Wintertime emissions and chemistry over the N.E. US: Role of oxidants and heterogeneous chemistry

Lyatt Jaeglé, Viral Shah, Joel Thornton, Felipe Lopez-Hilfiker, Ben Lee
Department of Atmospheric Sciences, University of Washington

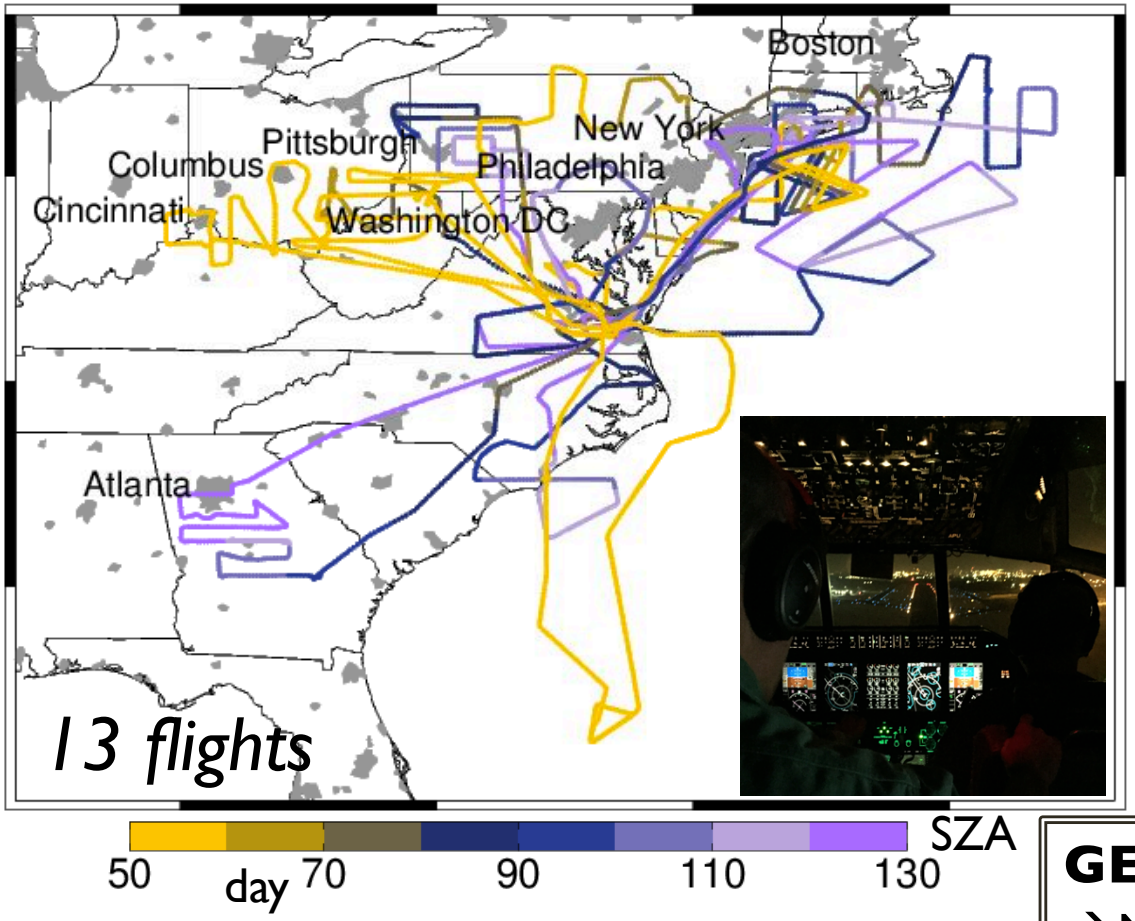
S. Brown (NOAA), J. Jimenez (U Colorado), J. Dibb (U New Hampshire), R. Cohen (UC Berkeley), R. Weber (Georgia Tech), A. Weinheimer, T. Campos, E. Apel (NCAR), G. Wolfe (UMBC), J. DiGangi (NASA Langley), T. Hanisco (NASA GSFC)

- How well do we understand wintertime emissions of pollutants?
- How important are nocturnal & multiphase processes?
- What factors control aerosol formation and aerosol/gas partitioning?

