NO_x Chemical Sinks in the Upper Troposphere

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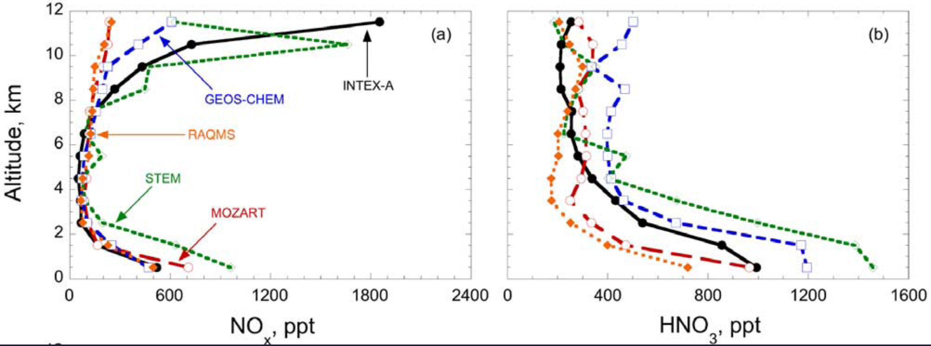
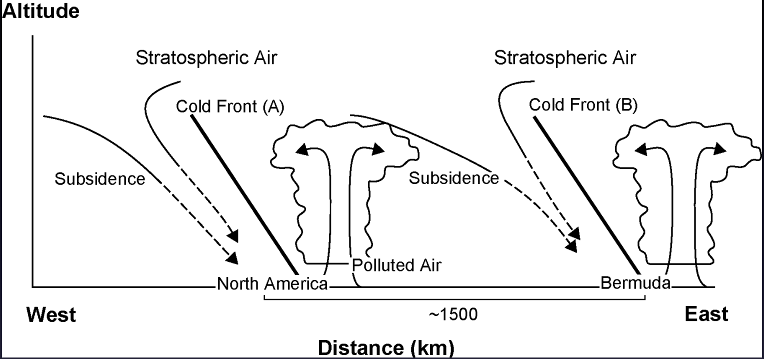
Aircraft analysis shows NO_x low-bias

Simulated NO_x vertical profiles from Singh 2007



- most models under-predict tropospheric NO_x
- STEM model uses out-dated emission inventory

