Ammonia Emissions and Nitrogen Deposition in the United States and China

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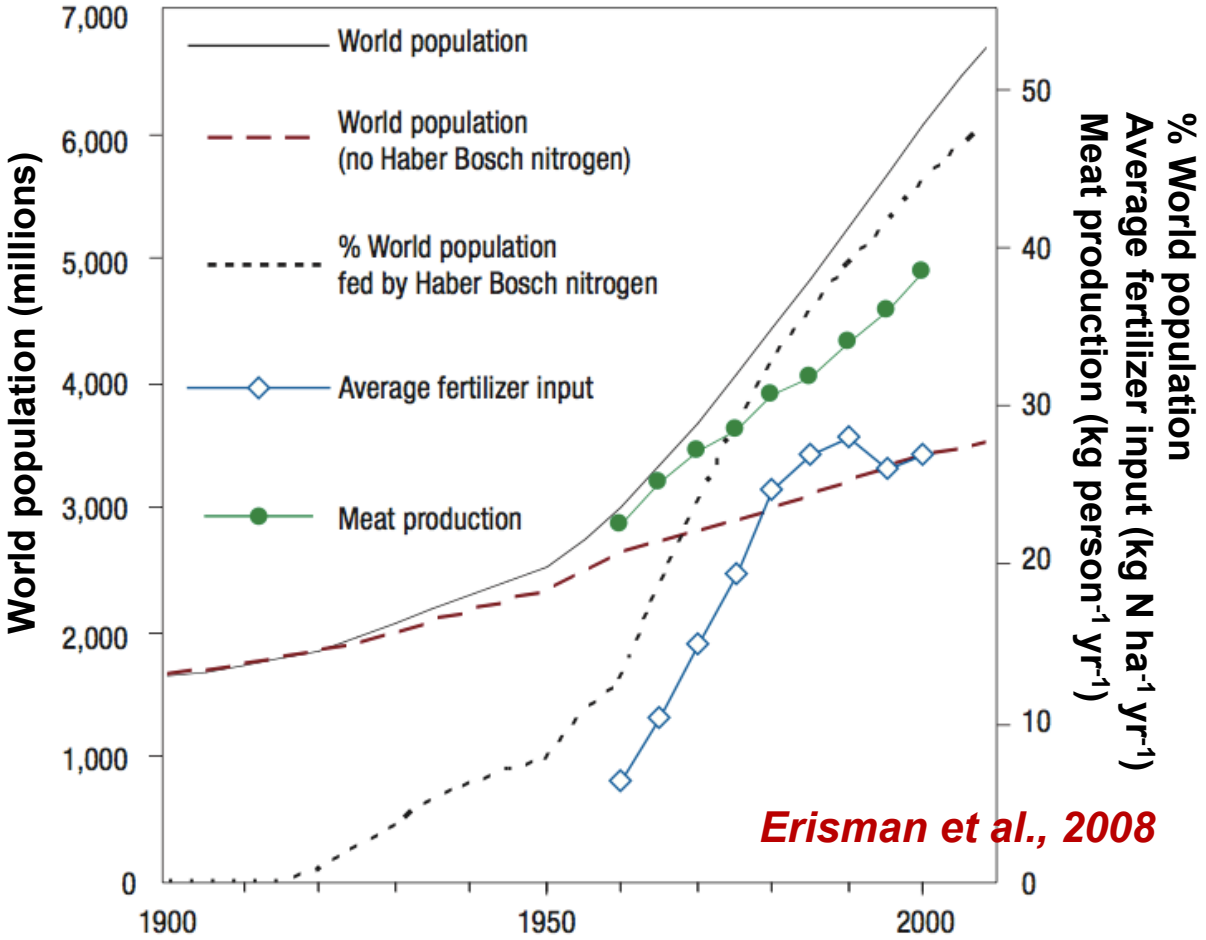
The Haber-Bosch process significantly changed the availability of fixed nitrogen

Fritz Haber (1868-1934)

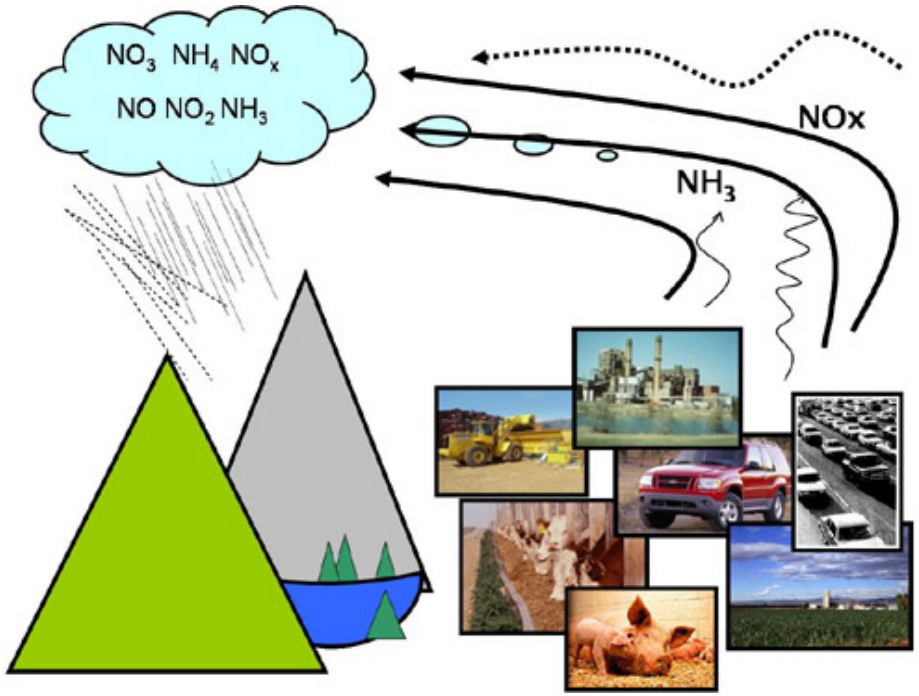
Carl Bosch (1874-1940)

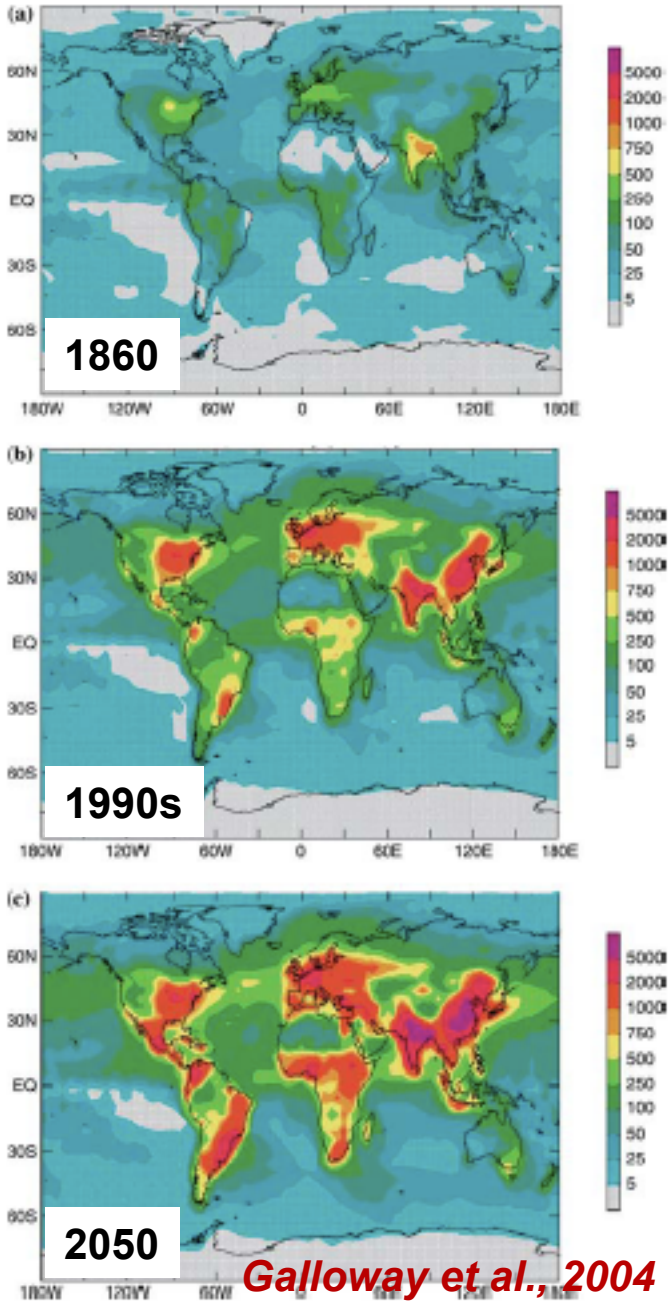
Agricultural production for food was limited by nitrogen availability. Most of them is in its chemically and biologically unusable gaseous form (N_2).

The Haber-Bosch process by generating NH_3 from N_2 and H_2 in the presence of iron at high pressures and temperatures now feeds 44% of the world's population.



Increasing inputs of fixed nitrogen from the atmosphere



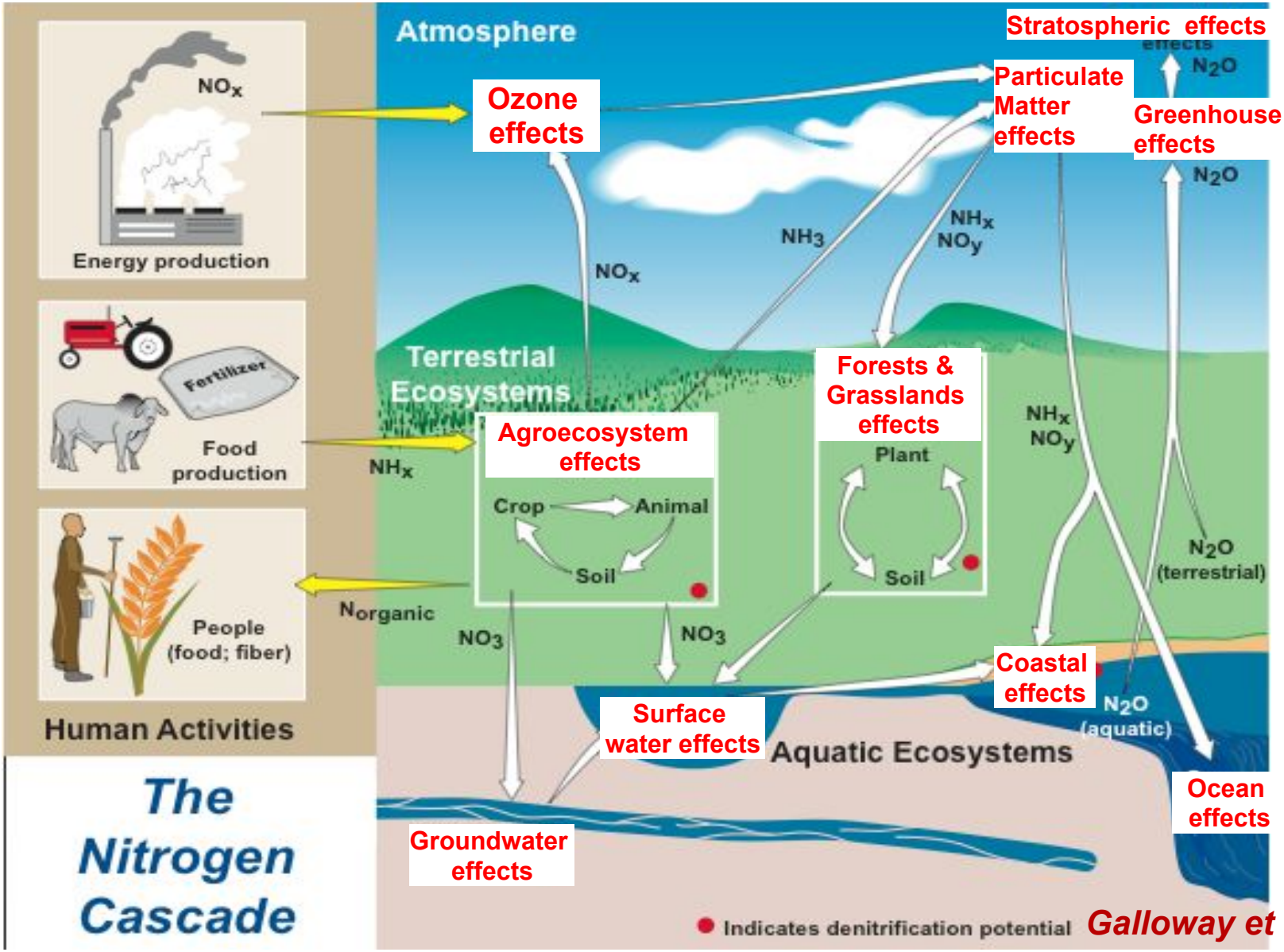


Atmospheric nitrogen deposition have increased by more than a factor of 3 globally due to human activity, causing effects including soil acidification, eutrophication, and a reduction in plant biodiversity.

