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

Measurements

- Gas-phase: NO₂, NO, HNO₃, N₂O₅, ΣPANs, ΣANs, HONO, NOy, CINO₂, HCl, Cl₂, CO, O₃, SO₂, NH₃, CH₂O, alkanes, alkenes, alkynes, CFCs, halons
- Aerosol composition (ToF-AMS, PILS, Filter): organic aerosol, SO₄²⁻, NH₃⁺, NO₃⁻, Cl⁻, Na⁺, Mg²⁺, Ca²⁺
- 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 SO₂ (2015 CEMS)

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

**NOx emissions**
- 58% transportation
- 29% stationary FF
- 13% industry

**HCHO emissions**
- 60% transportation
- 28% stationary FF
- 12% industry

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

**Impact on oxidants**
- 5xHCHO + ClNO2 chemistry
  - 40-80% increase in HOx
  - 10-20% increase in SO4²⁻ & OA

**Vertical profiles over land**
- NOy observations vs. model
- HCHO observations vs. model 5xNEI

- Increase NEI HCHO emissions by x5 (cold-start OVOC emissions?)
**NOy partitioning during WINTER**

NOy partitioning (<1km)

Nighttime NOz (NOy-NOx)

- **Model HNO₃ too high x4**  
  [Zhang et al., 2012; Heald et al, 2012]

- **Model N₂O₅ too low by x4**  
  → Problem with $\gamma(N₂O₅)$?  
  GEOS-Chem [Evans & Jacob, 2005]:  
  $\gamma(N₂O₅) = f(RH, \text{aerosol}, T) \sim 0.02$
Update $\gamma(N_2O_5)$ to more recent lab obs

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

- $\text{SO}_4^{2-}$-$\text{NO}_3^-$-$\text{NH}_4^+$ aerosol $\gamma = f(\text{H}_2\text{O}, \text{NO}_3^-, \text{Cl}^-)$ [Bertram & Thornton, 2009]
- Organic aerosol $\gamma = 0.0001$ (RH<50%), 0.001 (RH>50%) [Badger et al., 2006]

CINO$_2$ yield, $\phi$

- $\text{SO}_4^{2-}$-$\text{NO}_3^-$-$\text{NH}_4^+$ aerosol $\phi = f(\text{H}_2\text{O}, \text{Cl}^-)$ [Bertram & Thornton, 2009]
- Sea salt $\phi=1$, other aerosol $\phi=0$

New $\gamma(N_2O_5)$

- $\gamma(N_2O_5)<0.01$
- $\gamma(N_2O_5)>0.02$

Feb-Mar surface

New $\phi($CINO$_2$)

- $\phi < 0.2$
- $\phi = 1$
**Improved NOy partitioning**

\[ \text{HNO}_3 + p\text{NO}_3 \]

**Observations**
- Model, new $\gamma_{N_2O_5}$

**Updated model** (new $\gamma_{N_2O_5} + \nu_d$)

**Nighttime NOz (NOy-NOx) (<1 km)**

- **HNO$_3$**
- **HONO**
- **ClNO$_2$**
- **N$_2$O$_5$**
- **ANs**
- **PNs**

**$\rightarrow$ New $\gamma(N_2O_5)$ + Update dry deposition**

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

Set $R_c(\text{HNO}_3)=0$ [Wesely and Hicks, 2000] $\rightarrow \nu_d(\text{HNO}_3) \sim 1-4$ cm s$^{-1}$

Other species: limit $R_c$ increase by x2 $\rightarrow \nu_d(\text{O}_3)$ 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 $\rightarrow$ helps address long-standing winter HNO$_3$/nitrate overestimate problem

**GEOS-Chem budget (NE US 0-1 km)**

- $\tau_{NO_x} = 1.2$ days
- 75% $N_2O_5 + aero$ (55% $NO_2 + OH$ and 44% $NO_3 + VOC$)
- 10% $NO_3 + VOC$
- 15% CINO$_2$
- 53% NOy exported

- Org nit.