

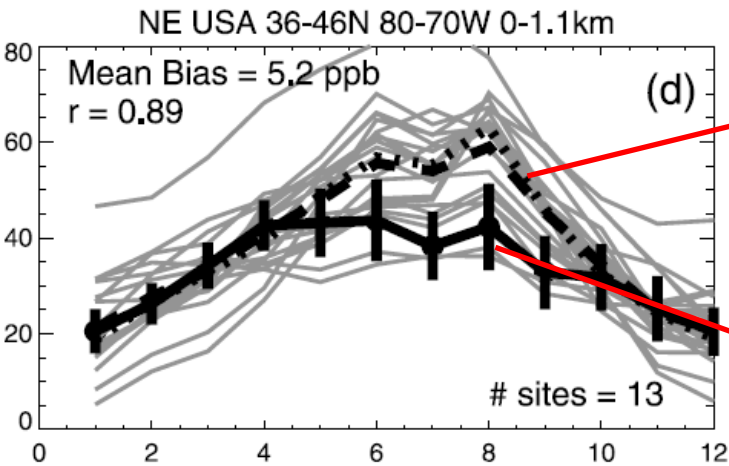


Ozone and organic nitrates over the eastern US: sensitivity to isoprene chemistry

Jingqiu Mao (NOAA GFDL), Fabien Paulot (Harvard), Daniel Jacob (Harvard), Ronald Cohen (UC Berkeley), John Crouse (Caltech), Paul Wennberg (Caltech), Christoph Keller (Harvard), Rynda Hudman (EPA), Michael Barkley (U Leicester), Larry Horowitz (NOAA GFDL)

Summertime ozone over eastern US is a classic problem for most models

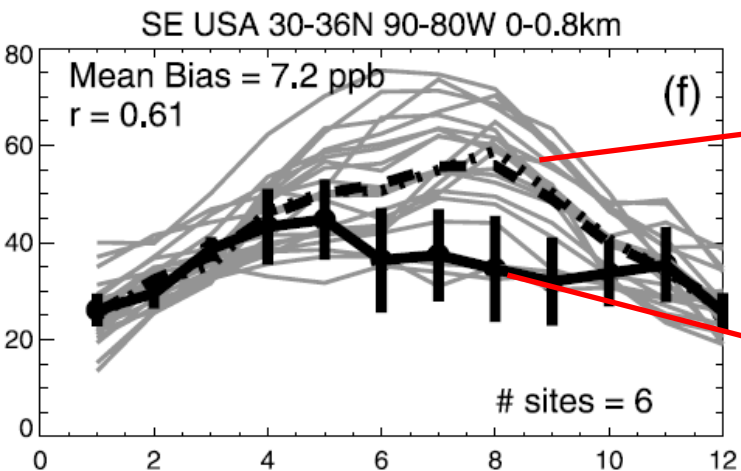
Northeast US



Multimodel mean

Obs from CASTNET surface sites

Southeast US

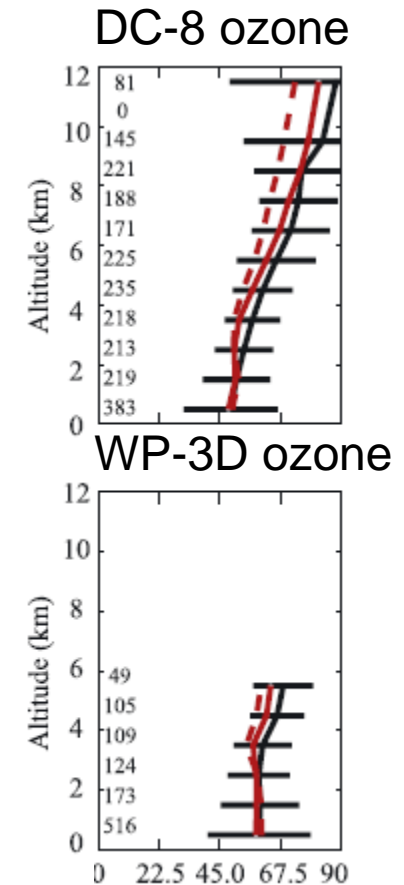


Multimodel mean

Obs from CASTNET surface sites

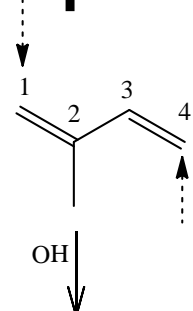
(Fiore et al., 2009, JGR)

We didn't have this problem during ICARTT!



