A51B-0036 Uncertain Isoprene Emissions and Chemistry: Implications for Ozone in the Eastern United States

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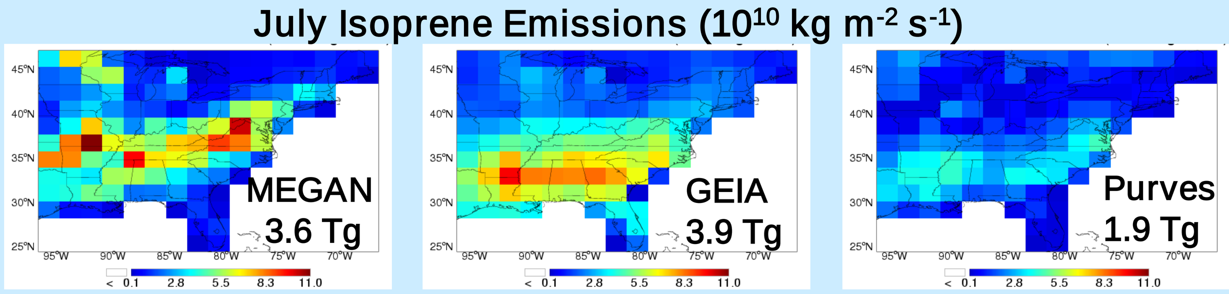
1. Introduction: Uncertain Isoprene Emissions and Chemistry

Eastern U.S. emission estimates vary by more than a factor of 2:

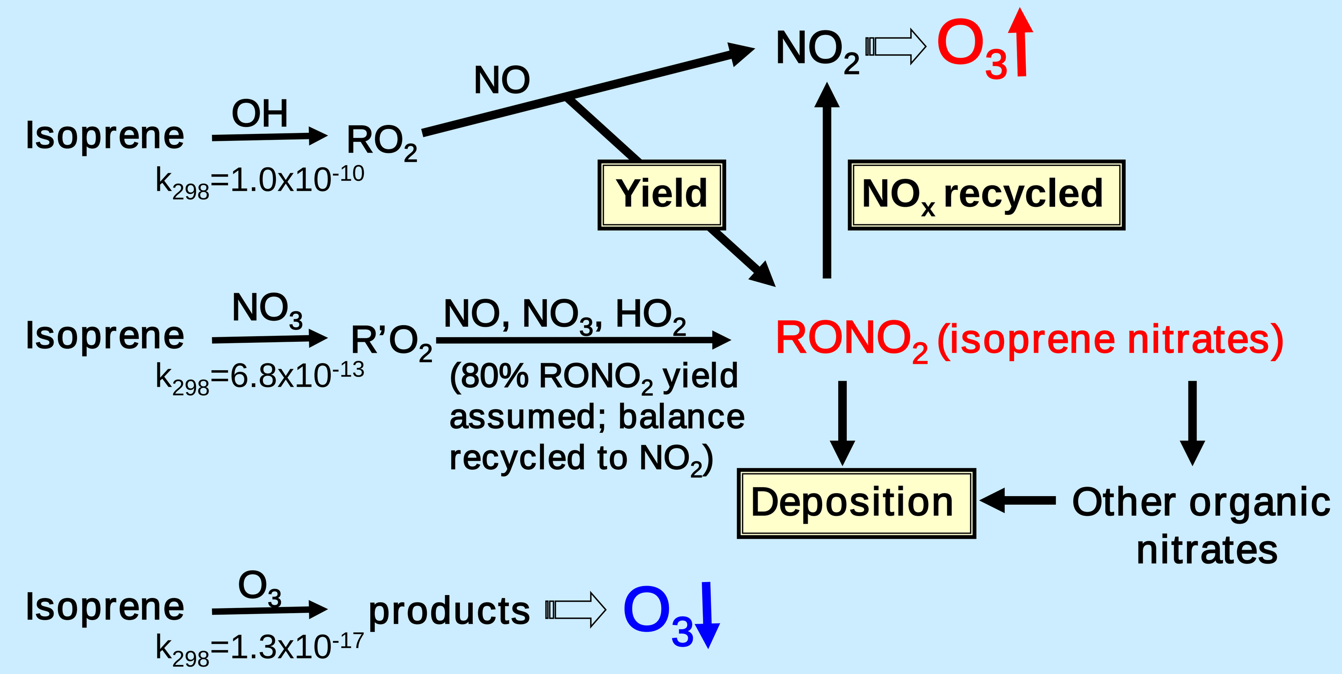
July Isoprene Emissions (10^{10} kg m^{-2} s^{-1})



