Evaluating the impact of recent changes in isoprene and anthropogenic emissions on surface ozone over the eastern United States

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AOS @PRINCETON

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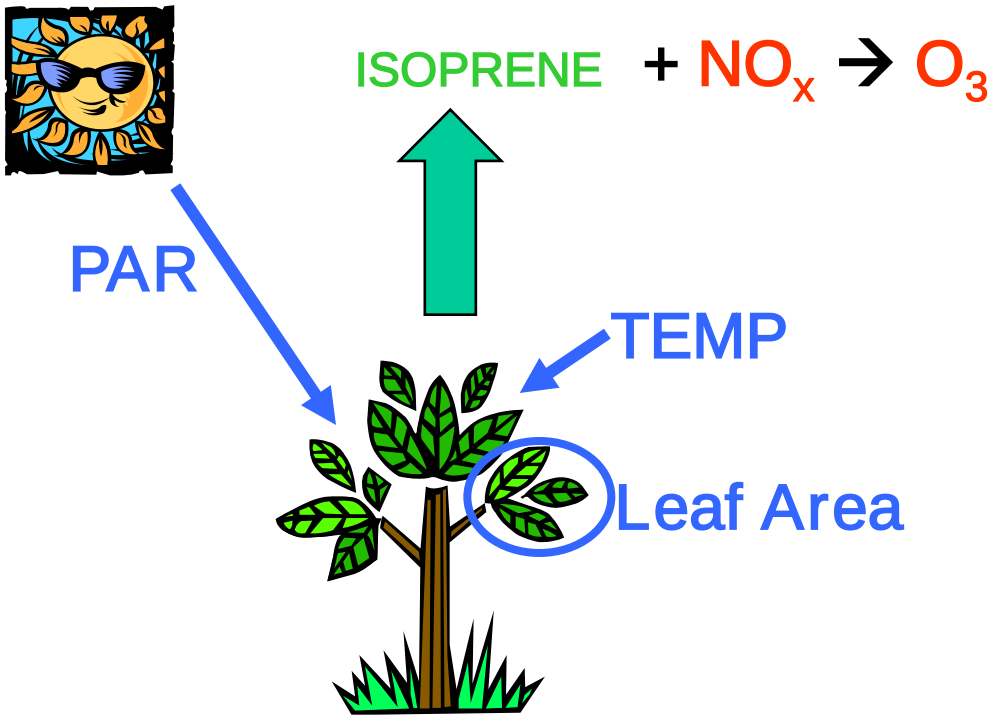
Isoprene Emissions are generally thought to contribute to O_3 production over the eastern United States
[*e.g. Trainer et al.*, 1987; *NRC* 1991]

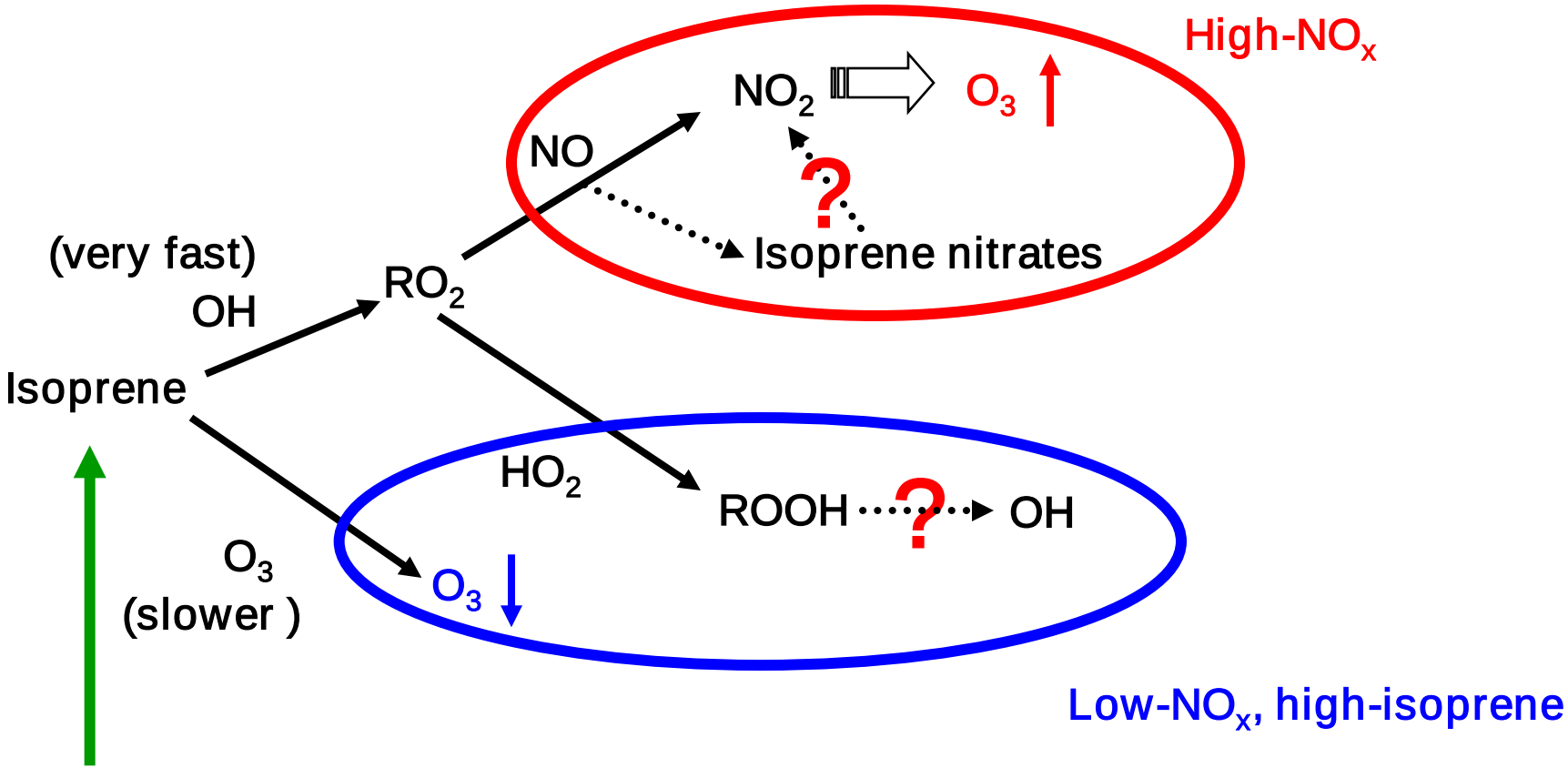


Vegetation changes → Impact on O_3?

Isoprene can also decrease surface O_3 by:

(1) Sequestering NO_x as organic isoprene nitrates

(2) Titrating OH and enabling direct reaction of isoprene with O_3

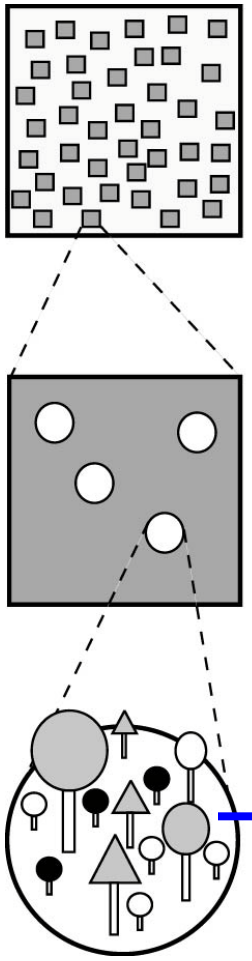


Isoprene emissions uncertain;

New evidence for recent changes over E. U.S.

Purves et al. [2004]: observation-based BVOC emission estimates for mid-1980s and mid-1990s

Forest Inventory Analysis



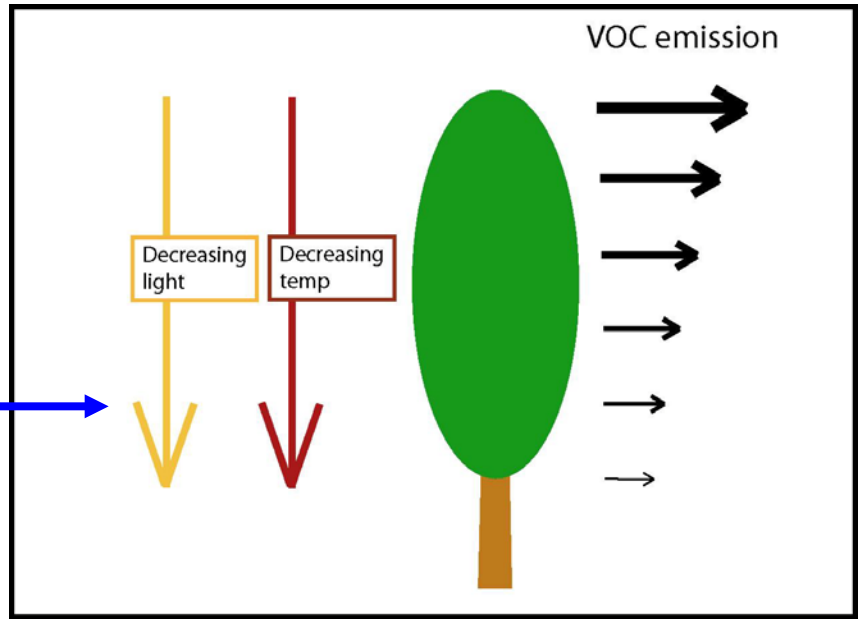
280,000 Re-surveyed plots

Estimate emissions from:

- **2.7 million trees**
- **species-specific emission capacities**
- **canopy model (FIA data for depth & LAI)**
- **f(T,PAR,LAI) [*Guenther et al*., 1993]**

→ Aggregate results to 1°x1°

→ Changes from mid-1980s to mid-1990s?



Adapted from D. Purves

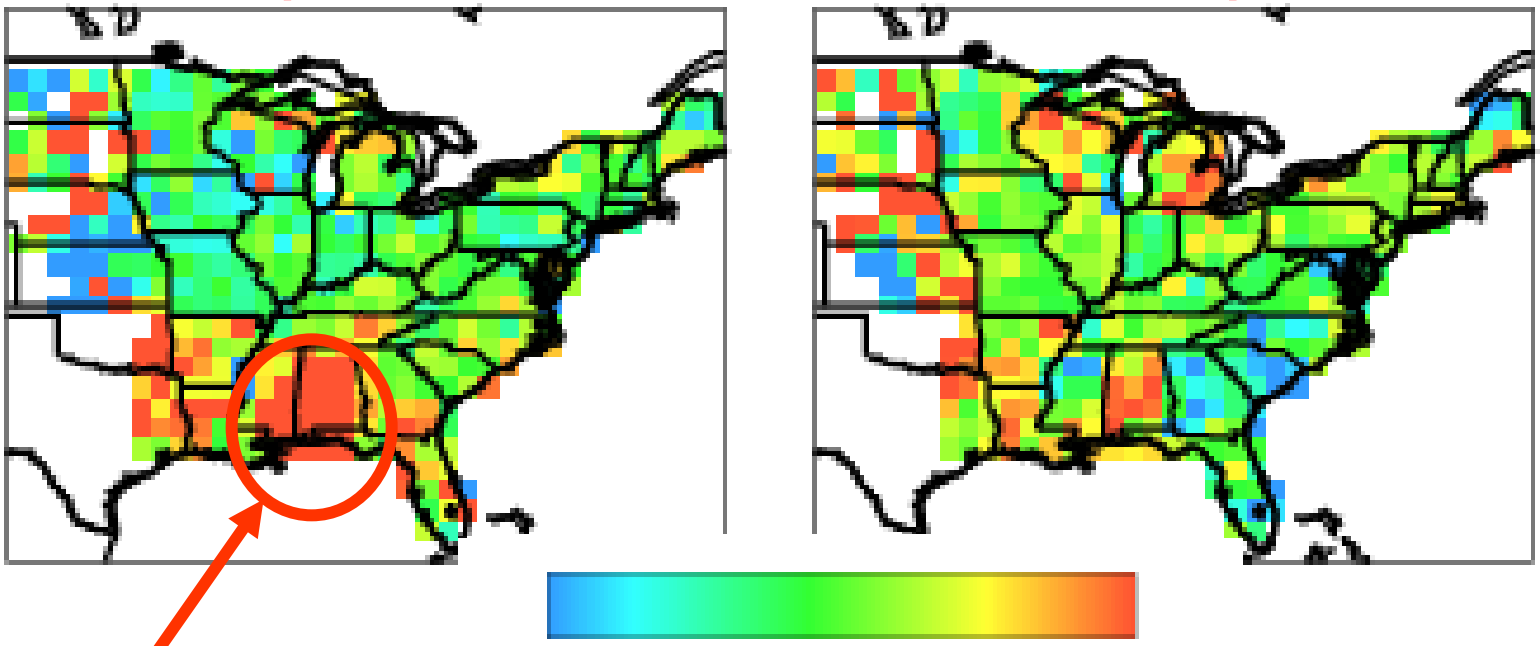
Recent Changes in Biogenic VOC Emissions

