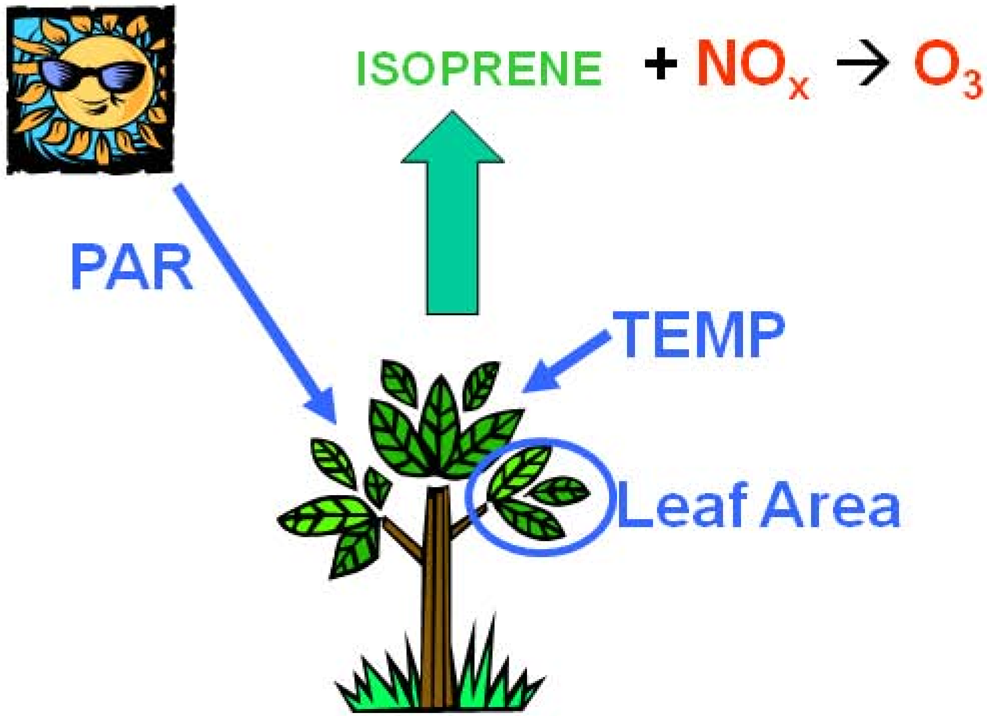
Uncertainties in isoprene-NO_x-O_3 chemistry: Implications for surface ozone over the eastern United States



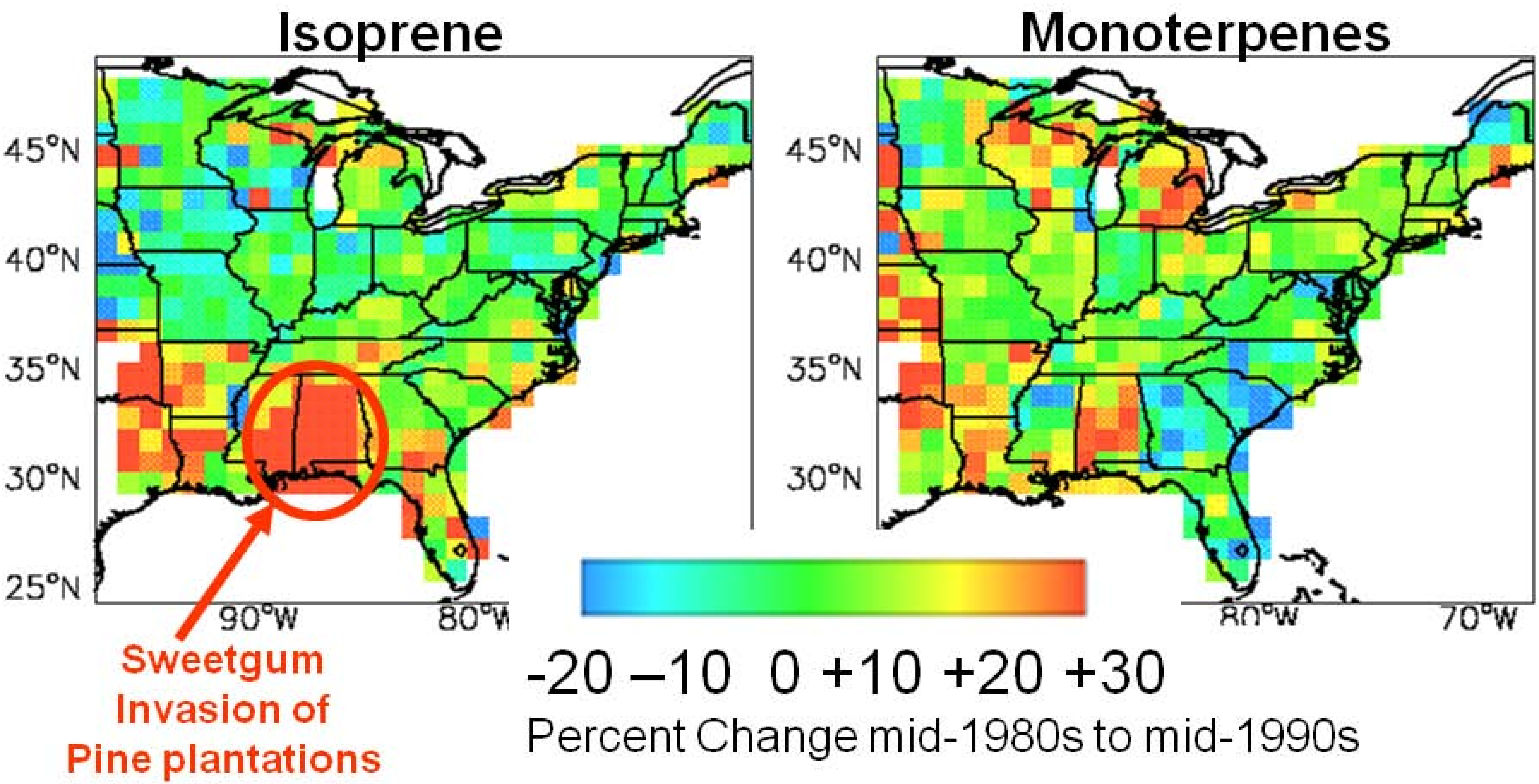
Arlene M. Fiore

Telluride Atmospheric Chemistry Workshop
August 11, 2004

Recent Changes in Biogenic VOC Emissions

- based upon analysis of > 280,000 forest plots
- substantial isoprene increases in southeastern USA
- largely driven by human land-use decisions

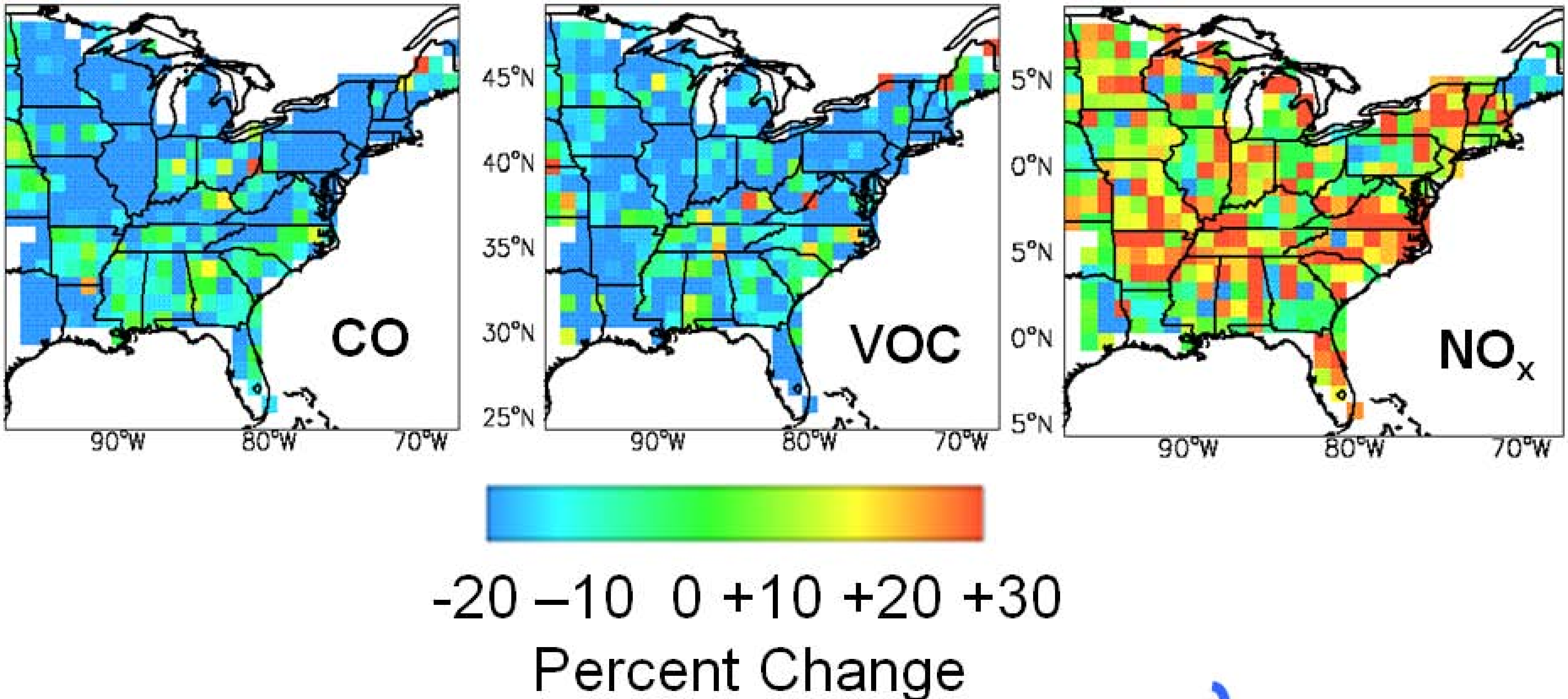
[*Purves et al.*, *Global Change Biology*, 2004]