Galloway et al., 2004

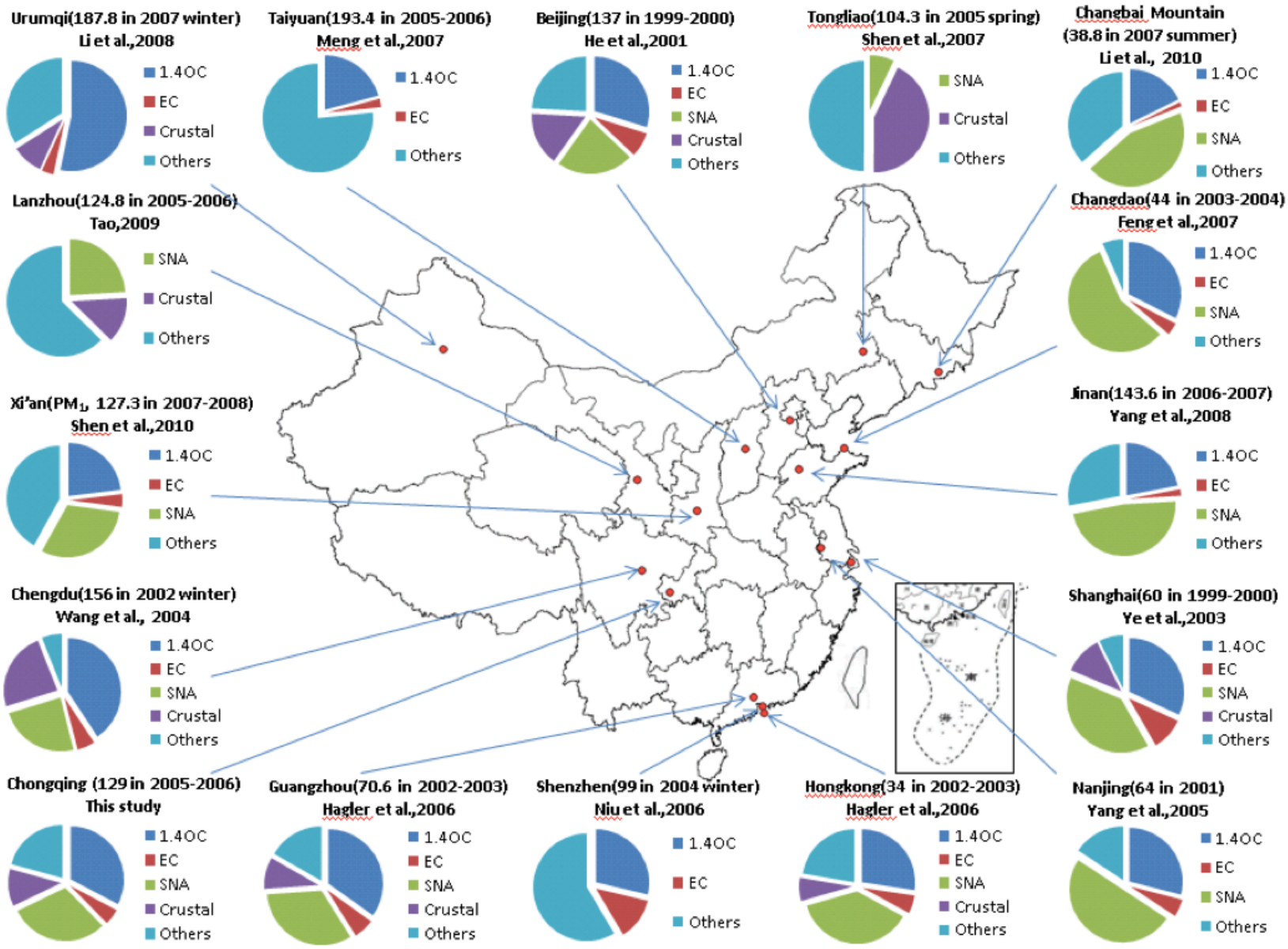
Unintended nitrogen deposition lead to a nitrogen cascade

One atom of fixed nitrogen can cause multiple effects in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on human health.