→ *Viral Shah (talk); Jessica Haskins, Kelsey Larson (posters) on Tuesday*

WINTER: Feb 3 - Mar 13 2015

NSF/NCAR C-130 aircraft flight tracks



- 50% of flights hours at night
- 71% within 1 km of the surface

Measurements

- Gas-phase: NO_2, NO, HNO_3, N_2O_5, ∑PANs, ∑ANs, HONO, NOy, $ClNO_2$, HCl, Cl_2, CO, O_3, SO_2, NH_3, CH_2O, alkanes, alkenes, alkynes, CFCs, halons
- Aerosol composition (ToF-AMS, PILS, Filter): organic aerosol, SO_4^{2-}, NH_3^+, NO_3^-, Cl^-, Na^+, Mg^{2+}, Ca^{2+}
- Aerosol size distribution, actinic flux, meteorological parameters

GEOS-Chem Model

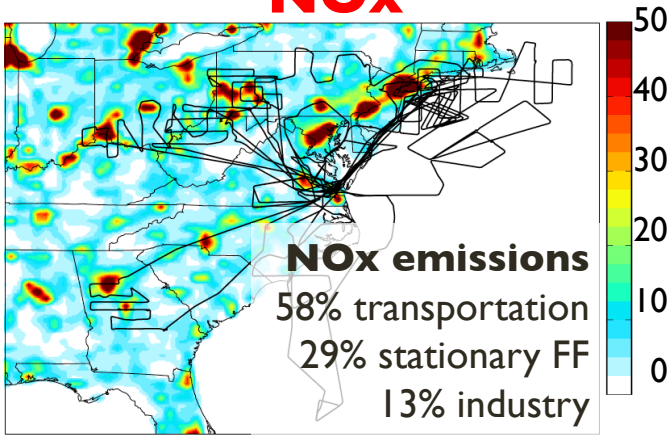
→Nested grid (0.5°x0.625°). v10-01

→Scale EPA NEI 2011 to 2015:

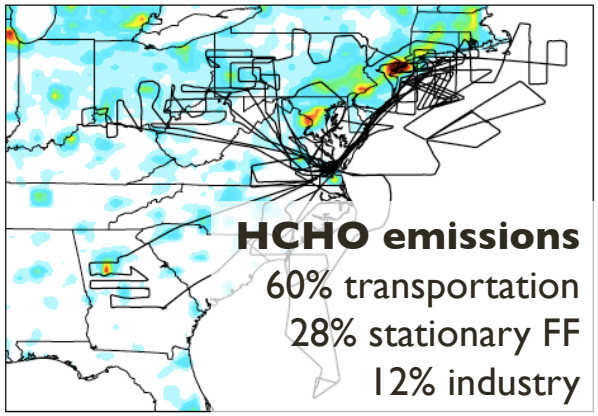
- 20% reduction in NOx (2015 CEMS + 7%/yr decrease in transportation)
- 32% reduction in SO_2 (2015 CEMS)

