Adjoint sensitivity analysis of $PM_{2.5}$ sources: constraining NH_3 emissions

Daven K. Henze

10/19/09

Mechanical Engineering
University of Colorado at Boulder

Collaborators

Atmospheric and Environmental Research, Inc. — Mark Shepard, Karen Cady-Pereria,

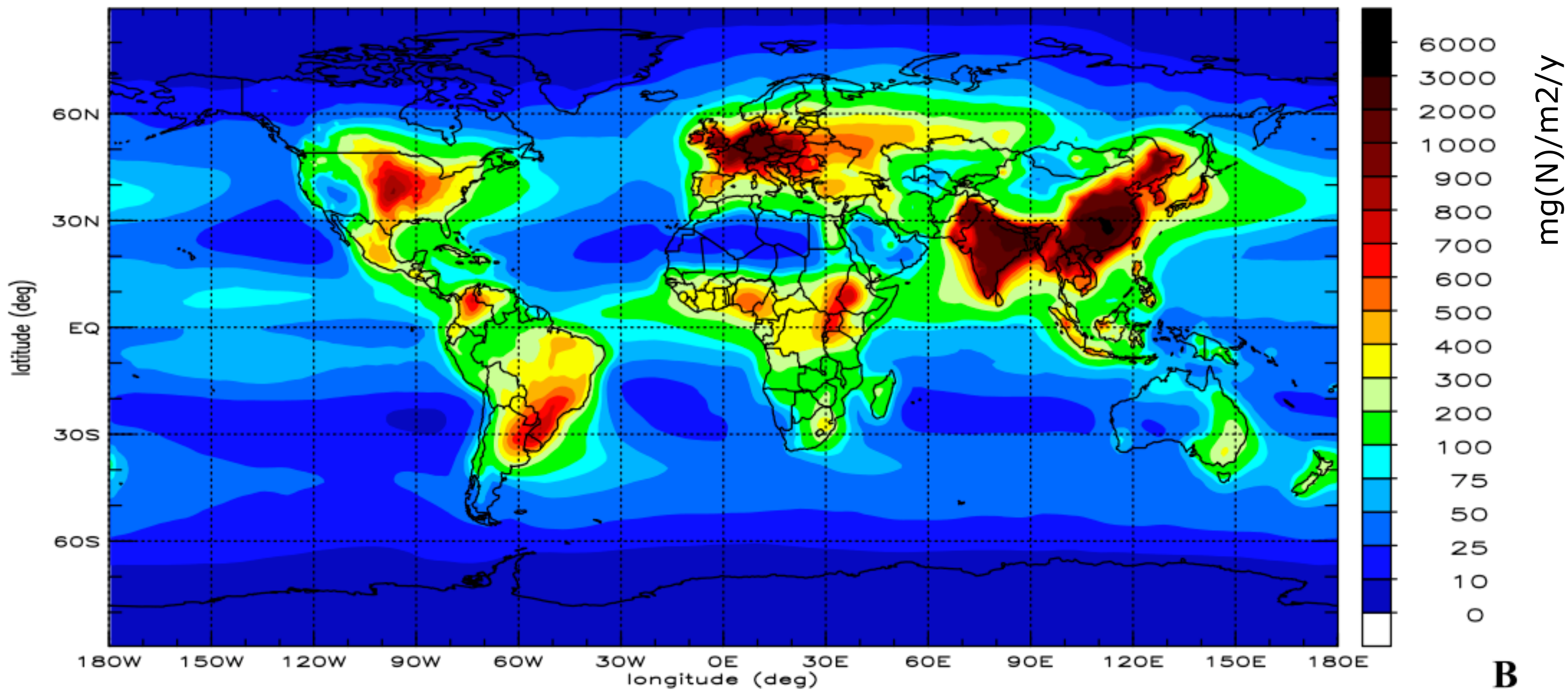
Ming Luo, Reinhard Beer, TES team

Rob Pinder, John Walker

NASA GSFC: NCCS
NASA JPL: SCC

Environmental impacts NH_3

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

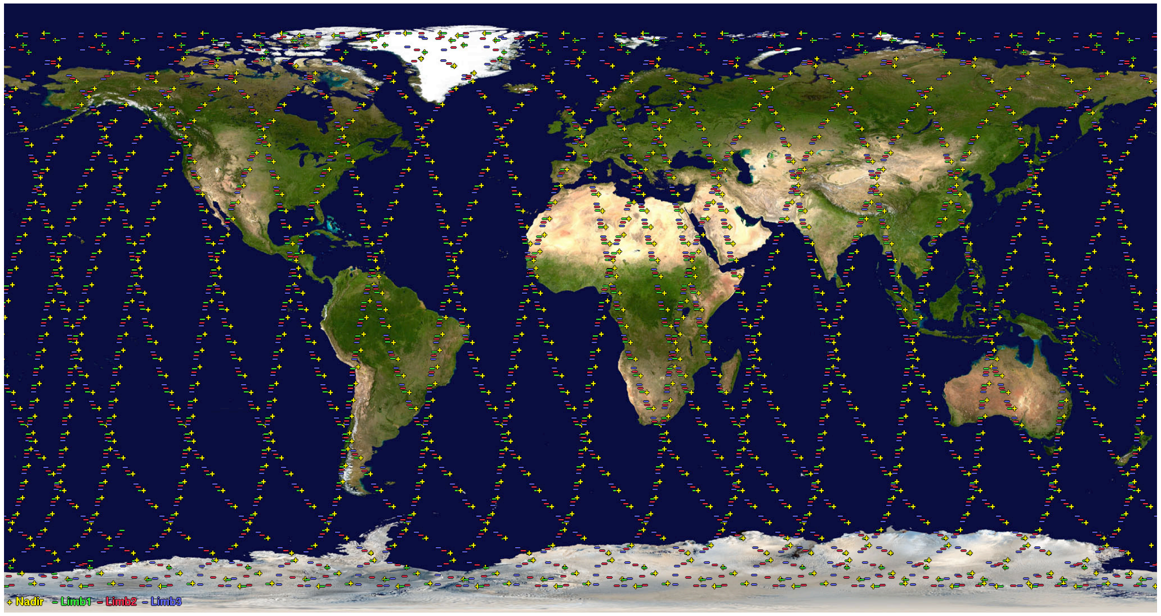


Denman et al. (2007), *IPCC*: NH_3 emissions to double by 2050.

Galloway et al. (2008), *Science:* Importance of atmospheric NHx transport

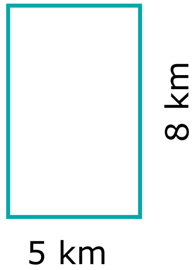
Schlesinger (2009), *PNAS:* a 46 Tg gap in N budget?

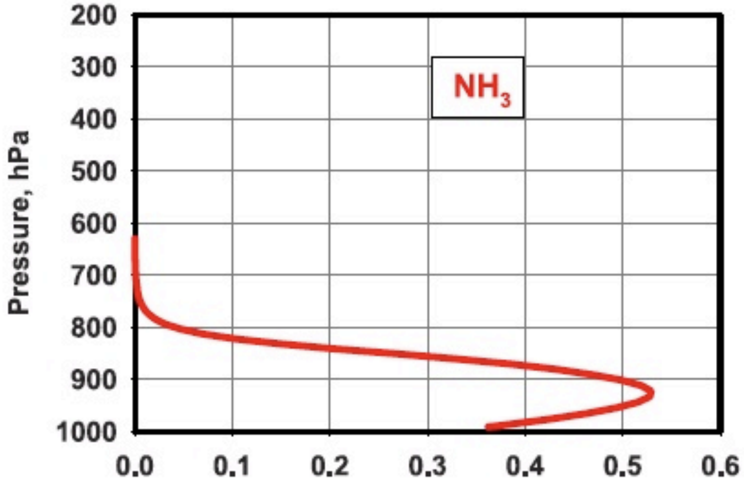
TES: remote sensing of NH_3



"covers" globe in 16 days

Footprint size:



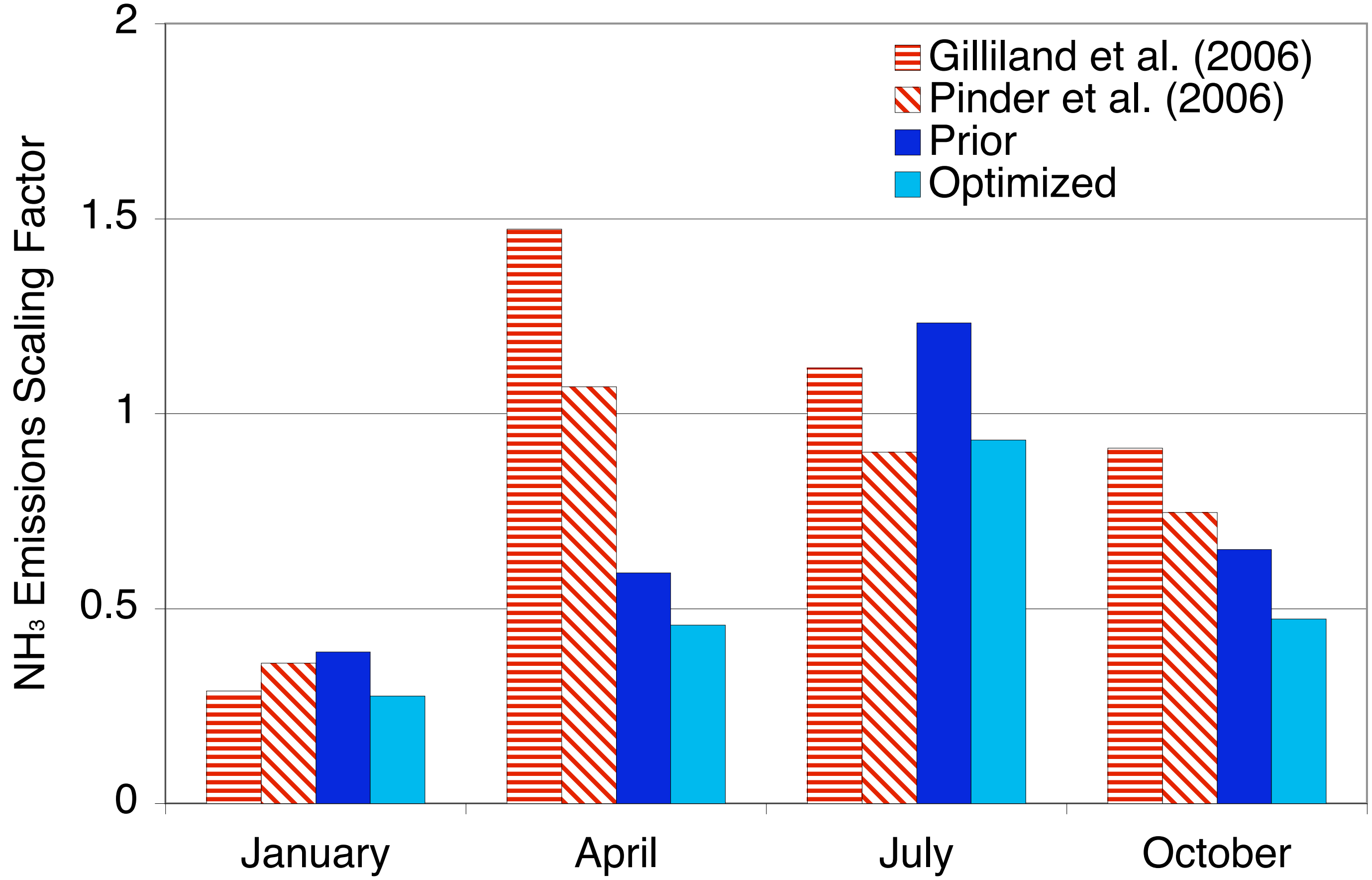


Vertical profile yields ~1 DOF near 900 hPa

Beer et al., 2008

Inverse modeling: NH_3

Sum changes to NH_3 over U.S., compare to other inverse modeling (Gilliland et al., 2006) and bottom up (Pinder et al., 2006)



Seasonal peak in April or July? (Henze et al., 2009)

NH_3 emissions variability and uncertainty: Beusen et al. (2008)

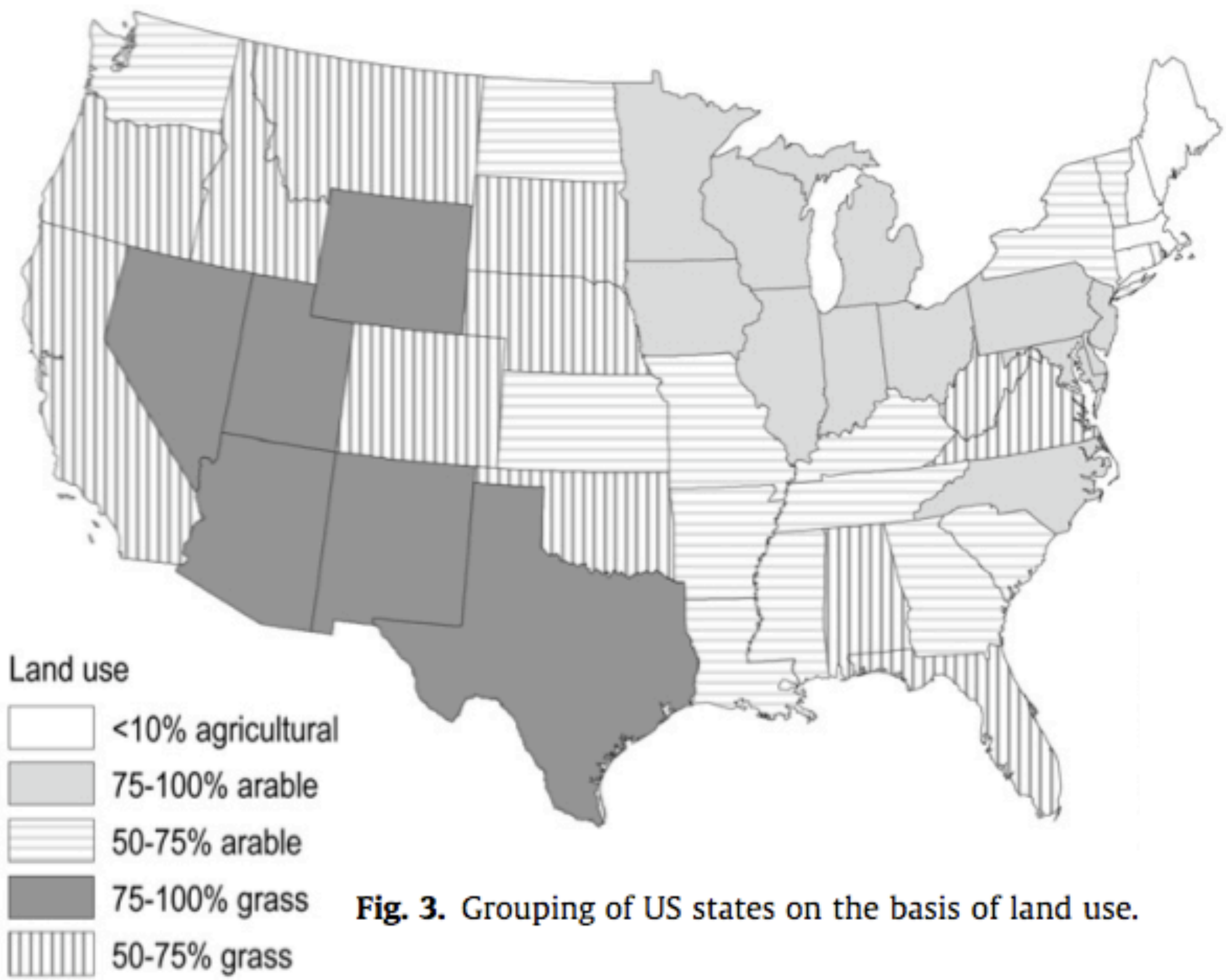
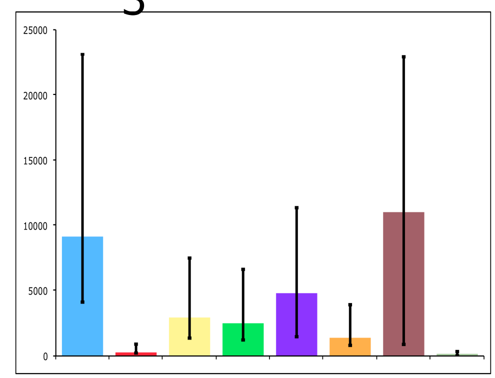


Fig. 3. Grouping of US states on the basis of land use.

Global animal NH_3 emissions



Source types
- housing mixed
- housing pastoral
- grazing mixed
- grazing pastoral
- spreading cropland
- spreading grassland
- fertilizer cropland
- fertilizer grassland

Model sensitivity

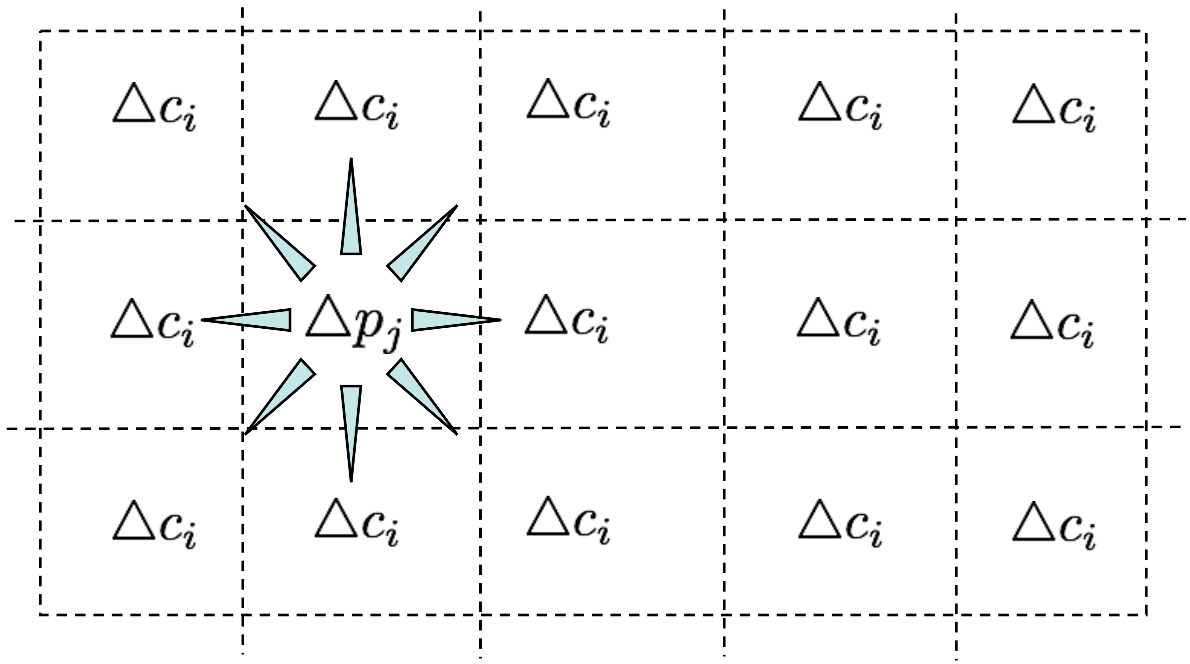
Model: estimates, c_i , and parameters, p_i

c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i
c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i
c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i	c_i, p_i

Ideally, want model Jacobian, $\frac{\partial \mathbf{c}}{\partial \mathbf{p}} = \begin{bmatrix} \frac{\partial c_1}{\partial p_1} & \cdots & \frac{\partial c_1}{\partial p_J} \\ \vdots & \ddots & \vdots \\ \frac{\partial c_I}{\partial p_1} & \cdots & \frac{\partial c_I}{\partial p_J} \end{bmatrix}$

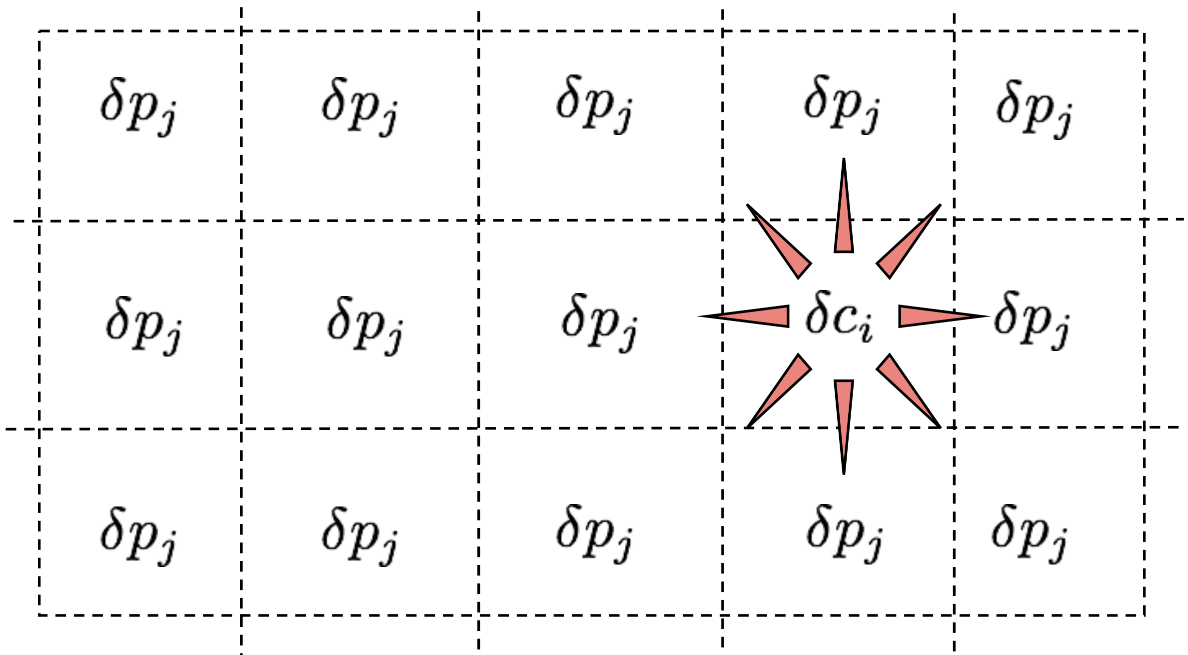
but it is generally much too large to calculate.

Forward sensitivity



$$\frac{\partial \mathbf{c}}{\partial p_j} = \begin{bmatrix} \frac{\partial c_1}{\partial p_1} & \cdots & \frac{\partial c_1}{\partial p_J} \\ \vdots & \ddots & \vdots \\ \frac{\partial c_I}{\partial p_1} & \cdots & \frac{\partial c_I}{\partial p_J} \end{bmatrix} \mathbf{u_j}$$

Adjoint sensitivity



$$\begin{bmatrix} \frac{\partial c_1}{\partial p_1} & \cdots & \frac{\partial c_1}{\partial p_J} \\ \vdots & \ddots & \vdots \\ \frac{\partial c_I}{\partial p_1} & \cdots & \frac{\partial c_I}{\partial p_J} \end{bmatrix}^T \quad \mathbf{u_i} = \frac{\partial c_i}{\partial \mathbf{p}}$$

4D-Var with GEOS-Chem Adjoint Model

Forward model v6-02-05 (*Bey et al.*, 2001; *Park et al.*, 2004)

emissions (gas)
SO_2, NO_x, NH_3

Gas-phase chemistry
Heterogeneous chem
Cloud processing
Aerosol thermo

Aerosol
SO_4^{2-}, NO_3^-, NH_4^+

All included in adjoint (*Henze et al.*, 2007)

Calculates sensitivity of single model response w.r.t. all model parameters in $t = 3 \times t_{forward}$

Testing the Adjoint Model: Gradient Check

Check gradient using finite difference calculation

$$\lambda \approx \frac{J(\sigma + \delta\sigma) - J(\sigma - \delta\sigma)}{2\delta\sigma}$$

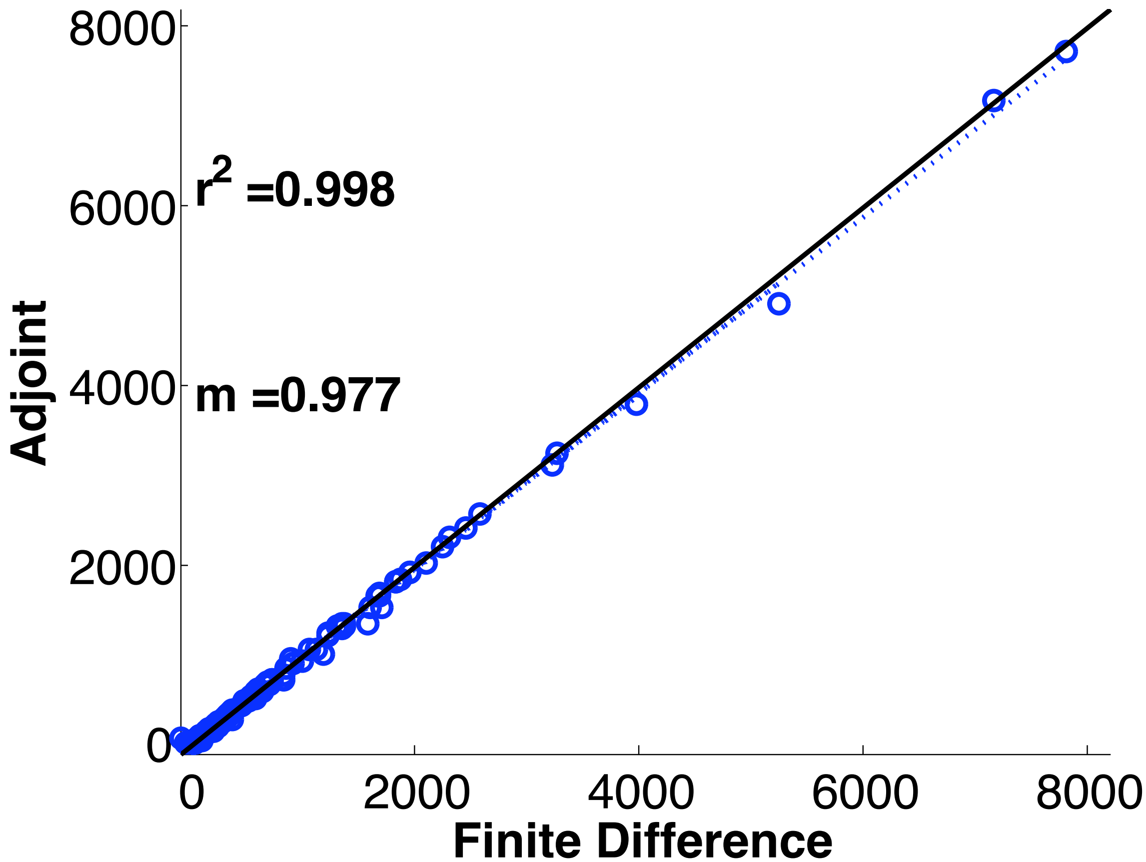
$J =$ model response

$\sigma =$ control parameter (emissions)

$\lambda =$ adjoint sensitivity

Component-wise analysis affords domain wide points-of-comparison (e.g., Hakami et al., 2007)

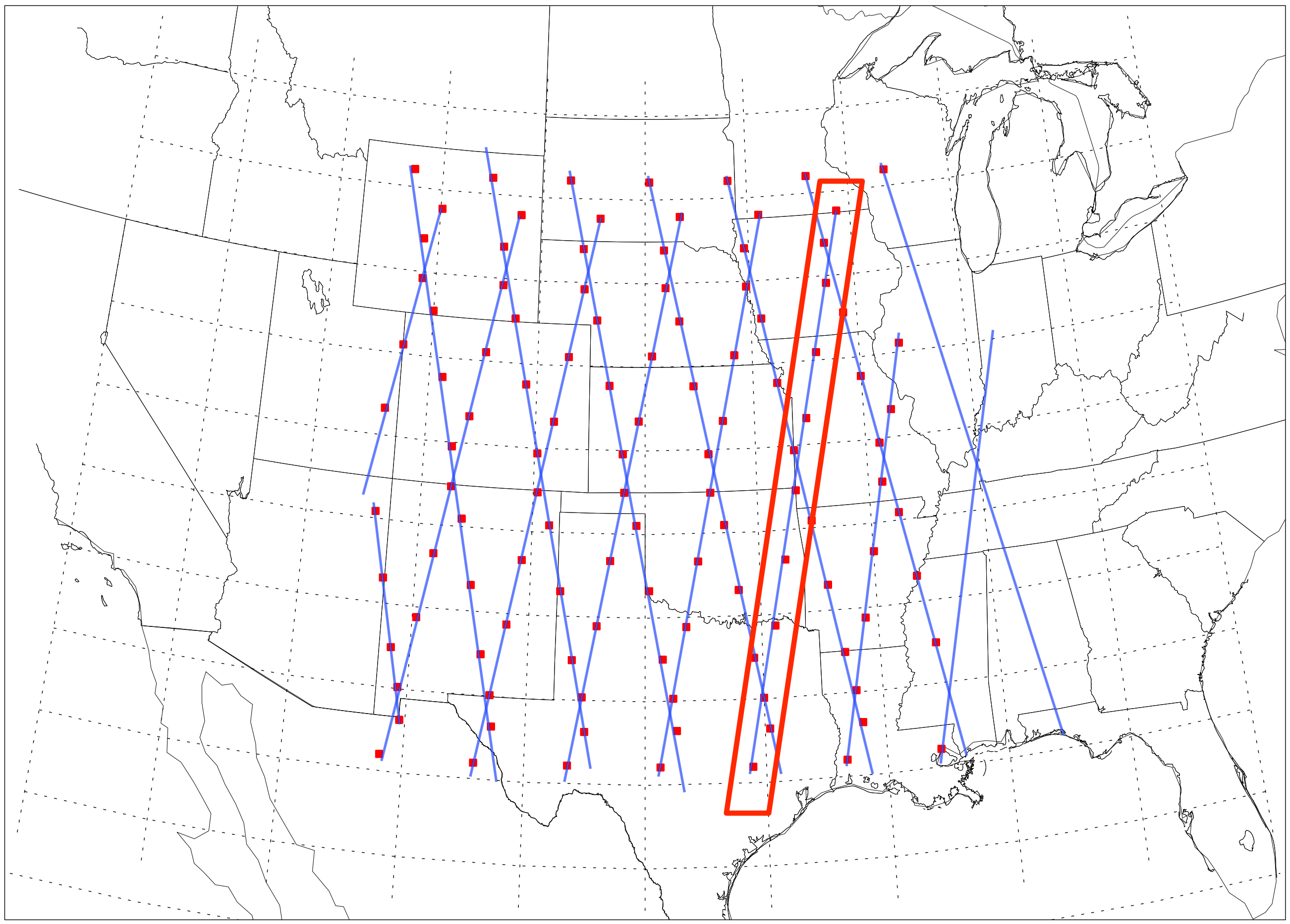
Adjoint model validation



Sensitivity of nitrate aerosol w.r.t ammonia emissions, 1 week, all processes other than horizontal transport

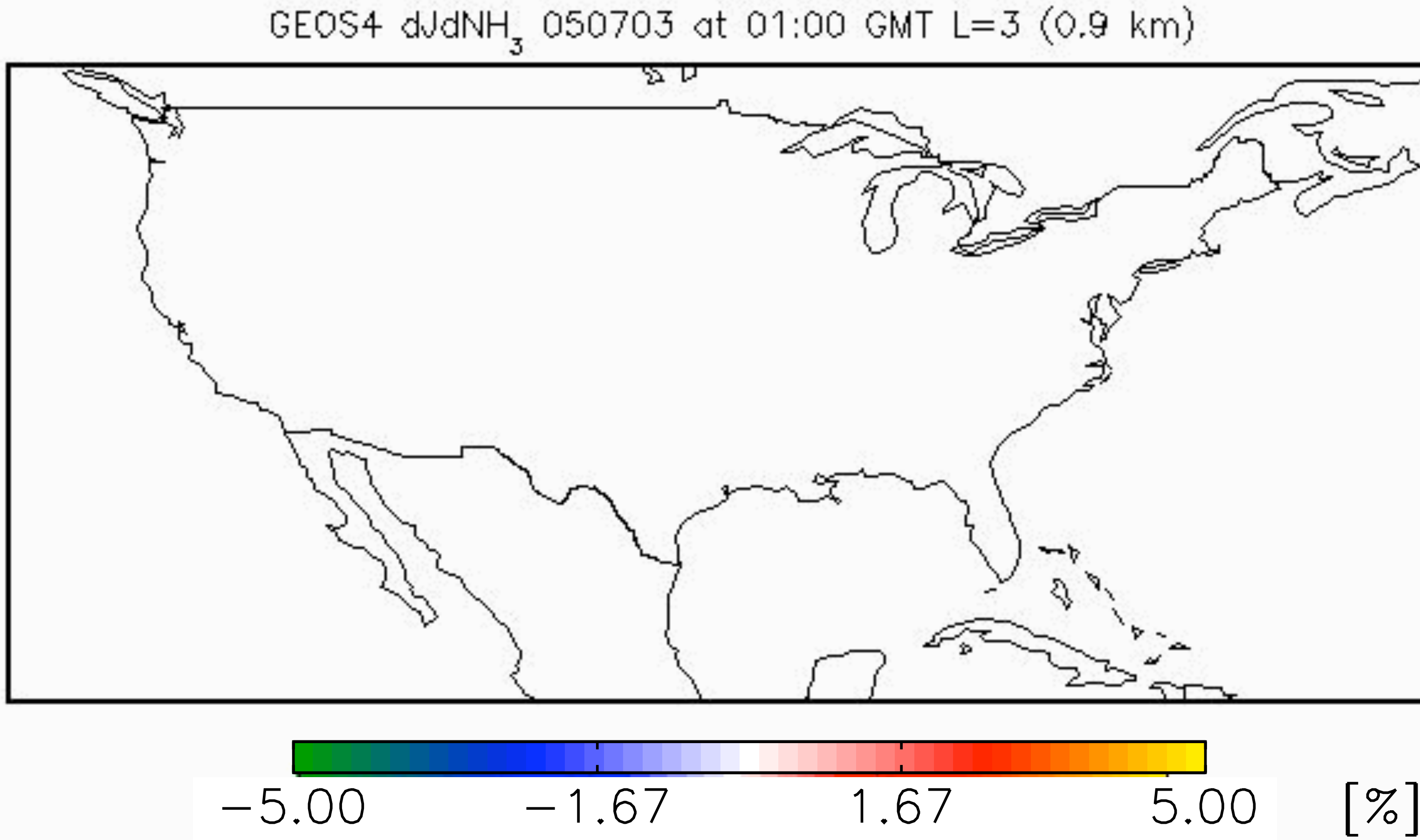
Potential for further constraints: TES coverage for 2 weeks in July 2005

TES GS Footprints, July 4-19, 2005



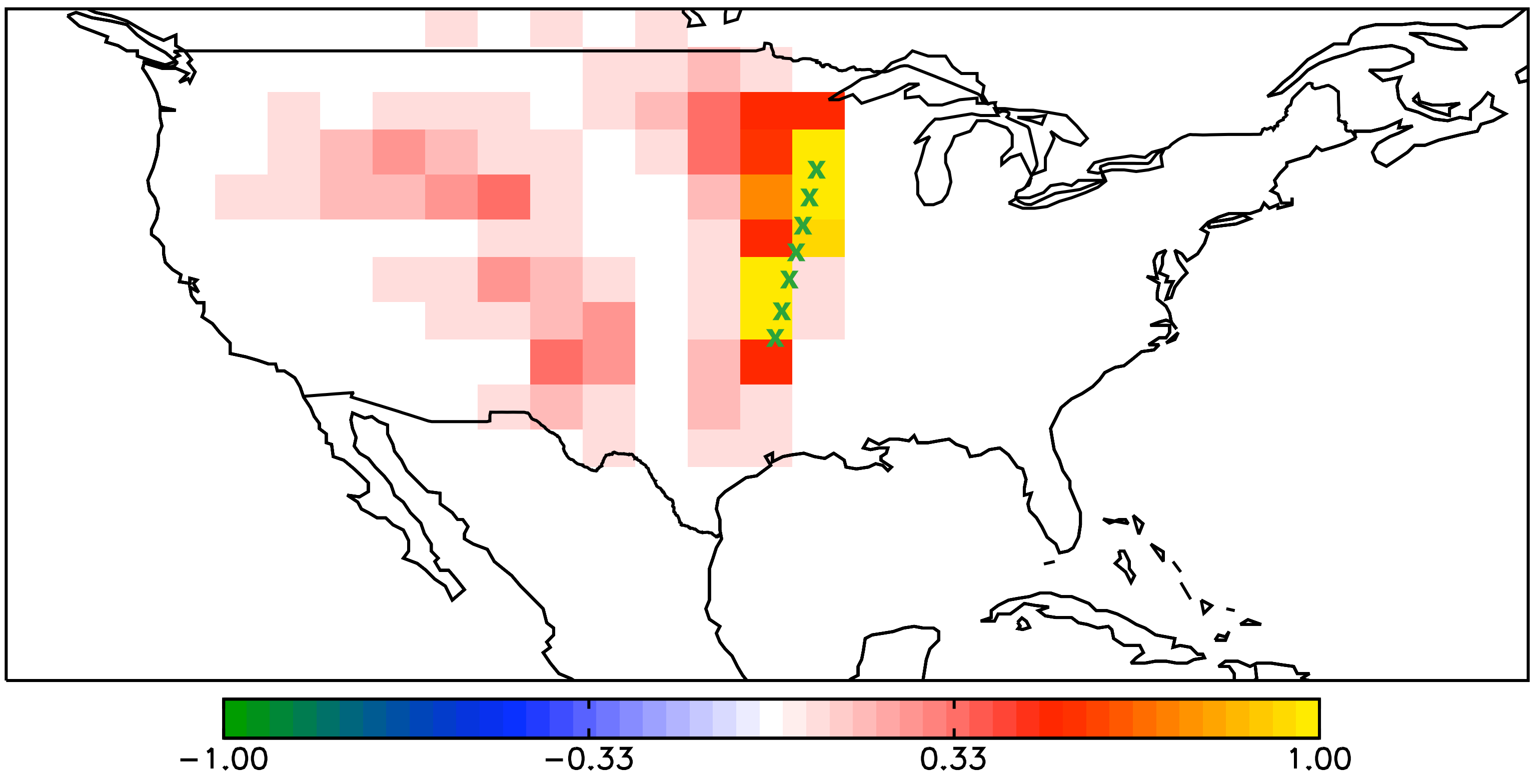
data selection: lat = [30.,45.], lon = [-110, -90.]; total number of profiles: 115

Adjoint sensitivities of modeled NH_3 retrievals



Sensitivities show the origins of the NH_3 that eventually will be "observed" by TES

Sensitivity of TES observation in the track highlighted on previous slide to NH_3 emissions from the week prior