Processes in the upper troposphere



Source: Prados et al., 2000

Sources

- Convection
- Lightning
- Aircraft

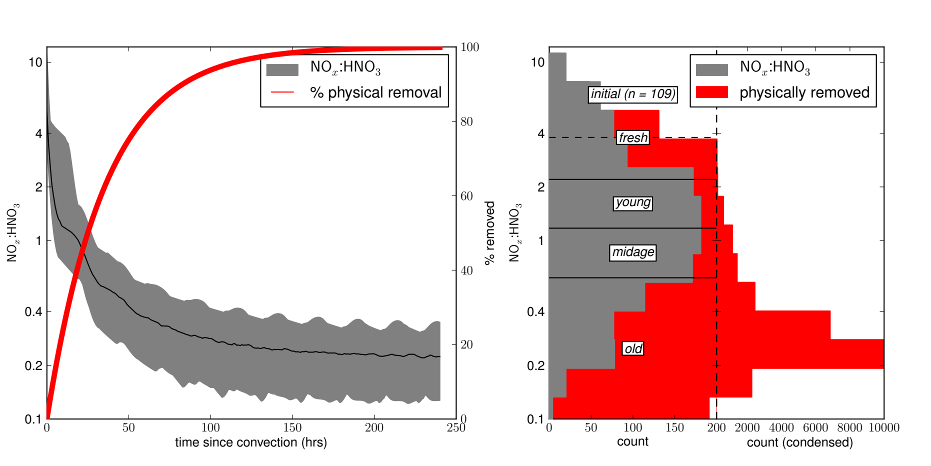
Sinks

- Chemistry
- Subsidence
- Rain, snow, ice

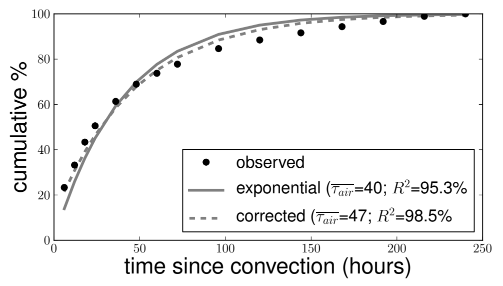
3D Models

- Simulate all
- Many uncertainty terms

NO_x Processing in the upper troposphere



Stochastic model of air parcel removal



Sample Bias

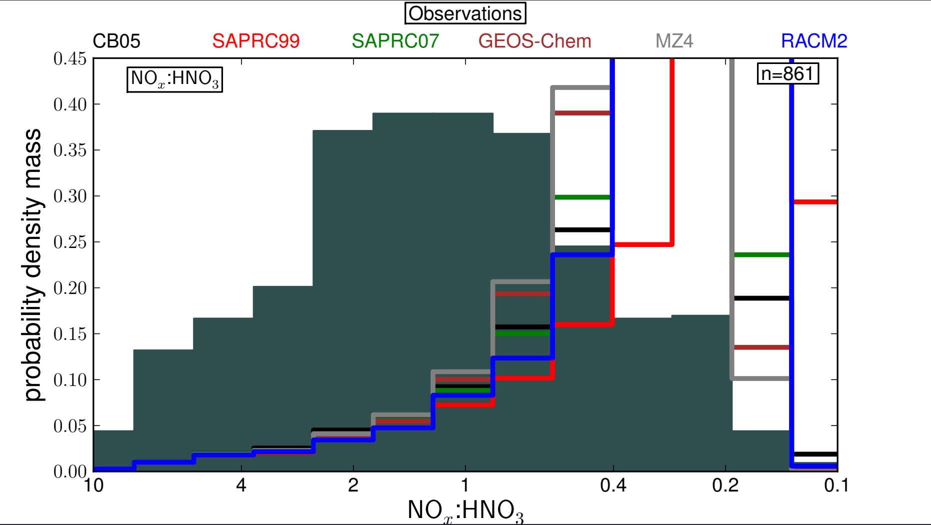
INTEX-NA observations have 21.4% near convection, but observed convection covers only 12.5% of sampling domain. Stochastic model adjusted to correct for this bias.

Simple Model	**Bias-Corrected**
$p(t) = \exp\left(\frac{-t}{\tau}\right)$ (1)	$p(t) = \begin{cases} \exp\left(\frac{-t}{\kappa}\right) & \text{if } t \leq 6 \\ \frac{\kappa}{\tau}\exp\left(\frac{-t}{\tau}\right) & \text{if } t > 6 \end{cases}$ (2) where $\kappa = \frac{-6}{\log\left(2\exp\left(\frac{-6}{\tau}\right) - 1\right)}$ and $\tau \geq 9$