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)



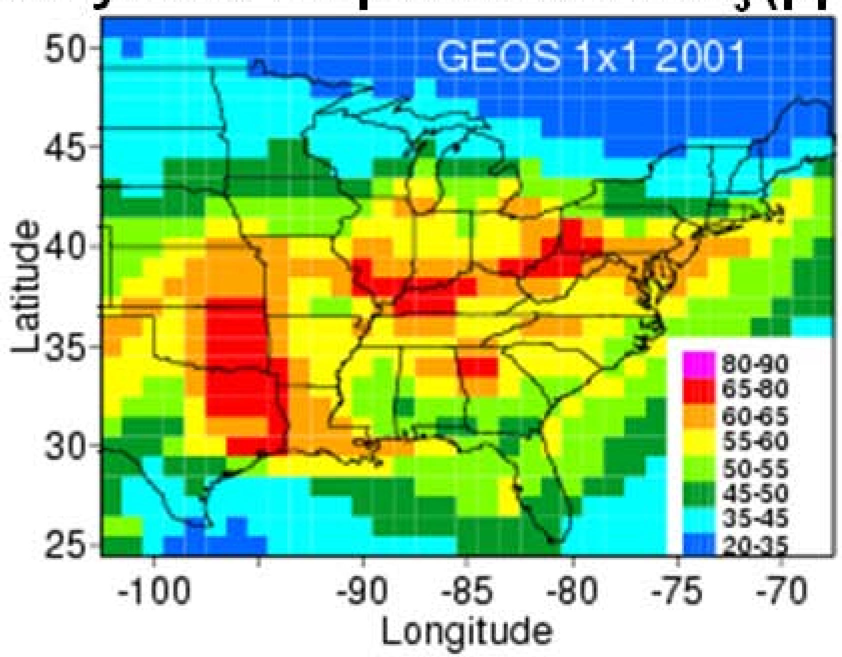
→Large decreases in CO and VOC Emissions
→Some local increases in NO_x
→Higher biogenic VOCs

Net effect On O_3?

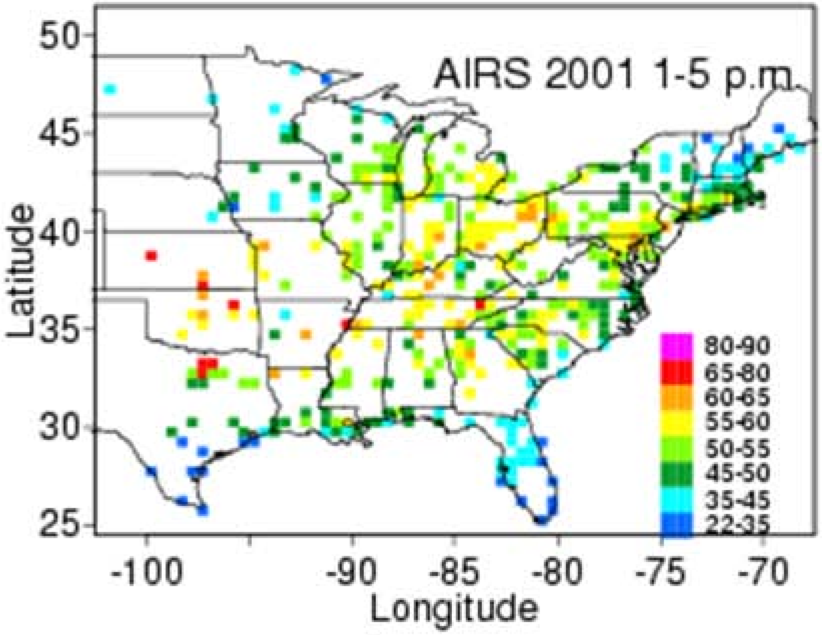
Tool: GEOS-CHEM tropospheric chemistry model [*Bey et al.*, 2001]

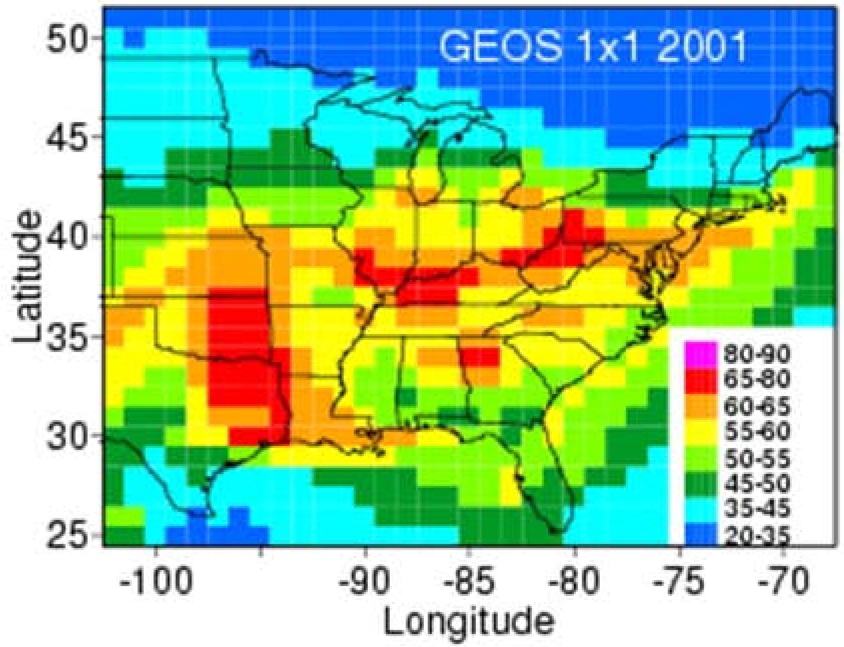
- Uses assimilated meteorology: GEOS-3 1°x1° fields for 2001
- 48 vertical levels (9 below 2 km)
- Regridded to 4°x5° for global spinup and boundary conditions for nested 1°x1° resolution over North America [*Wang et al.*, 2004; *Li et al.*, 2004]
- 31 tracers; NO_x-CO-hydrocarbon-O_3 chemistry coupled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

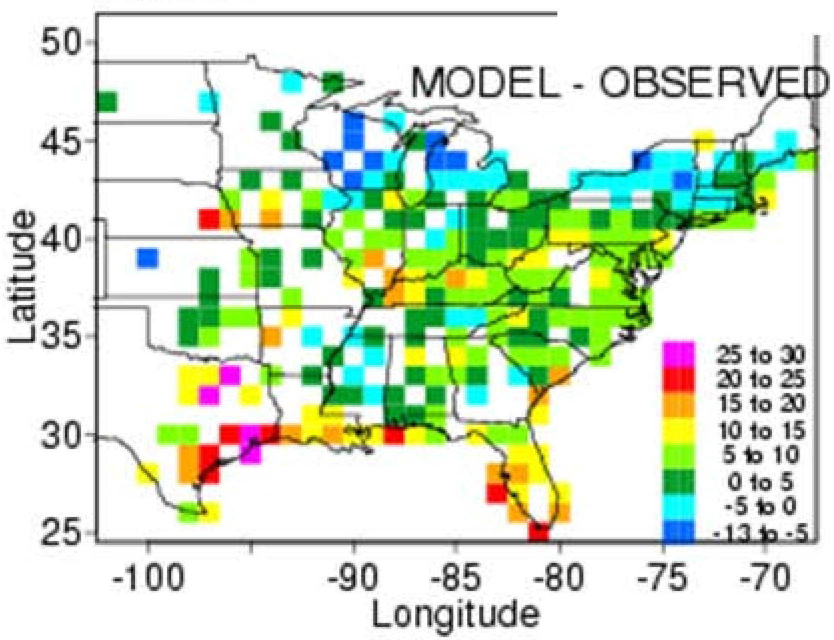
July 2001 1-5 p.m. Surface O_3 (ppbv)