Inverse Modeling: twin experiment

Parameter Estimate

$$\mathbf{p} = 2\mathbf{p}_a$$

Forward Model

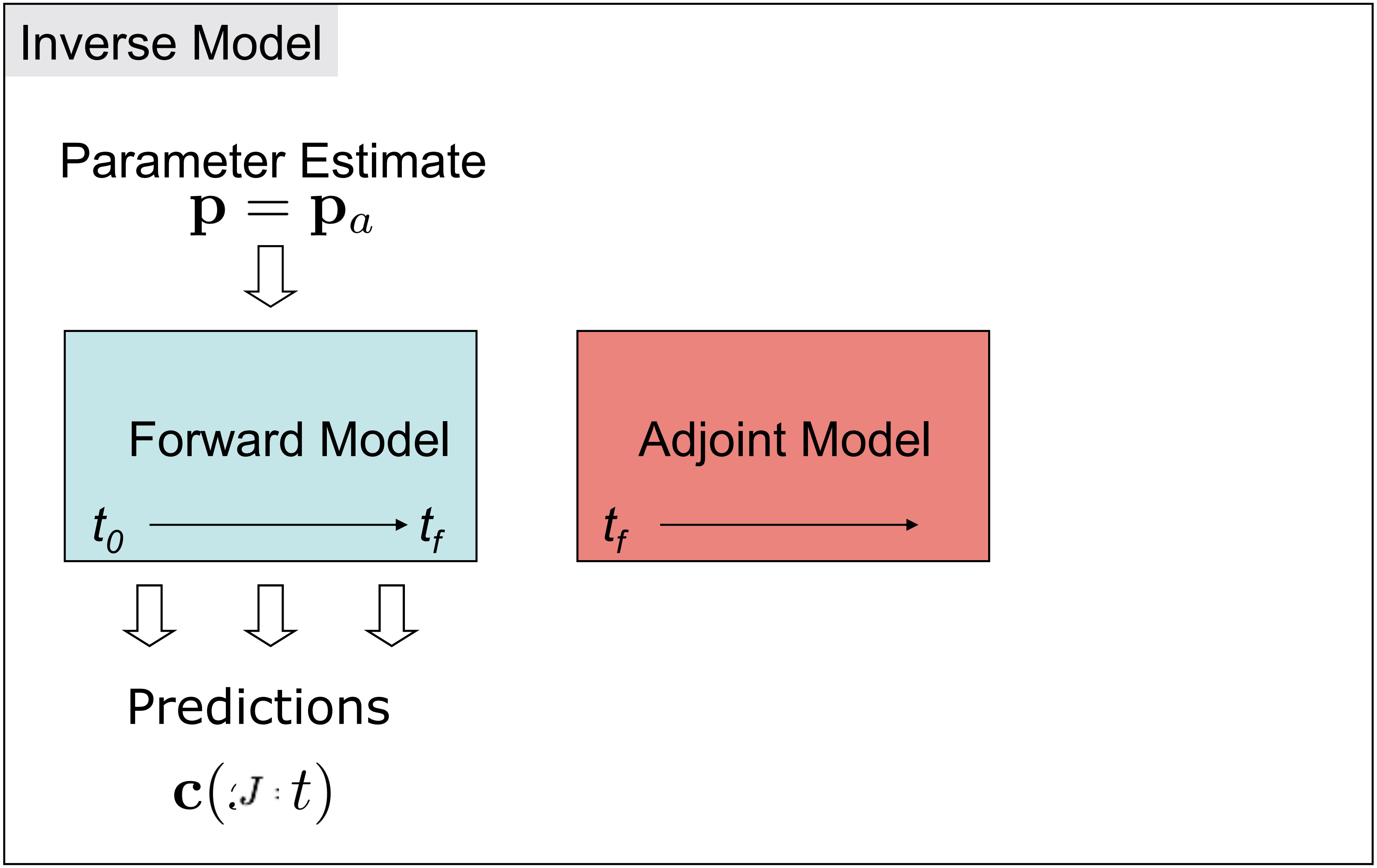
$t_0 \longrightarrow t_f$

Simulated NH_3 field

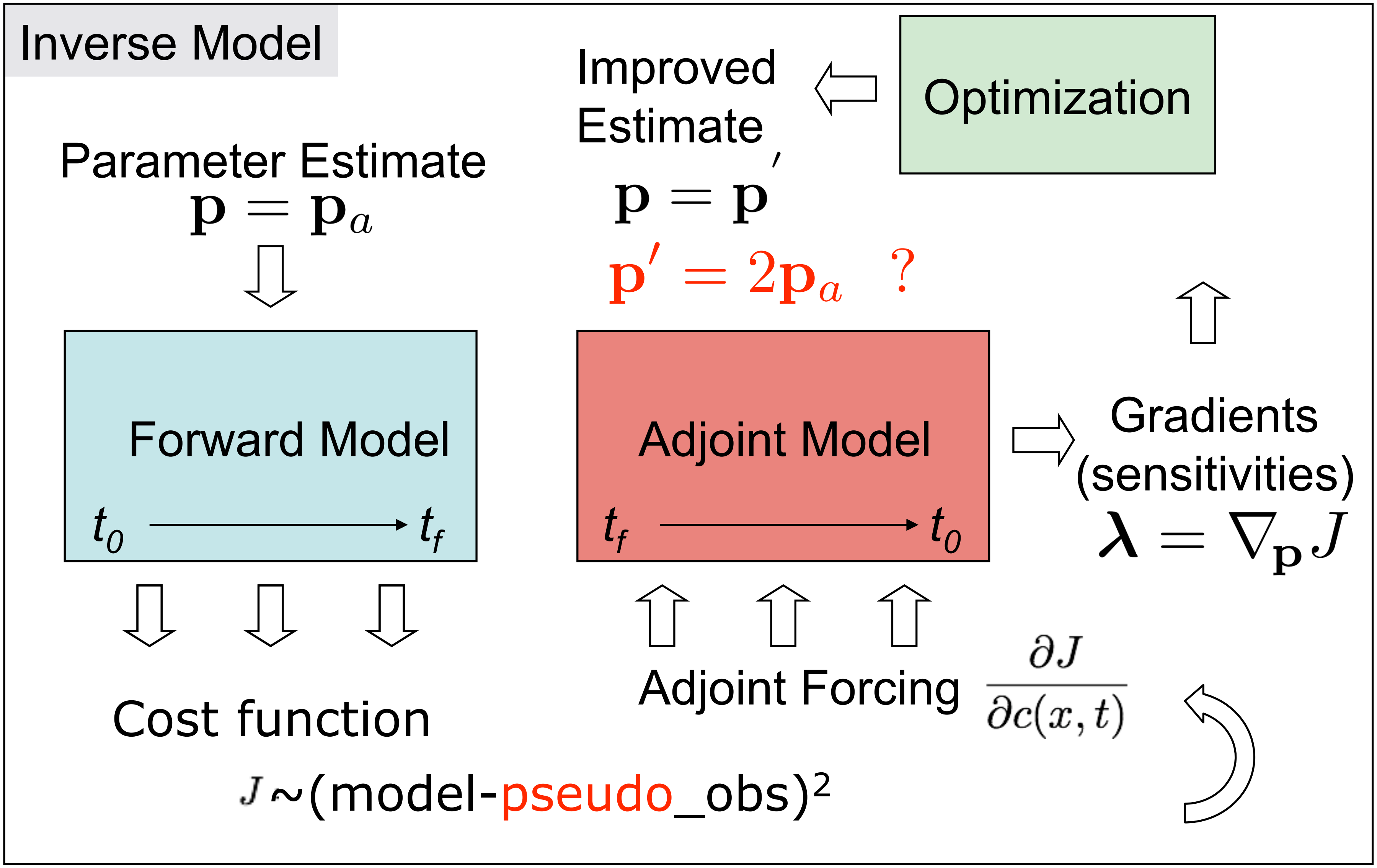
$$\mathbf{c}(x,t)$$

Pseudo retrievals, IMPROVE observations

Inverse Modeling using Adjoint Model

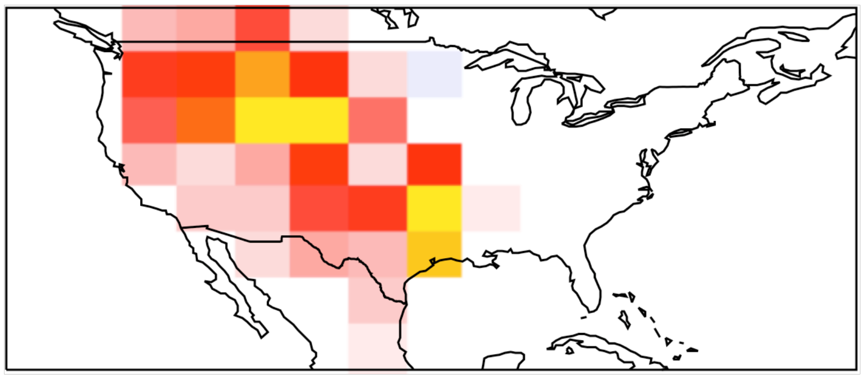


Inverse Modeling using Adjoint Model

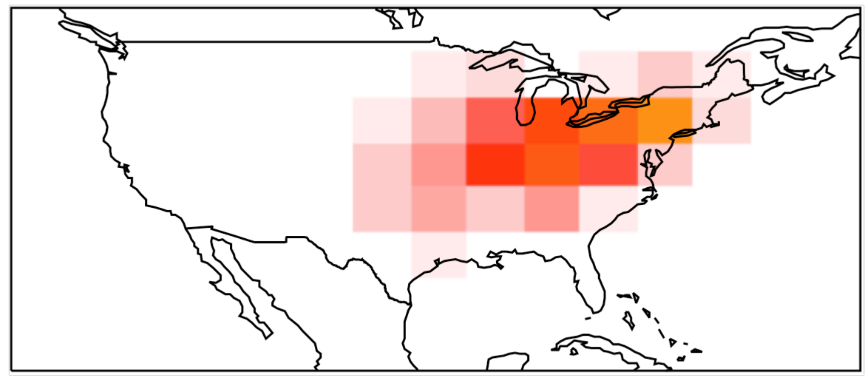


Inverse modeling tests with different obs

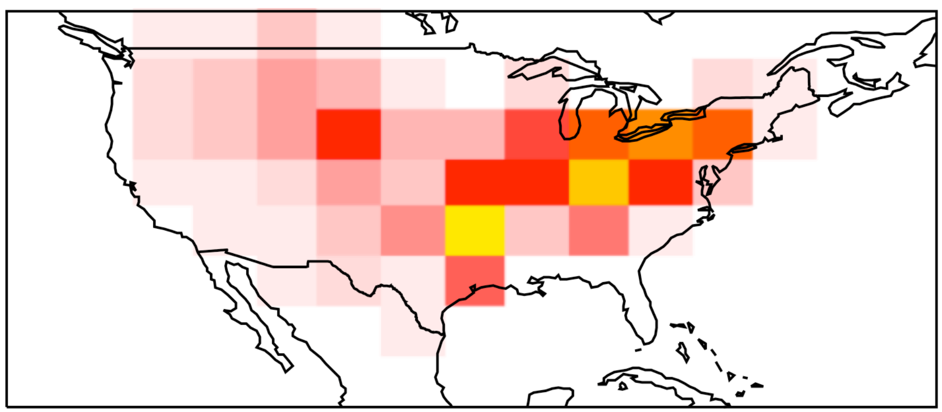
Using TES NH3



Using IMPROVE SO4, NO3



Using both



$$\sigma = ln(p/p_a)$$

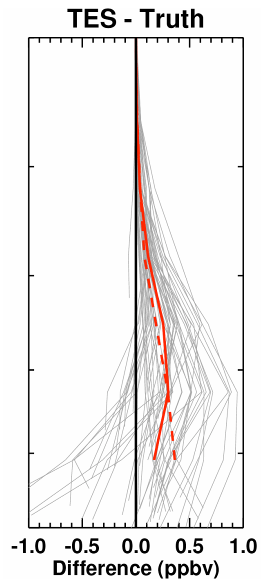
Ongoing efforts

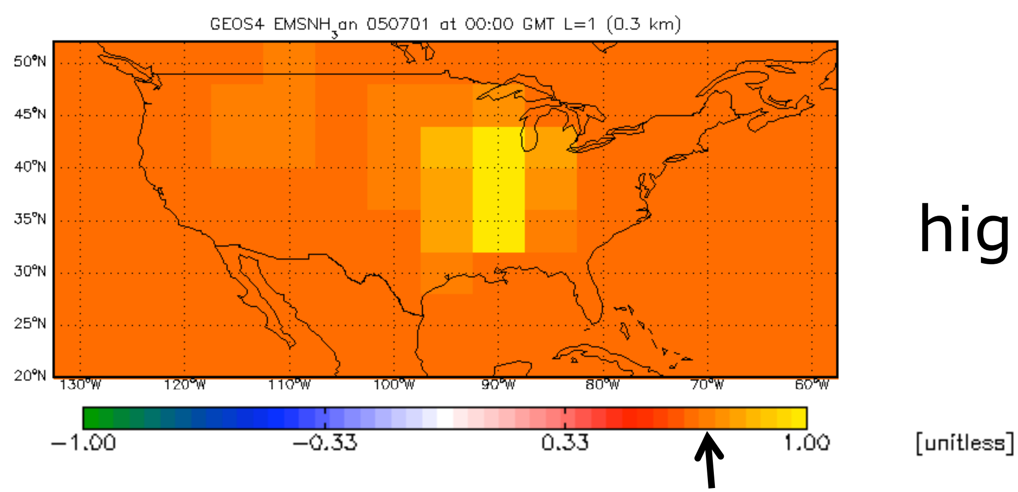
- Model transport bias – use GEOS 3 /4 / 5 met fields

- Intercomparison of TES / in situ obs / CMAQ

- Retrieval bias

    - inversion that starts with doubled emissions





high bias?

Final Remarks

- Remote sensing of NH_3 provides valuable constraints

- Multiple types of gas and aerosol observations required to constrain NH_3 emissions

- Adjoint approach spreads information from NH_3 observations across wide domain

- How well can we constrain magnitudes vs locations? Are we aliasing for bi-directional flux?

the end

Satellite: indirect observations

Arriving at an NH_3 “observation” is an inverse problem itself.

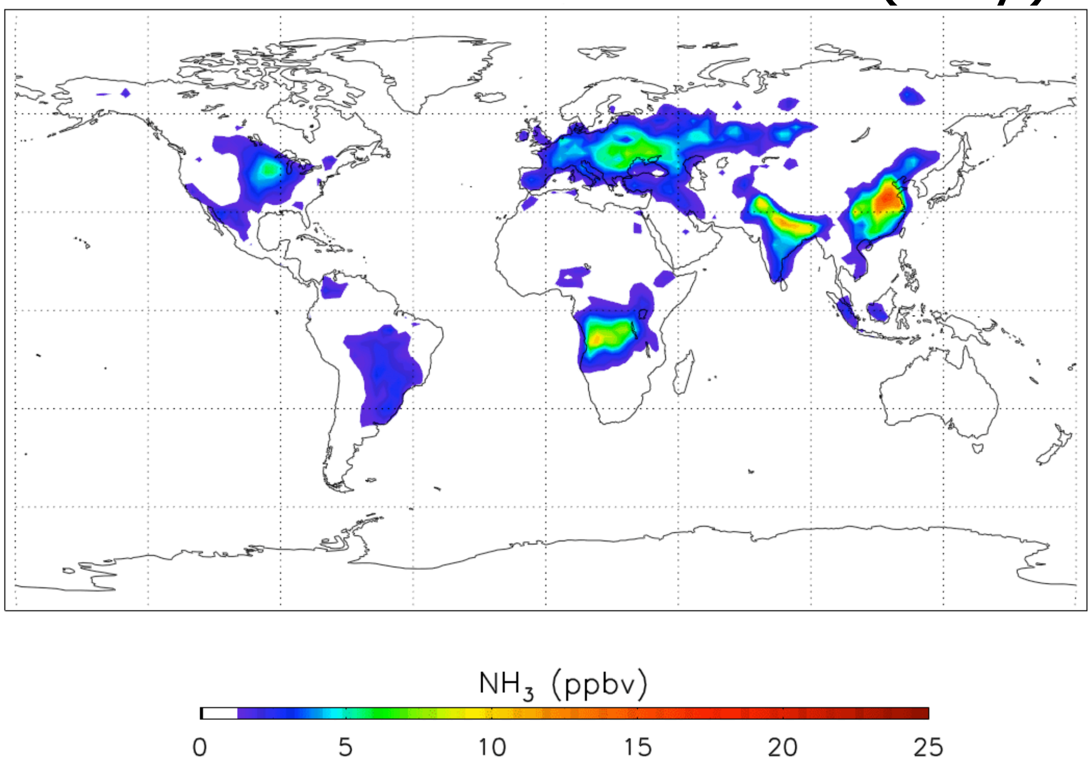
- ill posed (multiple atmospheric states look alike)
- constraints required

Satellite products are a mix of measured and modeled quantities.

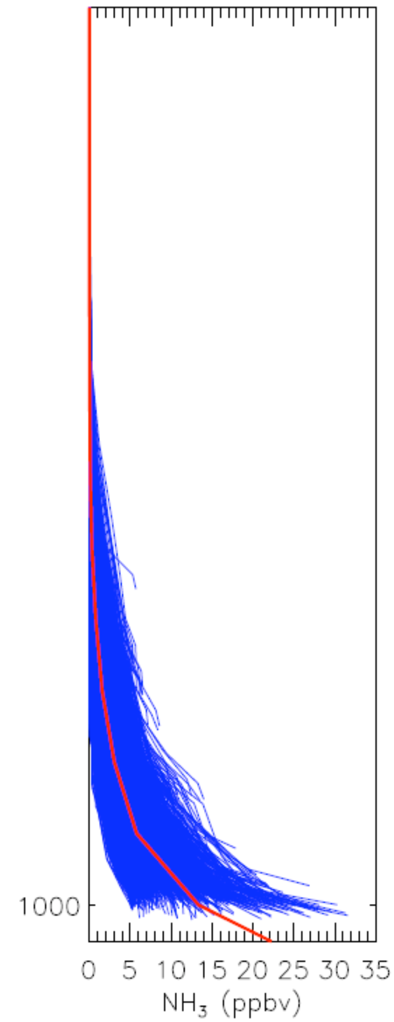
- model estimates used for initial profile
- profile scaled to match observations
- influence of model estimate can be removed

Global modeling support of NH_3 retrievals

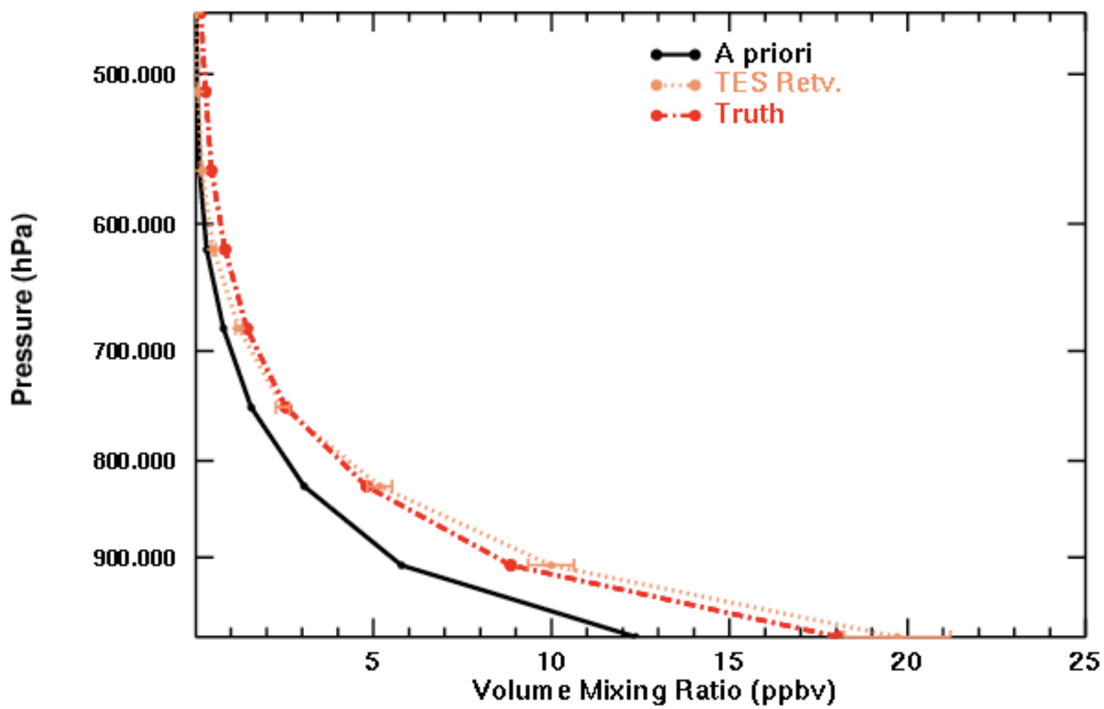
GEOS-Chem surface level (July)

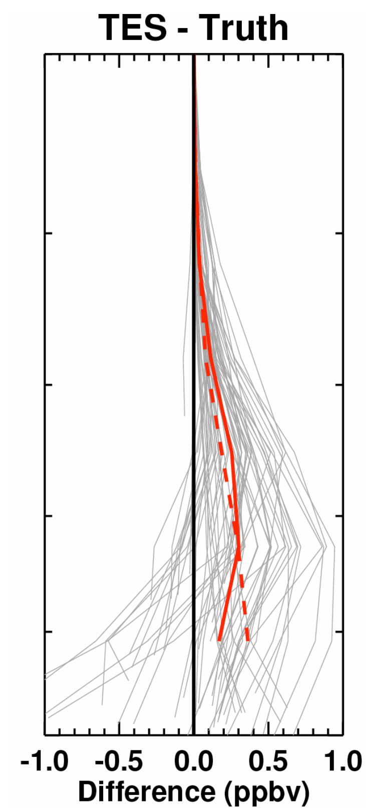


Vertical variance



Retrieval tests: simulated NH_3

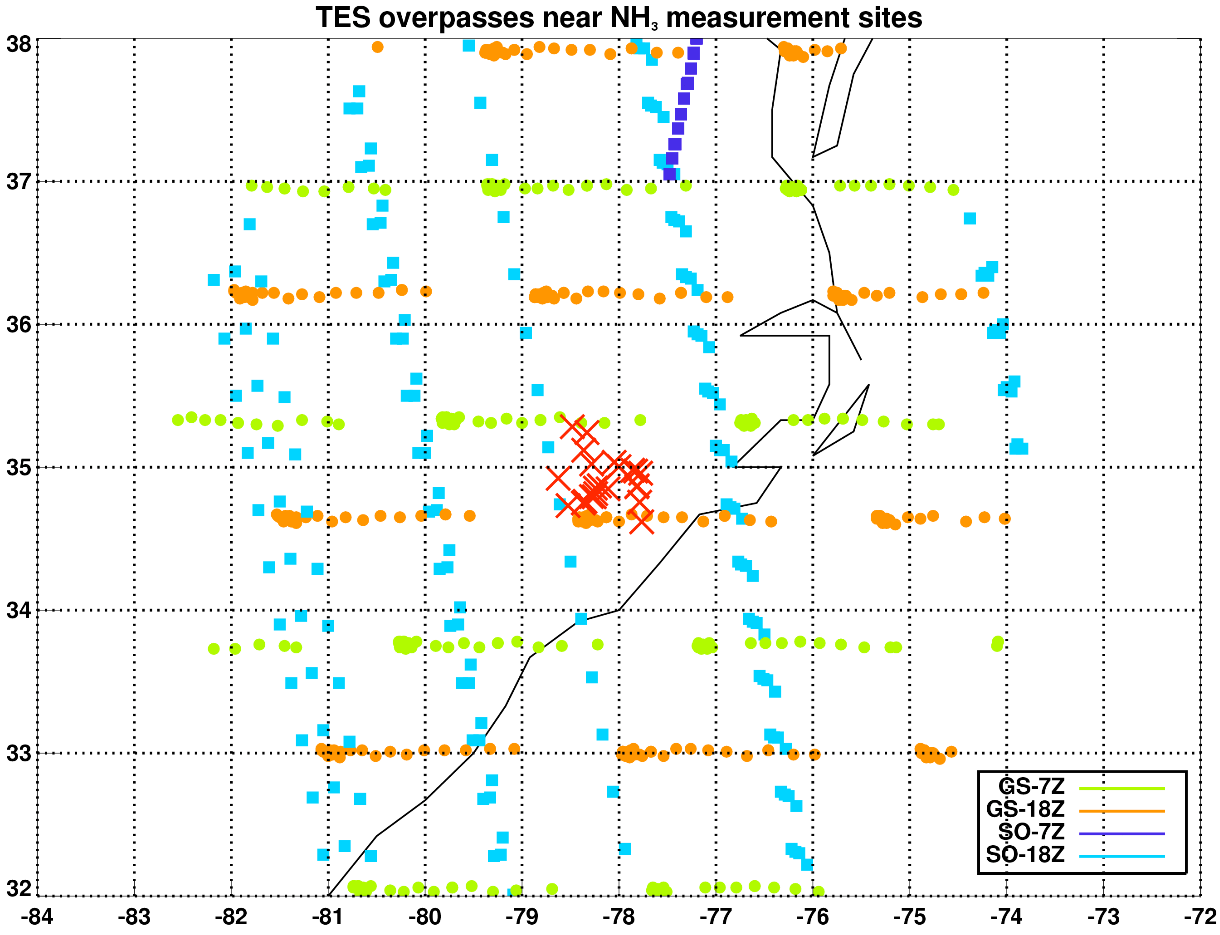




1. Simulate NH3 from a doubled emissions model run
2. Model what TES would see if "doubled" was truth
3. Starting from non-doubled run, can truth be recovered?

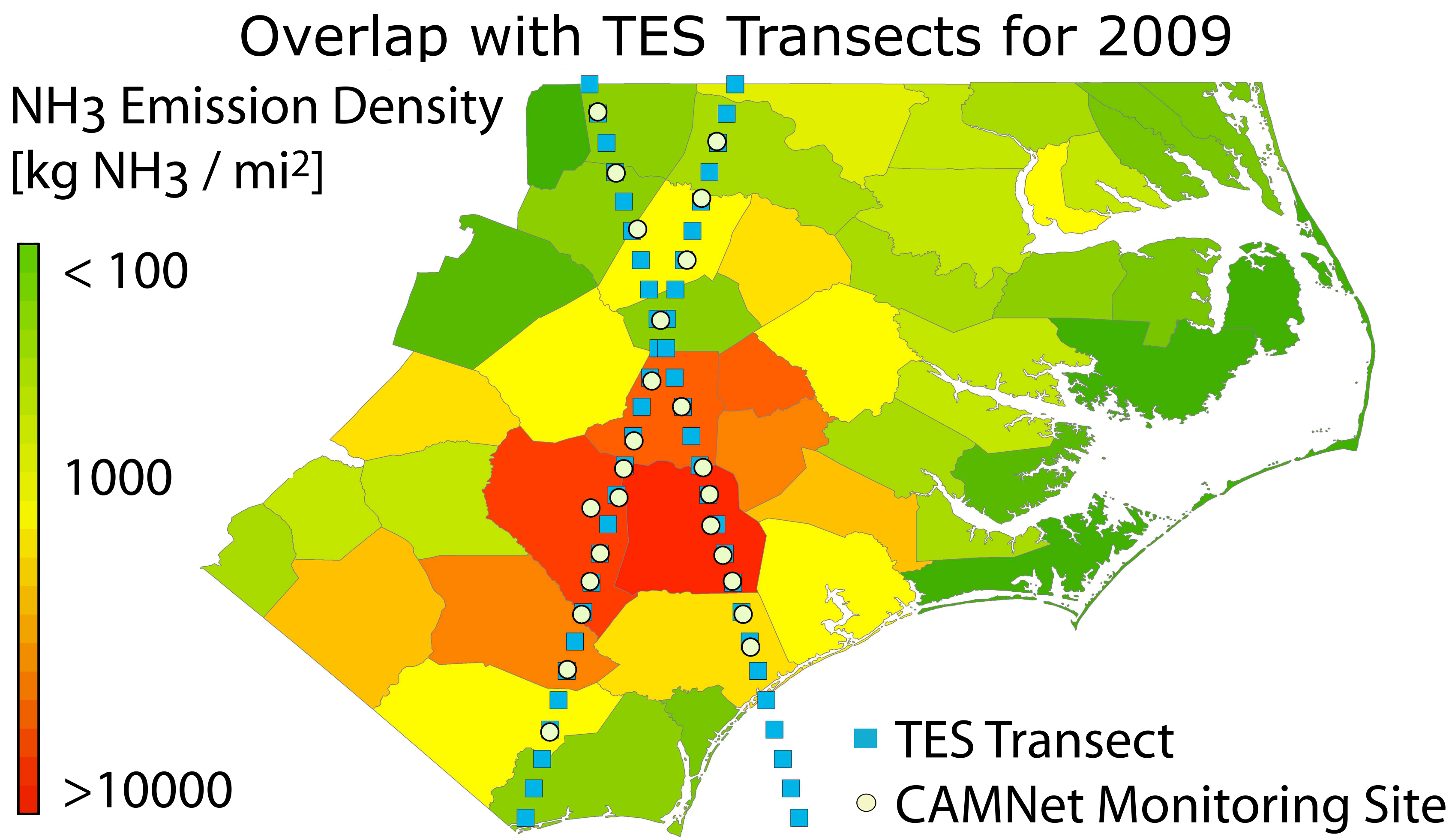
Validating TES NH_3 with surface observations

Standard overlap with North Carolina CAMNet sites



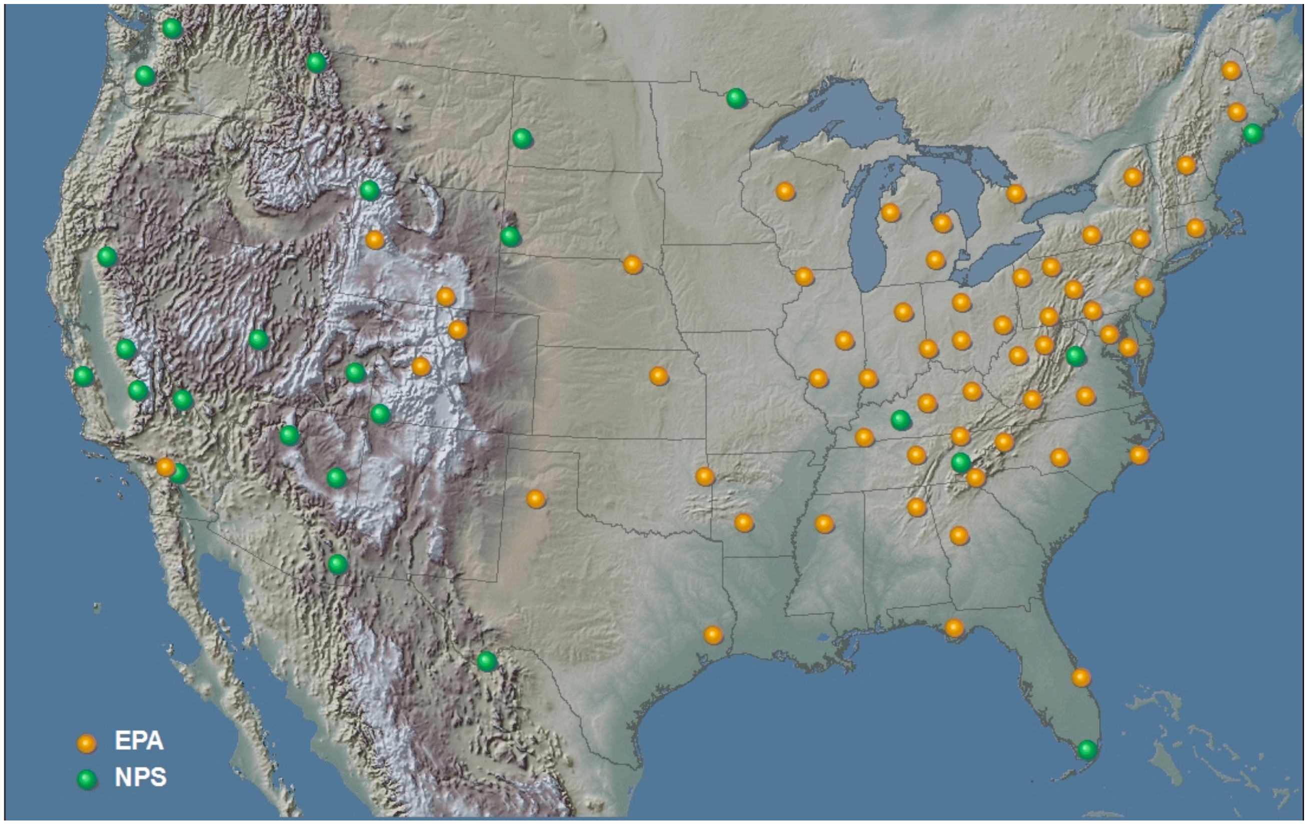
x = CAMNet NH_3 obs (John Walker, EPA)

Validating TES NH_3 with surface observations



NH_4^+ monitoring

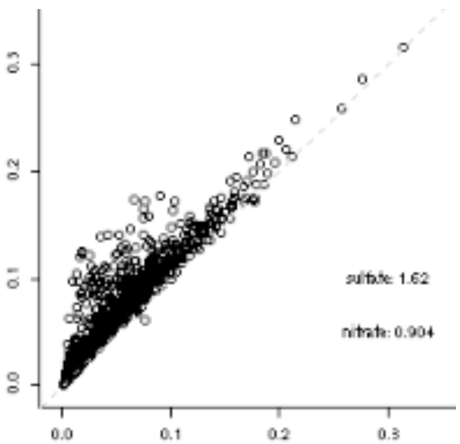
CASTNet



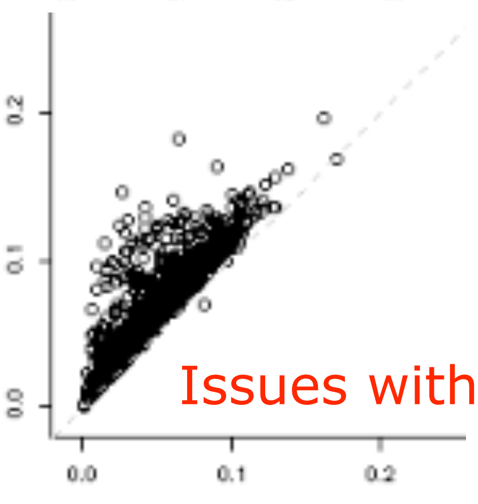
STN: another 200 sites

Checking ion balance: $n(NH_4^+) : 2n(SO_4^{2-}) + n(NO_3^-)$

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



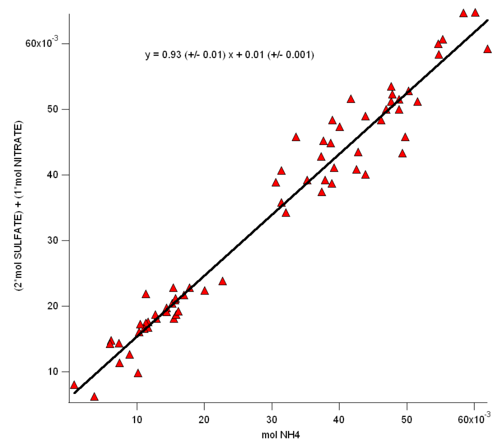
January



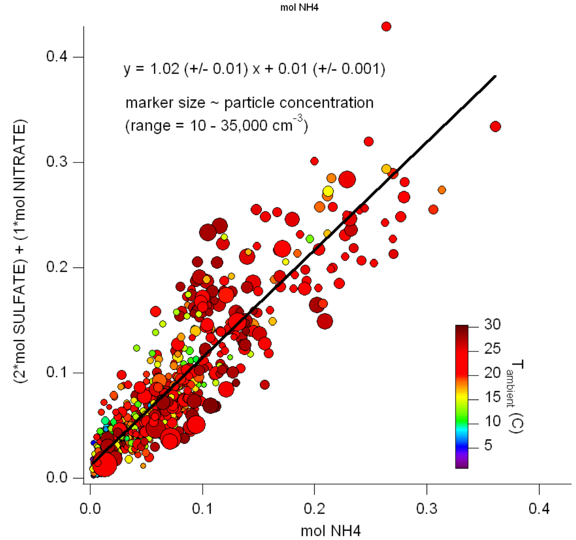
April

Issues with evaporation

Field campaigns (Sorooshian et al.)