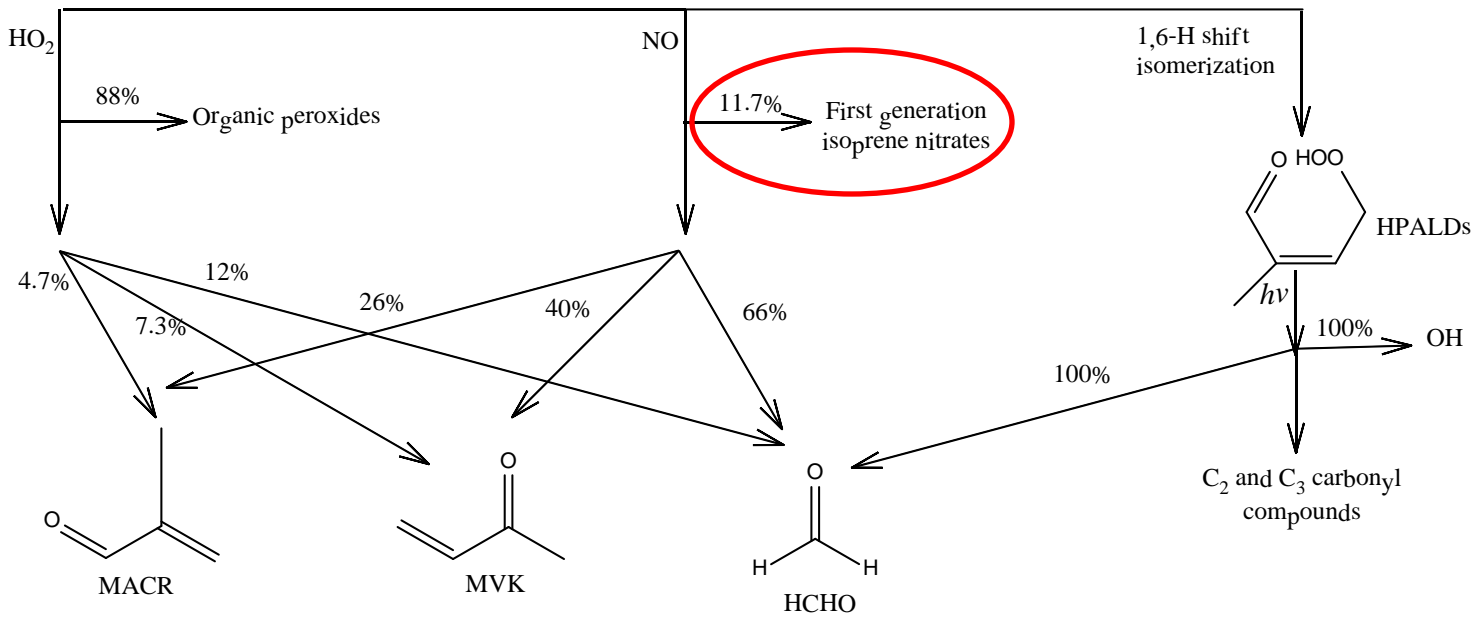
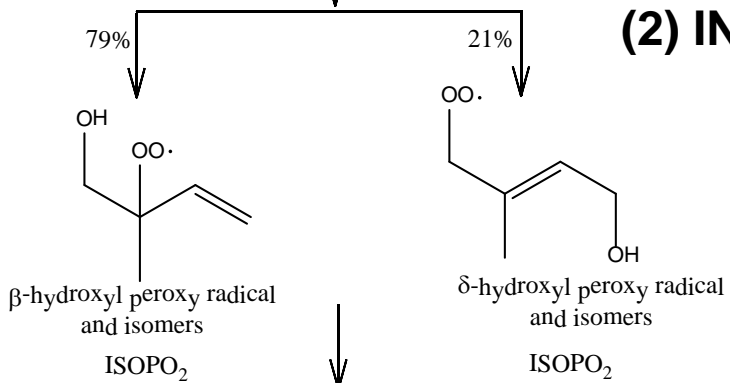
(Hudman et al., 2007, JGR)