τ is the average time an air parcel is in the upper troposphere

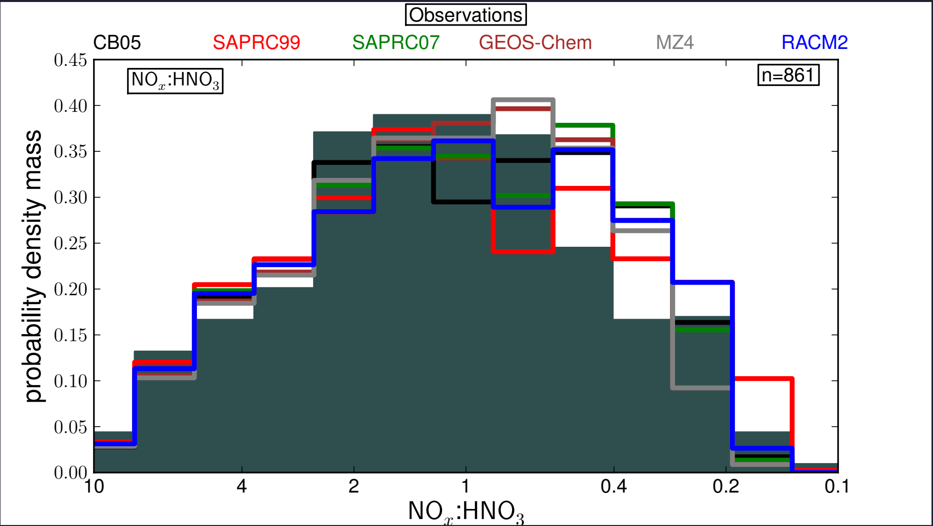
Simulation results for $NO_x:HNO_3$

IGNORING stochastic removal

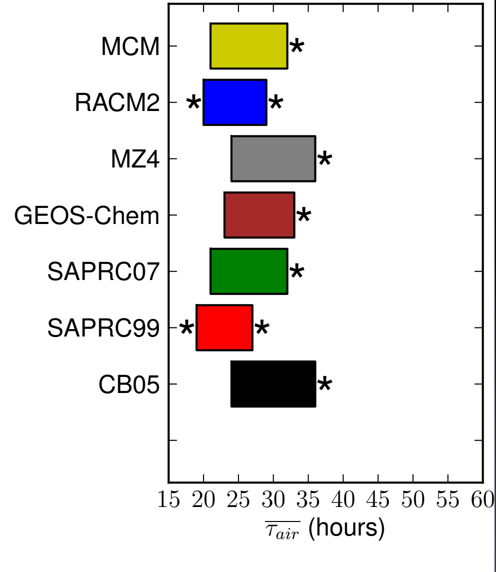


Simulation results for NO_x:HNO_3

INCLUDING stochastic removal



High Empirical Physical Sinks

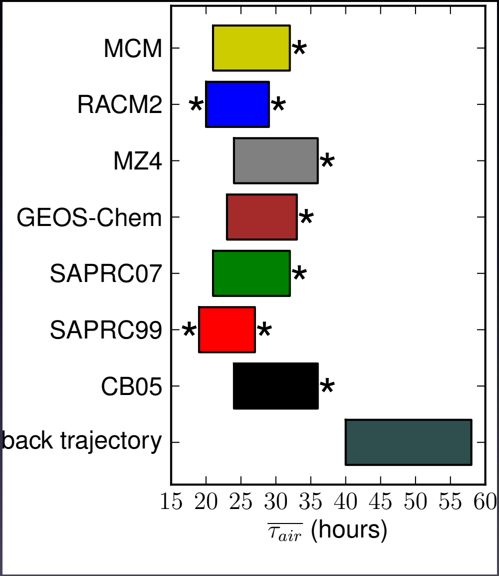


Henderson et al., 2010 ACPD

Best fit τ

Given a chemical oxidation rate, the average air parcel lifetime would have to be τ to reproduce observed NO_x:HNO_3

High Empirical Physical Sinks



Henderson et al., 2010 ACPD

Best fit τ

Given a chemical oxidation rate, the average air parcel lifetime would have to be τ to reproduce observed NO_x:HNO_3

Back Trajectory τ

Given observed air parcel ages, the average air parcel lifetime is τ

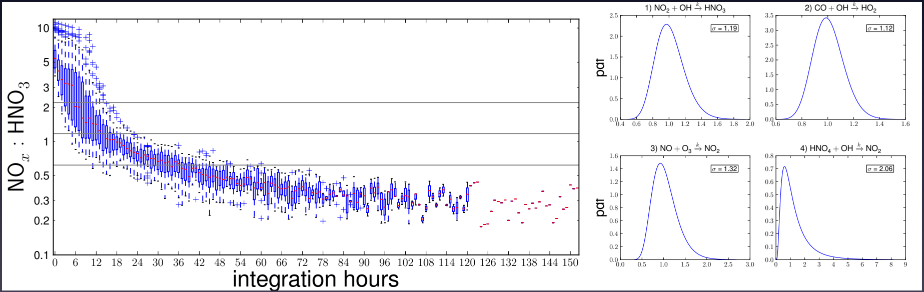
Using met τ with modeled chemical sinks causes 30% low-bias for NO_2

Can known uncertainty explain bias?