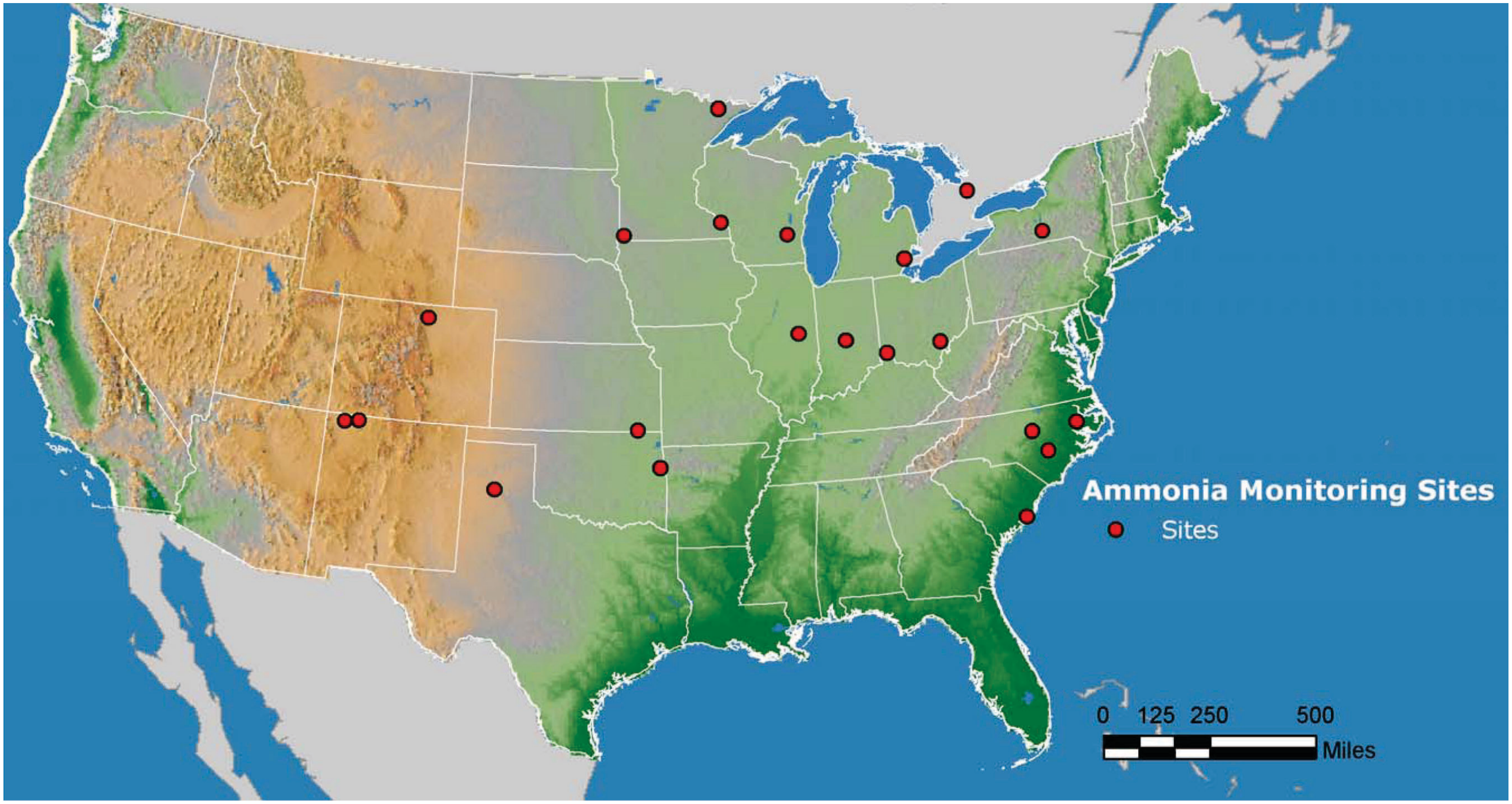


SJ Valley



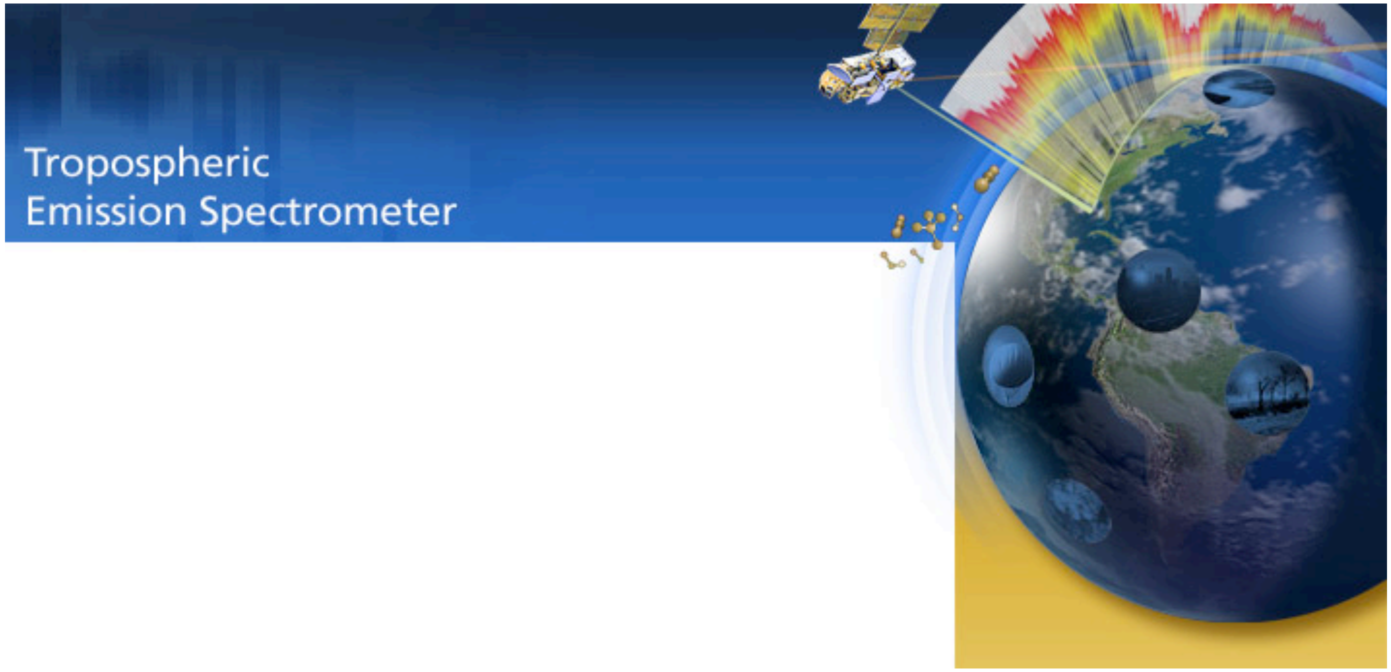
Houston

NH_3 Monitoring Sites



EPA's new AMoN sites (Gary Lear)

New NH_3 observations

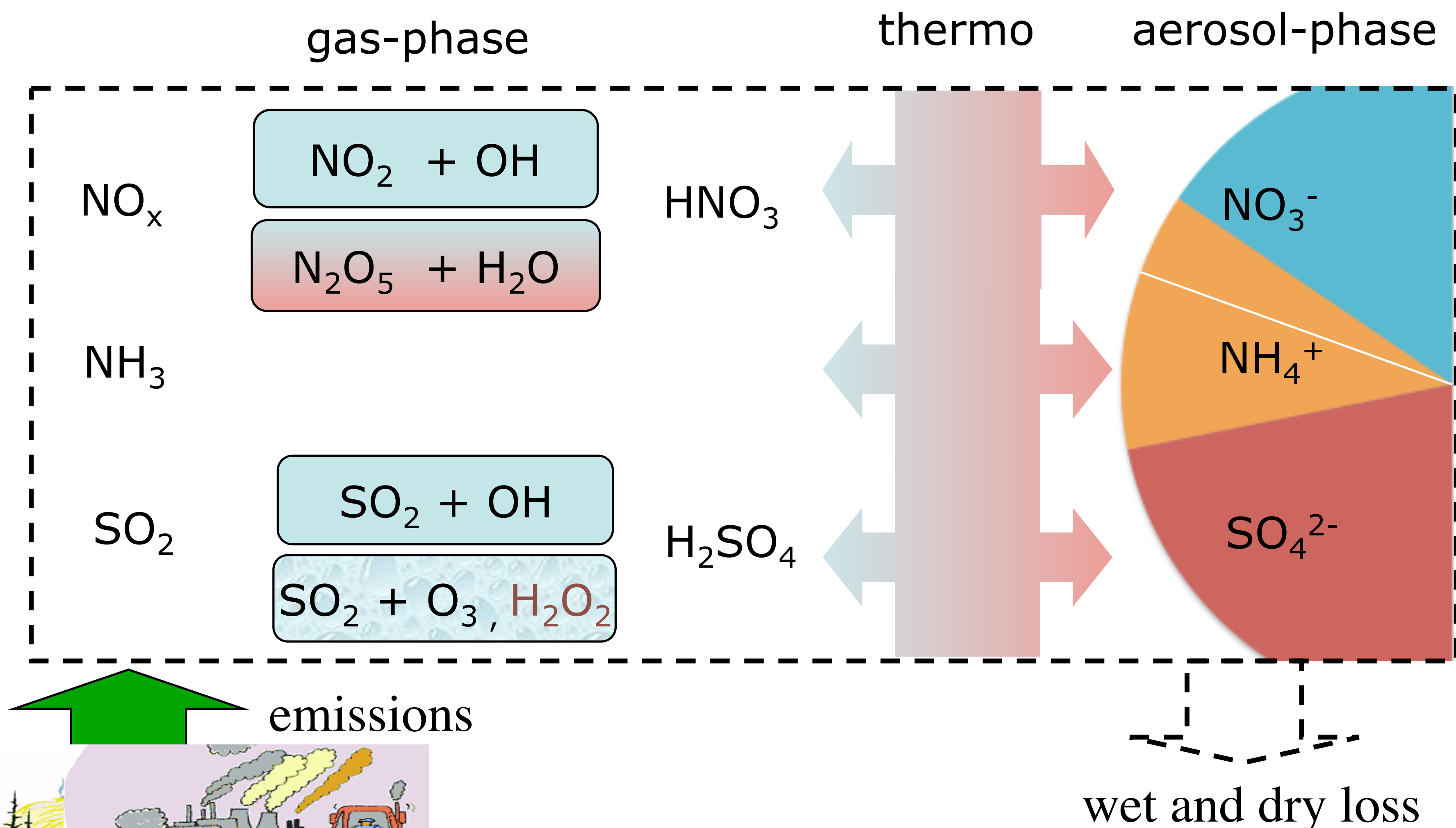


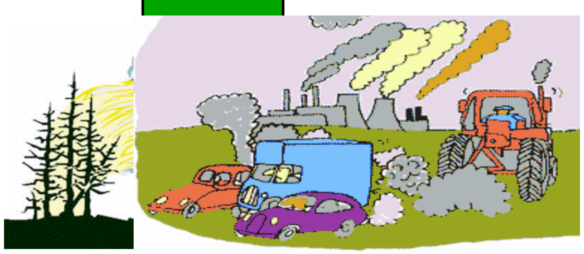
GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L09801, doi:10.1029/2008GL033642, 2008

First satellite observations of lower tropospheric ammonia and methanol

Reinhard Beer,[1] Mark W. Shephard,[2] Susan S. Kulawik,[1] Shepard A. Clough,[3] Annmarie Eldering,[1] Kevin W. Bowman,[1] Stanley P. Sander,[1] Brendan M. Fisher,[1] Vivienne H. Payne,[2] Mingzhao Luo,[1] Gregory B. Osterman,[1] and John R. Worden[1]

Why top-down constraints?





... because direct measurements of NH3 emissions are rare, if not entirely absent

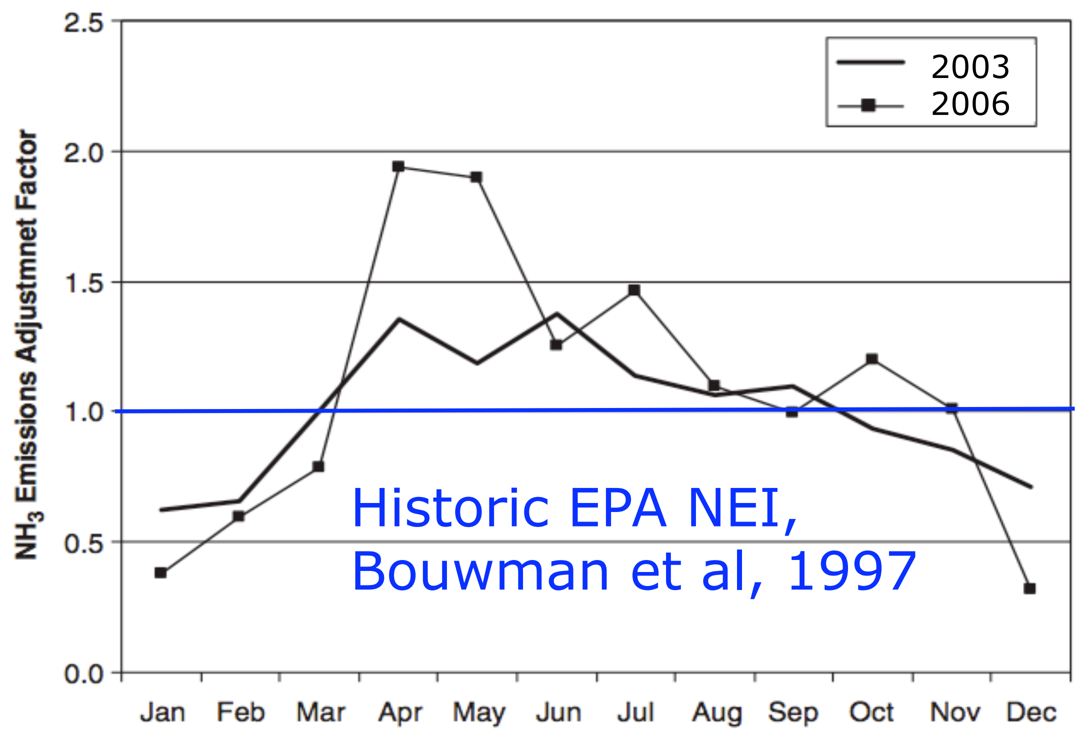
NH_3 inverse modeling: Gilliland et al.

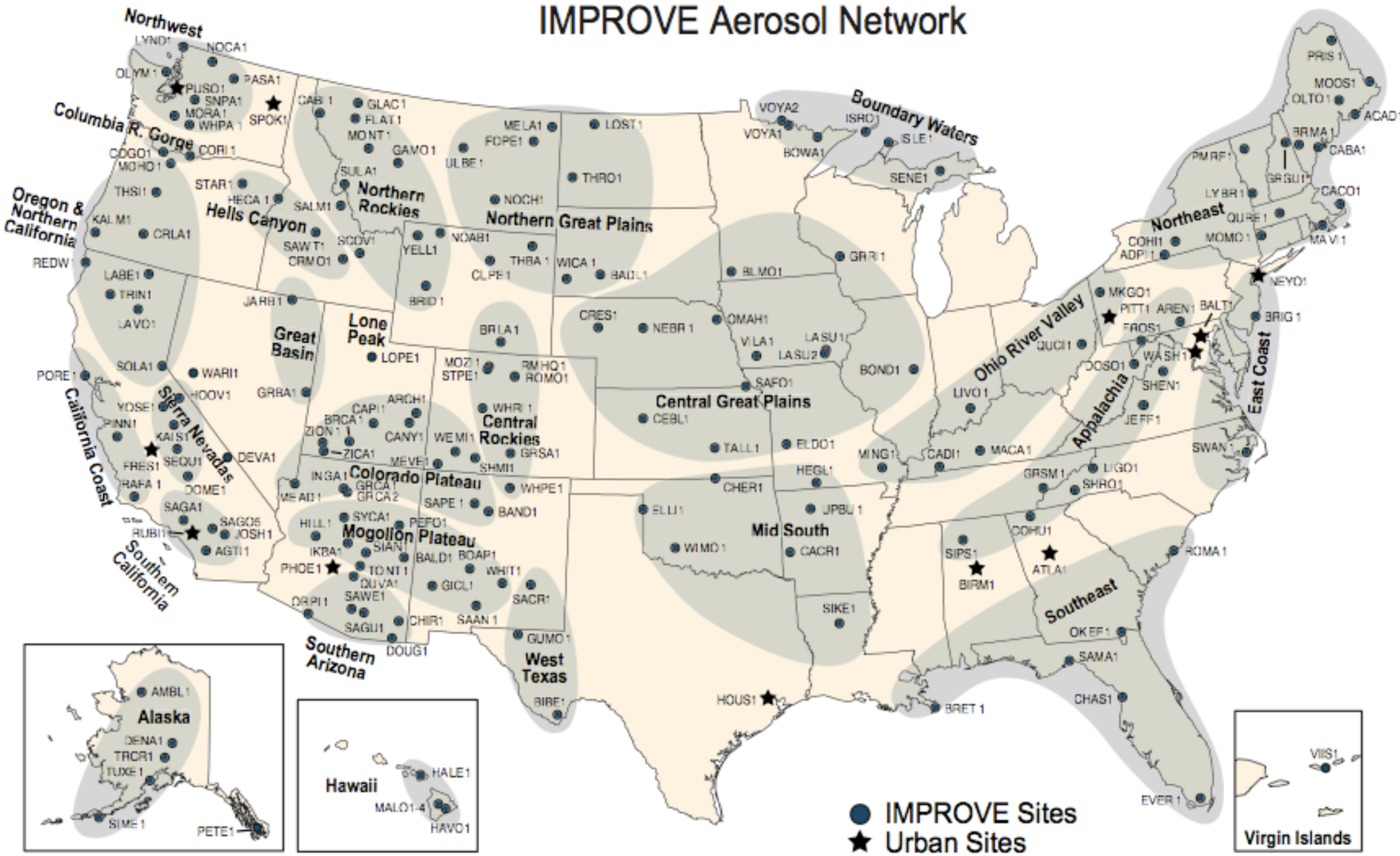
Observations: wet NH_x = aerosol NH_4^+ + gas NH_3

Method: Kalman filter (BF) to adjust monthly nation-wide scale factors

Results:

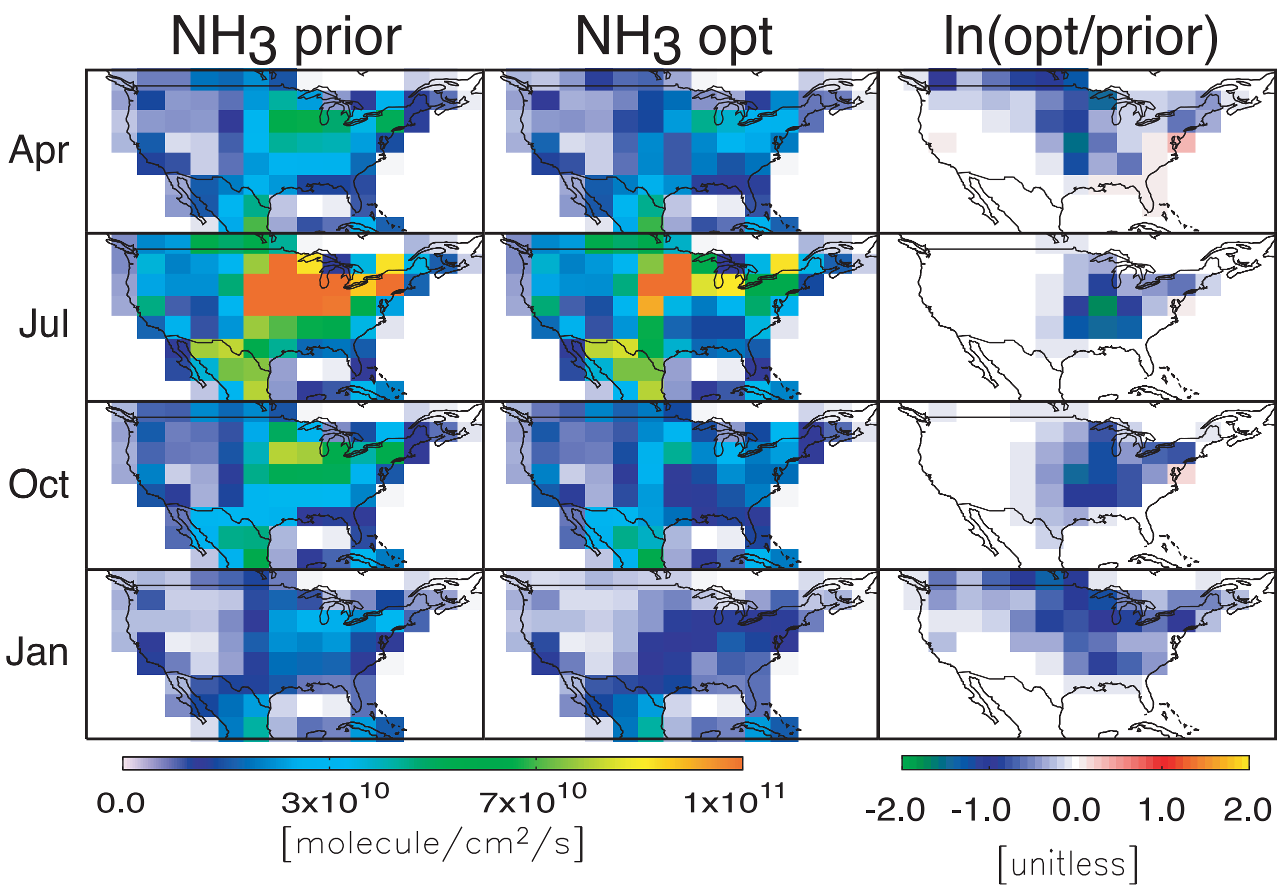
Gilliland et al., 2003;
Gilliland et al., 2006





Measures sulfate and nitrate.

Inverse modeling: anthro NH_3 emissions



- scaling is spatially variable
- scaling generally reductions
- some increases
- Each month treated separately
- reduction in RMSE ≈ 40%

Inverse modeling: assessing the solution

Dependence on inverse modeling assumptions:

- error covariance matrices
- regularization

Estimated uncertainty of solution

- approximate inverse hessian
- std error and correlations

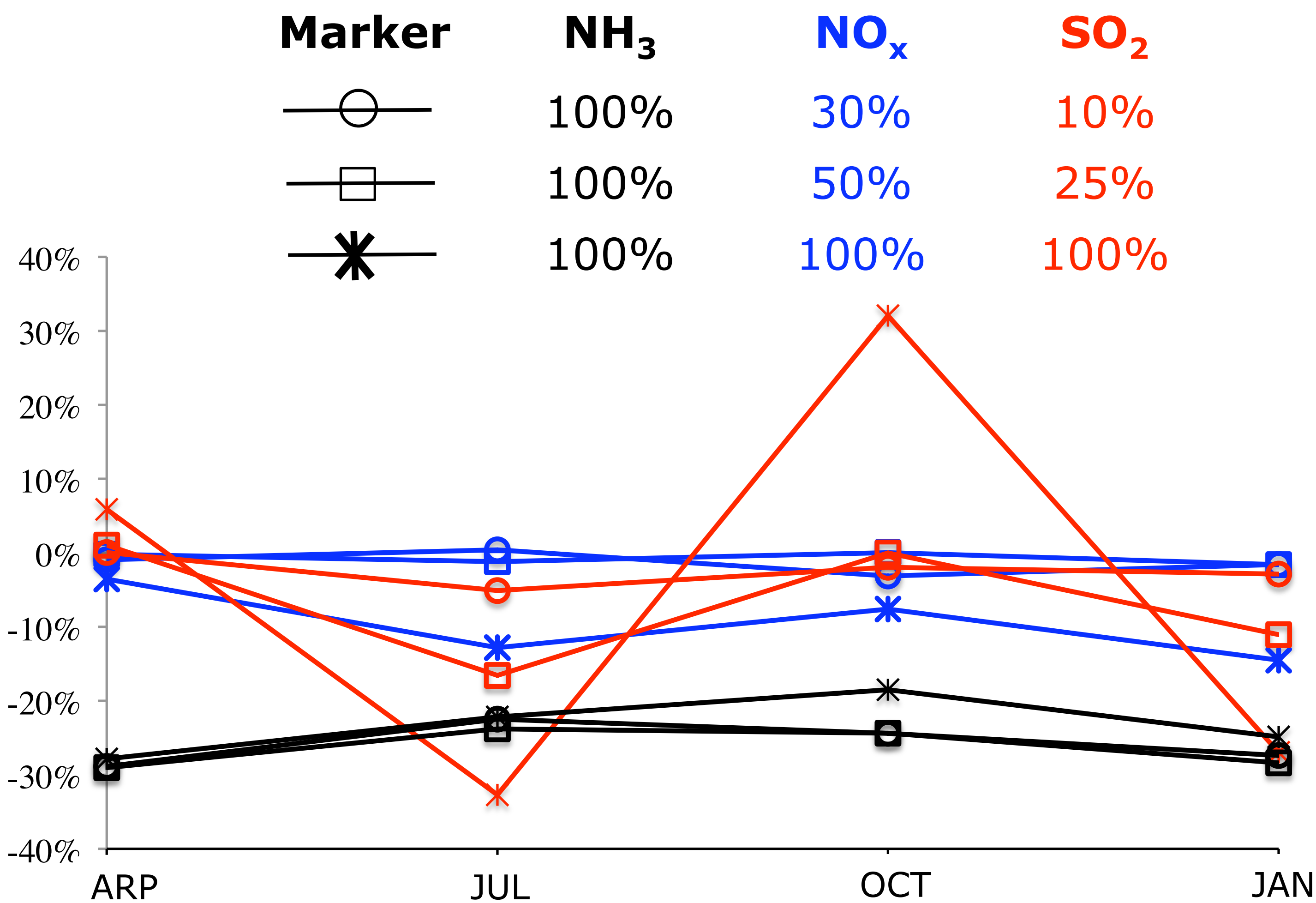
Compare to other studies

- inverse modeling
- bottom up inventories

Compare to NH_3 observations

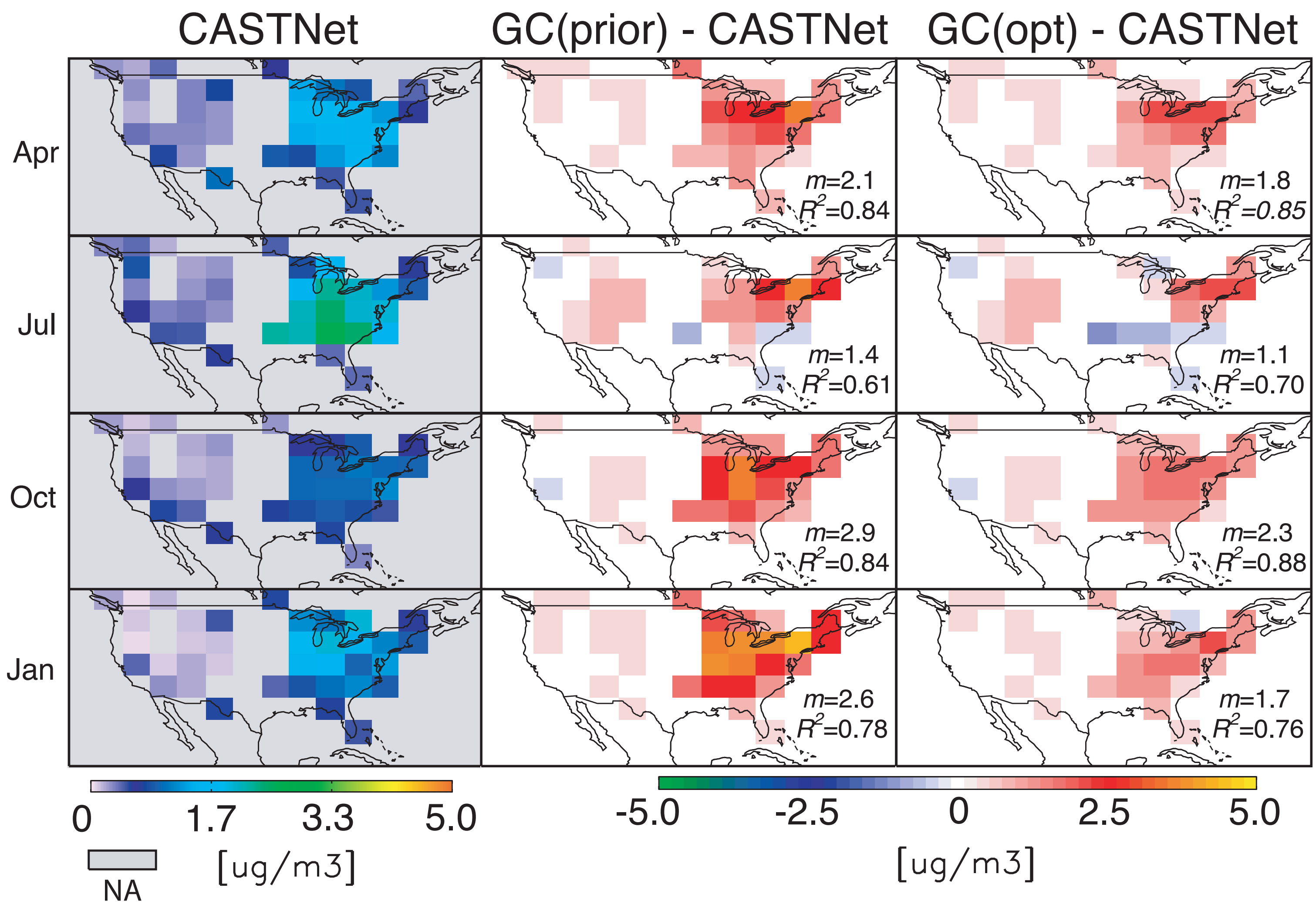
Inverse modeling: variable constraints

Repeat inversions with different emissions error estimates:



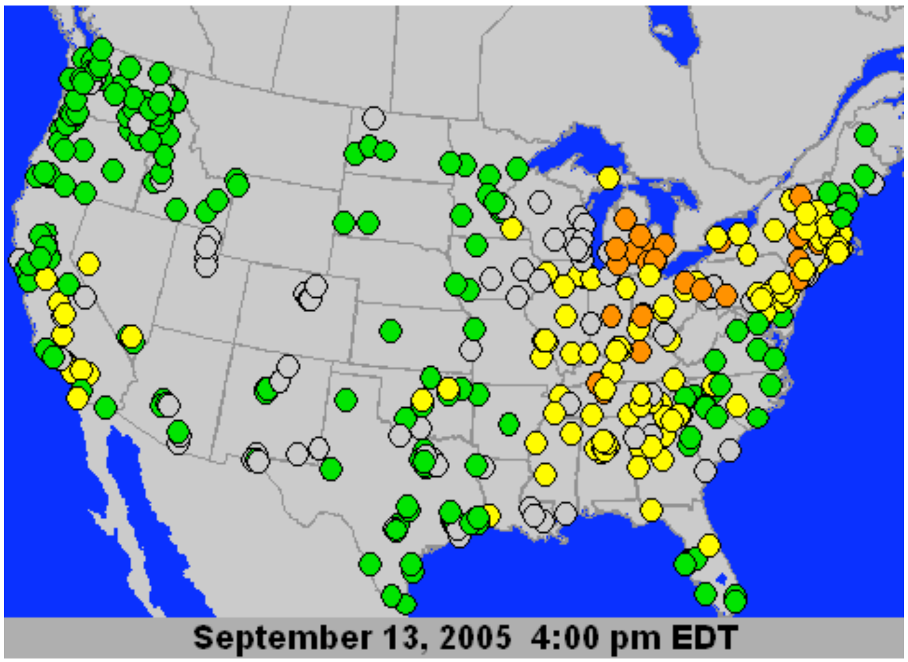
NH_3, and to lesser extent, NO_x, emissions estimates fairly invariant

Inverse: comparison to CASTNet NH_4^+

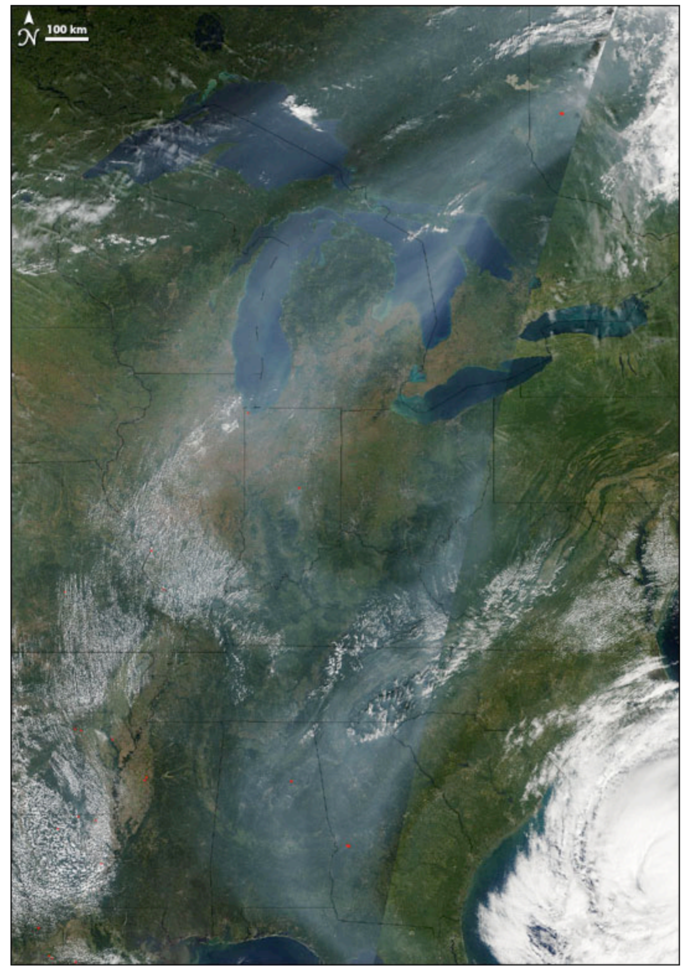


Air Pollution: Continental PM

EPA AIRNow



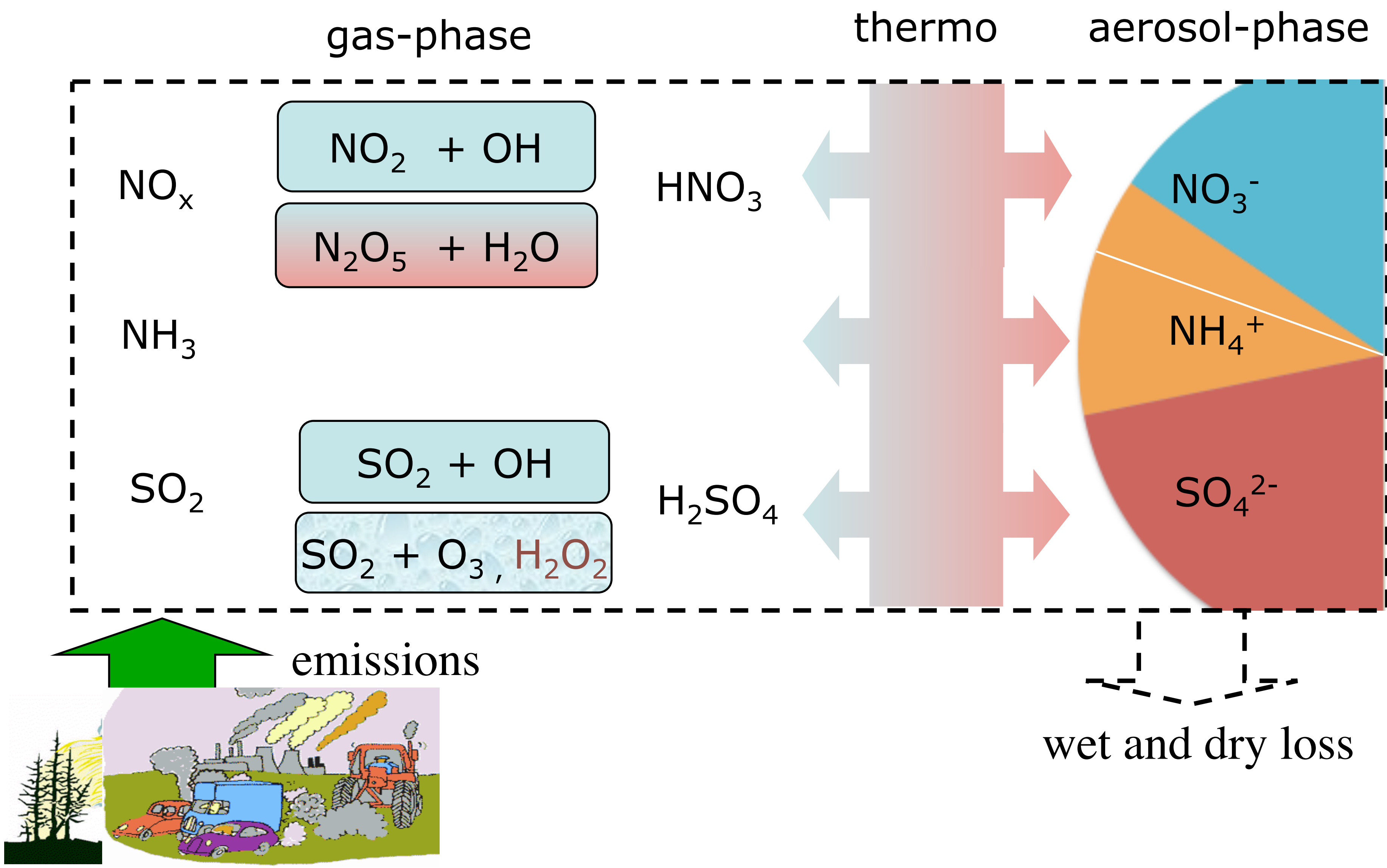
MODIS (TERRA)



September 11, 2005

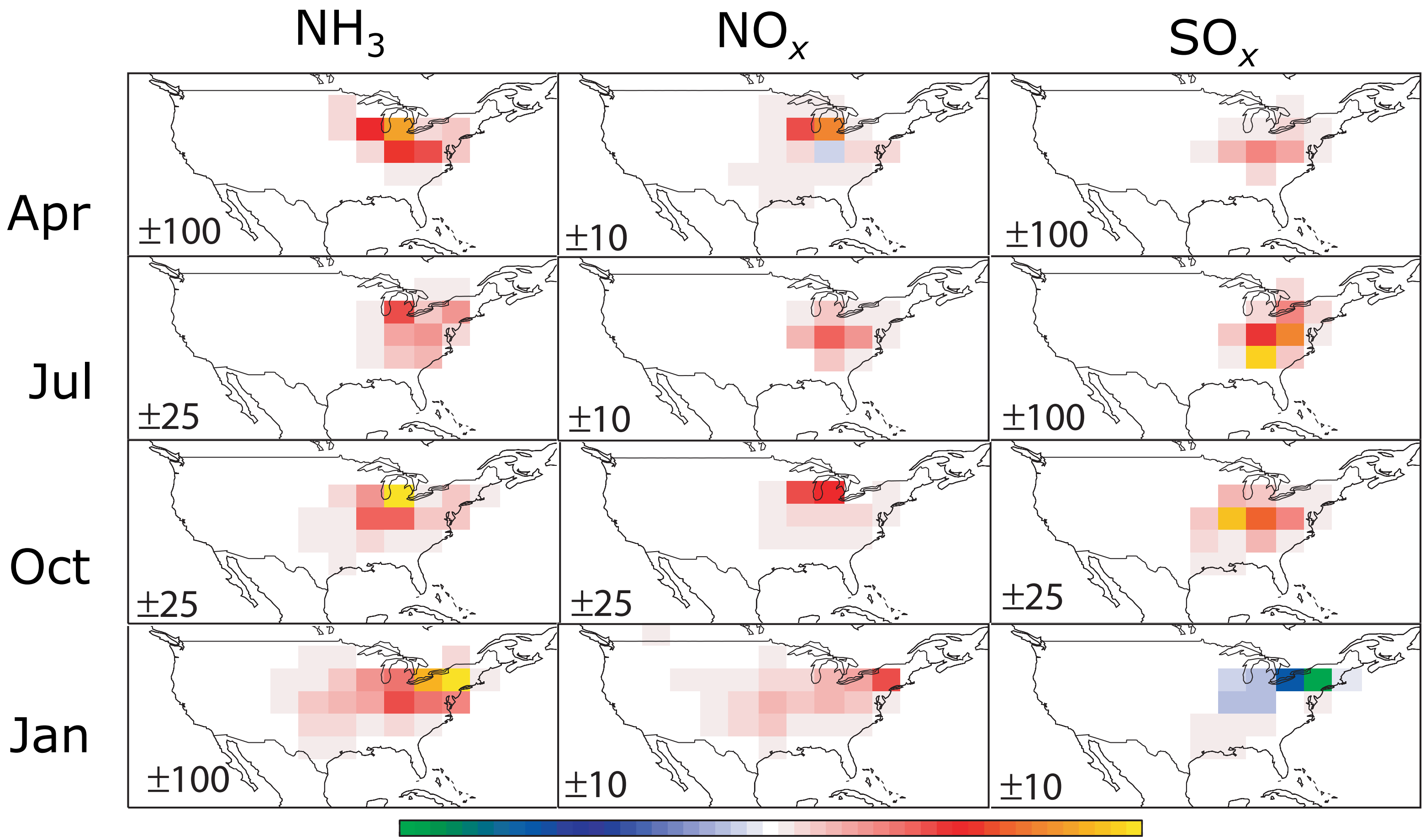
(smog blog, NASA's visible earth)

Secondary inorganic aerosol formation



AQ Attainment: seasonal variability

Seasonal variation in control effectiveness:



Ansari and Pandis, 1998; West et al., 1999; Vayenas et al., 2005; Pinder et al., 2007

Effectiveness of emissions controls have critical spatial, seasonal, sector and chemical variability

$(NH_4^+)_2SO_4^{2-}$ (mw = 132) → $2NH_4^+NO_3^-$ (mw = 2x80)

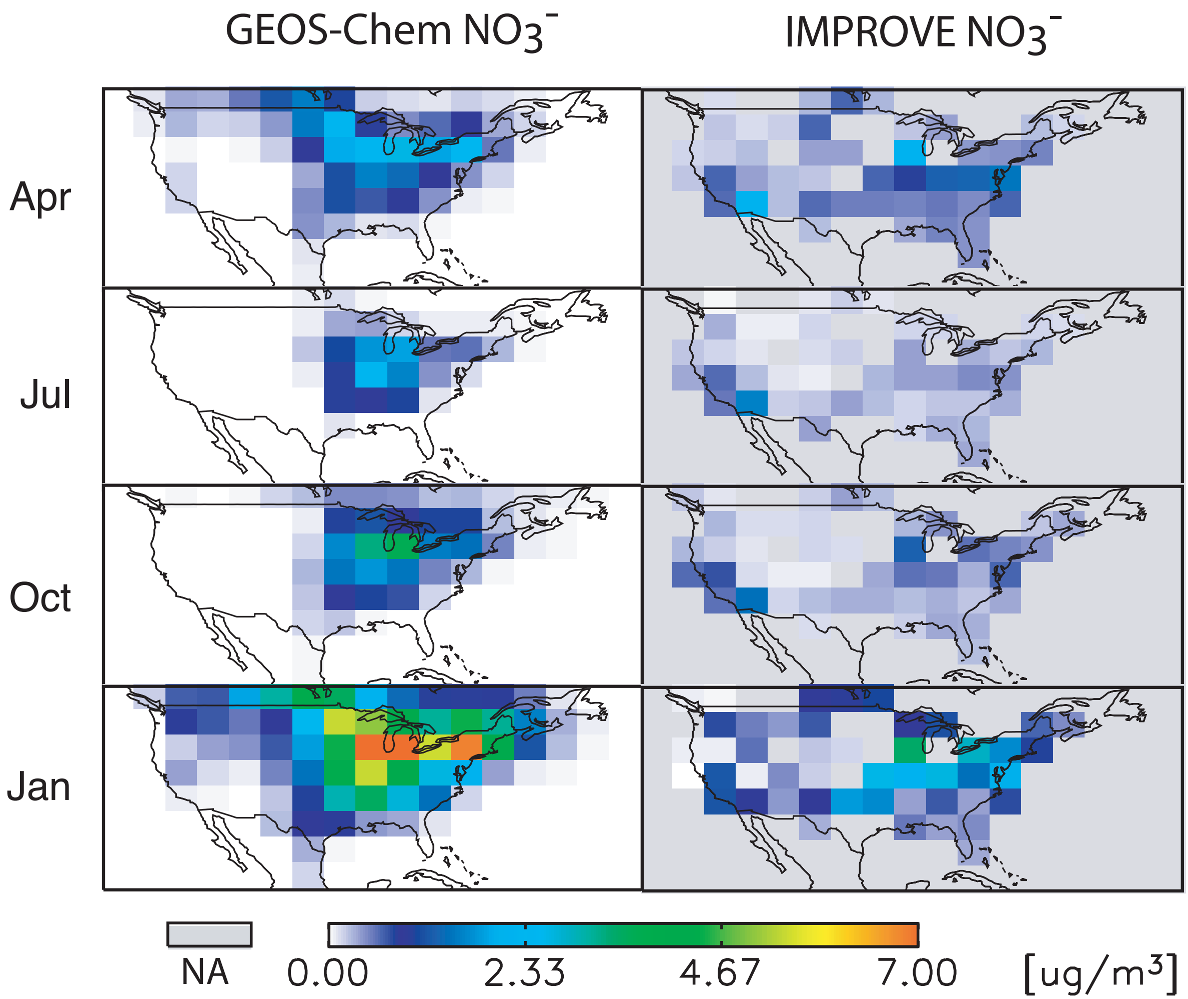
Why study NH_3 emissions?