Switching to Fabien's isoprene chemistry

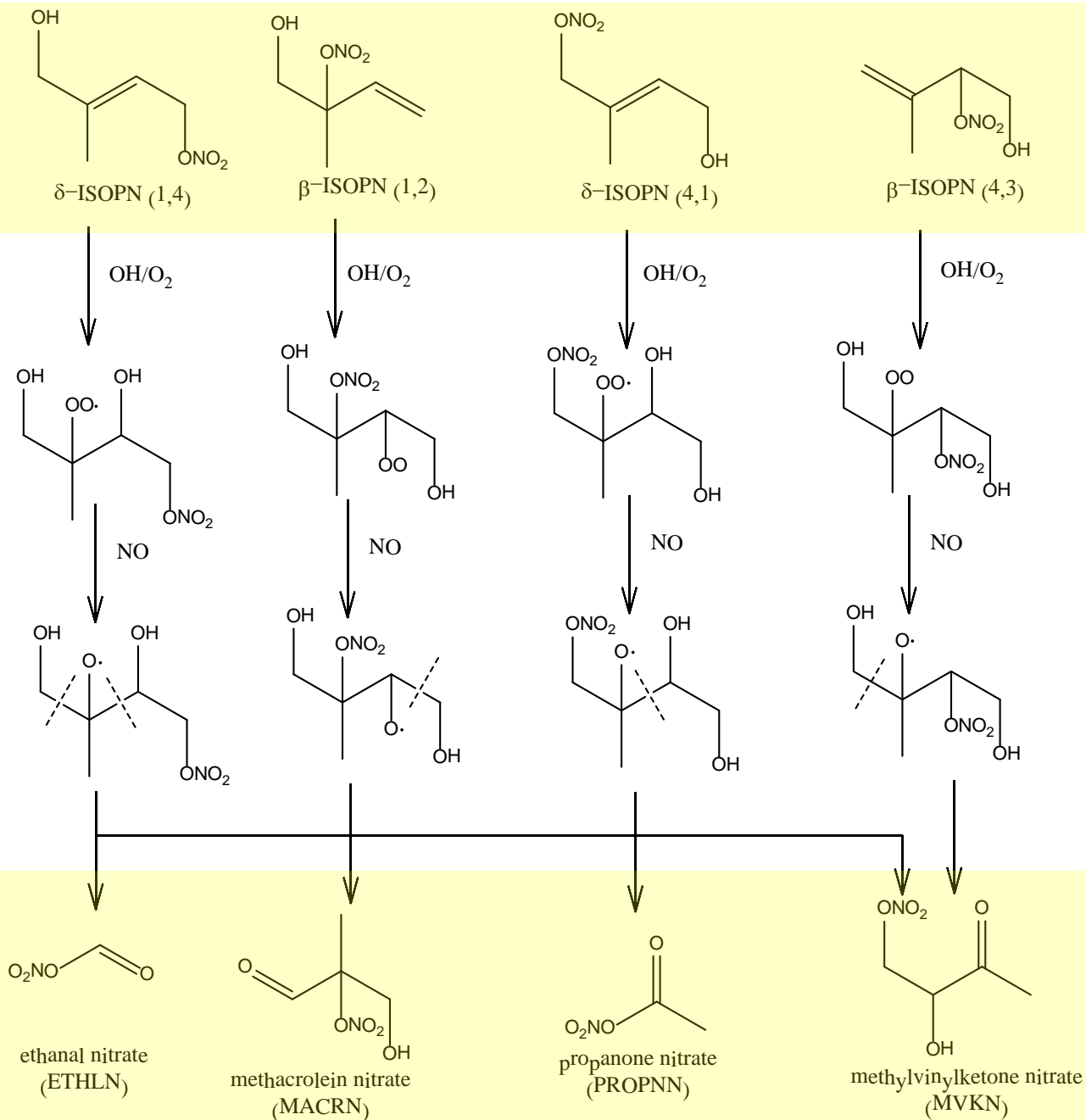


(1) smaller yield of isoprene Nitrate (IN)

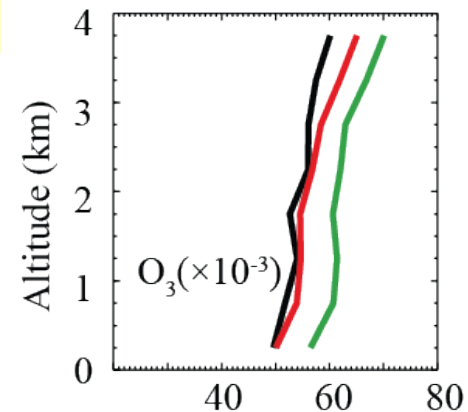
(2) IN is not a terminal sink!



First generation of isoprene nitrates degraded to second generation nitrates!



Obs
 Std chem (v8-2-3)
 Paulot isoprene chem



Ozone bias is about +5 ppb in both boundary layer and free troposphere!

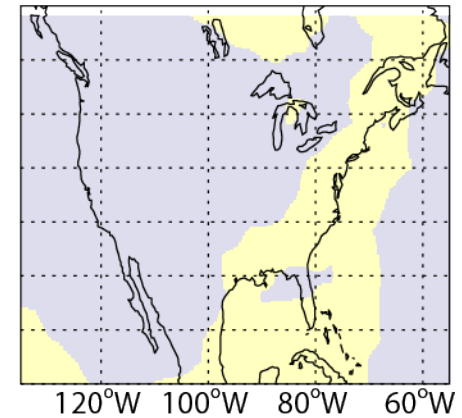
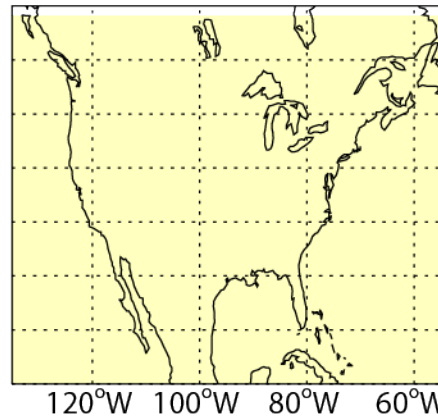
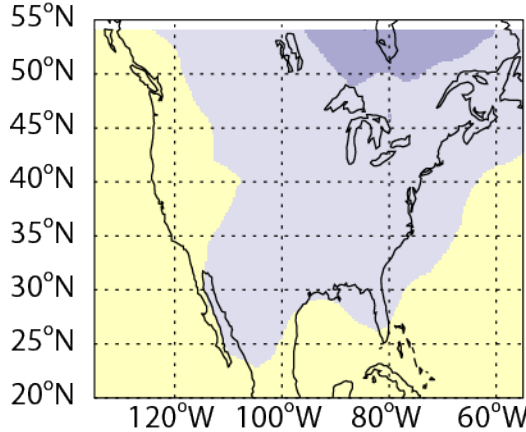
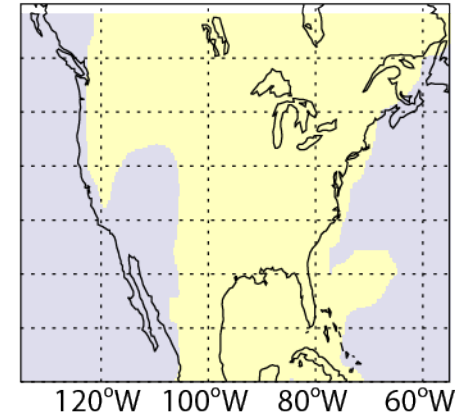
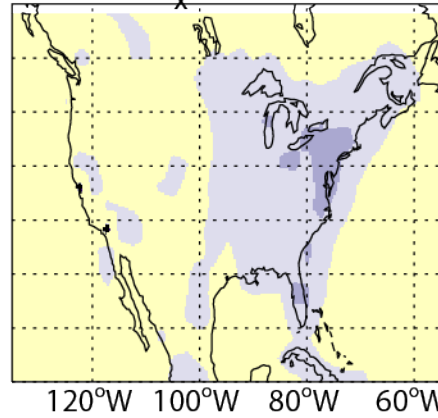
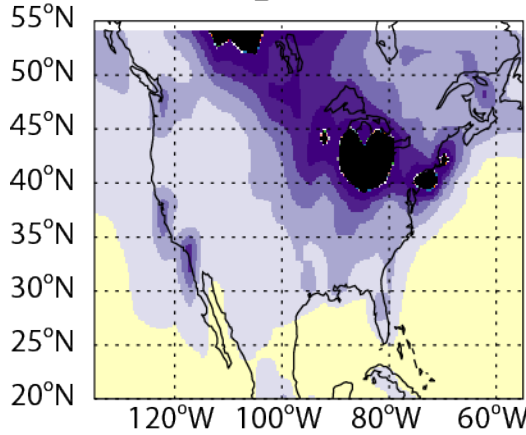
NO_x recycling efficiency is 55%!