Anthropogenic emissions

NOx

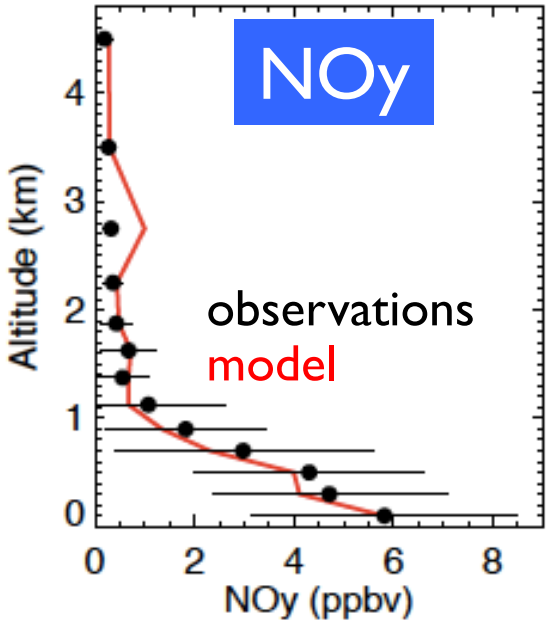


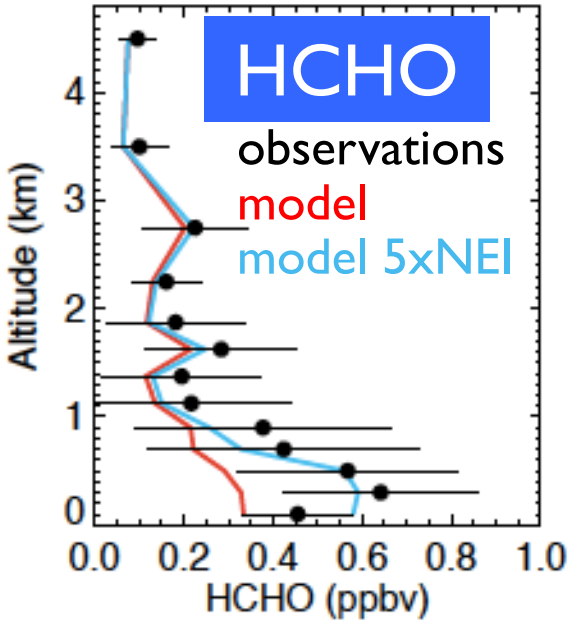
HCHO



10^{10} atoms cm^{-2} s^{-1}

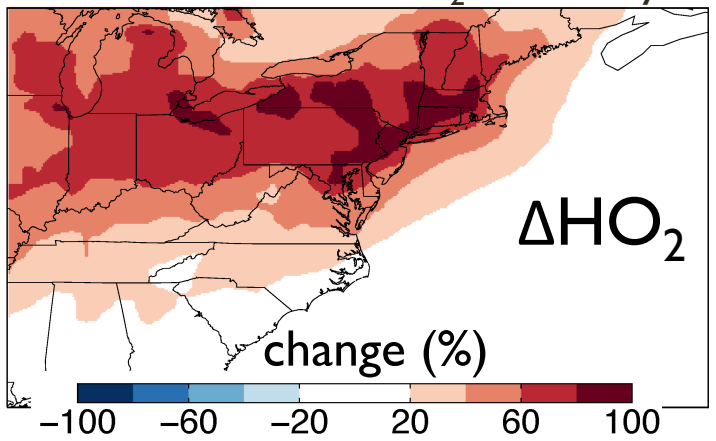
Vertical profiles over land





Impact on oxidants

5xHCHO + $ClNO_2$ chemistry



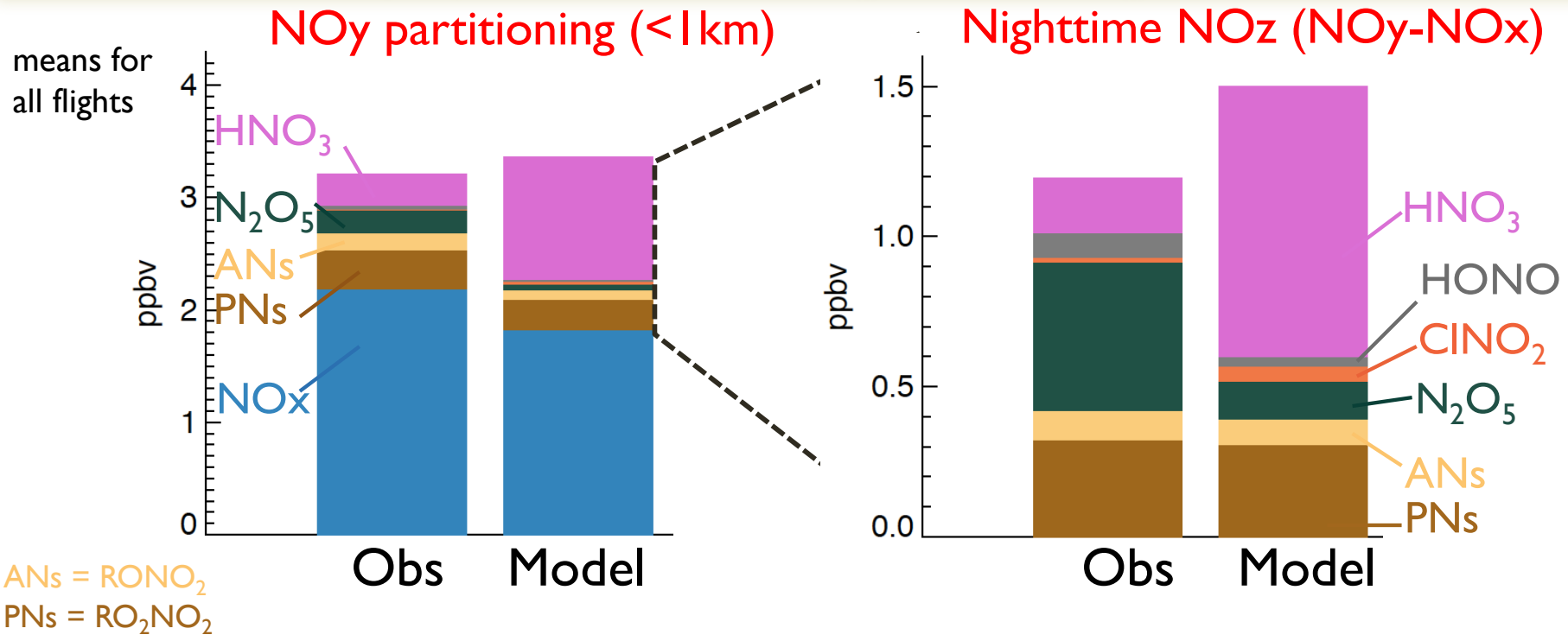
→ 40-80% increase in HOx

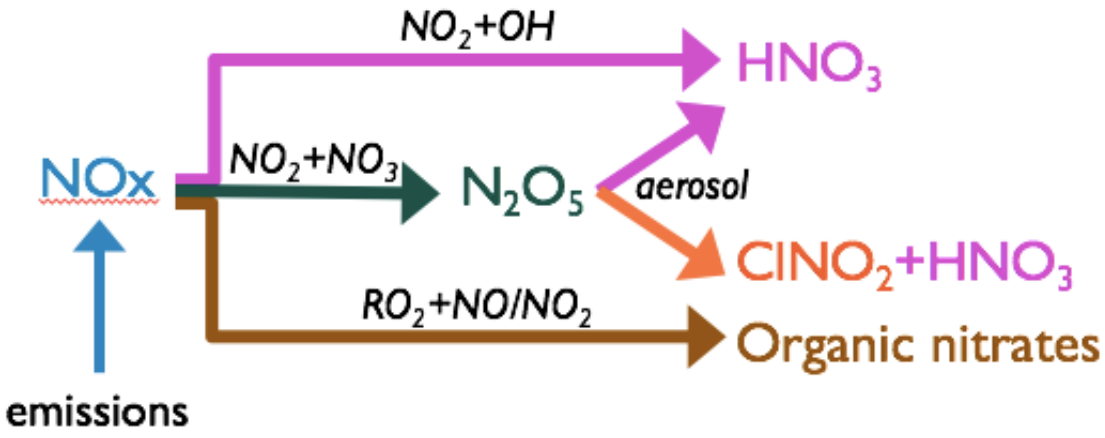
→ 10-20% increase in $SO_4^=$ & OA

→ NOy within 10% of observations, but HCHO too low by x2

→ Increase NEI HCHO emissions by x5 (cold-start OVOC emissions?)

NOy partitioning during WINTER





- Model HNO_3 too high x4
  [Zhang et al., 2012; Heald et al, 2012]
- Model N_2O_5 too low by x4
  → *Problem with* $\gamma(N_2O_5)$*?*
  GEOS-Chem [Evans & Jacob, 2005]:
  $\gamma(N_2O_5)$ = f(RH, aerosol, T)~0.02

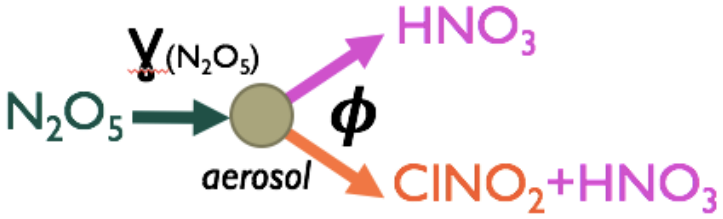
Update $\gamma(N_2O_5)$ to more recent lab obs