Sources of Uncertainty:

- Base emission capacities and leaf area index [*Guenther et al.*, 1995, *Purves et al.*, 2004]
- 4 to 13% range on lab measurements of isoprene nitrate yields from isoprene + OH reaction [*Tuazon and Atkinson*, 1990; *Chen et al.*, 1998, *Sprengnether et al.*, 2002]
- Importance of isoprene nitrates as a NO_x sink [*Chen et al.*, 1998, *Liang et al.*, 1998, *Horowitz et al.*, 1998]
- Fate of multifunctional organic nitrates; rapid deposition assumed in this study

Uncertainties in NO_x-isoprene-O_3 chemistry considered here:

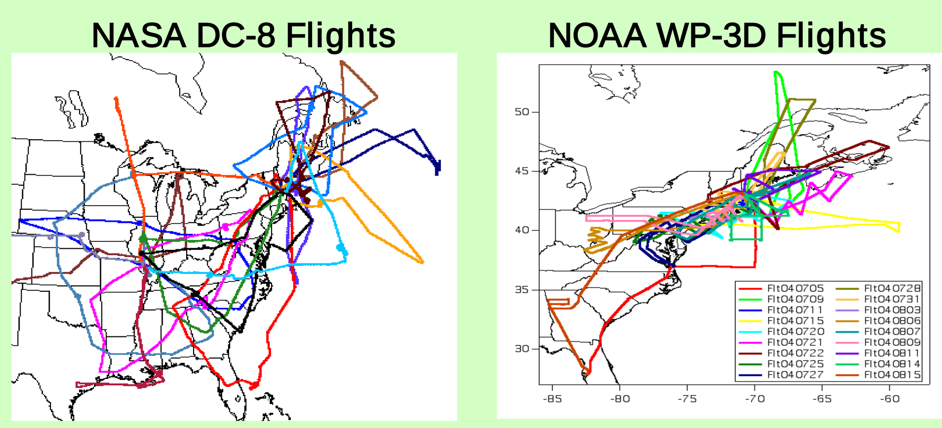


2. Apply MOZART-4 CTM to the ICARTT period (July-August 2004)

Base Case MOZART-4 Simulation

- ~100 gas and aerosol species, ~200 reactions
- NCEP Global Forecast System (GFS)
- 1.9° latitude x1.9° longitude x 64 vertical levels
- Emissions: ICARTT anthropogenic and *Turquety et al.* [2005] daily biomass burning from MODIS and NIFC (North America), POET 1997 (elsewhere) [*Olivier et al.*, 2003]
- MEGAN (v.0) isoprene emissions [*Guenther et al.*, 2005]

OBJECTIVES
→ Explore chemical uncertainty associated with isoprene emissions and chemistry
→ Attempt to constrain uncertainties using ICARTT measurements
→ Quantify NO_x sink via isoprene nitrates



Model is sampled along flight tracks at 1-minute intervals

3. Isoprene Nitrate Budgets (July, Eastern U.S. below 2 km)

Simulation Name	Selected Loss Pathways			Yield from RO_2+NO (Production)			Lifetime (hours)
	OH	WET DEP	DRY DEP	4%	8%	12%	
				Burden (Gg N)			
BASE	FAST	FAST	FAST	--	0.6	0.7	4.1-4.3
OHm	MEDIUM	FAST	FAST	--	1.0	1.1	7.2-7.3
OHmWDs	MEDIUM	SLOW	FAST	--	1.0	--	7.4
OHmDDs	MEDIUM	FAST	SLOW	--	1.4	--	10.1
OHs	SLOW	FAST	FAST	1.2	1.5	1.8	11.0-11.4
OHsWDs	SLOW	SLOW	FAST	1.2	--	--	11.5

Photochemical Loss (OH)