Health impacts of PM2.5, air quality control

Environmental impacts

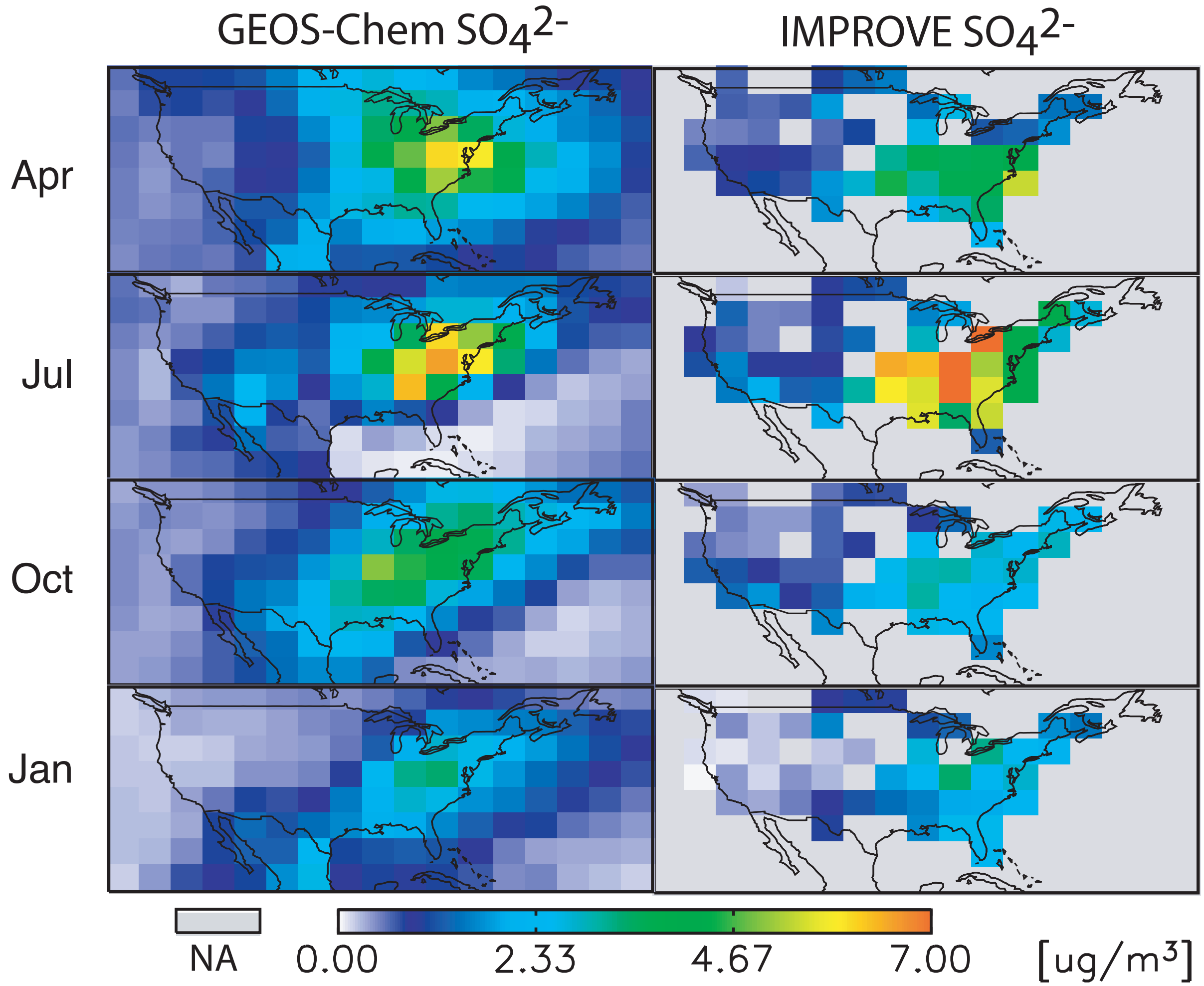
A large source of uncertainty

GEOS-Chem vs IMPROVE: nitrate

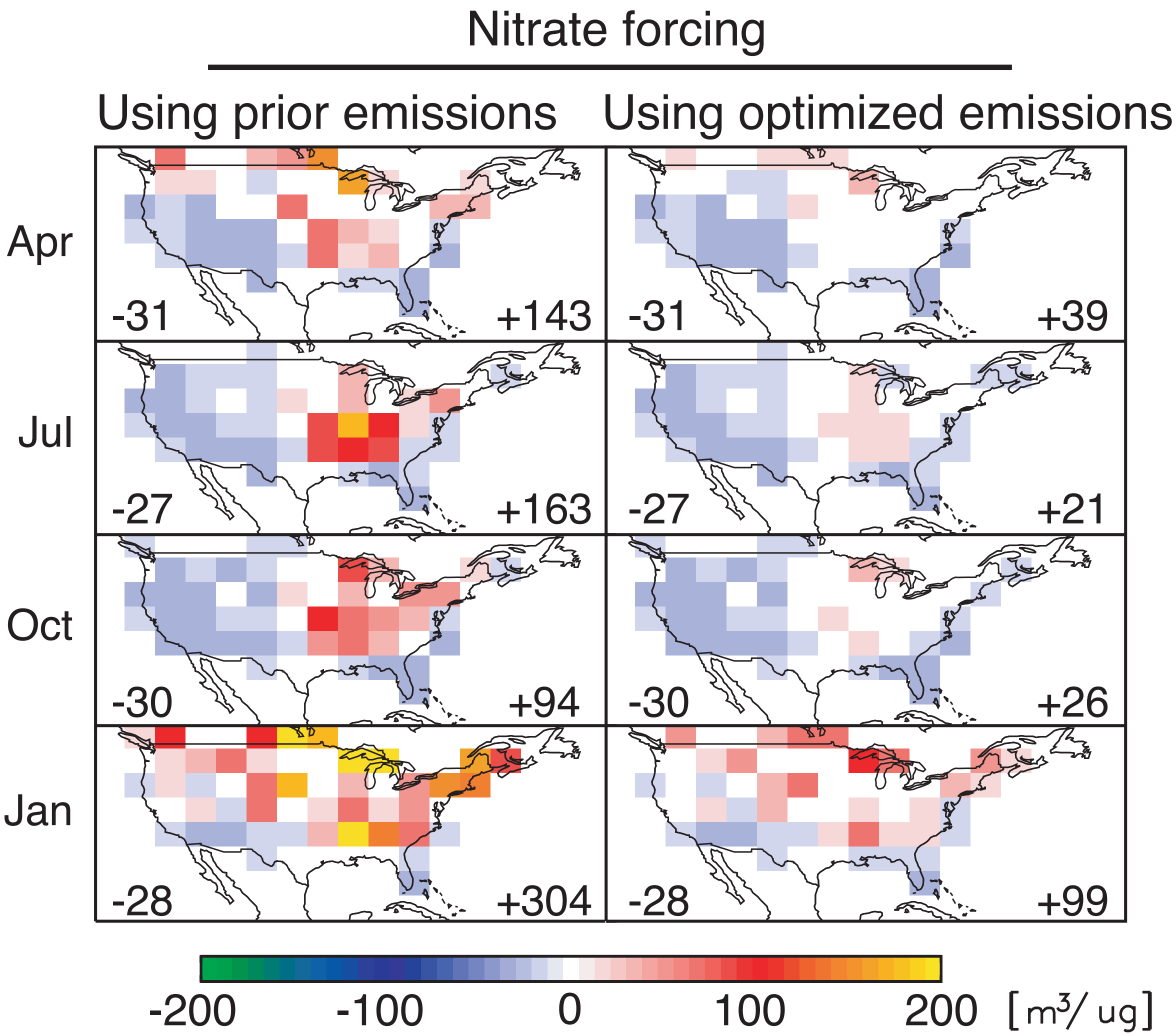


nitrate problematic: Park et al., (2004,2006), Liao et al. (2007), Pye et al. (2008)

GEOS-Chem vs IMPROVE: sulfate



Inverse modeling: reduction in error



$$\frac{\partial J}{\partial Hc} = (Hc - c_{obs})^T \mathbf{S}_{obs}^{-1}$$

= "forcing"

- #'s in corner are min/max of forcing
- Each month treated separately
- reduction in RMSE ≈ 40%

Importance of studying NH_3 emissions

PM2.5

- Itself leads to NH_4^+, 10-20% of $PM_{2.5}$ mass concentration
- Governs formation of NO_3^-, which can be 20-30% in winter

PM2.5 NAAQS Regulations

- Not a presumptively regulated species, but can be very efficient (Pinder et al., 2007; Henze et al., 2008)
- Can be regulated in place of SO_2 or NO_2

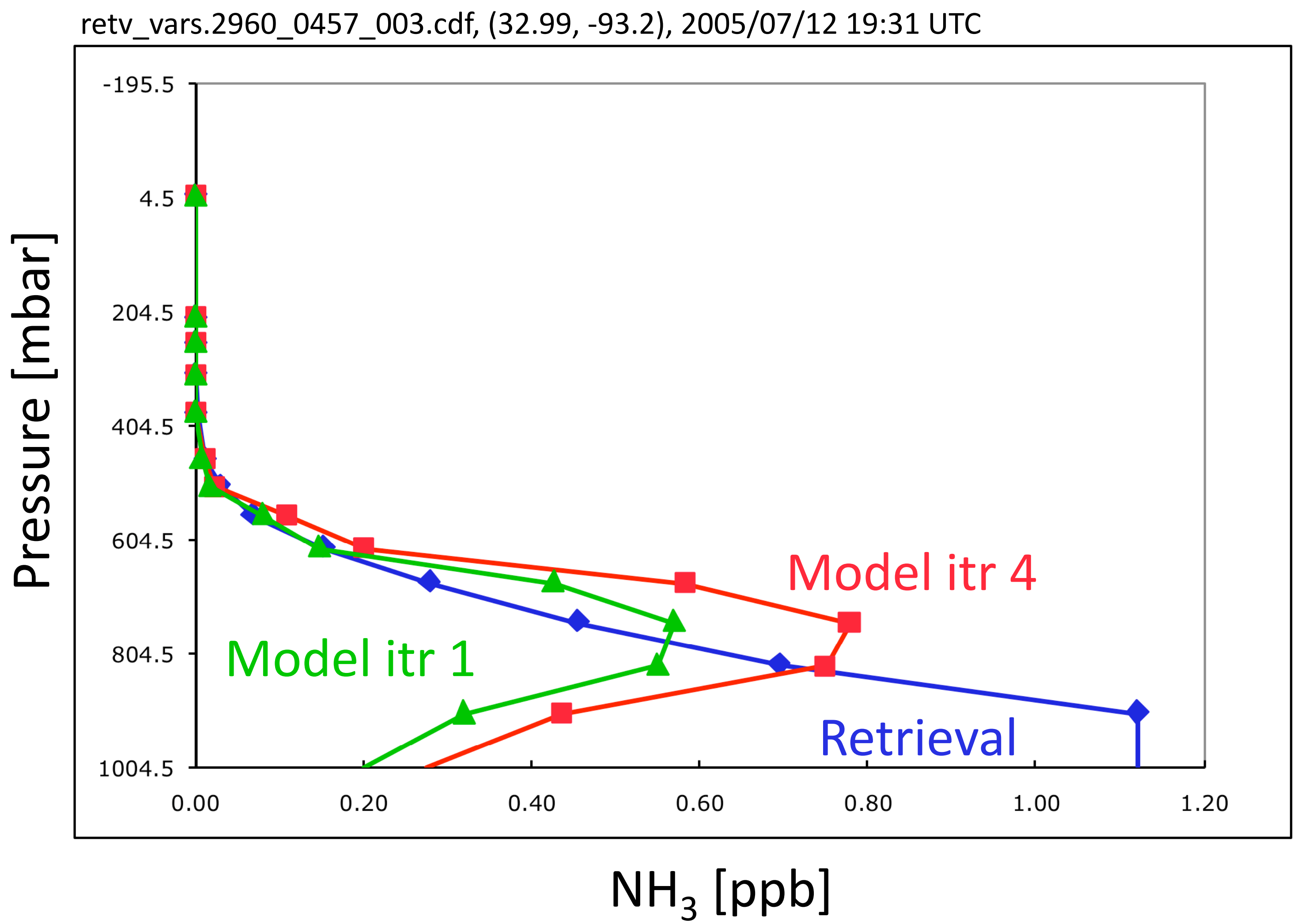
Ecosystem impacts

- 11% of worlds natural vegitation impacted by N dep (Dentener et al., 2006)
- N dep will increase 10-40% near NH_3 sources in U.S. by 2020 (Pinder et al., 2008)

Very large source of uncertainty

- estimating U.S. inorganic $PM_{2.5}$ levels (Yu et al., 2005; Simon et al., 2008)
- global N dep. (Sutton et al., 2007)

Inverse modeling: impact on profile estimates compared to pseudo retrieval. After only 4 iterations (would usually do about 20)



Inverse modeling: cost function

Define a cost function (want to minimize):

$$\mathcal{J} = \underbrace{\frac{1}{2}\sum_{\mathbf{c}\in\Omega}(H\mathbf{c}-\mathbf{c}_{obs})^T\mathbf{S}_{obs}^{-1}(H\mathbf{c}-\mathbf{c}_{obs})}_{\text{"error"}} + \underbrace{\frac{1}{2}\gamma_r(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)^T\mathbf{S}_a^{-1}(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)}_{\text{"penalty term"}}$$

where

$\mathbf{c}$ = Model predictions

Ω = Domain of observations

$\mathbf{S}^{-1}$ = Error covariance matrices

γ_r = Regularization parameter

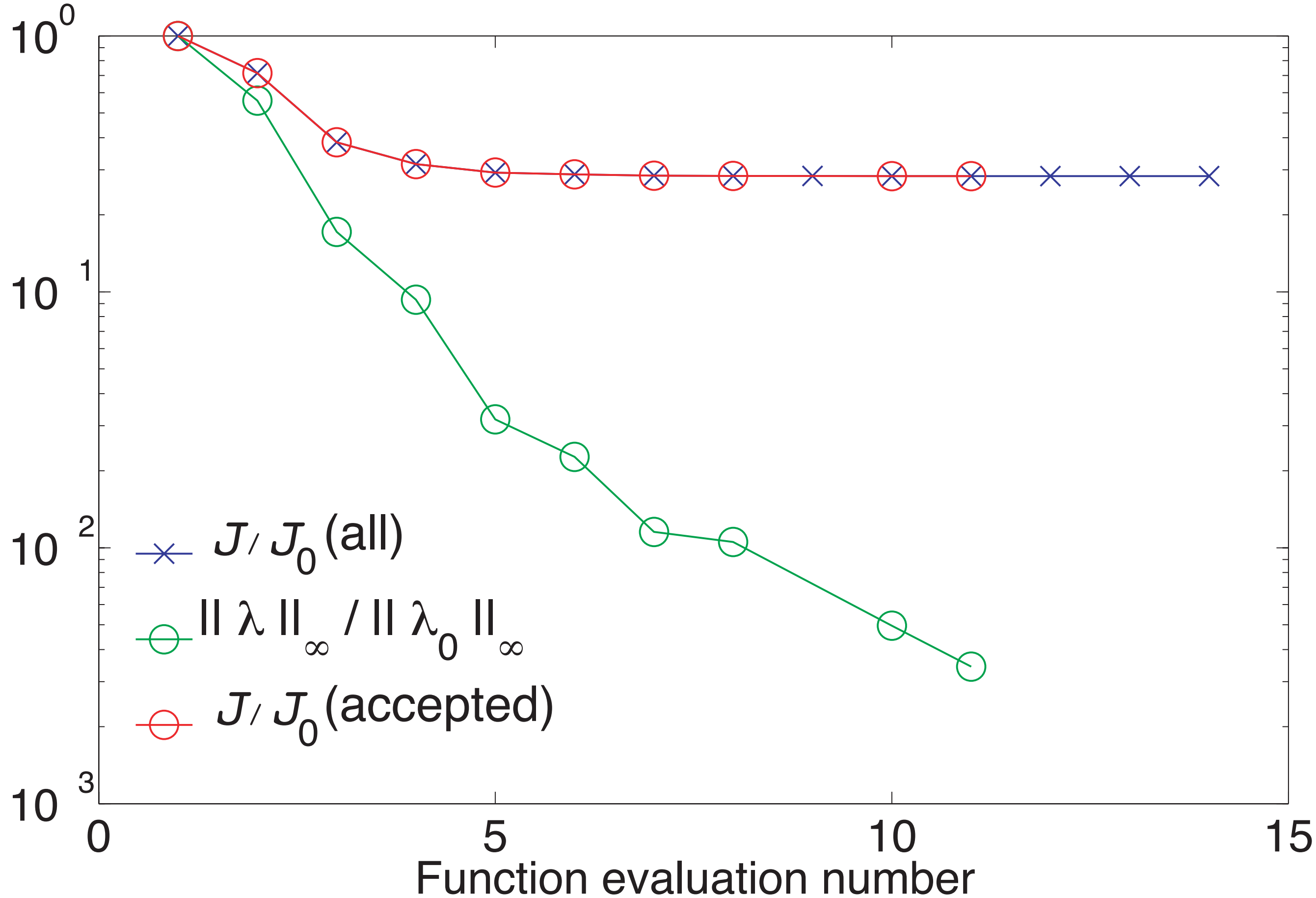
$\boldsymbol{\sigma}$ = free parameters, $\boldsymbol{\sigma} = ln\left(\frac{emission}{emission_a}\right)$

$\boldsymbol{\sigma}_a$ = initial guess of parameters (= 0)

$\mathbf{S}_{obs}$ = 30%

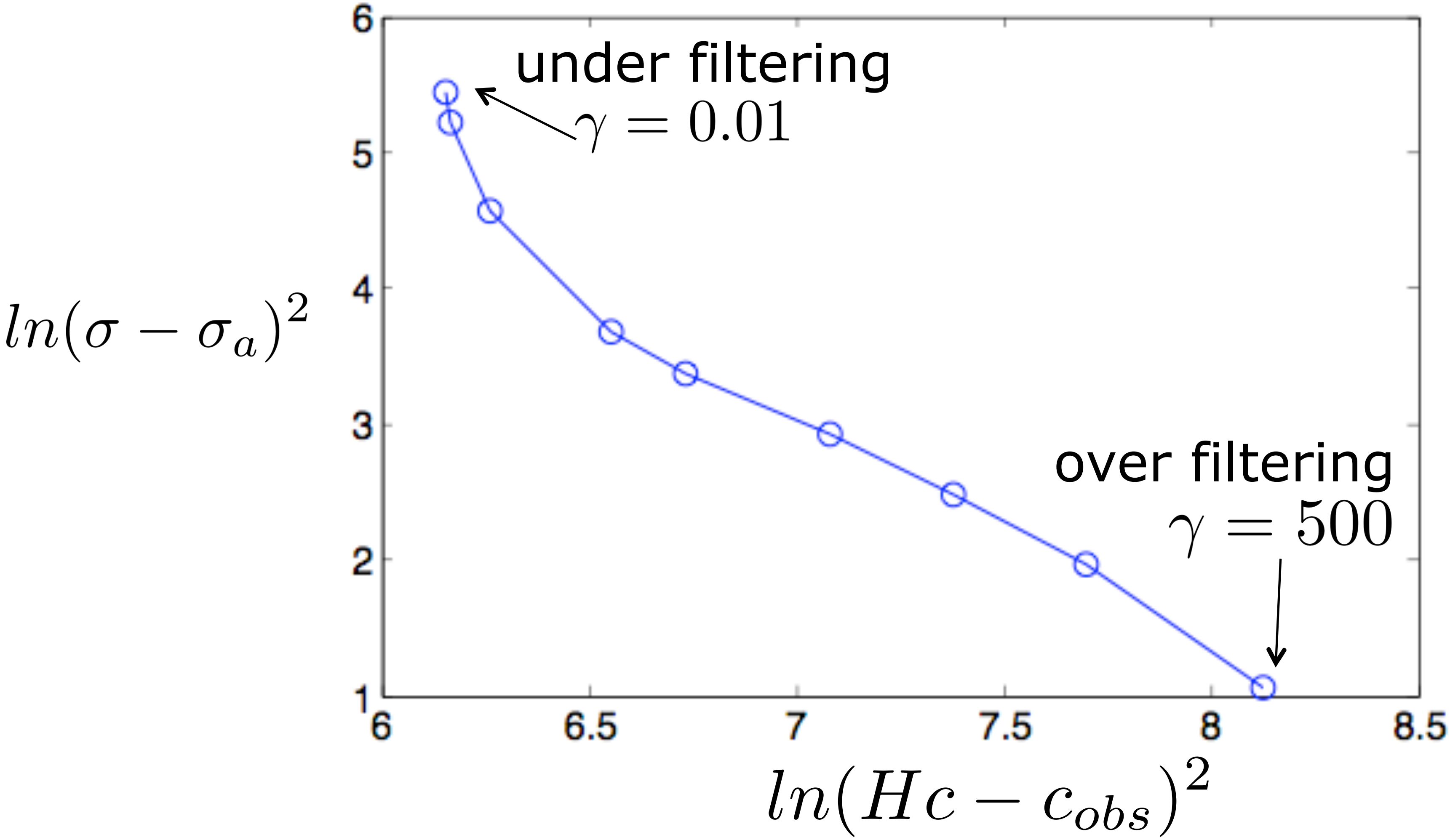
$\mathbf{S}_a$ = 100% for NH_3
= 30% for NO_x
= 10% for SO_x

Inverse modeling: minimization



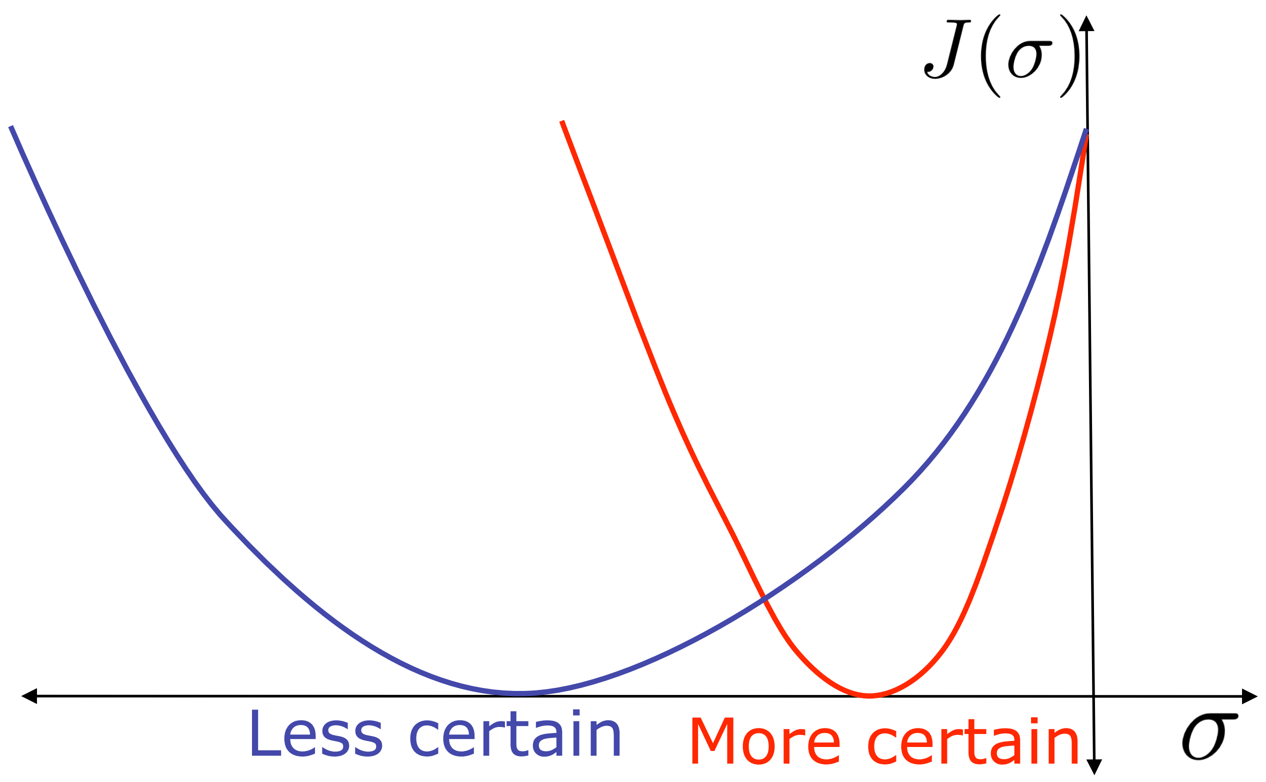
Regularization Parameter

$$J = \frac{1}{2}\sum_{\mathbf{c}\in\Omega}(H\mathbf{c}-\mathbf{c}_{obs})^T\mathbf{S}_{obs}^{-1}(H\mathbf{c}-\mathbf{c}_{obs}) + \frac{1}{2}\gamma_r(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)^T\mathbf{S}_{\sigma_a}^{-1}(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)$$



Posterior Error Covariance Estimates

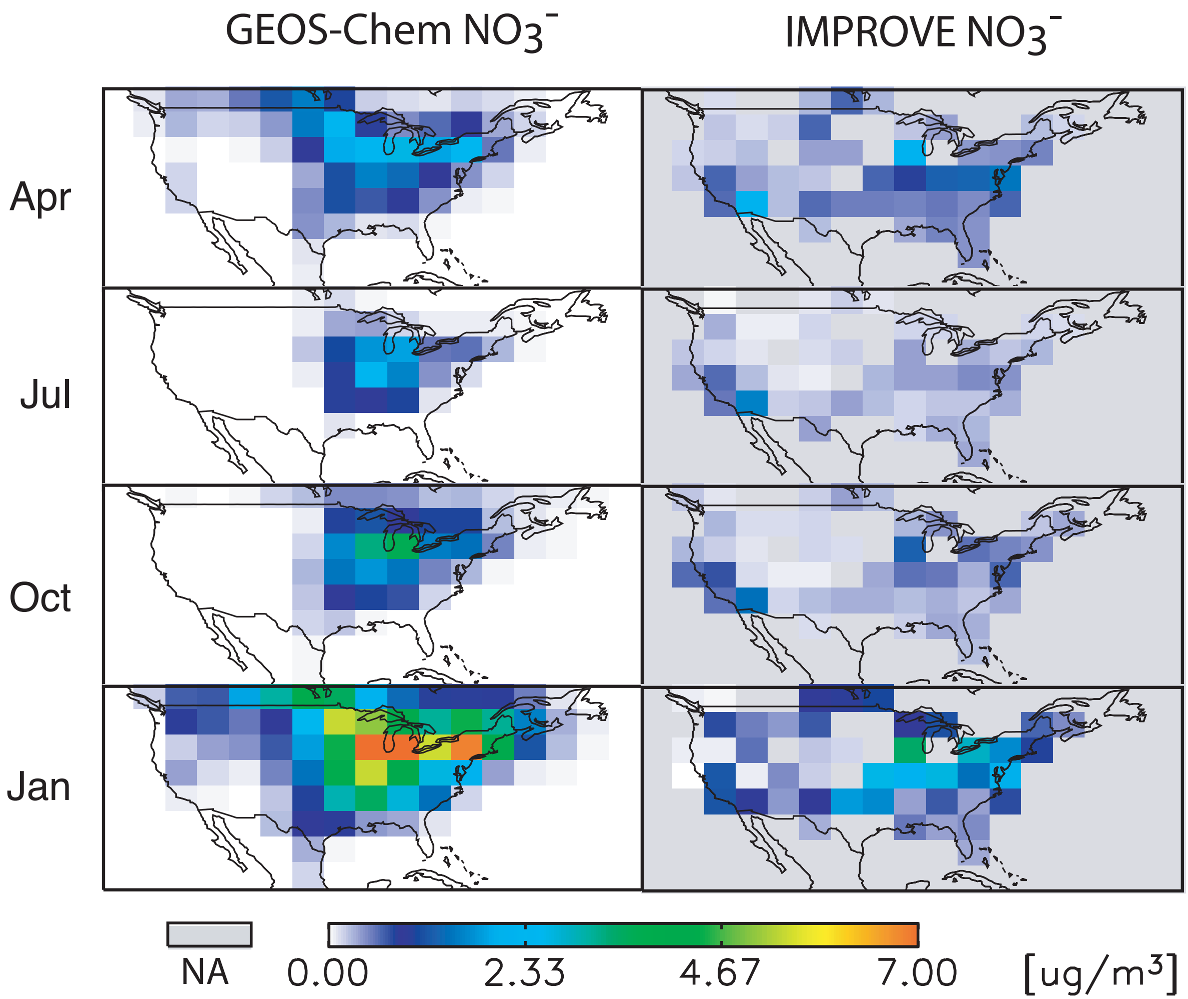
Certainty ~ curvature at minimum



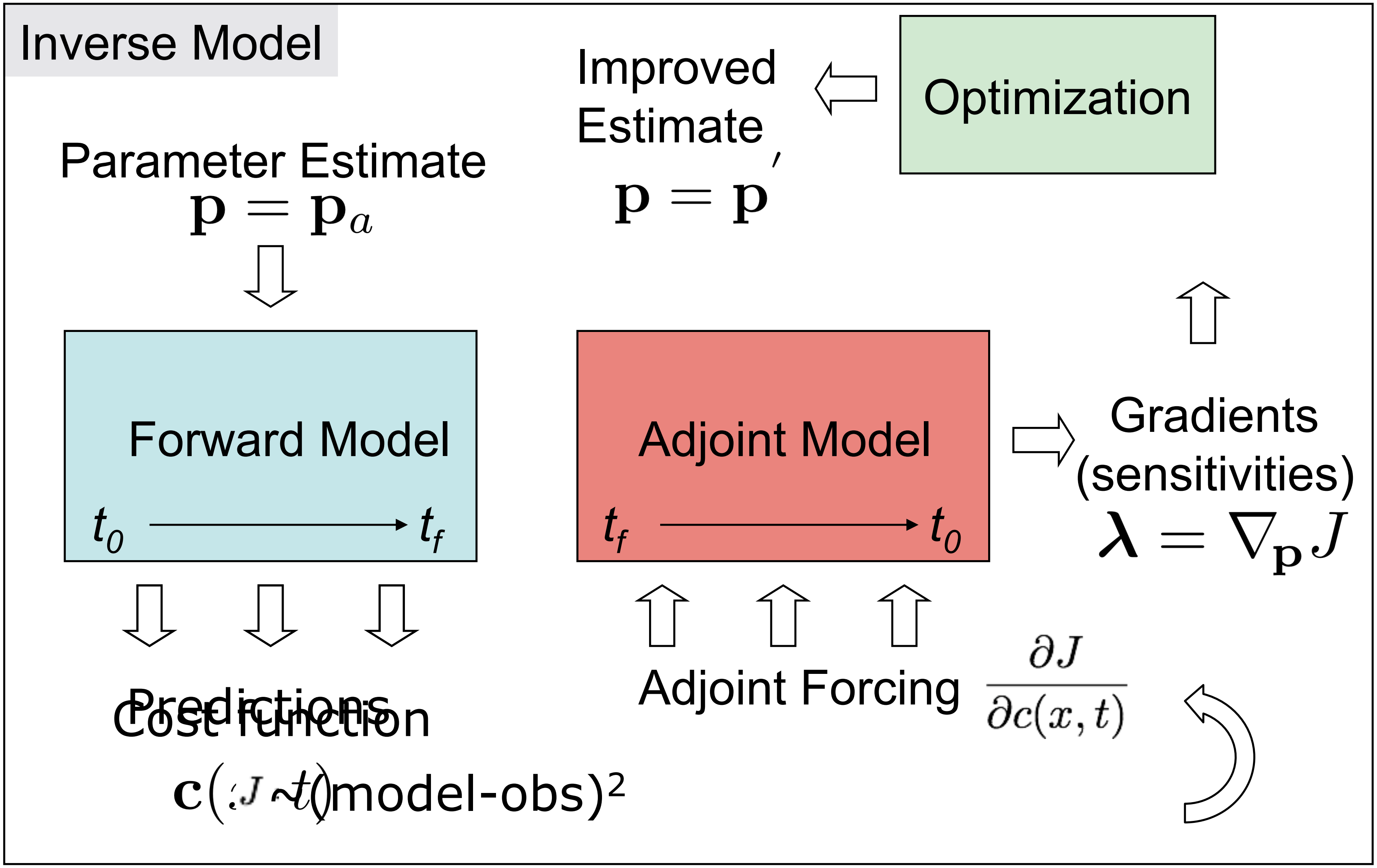
Can estimate inverse Hessian(J) by tracking the minimization

NH3 emissions uncertainty

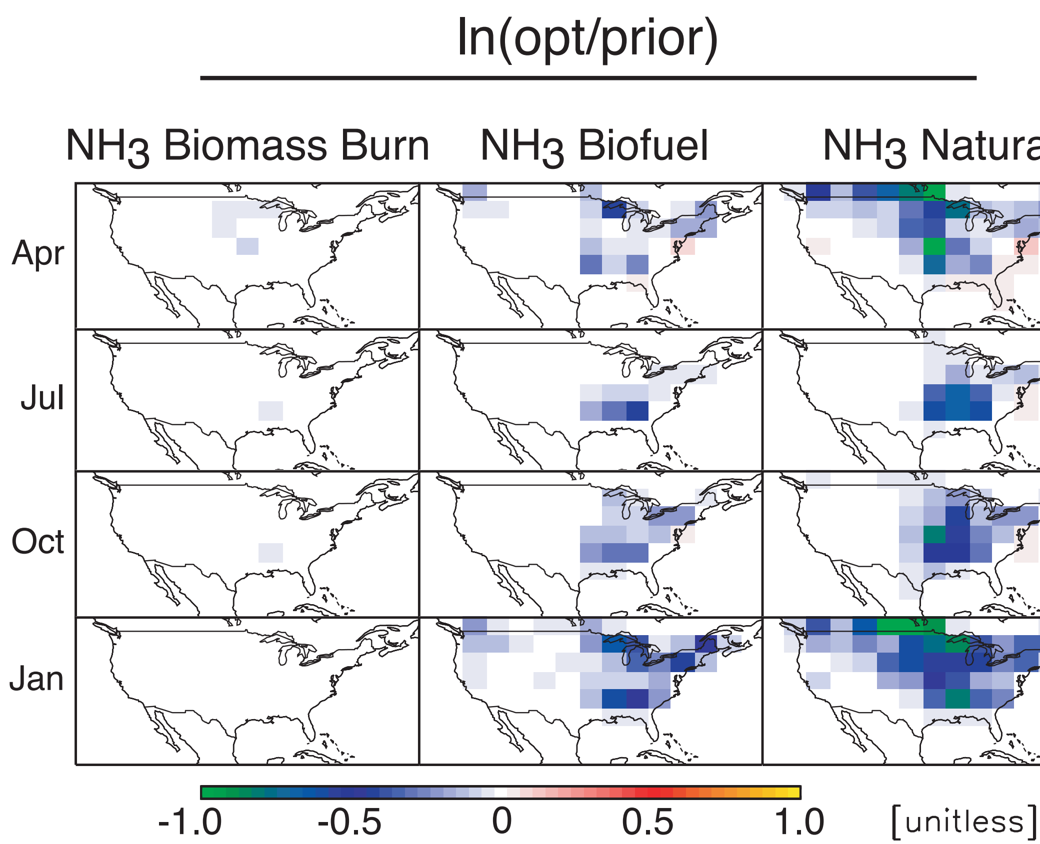
GEOS-Chem vs IMPROVE: nitrate



Inverse Modeling using Adjoint Model



Inverse modeling: other NH_3 emissions



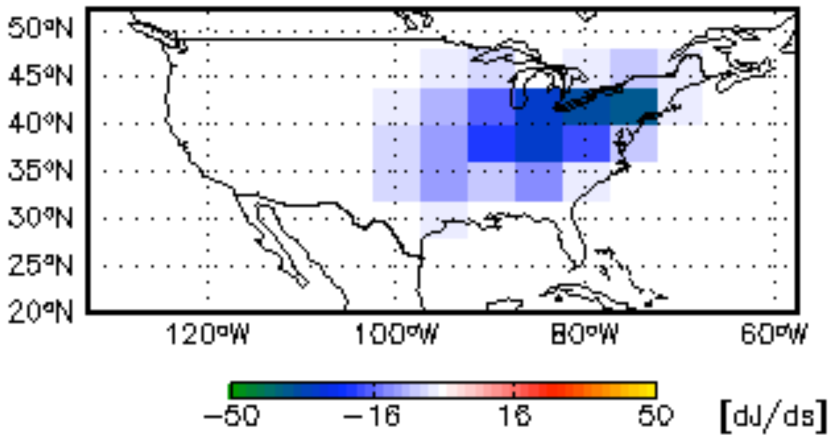
- scaling results from product of adjoints with prior emissions estimates
- reductions affect anthropogenic sources more than natural sources
- results across sectors are correlated

Can effectively distinguish between source sectors

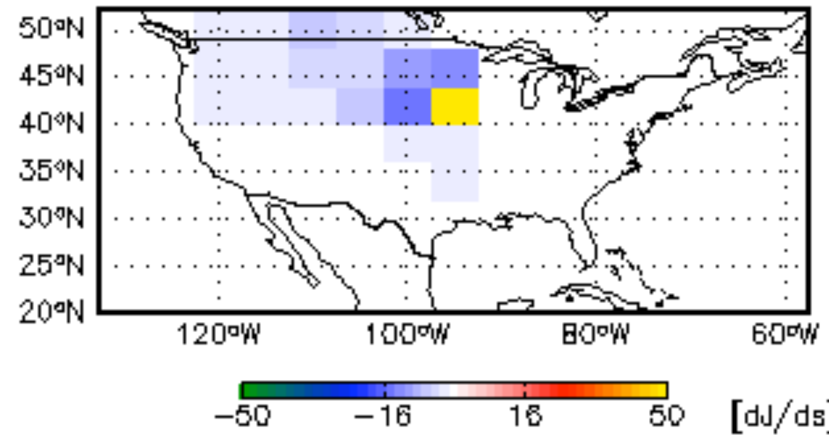
Sensitivities of various cost functions

Sensitivities with respect to anthro NH3 emissions:

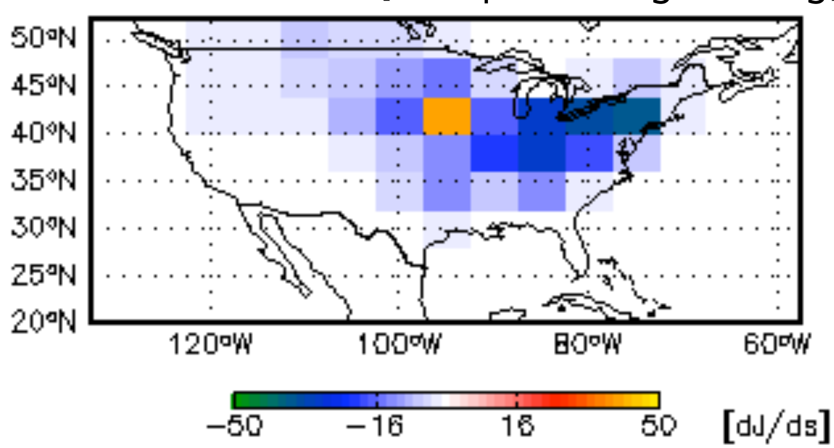
IMPROVE: $J = J(SO_4^{2-}, NO_3^{-})$



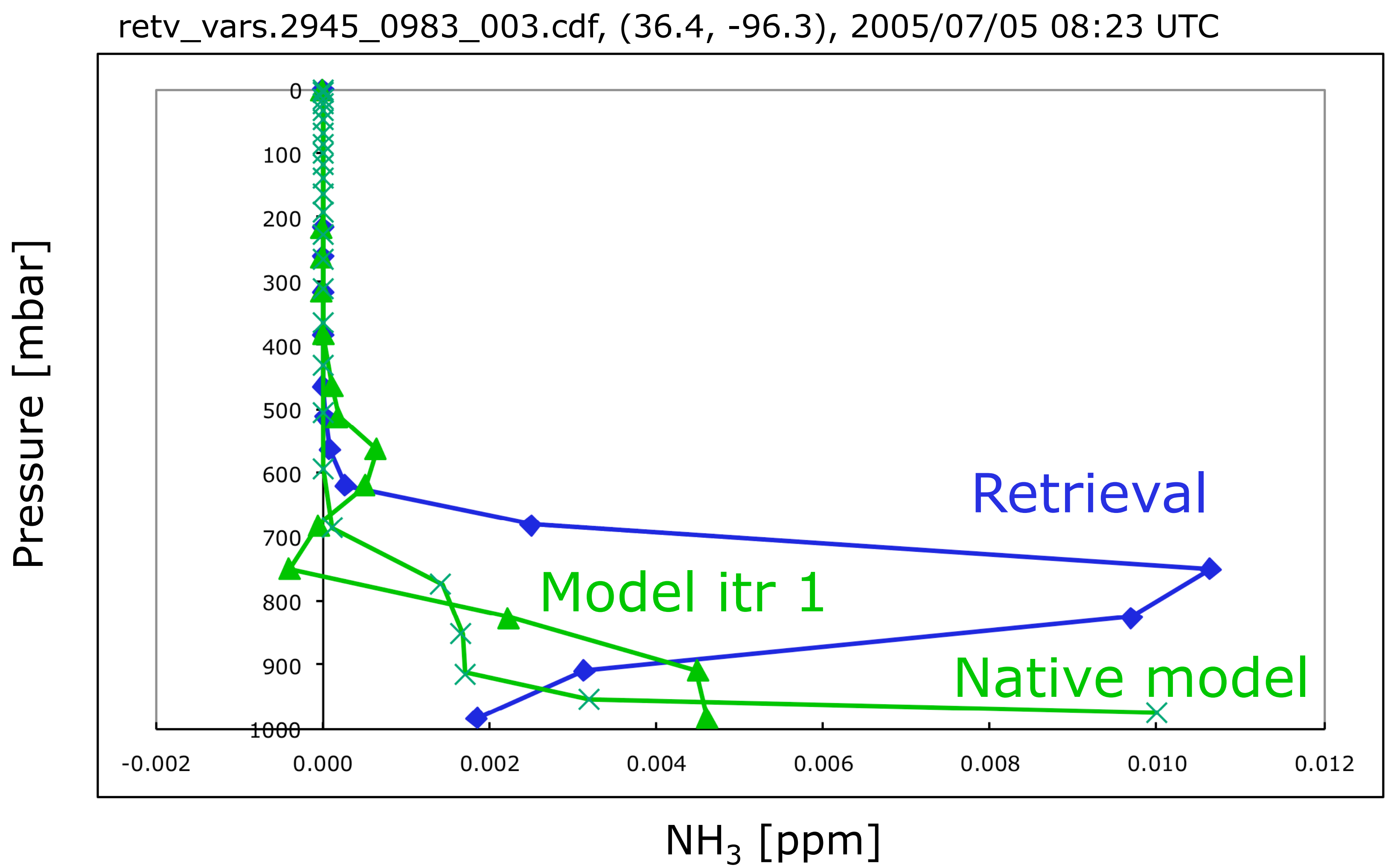
TES: $J = J(NH_3)$



BOTH: $J = J(SO_4^{2-}, NO_3^{-}, NH_3)$

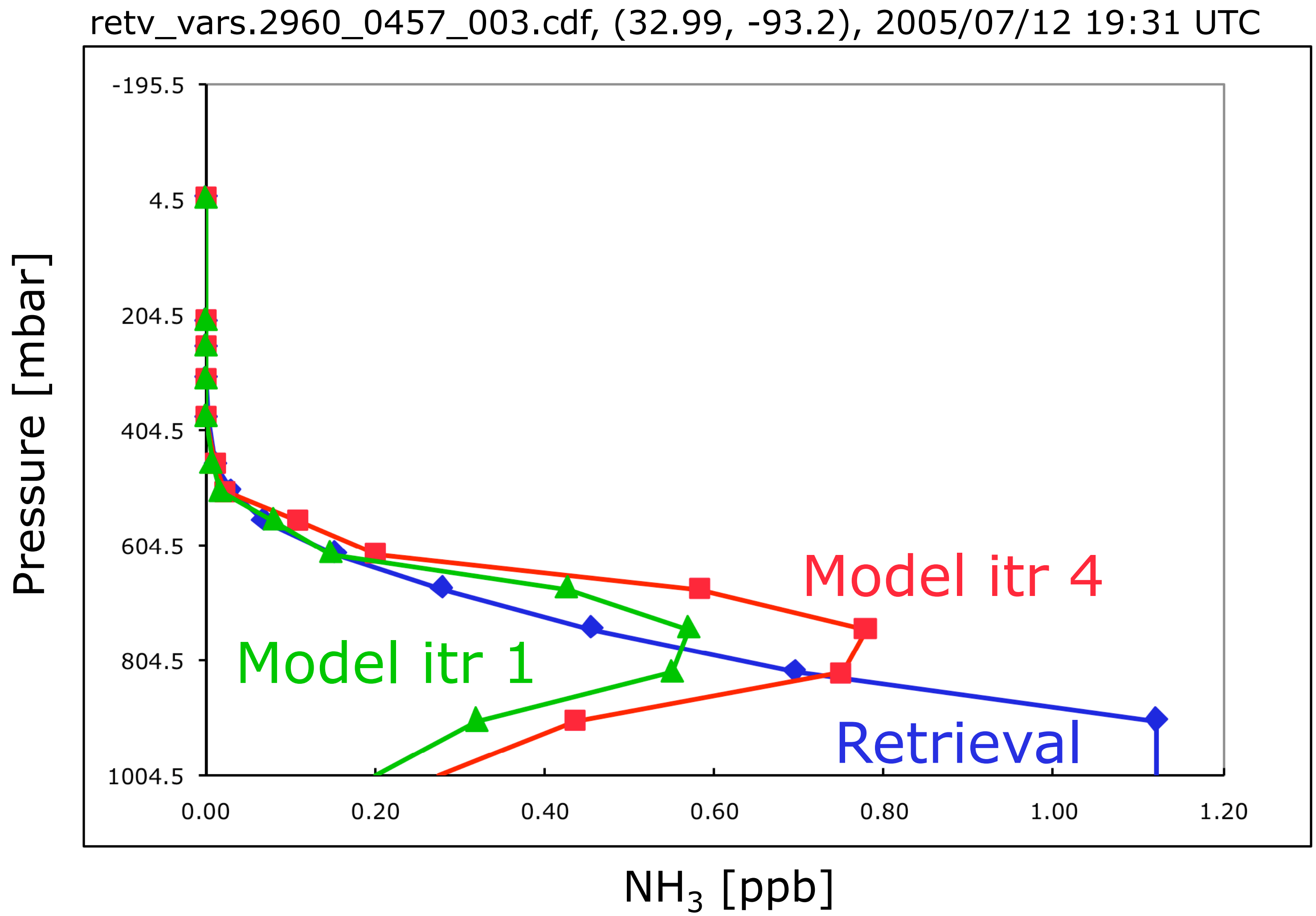


Why is the sensitivity positive in one spot?

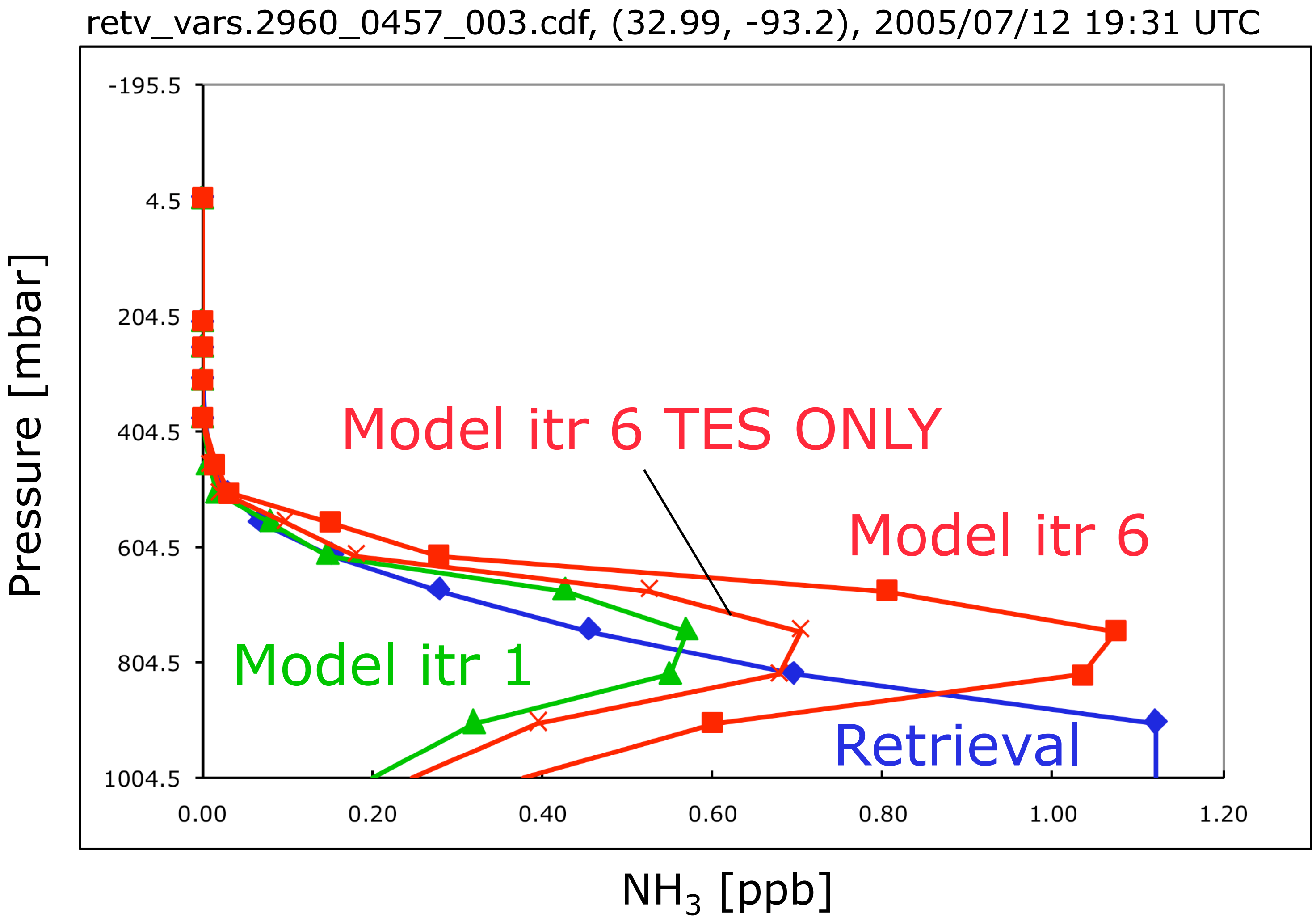


Resolution issue? Retrieval limitation?

Other locations perform better



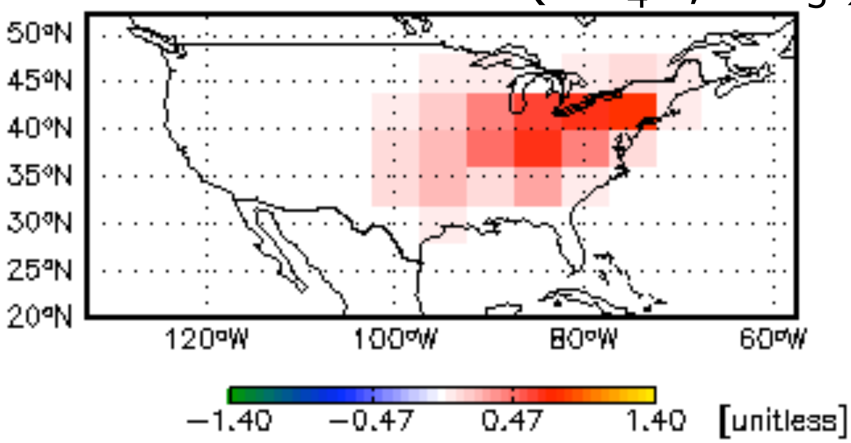
Other locations perform better



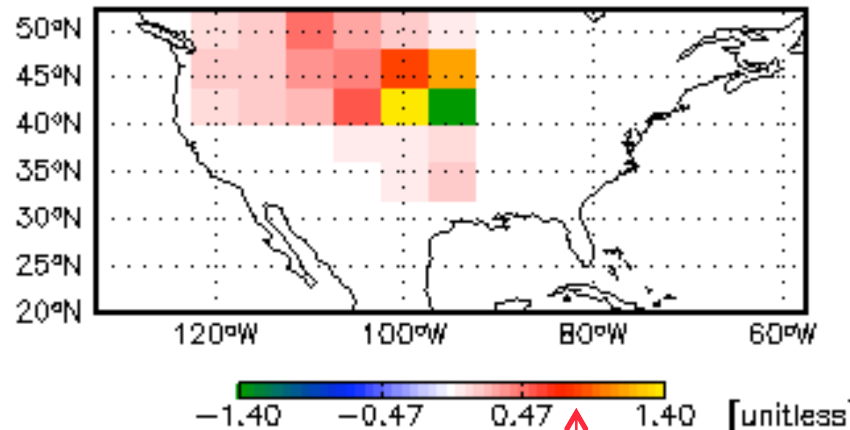
“optimized” scaling factors

Anthro NH3 emission scaling after 6 iterations

IMPROVE: J = J(SO_4^{2-}, NO_3^-)

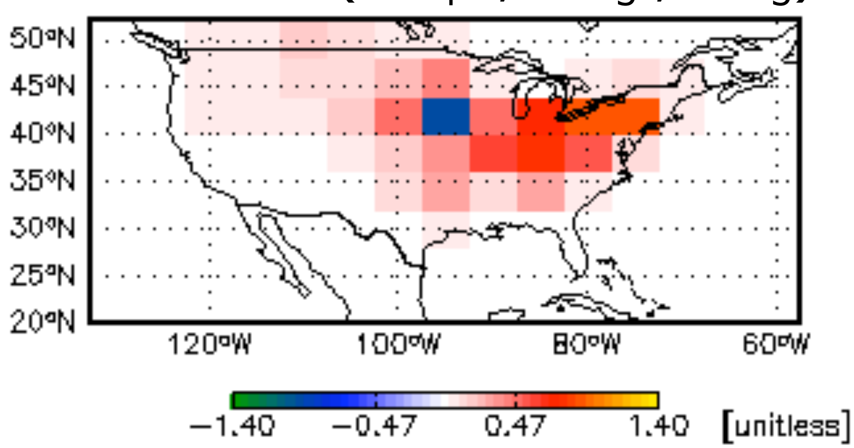


TES: J = J(NH_3)



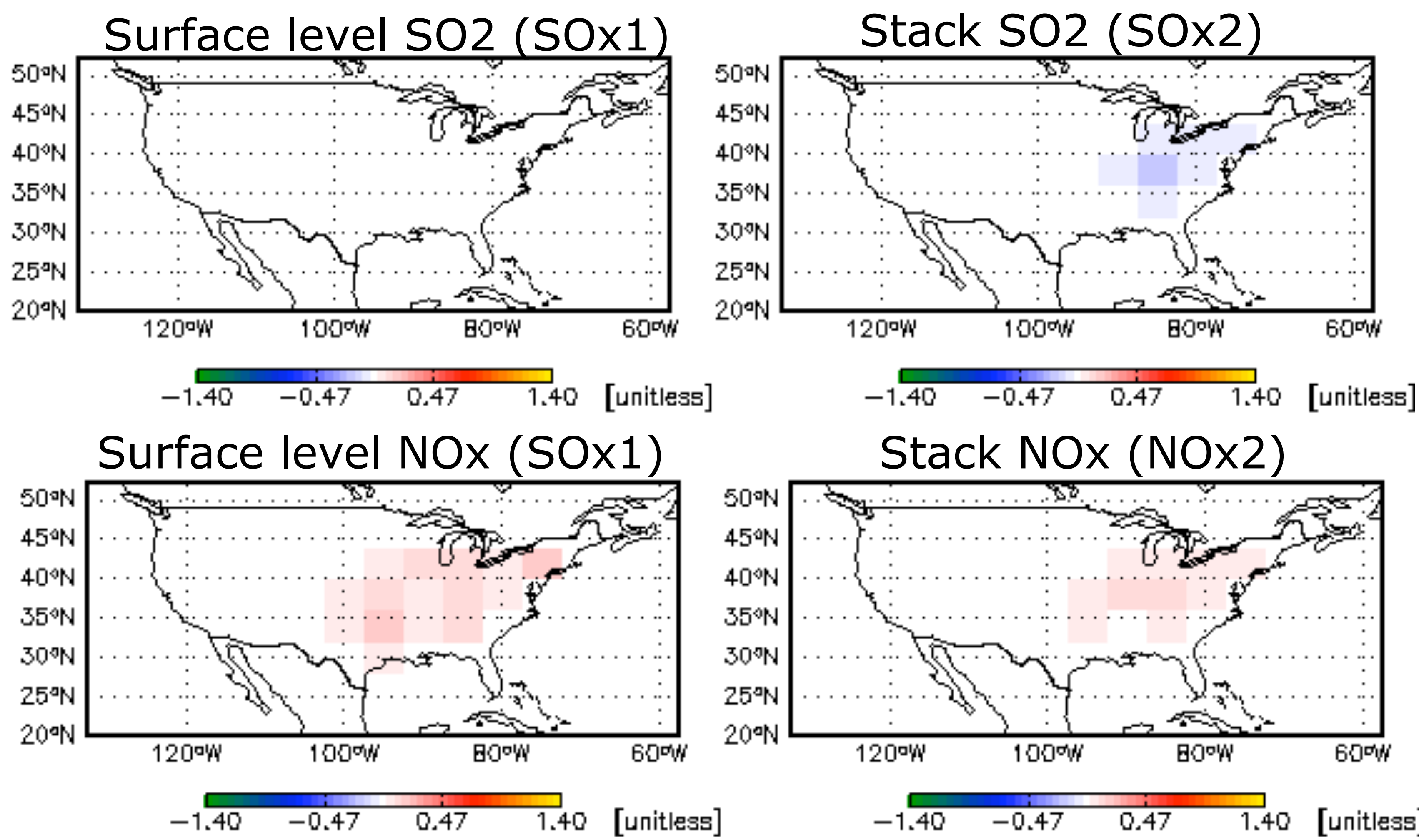
target solution

BOTH: J = J(SO_4^{2-}, NO_3^-, NH_3)



Scaling for other inventories

Anthro emission scaling after 6 iterations, J=J(**BOTH**)



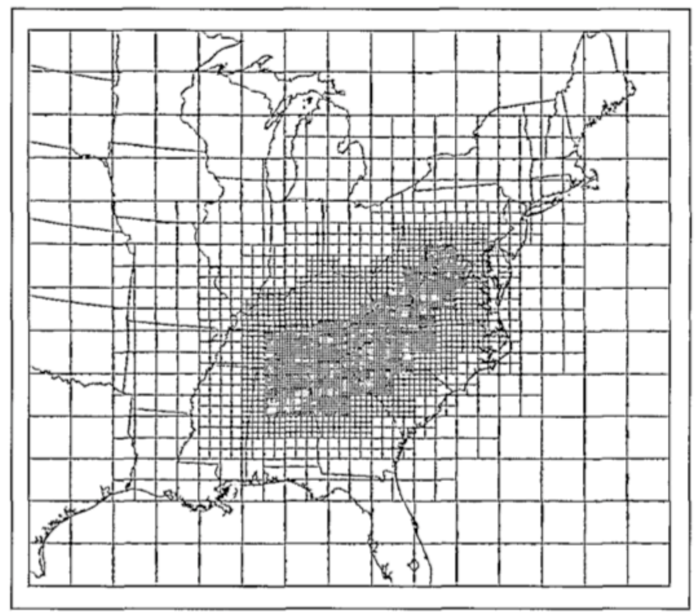
NH_3 inverse modeling: Mendoza-Dominguez et al. (2001)

Observations: $PM_{2.5}$ (speciated and total), gas precursors (NO_x, VOCs, SO_2)

Method: Kalman filter (DDM) to adjust single domain-wide scale factors

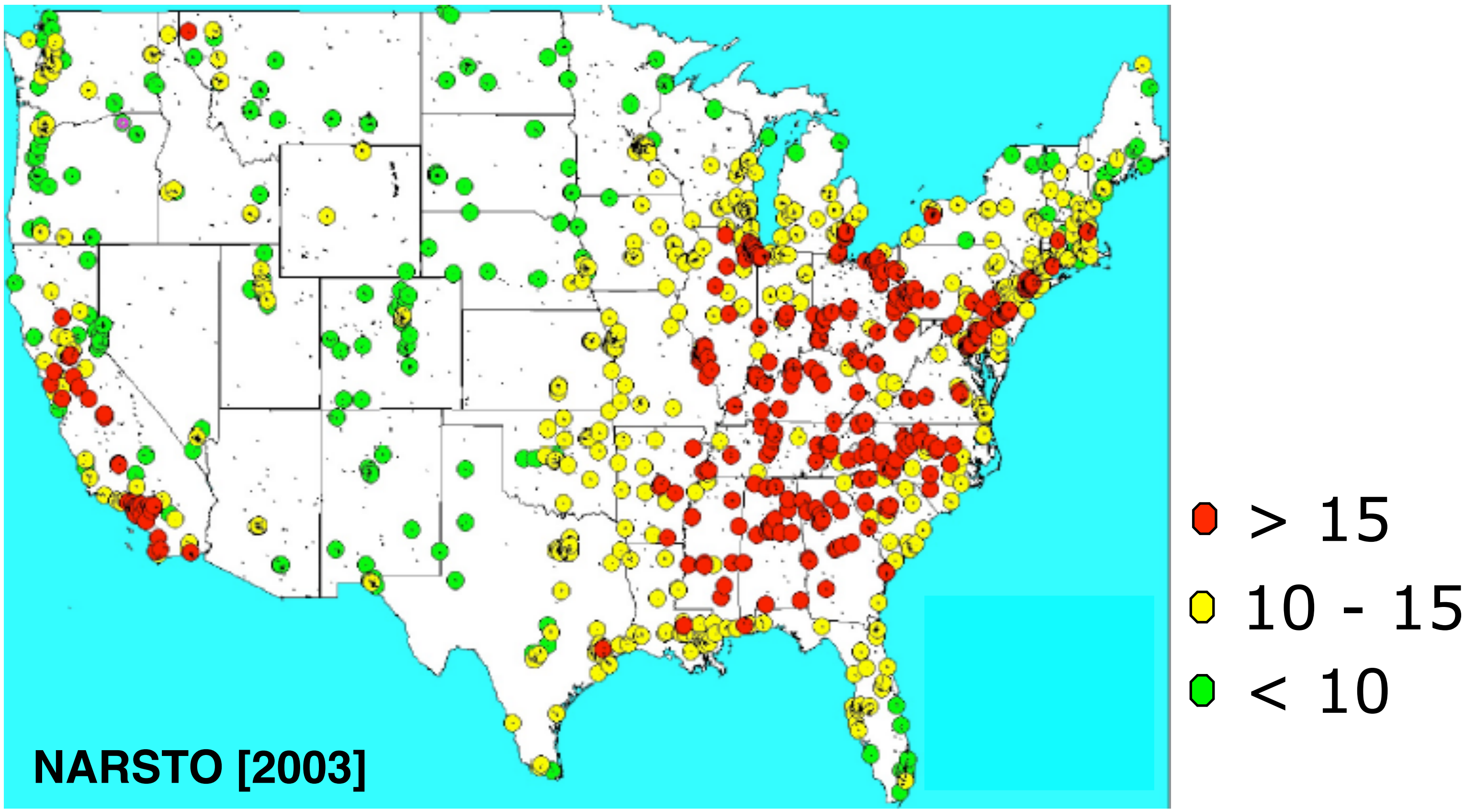
Results:

NH_3 emissions scaling factors:
- May 22-29, 1995: 0.59
- July 09-19, 1995: 0.59



Modeling domain

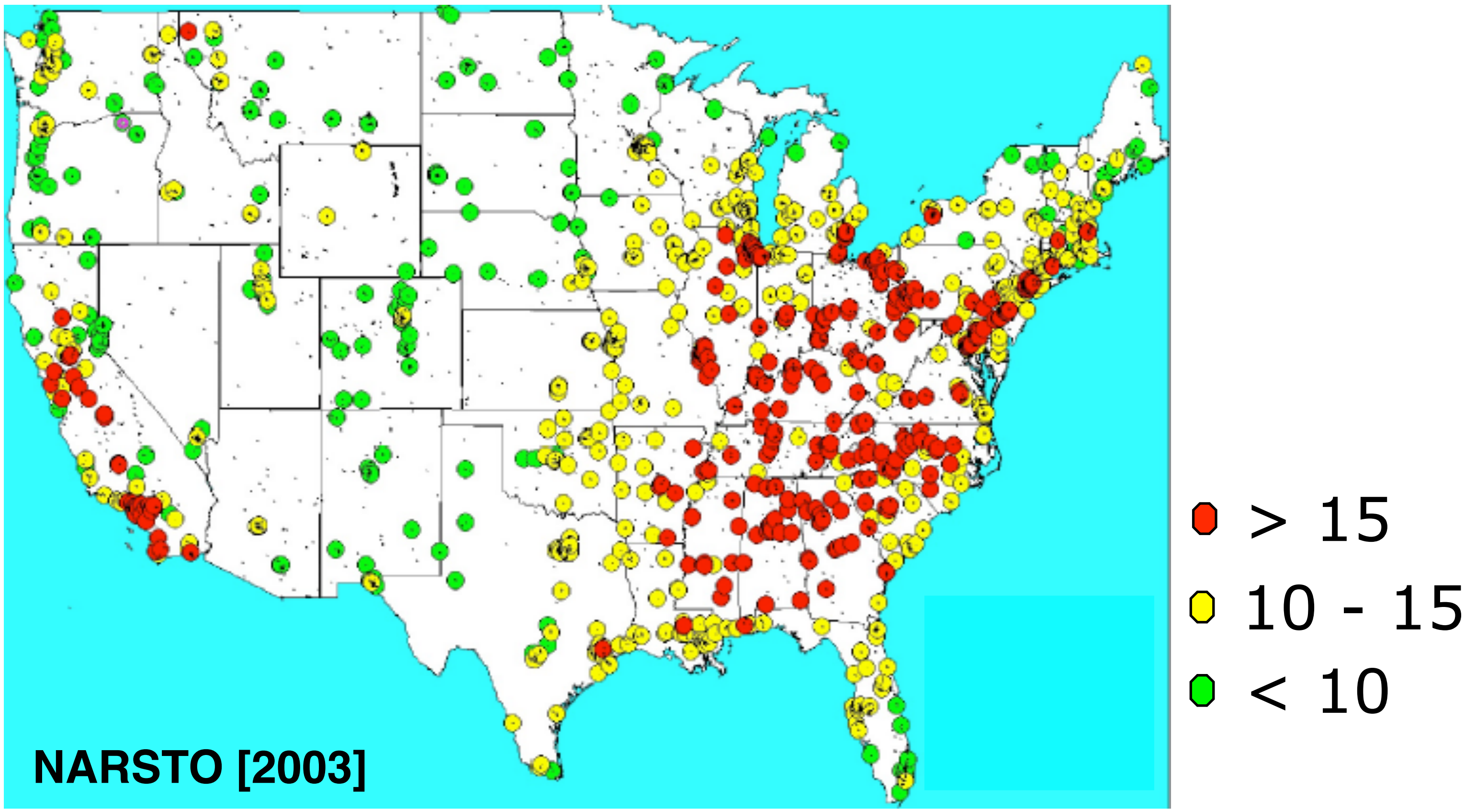
Air Pollution: $PM_{2.5}$



Annual average $PM_{2.5}$ concentrations, ug/m^3

90 million people live in counties which are in exceedance of NAAQS for $PM_{2.5}$ of 15 μg/m^3 (annual average). (*EPA*, 2003)

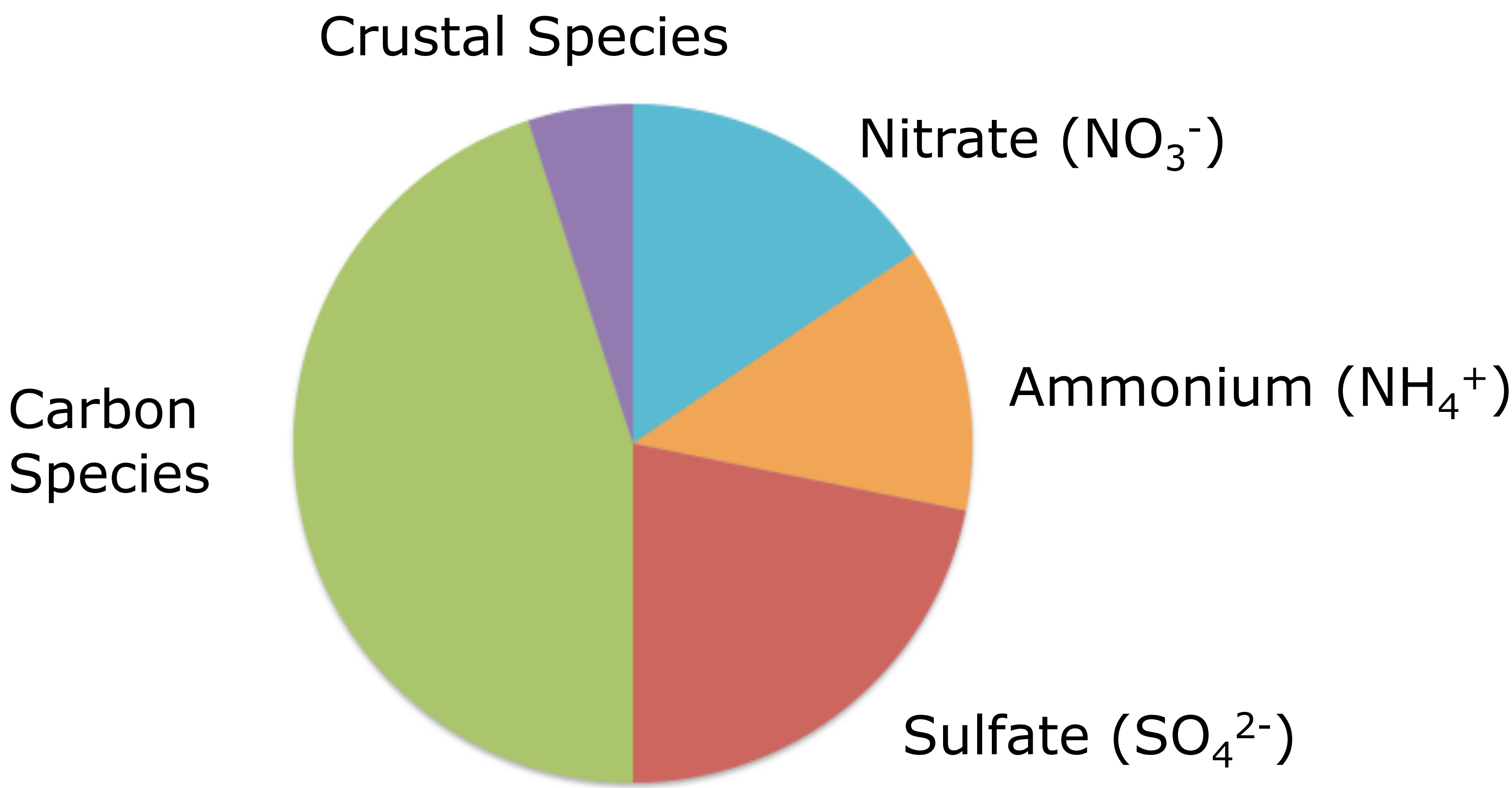
Air Pollution: PM



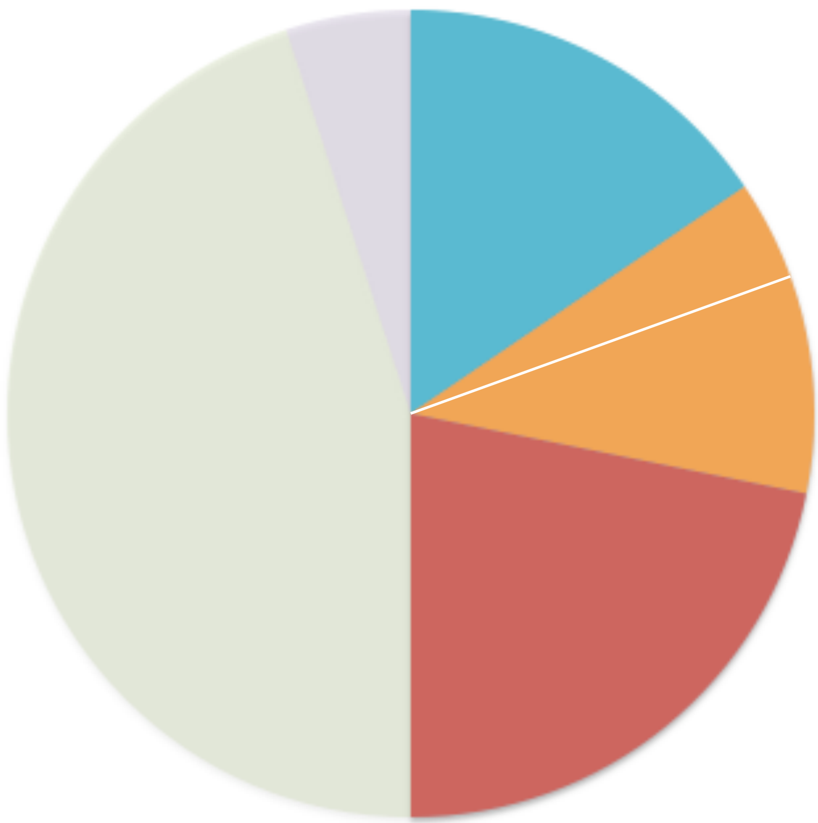
Annual average $PM_{2.5}$ concentrations, ug/m^3

Cardiovascular disease, inhibited lung development, premature mortality
Pope, (2000); *Pope et al.,* (2002); *Gauderman et al.,* (2004)

Air Pollution: $PM_{2.5}$ Composition



Air Pollution: $PM_{2.5}$ Composition



Ammonium Nitrate: NH_4NO_3

Ammonium Sulfate: $(NH_4)_2SO_4$

Inverse modeling: additional considerations

How does solution depend upon initial error estimates?

$$\mathcal{J} = \frac{1}{2}\sum_{\mathbf{c}\in\Omega}(H\mathbf{c} - \mathbf{c}_{obs})^T\mathbf{S}_{obs}^{-1}(H\mathbf{c} - \mathbf{c}_{obs}) + \frac{1}{2}\gamma_r(\boldsymbol{\sigma} - \boldsymbol{\sigma}_a)^T\mathbf{S}_a^{-1}(\boldsymbol{\sigma} - \boldsymbol{\sigma}_a)$$

vary “parameters” of the inversions

Questions

What do current network observations directly tell us about NH_3 emissions?

- Not enough

How can indirect observations and modeling be used to constrain NH_3 emissions estimates?

How do emission estimates affect emissions mitigation strategies?

What new measurements required?

Questions

What do current network observations directly tell us about NH_3 emissions?

How can indirect observations and modeling be used to constrain NH_3 emissions estimates?

How do emission estimates affect emissions mitigation strategies?

What new measurements required?

Inverse modeling and data assimilation

Using observations to constrain emissions is an inverse problem.

In data assimilation, models and measurements are combined to create an optimal estimate of the state of the system

Questions

What do current network observations directly tell us about NH_3 emissions?

How can indirect observations and modeling be used to constrain NH_3 emissions estimates?

- can spatial variability be improved?

How do emission estimates affect emissions mitigation strategies?

What new measurements required?

Inverse Modeling: 4D-Var

4D Variation Data Assimilation (Kalnay, 2003):

- Optimize parameters at resolution of forward model
- Forward model equations are strong constraints

Inverse Modeling: 4D-Var

4D Variation Data Assimilation (Kalnay, 2003):

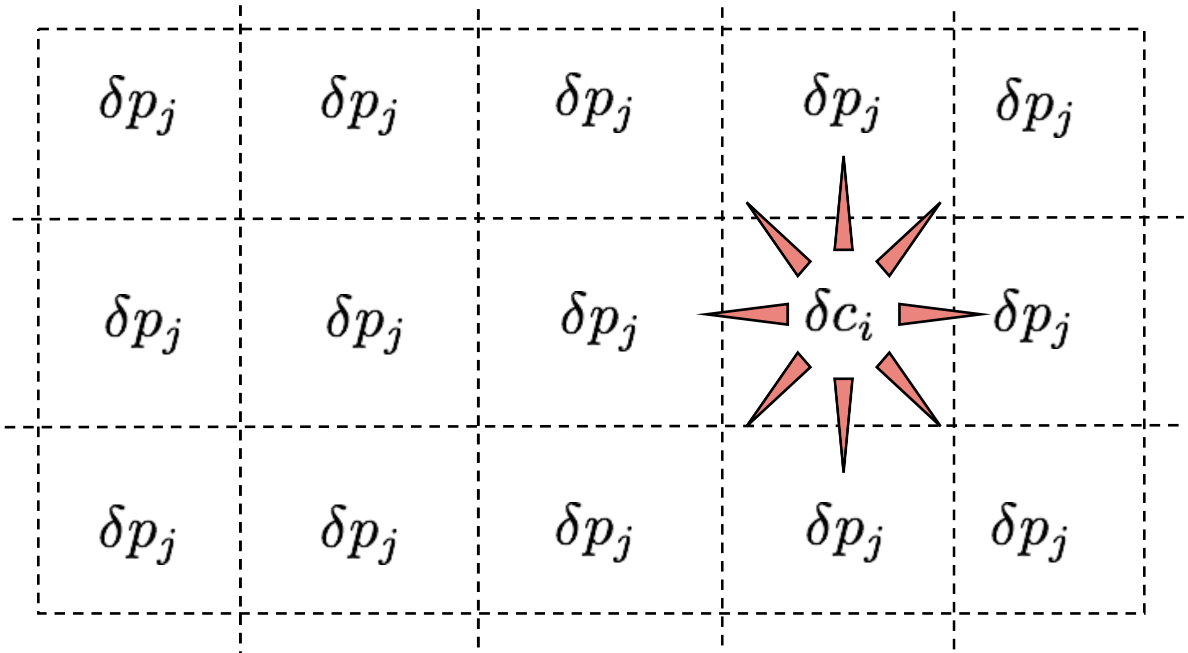
- Optimize parameters at resolution of forward model
- Forward model equations are strong constraints

Applications with GEOS-Chem adjoint:

- emissions estimates using remote sensing
  - MOPITT CO (Kopacz et al., 2008)
  - SCIAMACHY SO_2, NO_2 (C. Lee, C. Shim, Q. Li, R. V. Martin)
  - TES O_3 (K. Singh, A. Sandu, K. Bowman)

- NH_3 emissions estimates using surface obs. of sulfate and nitrate (IMPROVE)

Adjoint sensitivity



Method for calculating sensitivity of a single, scalar model response with respect to numerous (i.e., 10^6) model parameters that is very computationally efficient*:*

*time(adjoint model) = 3 * time(forward model)*

Questions

What do current network observations directly tell us about NH_3 emissions?