[*Purves et al.*, *Global Change Biology*, 2004]

→ Substantial isoprene increases in southeastern USA largely driven by human land-use decisions

→ Land-use changes not presently considered in CTMs

Isoprene **Monoterpenes**



Sweetgum Invasion of Pine plantations

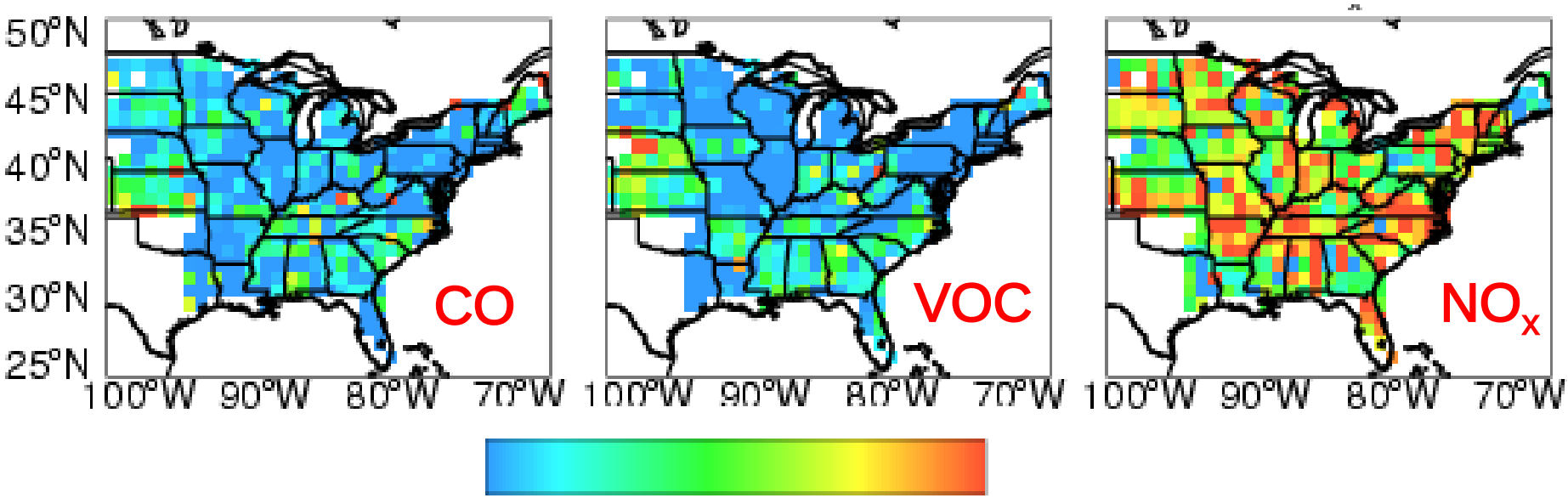
-20 –10 0 +10 +20 +30

Percent Change mid-1980s to mid-1990s

Trends in anthropogenic precursors?

Trends in Anthropogenic Emissions: 1985 to 1995

from US EPA national emissions inventory database
(http://www.epa.gov/air/data/neidb.html)



-20 –10 0 +10 +20 +30

Percent Change

→Large decreases in CO and VOC Emissions
→Some local increases in NO_x
→Higher biogenic VOCs

} Net effect On O_3?

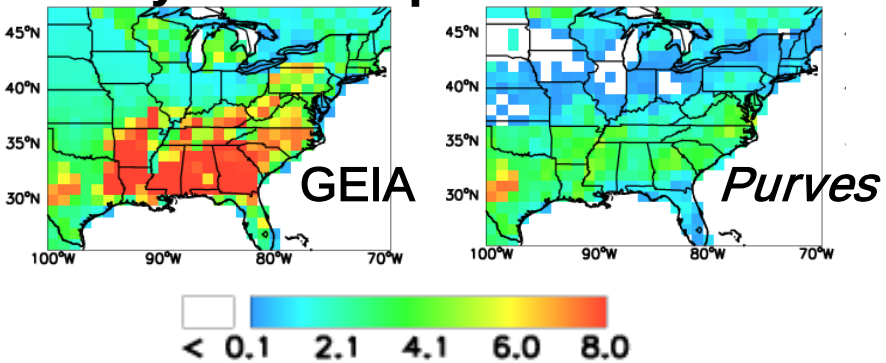
Approach: Insights from two chemical transport models

GEOS-CHEM

1. Quantify O_3 response to reported biogenic and anthropogenic emissions changes

2. Determine sensitivity to uncertainties in isoprene emissions

July mean isoprene emissions

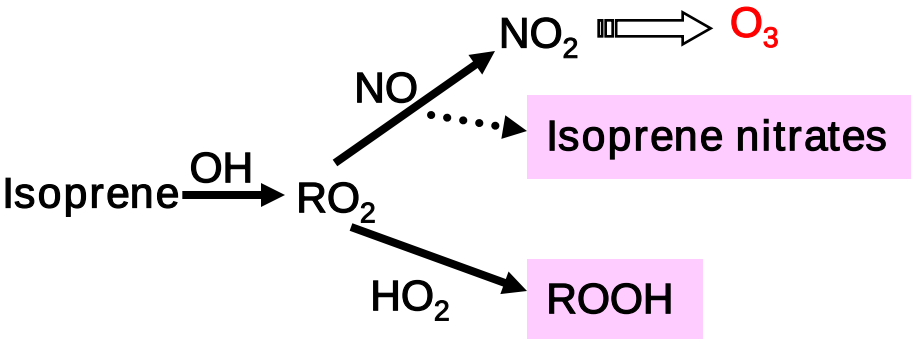


(10^{11} molecules isoprene cm^{-2} s^{-1})

MOZART-2

1. Test whether results are model-dependent

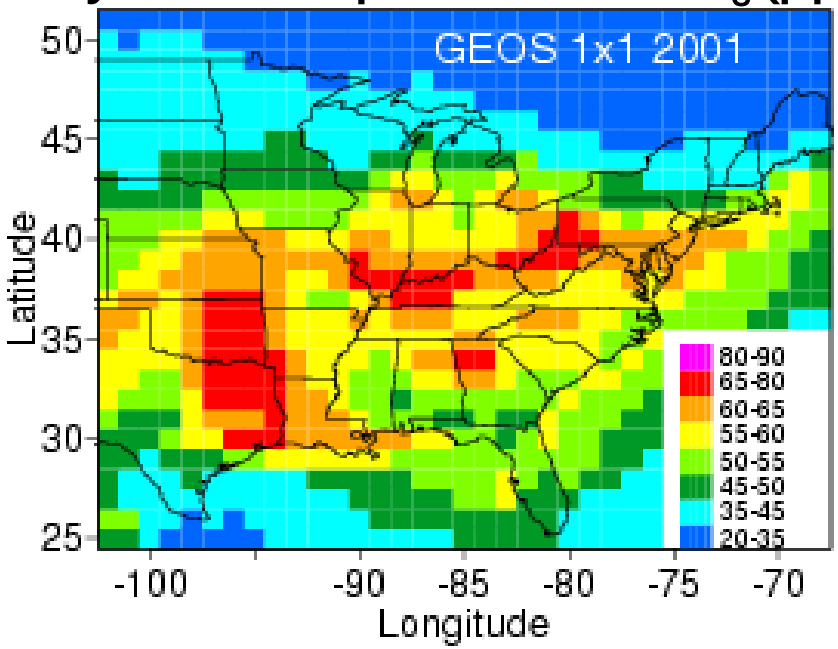
2. Determine sensitivity to uncertainties in isoprene-NO_x-O_3 chemistry



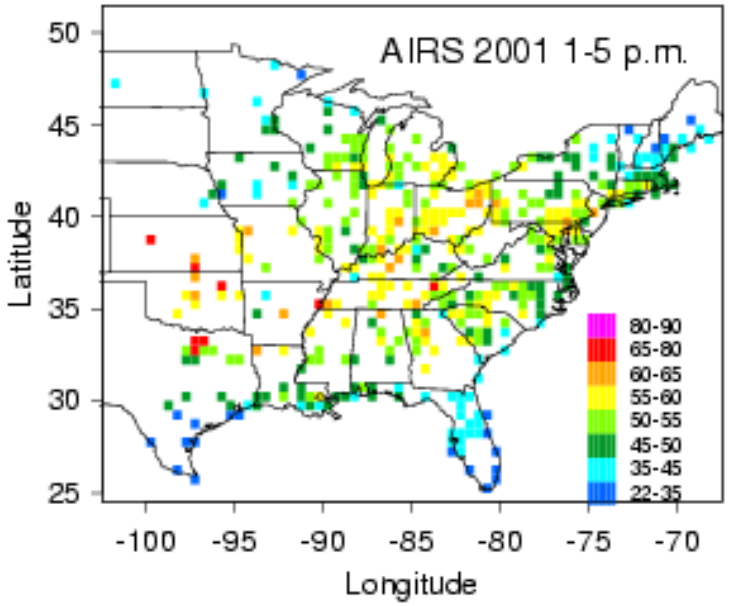
Tool #1: GEOS-CHEM tropospheric chemistry model [*Bey et al.*, 2001]

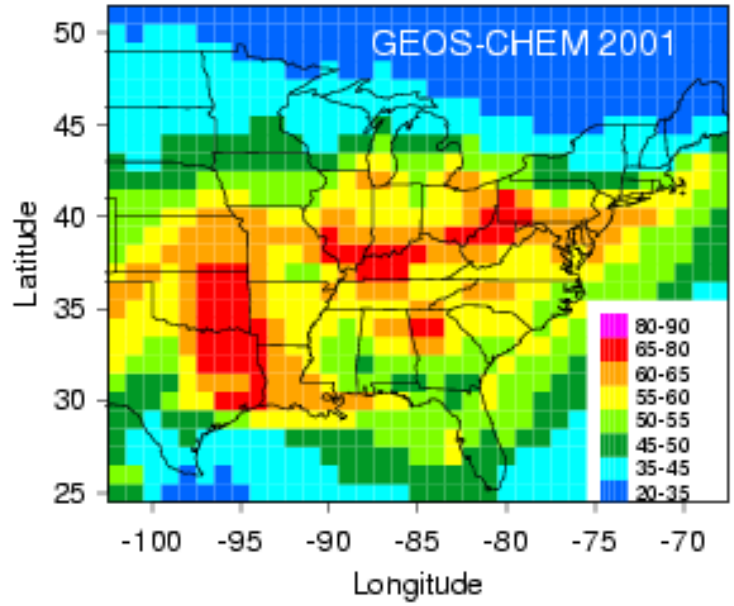
- Uses assimilated meteorology: GEOS-3 1°x1° fields for 2001
- 48 vertical levels (9 below 2 km)
- Regridded to 4°x5° for global spinup and boundary conditions for **nested 1°x1° over North America** [*Wang et al.*, 2004; *Li et al.*, 2004]
- 31 tracers; NO_x-CO-hydrocarbon-O_3 chemistry coupled to aerosols
- GEIA isoprene emission algorithms [*Guenther et al.*, 1995]
- v. 5-07-08 (http://www-as.harvard.edu/chemistry/trop/geos/index.html)

July 2001 1-5 p.m. Surface O_3 (ppbv)