$\gamma(N_2O_5)$ – inhibited by nitrate and organics

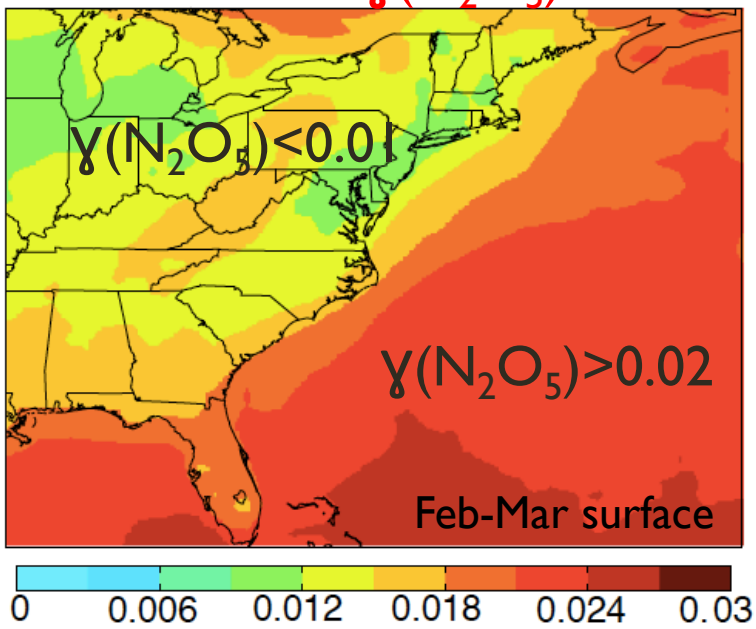
- $SO_4^{=}$-NO_3^{-}-NH_4^{+} aerosol $\gamma = f(H_2O, NO_3^{-}, Cl^{-})$ [Bertram & Thornton, 2009]
- Organic aerosol γ = 0.0001 (RH<50%), 0.001 (RH>50%) [Badger et al., 2006]

$ClNO_2$ yield, ϕ

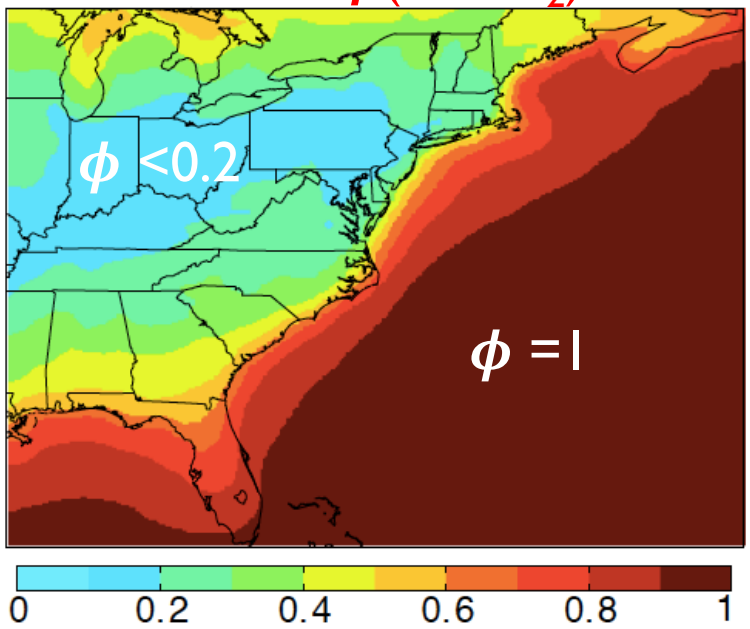
- $SO_4^{=}$-NO_3^{-}-NH_4^{+} aerosol $\phi = f(H_2O, Cl^{-})$ [Bertram & Thornton, 2009]
- Sea salt ϕ=1, other aerosol ϕ=0