How can indirect observations and modeling be used to constrain NH_3 emissions estimates?

How do emission estimates affect emissions mitigation strategies?

What new measurements required?

Questions

What do current network observations directly tell us about NH_3 emissions?

How can indirect observations and modeling be used to constrain NH_3 emissions estimates?

How do emission estimates affect emissions mitigation strategies?

What new measurements required?

Collaborators

Thanks to:

Mark Shepard, Karen Cady-Pereria,

Ming Luo, Kevin Bowman, TES team

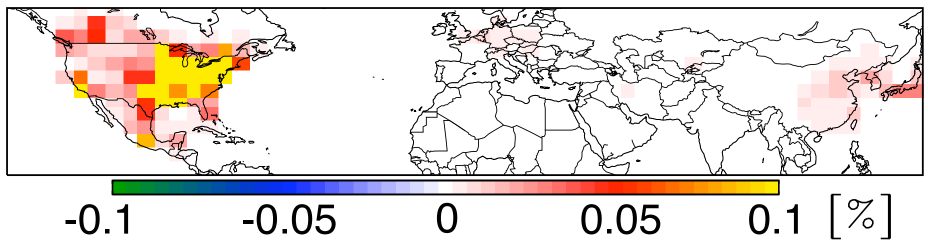
Rob Pinder, John Walker

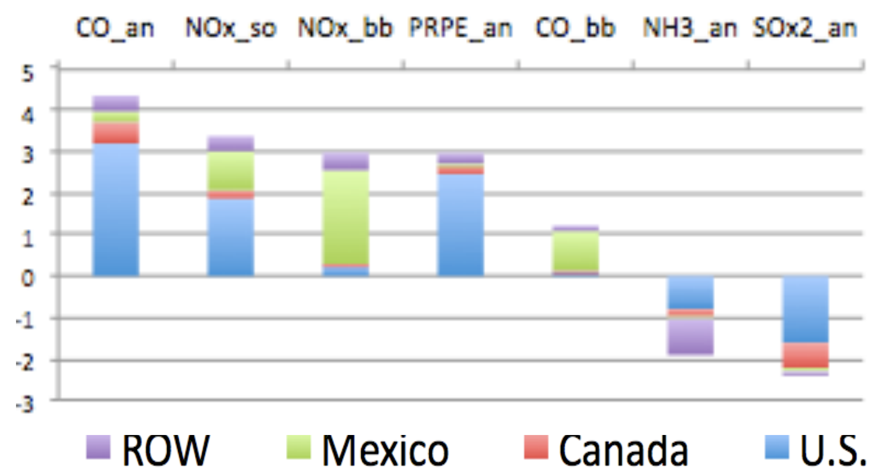
NASA GSFC: NCCS
NASA JPL: SCC

Additional projects

Assessing long-range influences on local air quality.

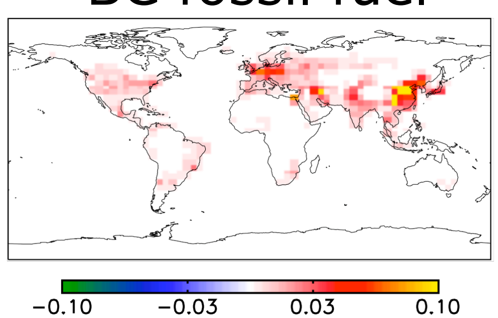
Sensitivity of US O_3 to alkane emissions



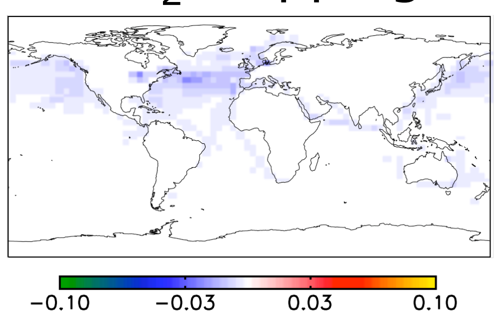


ClimateWorks: optimizing energy strategies to minimize global warming potential of aerosols.

BC fossil fuel

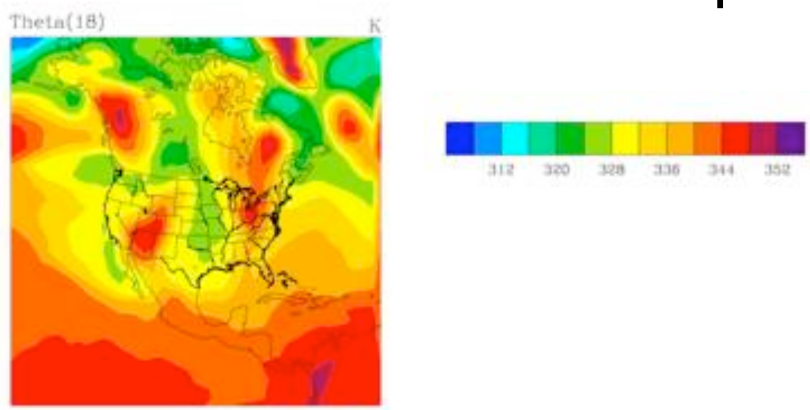


SO_2 shipping

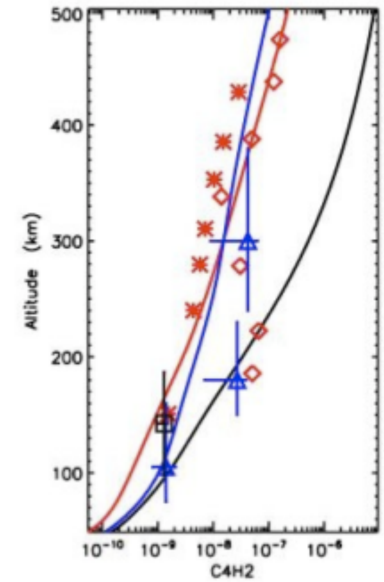


Additional projects

WRF-Chem / Var: how can chemical data assimilation improve weather and air quality forecasts?

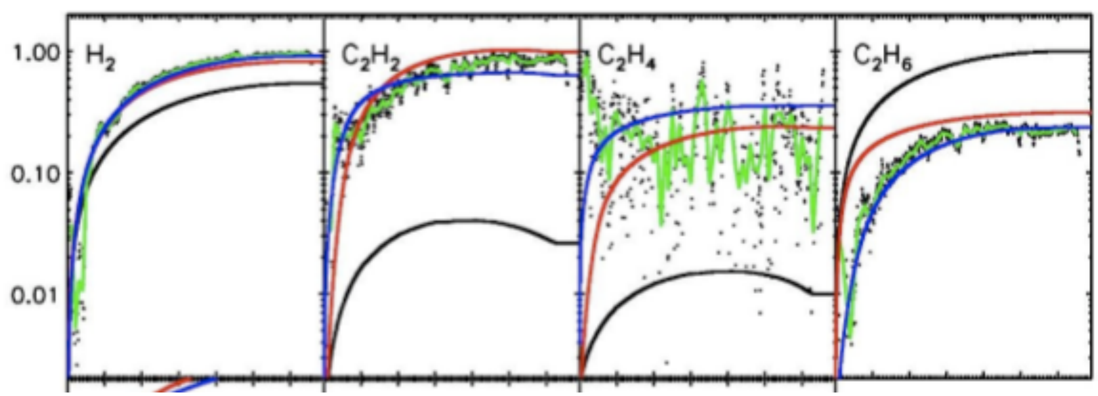


Titan



Chemistry of outer planets (sub. Liang et al.)

JPL chamber

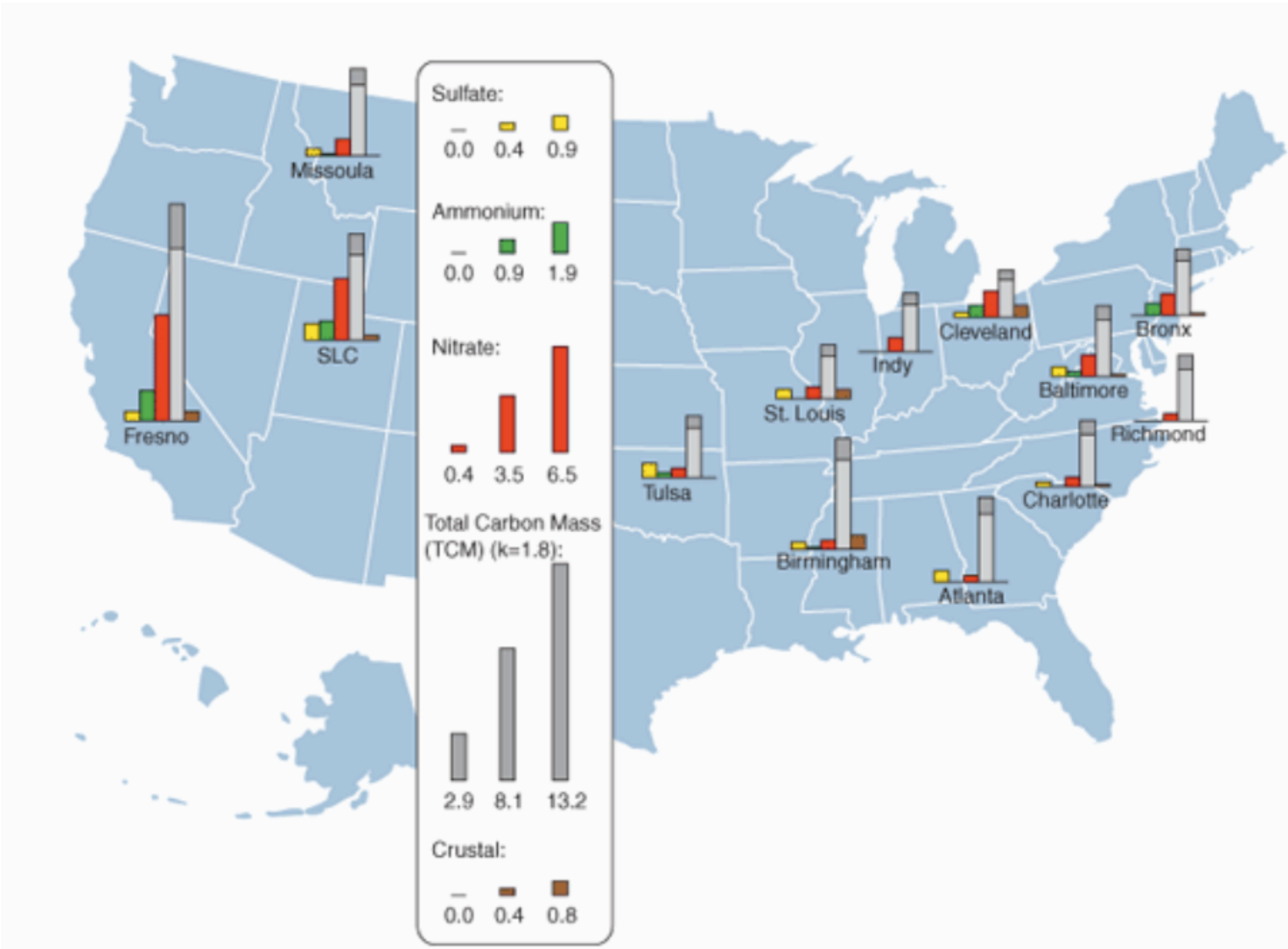


Directions

Emissions inverse modeling tests

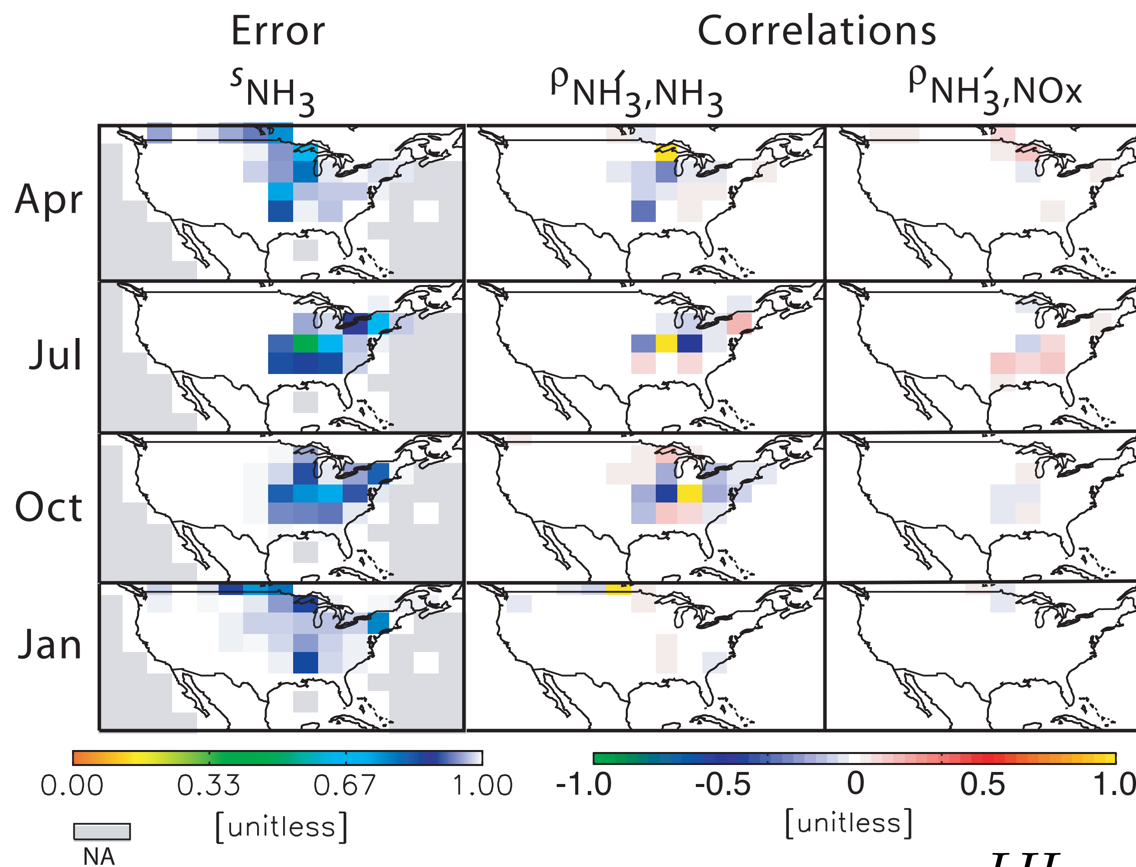
- simulate atmospheric NH_3 field
- simulate TES NH_3 observations
- can inverse model recover “true” emissions?

Air Pollution: Regional



Inverse modeling: uncertainty estimates

Inverse Hessian (*IH*) estimated by tracking progression towards minimum

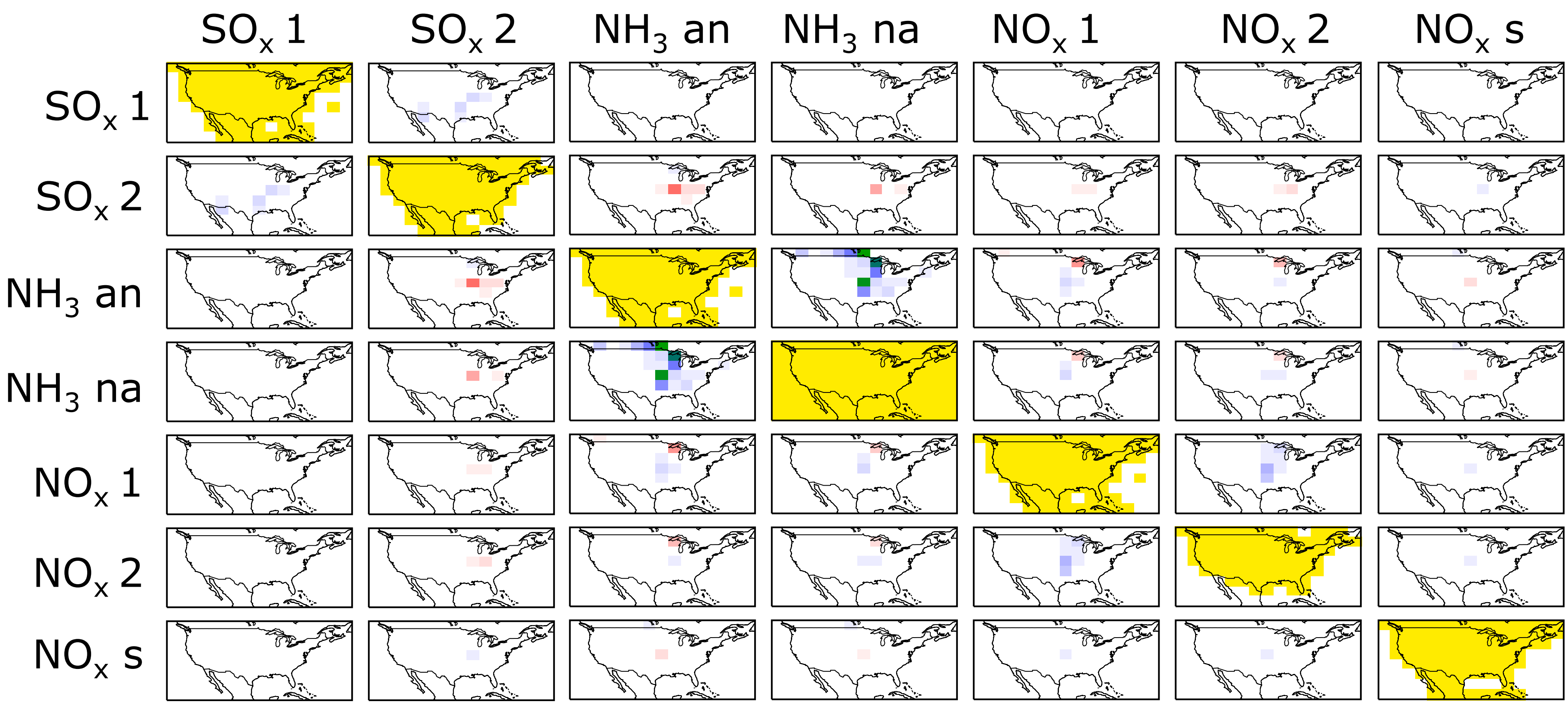


$$s_{\sigma_m} = (IH_{m,m})^{\frac{1}{2}}$$

$$\rho_{\sigma_{m_1},\sigma_{m_2}} = \frac{IH_{m_1,m_2}}{(IH_{m_1,m_1} IH_{m_2,m_2})^{\frac{1}{2}}}.$$

Inverse modeling: uncertainty estimates

Correlation of emissions between species, same location



$$\rho_{\sigma_{m_1},\sigma_{m_2}} = \frac{IH_{m_1,m_2}}{(IH_{m_1,m_1} IH_{m_2,m_2})^{\frac{1}{2}}}.$$

Adjoint modeling applications

Depending on "model response," can be used for:

Sensitivity analysis: quantifying influence of uncertain model parameters (emissions, reaction rates, …)
Response = Average concentrations of X in location Y...

Inverse modeling: using large data sets, optimizing parameters on resolution commensurate with forward model.
Response ~ sum(model – obs)^2

Attainment studies: assessing the effectiveness of emissions changes on an air quality
Response = total amount of nonattainment

Adjoint modeling: History

From principles of functional analysis (Hilbert)

Used extensively for optimal control problems (Lions, 1971)
- nuclear reactor design (classified?!)
- oceanography (Tziperman and Thacker, 1989)
- meteorology (Derber, 1985)
- aeronautics (Giles and Pierce, 2000)

Adjoint modeling: History

From principles of functional analysis (Hilbert)

Used extensively for optimal control problems (Lions, 1971)
- nuclear reactor design (classified?!)
- oceanography (Tziperman and Thacker, 1989)
- meteorology (Derber, 1985)
- aeronautics (Giles and Pierce, 2000)

Atmospheric chemistry
- proposed for tracer analysis (Marchuk, 1974)
- stratospheric chemistry (Larry et al, 1995)
- tropospheric chemistry (Elbern and Schmidt, 1999)

Adjoint modeling: History

From principles of functional analysis (Hilbert)

Used extensively for optimal control problems (Lions, 1971)
- nuclear reactor design (classified?!)
- oceanography (Tziperman and Thacker, 1989)
- meteorology (Derber, 1985)
- aeronautics (Giles and Pierce, 2000)

Atmospheric chemistry
- proposed for tracer analysis (Marchuk, 1974)
- stratospheric chemistry (Larry et al, 1995)
- tropospheric chemistry (Elbern and Schmidt, 1999)

Aerosols
- box model microphysics (Henze et al., 2004; Sandu et al., 2005)
- black carbon (tracer) (Hakami et al., 2005)
- coupled thermodynamics and chemistry (Henze et al., 2007)
- AOD (offline chemistry) (Dubovik et al., 2008)

Inverse Modeling: 4D-Var

4D Variation Data Assimilation (Kalnay, 2003):

- Optimize parameters at resolution of forward model
- Forward model equations are strong constraints

Inverse Modeling: 4D-Var

4D Variation Data Assimilation (Kalnay, 2003):

- Optimize parameters at resolution of forward model
- Forward model equations are strong constraints

Applications with GEOS-Chem adjoint:

- Top down NH_3 emissions estimates using surface obs. of sulfate and nitrate (IMPROVE)

- Top down emissions estimates using remote sensing
  - MOPITT CO (Kopacz et al., 2008)
  - SCIAMACHY SO_2, NO_2 (C. Lee, C. Shim, Q. Li, R. V. Martin)
  - TES O_3 (K. Singh, A. Sandu, K. Bowman)

- Potential for combining aerosol and gas-phase obs.

Inverse Modeling: 4D-Var

4D Variation Data Assimilation (Kalnay, 2003):

- Optimize parameters at resolution of forward model
- Forward model equations are strong constraints

Applications with GEOS-Chem adjoint:

- Top down NH_3 emissions estimates using surface obs. of sulfate and nitrate (IMPROVE)

- Top down emissions estimates using remote sensing
  - MOPITT CO (Kopacz et al., 2008)
  - SCIAMACHY SO_2, NO_2 (C. Lee, C. Shim, Q. Li, R. V. Martin)
  - TES O_3 (K. Singh, A. Sandu, K. Bowman)

- Potential for combining aerosol and gas-phase obs.

Adjoint modeling applications

Depending on “model response,” can be used for:

Sensitivity analysis: quantifying influence of uncertain model parameters (emissions, reaction rates, initial conditions, …)

Inverse modeling (Data Assimilation): using large data sets, optimizing parameters on resolution commensurate with forward model

Attainment studies: assessing the effectiveness of emissions abatement on an air quality

AQ Attainment

Consider a representative metric of $PM_{2.5}$ air quality,

$$J = \frac{1}{2} \sum \mathrm{MAX}[(\text{inorganic PM}_{2.5})_{24\mathrm{h}} - 10\mu\mathrm{g/m}^3, 0]^2$$

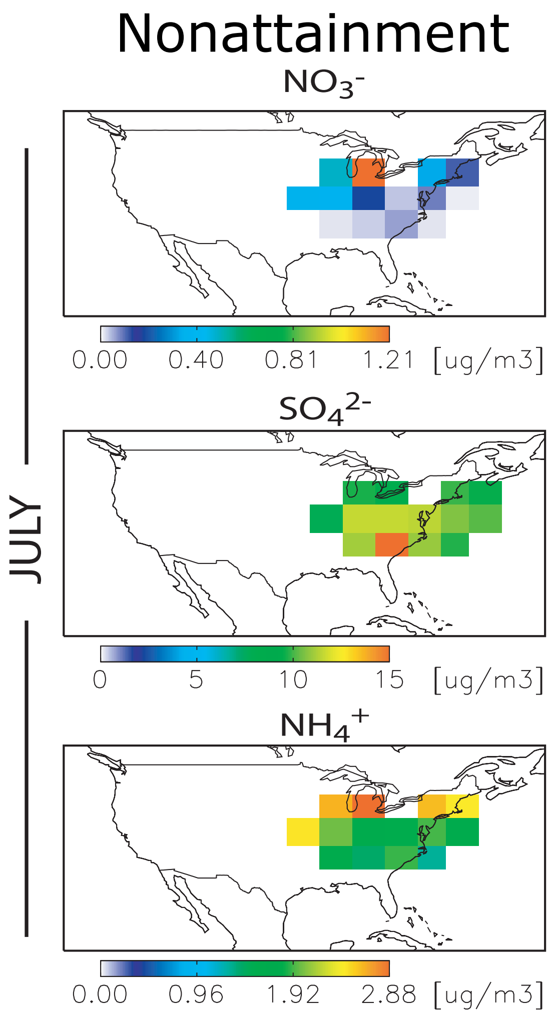
Calculate the sensitivity of this metric w.r.t. $PM_{2.5}$ precursor emissions, E.

Map adjoint sensitivities:

"Control effectiveness" = fully normalized sensitivities

$$\frac{\partial J}{\partial E} \times \frac{E}{J} \times 100\% \approx \frac{\triangle J[\%]}{\triangle E/E}$$

AQ Attainment: July



Spatial and chemical variability in effectiveness

AQ Attainment: sector specific influences

$$\chi_m = \left(\frac{|\sum_i \lambda_{p_{i,m}}|}{|\sum_{i,m} \lambda_{p_{i,m}}|} - \frac{\sum_i p_{i,m}}{\sum_{i,m} p_{i,m}} \right) \times 100\%$$

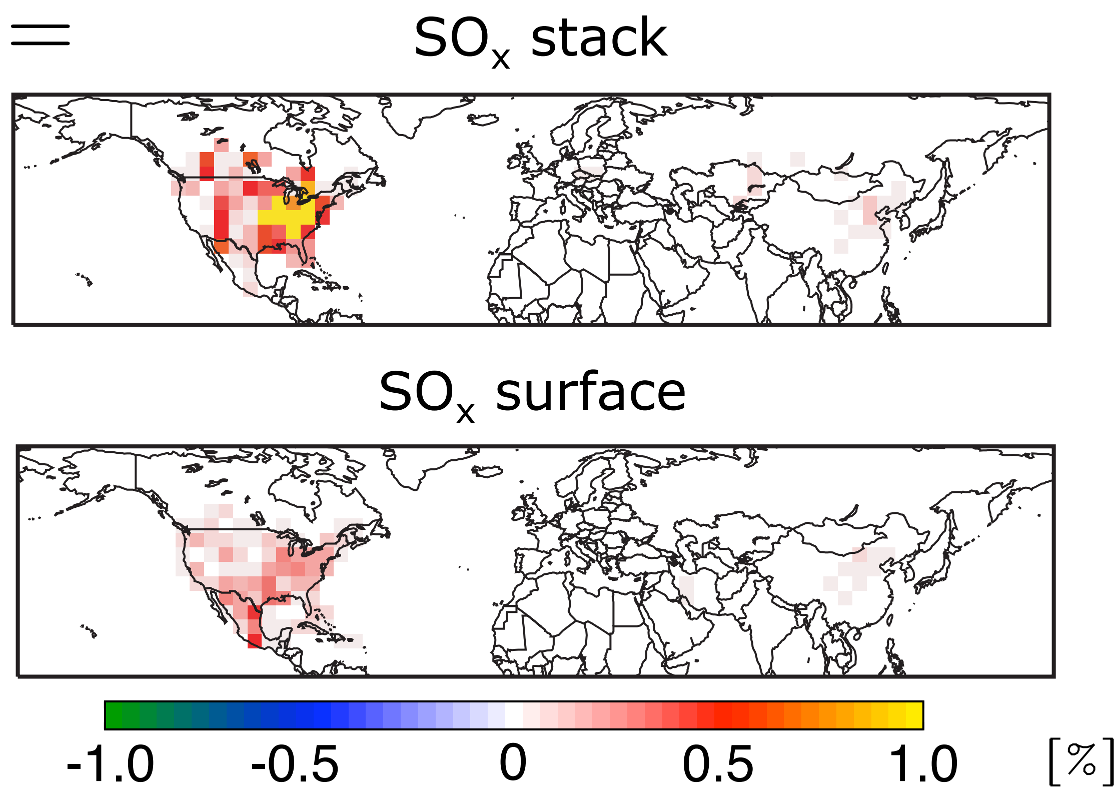
m = sector
i = location
p = emission
λ = sensitivity

Emission sector	January	April	July	October
SO_x surface	-11	-14	-11	-12
SO_x stack	16	17	13	13
SO_x shipping	-4	-2	-2	-1
NH_3 anthropogenic	-10	-11	-16	-23
NH_3 natural	9	11	12	14
NH_3 biomass burning	-18	-9	-3	0
NH_3 biofuel	18	9	8	10
NO_x surface	-2	-4	0	-6
NO_x stack	13	11	26	14
NO_x lightning	-6	-5	-19	-6
NO_x soil	-4	-2	-8	-2

AQ Attainment: long-range influences

$$J = \sum_{\text{in US}} \left([\mathrm{SO_4^{2-}}] + [\mathrm{NH_4^+}] + [\mathrm{NO_3^-}]\right)_{\text{24 h, surface level}}$$

$$\frac{\partial J}{\partial p}\frac{p}{J} \times 100\% \text{ for } p =$$



More than 25% of the influence of SO_x emissions on U.S. inorganic $PM_{2.5}$ comes from emissions outside the U.S.

AQ Attainment: long-range influences

Table shows the total influence of each sector (Total) and the percent of that total from each spatial domain on *J*. Sectors with largest influence are highlighted.

Emission sector	Total sensitivity	Percent from each region			
		U.S.	Canada	Mexico	ROW
SO_x surface	11.1	57.8	8.2	23.9	10.1
SO_x stack	30.1	75.1	16.7	3.4	4.7
SO_x shipping	2.0	67.9	6.9	6.4	19. 9
SO_x biomass burning	0.2	16.2	1.1	77.3	5.4
SO_x bio fuel	0.03	2.9	25.4	36.1	35.6
NH_3 anthropogenic	19.6	90.0	6.0	2.3	1.7
NH_3 natural	9.2	89.4	8.4	0.1	1.3
NH_3 biomass burning	0.6	60.1	2.3	33.3	3.1
NH_3 biofuel	3.48	95.4	3.9	0.4	0.2
NO_x surface	6.7	84.4	5.3	8.3	2.0
NO_x stack	2.7	97.7	1.1	0.4	0.8
NO_x lightning	0.1	68.3	1.1	24.3	6.2
NO_x soil	0.7	65.3	4.1	28.8	1.7

Final comments on adjoint sensitivities

Disadvantages

- sensitivities ≠ source attribution

Advantages

- Computational efficiency
- No perturbation to forward model
  - sensitivities around current model state
  - relevant for policy (+/- 10-30% Δemission)
- Models can be first conditioned to observations using 4D-Var
- Estimates of emissions influence side-by-side with estimates influence of other parameters

Towards actual decision making activities

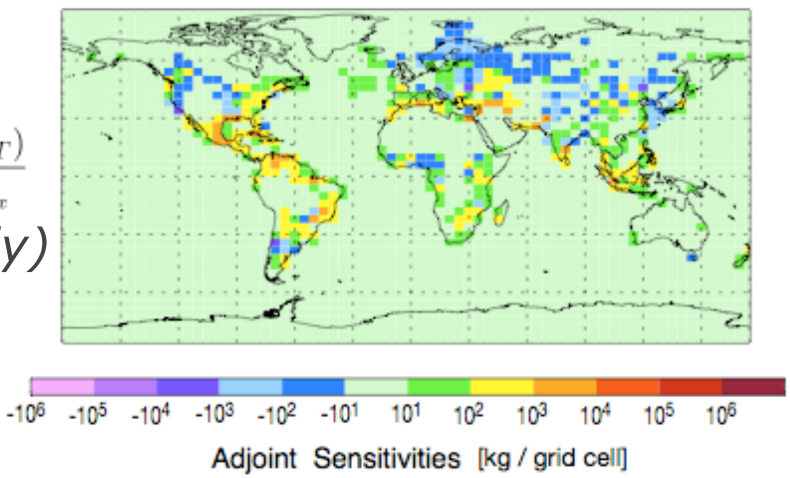
Consider additional observational constraints

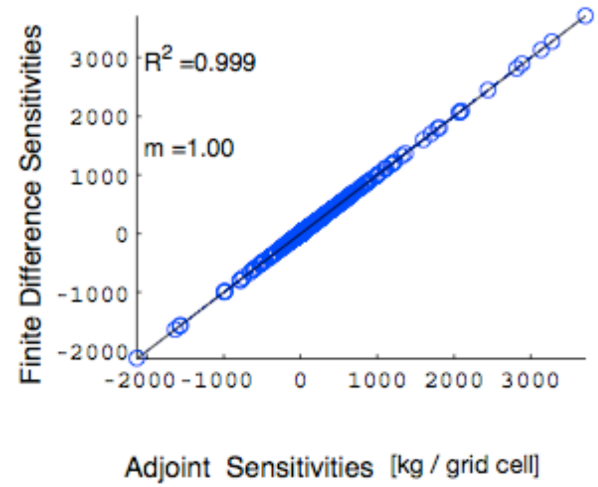
- combine remote sensing with surface observations
- gas- and aerosol-phase

Testing the Adjoint: single processes, 1 week

$$\frac{\partial J(g_{NIT})}{\partial \sigma_{ESO_x}}$$

(thermo only)

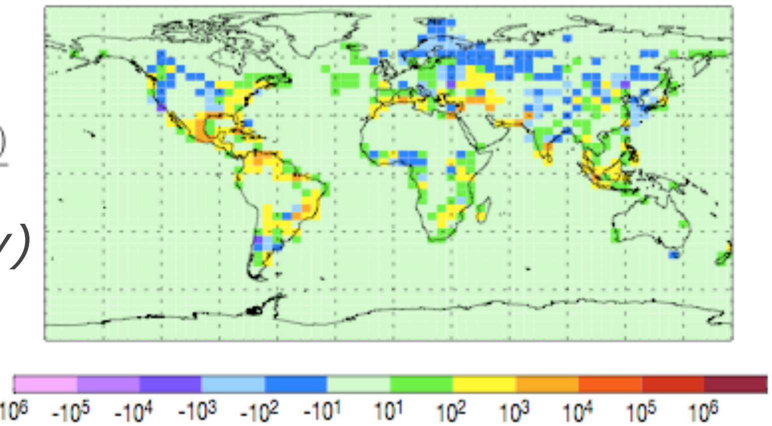


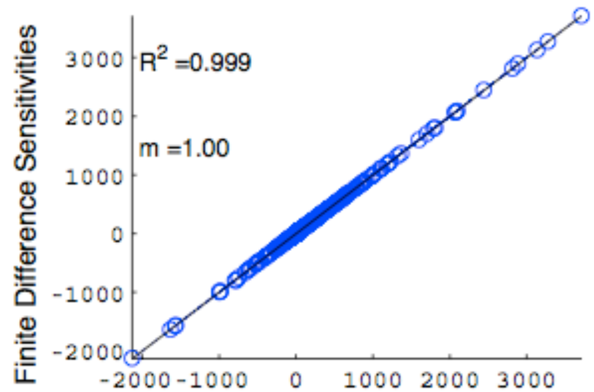


Testing the Adjoint: single processes, 1 week

$$\frac{\partial J(g_{NIT})}{\partial \sigma_{ESO_x}}$$

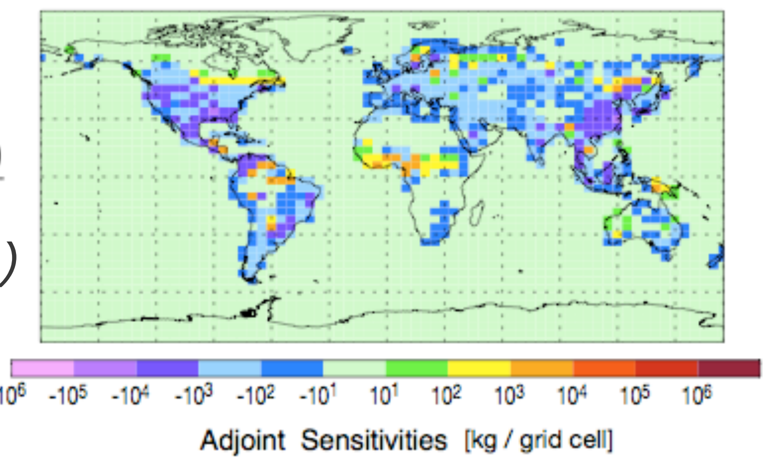
(thermo only)

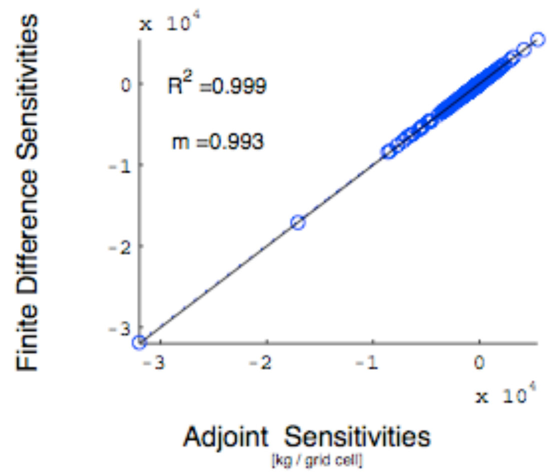




$$\frac{\partial J(g_{MACR})}{\partial \sigma_{ENO_x}}$$

(chem only)





AQ Attainment

Consider a representative metric of $PM_{2.5}$ air quality,

$$J = \frac{1}{2}\sum \mathrm{MAX}[(\mathrm{inorganic\ PM}_{2.5})_{\mathrm{24h}} - 10\mu\mathrm{g/m}^3, 0]^2$$

Calculate the sensitivity of this metric w.r.t. $PM_{2.5}$ precursor emissions, E.