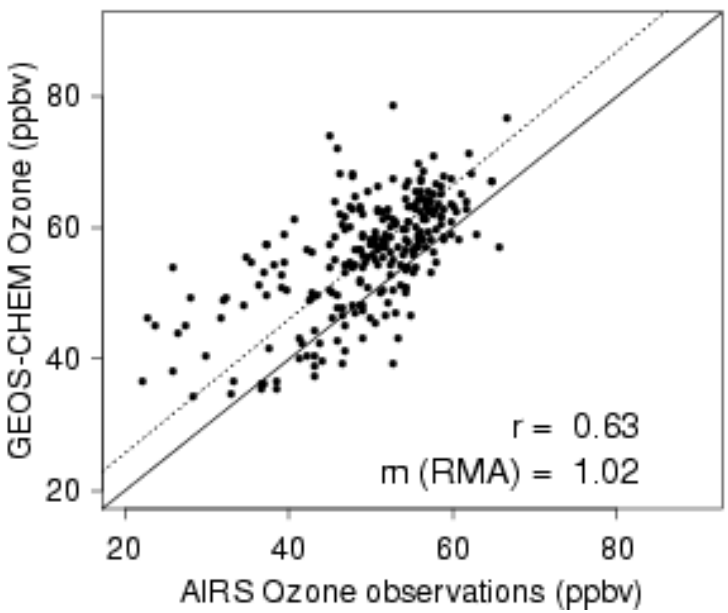


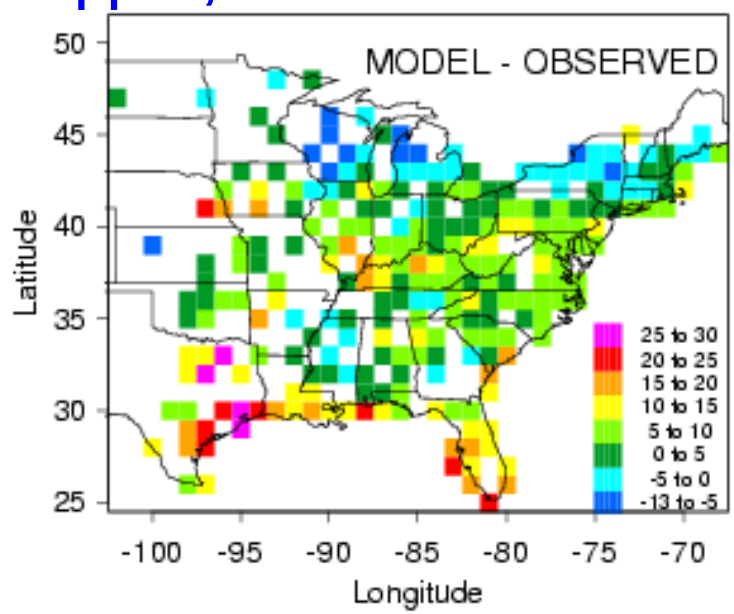
GEOS-CHEM Evaluation: July 2001 1-5 p.m. Surface O_3 (ppbv)





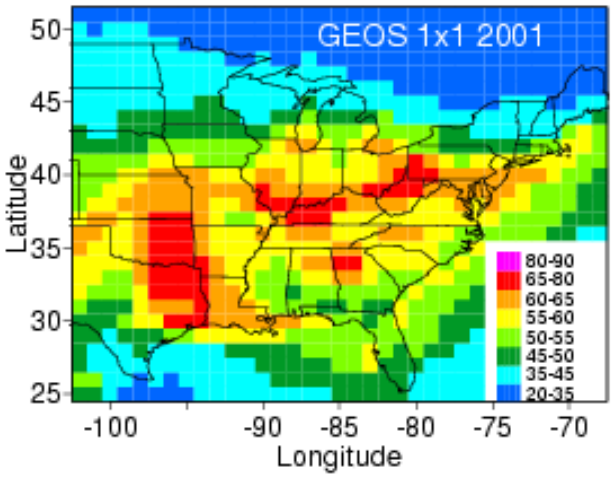
Mean Bias = 6±7 ppbv; r^2 = 0.40





Isoprene increases reduce O_3 in Southeastern US

GEOS-CHEM July 1-5 p.m. O_3



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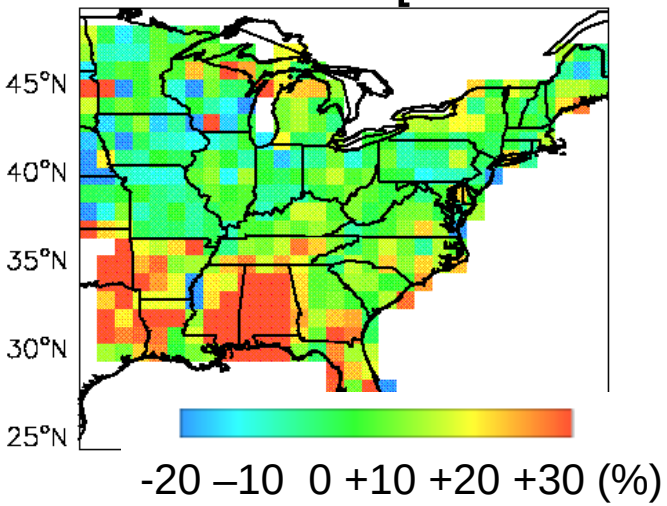
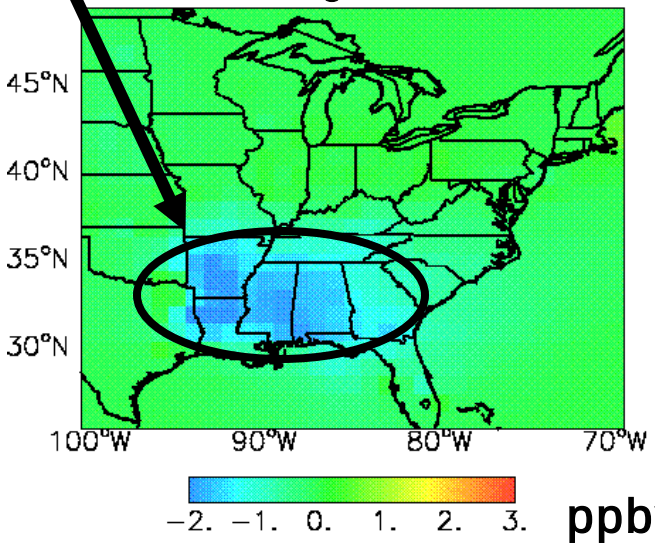
Isoprene emission changes from mid-80s to mid-90s [*Purves et al.*, 2004]



Change in July 1-5 p.m. surface O_3

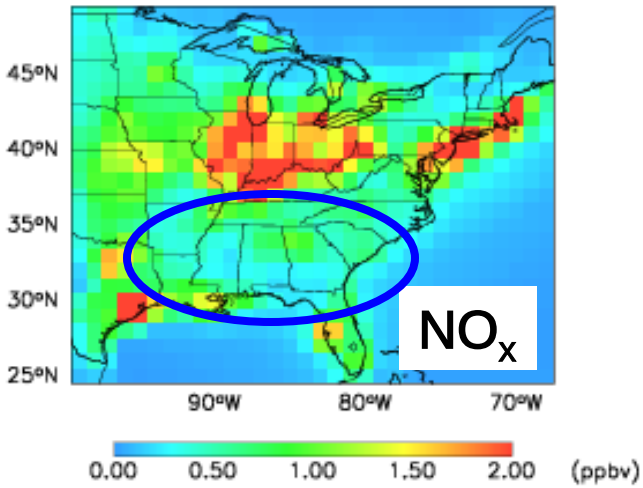


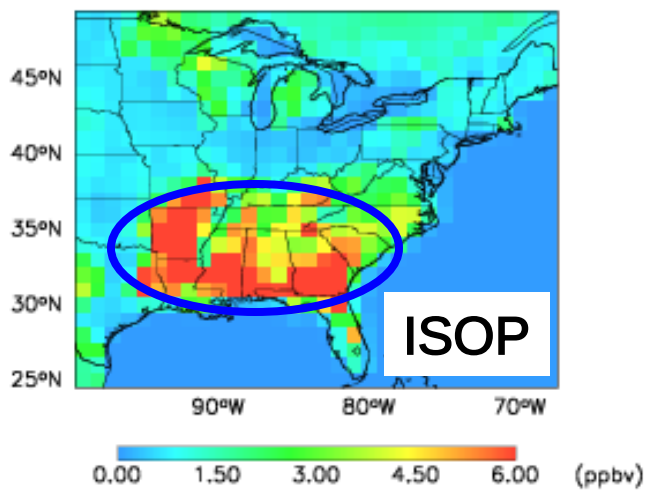
Low-NO_x regime?

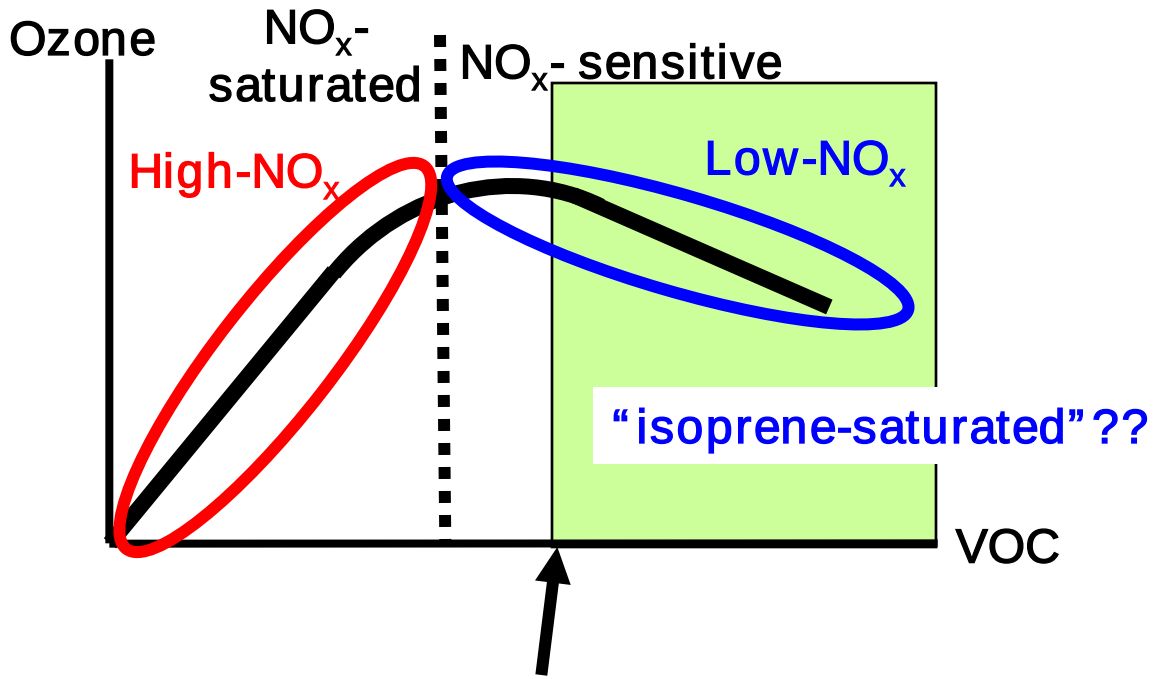
e.g. titration of boundary-layer OH in pre-industrial [*Mickley et al.*, 2001]; and present-day tropical regions [*von Kuhlmann et al.*, 2004]

Increasing Isoprene Decreases O_3 in Low-NO_x, High-isoprene regions

GEOS-CHEM base-case
July 1-5 p.m. mean







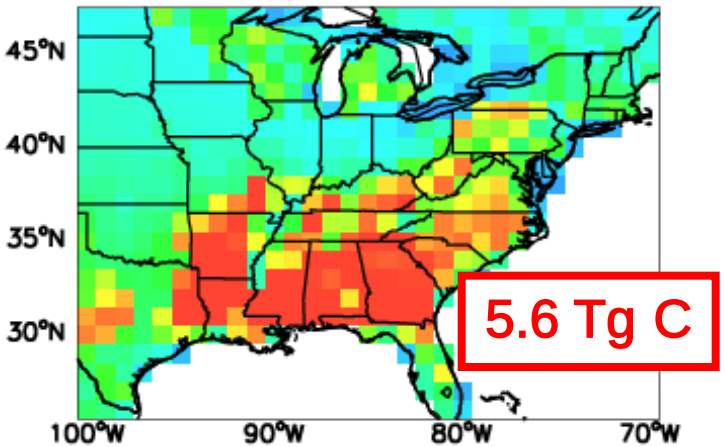
SE US is near "maximum VOC capacity point", beyond which VOCs suppress O_3 formation [*Kang et al.*, 2003].

