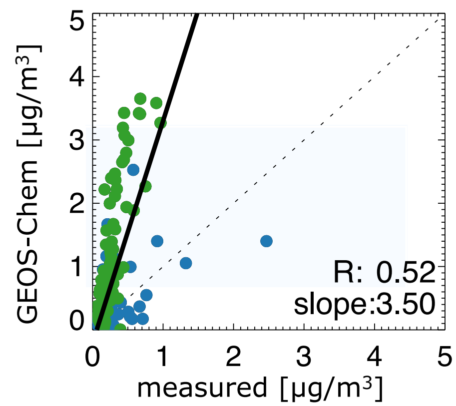
Uncertainties in NH_3 emissions: Implications for air quality and environment

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

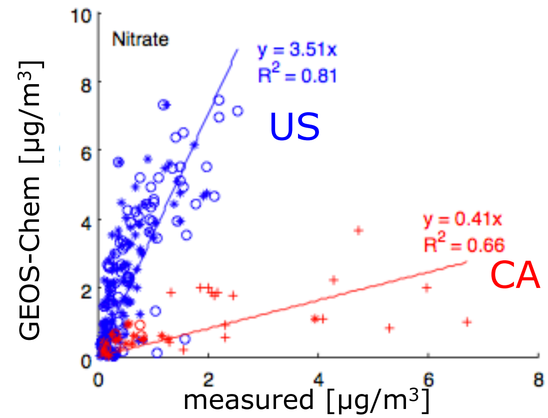
Ex: GEOS-Chem overestimates nitrate at IMPROVE / CASTNET (July)



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

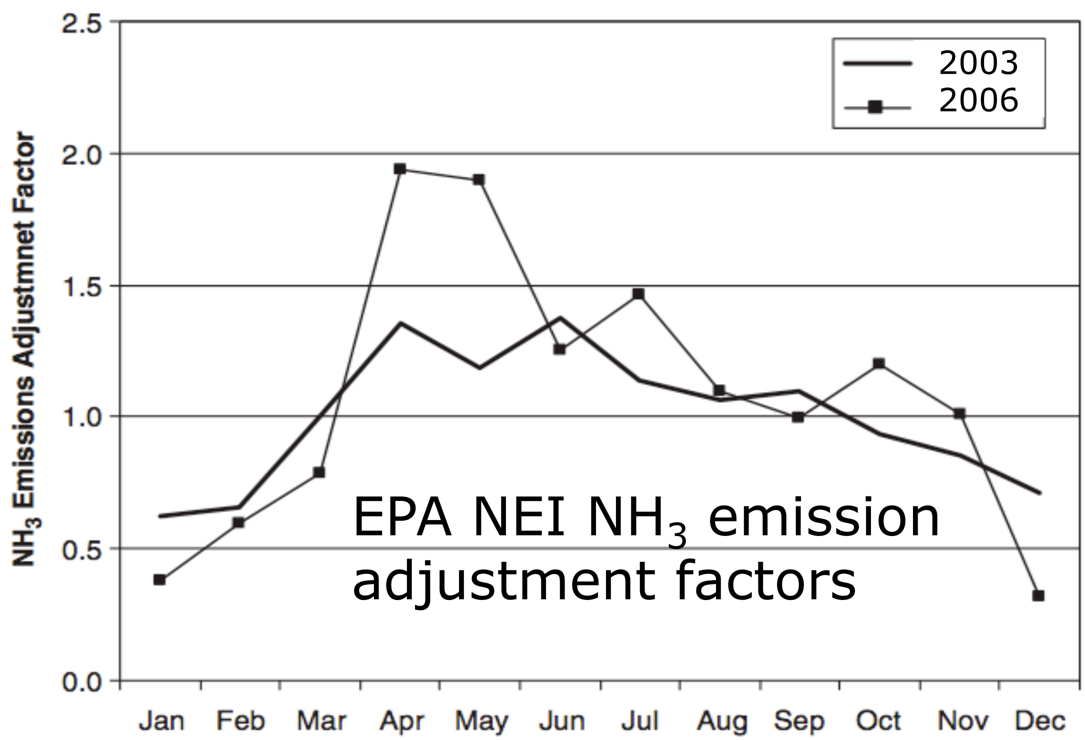
Many US air quality models get NHx deposition correct via assimilation.

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

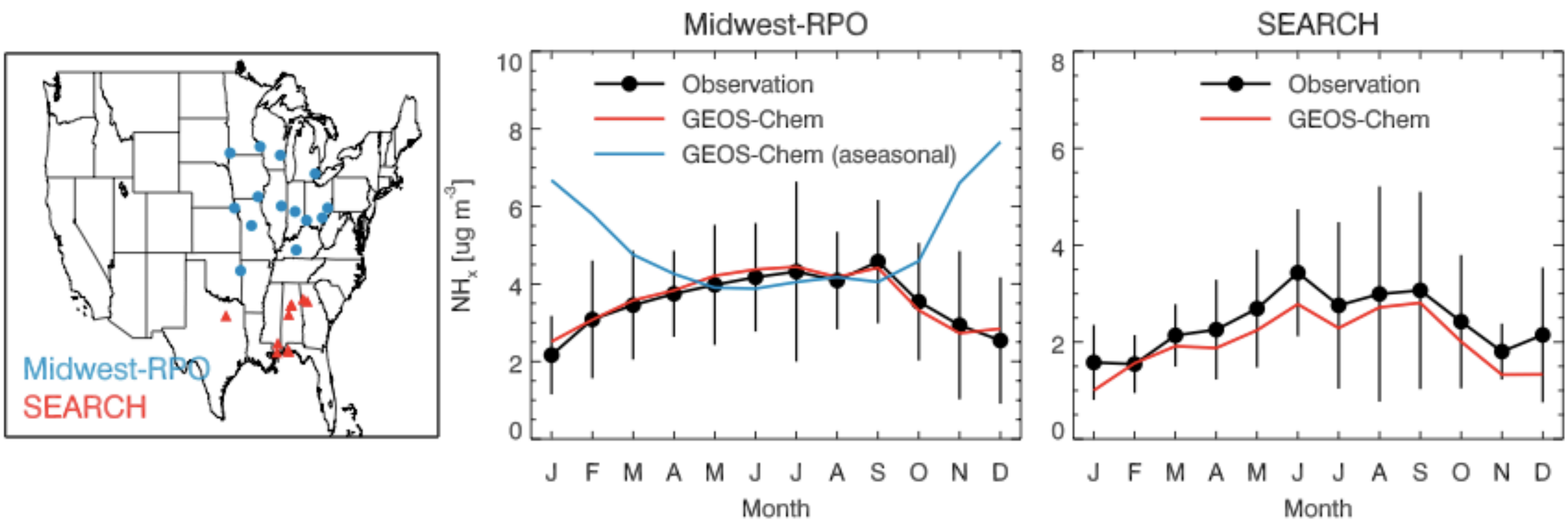
Assumptions:
- uniform seasonality throughout broad regions of US



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

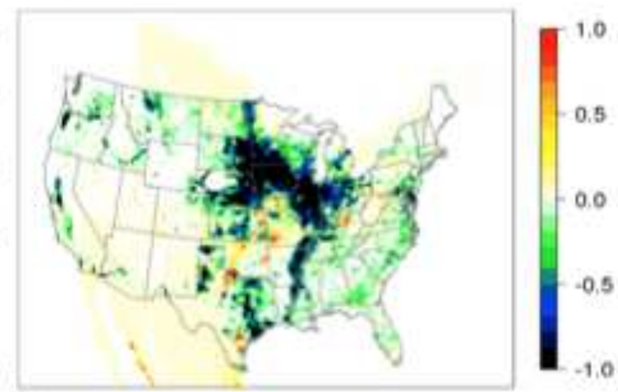


- Resulting annual NHx and NO3 deposition unbiased.
- Enforces a spatially uniform seasonality / correction factor across the US.

Spatial heterogeneity in source-receptor relationships for NH_3

Consider emissions perturbation, Δemiss:

April



July

Kg NH_3/ha/month

Jeong et al., submitted

Spatial correlations of Δemiss with:

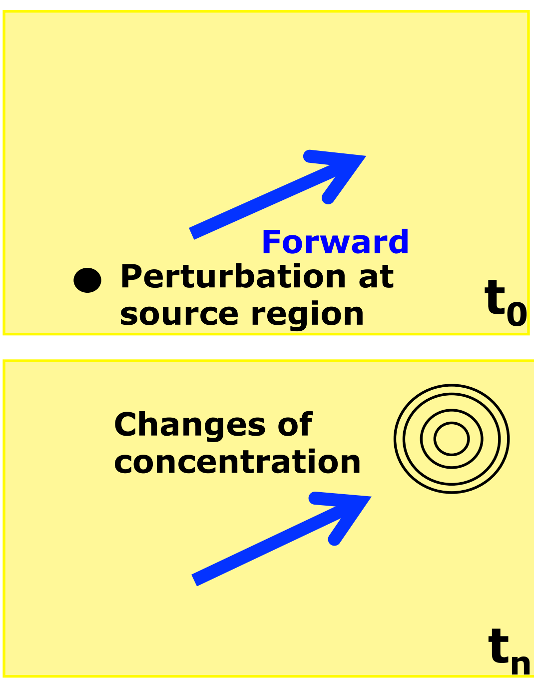
	Δ[NH_3]	Δ wet dep [NH_x]
April	0.83	0.54
July	0.17	-0.06

Spatially heterogeneous impacts of NH3 emissions – can be accounted for using 4D-Var / adjoint inversions

Source attribution techniques

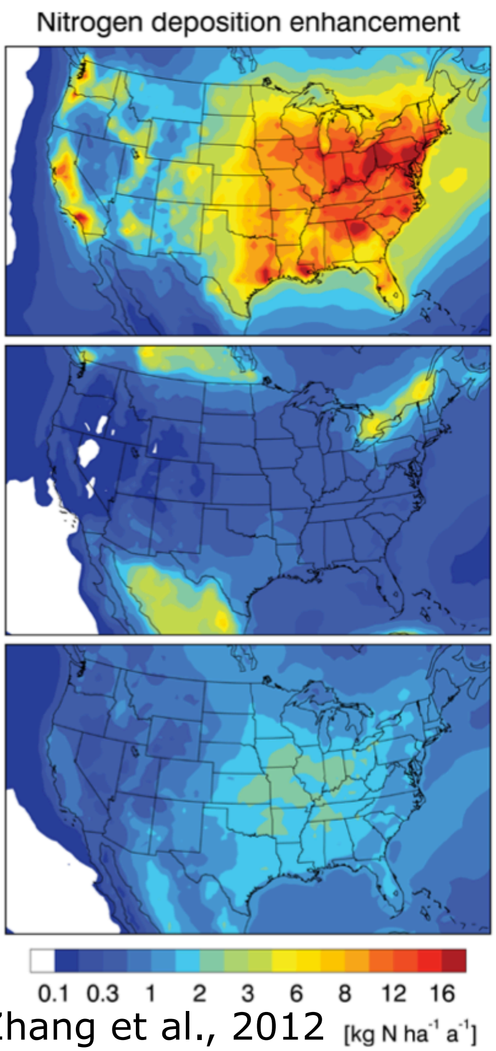
Forward Model (source-oriented)

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

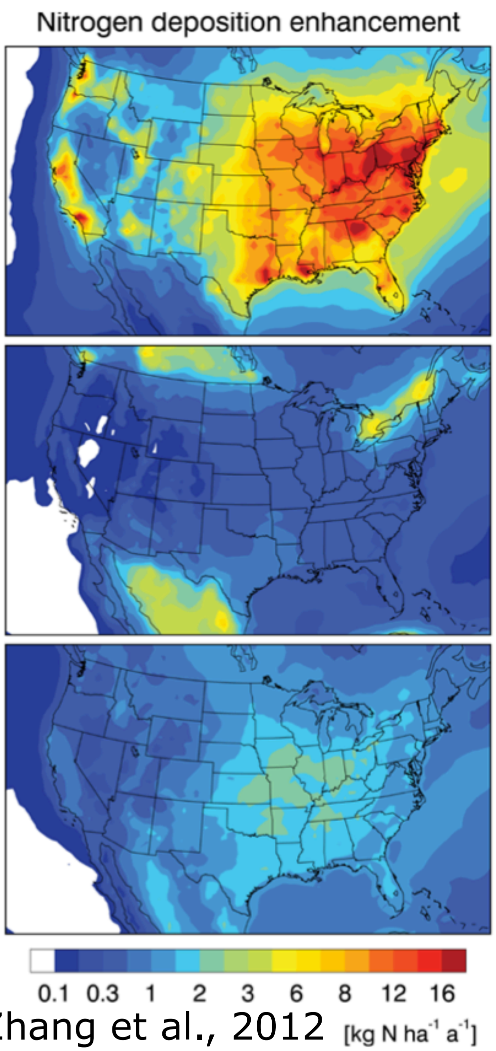
Foreign
Anthropogenic
0.42 Tg N / yr

Natural
1.0 Tg N / yr

Zhang et al., 2012

Source attribution techniques

Forward Model (source-oriented)