A few more updates (impact on July afternoon ozone of 2004)

HO₂ uptake

Improved Diurnal Cycle of NO_x emissions

bromine chemistry



< -5.0 -3.6 -2.2 -0.9 0.5 ppb

(Mao et al., ACP 2013)

Implemented by
Christoph Keller

(Parrella et al.,
ACP 2012)

Surface

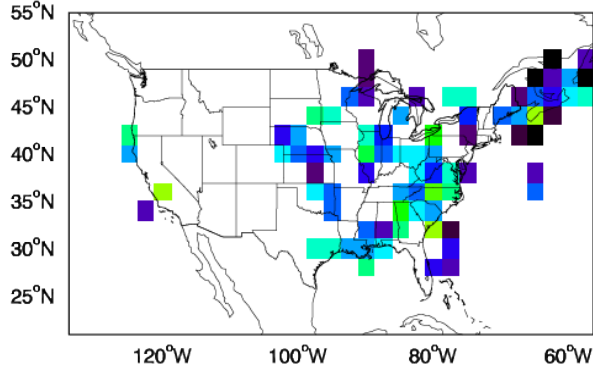
500 hPa

We are now in good shape...

Ozone in the boundary layer during ICARTT

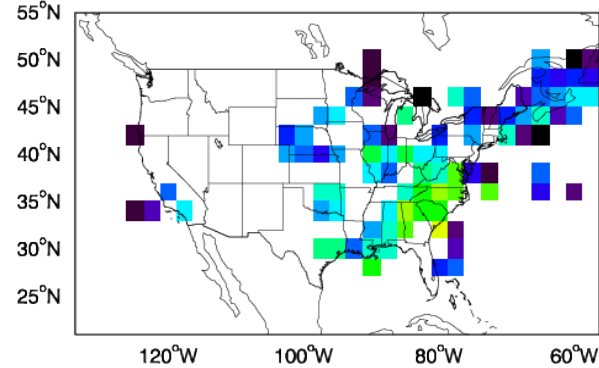
Observations

Observations (0 - 1.5 km)

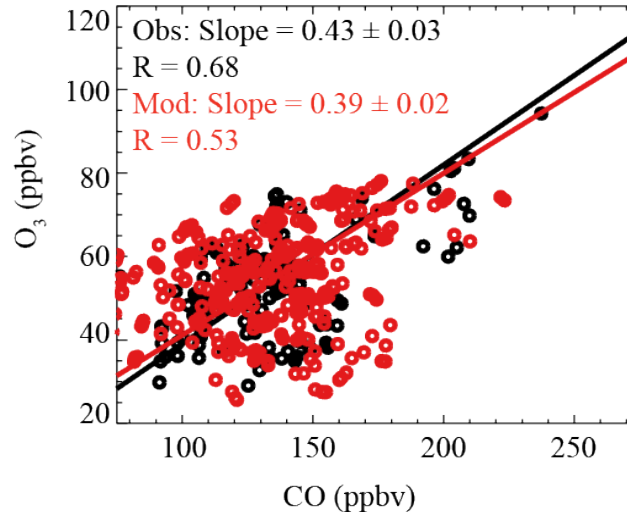
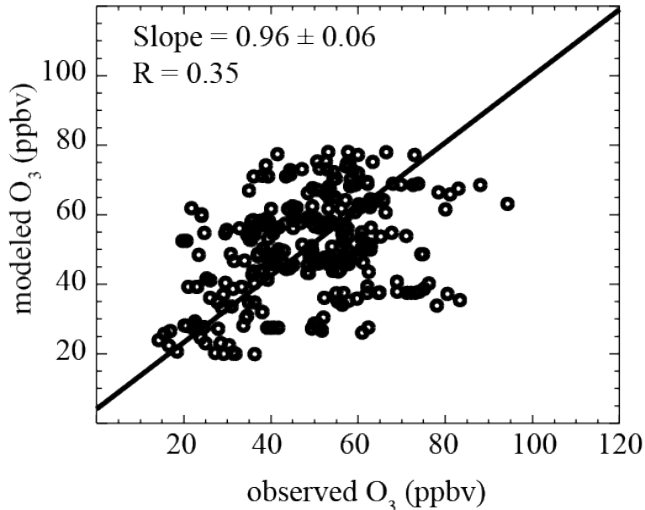