"Isoprene-saturated" GEIA SE US: biogenics+O_3 (10d) comparable to O_3+HO_x (16d), O_3+hν -> OH (11d)

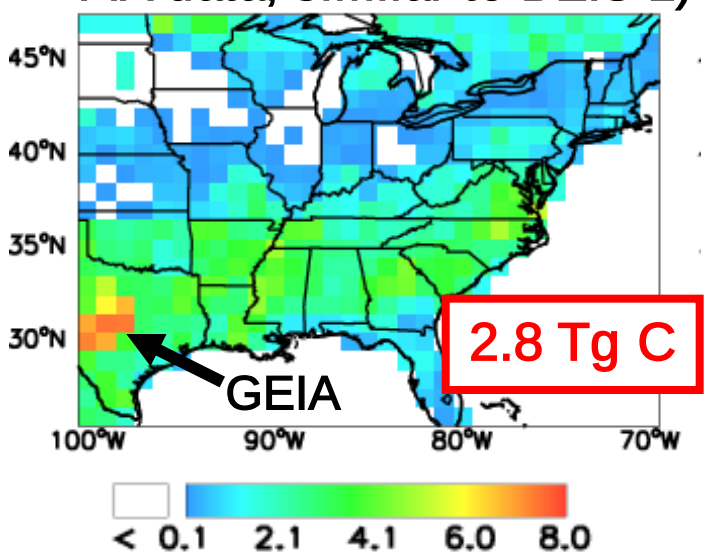
Choice of isoprene inventory critical for predicting base-case O_3

July isoprene emissions

GEIA: global inventory

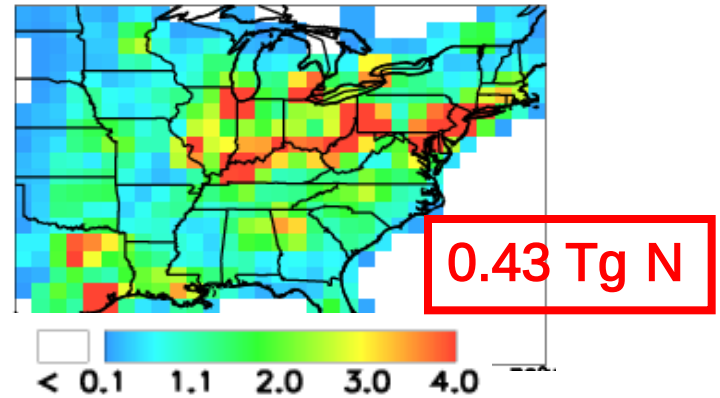


Purves et al., [2004] (based on FIA data; similar to BEIS-2)



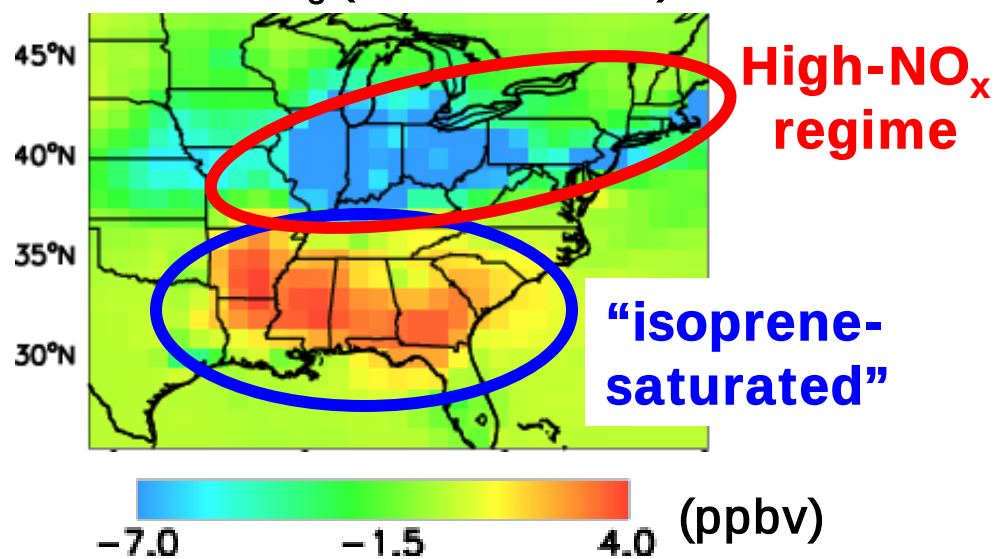
(10^{11} molecules isoprene cm^{-2} s^{-1})

July Anthrop. NO_x emissions



(10^{11} molec cm^{-2} s^{-1})

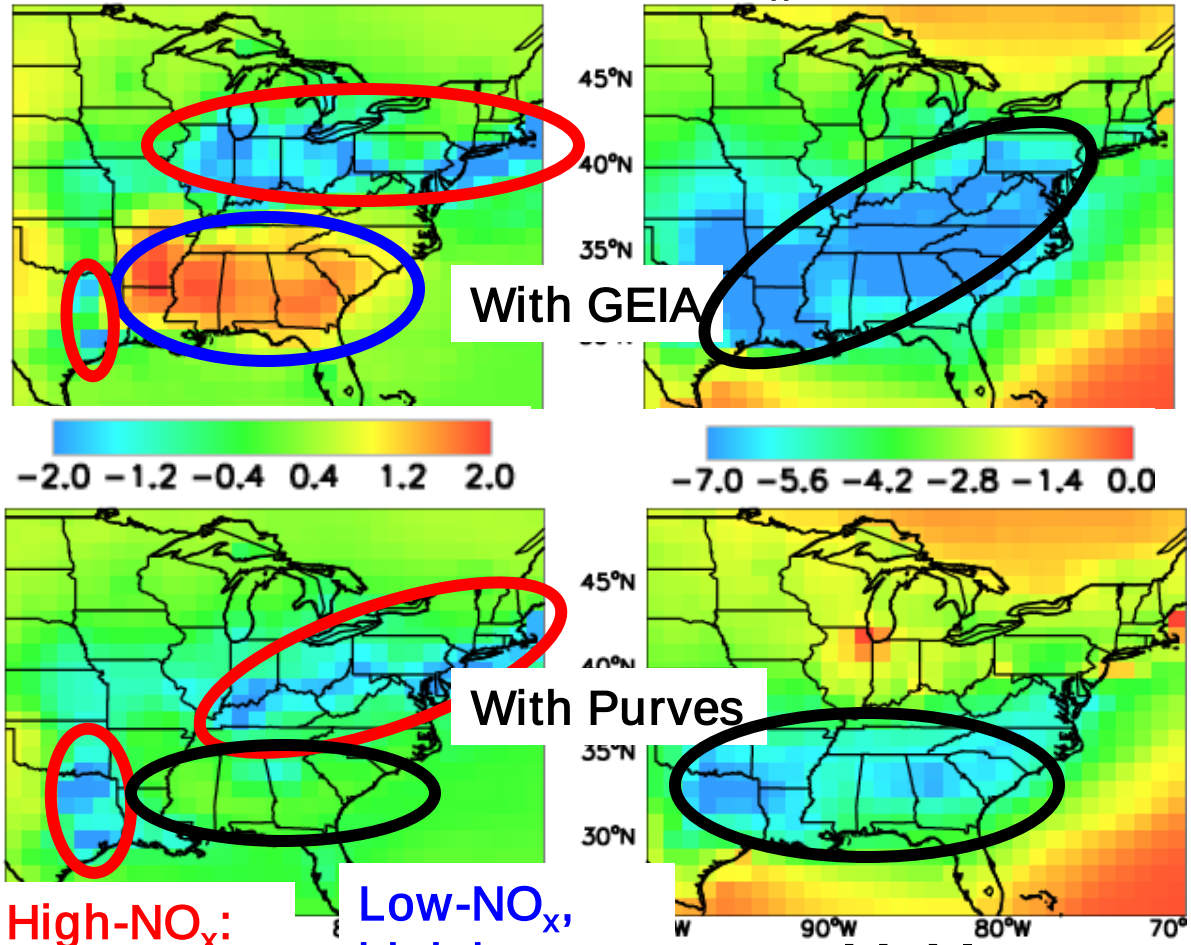
Difference in July 1-5 p.m. surface O_3 (Purves–GEIA)



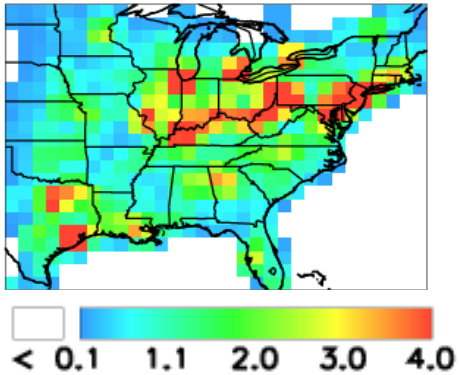
Identify O_3 chemistry regime with precursor emissions reductions

Change in July O_3 (ppbv; 1-5 p.m.)

Isoprene reduced 25% | NO_x reduced 25%



July Anthropogenic NO_x Emissions



(10^{11} molec cm^{-2} s^{-1})

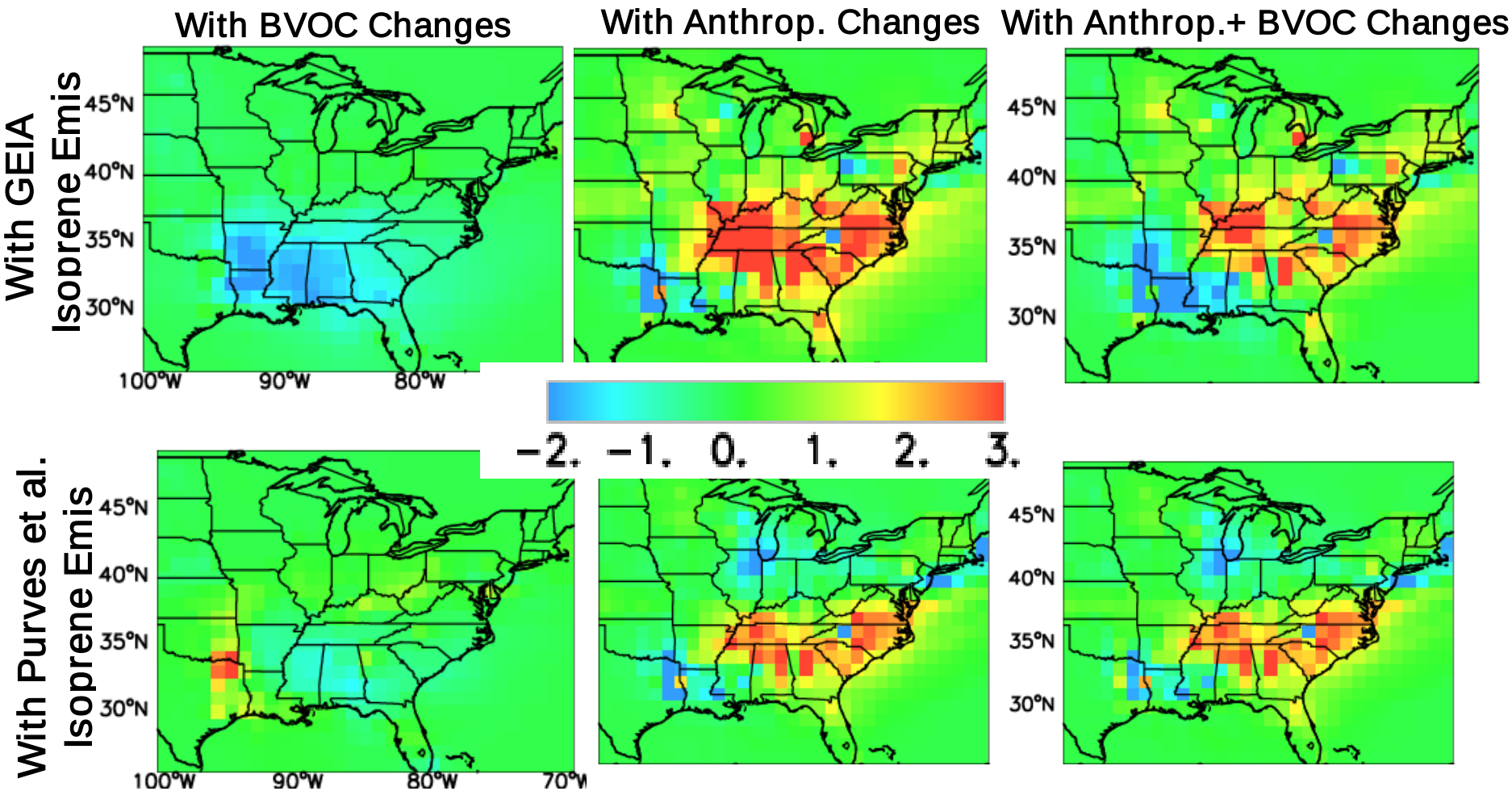
High-NO_x: O_3 ↓ as isop ↓

Low-NO_x, high isop: O_3 ↑ as isop ↓

highly NO_x-sensitive

Choice of isoprene inventory also critical for predicting O_3 response to changes in isoprene and anthropogenic NO_x emissions