FAST (BASE) $k_{RONO2-OH}$ = 4.5 x 10^{-11} ; J_{RONO2} = J_{CH3CHO}
MEDIUM $k_{RONO2-OH}$ = 1.3 x 10^{-11} ; J_{RONO2} = J_{HNO3}
SLOW $k_{RONO2-OH}$ = 4.5 x 10^{-12}; J_{RONO2} = J_{HNO3}

Wet Deposition (WD)

FAST (BASE) K_H = 7510 M atm^{-1} at 298K
SLOW K_H reduced by a factor of 10

Dry Deposition (DD)

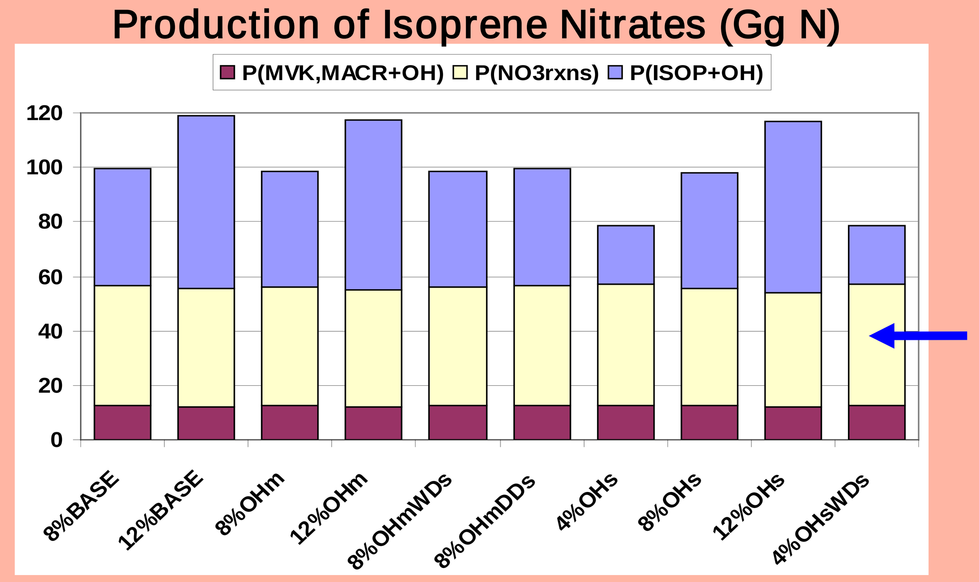
FAST (BASE): V_d ($RONO_2$) = V_d (HNO_3)
SLOW: V_d ($RONO_2$) = V_d (PAN)

Shepson et al. [1996] used loss rates similar to simulation OHmDDs

If dry deposition is slow then reaction with OH is the dominant loss

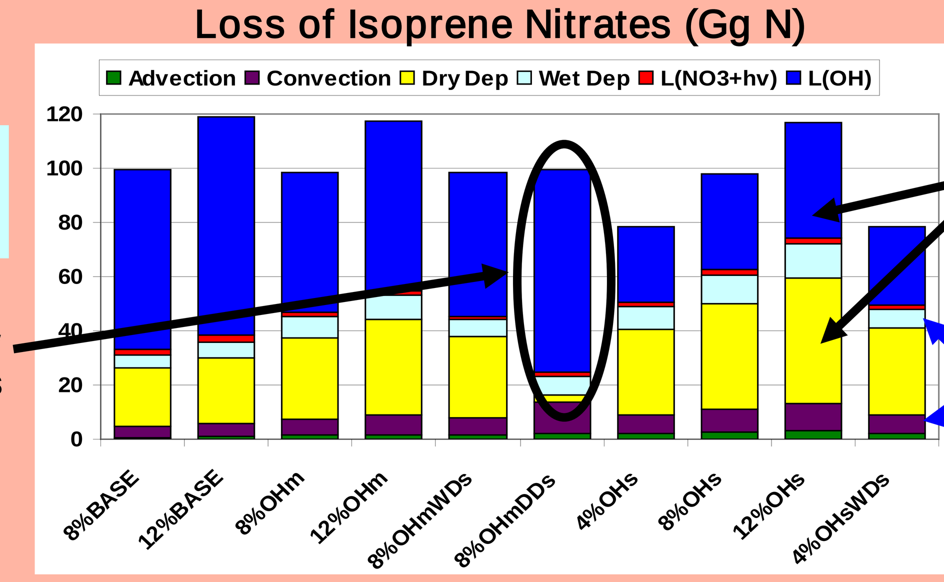
Simulations falling within observational constraints (Section 4) are highlighted in white in the Table