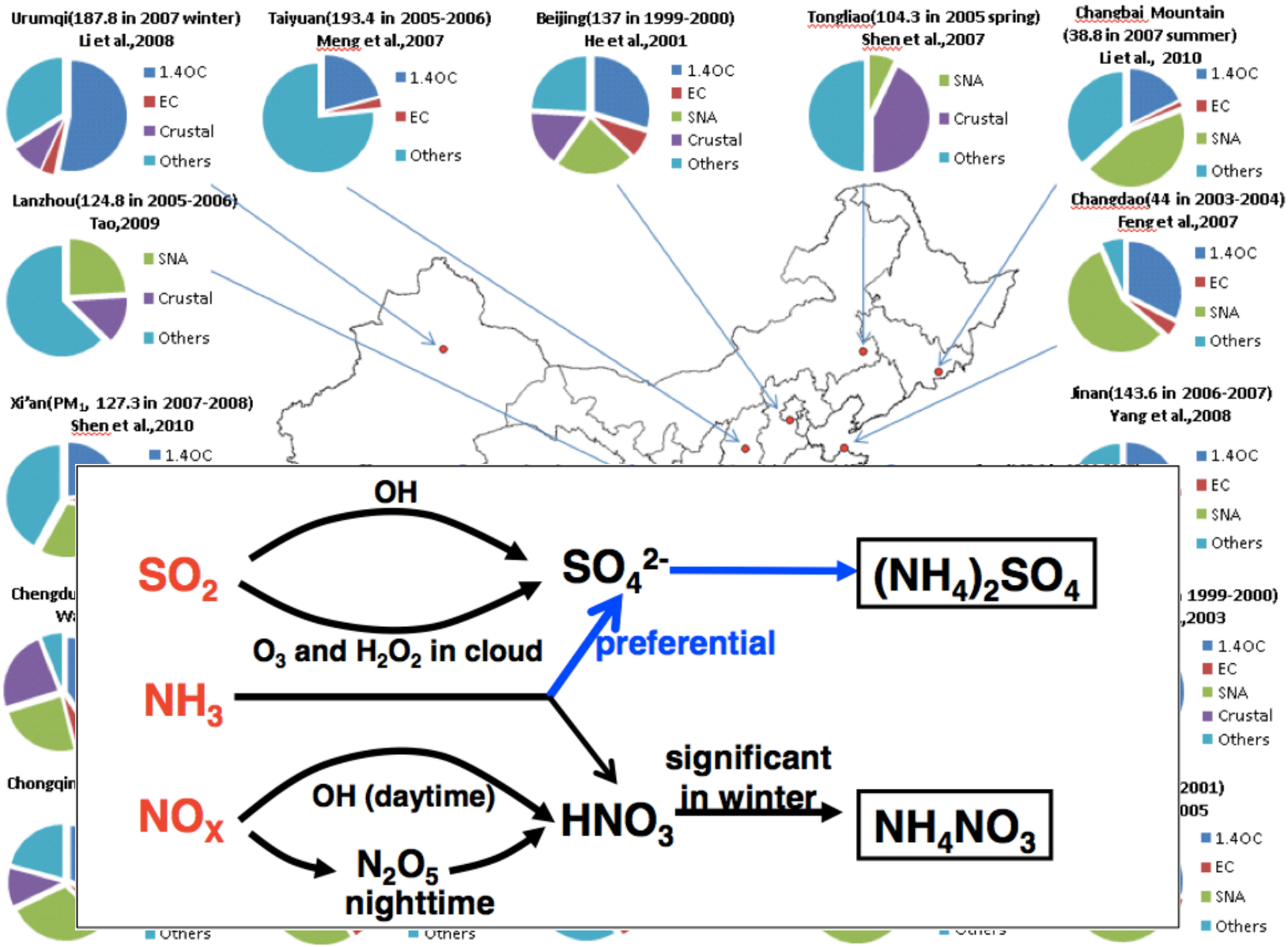
Galloway et al., 2003

Sulfate-Nitrate-Ammonium (SNA) aerosols are important components of PM2.5



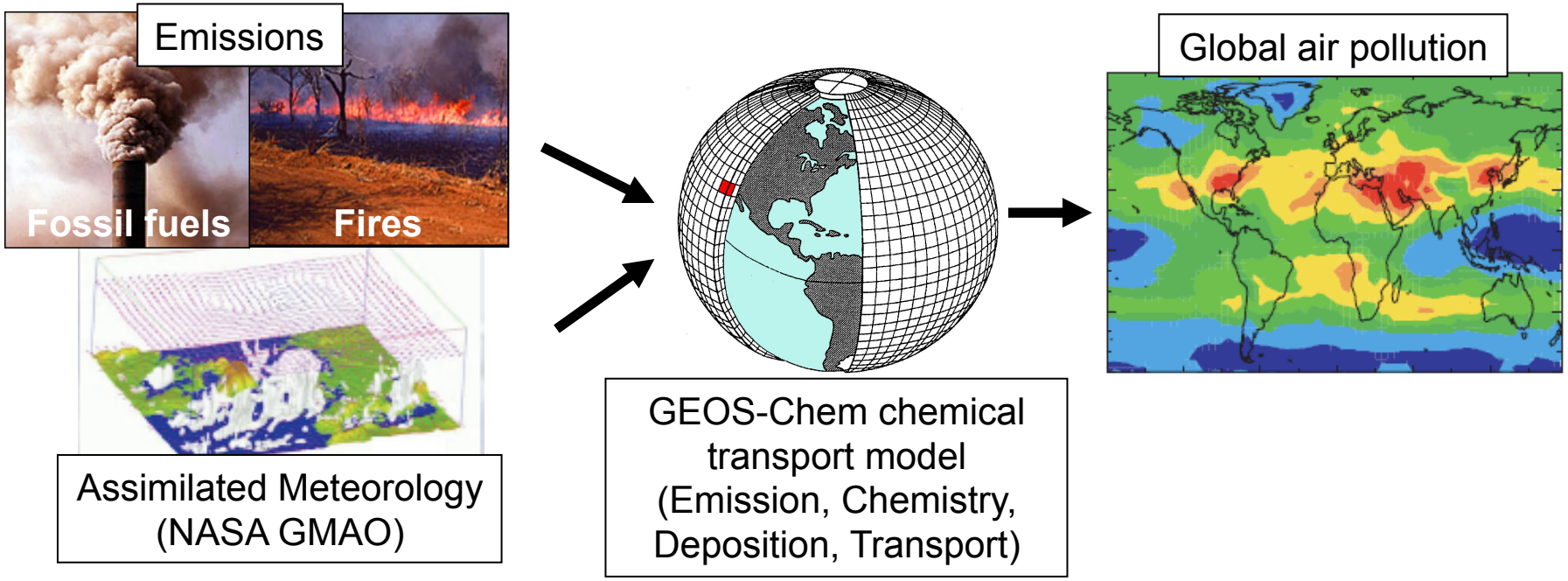
Yang et al., ACP, 2011

Sulfate-Nitrate-Ammonium (SNA) aerosols are important components of PM2.5



Yang et al., ACP, 2011

The GEOS-Chem chemical transport model

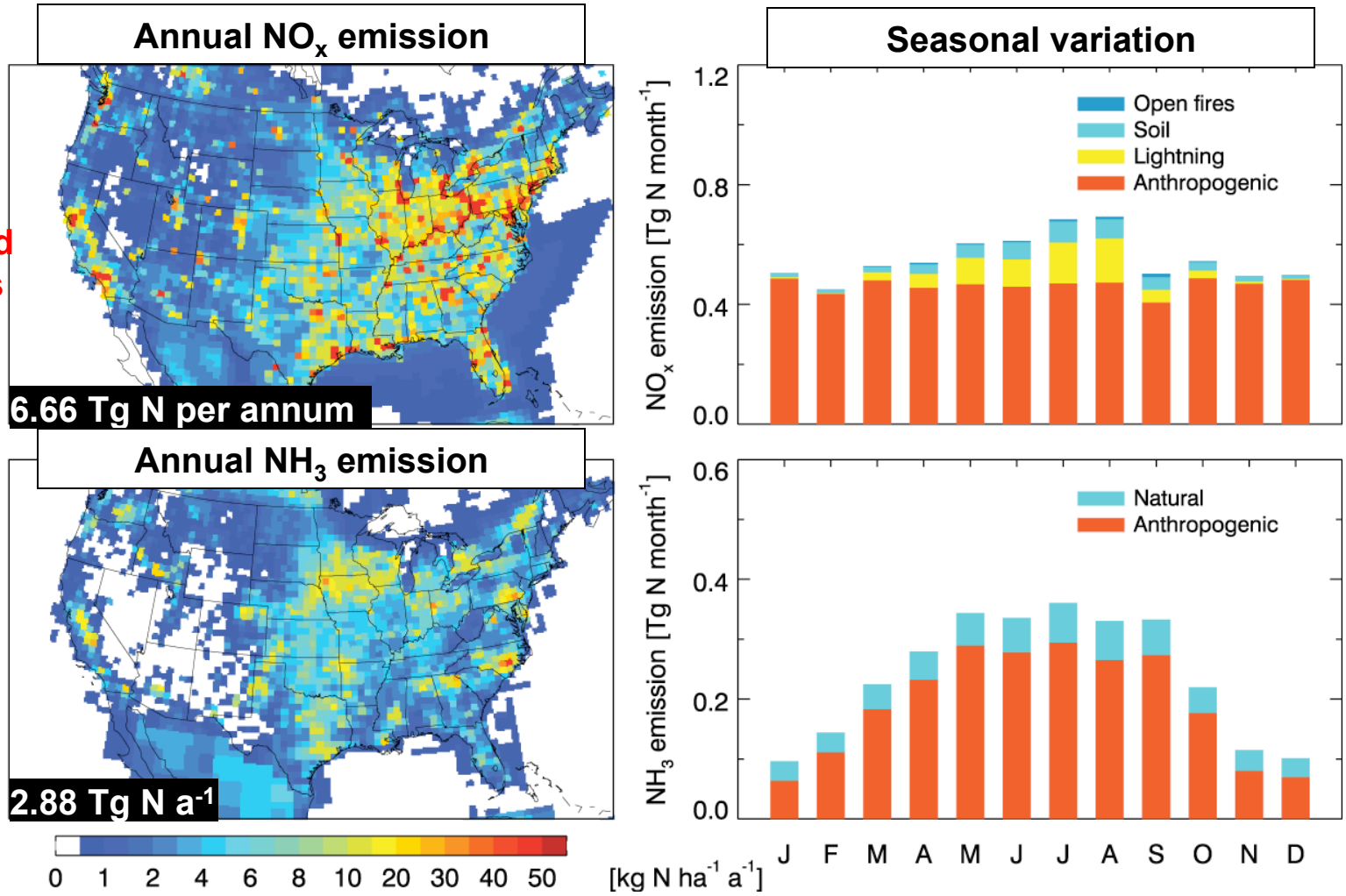


- 3-D global model of atmospheric composition, driven by GEOS-5 assimilated meteorological fields
- Detailed simulation of tropospheric ozone-NO_x-VOC-aerosol chemistry
- $1/2^o$ x $2/3^o$ resolution over the nested domain (North America or Asia), and 2^ox2.5^o resolution over rest of world.

NO_x and NH_3 emissions in the United States (2006)

Mostly from transport and power plants

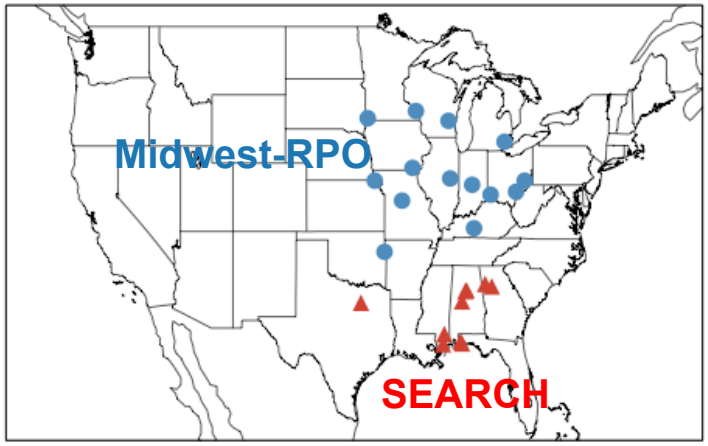
Mostly from agriculture



- NO_x: anthropogenic (83%), lightning (9.5%), soil (6.2%), and fire (0.7%)
- NH_3: anthropogenic (81%), natural (19%). The emission seasonality is constrained with surface measurements of total reduced nitrogen (NH_3+NH_4^+)

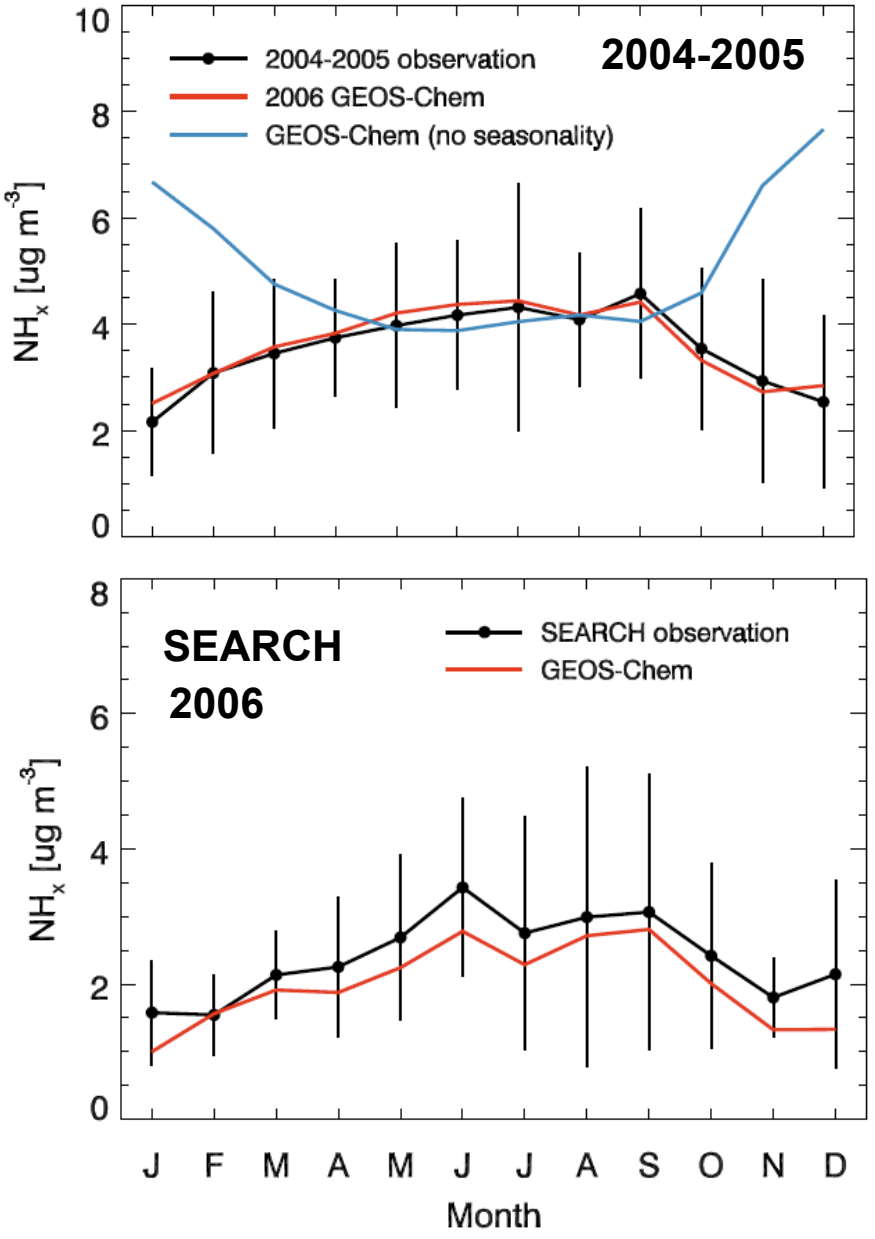
Constrain NH_3 emissions using NH_x measurements

NH_x measurements at Midwest-RPO and SEARCH sites

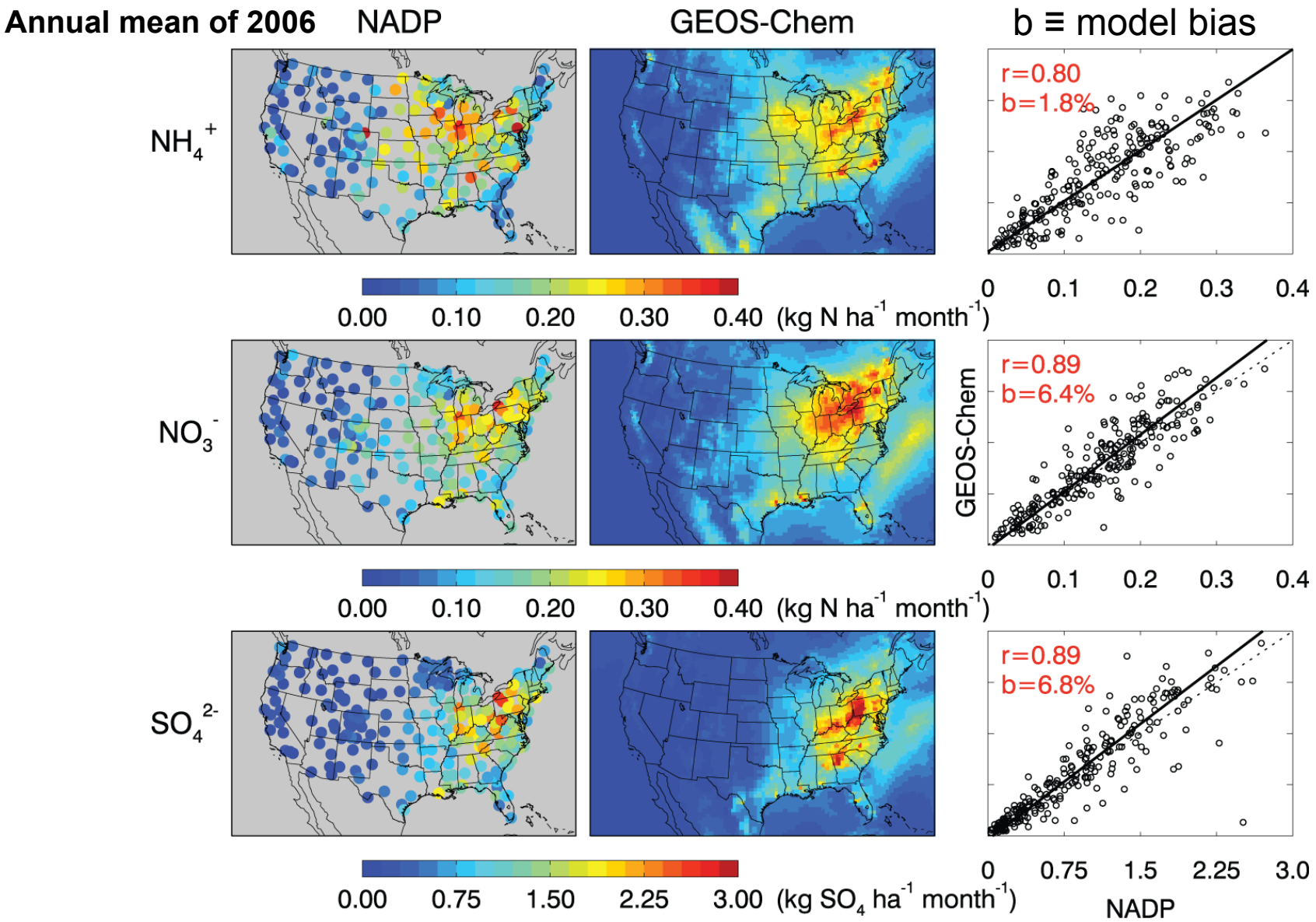


- We derive monthly scaling factors to match the mean NH_x concentrations observed at Midwest-RPO sites. These scaling factors are applied nationwide.
- The seasonality is independently verified by NH_x measurements at SEARCH sites.