Change in Mean July Surface O_3 (ppbv; 1-5 p.m.) reflecting 1980s to 1990s emissions changes



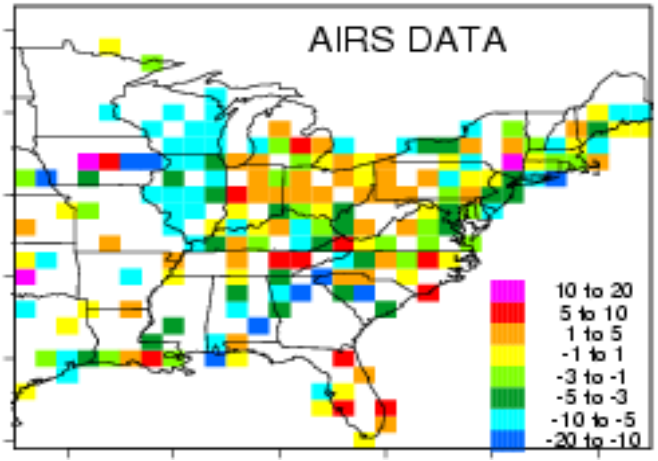
Changes in Anthropogenic NO_x emissions dominate O_3 response

But response depends upon choice of isoprene emission inventory

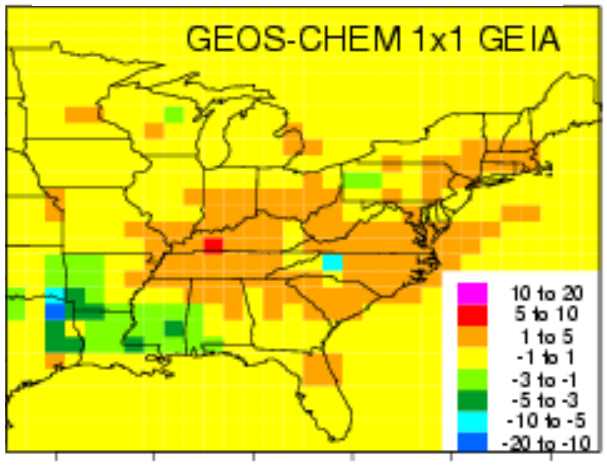
Comparison with observed changes? Impact on high-O_3 events?

Model vs. Obs.: Change in July O_3 1980s to 1990s (ppbv; 1-5 p.m.)

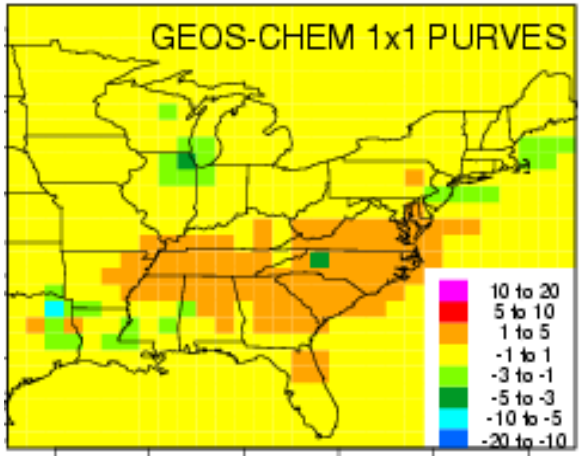
Obs: EPA AIRS



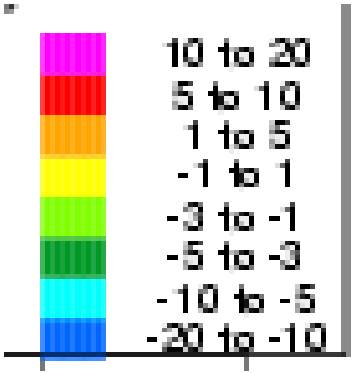
GEOS-CHEM: GEIA



GEOS-CHEM: Purves



(1993-1997) – (1983-1987)

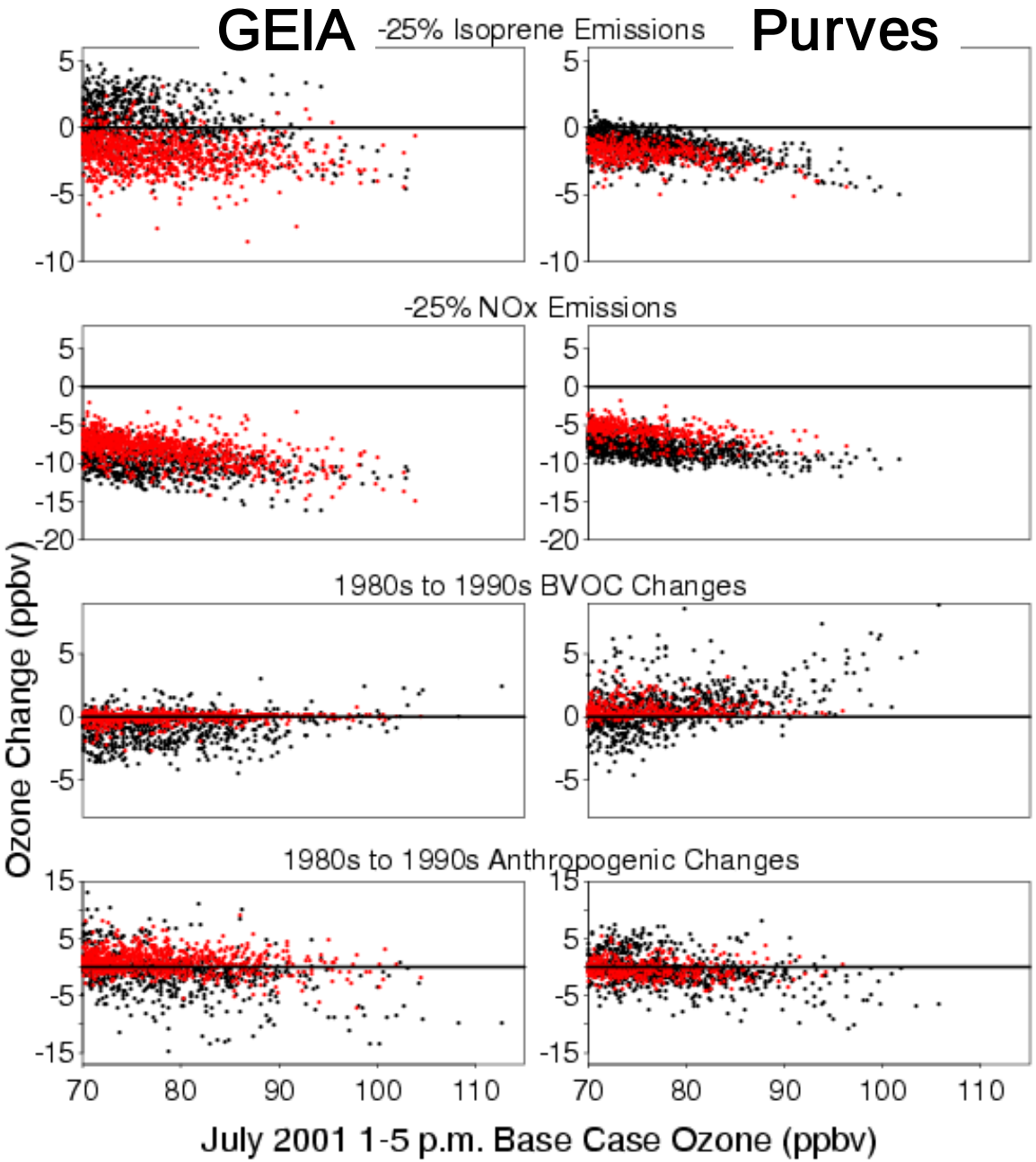


Poor correlation ($r^2 \sim 0$) between observed and simulated changes

Observed changes in O_3 are not explained by regional emission changes alone…

● Northeast
● Southeast

Impact of Sensitivity Simulations on High-O_3 Events:



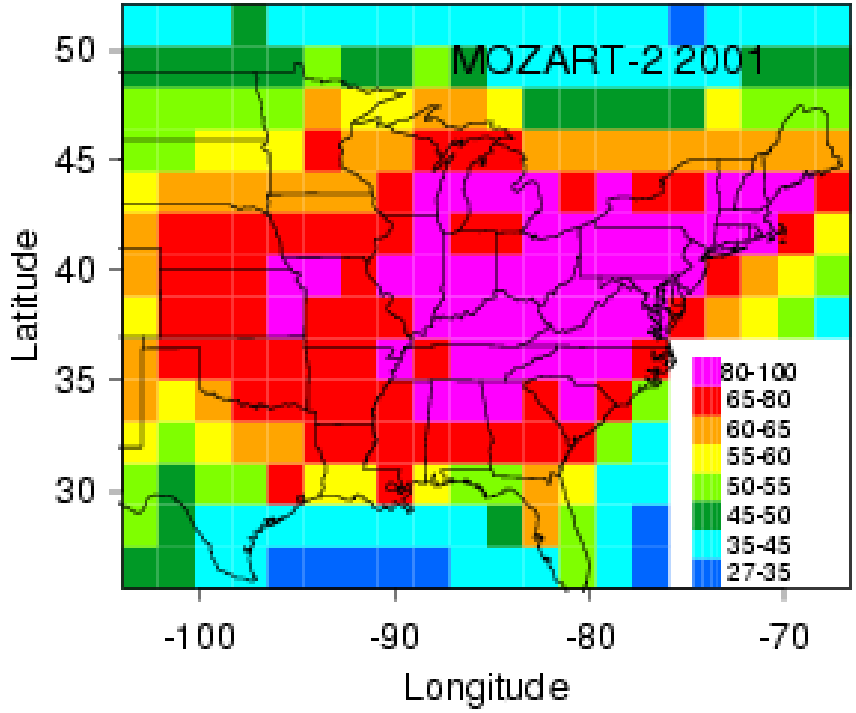
- decrease with isoprene except for GEIA SE
- decrease with NO_x, larger response with GEIA
- dominated by anthrop. (NO_x) emissions but BVOC changes may offset for most extreme events

Unclear whether recent BVOC emission changes mitigated / exacerbated high-O_3 events