- 323 independent variables
  - Initial conditions come from experimental techniques
  - JPL and IUPAC cite experimental and systematic uncertainty for all reactions

Can known uncertainty explain bias?

- 323 independent variables
  - Initial conditions come from experimental techniques
  - JPL and IUPAC cite experimental and systematic uncertainty for all reactions
- Pre-screen influential variables
  - slow NO_x to HNO_3 conversion
  - characterized uncertainty



Cost functions for optimization

- Problem: do not have paired observations and model outputs
- Solution: Use Mann Whitney Wilcoxon U statistic (used for distribution comparison in original paper)

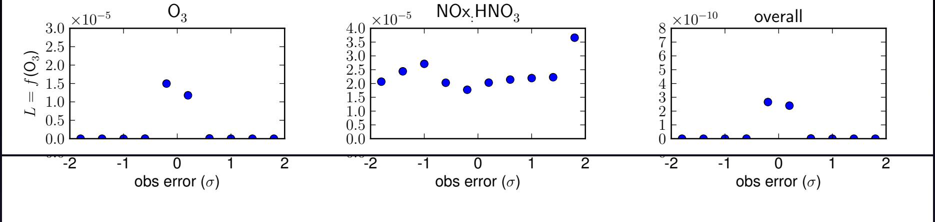
- *U* is normally distributed
  - mean: $\frac{n_1 n_2}{2}$
  - sigma: $\sqrt{\frac{n_1 n_2 (n_1 + n_2 + 1)}{12}}$
- Calculate the likelihood (*L*) of *U* from predictions (*Y*) given observations (*O*) of species (*s*)

$$L(Y_s|O_s) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2}\left[\frac{O - Y}{\sigma}\right]^2\right) \tag{3}$$

- Combine likelihoods as the product of individuals

$$L = L(Y_{\mathrm{O_3}}|O_{\mathrm{O_3}}) \times L(Y_{\mathrm{NO_x:HNO_3}}|O_{\mathrm{NO_x:HNO_3}}) \tag{4}$$

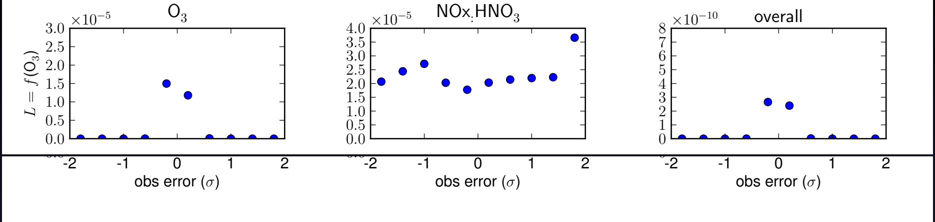
Observational Uncertainty Evaluation Results



For example, with ozone the model reproduces:

- adjusted ozone observation best near reported value
- NO_x:HNO_3 somewhat better at a lower (or very high) value
- overall, best estimate of ozone is near reported value