Midwest-RPO Ammonia monitoring sites



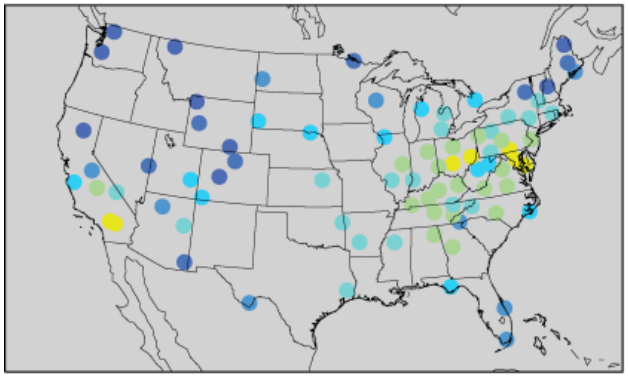
Model evaluation of NH_4^+, NO_3^- and SO_4^{2-} wet deposition



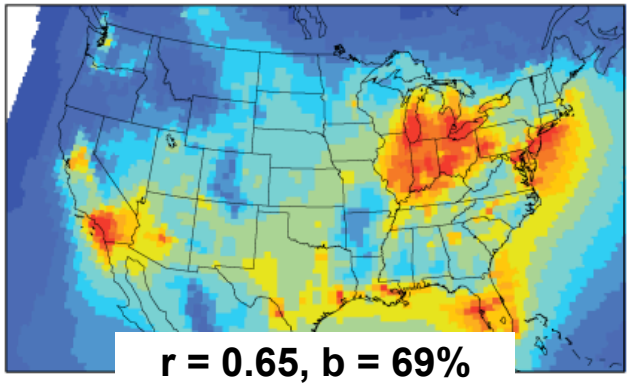
Comparison of wet deposition fluxes shows a good agreement, also verifies the emissions in the model.

Model evaluation of HNO_3 concentrations (2006)

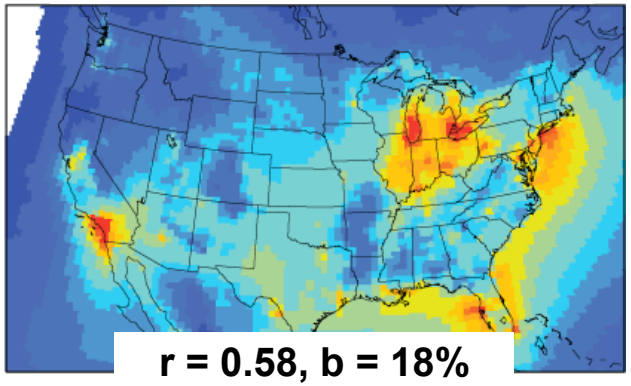
Annual mean HNO_3 at CASTNet (10m)

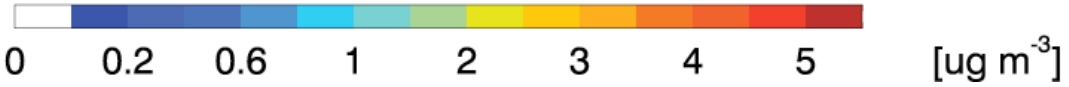


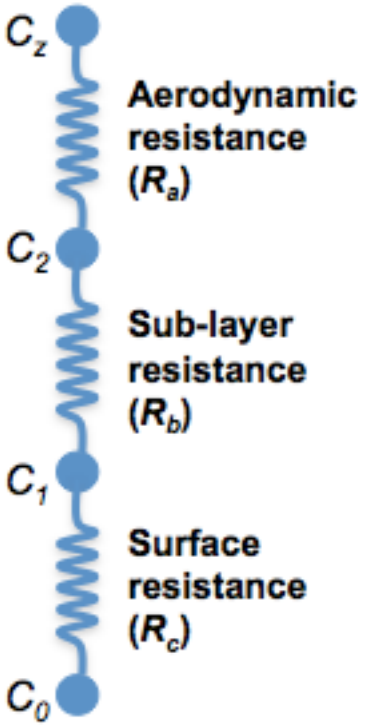
GEOS-Chem (70m)



GEOS-Chem (10m)







Deposition flux: $F_d = C_z \times v_d$

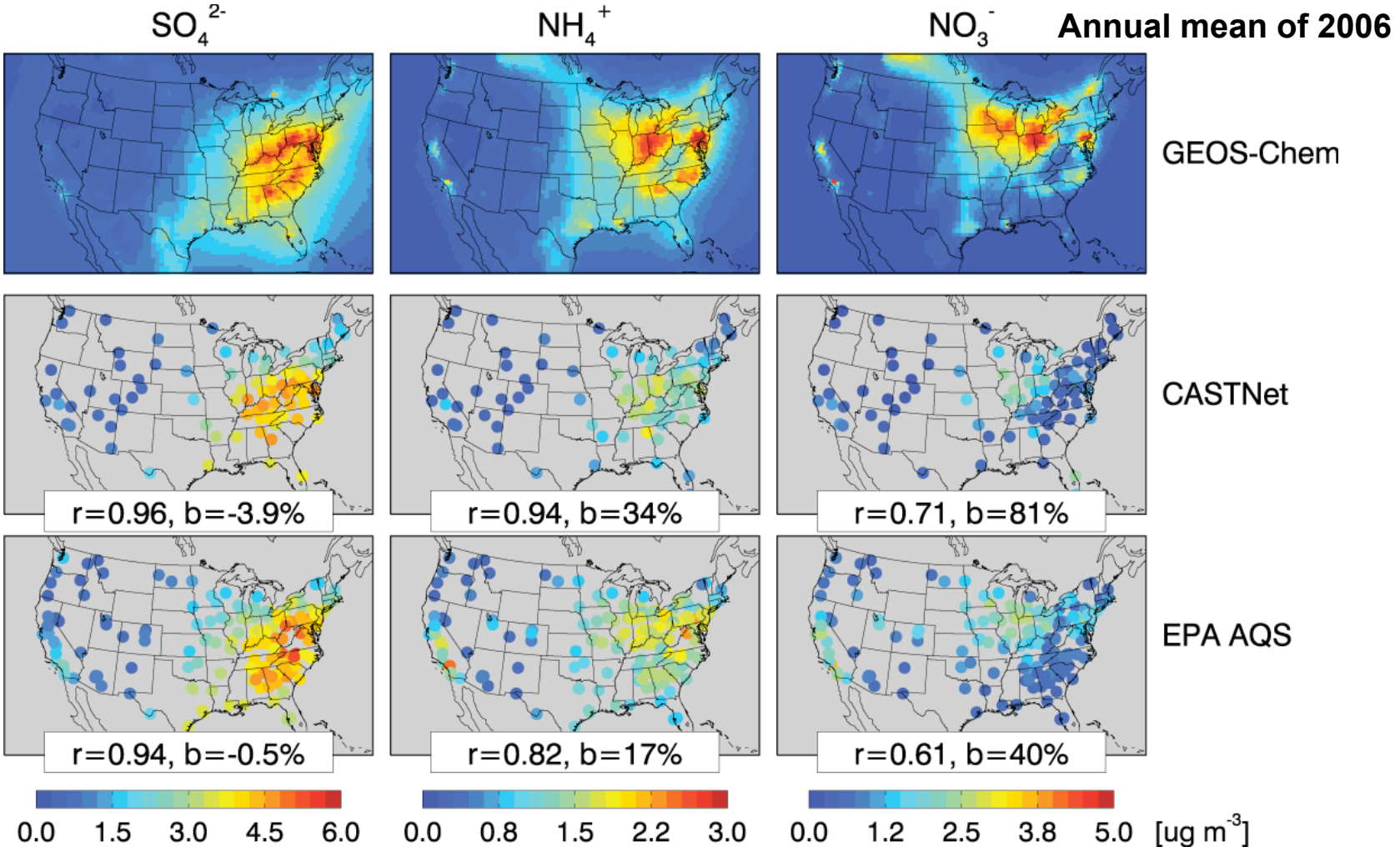
$v_d = 1 / (R_a + R_b + R_c)$

From the Monin-Obukhov similarity theory, we can compute the aerodynamic resistance from 70m to 10m R_a', and estimate the C_{10m}/C_{70m} ratio:

$C_{10m} = (1 - R_a' \times v_d) \times C_{70m}$

The remaining bias mainly occurs in winter reflecting an overestimate of HNO_3 formation in winter.

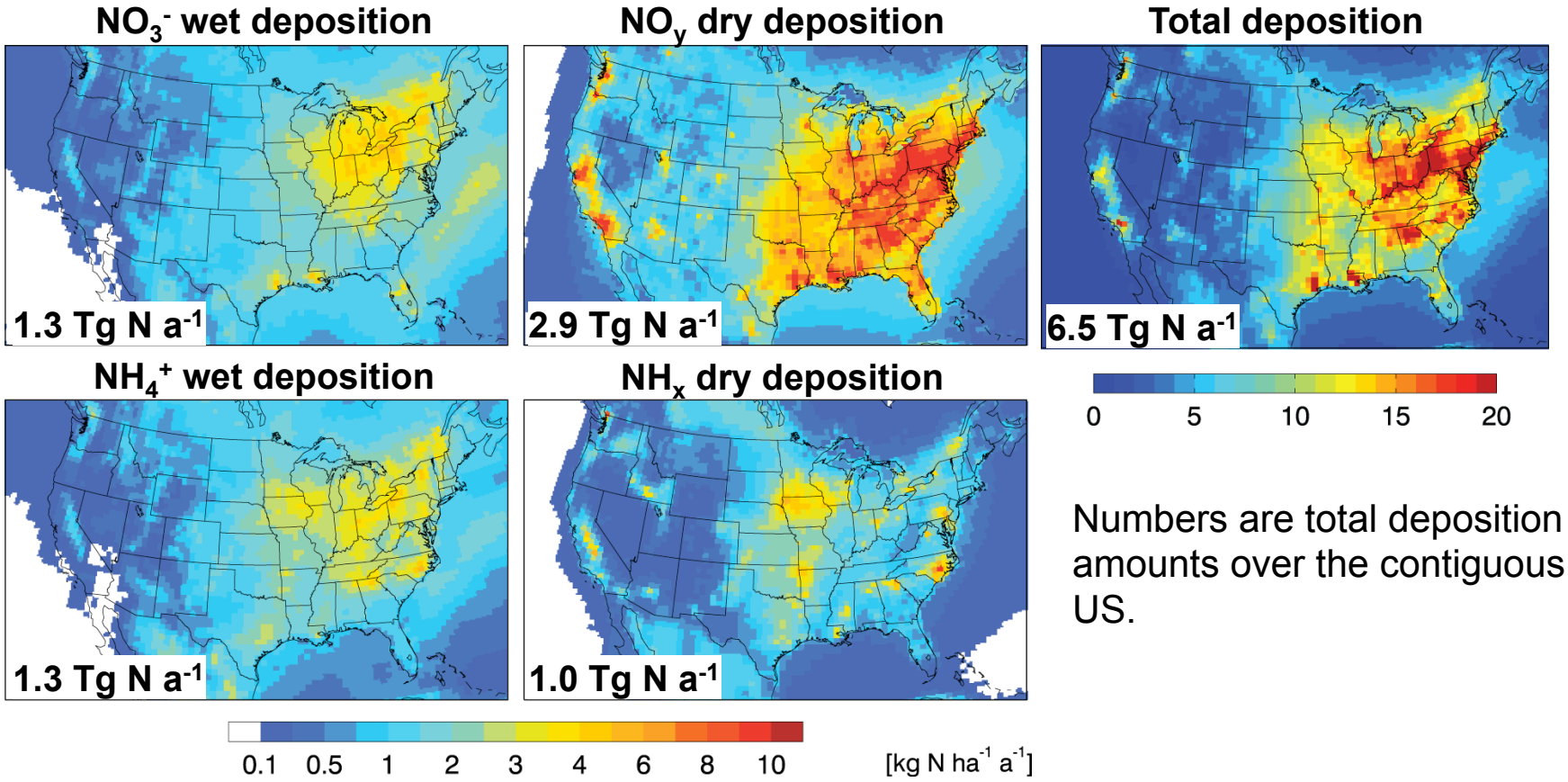
Model evaluation of surface aerosol concentrations



- The vertical gradient correction is not applied here because aerosol dry deposition is slow and the gradient is much weaker.
- Model overestimates of NH_4^+ and NO_3^- concentrations are also most severe in winter.