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





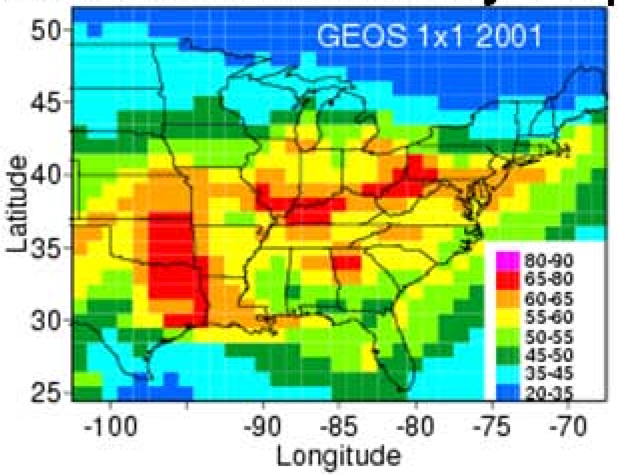


Mean Bias = 6±7 ppbv

r^2 = 0.4

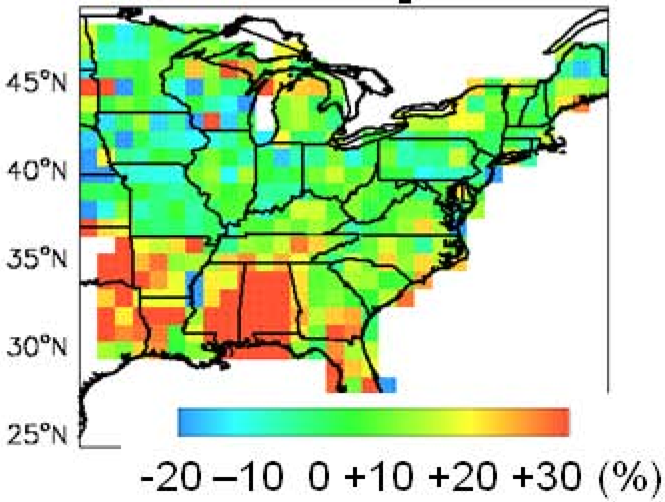
Isoprene increases reduce O_3 in Southeastern US

Standard GEOS-CHEM 1x1 N. American Nested simulation: July 1-5 p.m. O_3

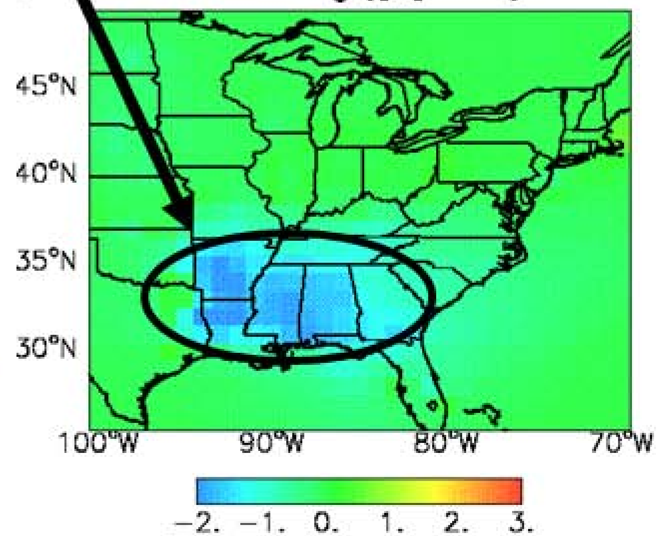


+

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



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

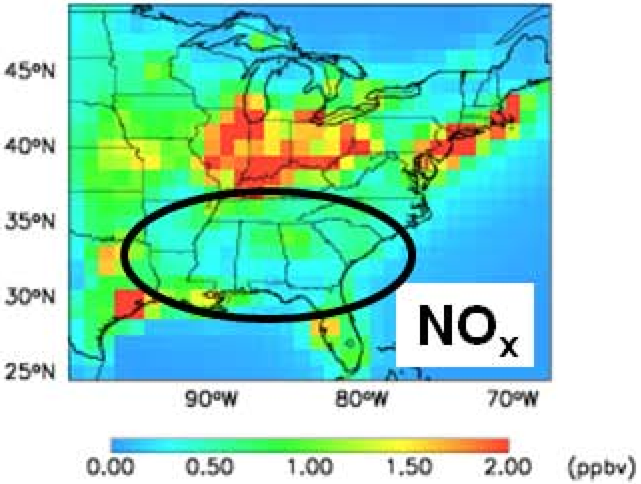


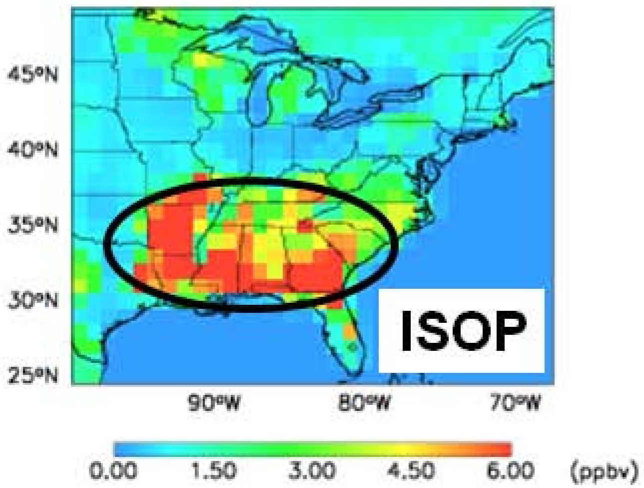
Low-NO_x regime?

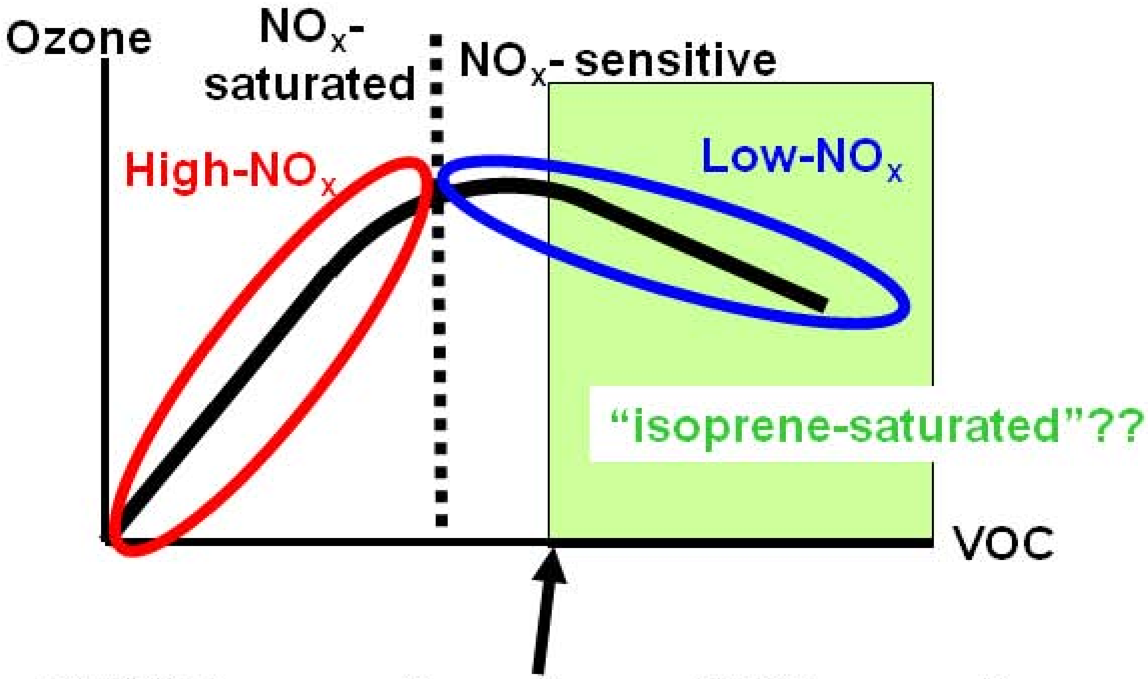
e.g. titration of OH in pre-industrial [*Mickley et al.*, 2001] & tropical [*von Kuhlmann et al.*, 2004] boundary layers