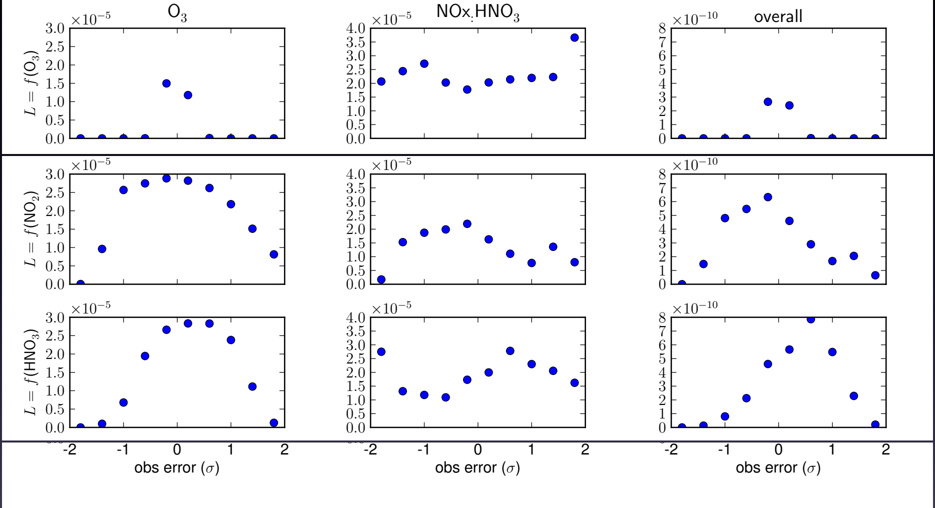
Observational Uncertainty Evaluation Results



For example, with ozone the model reproduces:

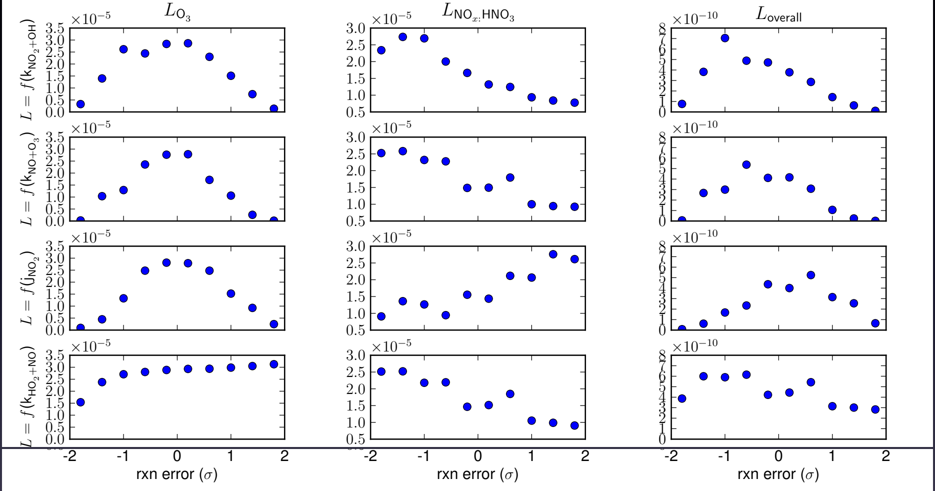
- adjusted ozone observation best near reported value
- NO_x:HNO_3 somewhat better at a lower (or very high) value
- overall, best estimate of ozone is near reported value
- What about other species?

Observational Uncertainty Evaluation Results



- NO_2 performs best at a slightly lower value
- HNO_3 performs best at a slightly higher value

Reaction Uncertainty Evaluation Results



- $k_{NO_2+OH \longrightarrow HNO_3}$ best at lower value (Mollner et al., 2010)

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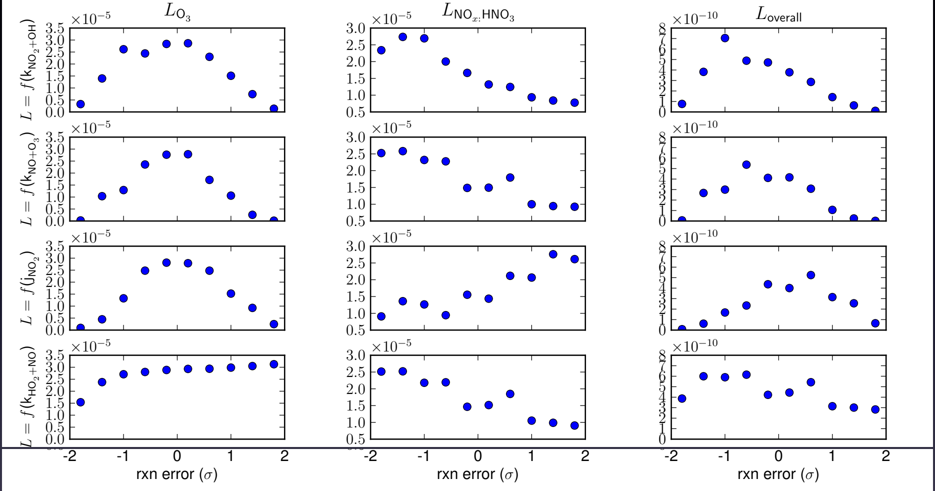