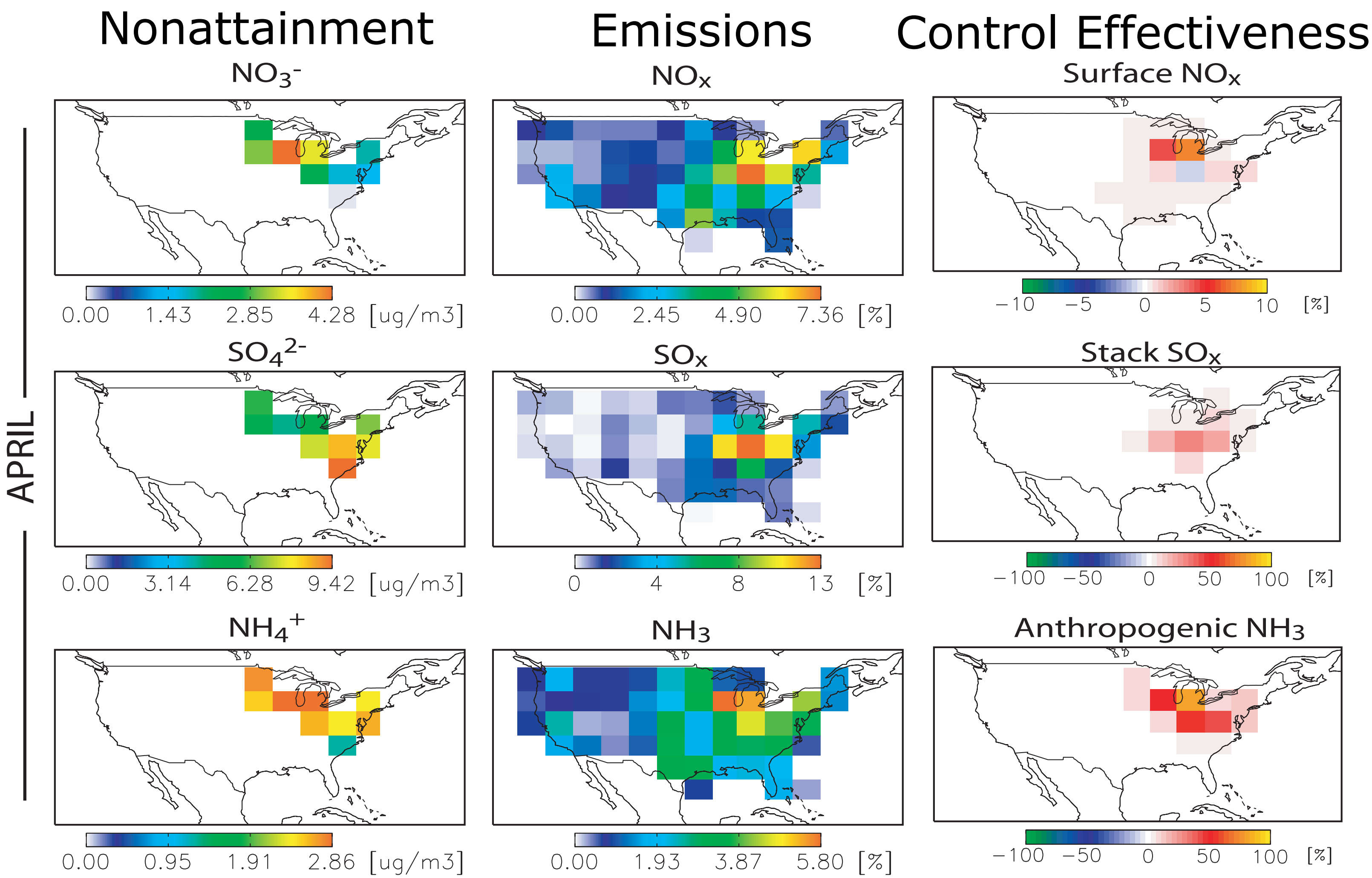
"Susceptibility" = semi normalized sensitivities

$$\frac{\partial J}{\partial E} \times \frac{100\%}{J} \approx \frac{\triangle J[\%]}{E[molec/cm2/s]}$$

"Control effectiveness" = fully normalized sensitivities

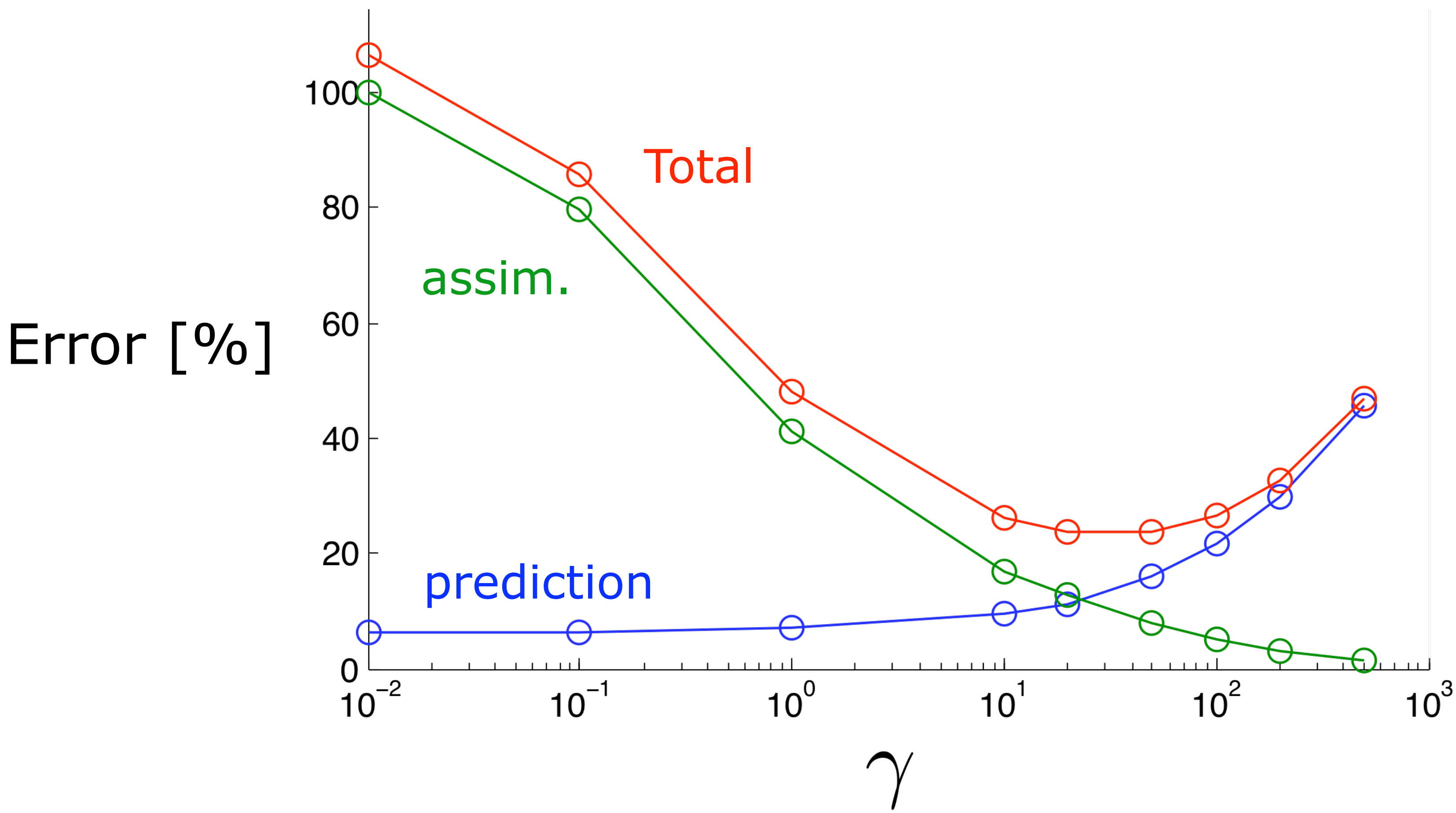
$$\frac{\partial J}{\partial E} \times \frac{E}{J} \times 100\% \approx \frac{\triangle J[\%]}{\triangle E/E}$$

AQ Attainment: April



Regularization Parameter

$$J = \frac{1}{2}\sum_{\mathbf{c}\in\Omega}(H\mathbf{c}-\mathbf{c}_{obs})^T\mathbf{S}_{obs}^{-1}(H\mathbf{c}-\mathbf{c}_{obs}) + \frac{1}{2}\gamma_r(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)^T\mathbf{S}_{\sigma_a}^{-1}(\boldsymbol{\sigma}-\boldsymbol{\sigma}_a)$$



Discrete Adjoints (general)

Consider a discrete governing equation that propagates the vector of concentrations from time step *n* to step *n+1:*

$$\mathbf{c}^{n+1} = F^n(\mathbf{c}^n, \mathbf{p}), \qquad \mathbf{c}^n = [c_1^n, \ldots, c_k^n, \ldots, c_K^n]^T$$ Concentrations of species *k*

$$p = [p_1, \ldots, p_m, \ldots, p_M]$$ Parameters (emissions)

$J(\mathbf{c}, \mathbf{p}) = \sum_{n=1}^{N} g^n(\mathbf{c}^n)$ is a model response; we are interested in sensitivity w.r.t. parameters, $\nabla_{\mathbf{p}} J$.

1. Define the local Jacobians:

$$\frac{\partial \mathbf{c}^{n+1}}{\partial \mathbf{c}^n} = \frac{\partial F^n(\mathbf{c}^n)}{\partial \mathbf{c}^n} \equiv \mathbf{F}_c^n, \qquad \frac{\partial \mathbf{c}^{n+1}}{\partial \mathbf{p}} = \frac{\partial F^n(\mathbf{c}^n)}{\partial \mathbf{p}} \equiv \mathbf{F}_p^n$$

2. Define the adjoint variable:

$$\lambda_c^n = \nabla_{\mathbf{c}^n} J = \sum_{n'=n}^{N} \frac{\partial g^{n'}}{\partial \mathbf{c}^n}$$

3. Expand the RHS of (2) using the chain rule

$$\lambda_c^n = \sum_{n'=n+1}^{N} \left(\prod_{n''=n}^{n'-1} (\mathbf{F}_c^{n''})^T \right) \frac{\partial g^{n'}}{\partial \mathbf{c}^{n'}} + \frac{\partial g^n}{\partial \mathbf{c}^n}$$

4. Solve iteratively (& backwards)

initialize: $\lambda_c^N = \dfrac{\partial g^N}{\partial \mathbf{c}^N}$

iterate:

```
DO n = N, 1, -1
```

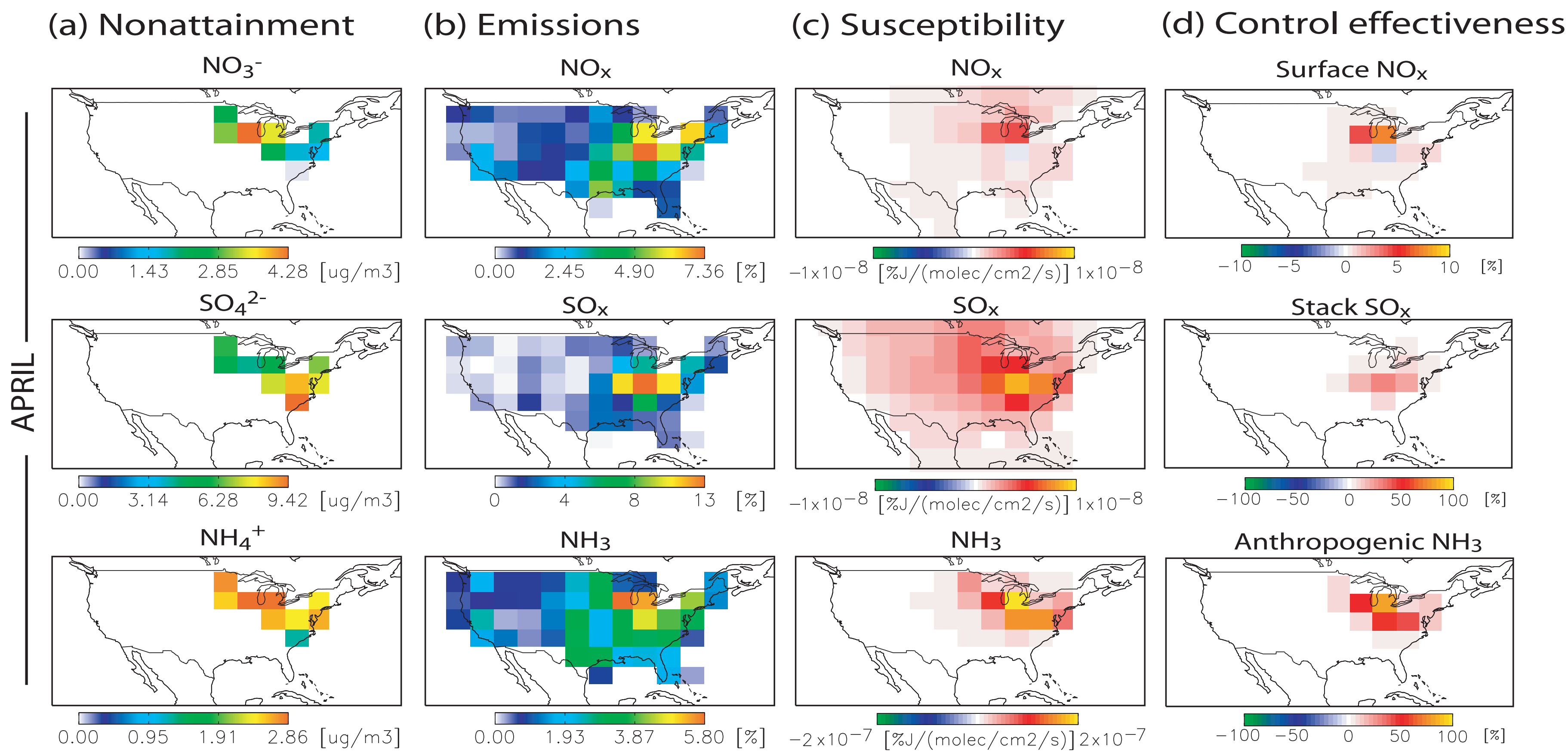
$$\lambda_c^N = (\mathbf{F}_c^{n-1})^T \lambda_c^n + \frac{\partial g^{n-1}}{\partial \mathbf{c}^{n-1}}$$

```
END DO
```

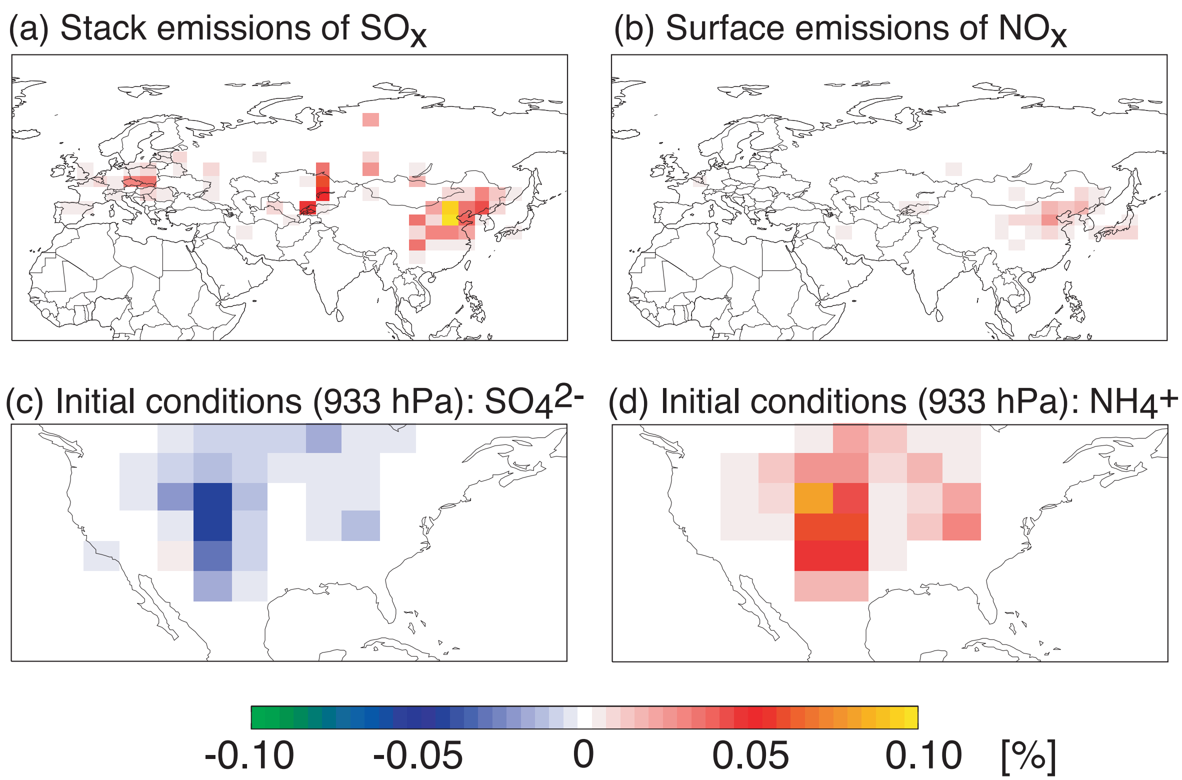
result: $\lambda_c^0 = \nabla_{\mathbf{c}^0} J$

$$\lambda_p = \nabla_{\mathbf{p}} J = \sum_{n=1}^{N} (\mathbf{F}_p^{n-1})^T \lambda_c^n$$

AQ Attainment



GEOS-Chem vs IMPROVE



Aerosols and Radiative Forcing

IPCC 4, WGI, Ch 2, p180:

"It would be useful to identify the RF contribution attributable to different source categories (Section 2.9.3 investigates this).

However, few models have separated out the RF from specific emission source categories."

Forster et al., 2007: Changes in Atmospheric Constituents and in Radiative Forcing. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*

Aerosols and Radiative Forcing

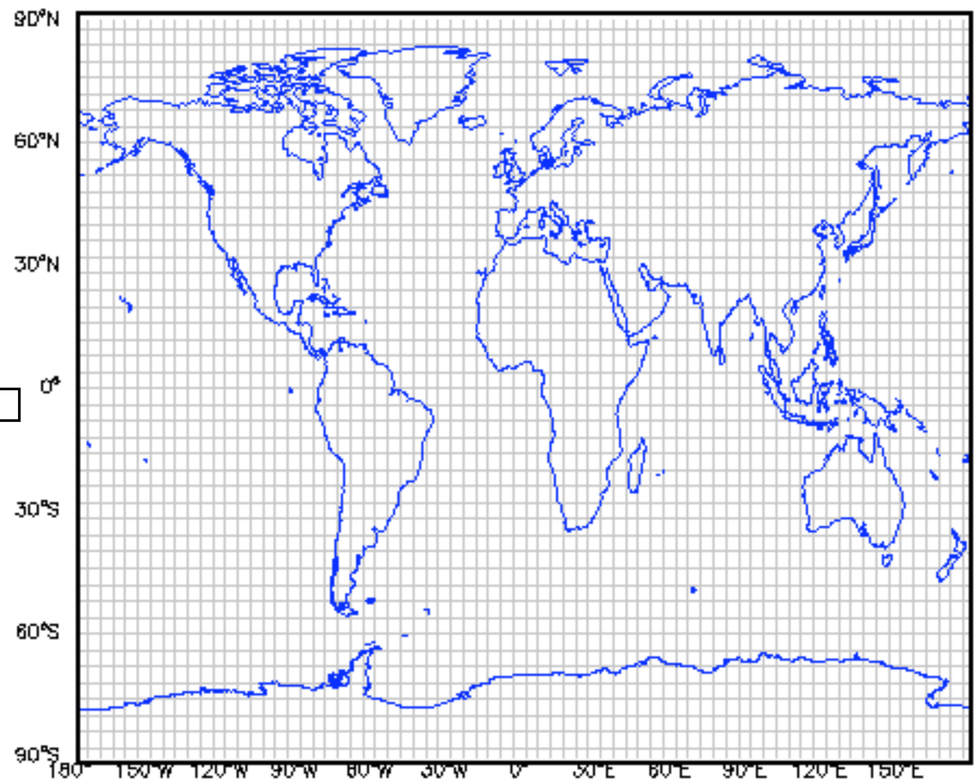
Sensitivities from every sector and every region:

δE_1

δE_2

$\vdots$

δE_{10^4} $\Leftarrow$



$\Leftarrow$ δRF

Calculated efficiently (3 x t_{fwd}) with an adjoint model

GEOS-Chem direct RF

Implement radiative transfer, LIDORT, with derivative capabilities (Spurr, 2002).

Approximations made:
Macro
- Clear sky
- Only direct effects
- Only SO_4-NO_3-NH_4-H_2O and BC aerosol

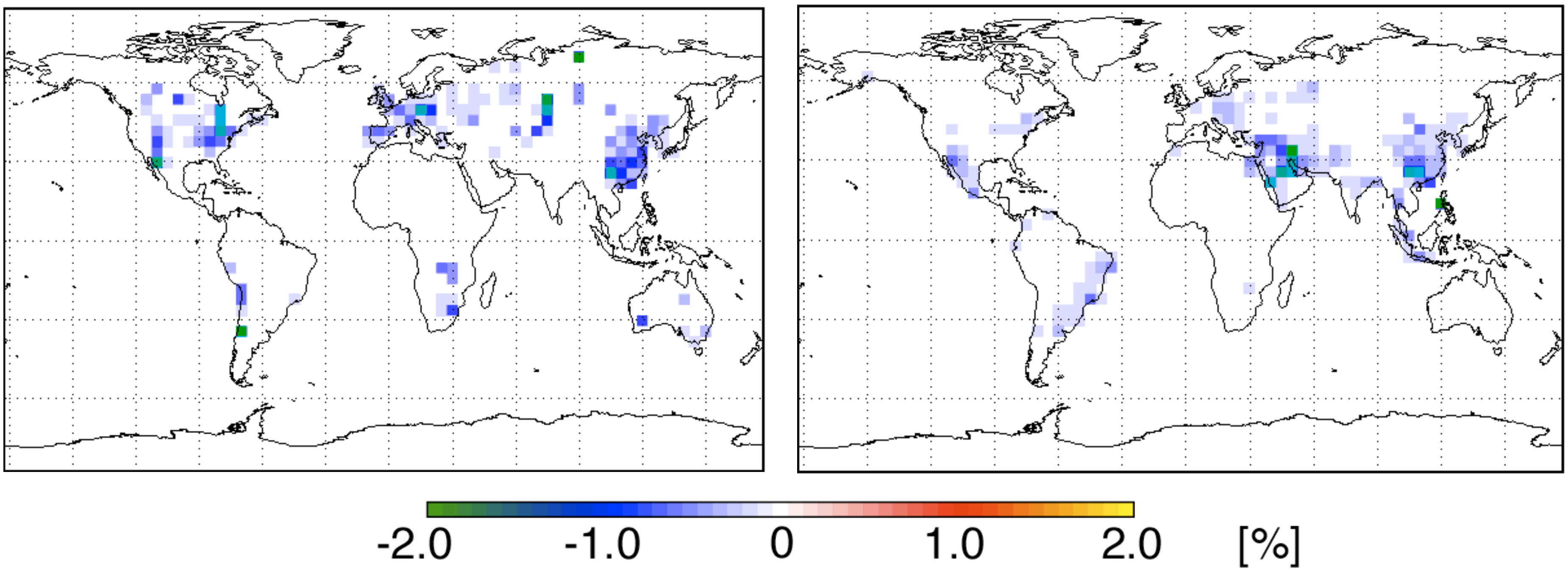
Micro
- Refractive index of SO_4-NO_3-NH_4-H_2O is that of SO_4.
- Assumed dry size
- External mixture

Timescale
- 1 week in July

Clear sky aerosol direct radiative forcing

Sensitivities with respect to different emissions sectors:

Stack SO_x emissions　　Transportation SO_x emissions

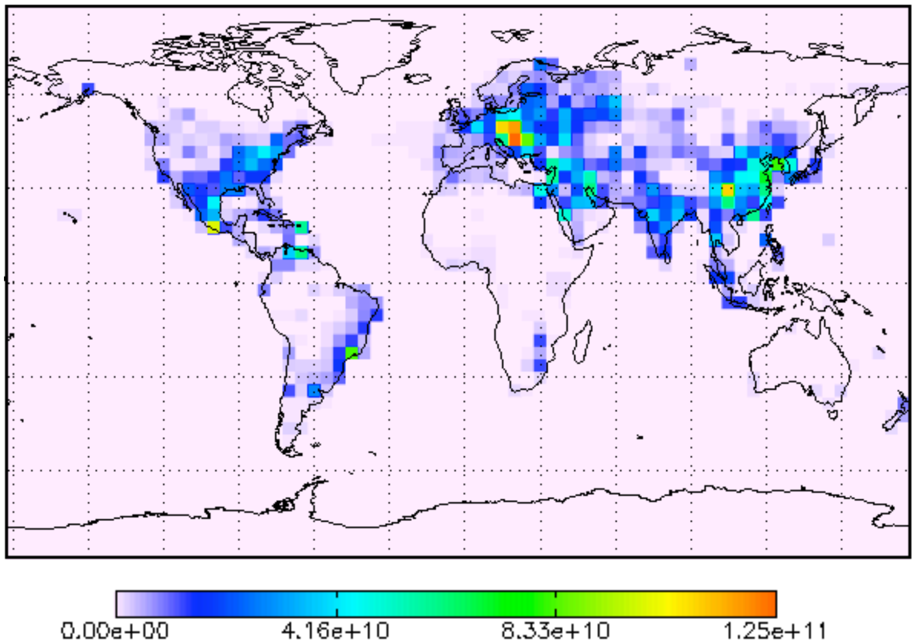


$$\text{sensitivities} = \frac{\partial RF}{\partial E}\frac{E}{RF} \times 100\% \approx \frac{\triangle RF[\%]}{100\% \triangle E}$$

Clear sky aerosol direct radiative forcing

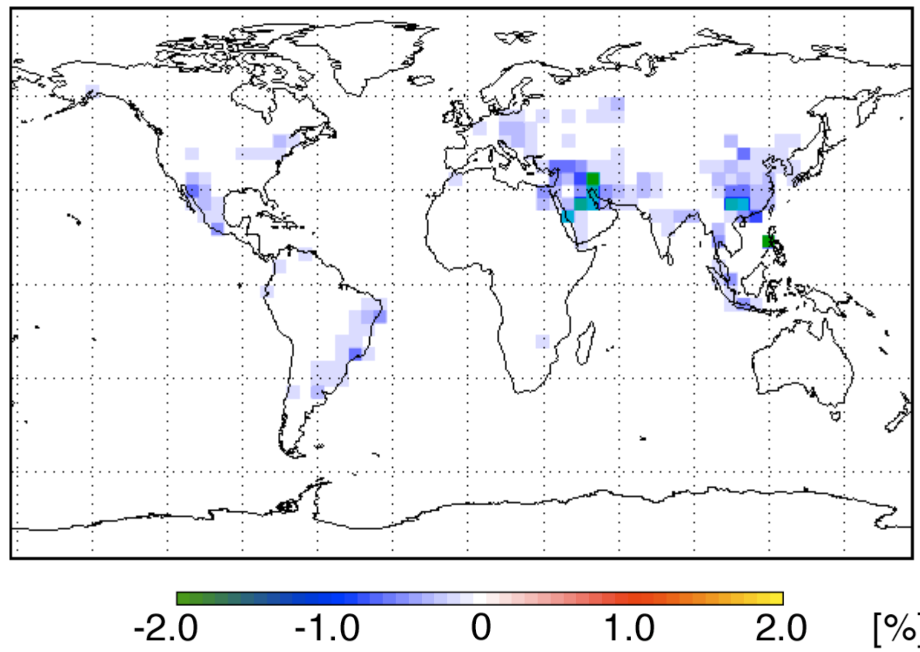
Consider transport sector SO_x

emissions



[molec / cm^2 / s]

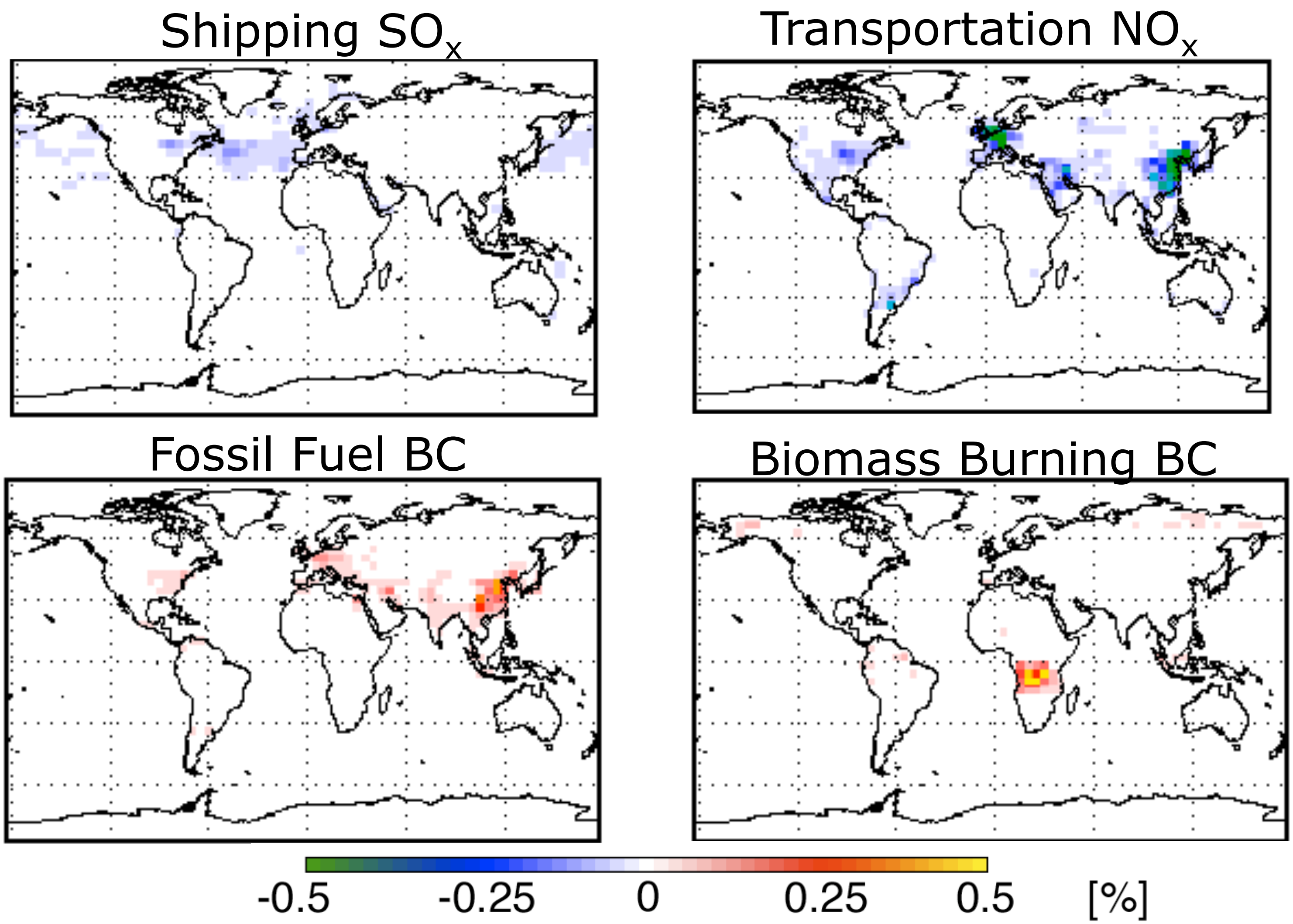
sensitivities



Location matters

Clear sky aerosol direct radiative forcing

Sensitivities with respect to different species & sectors:



Future work

Additional factors to consider

- Organic carbon
- Refractive index / mixing state
- Clouds
- Additional days / seasons
- Indirect effects
- Use GISS climatology, future emissions scenarios

Final comments on adjoint sensitivities

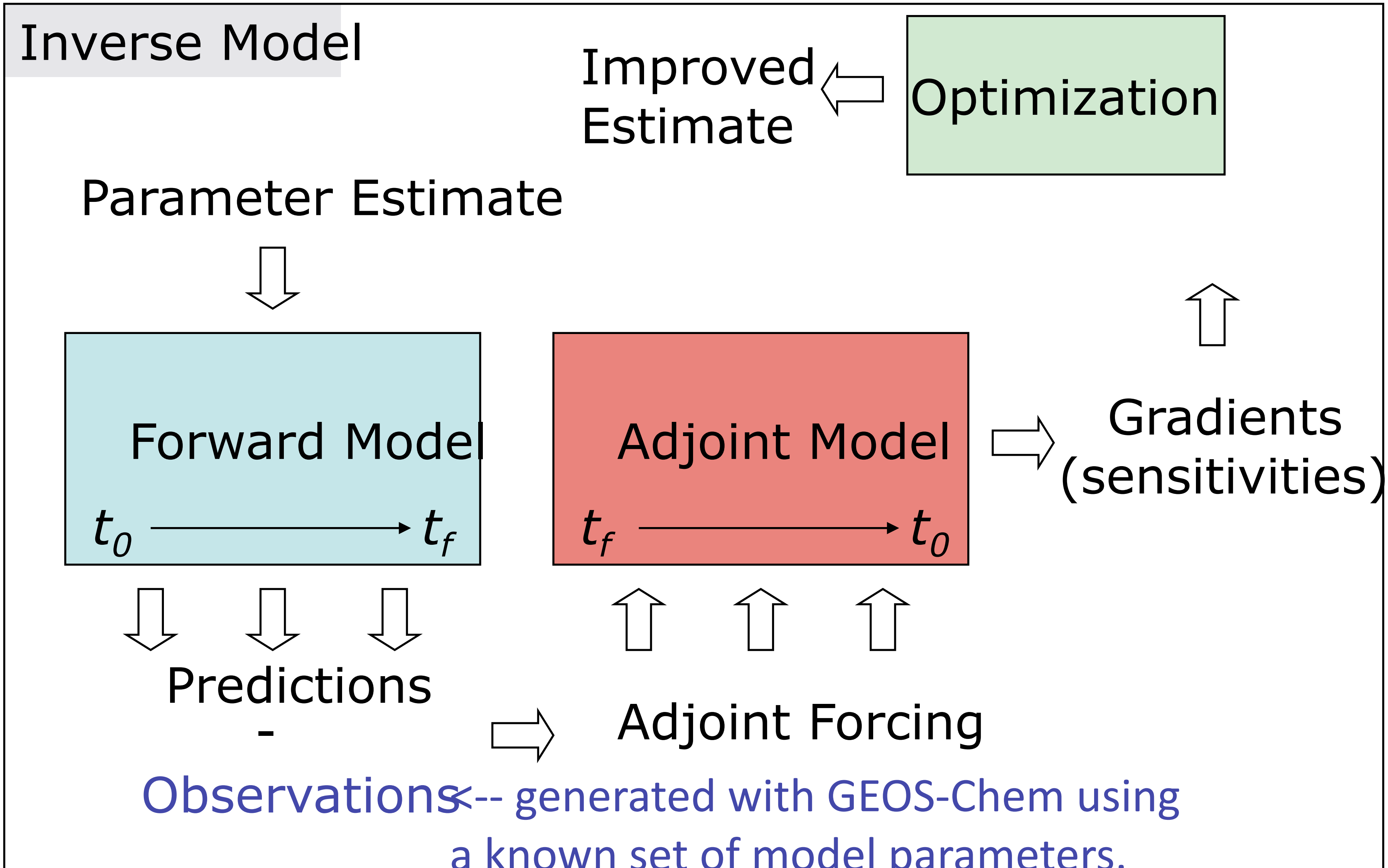
Disadvantages

- sensitivities ≠ source attribution

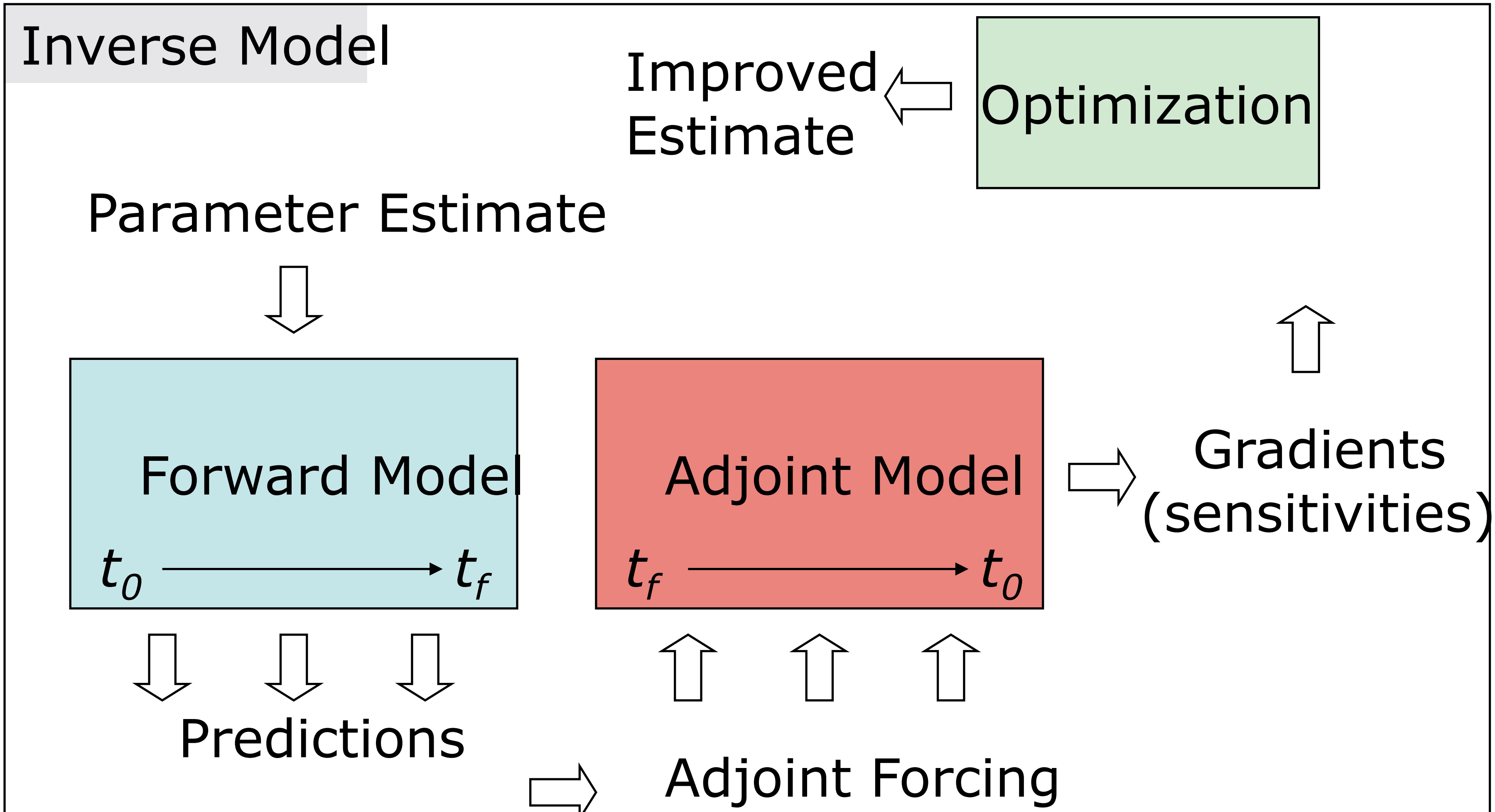
Advantages

- Computational efficiency
- No perturbation to forward model
  - sensitivities around current model state
  - relevant for policy (+/- 10-30% Δemission)
- Models can be first conditioned to observations using 4D-Var
- Estimates of emissions influence side-by-side with estimates influence of other parameters (ex: D_{dry})