Annual wet, dry and total nitrogen deposition over the US

GEOS-Chem simulation at 1/2x2/3 resolution averaged for 2006-2008

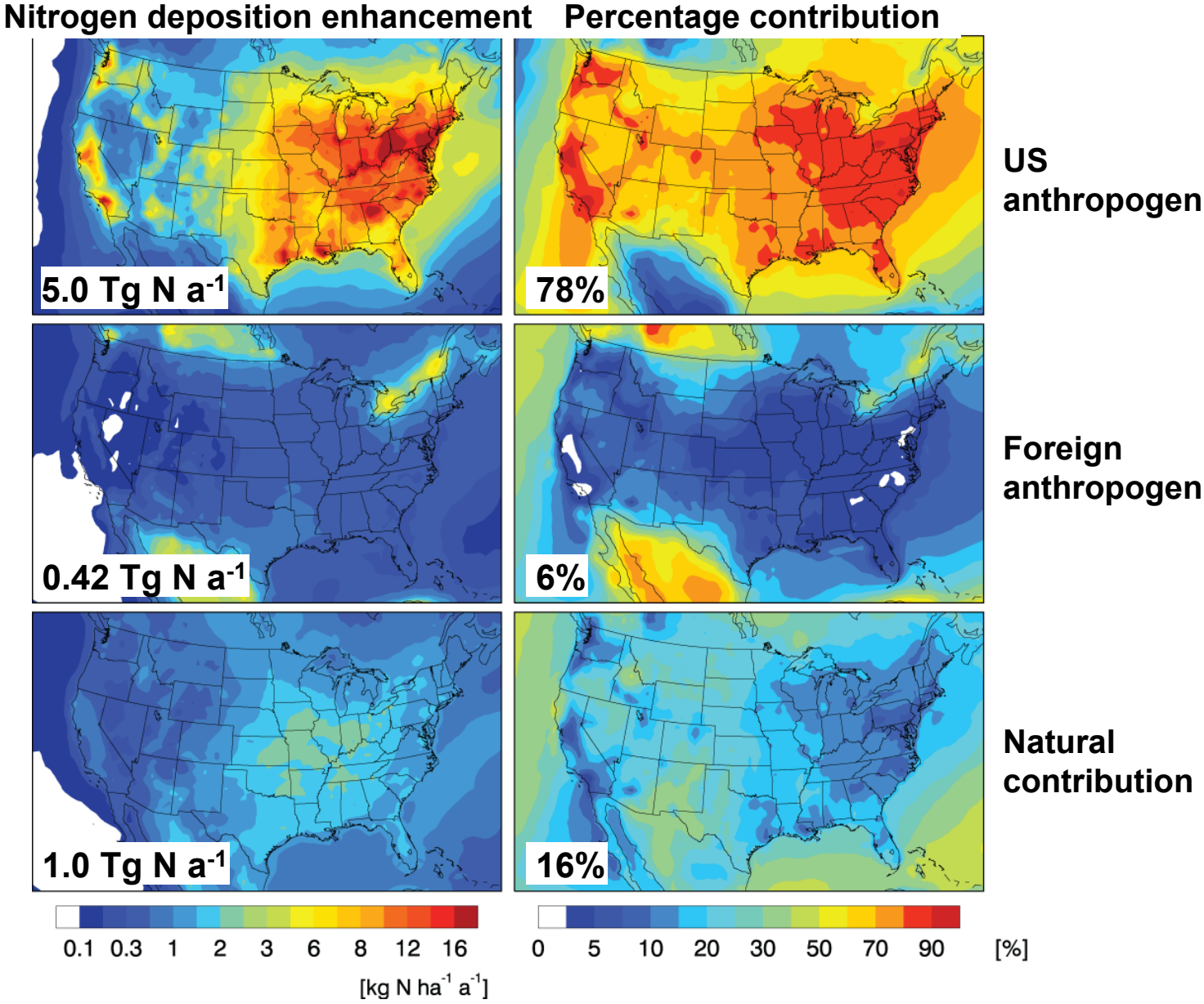


Numbers are total deposition amounts over the contiguous US.

- NO_y dry deposition is the largest pathway. HNO_3 accounts for 55% of the NO_y dry deposition, followed by NO_2 22%, and isoprene nitrates 9%.
- Wet and dry NH_x deposition is at similar amounts. NH_x contribute 35% of the total nitrogen deposition;

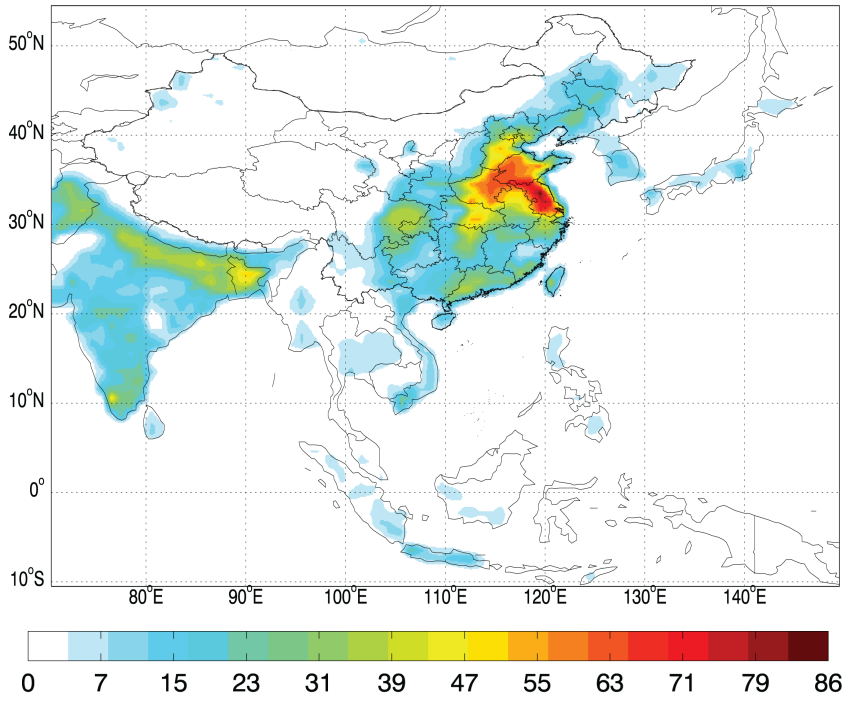
Contributions from anthropogenic versus natural sources

2006 annual totals

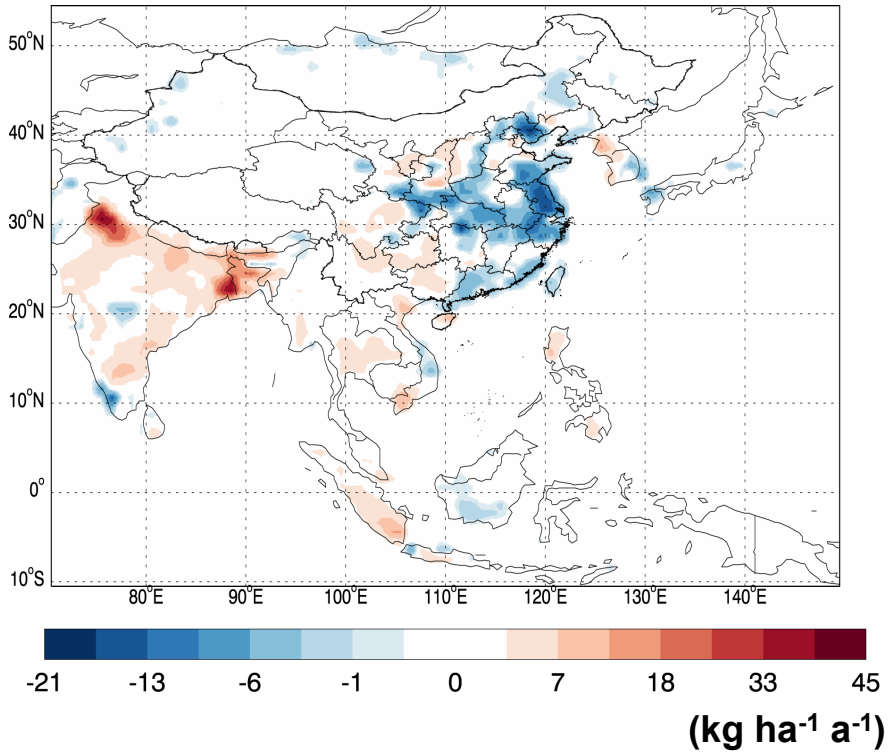


Large uncertainties in bottom-up Asian ammonia emissions

2000 NH_3 emissions from Streets et al. (2003)



REAS minus Streets differences

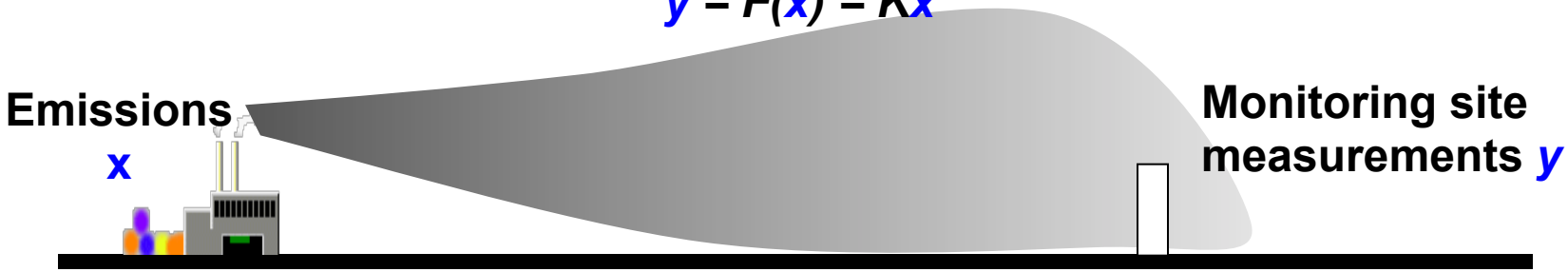


Bottom-up emission estimates are based on statistics of energy use/ agriculture activity and emission factors, which are all subject to large uncertainties.

Inverse modeling approach

Atmospheric "forward" model (GEOS-Chem)

$y = F(x) = Kx$



(fuel burned) X (emission factor)
⇨ *a priori* "bottom-up" estimate
$x_a \pm S_a$

Inverse model $x = K^{-1}y$
⇨ "top-down" estimate
$x_\varepsilon \pm S_\varepsilon$

Inverse Solution: consistent with both observations and *a priori* knowledge (weighted by respective errors)

This can be solved by minimizing the cost function:

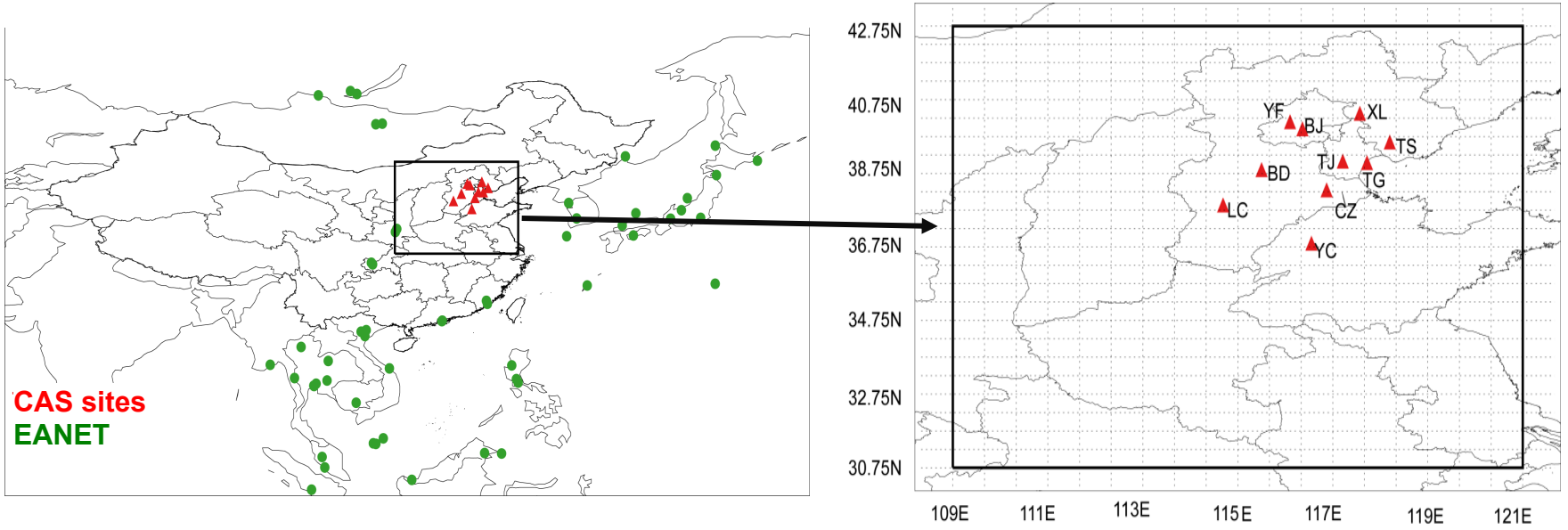
$$J(\mathbf{x}) = (\mathbf{F}(\mathbf{x}) - \mathbf{y})^T \mathbf{S}_\varepsilon^{-1} (\mathbf{F}(\mathbf{x}) - \mathbf{y}) + (\mathbf{x} - \mathbf{x}_a)^T \mathbf{S}_a^{-1} (\mathbf{x} - \mathbf{x}_a)$$