Production of Isoprene Nitrates (Gg N)



36-56% of $RONO_2$ forms via NO_3 pathway; needs further investigation

Loss of Isoprene Nitrates (Gg N)



OH reaction and dry deposition are dominant losses

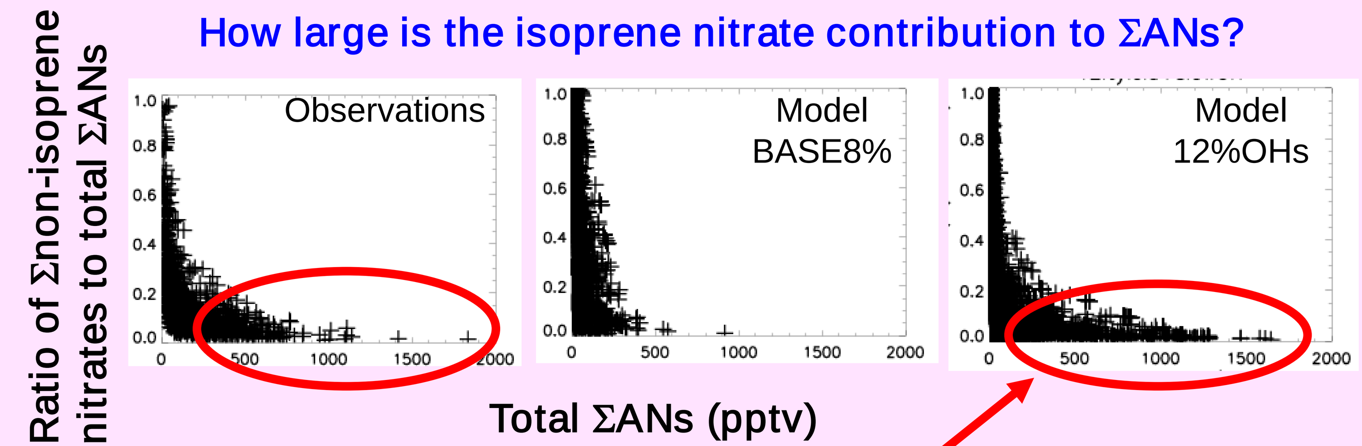
Smaller contributions from wet deposition and convection

Isoprene nitrates account for 7-16% of NO_x sink

4. Constraints from Observations

Use ICARTT measurements of total alkyl nitrates (ΣANs) and several individual alkyl nitrates to constrain uncertainties discussed in Section 1.

How large is the isoprene nitrate contribution to ΣANs?

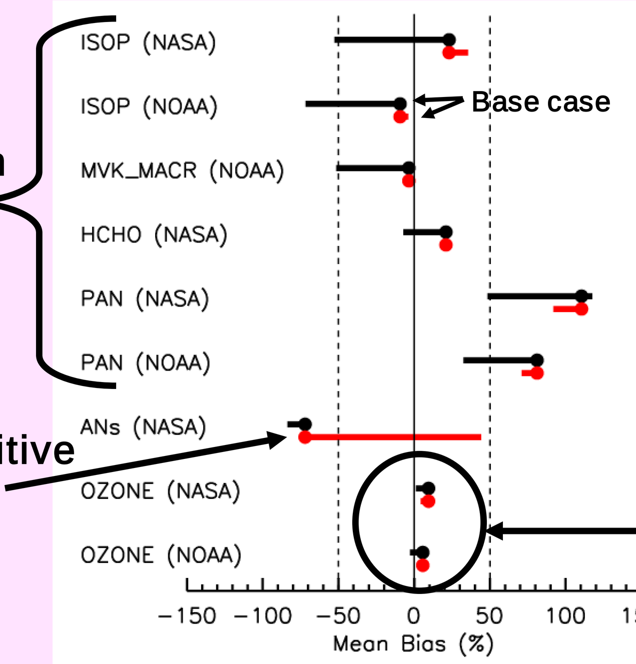


In simulation with slower $RONO_2$ loss, non-isoprene nitrates contribute <15% to ΣANs, in better agreement with observations