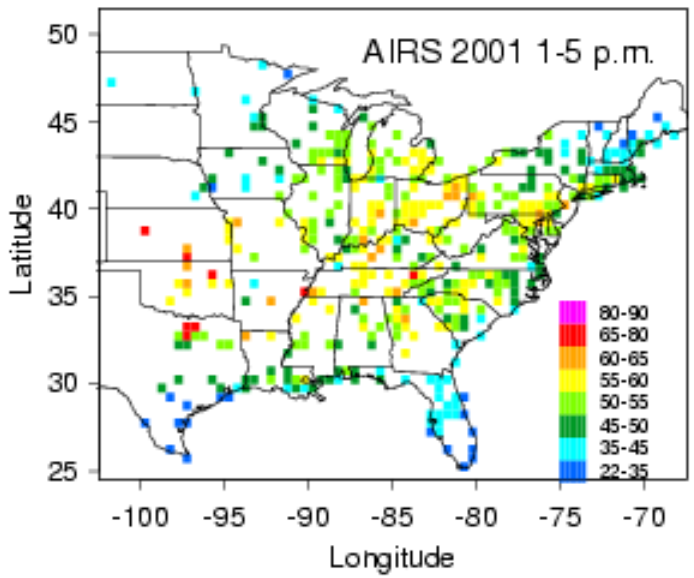
Tool #2: MOZART-2 tropospheric chemistry model [*Horowitz et al.*, 2003]

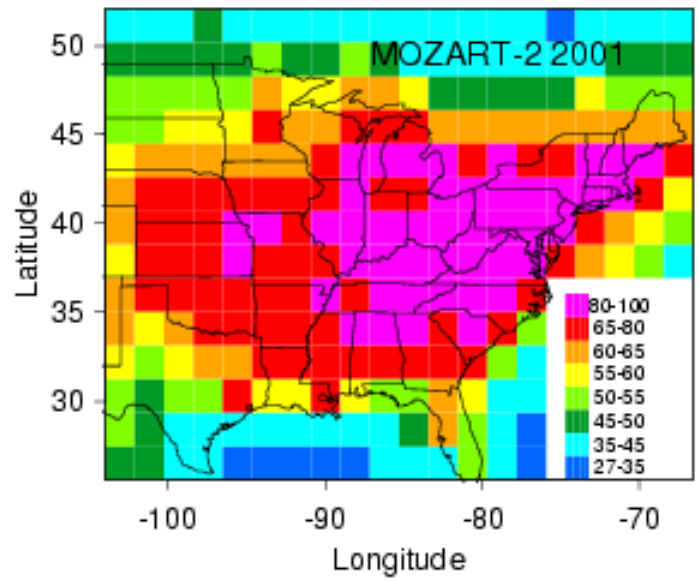
- **Uses assimilated meteorology: NCEP T62 (~1.9°) 2001**
- **28 vertical levels (8 below 2 km)**
- **75 tracers; NO_x-CO-hydrocarbon-O_3 chemistry coupled to BC, sulfate, nitrate aerosols**
- **GEIA isoprene inventory [*Guenther et al.*, 1995] implemented as monthly mean emission with diurnal cycle**

July 2001 1-5 p.m. Surface O_3 (ppbv)

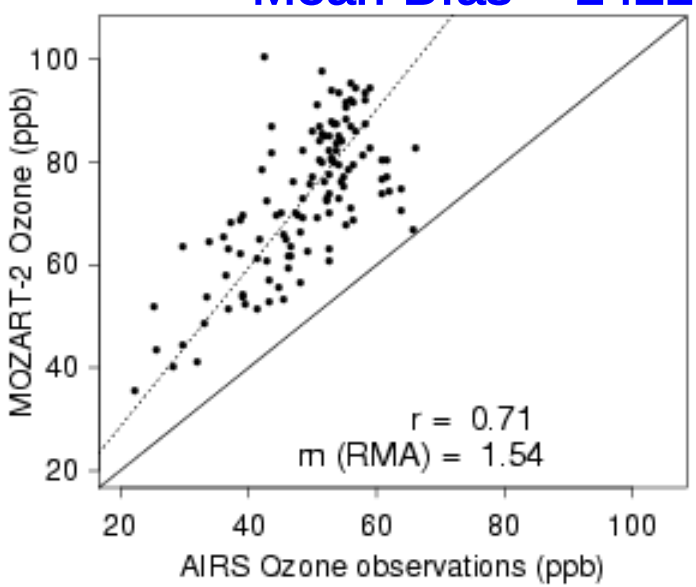


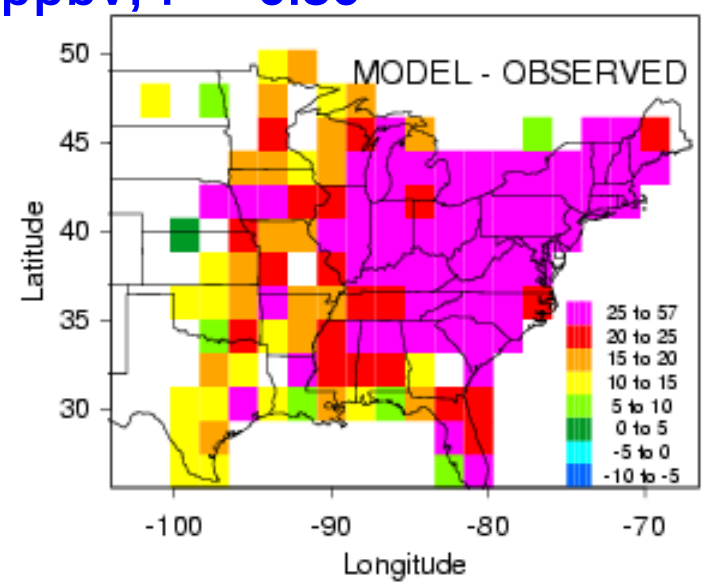
MOZART-2 Evaluation: July 2001 1-5 p.m. Surface O_3 (ppbv)





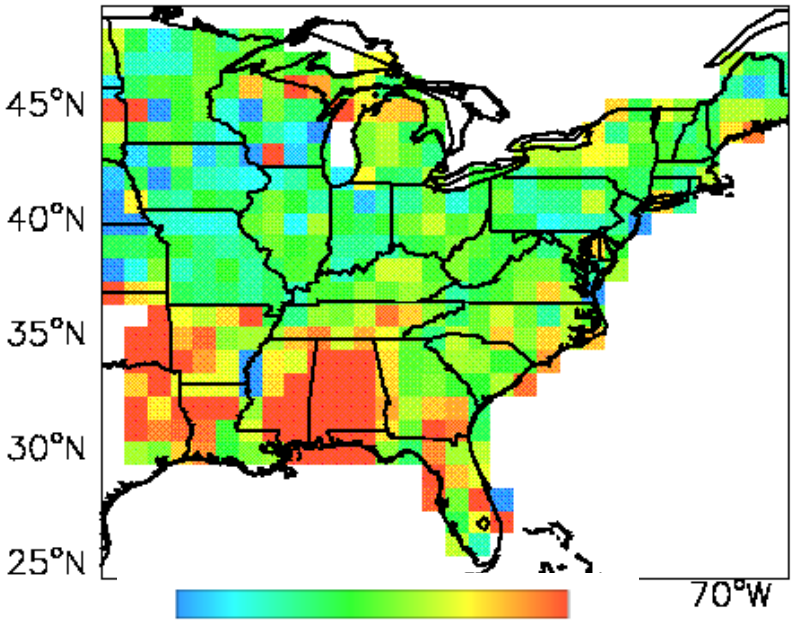
Mean Bias = 24±10 ppbv; r^2 = 0.50





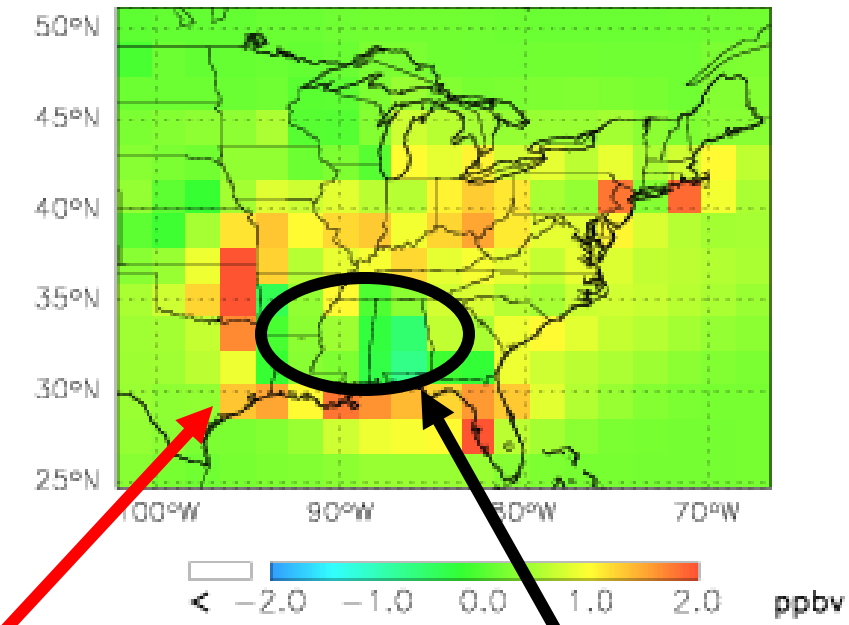
Does MOZART-2 also predict decreases in O_3 resulting from increases in isoprene emissions?

Isoprene emission changes from mid-80s to mid-90s [*Purves et al.*, 2004]



-20 –10 0 +10 +20 +30 (%)

MOZART-2: Change in July 1-5 p.m. surface O_3 (ppbv)



O_3 increases (1-2 ppbv)

Little change (NO_x-sensitive)

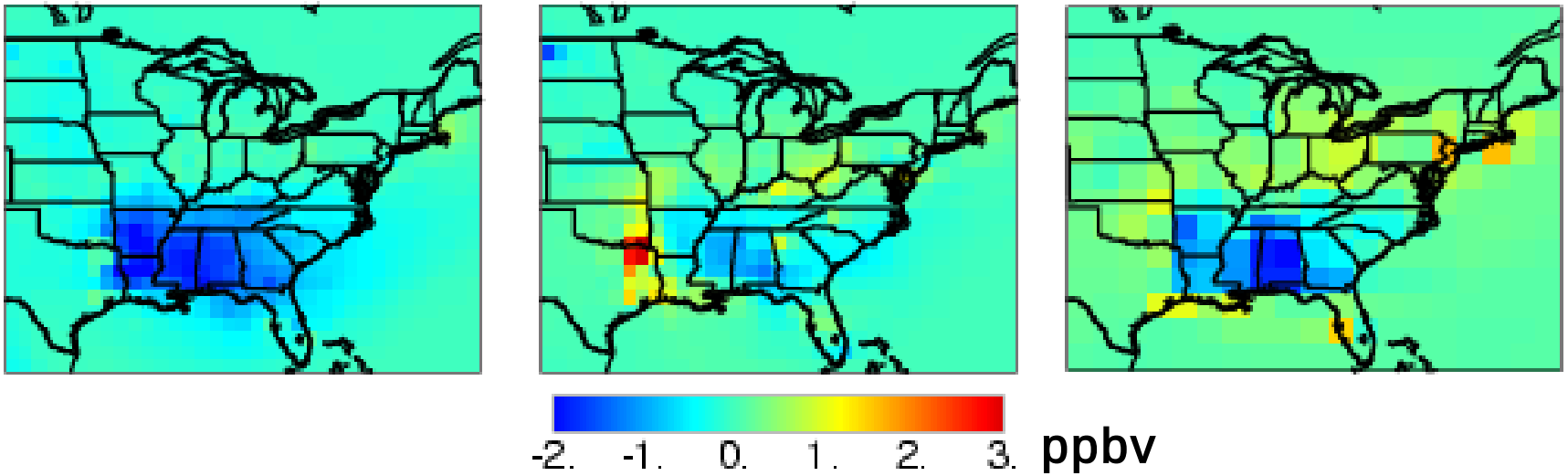
What if we assume isoprene nitrates are a NO_x sink?