Increasing Isoprene Decreases Ozone in "Low-NO_x" environment

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







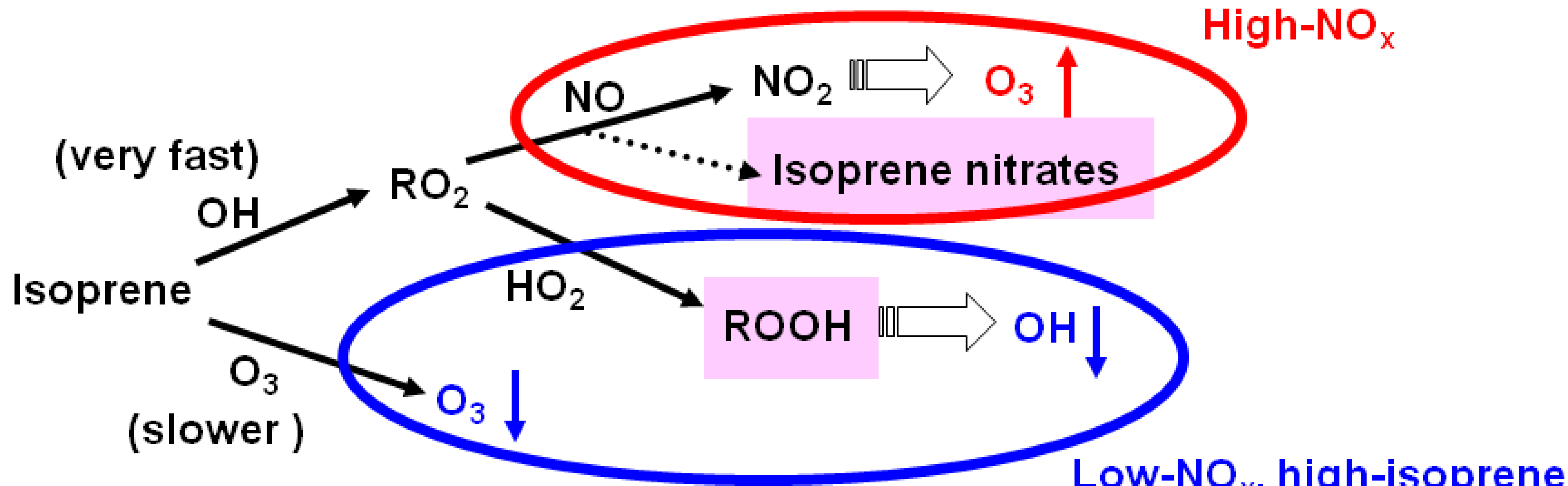
SE US is near "maximum VOC capacity point", beyond which VOCs suppress O_3 formation; [*Kang et al.*, 2003].

"Isoprene-saturated" GEIA simulation:
biogenics+O_3 (10d) comparable to
O_3+HO_x(16d), hν -> OH (11d)
in SE US (31-37N; 81-91W)

Isoprene can decrease surface O_3 by:

(1) Sequestering NO_x as organic isoprene nitrates

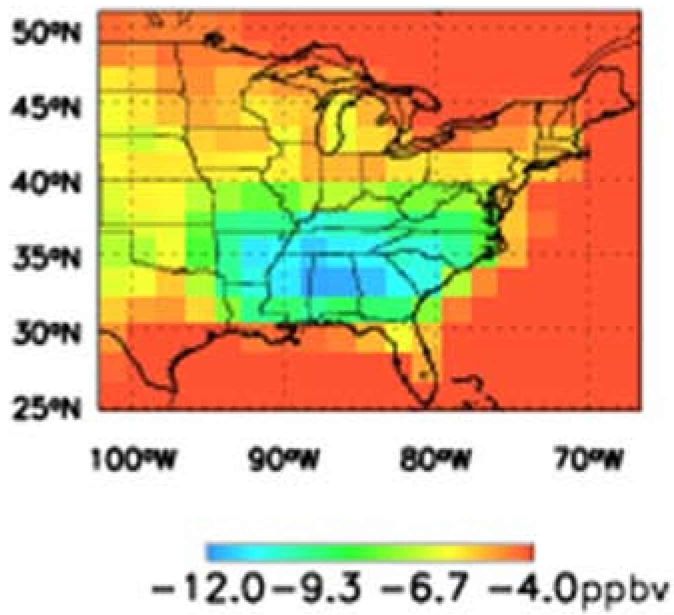
(2) Titrating OH and enabling direct reaction of isoprene with O_3



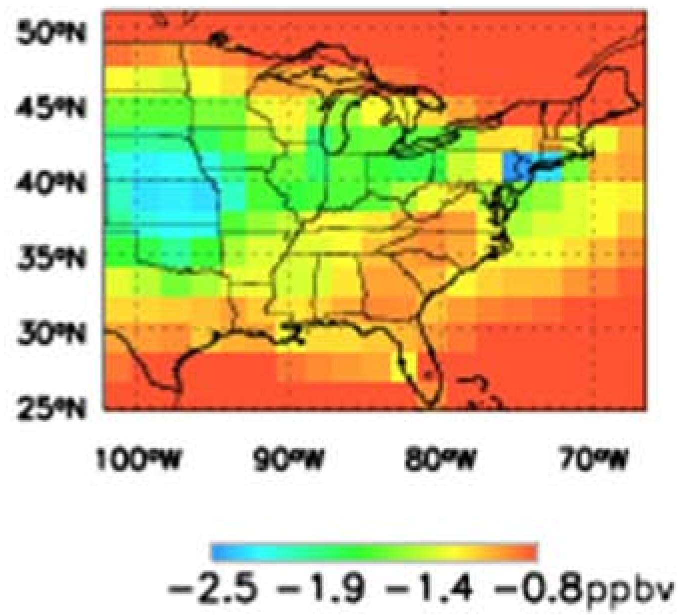
Uncertainties in the fate of organic nitrates and peroxides: Sinks of HO_x / NO_x vs. recycling of radicals?

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

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



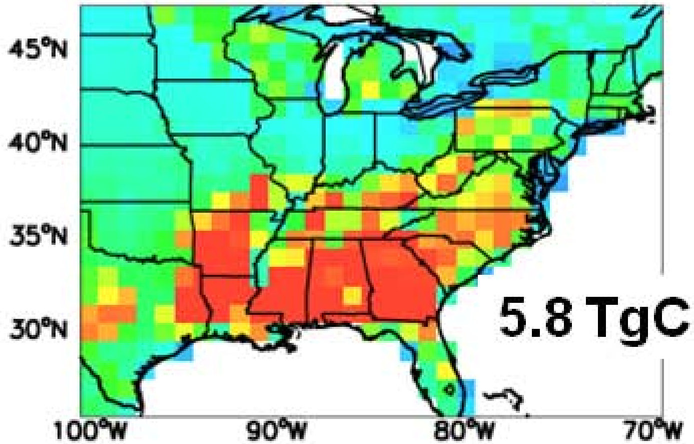
When isoprene nitrates act as a NO_x sink



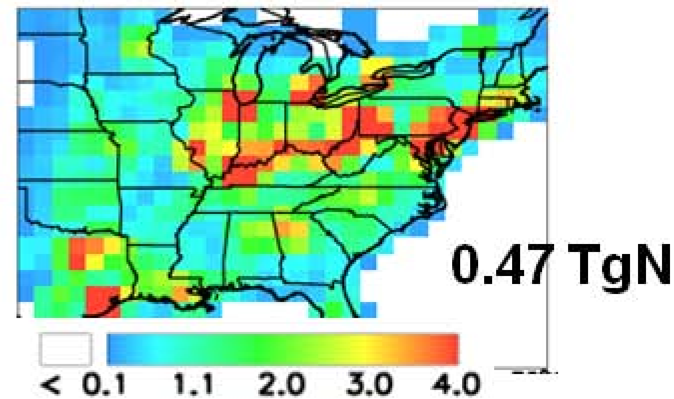
When organic peroxides act as a HO_x sink