Ranges in model bias due to uncertain emissions and chemistry (Eastern U.S. land boxes below 2 km, 10 a.m.–6 p.m. local time)

Uncertainty in isoprene and most oxidation products dominated by emission uncertainties

ΣANs most sensitive to uncertainties in chemistry

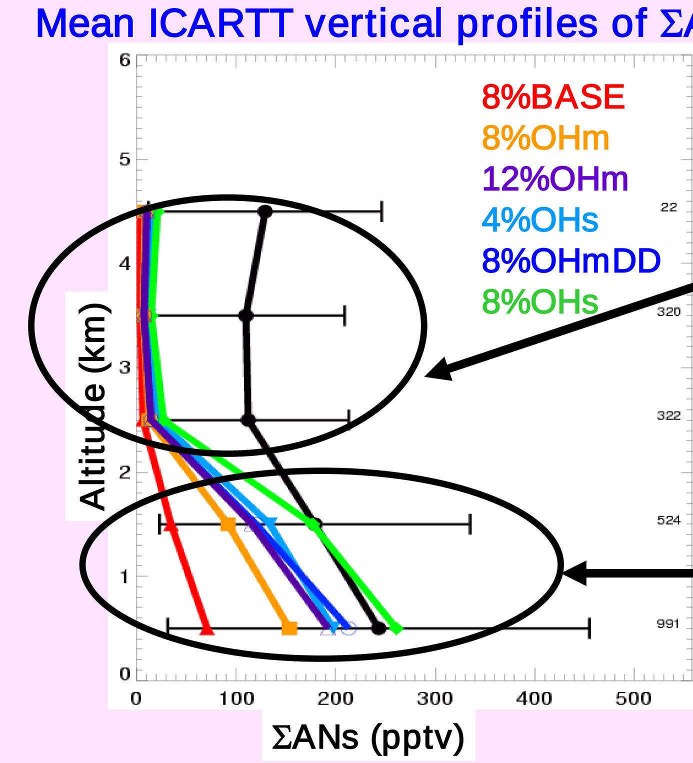


Statistics based on values averaged to model grid for each flight

Note: PAN bias always <15% in free troposphere

Ozone sensitive to both emissions and chemistry (see also Section 5)

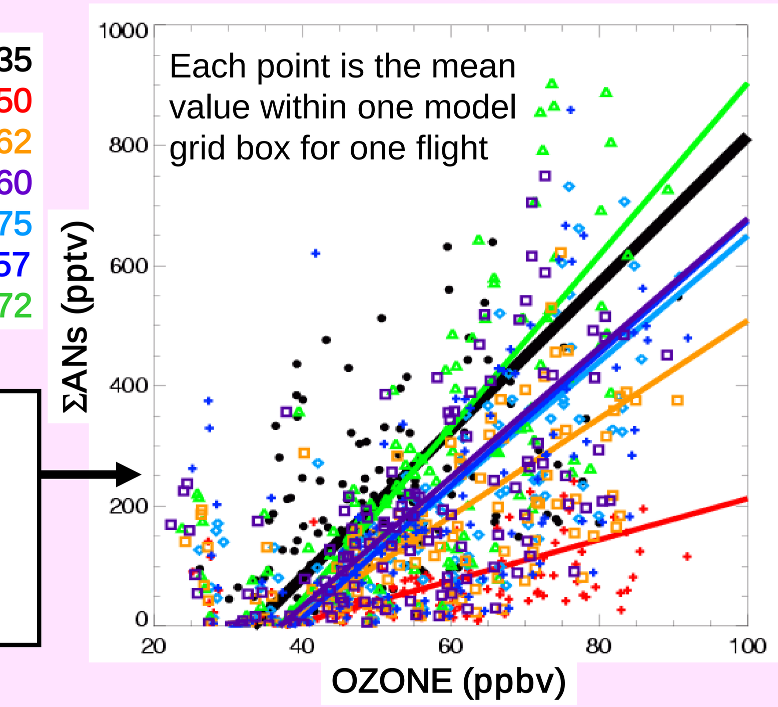
Mean ICARTT vertical profiles of ΣANs



Model underestimates free tropospheric ΣANs in all cases. Due to assumed loss of multifunctional organic nitrates?