US Anthropogenic 5.0 Tg N / yr

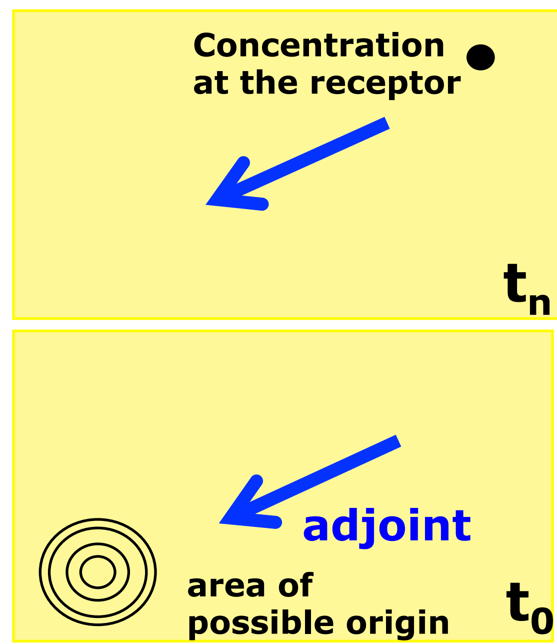
Foreign Anthropogenic 0.42 Tg N / yr

Natural 1.0 Tg N / yr

Zhang et al., 2012

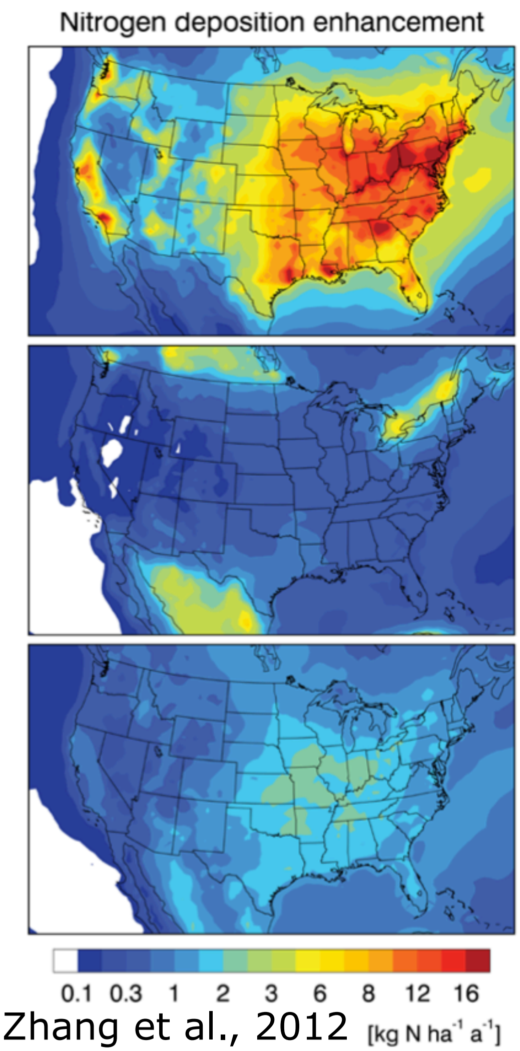
Adjoint Model (receptor-oriented)

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

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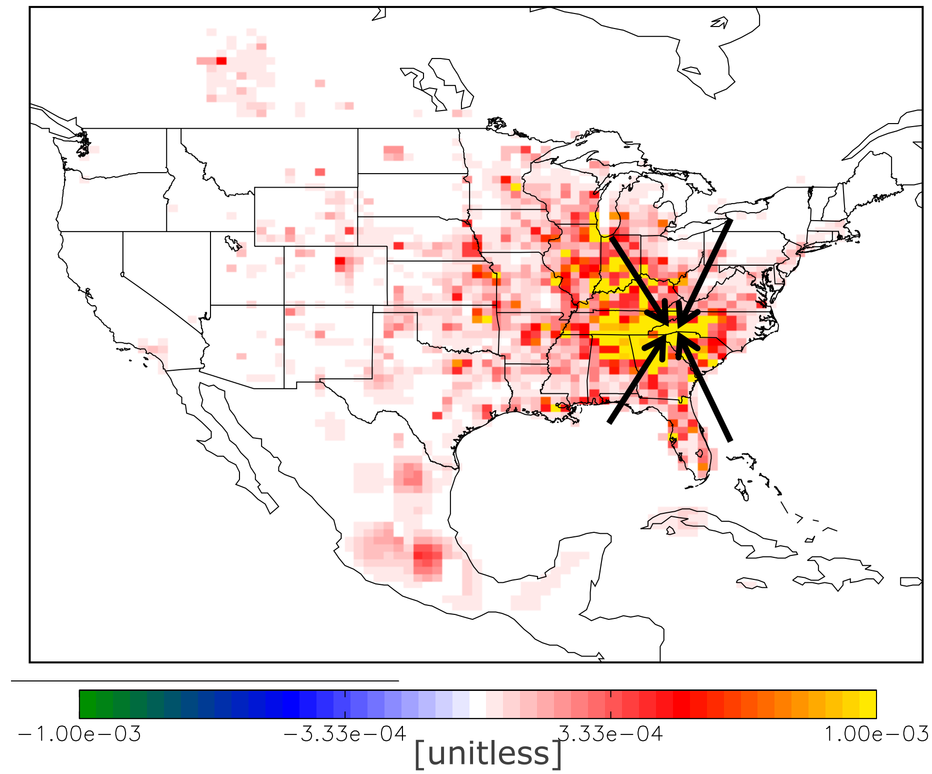
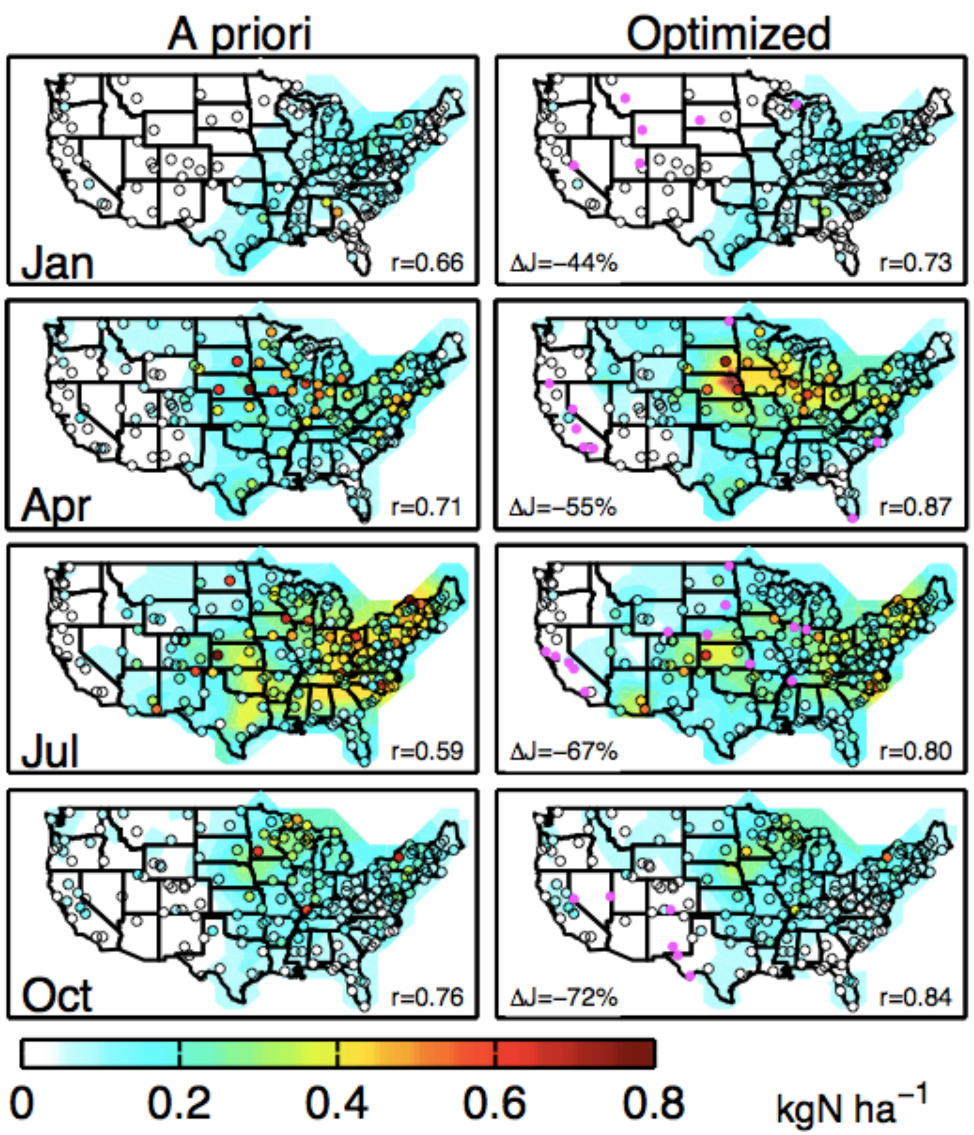
Zhang et al., 2012

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



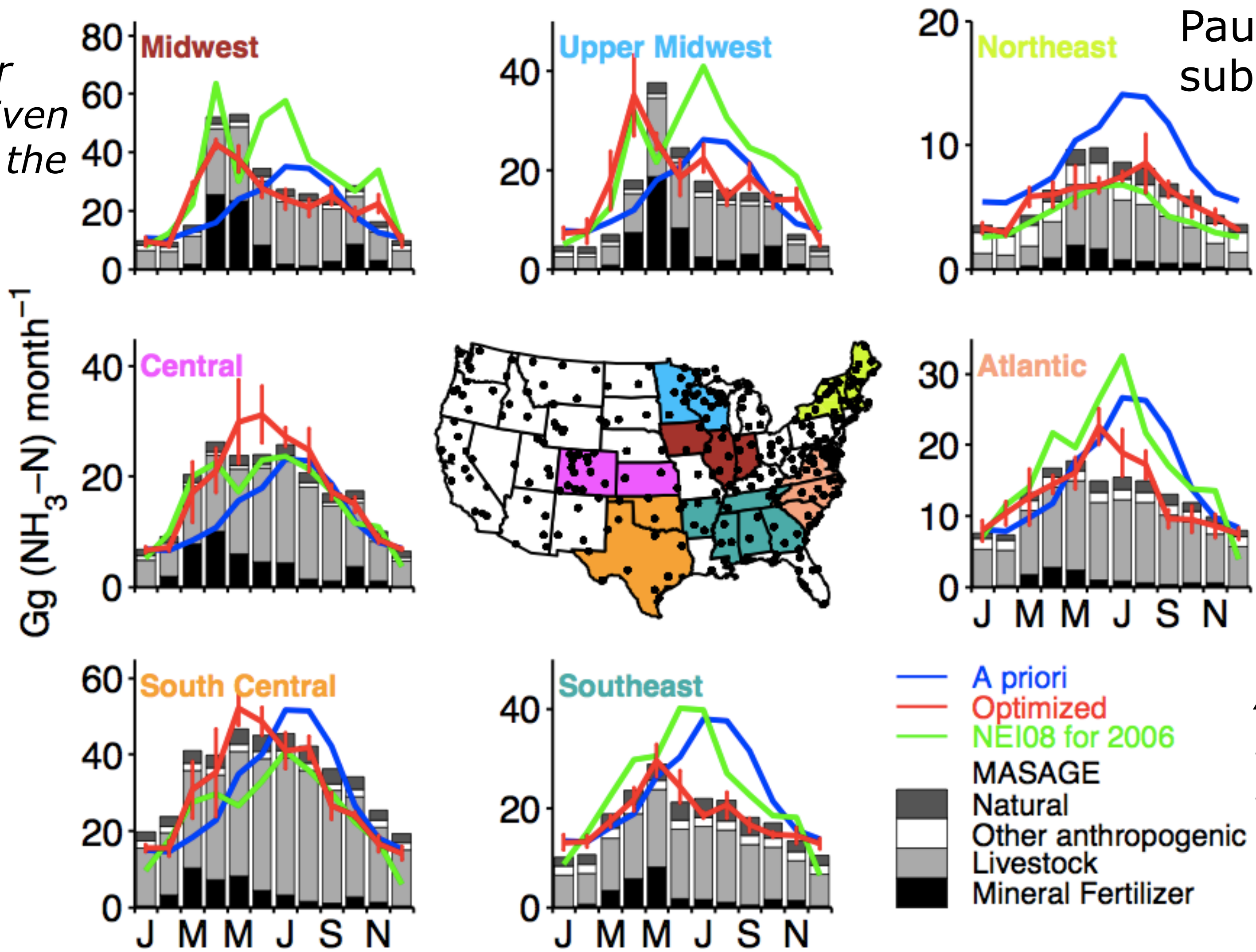
Paulot et al., submitted

- 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

Evidence for fertilizer-driven Emission in the Midwest?