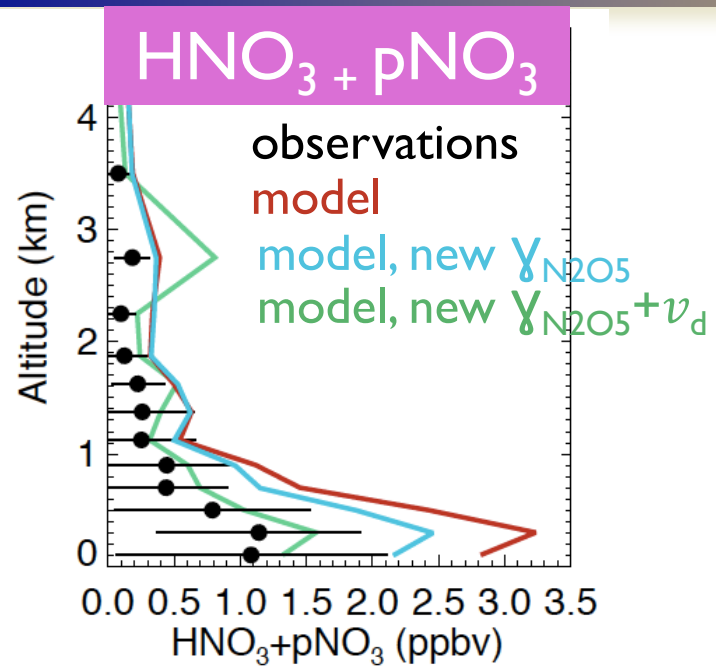
New $\gamma(N_2O_5)$

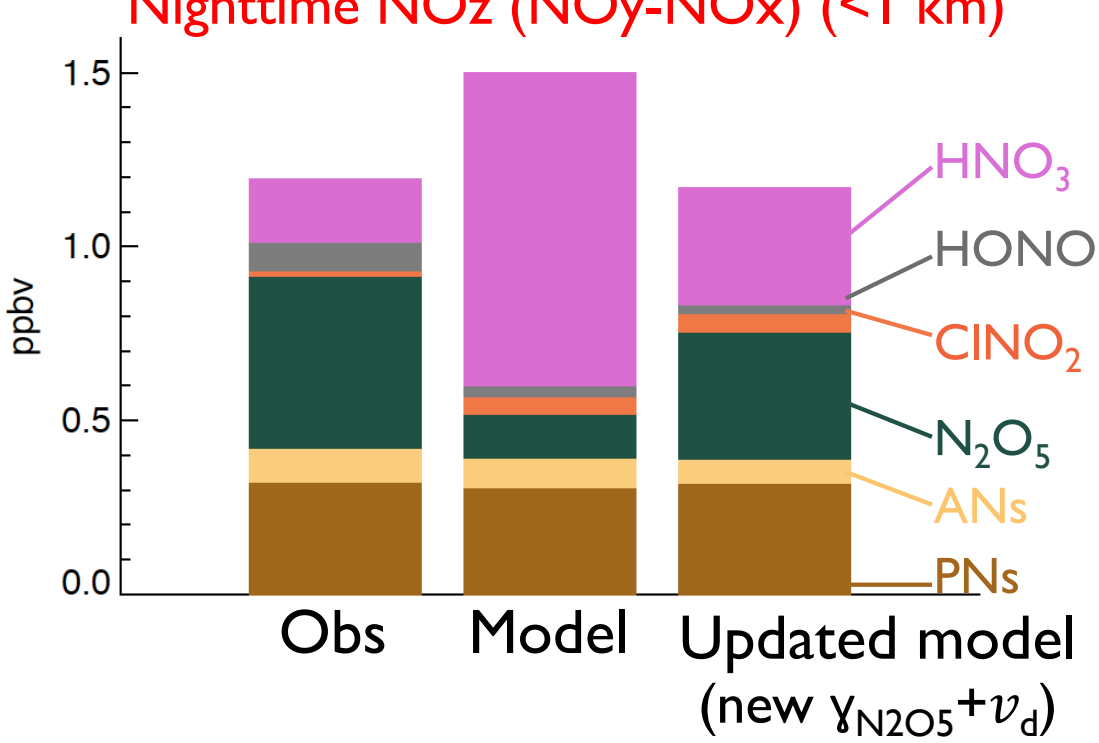


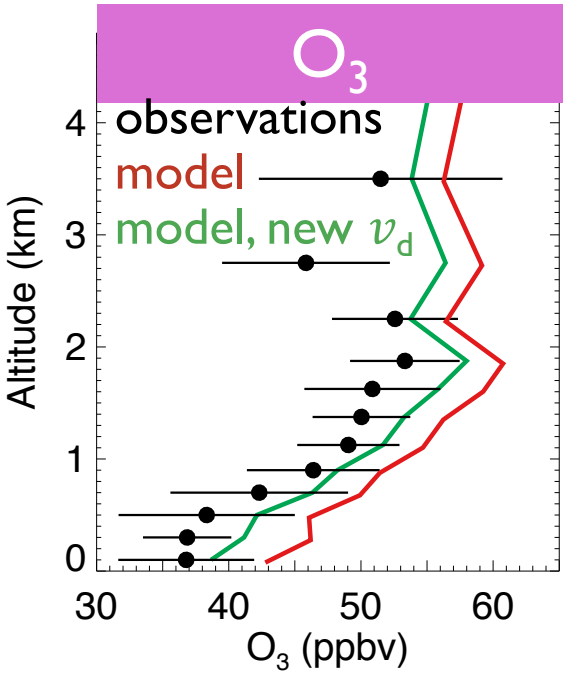
New $\phi(ClNO_2)$



Improved NOy partitioning







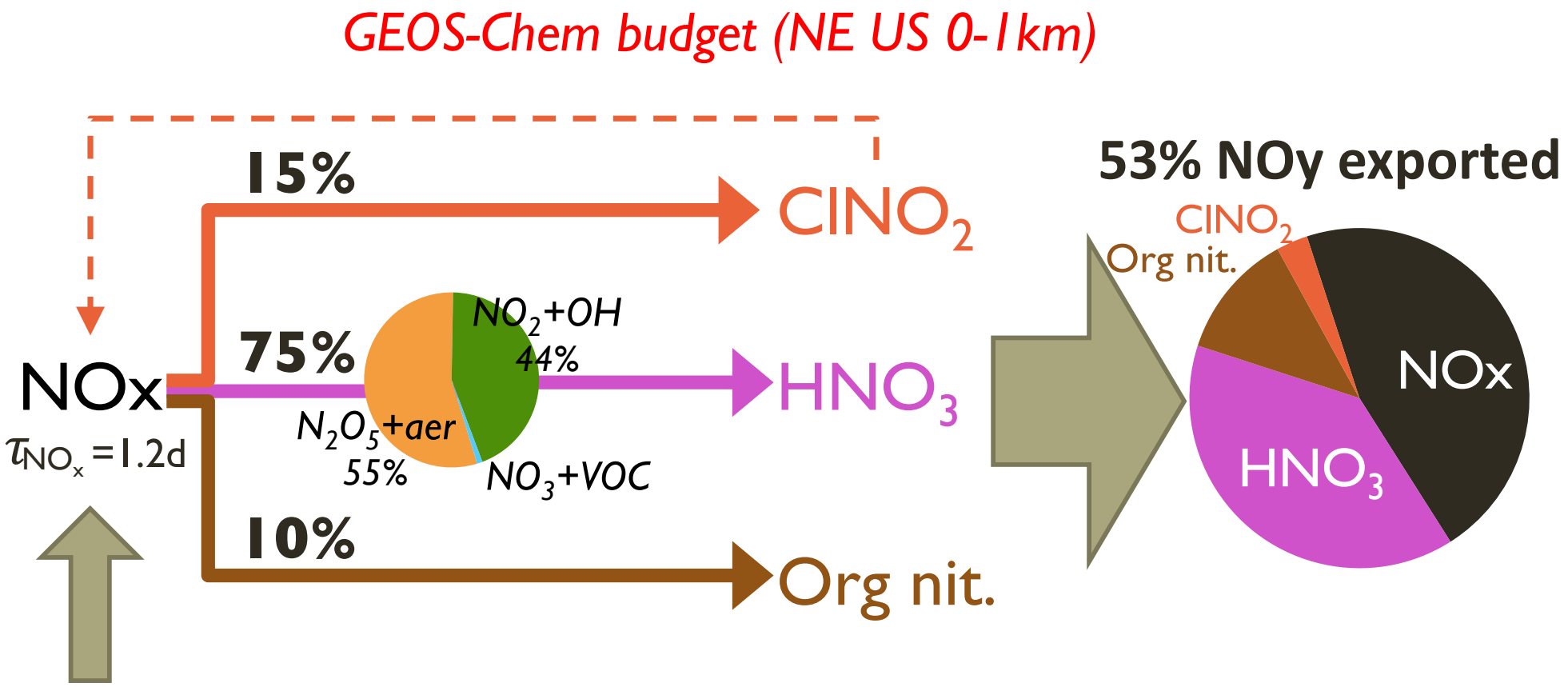
→New $\gamma(N_2O_5)$ + Update dry deposition

Surface resistance (R_c) ↑ at cold temp ~ exp(-T-4) [Wesely, 1989]

Set $R_c(HNO_3)=0$ [Wesely and Hicks, 2000] → *$v_d(HNO_3)$~1-4 cm s^{-1}*

Other species: limit R_c increase by x2 → $v_d(O_3)$ increases by 40%

Summary

- Oxidative capacity of wintertime polluted air controlled by regional anthropogenic emissions and multiphase chemistry

- Nitrate + OA suppression of $\gamma(N_2O_5)$ + corrected dry dep → helps address long-standing winter HNO_3/nitrate overestimate problem