Choice of isoprene emissions critical for predicting surface O_3

GEIA: global inventory

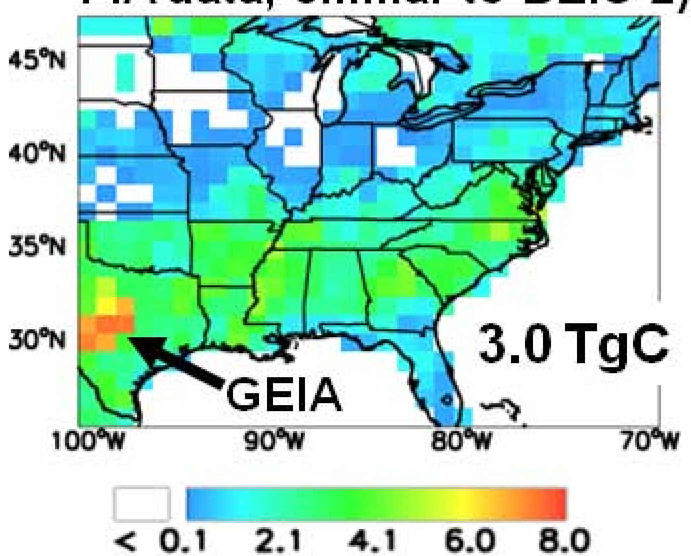


Anthrop. NO_x emissions



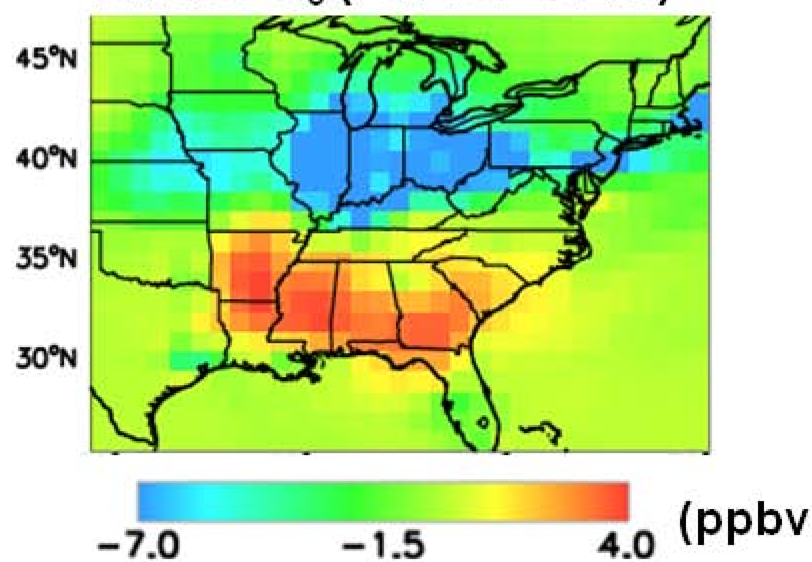
(10^{11} molec cm^{-2} s^{-1})

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



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

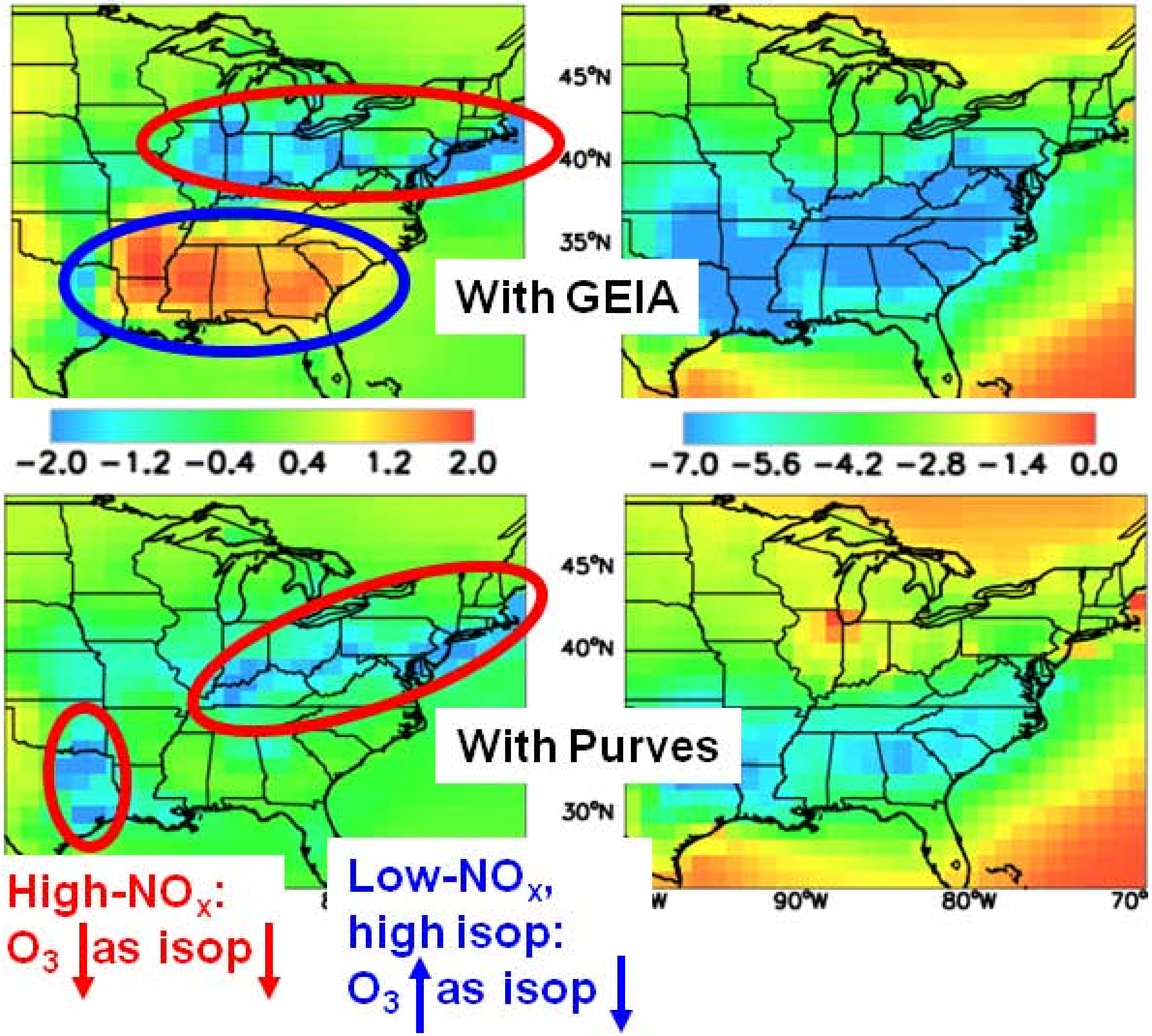
Difference in July 1-5 p.m. surface O_3 (Purves–GEIA)



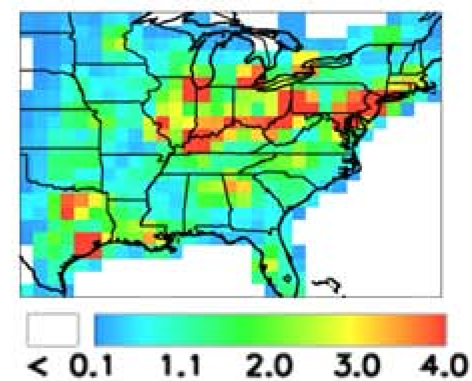
Surface Ozone Response to isoprene and anthropogenic NO_x emissions: sensitive to isoprene inventory choice