ΣANs – Ozone Correlations (Eastern U.S. land boxes below 2 km, 10 a.m.–6 p.m. local time)

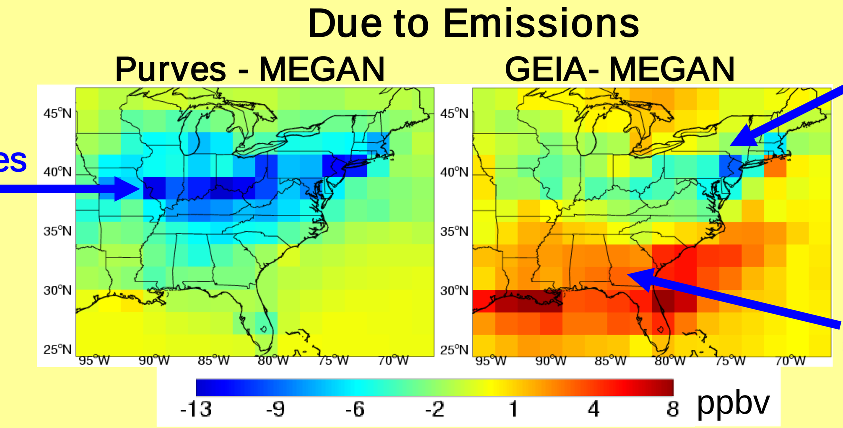
OBS	m=12.2, r=0.35
8%BASE	m=3.4, r=0.50
8%OHm	m=8.1, r=0.62
12%OHm	m=10.8, r=0.60
4%OHs	m=10.5, r=0.75
8%OHmDD	m=11.0, r=0.57
8%OHs	m=14.3, r=0.72



Model can capture observed O_3-ΣANs relationship with:
→ high $RONO_2$ yields (12%) with fast loss
→ moderate yields and loss
→ small yields (4%) and slow loss
Best guess simulations highlighted in white (Section 3)

5. Impacts on Surface Ozone: Change in July mean afternoon (1-5 p.m. local time) surface O_3

Due to Emissions

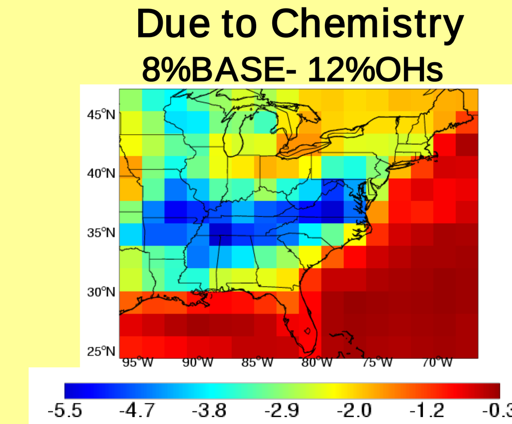


Largest O_3 decreases coincide with high NO_x emissions

Lower northeastern isoprene emissions reduce O_3 (up to 9 ppbv)

Higher southeastern emissions increase O_3

Due to Chemistry



Maximum O_3 decrease with a 12% isoprene nitrate yield and slow loss

→ NO_x sink via isoprene nitrates increases from 13% (Base) to 16% (12%OHs) and surface O_3 decreases by 2-5 ppbv

6. Conclusions

- MEGAN isoprene emissions are consistent with observed isoprene and oxidation products; O_3 increases in the northeast (up to 9 ppbv) and decreases in the southeast (up to 8 ppbv) compared to GEIA
- Simulated ΣANs-O_3 correlations approach the observed relationship for an isoprene nitrate burden of 1.1-1.5 Gg N (EUS below 2 km). This burden is obtained with either high yields and fast loss or small yields and slow loss
- Model underestimates observed ΣANs in free troposphere by a factor of ~10, possibly due to assumed loss of multifunctional organic nitrates
- ~45% (36-56%) of isoprene nitrate production in the model occurs through highly uncertain NO_3 chemistry
- ~7-16% of NO_x emitted in the eastern U.S. is lost through isoprene nitrates and an additional 4-9% cycles through isoprene nitrates

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