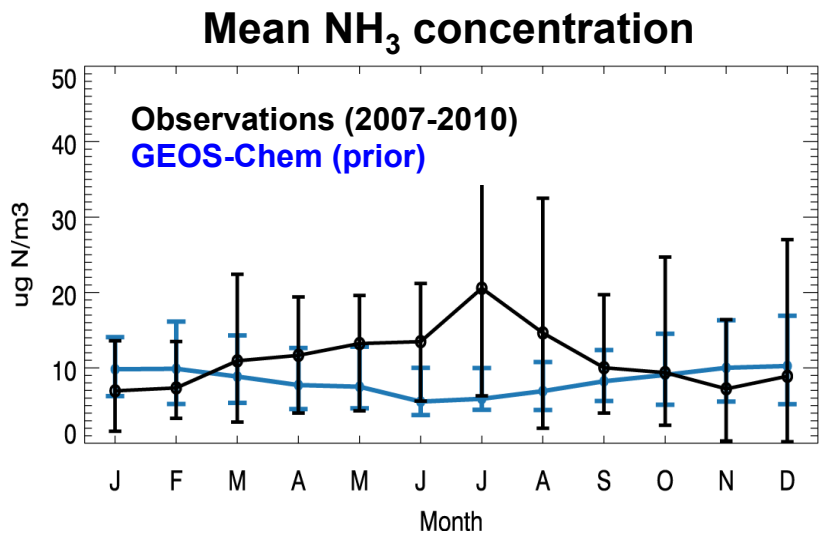
Analytical solution:

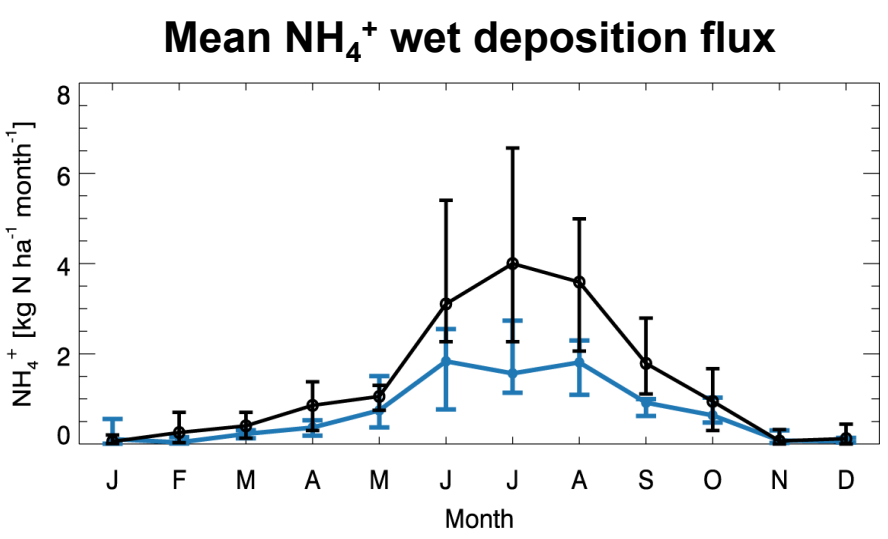
$$\hat{\mathbf{x}} = \mathbf{x}_a + \left(\mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1} \mathbf{K}^T \mathbf{S}_\varepsilon^{-1} (\mathbf{y} - \mathbf{K}\mathbf{x}_a)$$

$$\hat{\mathbf{S}}^{-1} = \mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1}$$

Surface measurements of ammonia concentrations and ammonium wet deposition fluxes







Prior emissions from Streets et al. (2003) with no seasonality.

Optimized ammonia emissions in North China

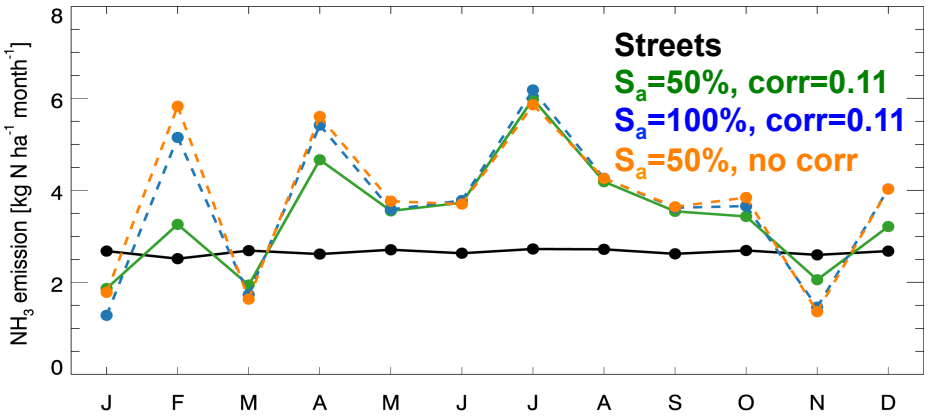
Optimized emissions

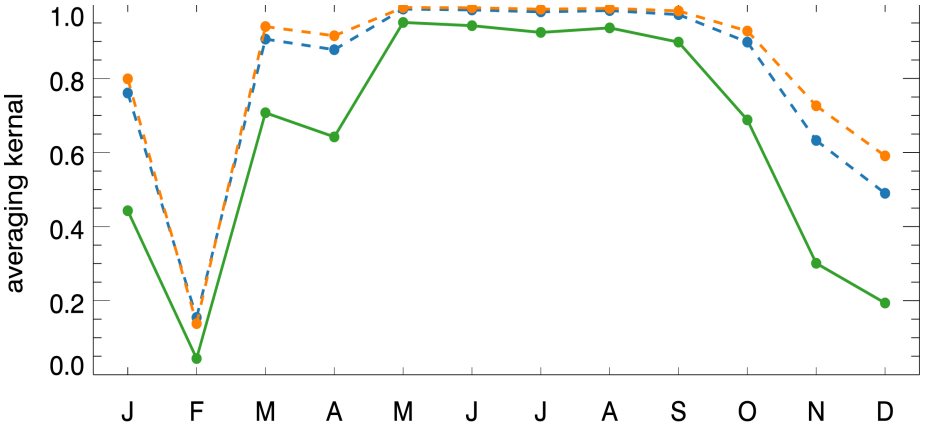
$$\hat{\mathbf{x}} = \mathbf{x}_a + \left(\mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1}\mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\left(\mathbf{y} - \mathbf{K}\mathbf{x}_a\right)$$

Averaging kernels (AK)

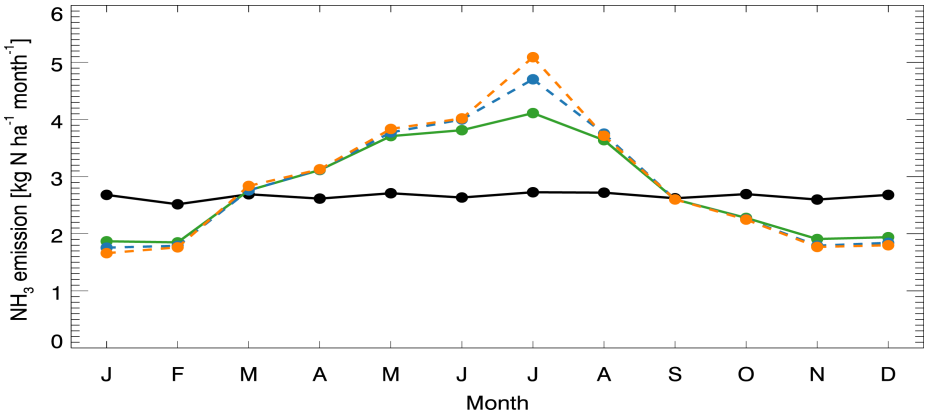
$$\mathbf{AK} = \left(\mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1}\mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\mathbf{K}$$

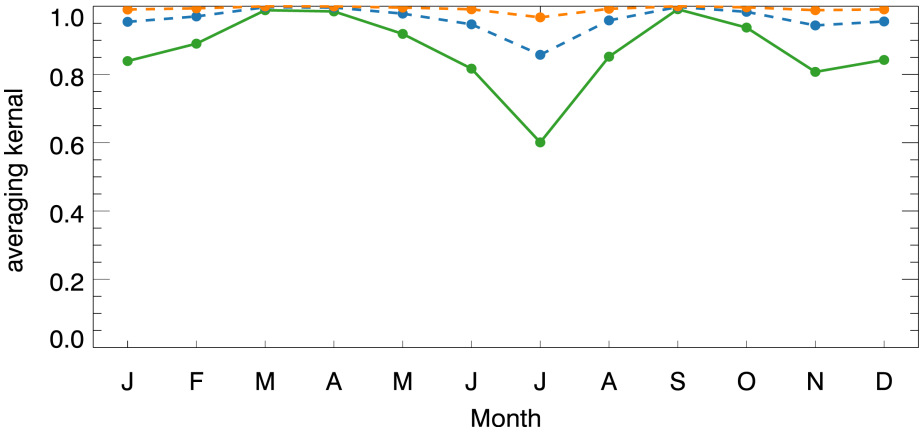
(1) Inversion with wet deposition measurements





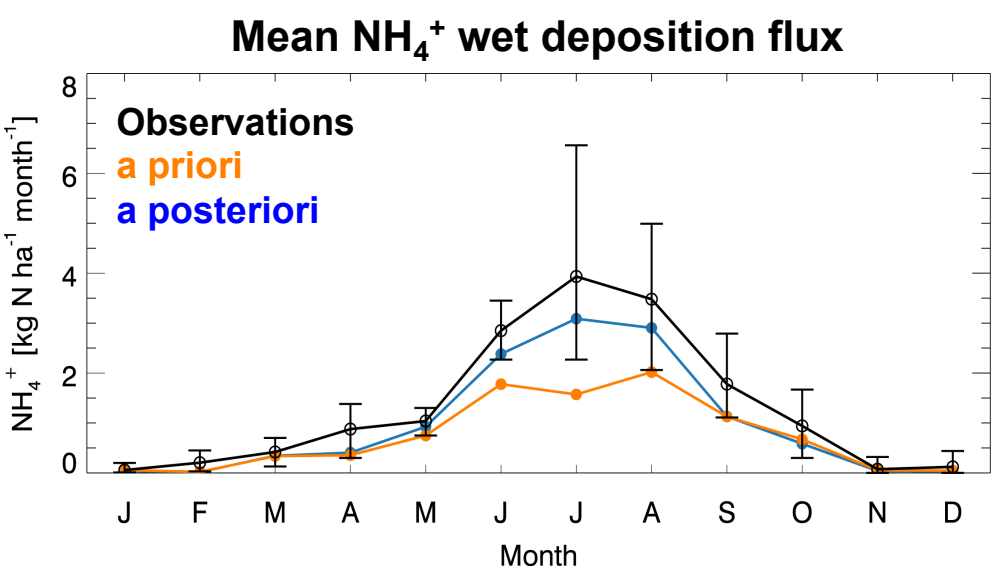
(2) Inversion with concentration measurements