Chemical uncertainty: MOZART-2 shows similar results to GEOS-CHEM if isoprene nitrates are a NO_x sink

Change in July 1-5 p.m. surface O_3 (ppbv)
(due to isop emis changes from mid-1980s to mid-1990s)

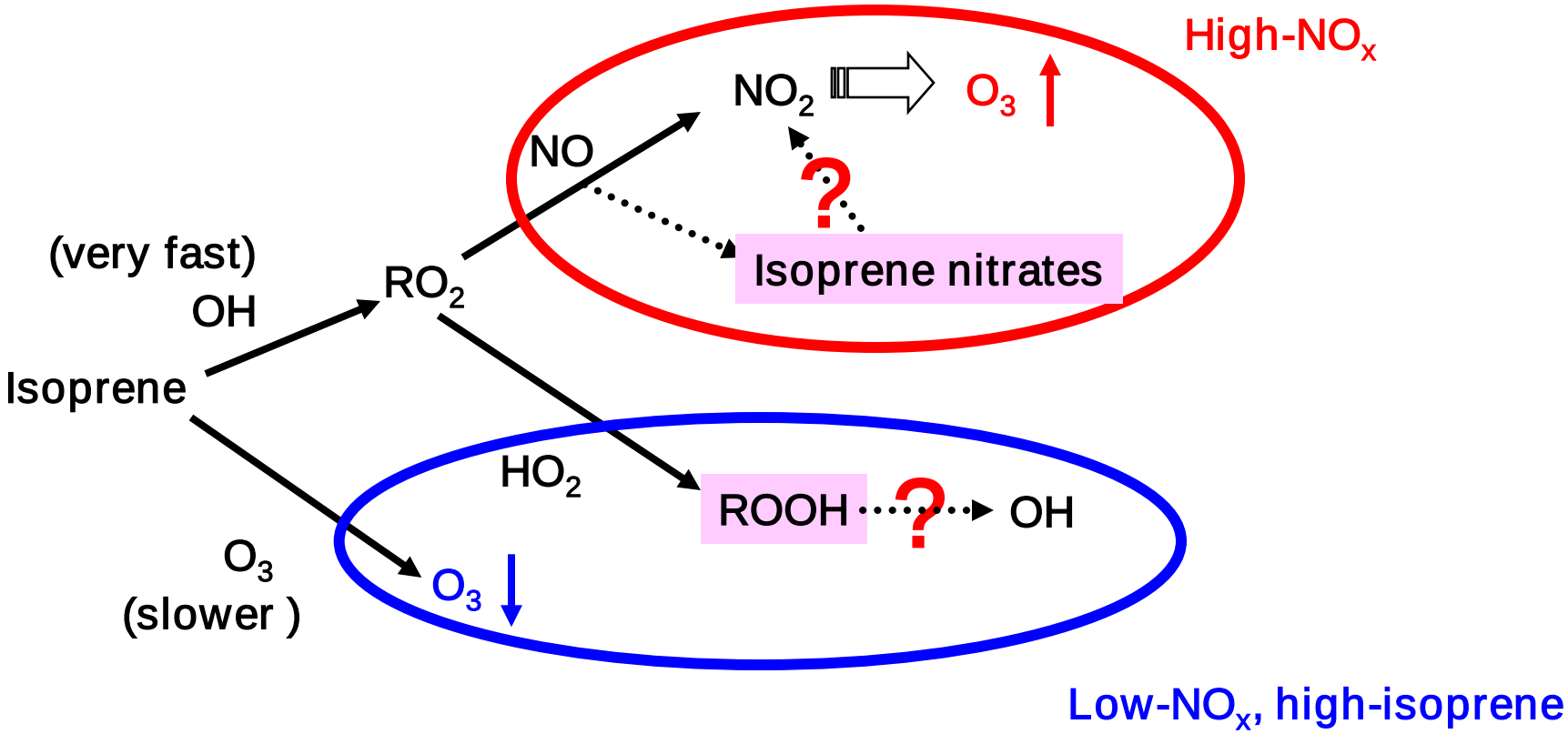
With 12% yield of isoprene nitrates

GEOS-CHEM: GEIA **GEOS-CHEM: Purves** **MOZART-2: GEIA**



Understanding fate of isop. nitrates essential for predicting sign of response to changes in isoprene emissions

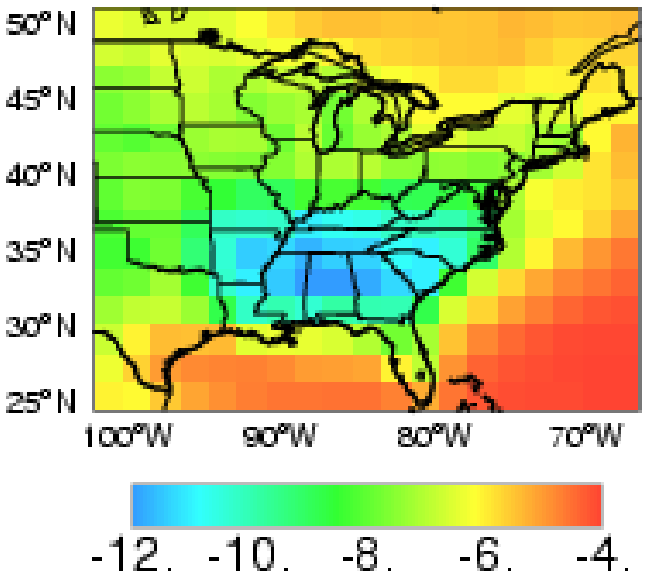
What is the O_3 sensitivity to the uncertain fate of organic nitrates and peroxides?



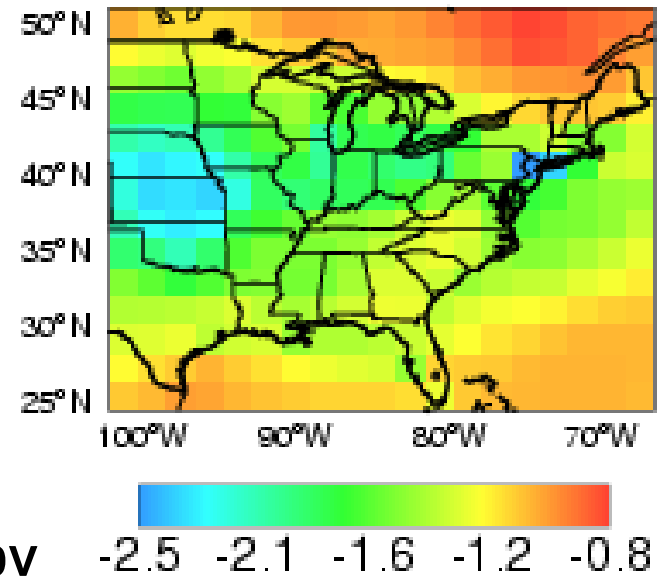
Sinks of HO_x / NO_x vs. recycling of radicals?

Impact on surface O_3 from uncertainties in chemical fate of organic isoprene nitrates and peroxides

Change in July mean 1-5 p.m. surface O_3 (MOZART-2)



ppbv



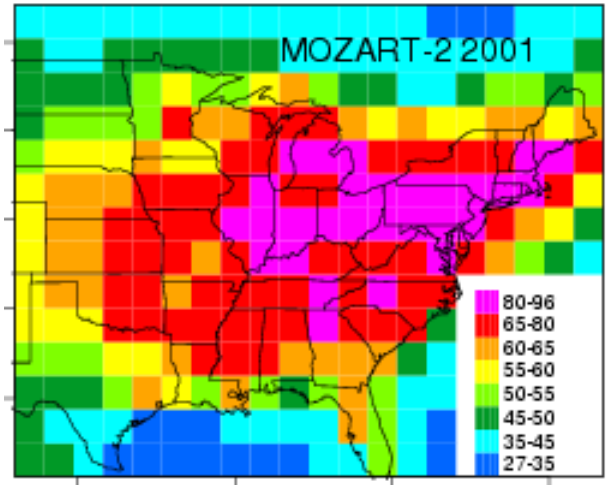
When isoprene nitrates act as a NO_x sink

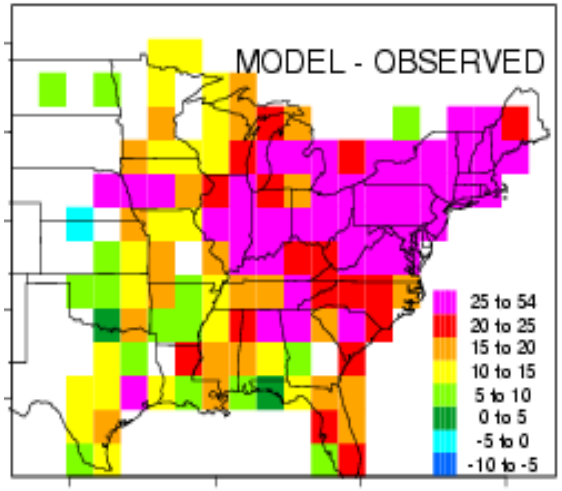
When organic peroxides act as a HO_x sink