Paulot et al., submitted

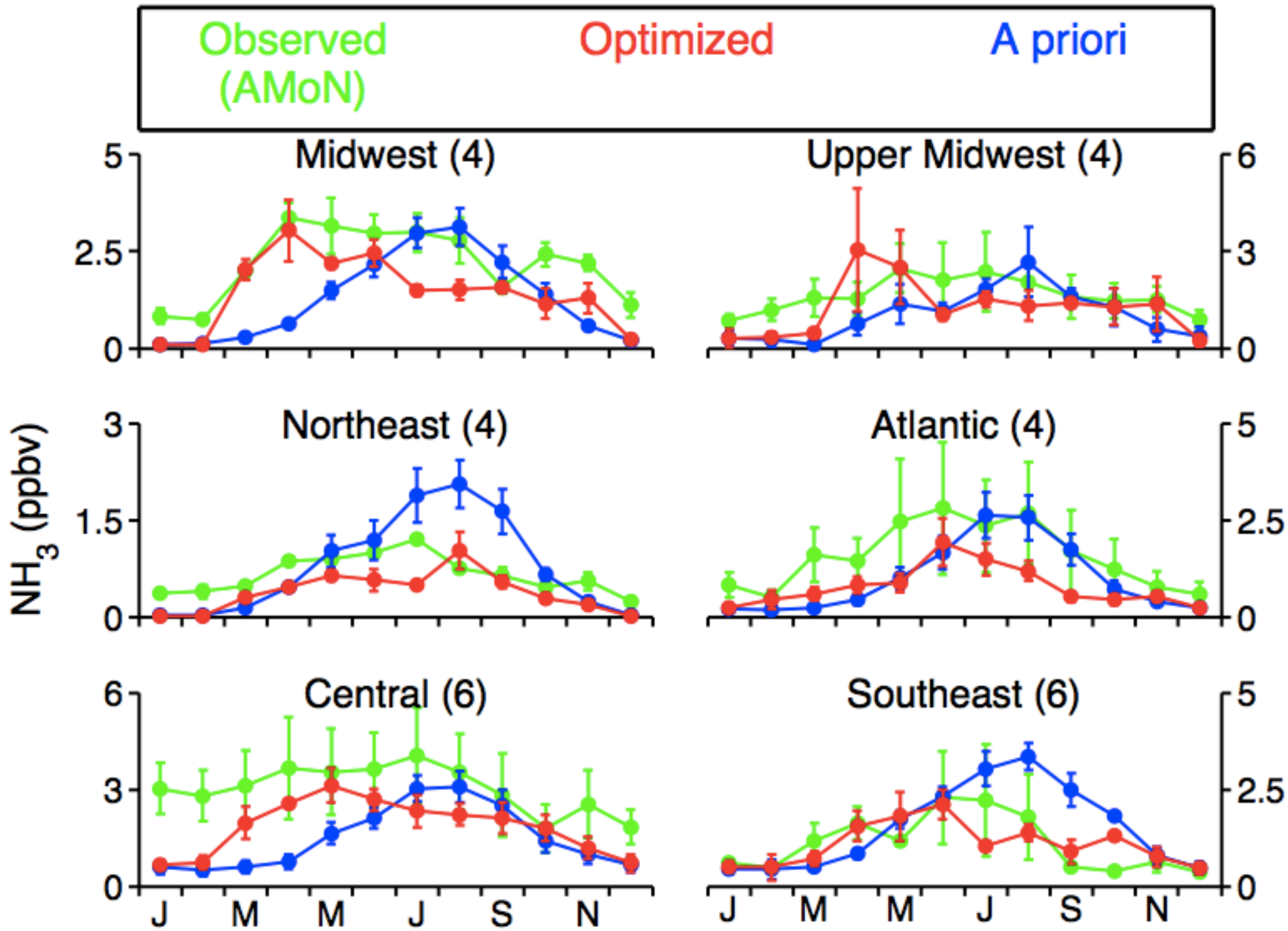


Alternate bottom-up inventory

No support for homogeneous seasonality in the US. Alternate bottom-up inventory has some success reproducing patterns of optimized emissions.

Constraints from NH_x deposition, and an alternate bottom up inventory

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



Paulot et al., submitted

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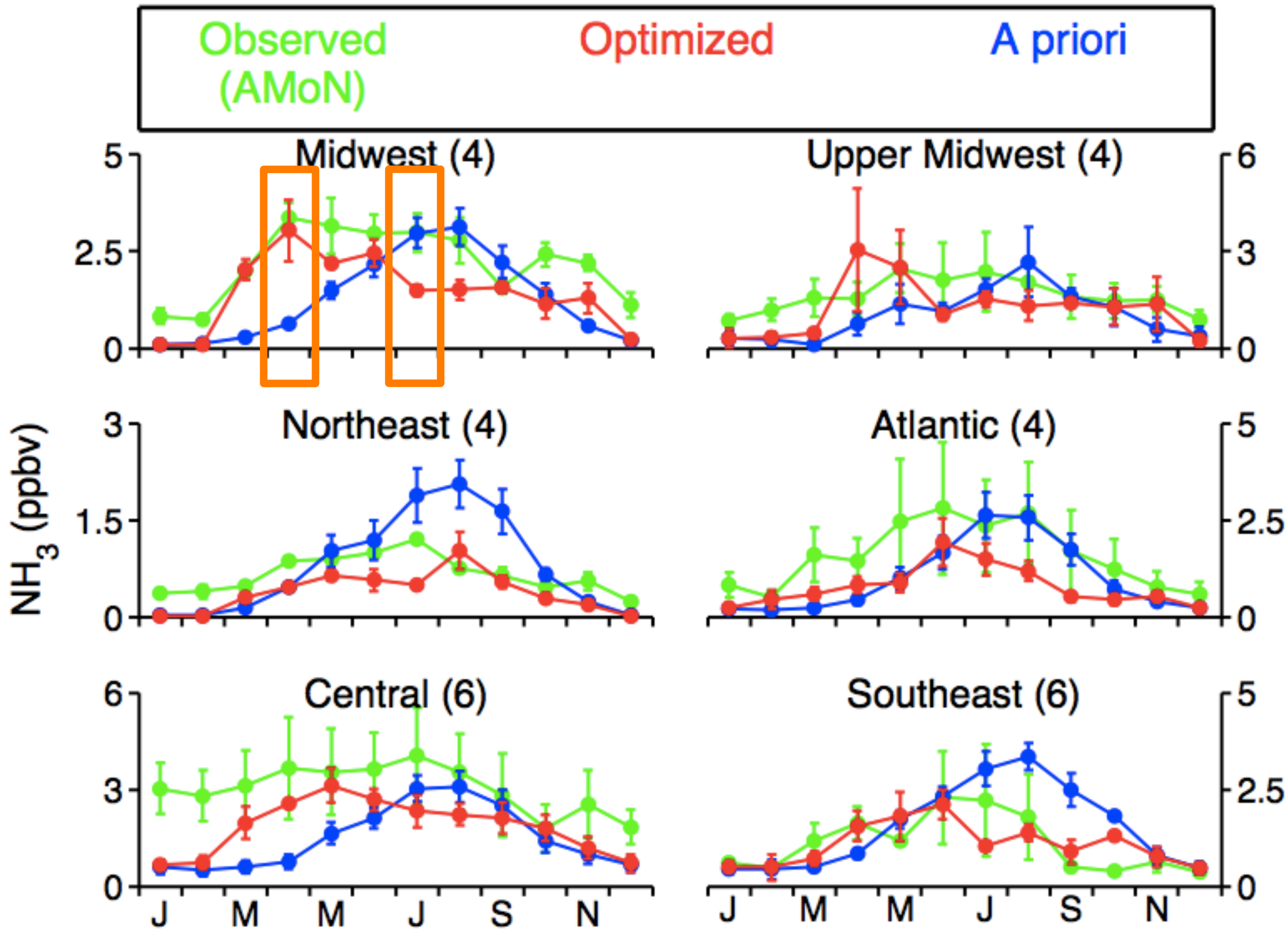


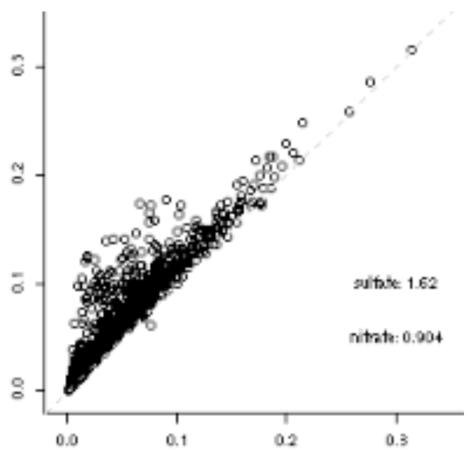
Paulot et al., submitted

Closure for NHx deposition does not necessarily imply better model NH3

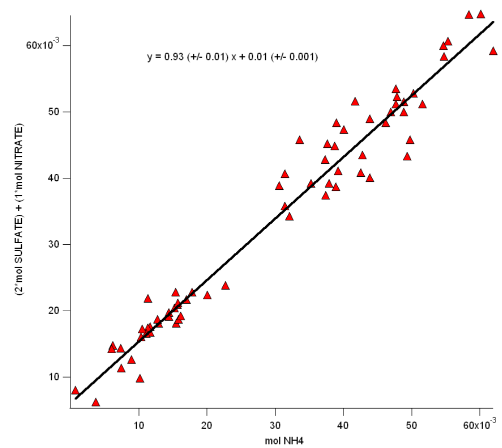
Constraints from CASTNet NH_4+?
$n(NH_4^+) : 2n(SO_4^{2-}) + n(NO_3^-)$

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

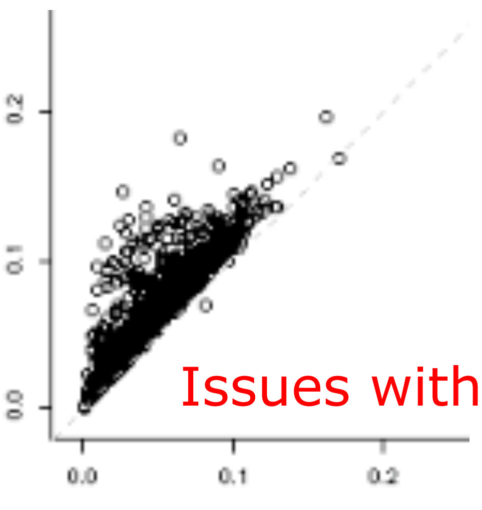
Field campaigns
(Sorooshian et al.)