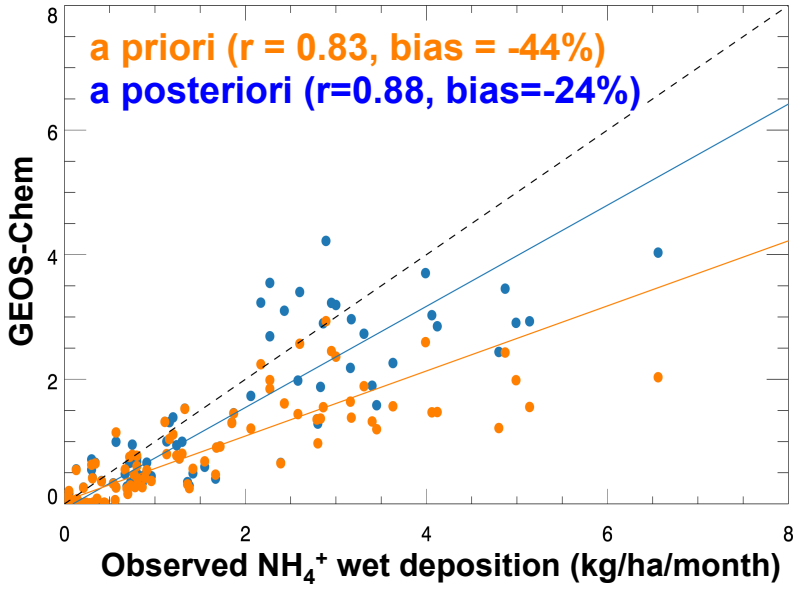


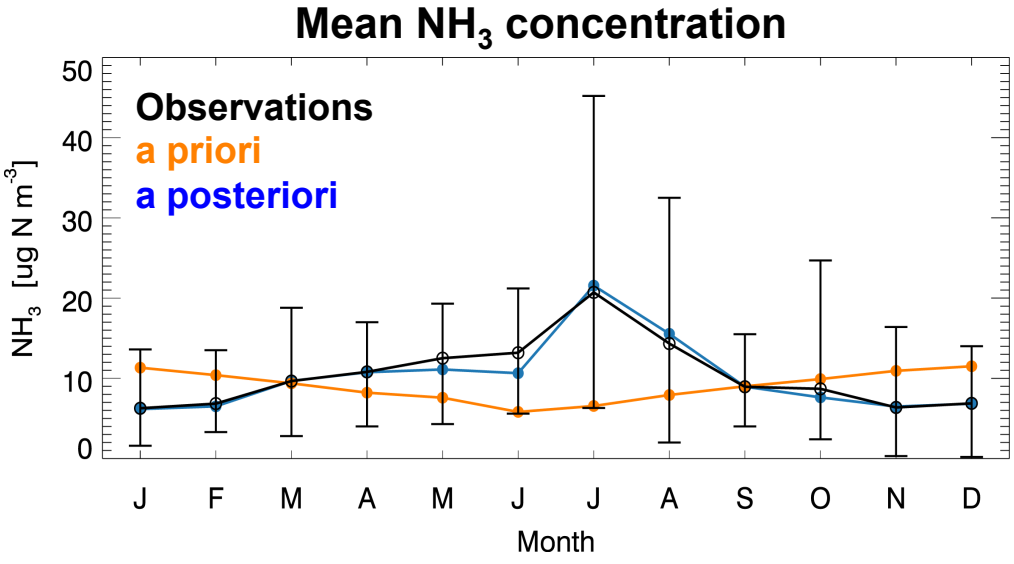


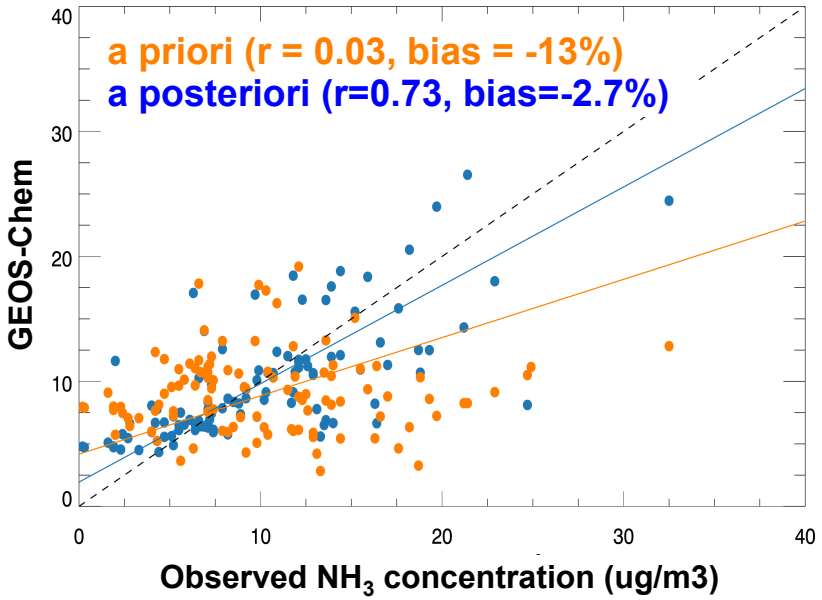
Our “best” inversion case uses wet deposition fluxes for May-August, and concentrations for the rest months; 28% decrease in winter, 72% increase in summer, 12% increase annually.

Evaluation of the optimized ammonia emissions

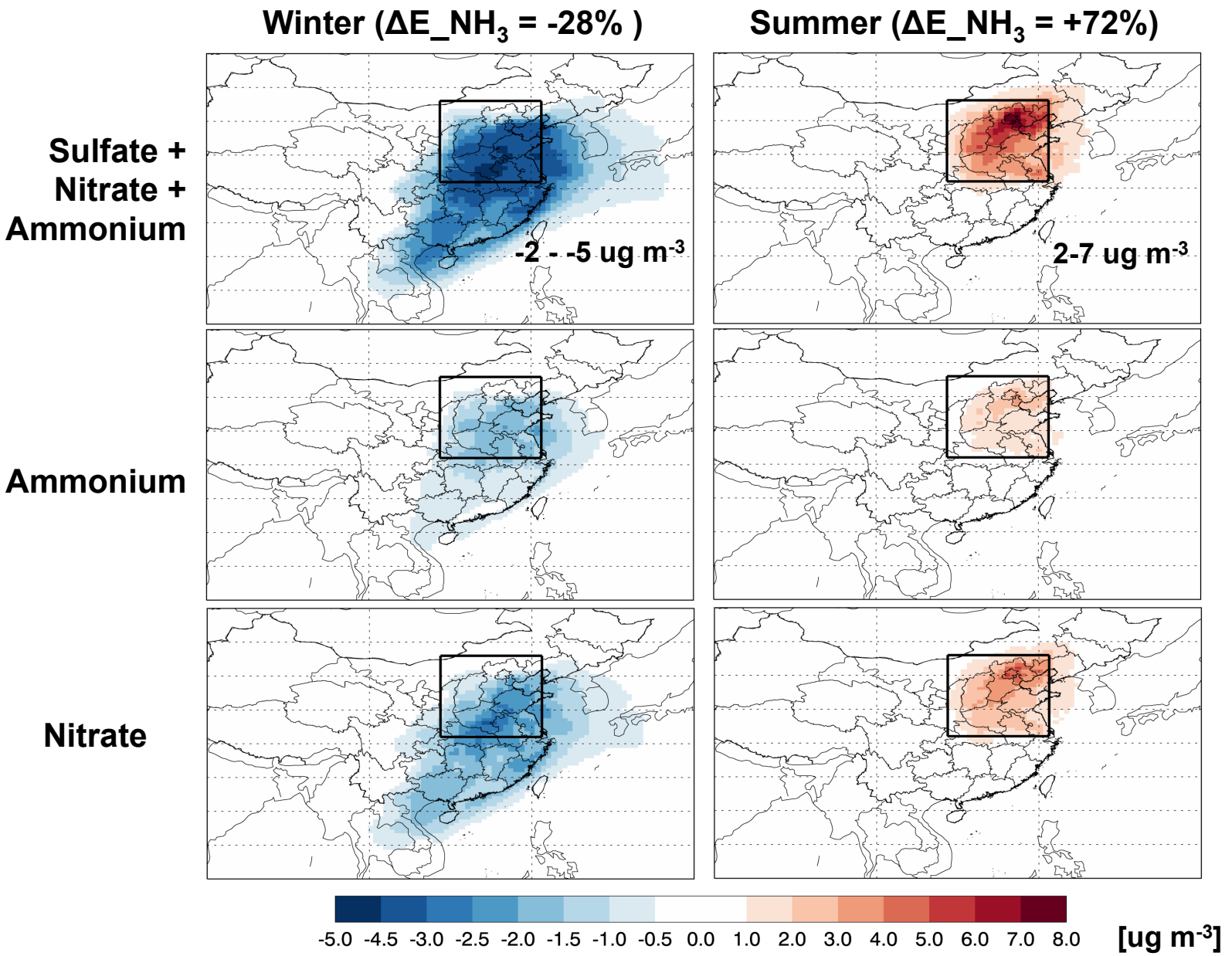








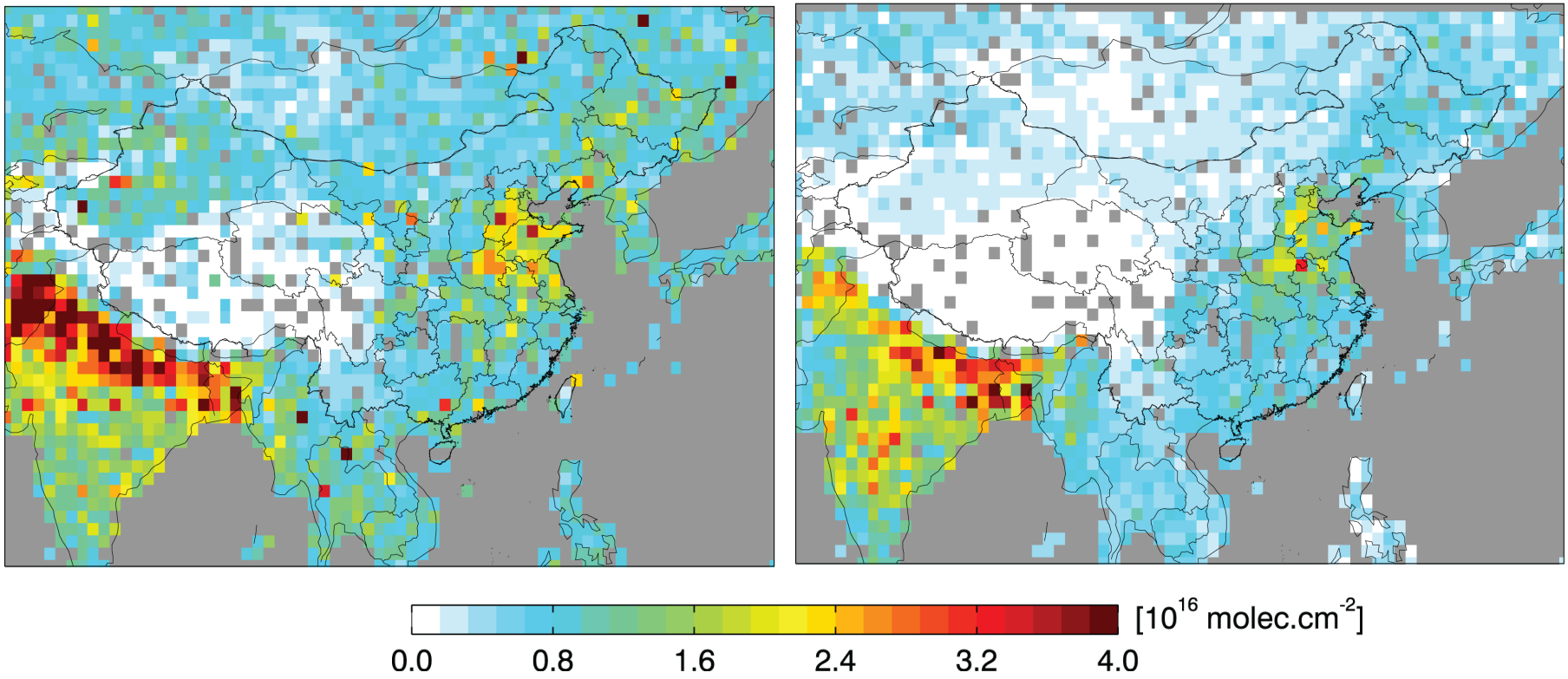
Sensitivity of surface aerosol concentrations to NH_3 emissions



TES satellite observations of NH_3 columns over Asia

2005-2010 annual mean NH_3 columns observed from TES

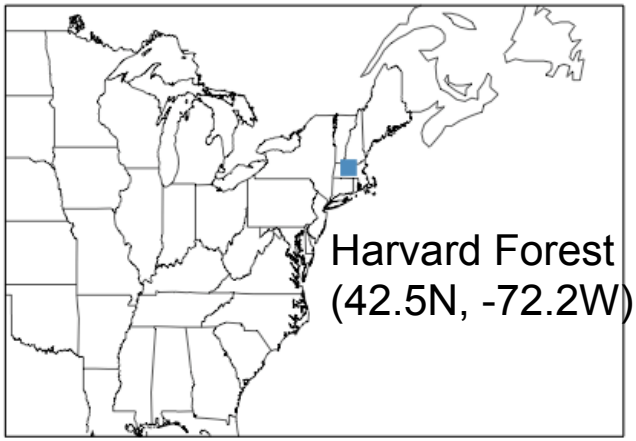
2008 GEOS-Chem simulated NH_3 columns smoothed by TES averaging kernels