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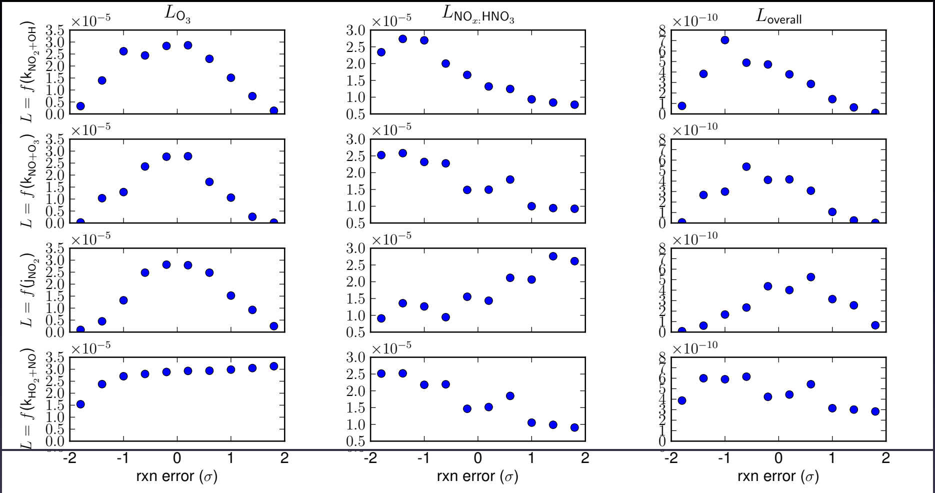
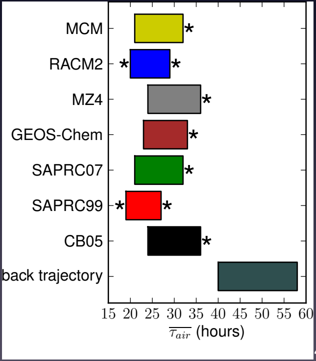


- $k_{NO_2+OH \longrightarrow HNO_3}$ best at lower value (Mollner et al., 2010)
- $k_{NO+O_3 \longrightarrow NO_2+O_2}$ best at lower value
- $k_{NO+HO_2 \longrightarrow NO_2+HO}$ has a broad range of acceptable values

Ranking influential variables

Parameter	**%Error**	τ **hrs**
NO_2	(-5,-22%)	(+0,+4.8)
$HO_2 + NO \longrightarrow NO_2$	(-7,-16%)	(+0,+2)
HNO_3	(+4,+12%)	+0
$NO_2 + OH \longrightarrow HNO_3$	-10%	+0
$NO + O_3 \longrightarrow NO_2$	-10%	+0
$NO_2 \longrightarrow NO + O$	+7%	+0



Summary and Conclusions

- Evaluation:
  1. Ensure proper understanding of the upper troposphere
  2. Accurately attribute and apportion radiative forcing of UT O_3
- Completed a thorough uncertainty analysis for the model evaluation framework and application in Henderson et al., 2010 ACPD
- Excluded many variables due to confounding influence on key species
- Identified observations and reactions that have the potential to improve model evaluation and lengthen inferred air parcel lifetime
  - $[NO_2]$
  - $k_{\mathrm{HO_2+NO \longrightarrow NO_2+HO}}$

Next steps

- Use Bayes Theorem to constrain uncertainty of key reactions
  - posterior: updated using likelihood function
  - prior: JPL reported uncertainty

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