January

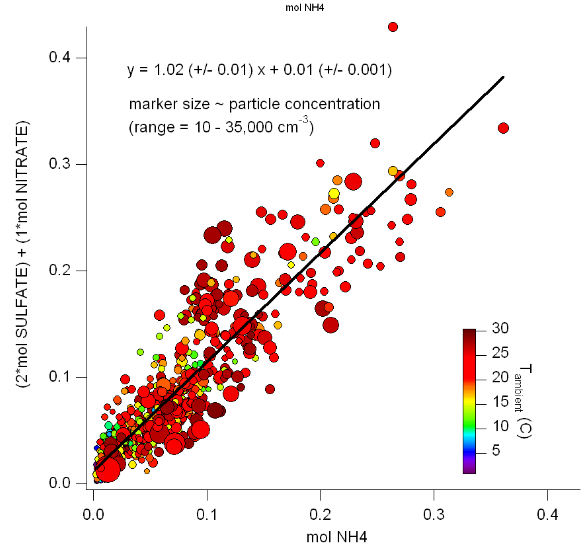


SJ Valley



April

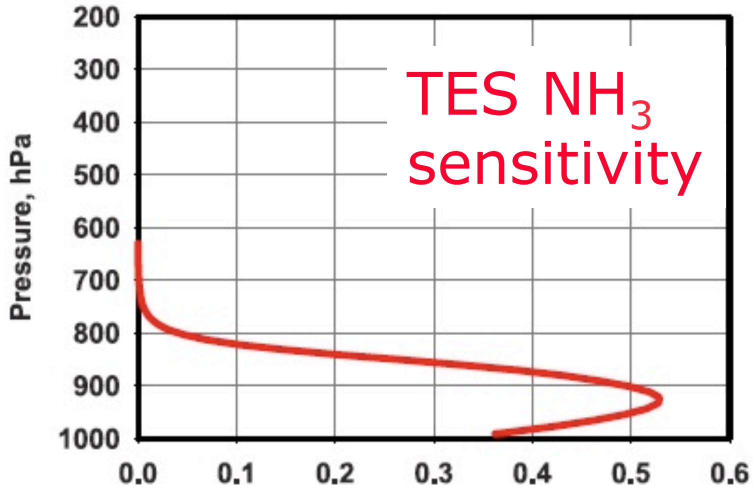
Issues with evaporation

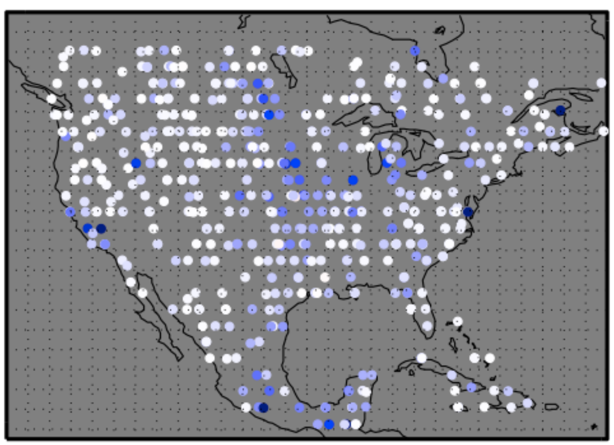


Houston

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

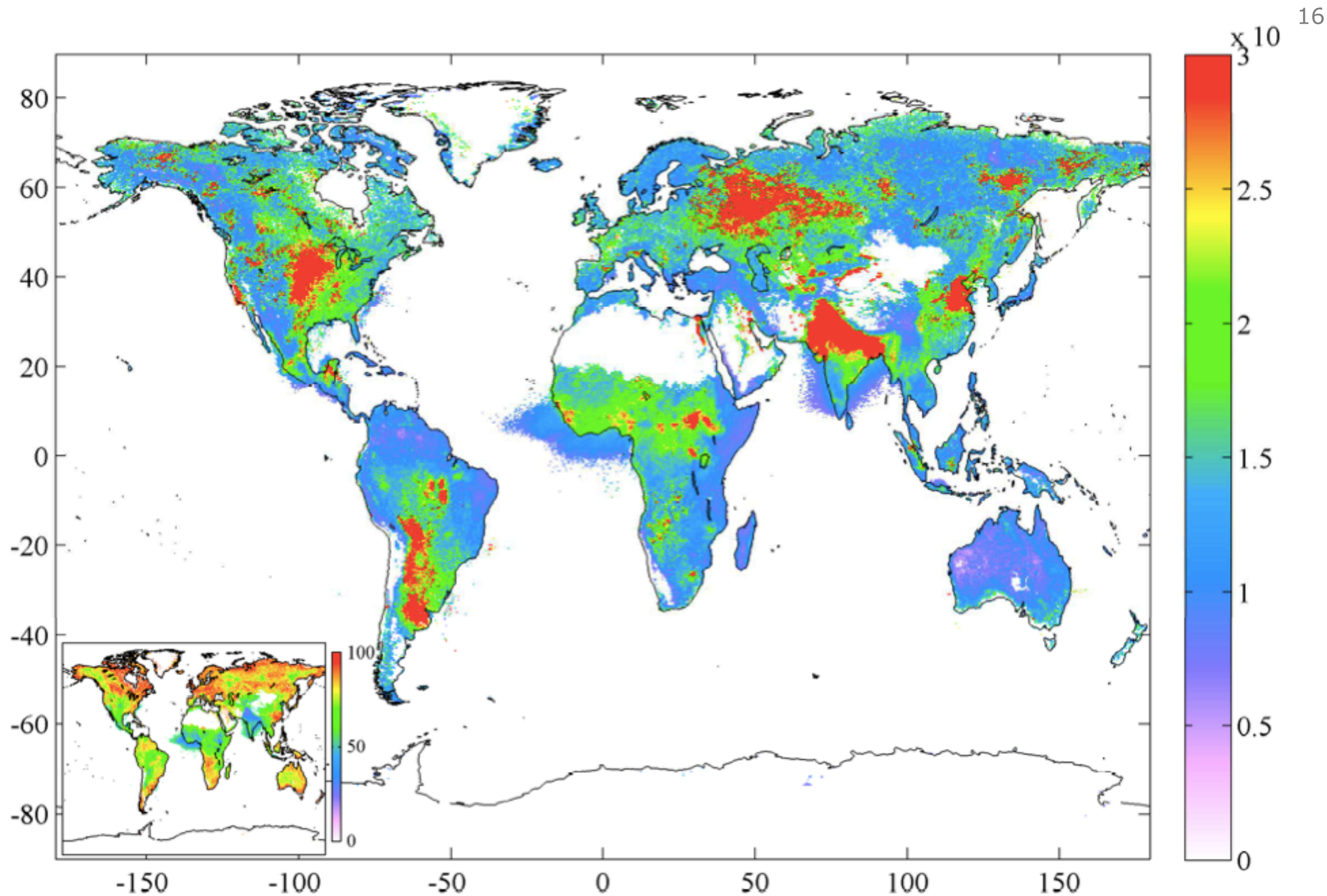
(Beer et al., 2008; Clarisse et al., 2009; Clarisse et al., 2010; Mark Shephard et al., 2011)

Passive surface measurements:

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

Also LADCO, SEARCH, CSU, ANARChE

Remote sensing of NH_3: IASI

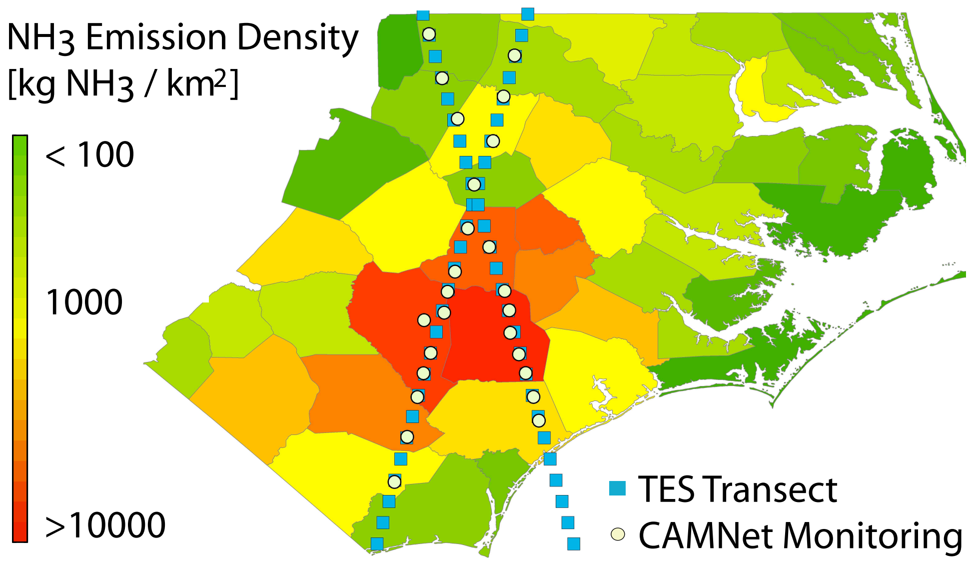


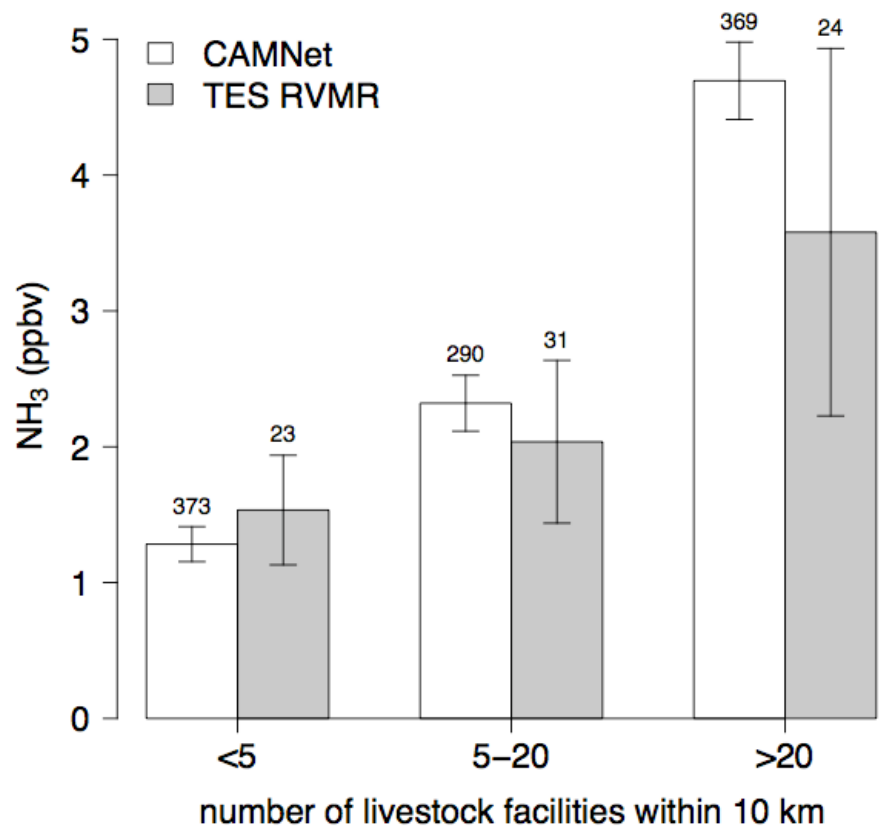
Van Damme et al., ACPD, 2013

TES NH_3 visualization

Validating TES NH_3 with surface observations

Overlap surface obs with TES Transects for 2009:



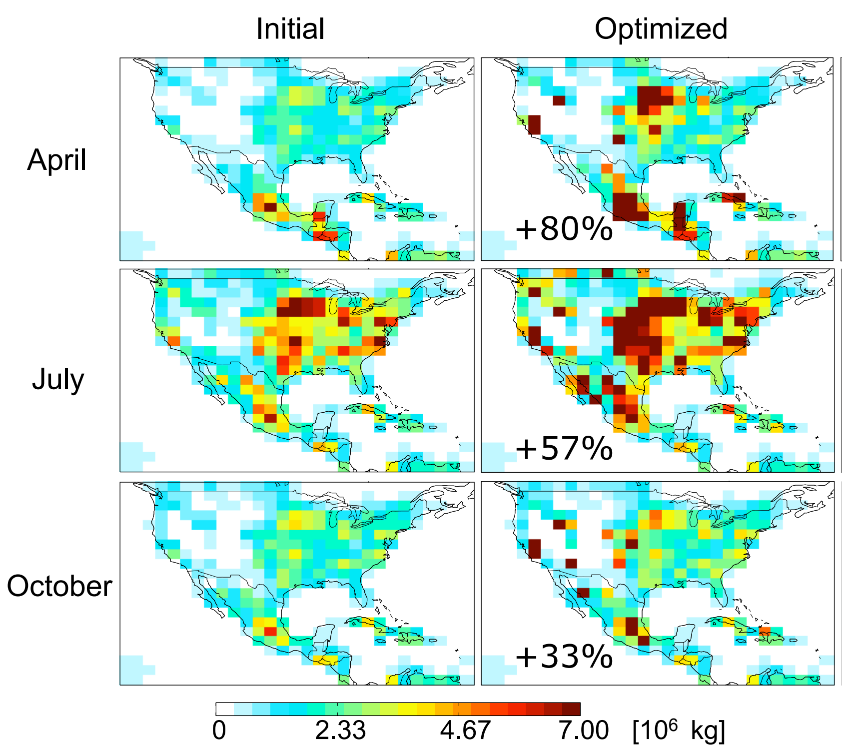


TES reflects real-world spatial gradients and seasonal trends

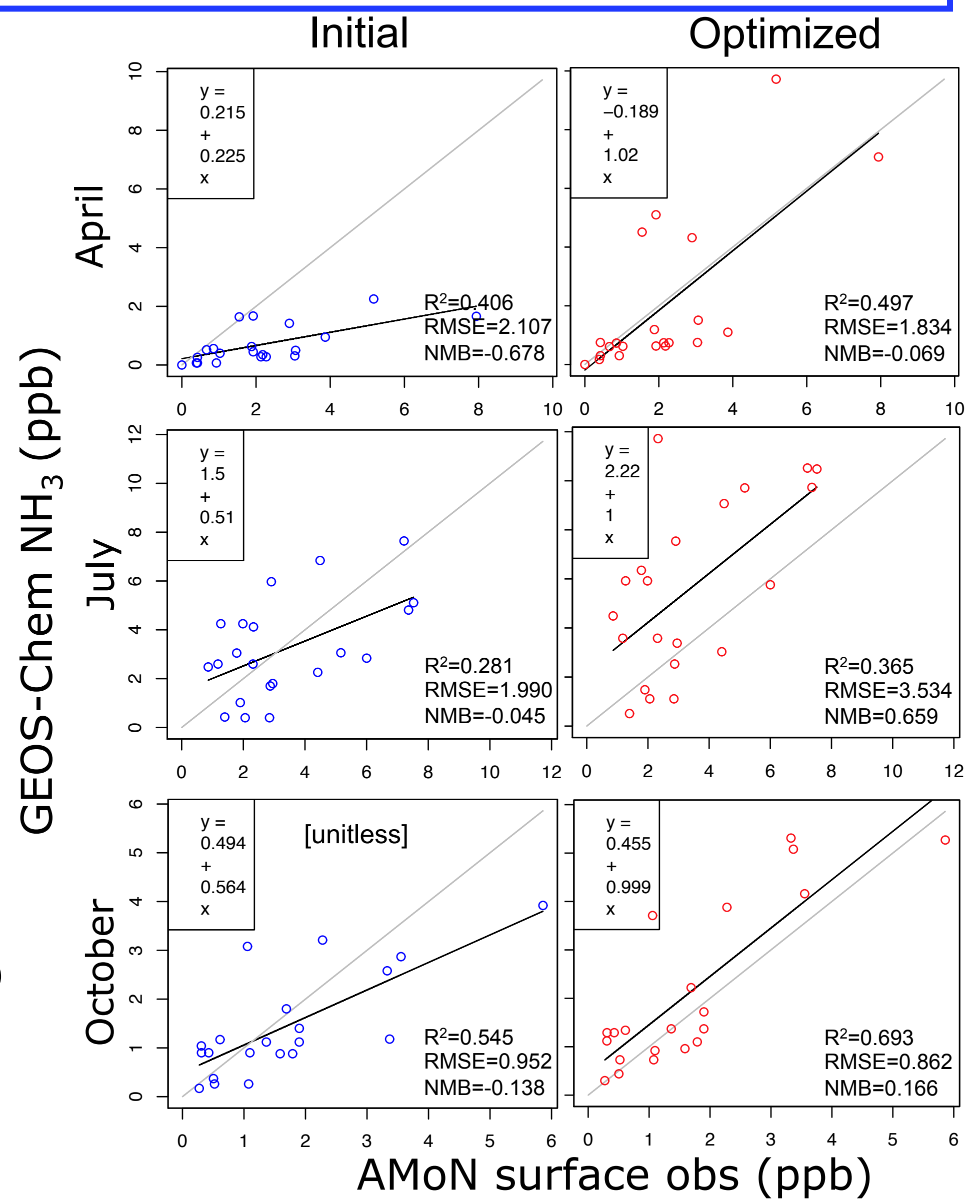
Pinder et al., 2011

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

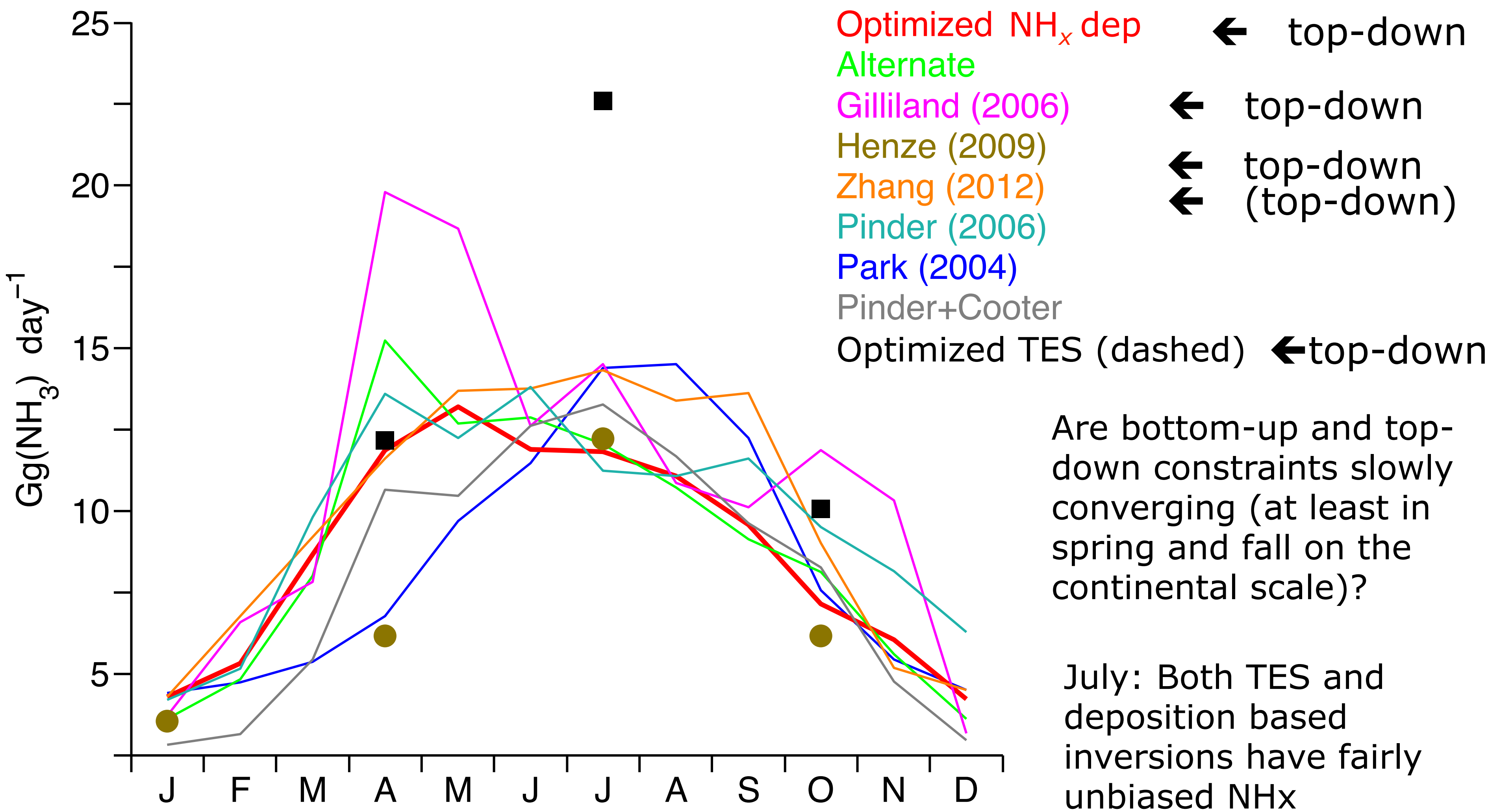
NH_3 emissions in GEOS-Chem



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



Uncertainties in the NH_3 emissions in the contiguous US

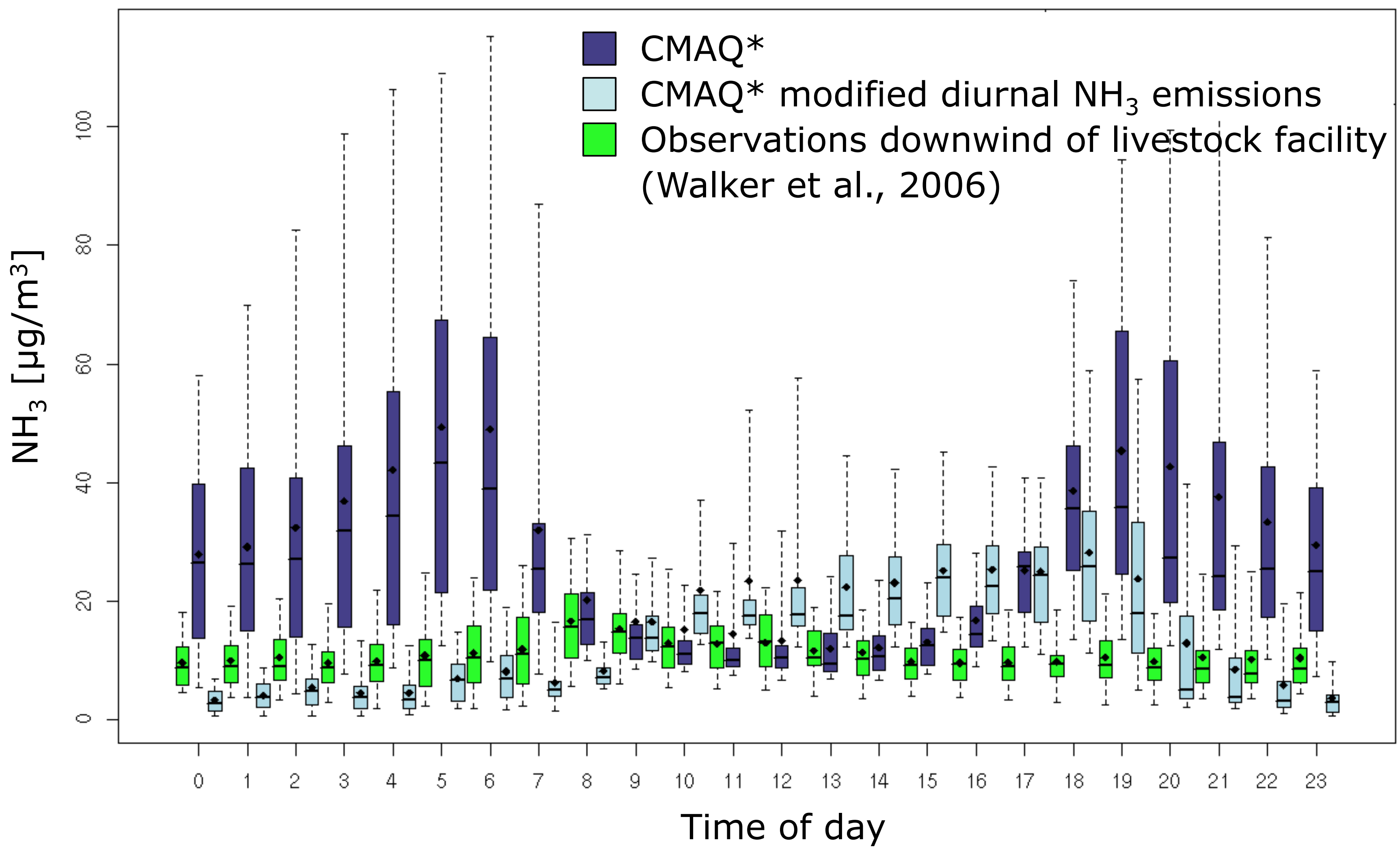


Paulot et al., submitted

Are bottom-up and top-down constraints slowly converging (at least in spring and fall on the continental scale)?