Model

Simulation (0 - 1.5 km)



Obs vs. Model

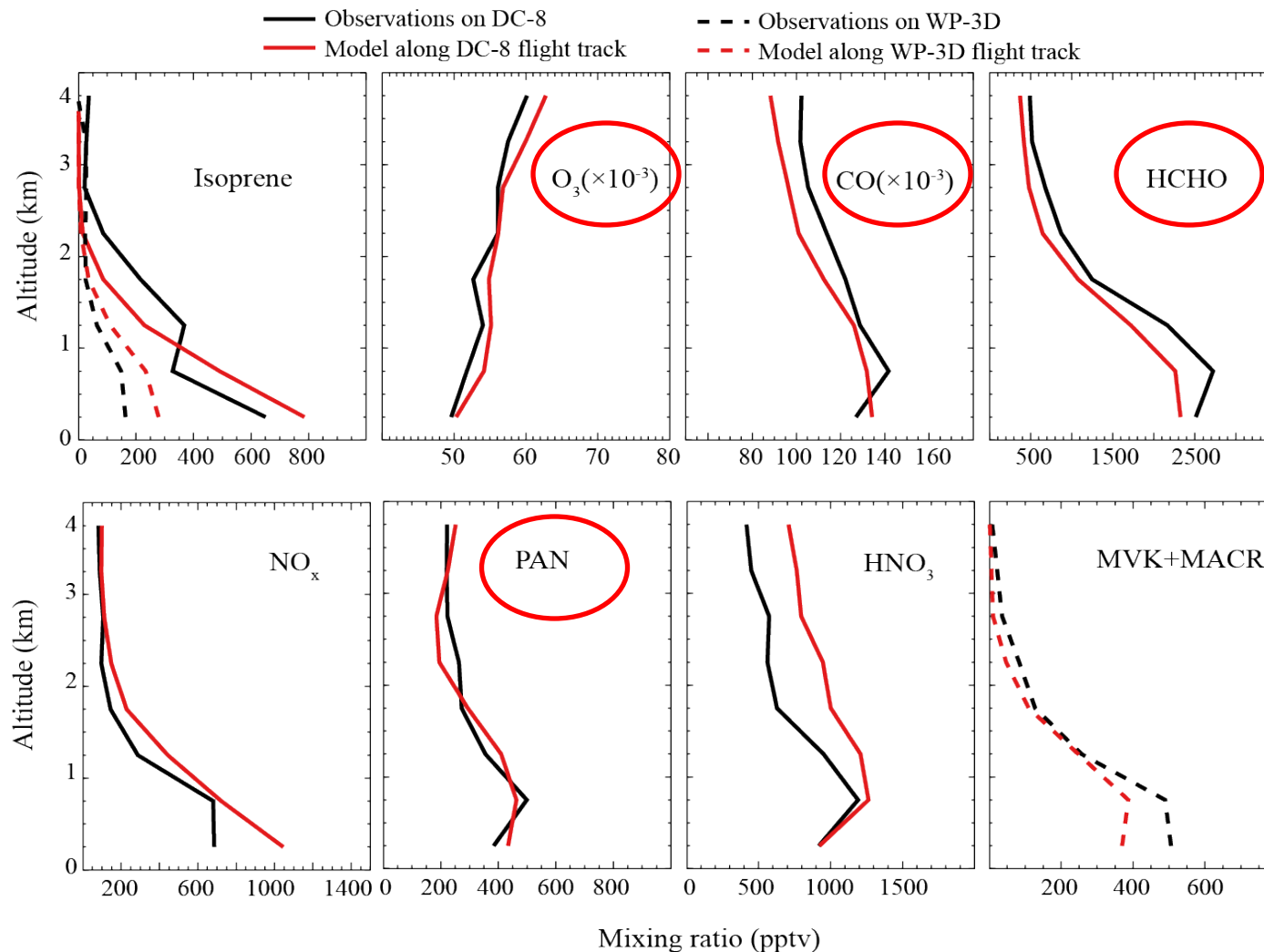


Improved O_3 -CO correlations due to:

1. Recycling of NO_x from isoprene nitrates
2. HO_2 uptake (lower OH and increase NO_x lifetime).

Mean vertical profiles during ICARTT

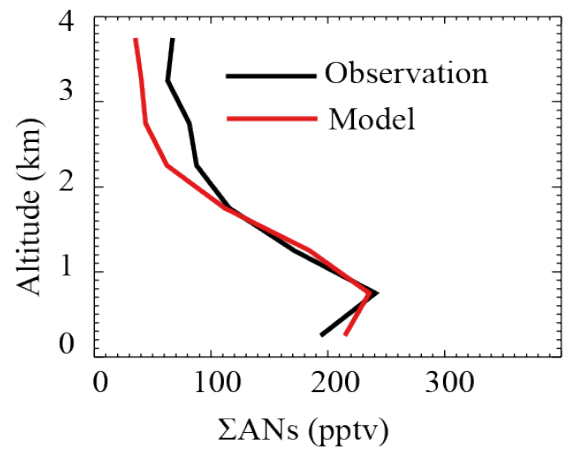
Observations
Model (this work)