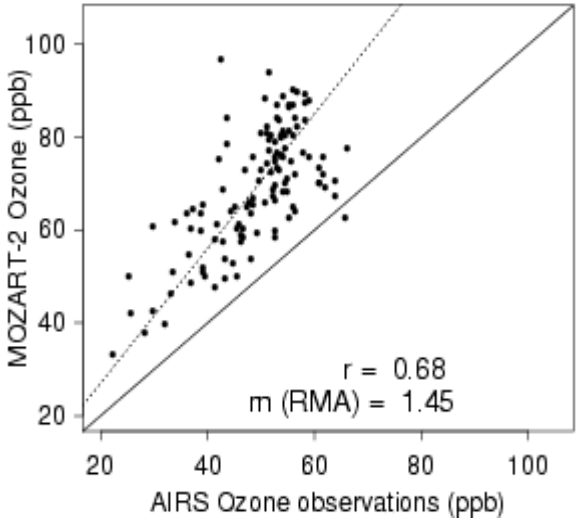
Revisit MOZART-2 vs. observations…

Isoprene nitrates as a NO_x sink → better MOZART-2 O_3 vs. observations

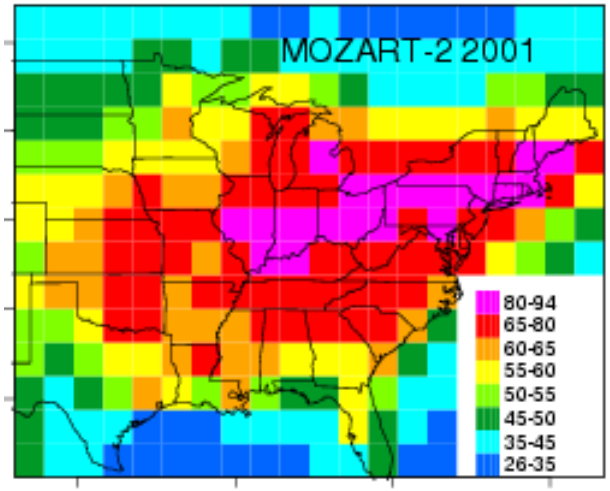
8% yield: bias = 20±10 ppbv; r^2=0.46

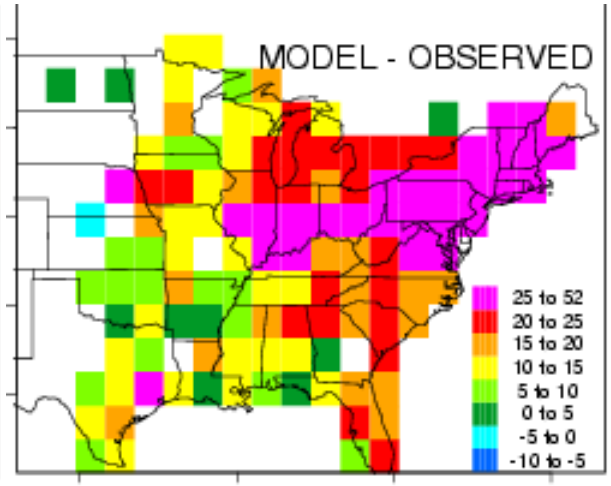


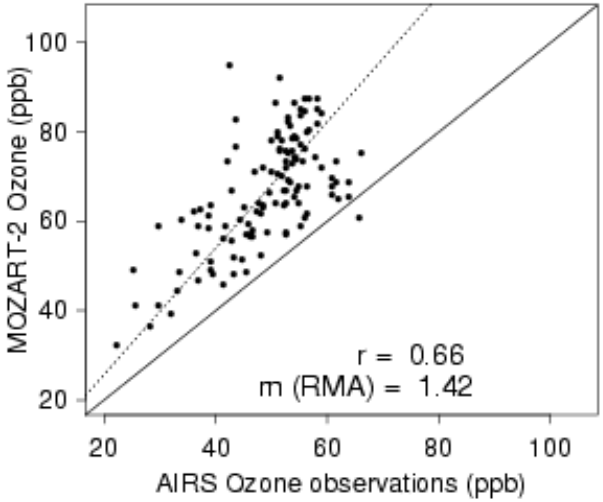




12% yield: bias = 18±10 ppbv; r^2=0.44

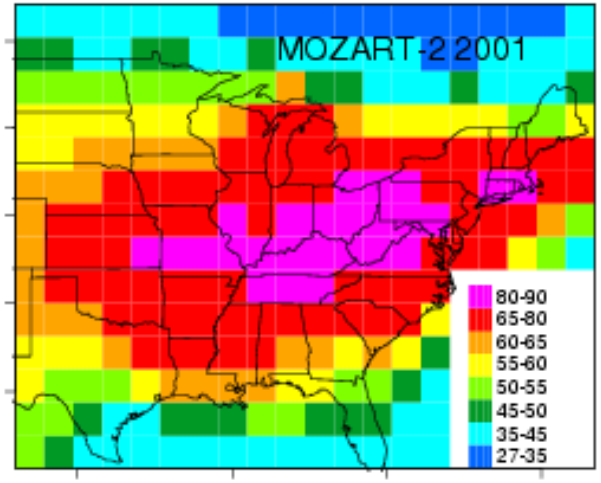


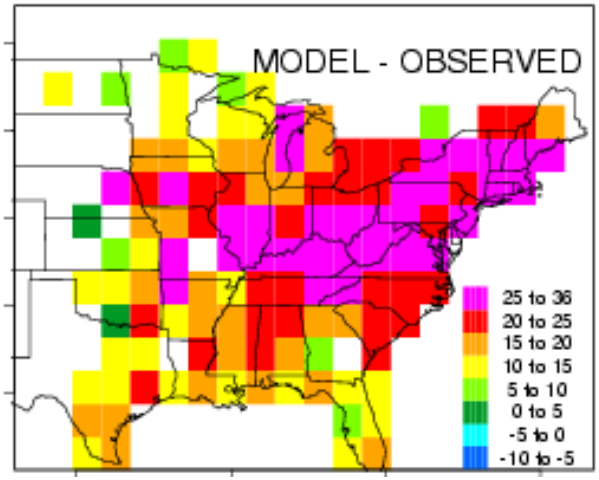


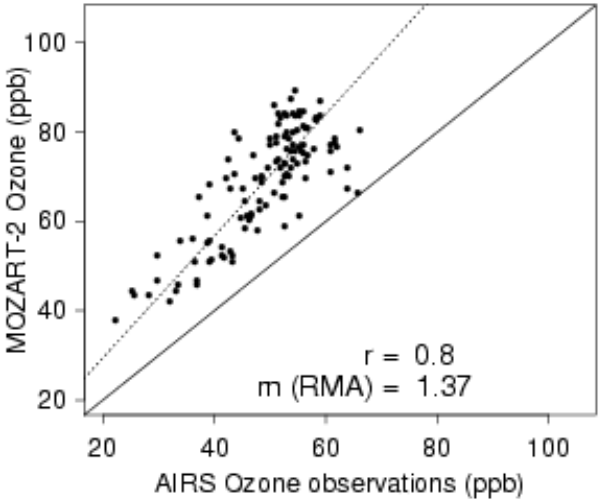


Using GEOS-CHEM NO_x emissions in MOZART-2…

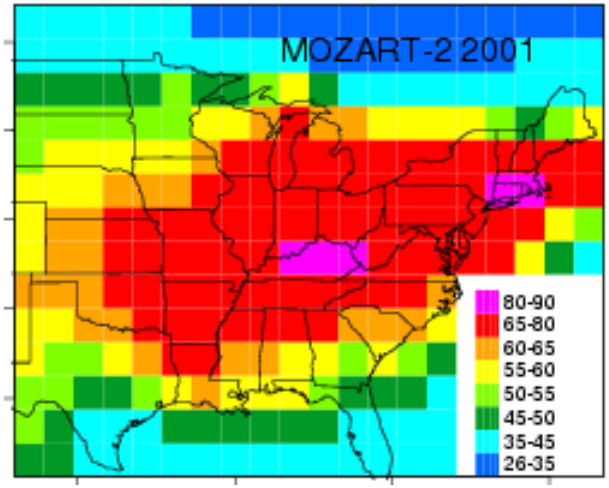
bias = 20±7 ppbv; r^2=0.64

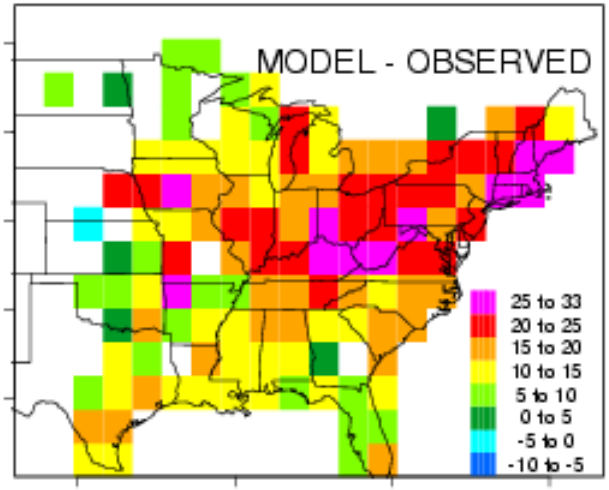


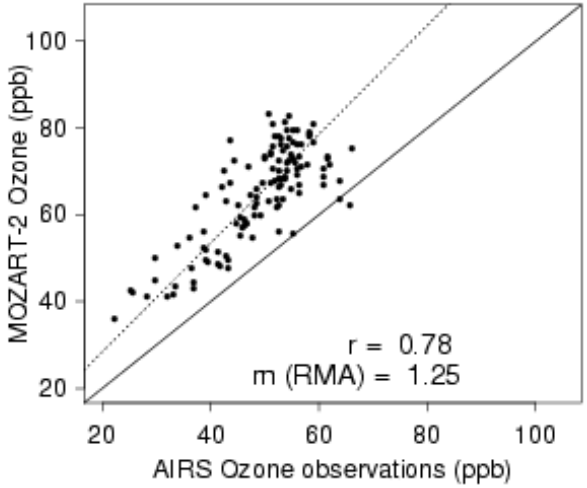




With organic nitrates as NO_x sink: bias = 16±7 ppbv; r^2=0.61







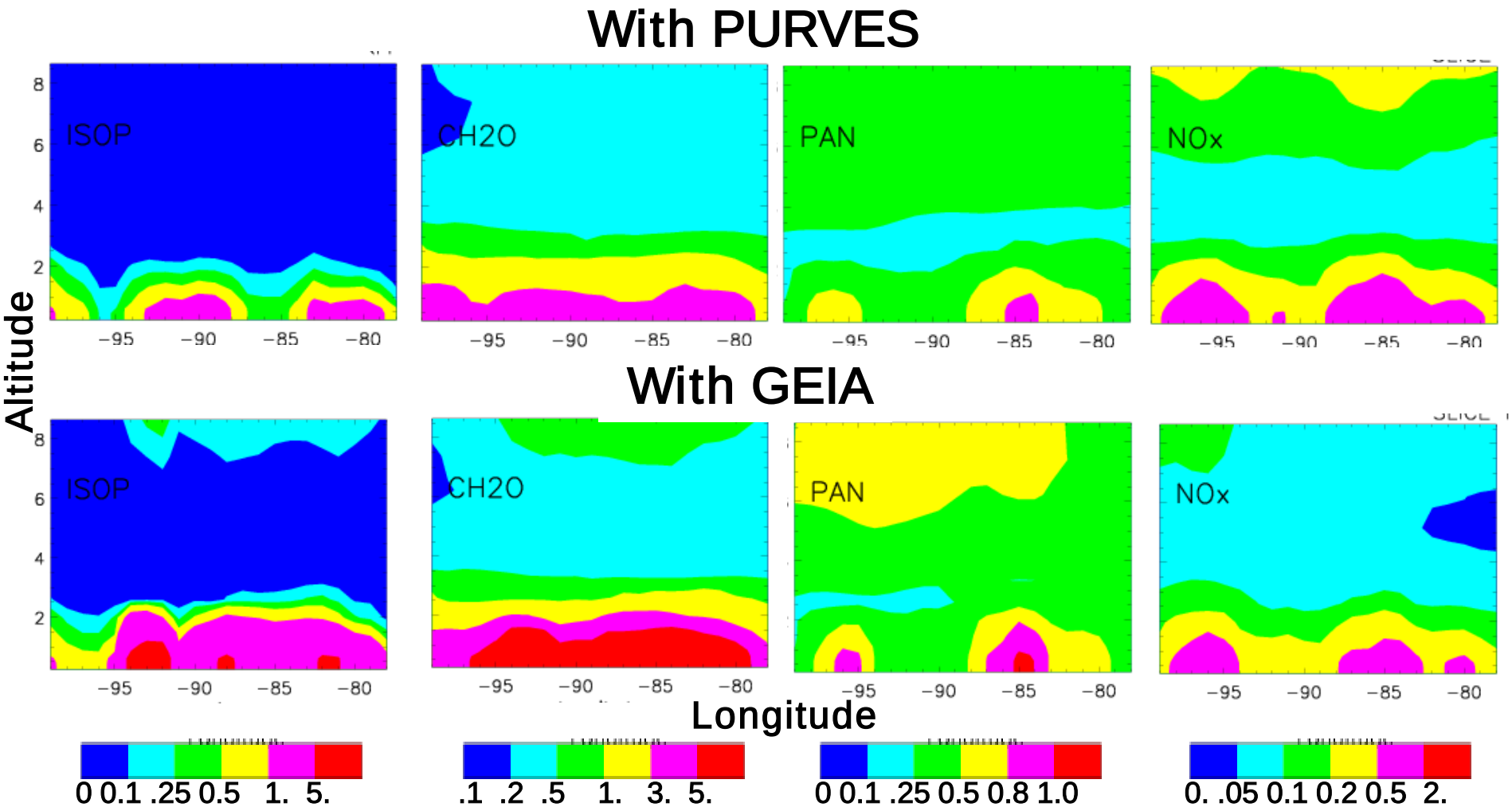
Conclusions… and Remaining Challenges

- Better constrained isoprene emissions are needed to quantify:
  1. isoprene contribution to E. U.S. surface O_3
  2. how O_3 responds to both anthrop. and biogenic emission changes

  → satellite CH_2O columns?
  → New inventories (MEGAN, BEIS-3) more accurate?
  → ICARTT observations?

Potential for ICARTT data over the Southeast U.S. to help determine which isoprene inventory is closer to reality?

Vertical slices through 34N in GEOS-CHEM: Differences in surface & upper trop ISOP, CH_2O, PAN, NO_x



Conclusions and Remaining Challenges

- Better constrained isoprene emissions are needed to quantify:
  1. isoprene contribution to E. U.S. surface O_3
  2. how O_3 responds to both anthrop. and biogenic emission changes

  → Utility of satellite CH_2O columns?
  → New inventories (MEGAN, BEIS-3) more accurate?
  → ICARTT observations?

- Recent isoprene increases may have reduced surface O_3 in the SE

  → Does this regime actually exist?
  → Fate of organic nitrates produced during isoprene oxidation?
  → Results consistent in MOZART-2 and GEOS-CHEM

- Reported regional emission changes from 1980s to 1990s alone do not explain observed O_3 trends
  → Are anthropogenic emissions inventories sufficient to support trend studies? (*Parrish et al.*, *JGR* 2002: inconsistencies with $CO:NO_x$ ratios from road traffic in EPA inventories vs. ambient msmts)
  → Decadal shifts in meteorology?
  → Changing global O_3 background?