July: Both TES and deposition based inversions have fairly unbiased NHx deposition

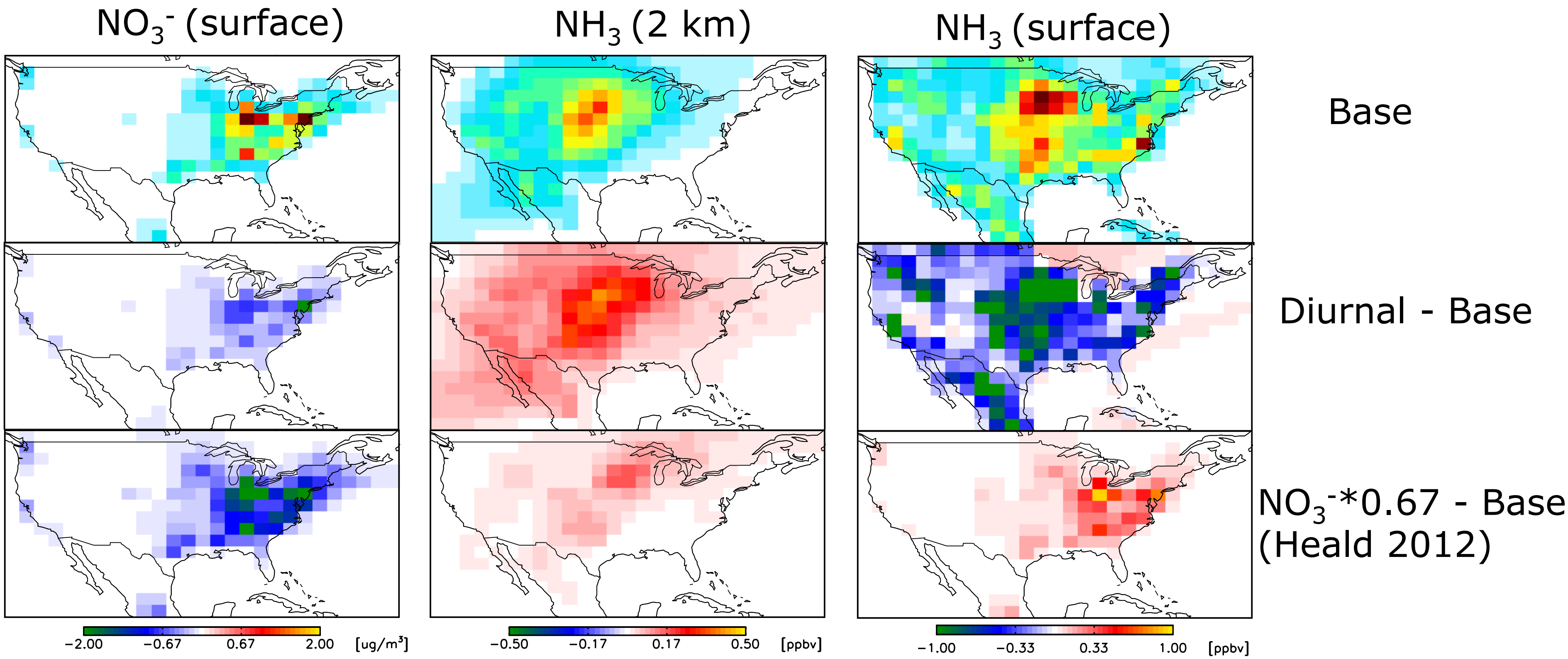
Diurnal variability of NH_3: case study in Warsaw, NC, with CMAQ regional model



* Using NEI05 emissions, simulated year not same as observations

Gill-Ran Jeong et al., submitted

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.

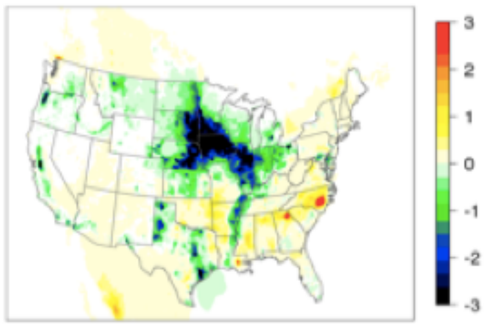
Other factors:

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

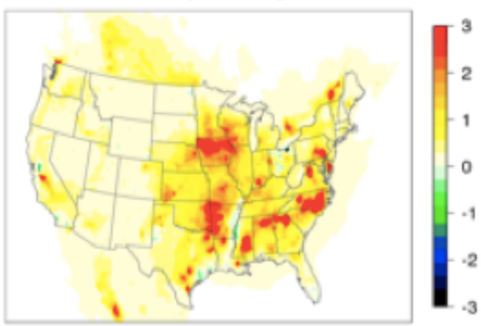
Impacts of bidirectional exchange in GEOS-Chem

NH3: $CMAQ_{bidi}$ - $CMAQ_{base}$

April

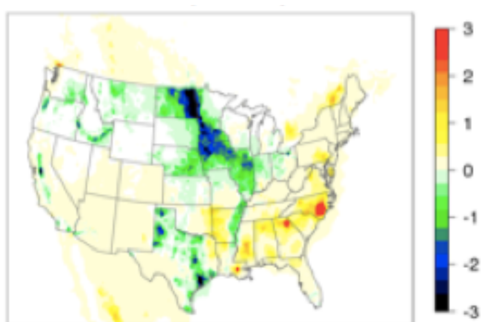


July



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

October

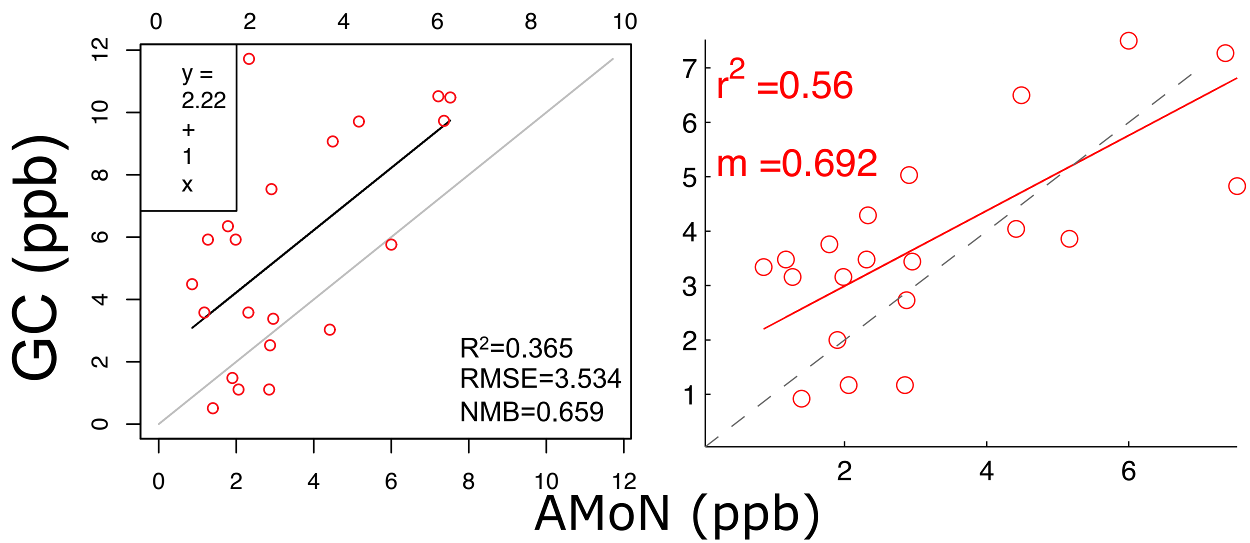


Jeong et al., submitted

Impacts of bidirectional exchange in GEOS-Chem

Optimized
(Zhu et al 2013)

Bidi applied to optimized emissions



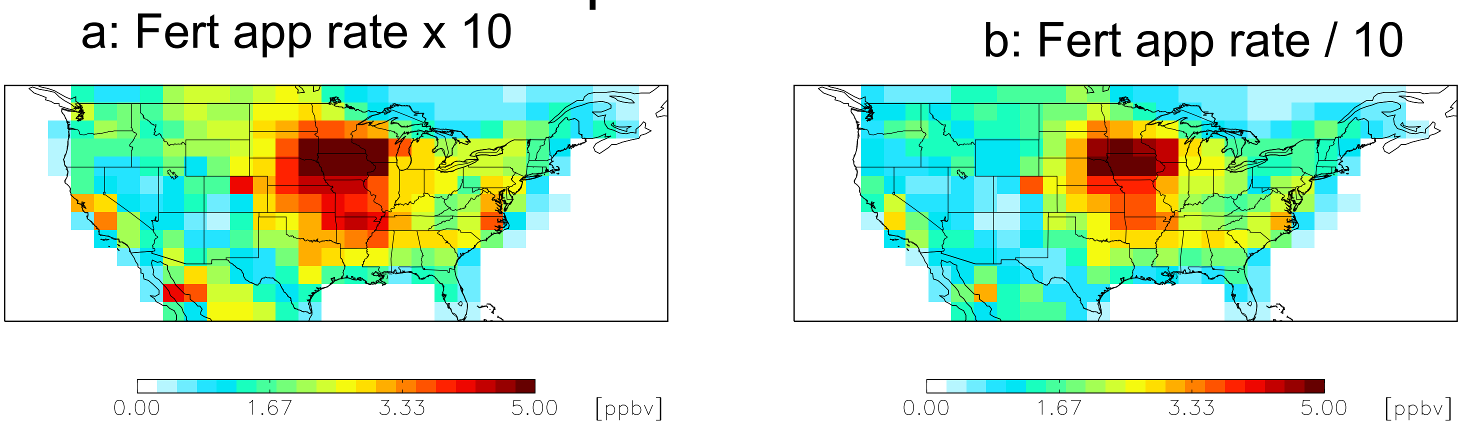
Improved (mechanistic) representation of NH3 fluxes may help resolve inconsistencies between NH_3 and $[NH_x]_{dep}$ constraints.

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

Next steps: Which factors drive uncertainty in model estimated bidirectional exchange?