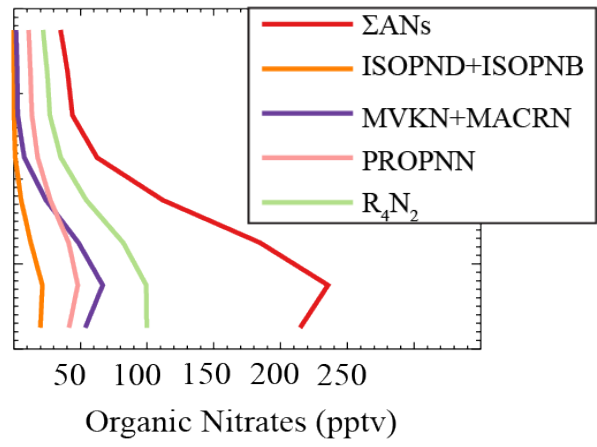
O_3 has no bias in boundary layer and free troposphere.
HCHO provides good constraint on isoprene emissions.

Total organic nitrates excluding peroxyacylnitrates (Σ ANs)

Vertical profiles



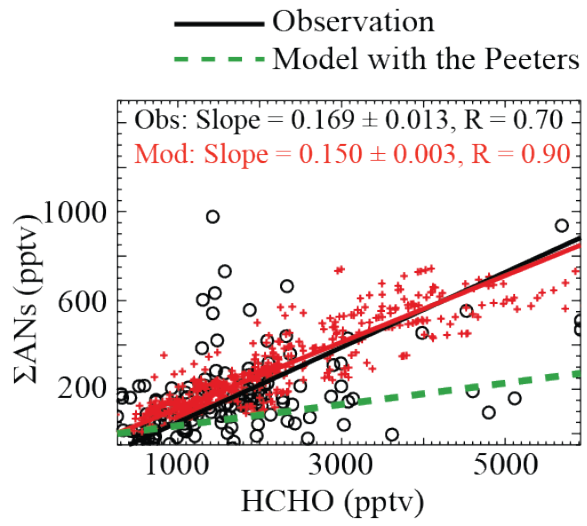
Speciation of Σ ANs



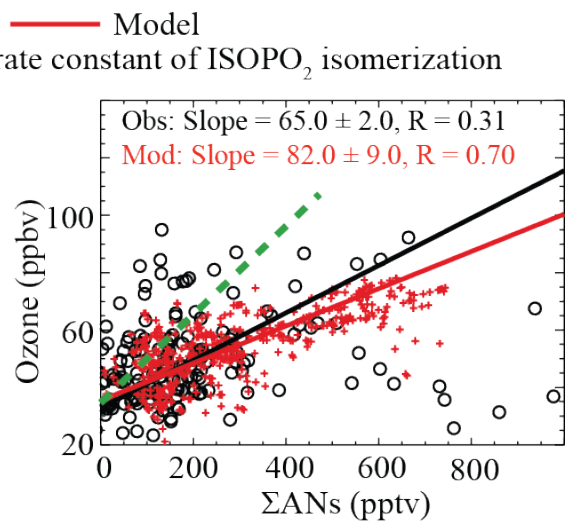
Model well reproduced Σ ANs.

Σ ANs is dominated by secondary organic nitrates.

Σ ANs vs. HCHO



Σ ANs vs. O_3



Model well reproduced Σ ANs vs HCHO and Σ ANs vs. O_3 correlations.

These correlations cannot be reproduced by a fast isomerization channel of $ISOPO_2$.

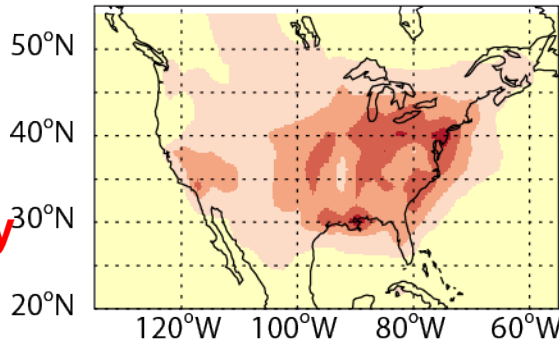
NO_y budget in eastern U.S. boundary layer for July 2004

Species	Emission	Chemical (P-L)	Dry Deposition	Wet Deposition	Net Export
NO _x	386	-337	44	-----	5
PANs		24	13	-----	11
∑ANs					
ANs		18	7.4	3.6	7
R ₄ N ₂		10	0.5	-----	10
HNO ₃		277	180	110	-3

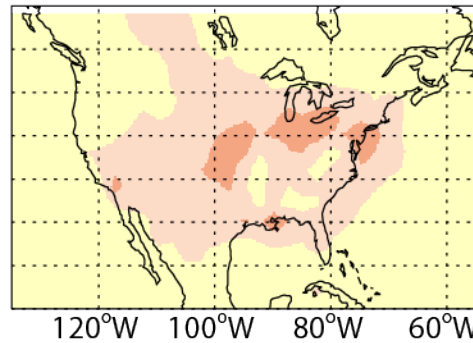
Export of ∑ANs > Export of PANs

Surface ozone response to isoprene emissions

+25% isoprene emissions



+25% isoprene emissions
(-50% NO_x emissions)