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

Isoprene reduced 25% — **NO_x reduced 25%**

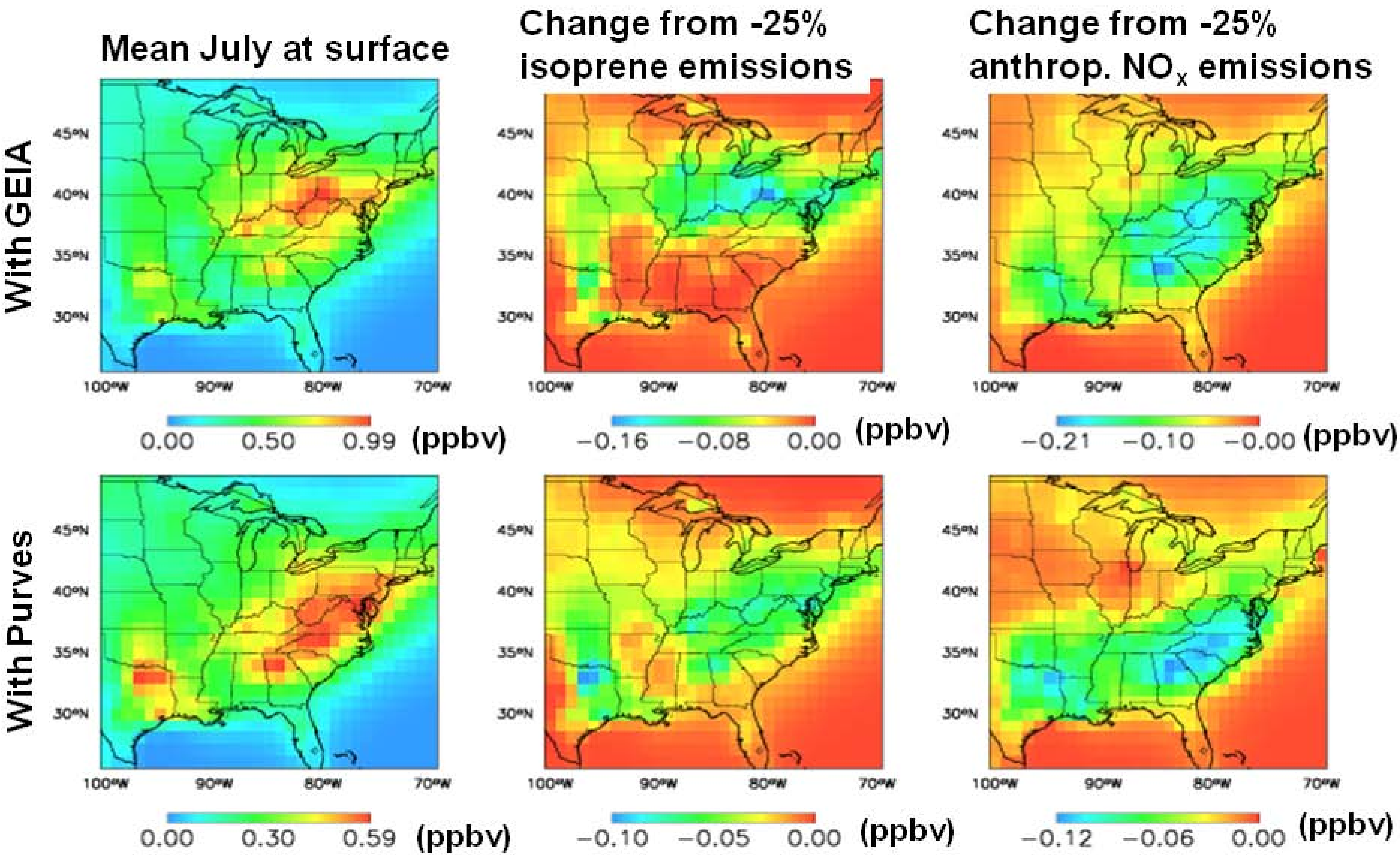


July Anthropogenic NO_x Emissions



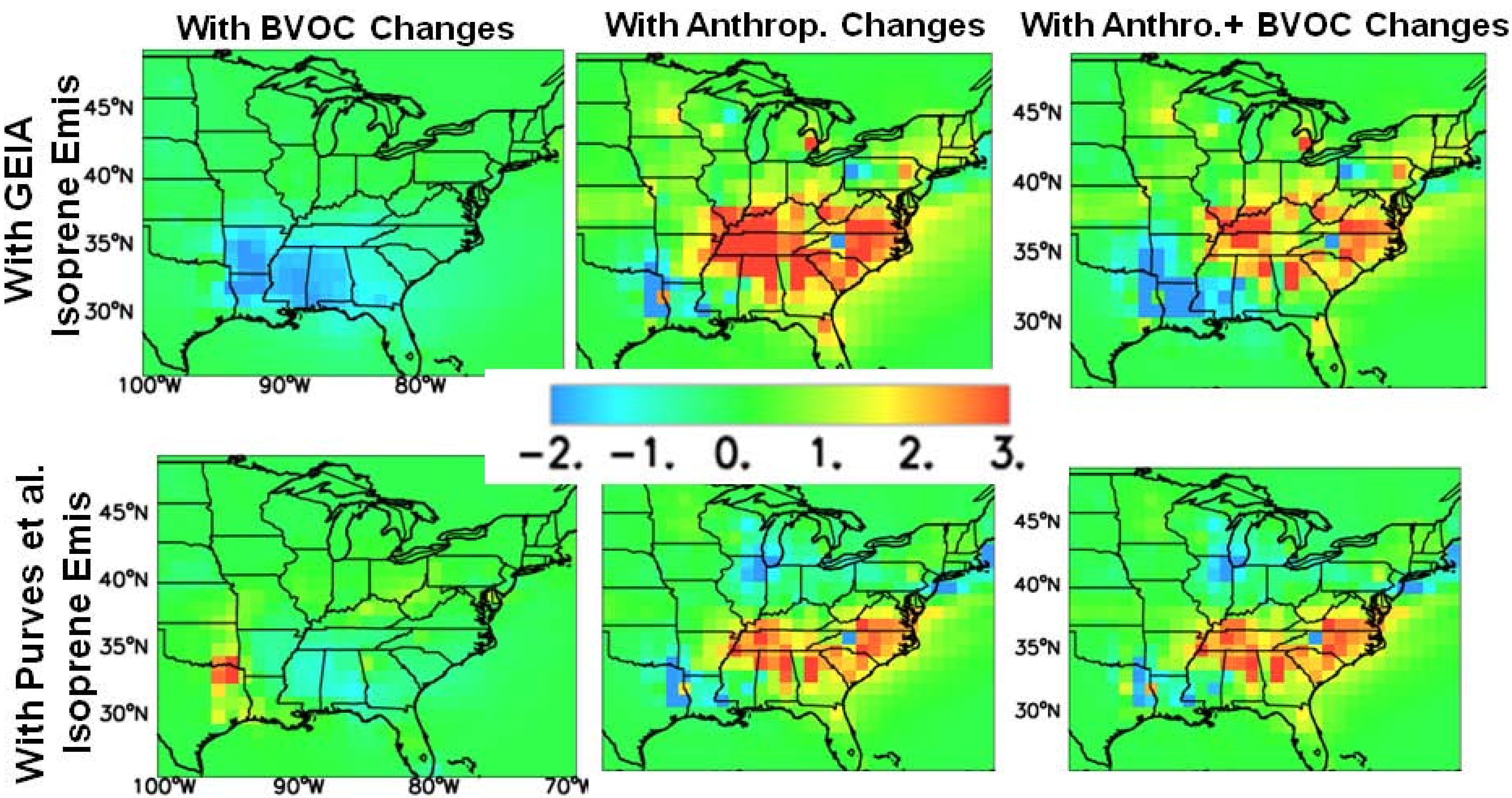
(10^{11} molec cm^{-2} s^{-1})

PAN most influenced by isoprene in high-NO_x locations



Little effect on PAN in SE US where isoprene changed most

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



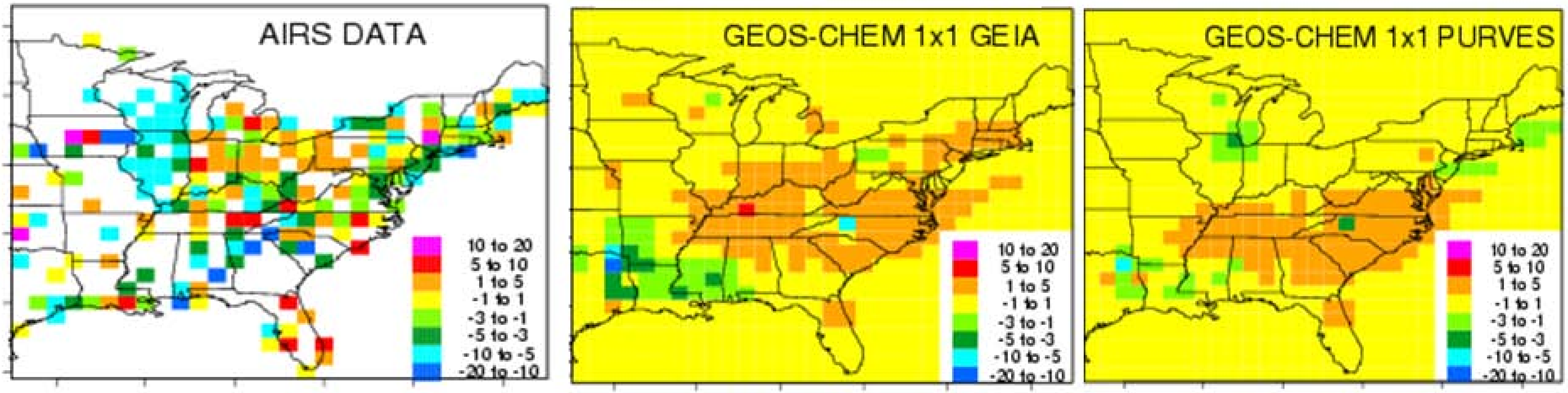
Changes in Anthropogenic NO_X emissions dominate O_3 response

But response depends upon choice of isoprene emission inventory

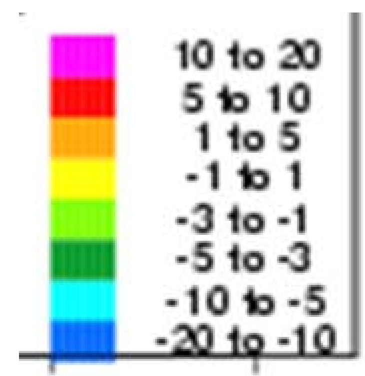
Comparison with observed changes? Impact on high-O_3 events?