From adjoint sensitivity analysis:
(in progress)

From forward model perturbations:



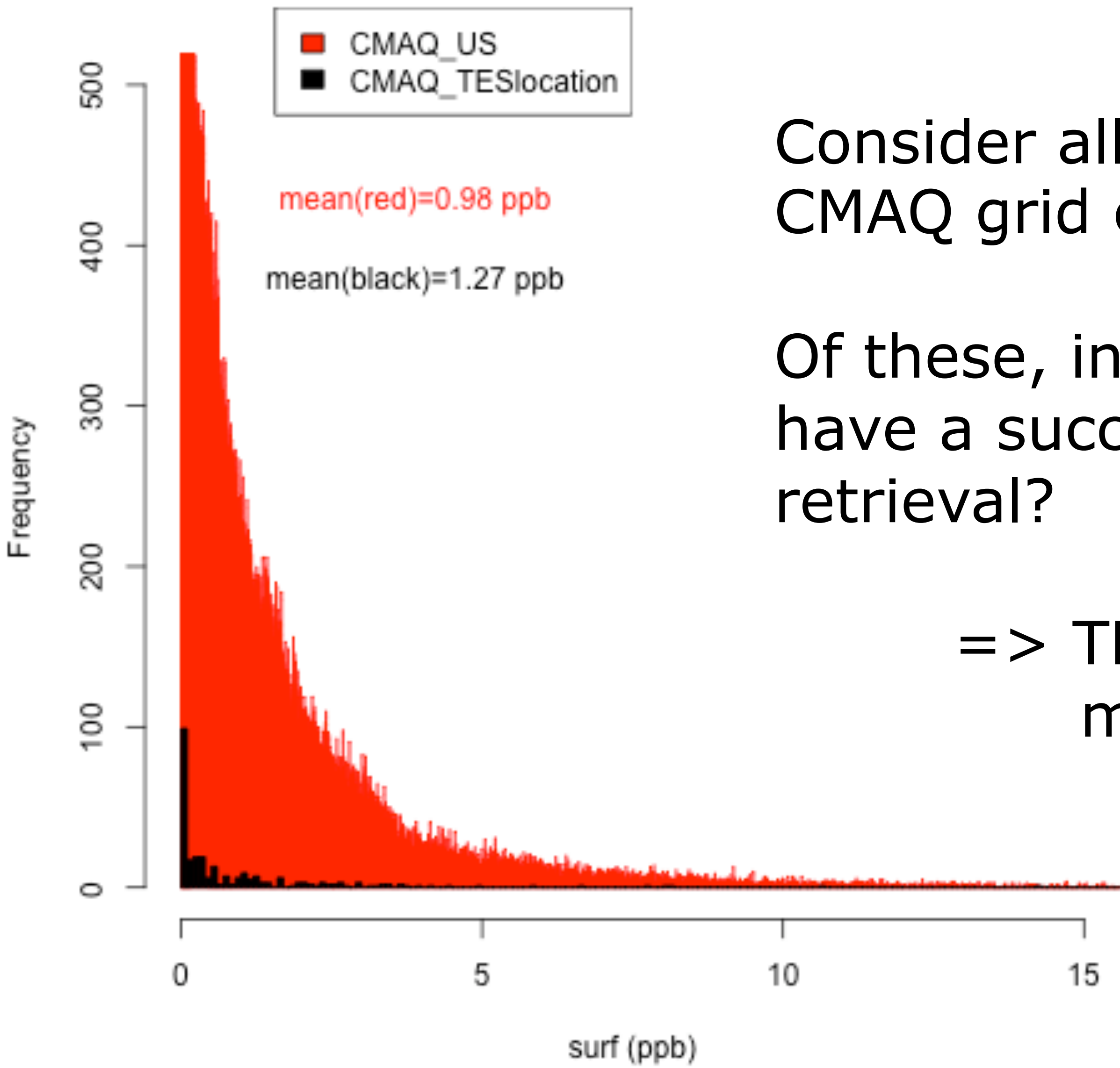
$[H+]_{soil}$
X_c
X_{st}
X_g

R_a
R_{inc}
R_{gbl}
R_{soil}

R_{bl}
R_{st}
R_w

Most influential
Least influential

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



Consider all 12 x 12 km2 CMAQ grid cells

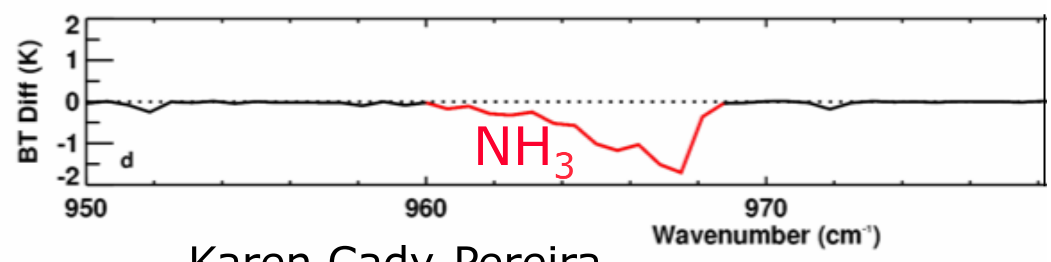
Of these, in which did we have a successful TES retrieval?

=> TES constraints may be ~30% high

Future work: new and possible remote-sensing measurements to constrain NH3 bidi exchange

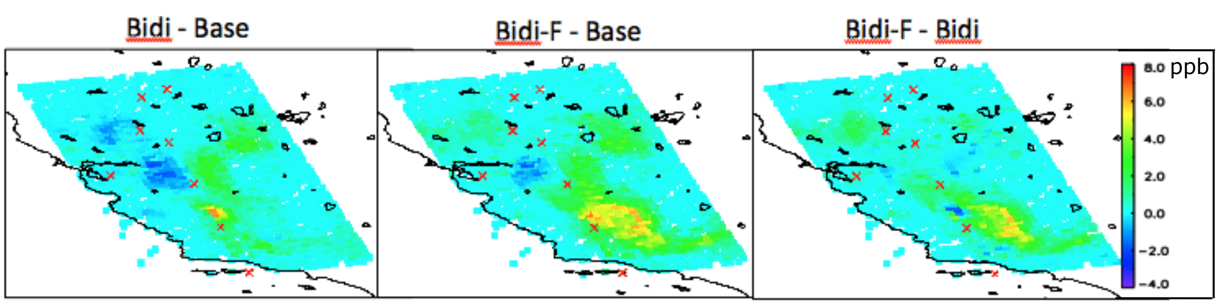
- More [NH_3] and NH_3 dry dep monitoring at the surface

- Potential for observations from CrIS



Karen Cady-Pereira

- Hourly data from geostationary satellite (GEO-CAPE)
  - could constrain diurnal cycle of NH_3 sources (?)
  - could distinguish between primary and bidi fluxes



Simulated retrievals from GEO-CAPE (map) and TES (x)

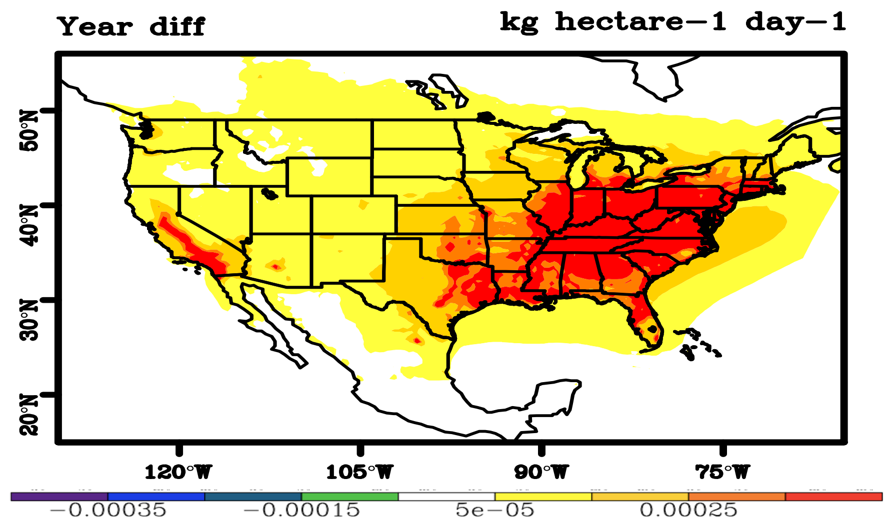
Base = only primary
Bidi = include bide fluxes
Bidi-F = bidi fluxes with fertilizer x 2

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

CMAQ 5.0 2010
NOy dry deposition
base – 20% less NOx



Yanko, GIT

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)

Tools / Observations:

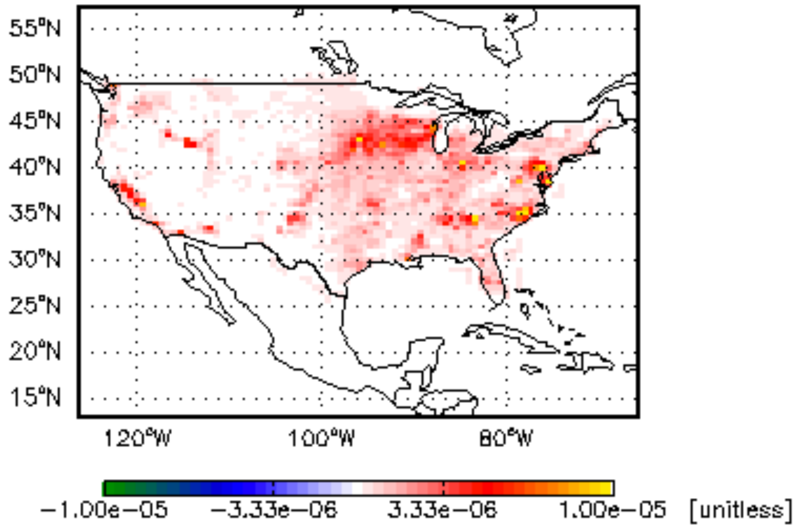
- NH_3 remote sensing, in situ observations (RMNP,…)
- GEOS-Chem and CMAQ models
- Source attribution techniques: sector perturbations, DDM, adjoint

Source contributions: NH_3 dry deposition in the entire US (January, 2010)

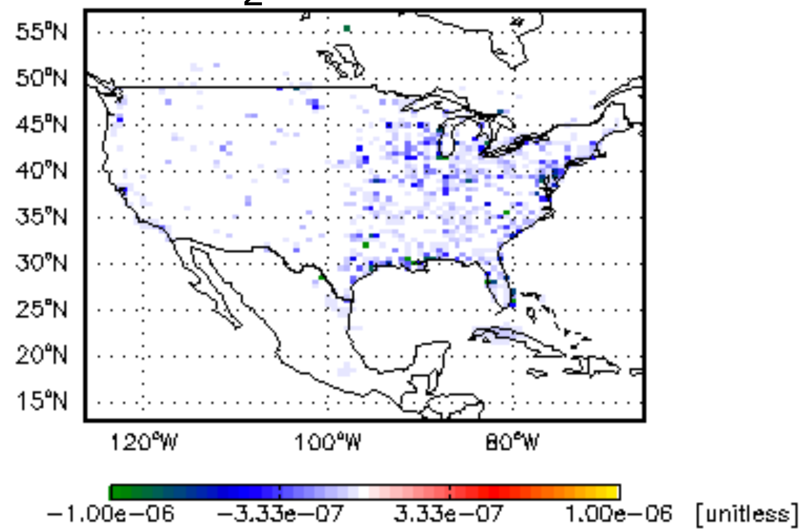
(ignore previous 30 slides)

Source contributions: NH_3 dry deposition in the entire US (January, 2010)