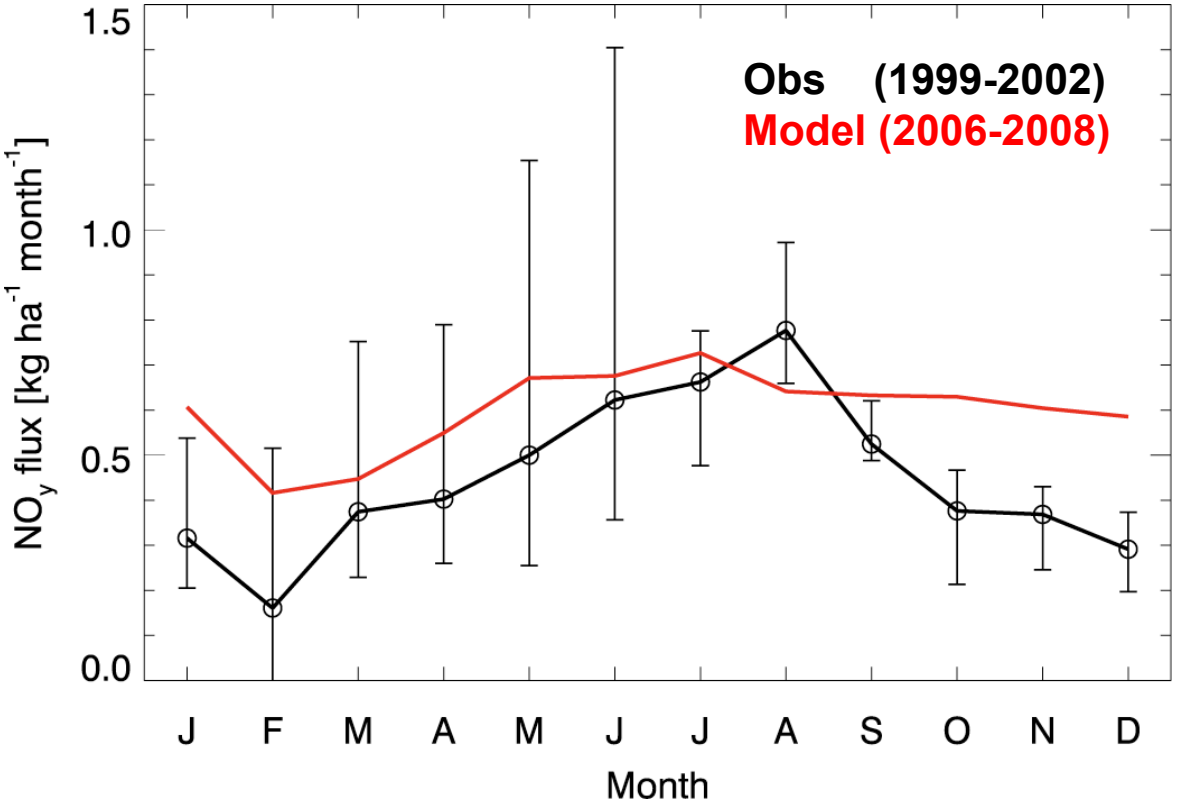


Our next step will use the satellite observations of ammonia columns to better quantify Asian ammonia emissions.

Extra slides

NO_y dry deposition measurements at the Harvard Forest

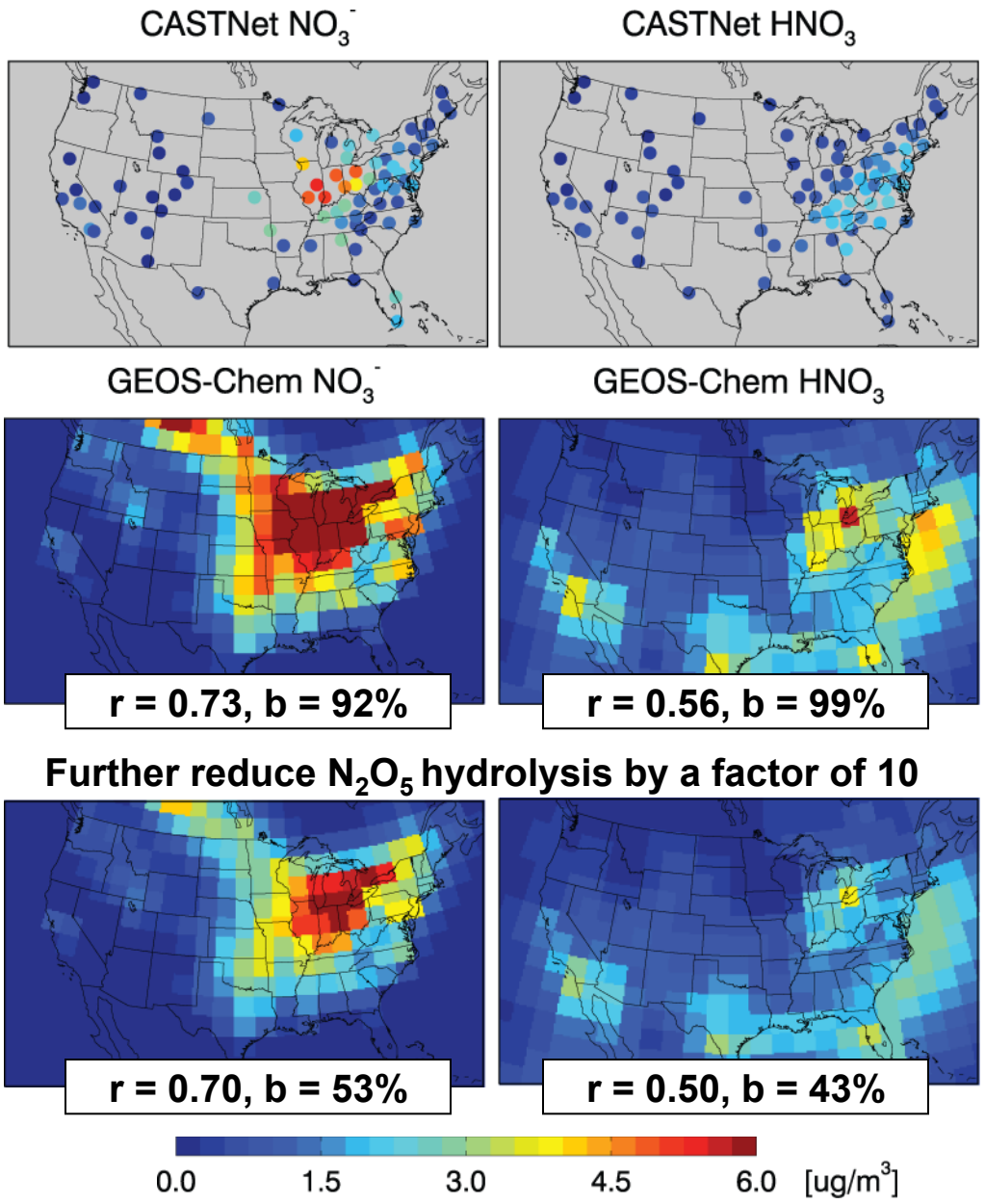


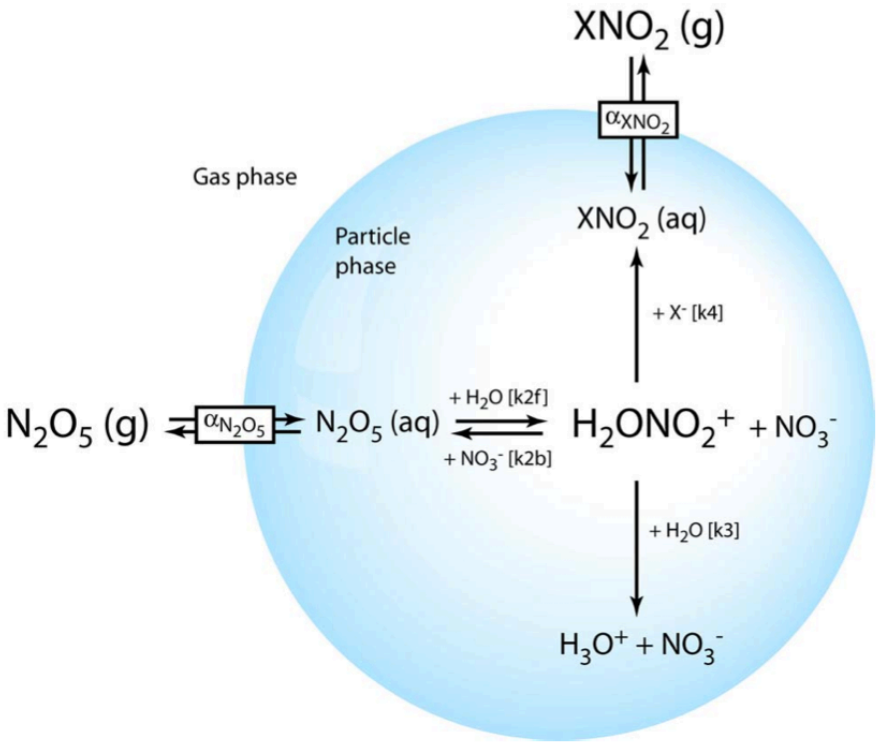


- The annual NO_y deposition flux is 5.4 kg N/ha/yr in the measurements, and 7.2 kg N/ha/yr in the model.
- The model overestimates reflect formation of HNO_3 is too high, particularly in winter.

Model overestimate of the N_2O_5 hydrolysis in aerosols

February 2006



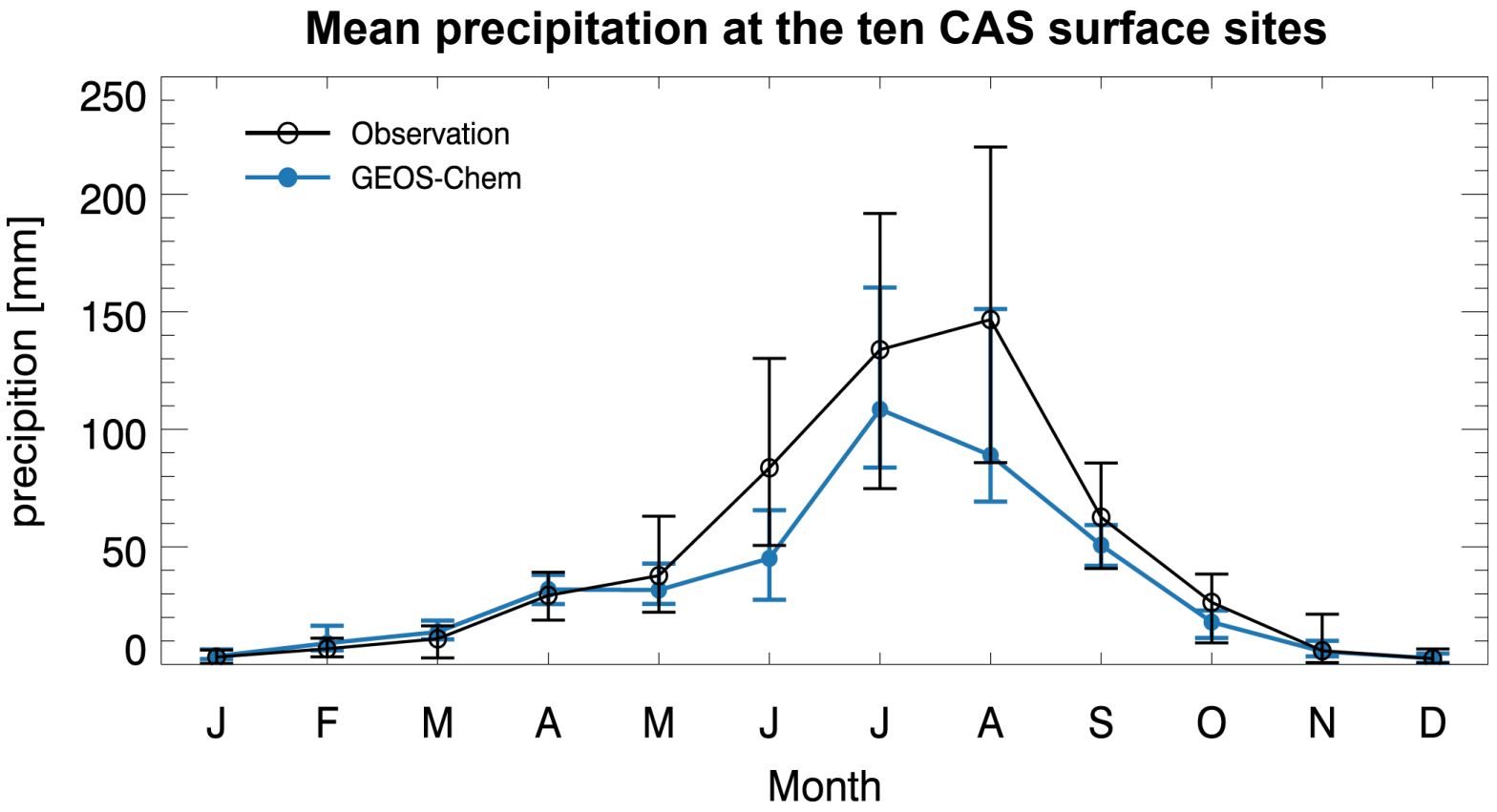


Bertram and Thornton, 2009

Missing in current GEOS-Chem:

1. Nitrate inhibits N_2O_5 dissociation
2. N_2O_5 reacts in chloride to produce $ClNO_2$

Model underestimates of precipitation over North China



Part of the underestimates in wet deposition fluxes is due to model underestimates of precipitation. This needs to be corrected in the inverse analysis.