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**



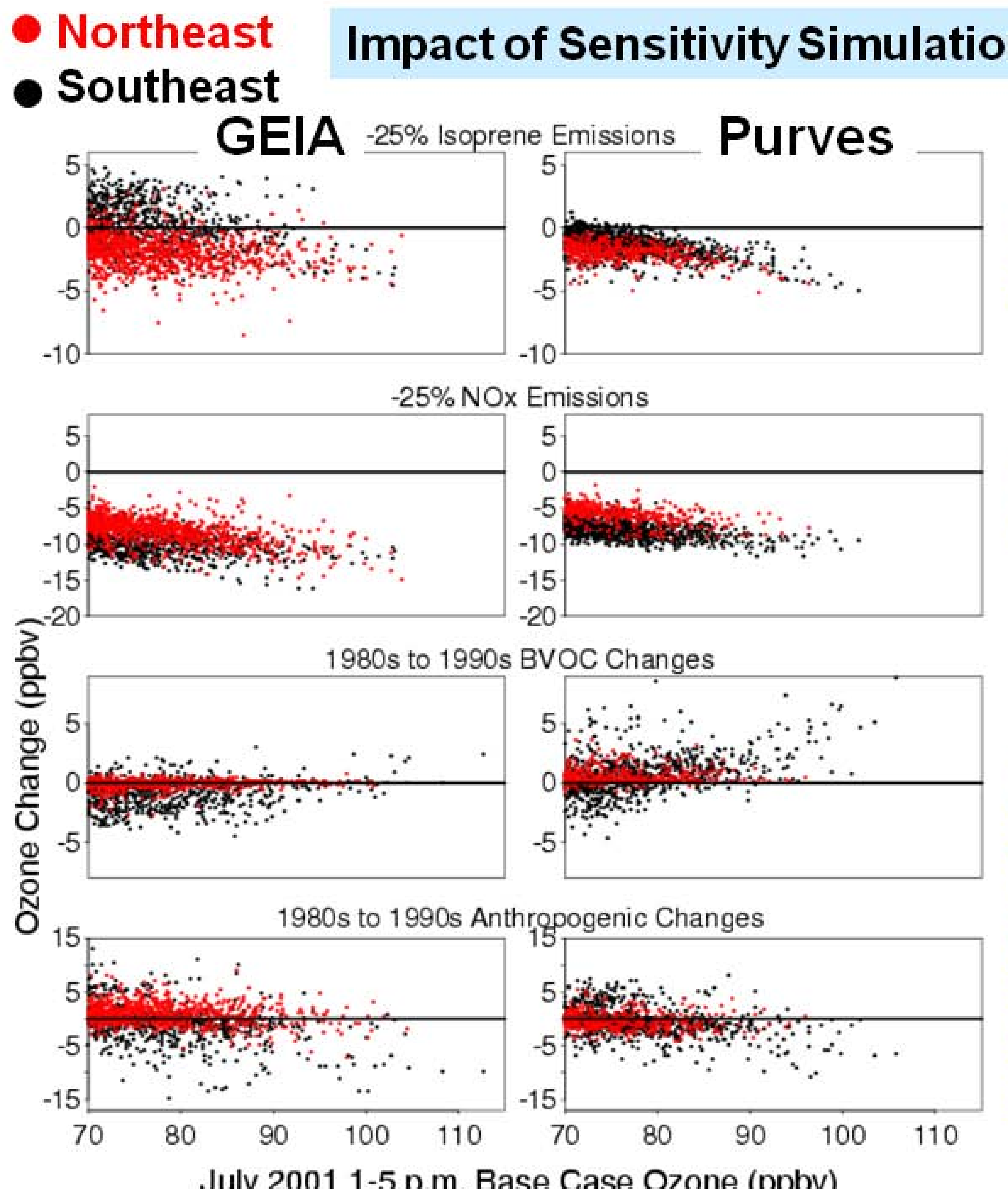
(1993-1997) – (1983-1987)



Poor correlation (r^2 ~ 0) between observed and simulated changes

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

Impact of Sensitivity Simulations on High-O_3 Events:



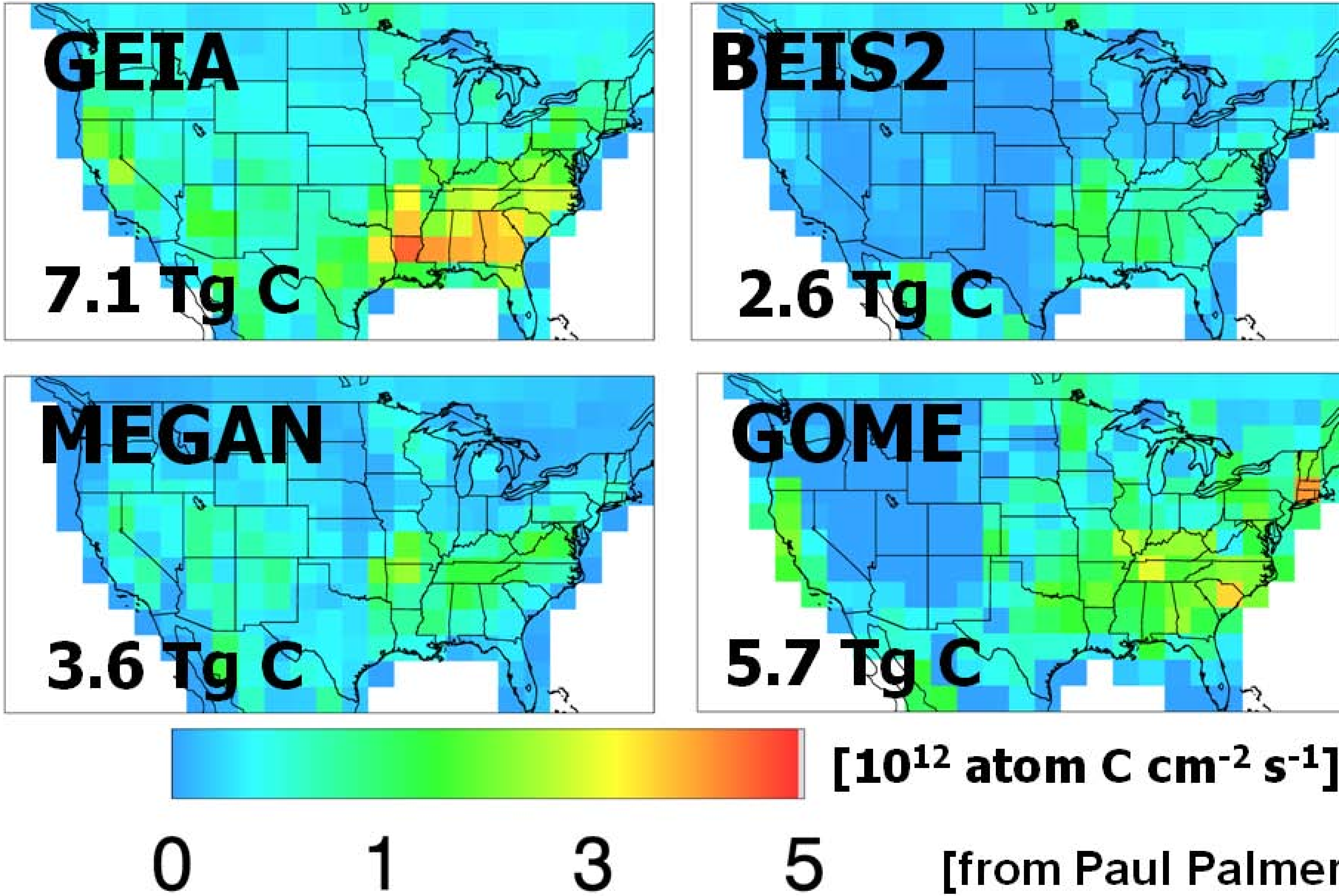
- decrease with isoprene except for GEIA SE
- decrease with NO_x, larger response with GEIA
- dominated by anthrop. (NO_x) emissions changes from 1980s to 1990s but BVOC changes may offset (Purves case) decreases of most extreme events

Preliminary Conclusions & Remaining Challenges

- Better constrained isoprene emissions are needed to predict O_3 response to both anthrop. and biogenic emission changes