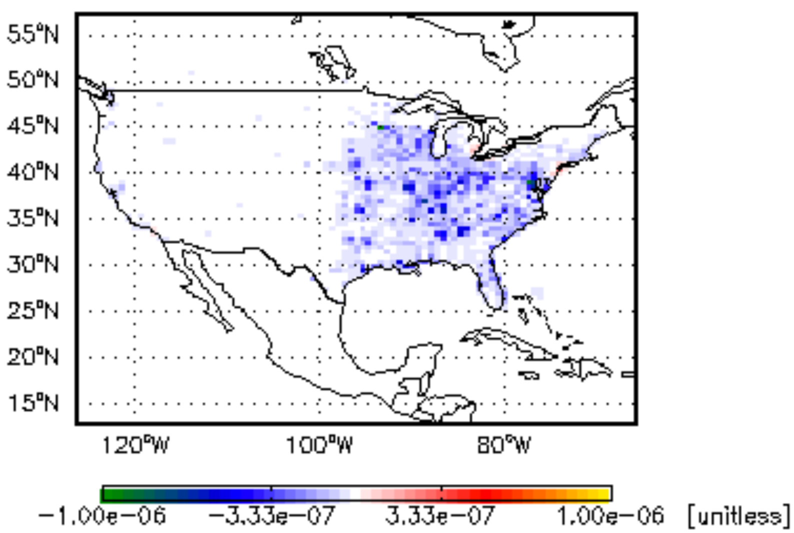
NH_3 emissions



SO_2 emissions



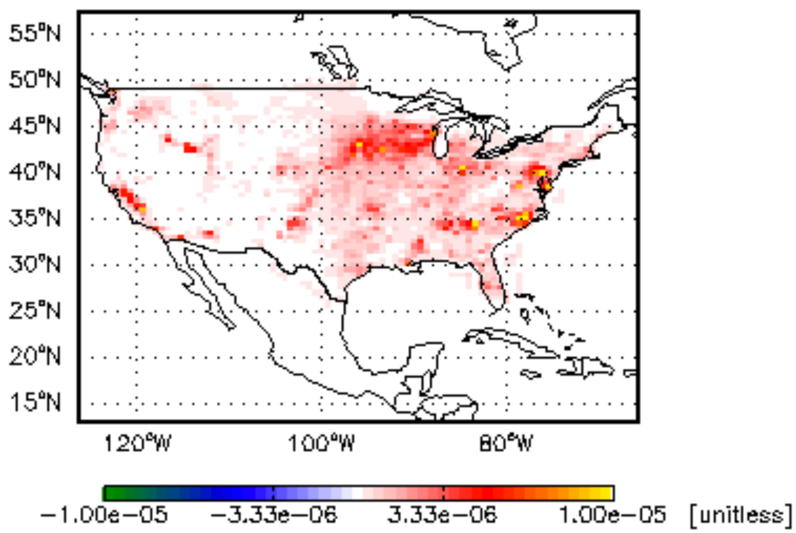
NOx emissions



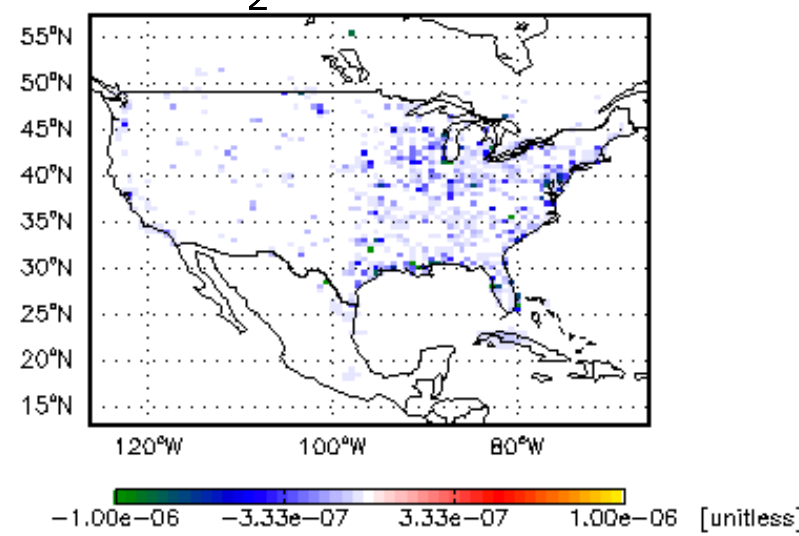
Plots show the contributions of fractional changes in grid-scale emissions to the national total NH_3 dry deposition flux during one week

Source contributions: NH_3 dry deposition in the entire US (January, 2010)

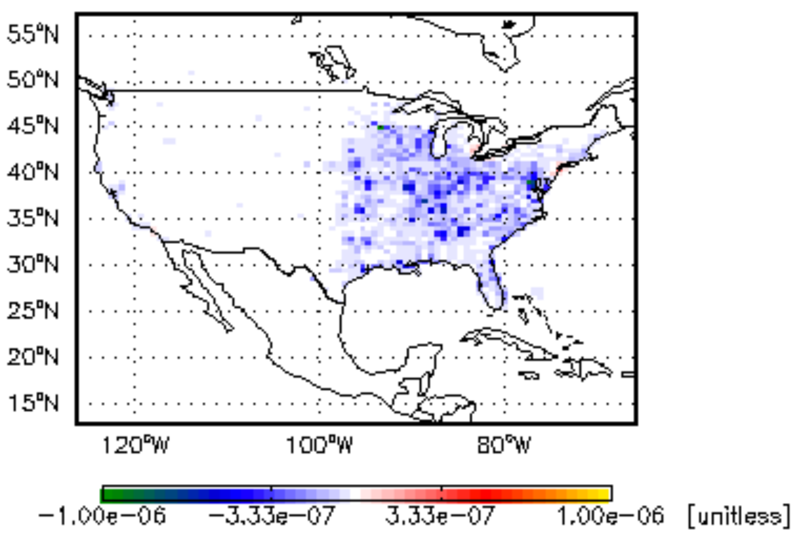
NH_3 emissions



SO_2 emissions



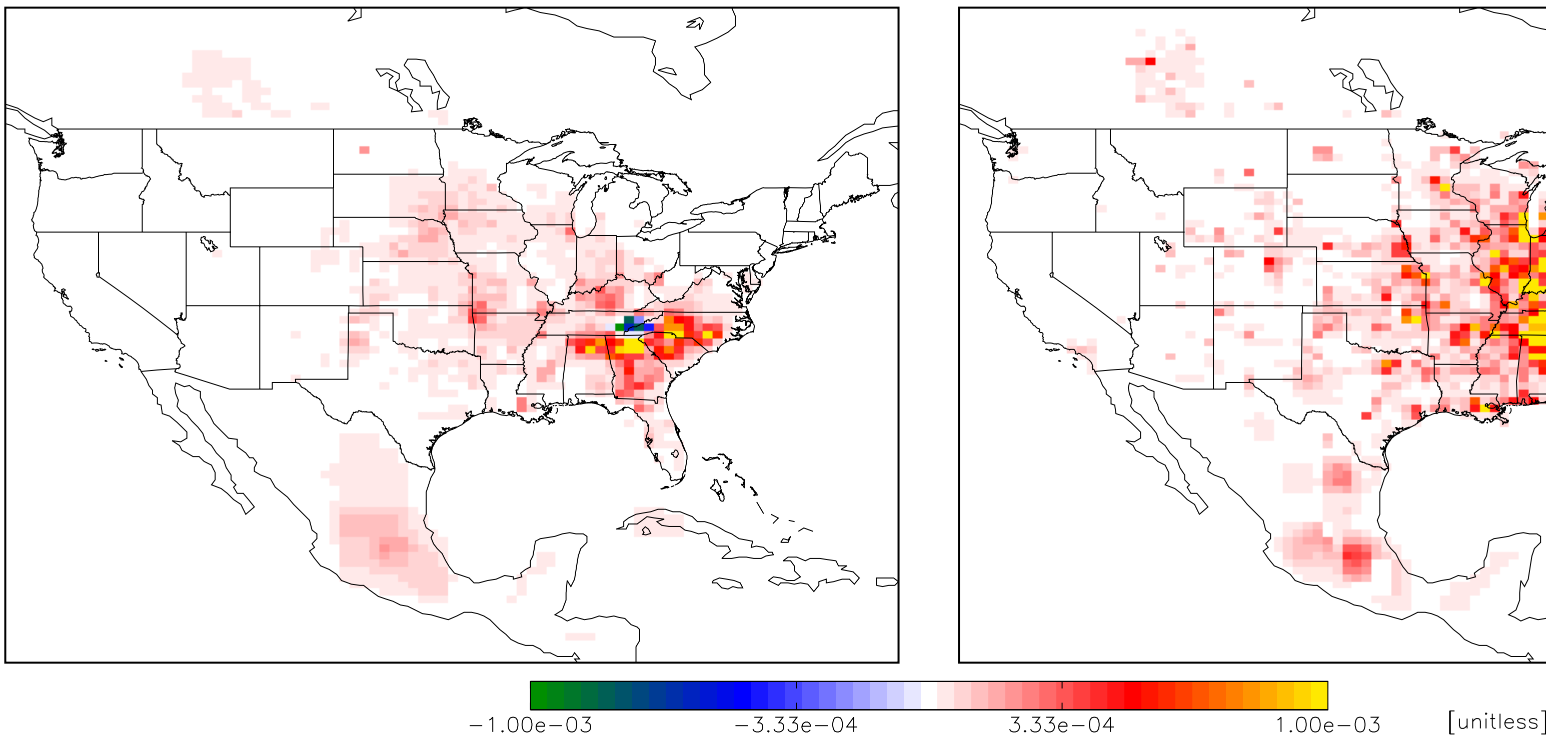
NOx emissions



Changes in NOx (and SO_2) emissions will change the distribution of NHx deposition (further from sources)
Pinder et al. (2008)

Source contributions: Nr deposition in Great Smokey National Park (January, 2010)

NH_3 emissions | NOx emissions



- Nr deposition from HNO_3
- NH_3 locally contributes to NH_4NO_3, which has a longer lifetime than HNO_3

Ongoing activities

- Impacts of NH_3 flux uncertainty on model estimates of N_r dep:

  => able to apportion detailed daily variations in observed Nr dep from field campaigns?

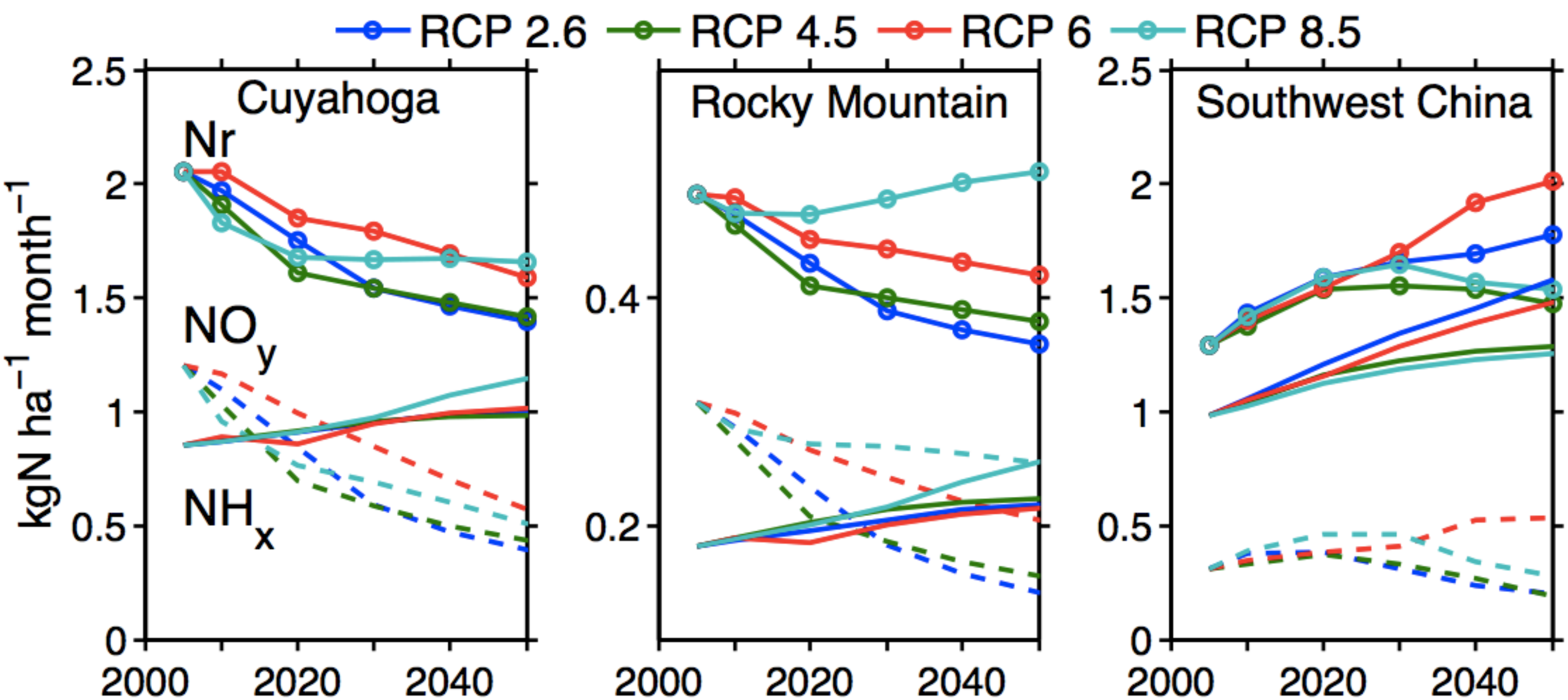
- Source attribution of N_r dep above critical levels:
  - in specific Class I areas
  - across the entire US

  => what is the best metric?

- Can we better estimate the response of Nr dep to emissions controls (NH3, but also NOx, SO2)?

Source attribution of Nr deposition: projections

Projections of the evolving roles of NH3 and NOx 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 NH3 increasing

End