New
chemistry

NO_x emissions ↓

Sensitivity of ozone to
isoprene emissions ↓

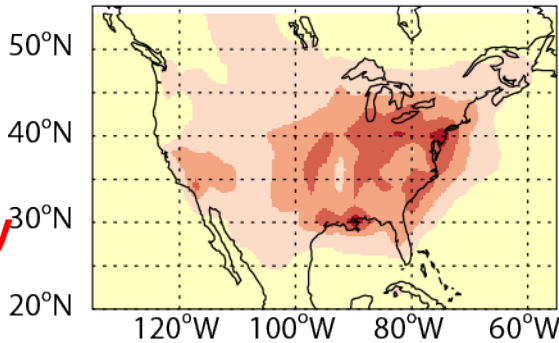
-4.0 -2.0 0.0 2.0 4.0 ppb

Current anthro
NO_x emissions

Reduce current anthro NO_x
emissions by 50%

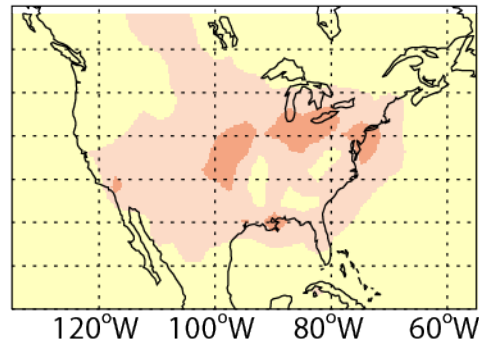
Surface ozone response to isoprene emissions

+25% isoprene emissions



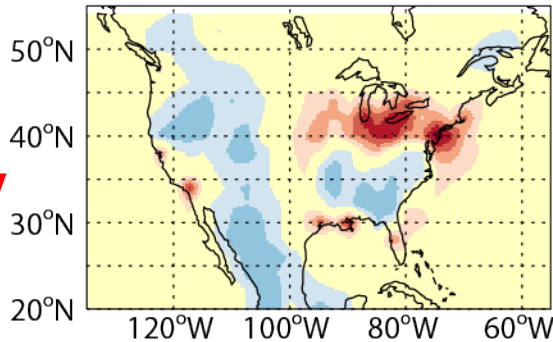
New
chemistry

+25% isoprene emissions
(-50% NO_x emissions)