Inverse Modeling Tests: Psuedo Observations

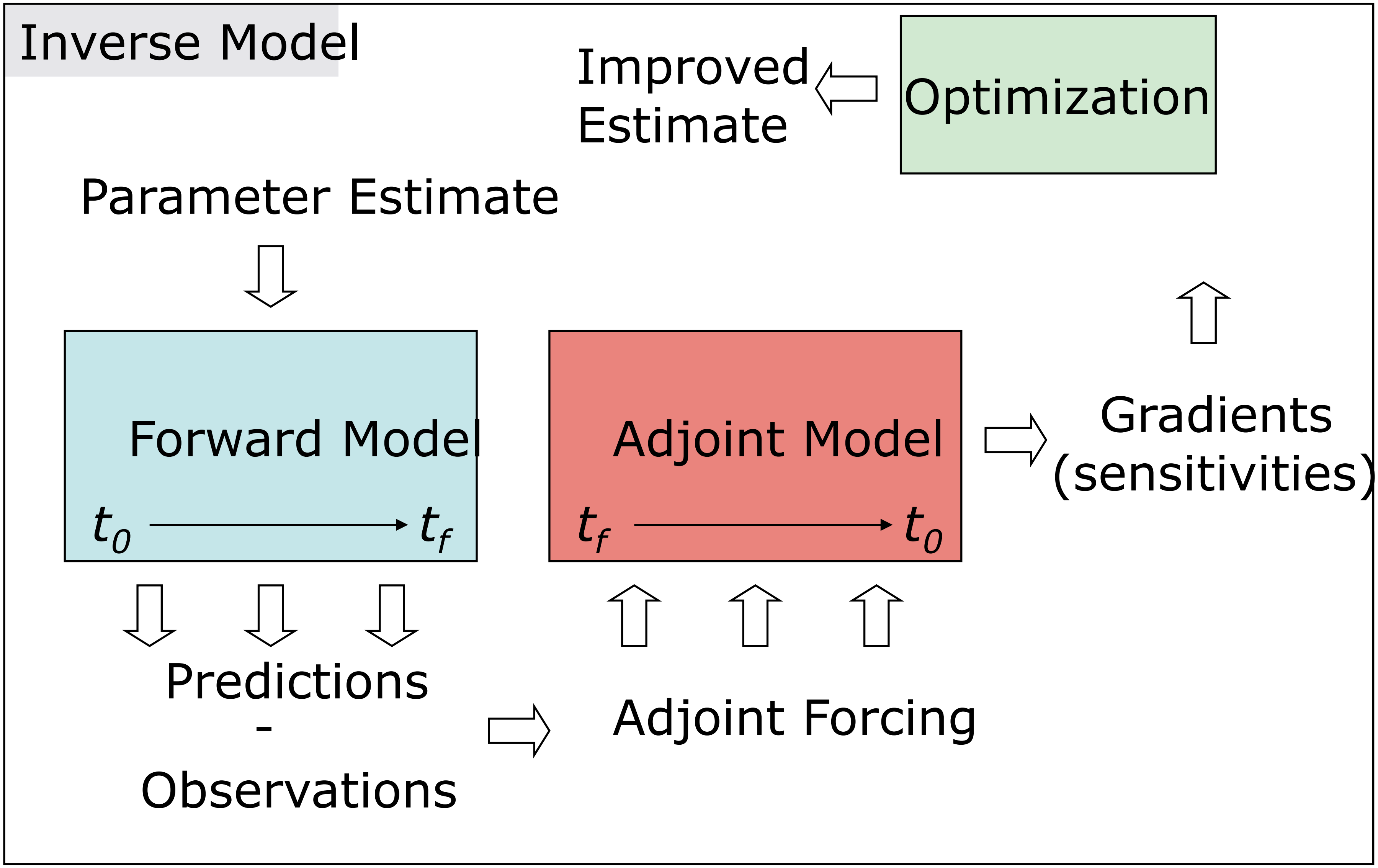


Inverse Modeling Tests: Psuedo Observations

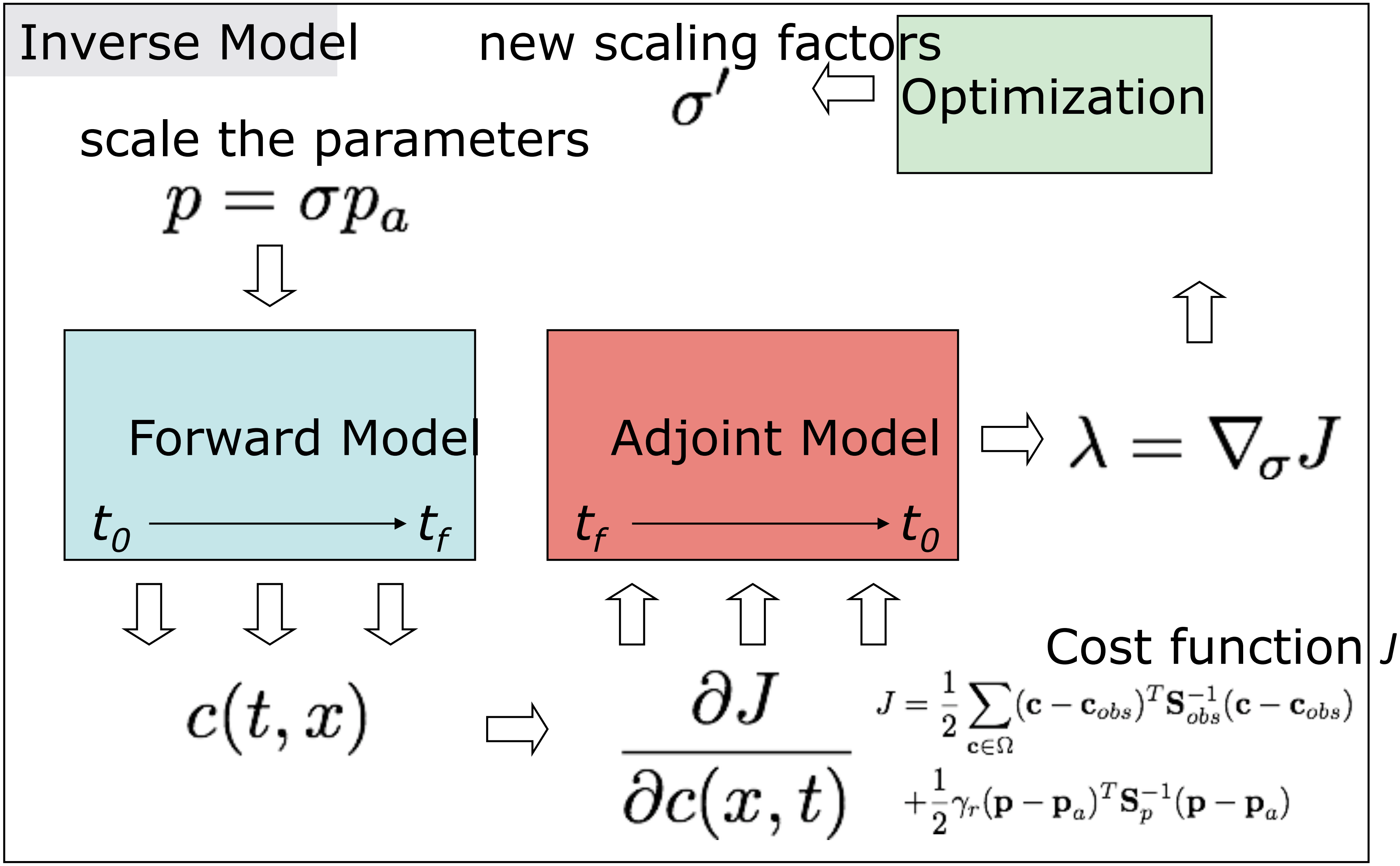


$$J = \frac{1}{2}\sum_{\mathbf{c}\in\Omega}(\mathbf{c}-\mathbf{c}_{obs})^T\mathbf{S}_{obs}^{-1}(\mathbf{c}-\mathbf{c}_{obs}) + \frac{1}{2}\gamma_r(\mathbf{p}-\mathbf{p}_a)^T\mathbf{S}_p^{-1}(\mathbf{p}-\mathbf{p}_a)$$

Inverse Modeling using Adjoint Model



Inverse Modeling using Adjoint Model



Discrete Adjoint of Chemical Reaction Kinetics

Consider reaction rate equations:

$$\frac{dc}{dt} = f(c, t)$$

$$\frac{dc}{dt} = \underbrace{p_1 c_1 - p_2}_{\text{Reaction rate parameters}} c_2 c_3$$

Discrete Adjoint of Chemical Reaction Kinetics

Numerical model (Rosenbrock solver):

$$c^{n+1} = c^n + \sum_{i=1}^{s} m_i k_i, \quad \mathrm{Err}^{n+1} = \sum_{i=1}^{s} e_i k_i$$

$$T_i = t^n + \alpha_i h, \quad C_i = c^n + \sum_{j=1}^{i-1} a_{ij} k_j$$

$$A = \left[\frac{1}{h\gamma} - \hat{J}^T(t^n, c^n) \right]$$

$$A \cdot k_i = f(T_i, C_i) + \sum_{j=1}^{i-1} \frac{b_{ij}}{h} k_j + h\gamma_i f_t(t^n, c^n)$$

Lots of numerical tricks for handling stiff ODEs

Discrete Adjoint of Chemical Reaction Kinetics

Adjoint of numerical model with respect to …

… concentrations (Sandu et al., 2002):

$$\lambda_c^n = \lambda_c^{n+1} + \sum_{i=1}^{s} (H(t^n, c^n) \times k_i)^T \cdot u_i$$
$$+ \sum_{i=1}^{s} \hat{J}^T(T_i, C_i) \cdot u_i.$$

$$\hat{J} = f_c = \frac{\partial f}{\partial c}$$ (Jacobian) $$H = \frac{\partial^2 f}{\partial c_i \partial c_j}$$ (Hessi an)

… reaction rate parameters (Henze et al., 2007):

$$\lambda_p^n = \lambda_p^{n+1} + \sum_{i=1}^{s} (\hat{J}_p(t^n, c^n) \times k_i)^T \cdot u_i$$
$$+ \sum_{i=1}^{s} f_p^T(T_i, C_i) \cdot u_i.$$

KPP automatically generates simulation and direct/adjoint sensitivity code for chemistry

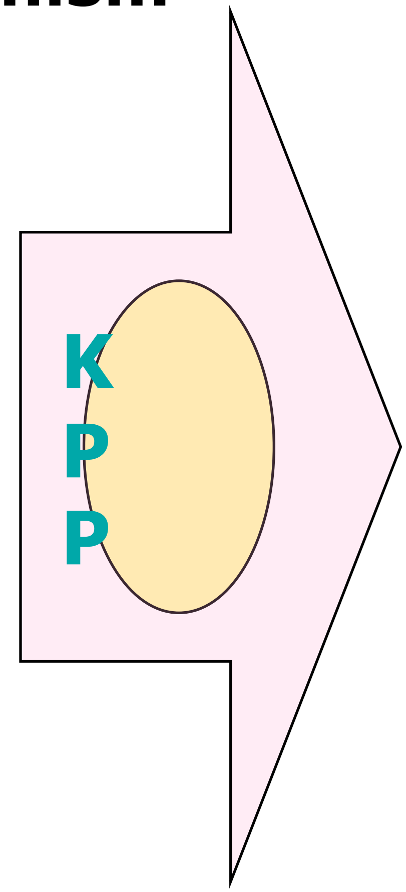
Chemical mechanism

```
#INCLUDE atoms

#DEFVAR
O  =  O;  O1D  =  O;
O3   =   O + O + O;
NO  =   N + O;
NO2  =  N + O + O;

#DEFFIX
O2   =   O + O;  M  =   ignore;

#EQUATIONS  { Small Stratospheric }
O2  + hv = 2O            :   2.6E-10*S;
O    + O2 = O3           :   8.0E-17;
O3  + hv = O   + O2      :   6.1E-04*S;
O    + O3 = 2O2          :   1.5E-15;
O3  + hv = O1D + O2      :   1.0E-03*S;
O1D  + M  = O   + M      :   7.1E-11;
O1D  + O3 = 2O2          :   1.2E-10;
NO    + O3 = NO2 + O2    :   6.0E-15;
NO2  + O  = NO  + O2     :   1.0E-11;
NO2  + hv = NO  + O      :   1.2E-02*S;
```

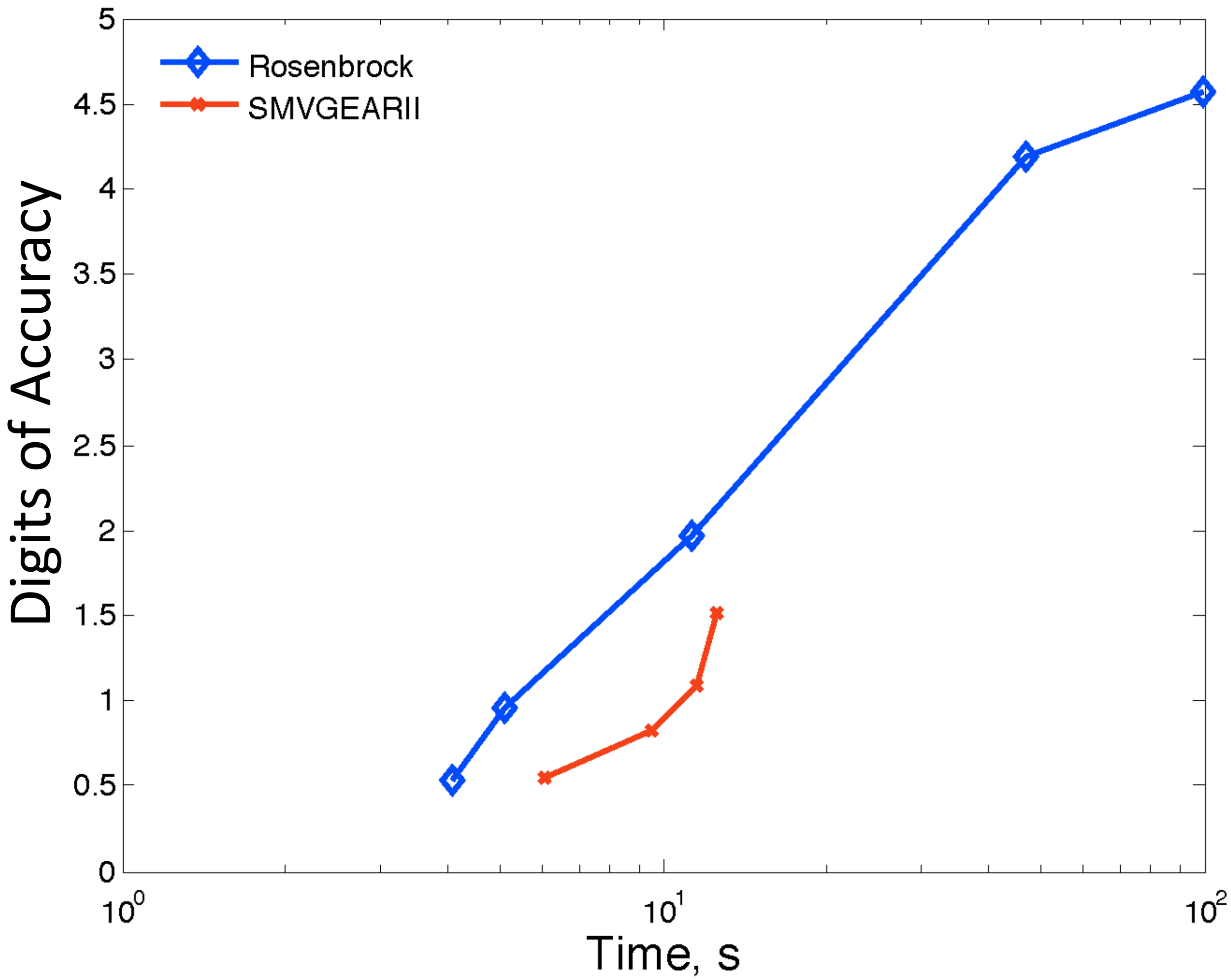


Simulation code

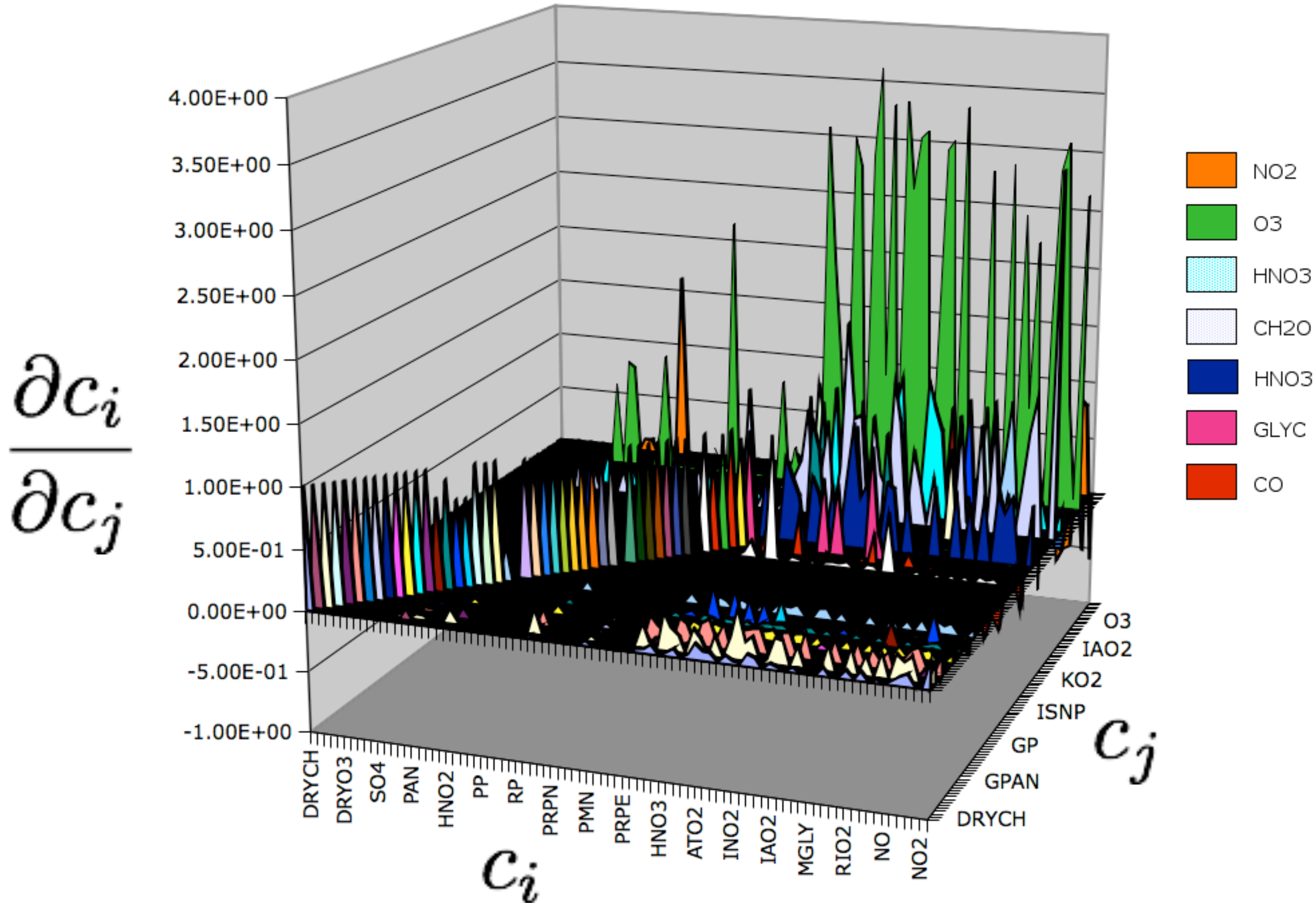
```
SUBROUTINE FunVar ( V,  F, RCT, DV )
   INCLUDE 'small.h'
    REAL*8 V(NVAR), F(NFIX)
    REAL*8 RCT(NREACT), DV(NVAR)
C A - rate for each equation
    REAL*8 A(NREACT)
C Computation of equation rates
    A(1) = RCT(1)*F(2)
    A(2) = RCT(2)*V(2)*F(2)
    A(3) = RCT(3)*V(3)
    A(4) = RCT(4)*V(2)*V(3)
    A(5) = RCT(5)*V(3)
    A(6) = RCT(6)*V(1)*F(1)
    A(7) = RCT(7)*V(1)*V(3)
    A(8) = RCT(8)*V(3)*V(4)
    A(9) = RCT(9)*V(2)*V(5)
    A(10) = RCT(10)*V(5)
C Aggregate function
    DV(1) = A(5)-A(6)-A(7)
    DV(2) = 2*A(1)-A(2)+A(3)-A(4)+A(6)-&A(9)+A(10)
    DV(3) = A(2)-A(3)-A(4)-A(5)-A(7)-A(8)
    DV(4) = -A(8)+A(9)+A(10)
    DV(5) = A(8)-A(9)-A(10)
    END
```

[Damian et.al., 1996; Sandu et.al., 2002]

KPP generated code is fast: compare to widely used GEAR solver

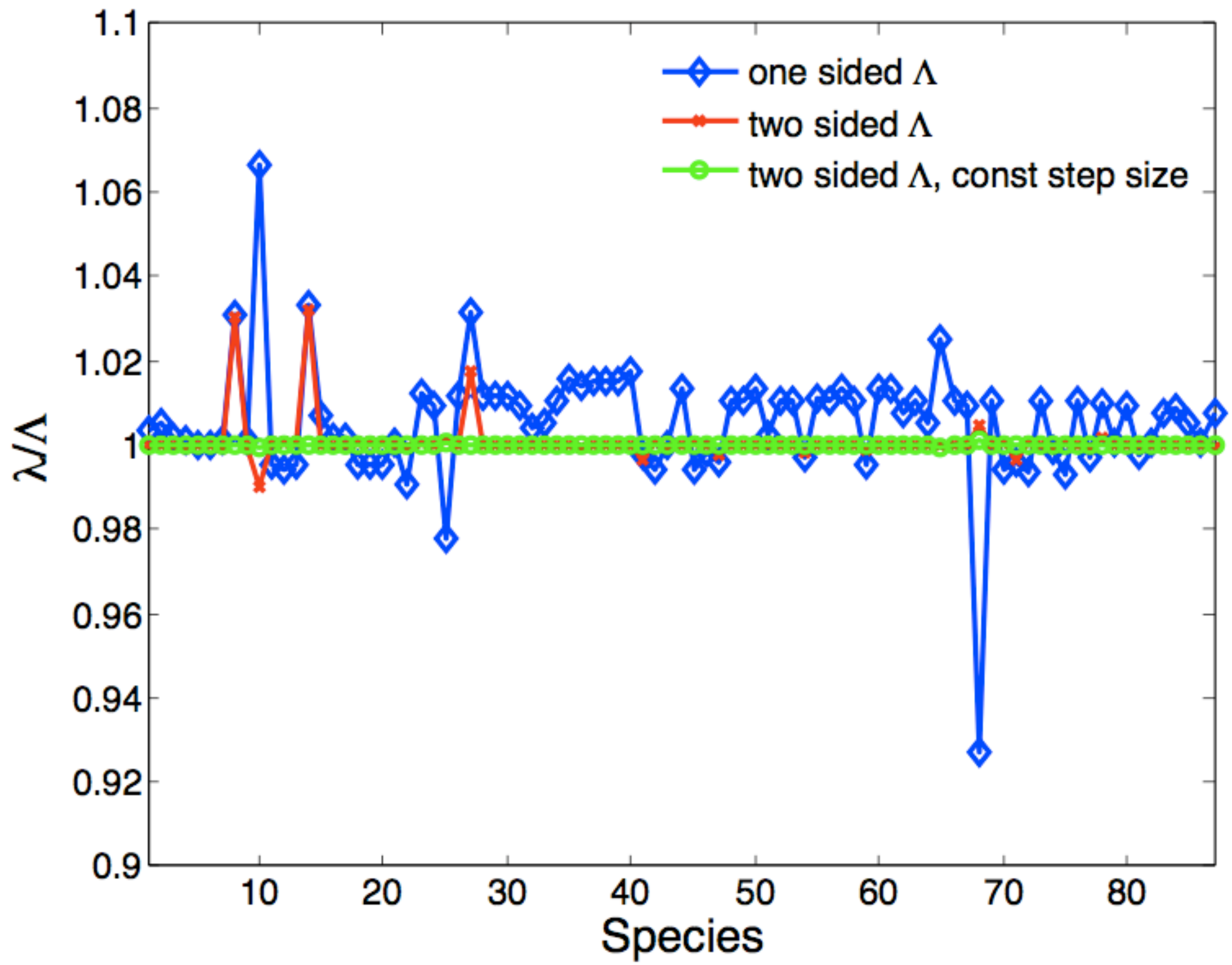


Box model test with KPP

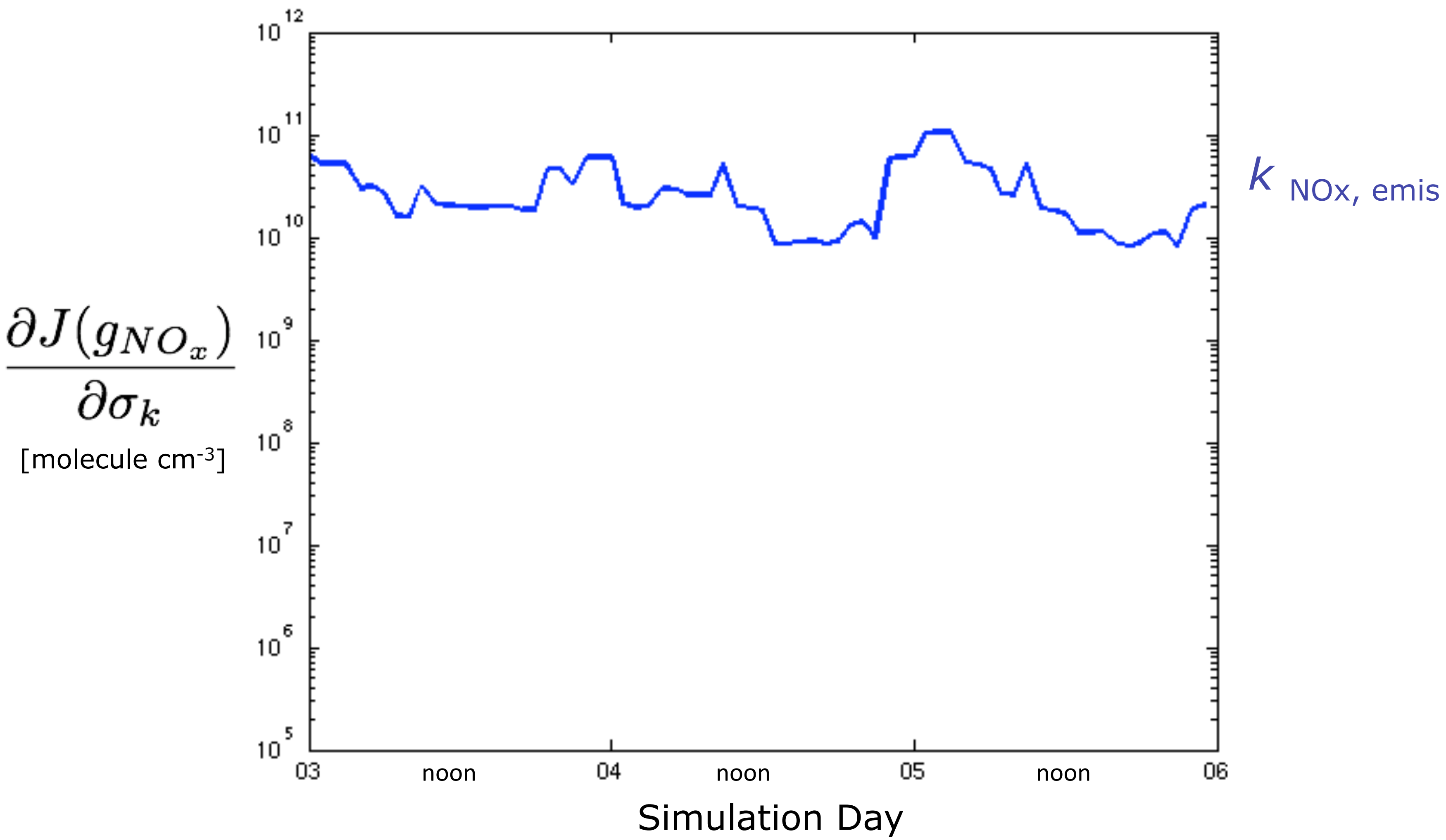


87 species, 307 reactions: Note the sparse structure --> Fast!

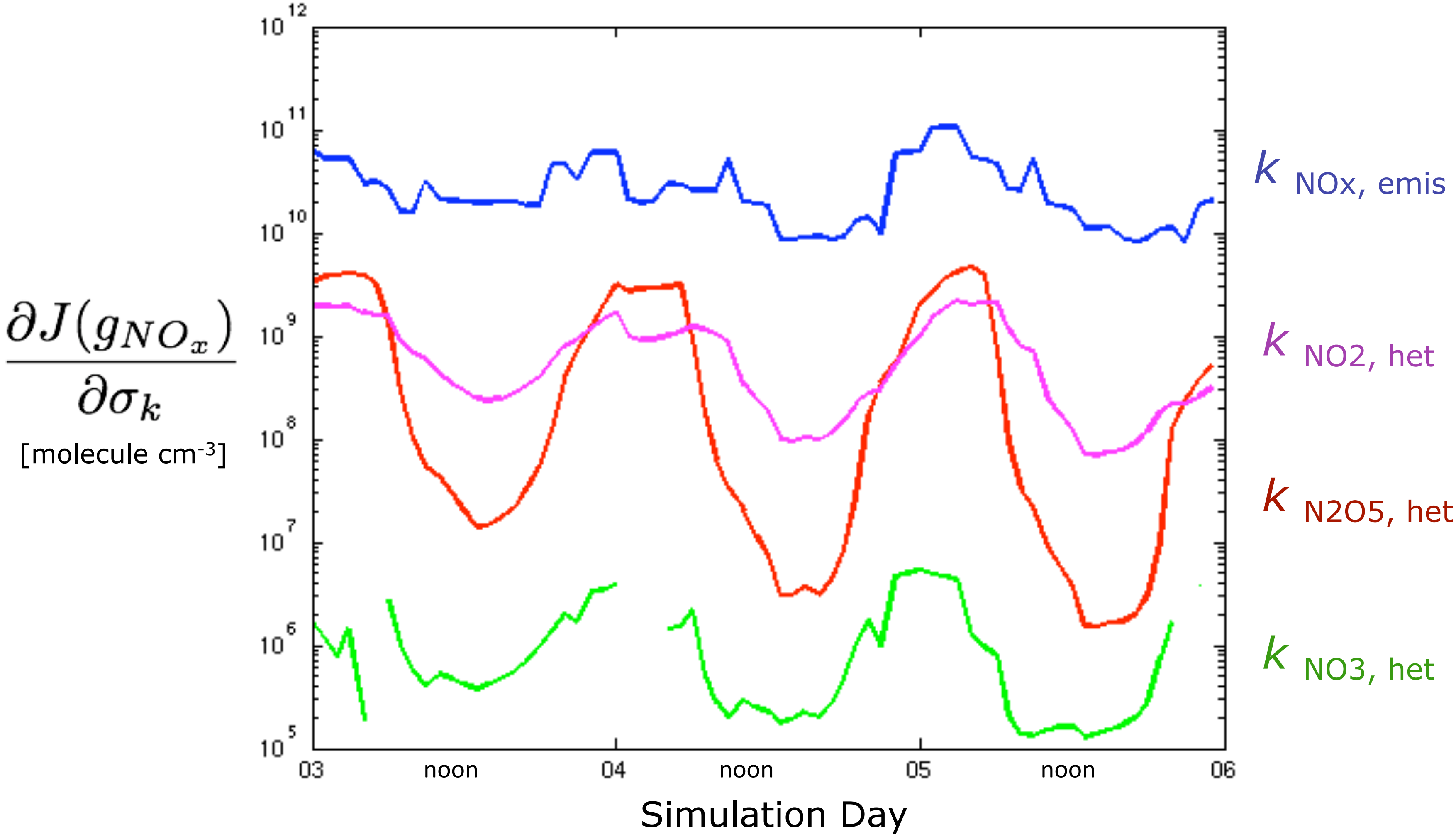
Box Model Test: **Discrete** sensitivity with respect to p_1



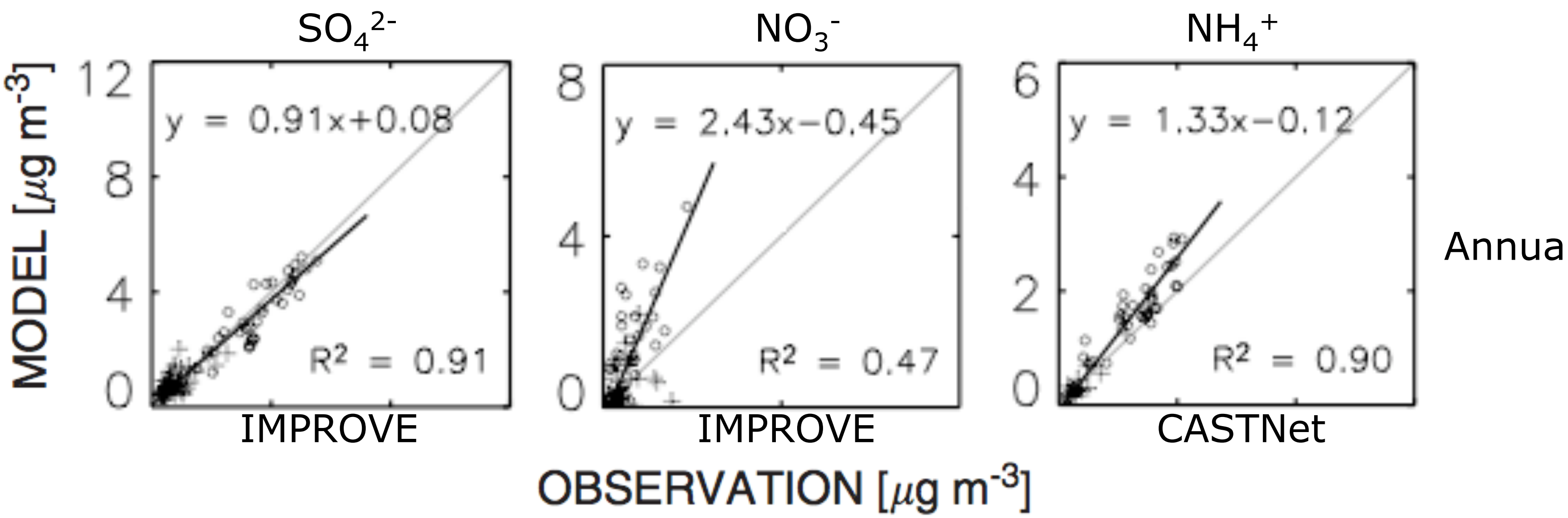
Sensitivity of NO_x on rate constants in chemical mechanism



Sensitivity of NO_x on rate constants in chemical mechanism

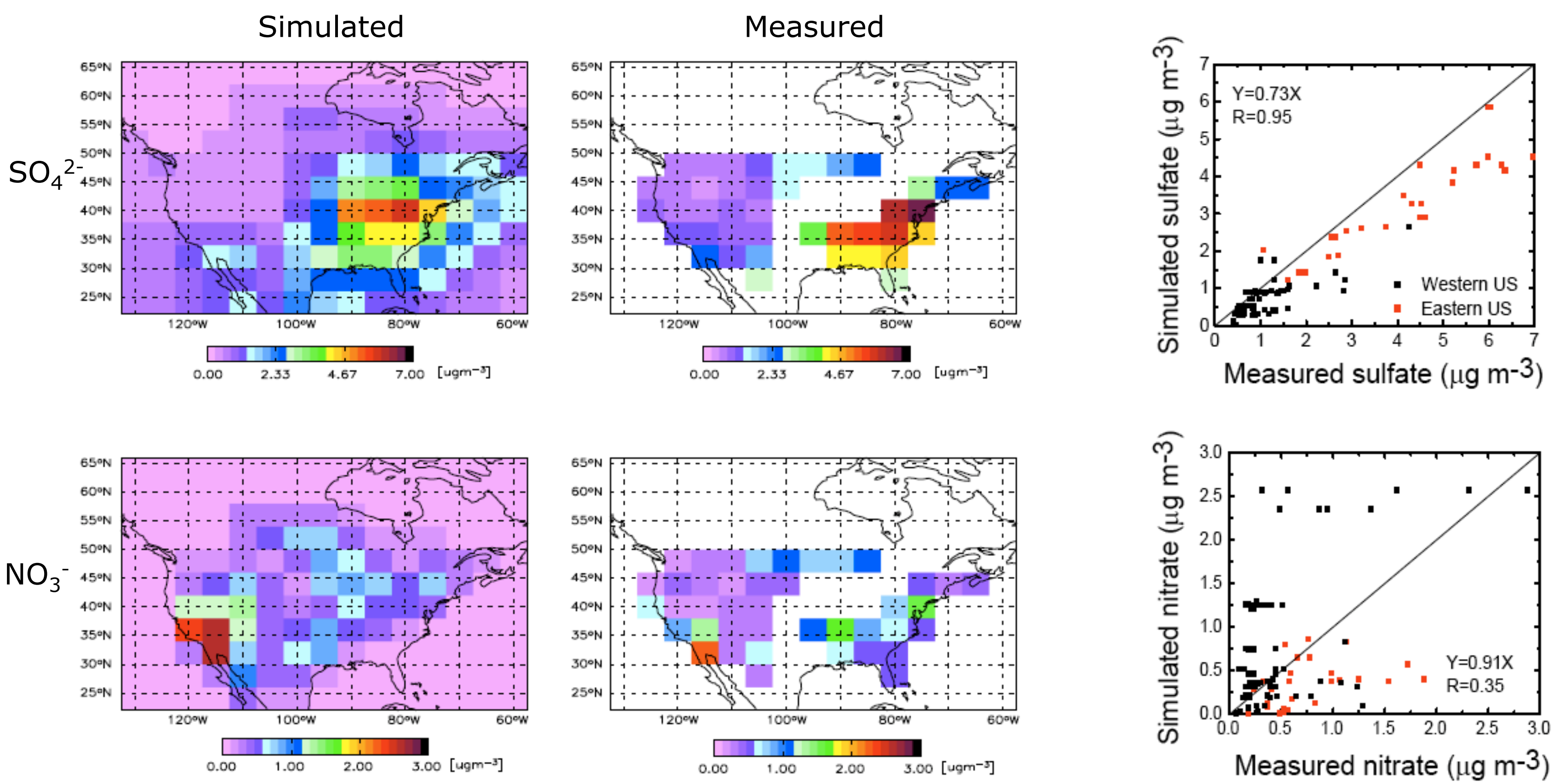


GEOS-Chem vs Observations



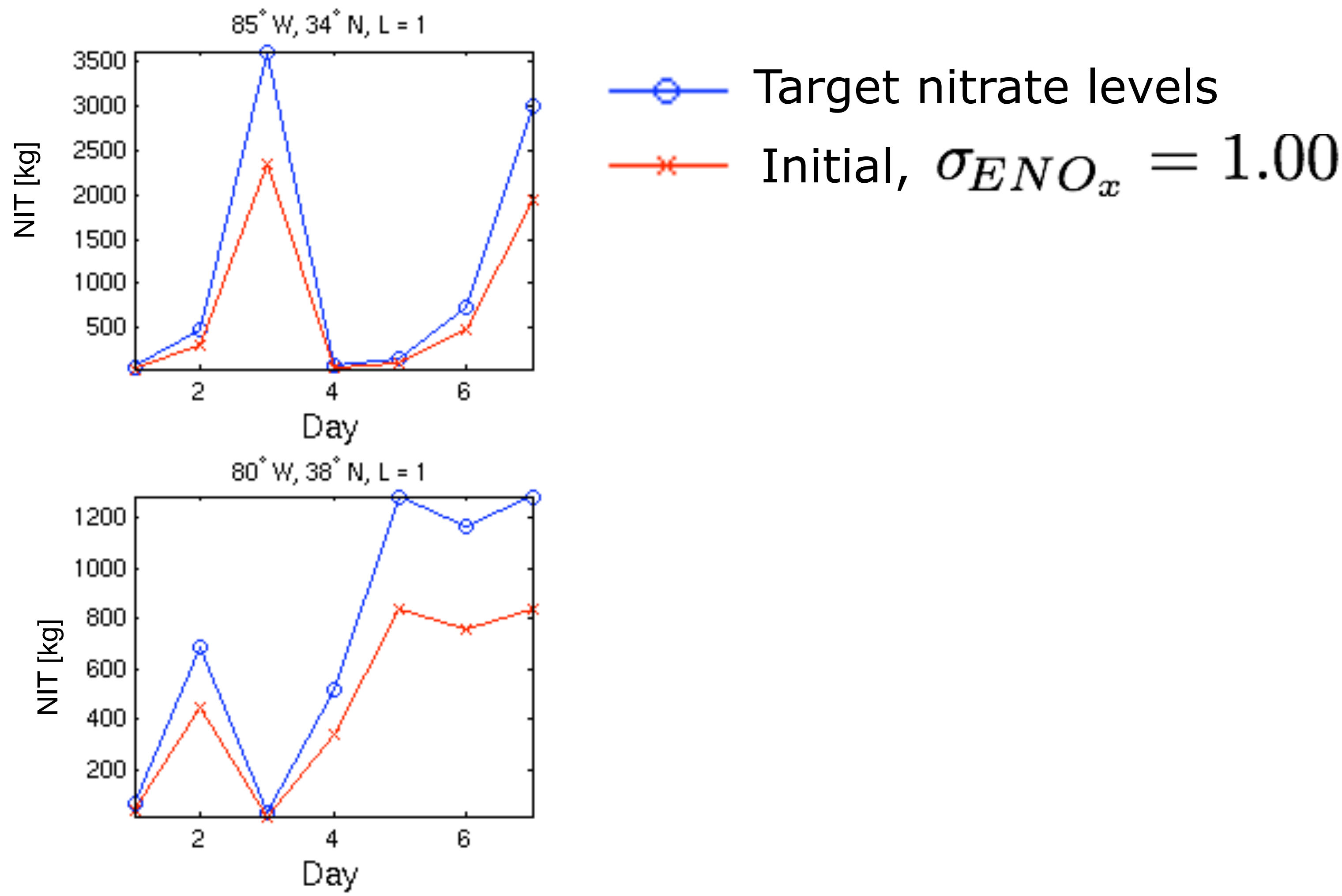
Model description: Park et al., (2004)

GEOS-Chem vs Observations



Liao et al., (2007)

Nitrate dependence on NO_x



Nitrate dependence on NO_x