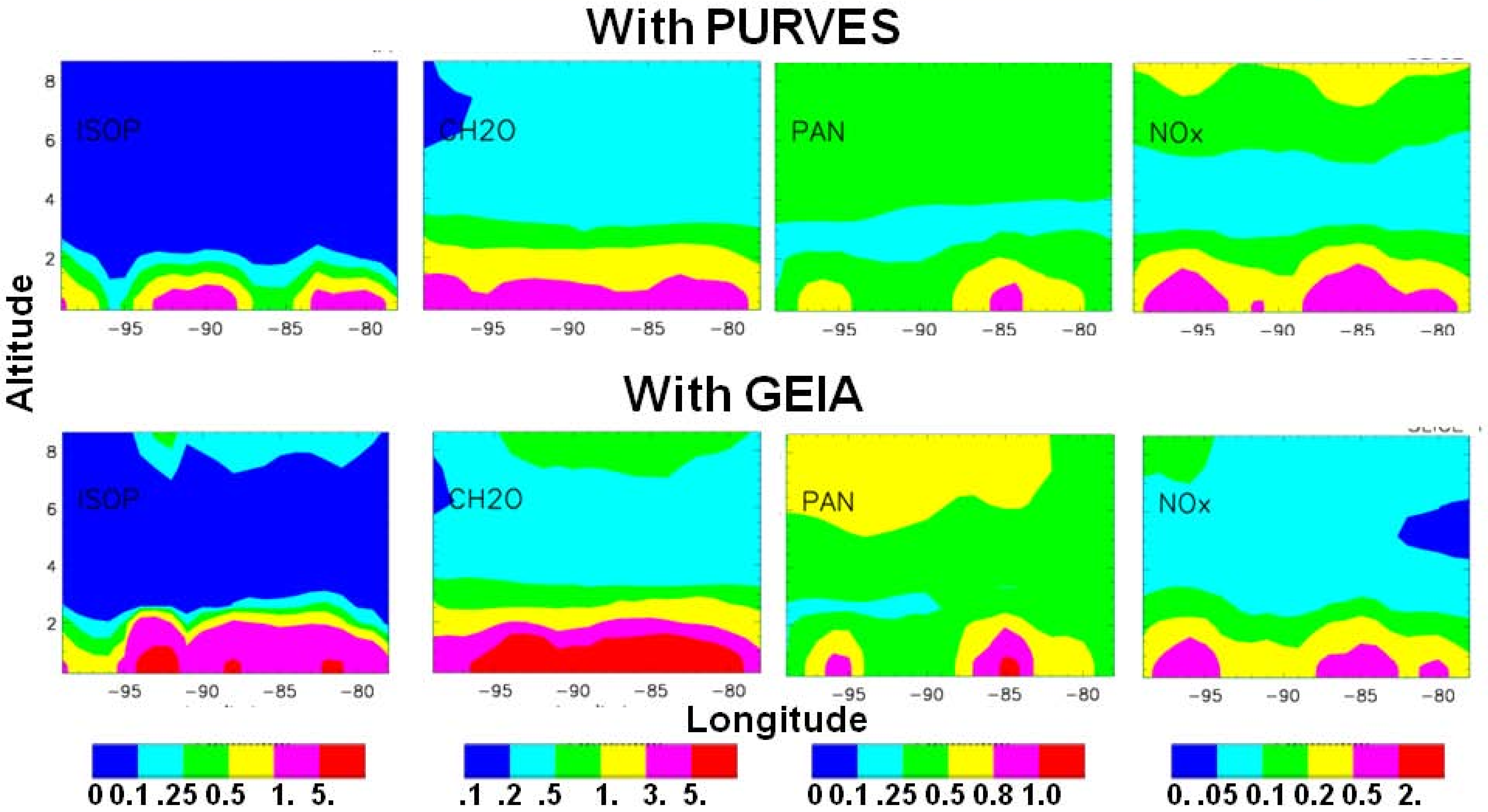
  → Utility of satellite CH_2O columns?
  → New inventories (MEGAN, BEIS-3) more accurate?
  → NASA INTEX-NA observations?

Isoprene emissions – July 1996



[from Paul Palmer]

Vertical slices through 34N: enhanced isoprene, CH_2O, PAN at surface & upper trop for GEIA compared to Purves

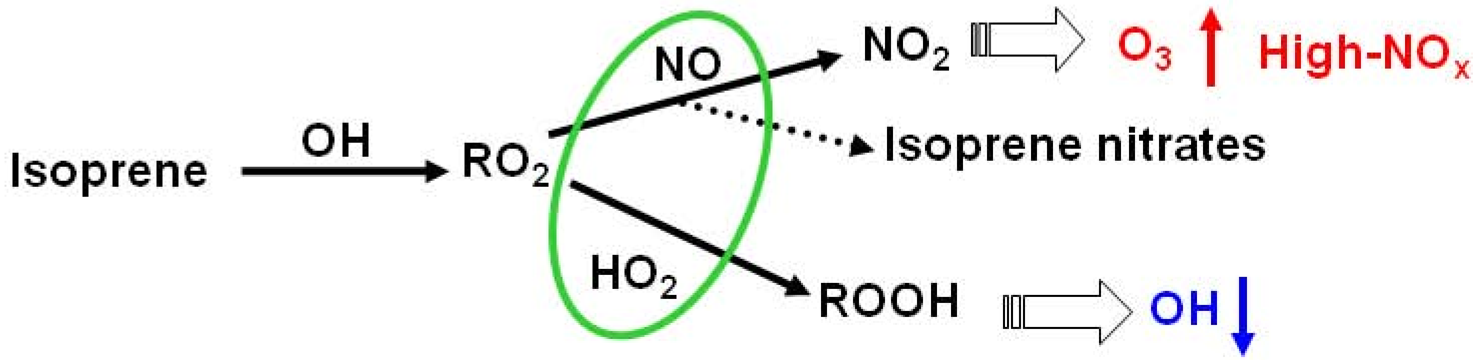


→ Insights from NASA INTEX-NA flights over SE US?

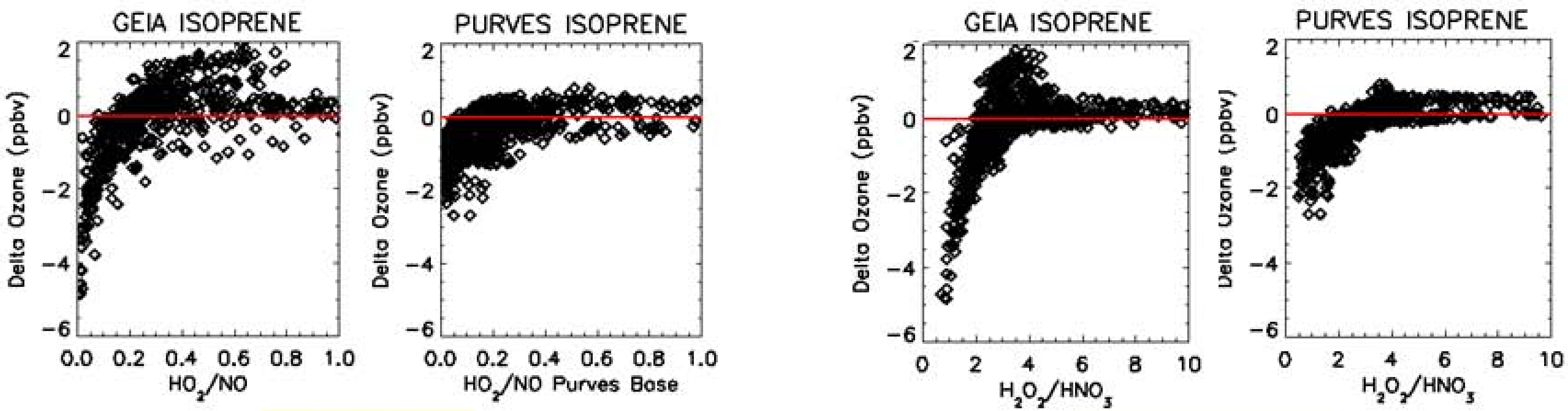
Preliminary Conclusions & Remaining Challenges

- Better constrained isoprene emissions are needed to predict O_3 response to both anthrop. and biogenic emission changes
  - → Utility of satellite CH_2O columns?
  - → New inventories (MEGAN, BEIS-3, GLOBEIS) more accurate?
  - → NASA INTEX-NA observations?
- Recent isoprene increases may have reduced surface O_3 in the SE
  - → Does this regime actually exist? Can chemical indicators help?
  - → Fate of organic nitrates produced during isoprene oxidation?

Chemical indicators for O_3 ↑ or ↓ as Isoprene ↑



Change in O_3 for 25% decrease in isoprene emissions



HO_2/NO H_2O_2/HNO_3

Potential for using observations to diagnose isoprene-saturated regime, as for NO_x-sensitive vs. NO_x-saturated [e.g. *Sillman*, 1995]

Preliminary Conclusions & Remaining Challenges

- **Better constrained isoprene emissions are needed to predict O_3 response to both anthrop. and biogenic emission changes**
  - → Utility of satellite CH_2O columns?
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- **Recent isoprene increases may have reduced surface O_3 in the SE**
  - → Does this regime actually exist? Can chemical indicators help?
  - → Fate of organic nitrates produced during isoprene oxidation?

- **Reported emission changes from 1980s to 1990s alone do not explain observed O_3 trends**
  - → Role of decadal shifts in meteorology?
  - → 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)

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