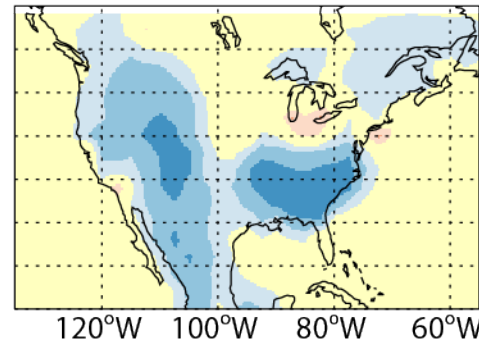


-4.0 -2.0 0.0 2.0 4.0 ppb

V8-02-03
chemistry



-2.0 -1.0 0.0 1.0 2.0 ppb



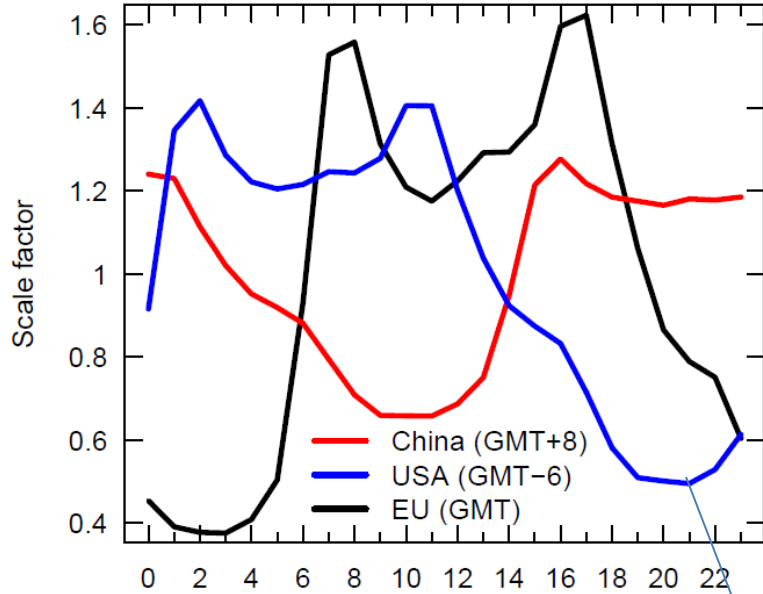
Isoprene↑
NO_x↓
OH↓
O₃↓ due to O₃+ISOP

Current anthro
NO_x emissions

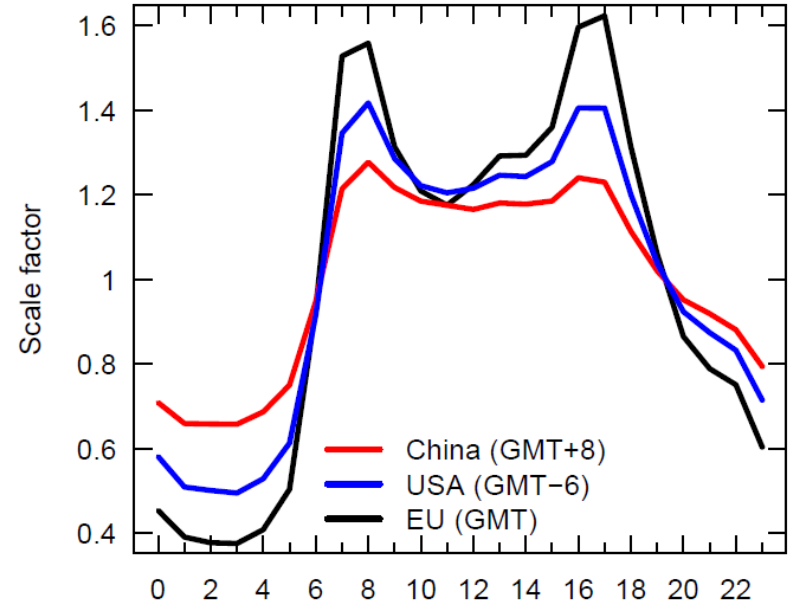
Reduce current anthro NO_x
emissions by 50%

Extra slides

Old diurnal cycle for NOx emissions



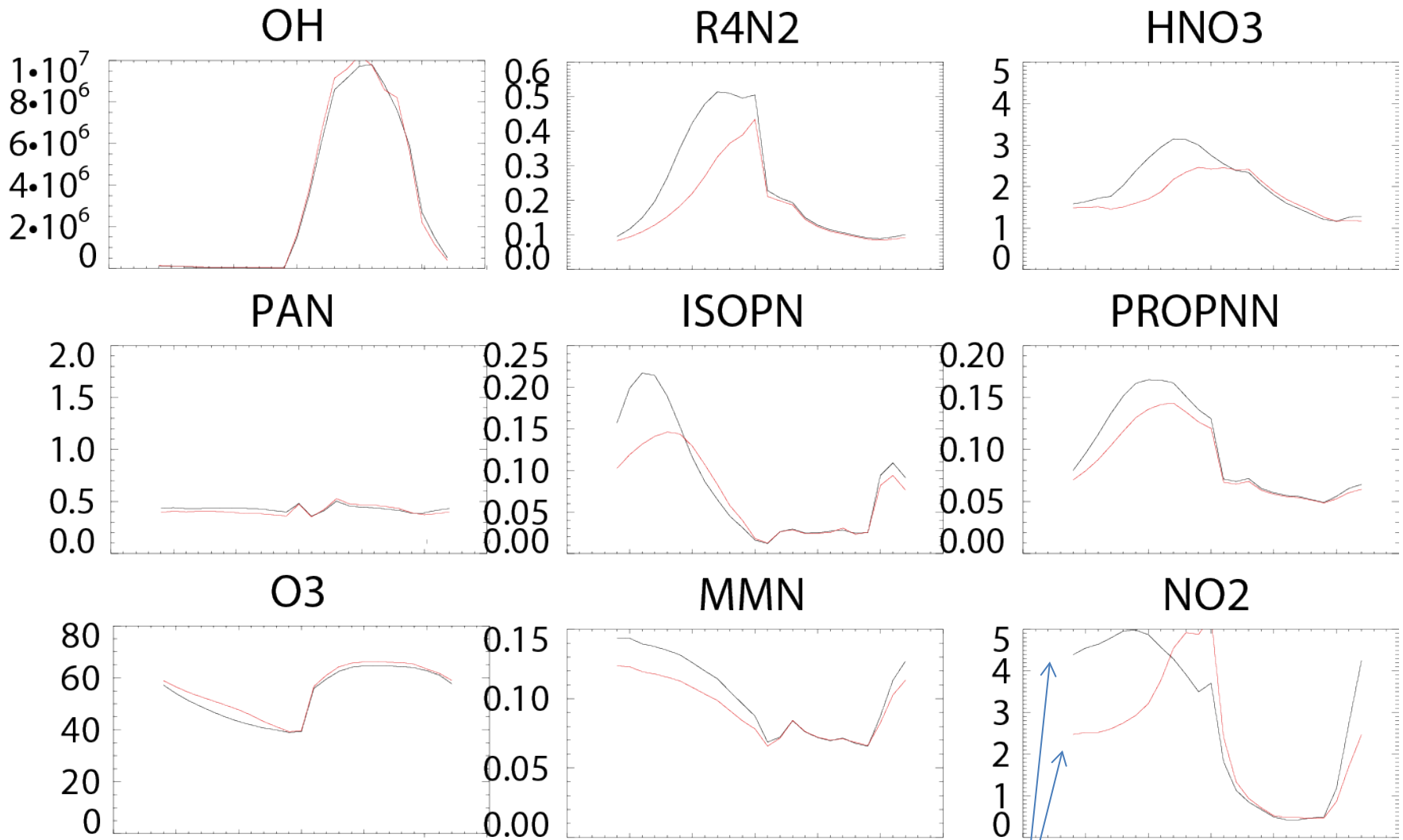
New diurnal cycle for NOx emissions



In the old diurnal cycle, very little NOx is emitted in the late afternoon.

Diurnal cycle in southeast US in summer

Red: old version Black: new version



Consequently NO_x in new version is higher than in old version by a factor of 2.