Measurements and Modeling of Atmosphere-Snowpack Exchange of Ozone and Nitrogen Oxides at Summit, Greenland

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Why is the Arctic $NO_x$ budget important?

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

Is this the termination of $NO_x$?

Maximum extent of snow cover in Northern Hemisphere
Retrieved on 10/6/13
http://nsidc.org/cryosphere/sotc/snow_extent.html

Honrath, J. Geophys. Res, 2000
Summit, Greenland

- Two year campaign
- Elevation – 3km above sea level
- Over 300 km to ocean
  - Minimal halogen chemistry
- Pollution controlled camp
  - Electrical vehicles

Map of Greenland depicting the location of Summit Camp.
Retrieved on 9/30/13 from maps.google.com
Met and Snow Towers
Seasonal Trends in the Measurements

Toro, Michigan Technological University, 2011
Chemical measurements

$O_3$, $NO$, $NO_2$
Physical measurements

Temperature

Wind Direction and Speed
1-D Process-scale snowpack model

• Goals
  – Reproduction of observed chemical trends in snowpack
  – Creation of a simplified model for estimation of NO\textsubscript{x} fluxes from snowpack.

• Overview of Components
  – Physical representation – Snow density, porosity, snowflake radius, aqueous phase (QLL) on surface of snowflakes
  – Chemistry – Gas and Aqueous phase
  – Physical Transport – Diffusion, wind pumping, and mass transfer between phases
Physical Representation of Snow

\[ SSA = -308.2 \times \log(\rho_{\text{snow}}) - 205.96 \]

\[ r = \frac{3}{SSA \times \rho_{\text{ice}}} \]

\[ \text{por} = 1 - \frac{\rho_{\text{snow}}}{\rho_{\text{ice}}} \]

- \( \rho_{\text{snow}} \) - density of snow (0.3-0.6 g/cm\(^3\))
- SSA – specific surface area [cm\(^2\)/g]
- \( r \) – radius of snowflake
- \( \text{por} \) – porosity of snowpack

Domine, Atmos. Chem. Phys., 2008

Rosenberg, Physics Today, 2005
### Chemistry

**Aqueous Light Reactions**

1. \( NO_3^- + hv \rightarrow NO_2 + OH \)
2. \( NO_2^- + hv \rightarrow NO + OH \)
3. \( NO_3^- + hv \rightarrow NO_2^- + O \)

**Aqueous Dark Reactions**

1. \( O_3 + NO_2^- \xrightarrow{H^+} NO_2 + OH + O_2 \)
2. \( NO + NO_2 \rightarrow 2NO_2^- + 2H^+ \)
3. \( NO_2 + NO_2 \rightarrow HNO_3 + HONO \)

- Photolysis rates calculated with Fast-JX
- Chemistry calculated with Kinetic Pre-Processor (KPP)
Physical Transport Part 1
Wind pumping and Diffusion

\[ \frac{\partial c_g}{\partial t} = - \nabla \cdot (U_{\text{firn}} c_g) + \nabla \cdot (D_g \nabla c_g) \]

\[ U_{\text{firn}} = \frac{6k\rho_{\text{air}} h}{\pi \mu \lambda_{\text{surf}} \lambda_{\text{surf}}} \frac{\sqrt{\alpha^2 + 1}}{\alpha} u_{10}^2 \left( C_1 \exp \left( \frac{Z}{\delta} \right) - C_2 \exp \left( \frac{-Z}{\delta} \right) \right) \]

\[ \delta = \frac{1}{2} \frac{\alpha}{\sqrt{\alpha^2 + 1}} \frac{\lambda_{\text{surf}}}{\pi} \exp \left( \frac{H_s}{\delta} \right) + \exp \left( -\frac{H_s}{\delta} \right) \]

\[ C_1 = \frac{\exp \left( \frac{H_s}{\delta} \right)}{\exp \left( \frac{H_s}{\delta} \right) + \exp \left( -\frac{H_s}{\delta} \right)} \]

\[ C_2 = \frac{\exp \left( -\frac{H_s}{\delta} \right)}{\exp \left( \frac{H_s}{\delta} \right) + \exp \left( -\frac{H_s}{\delta} \right)} \]

- \( U_{\text{firn}} \) – vertical wind speed in snow
- \( u_{10} \) – wind speed 10 meters high
- \( k \) – permeability of snow
- \( \mu \) – dynamic viscosity of air
- \( \lambda_{\text{surf}} \) – relief wavelength
- \( h \) – relief amplitude
- \( \rho_{\text{air}} \) – density of air
- \( \alpha \) – horizontal aspect ratio
- \( D_g \) – Gas diffusion coefficient
- \( c_g \) – Gas phase concentration
- \( H_s \) – Depth of ventilated snow

Toyota and McConnell via Liao, “Atmos. Chem. Phys, 2008”
Physical Transport Part 2
Mass Transfer

\[ \frac{dc_g}{dt} = -L \frac{dc_a}{dt} = -Lk_{mt} \left( \frac{c_g - c_a}{K_H} \right) \]

\[ k_{mt} = \left( \frac{r^2}{3D_g} + \frac{4r}{3v\alpha} \right)^{-1} \]

\[ c_g \] – Gas phase concentration
\[ c_a \] – Aqueous phase concentration
\[ L \] – Volumetric ratio aqueous/gas phases
\[ k_{mt} \] – Mass transfer coefficient
\[ K_H \] – Henry’s Law constant [dimensionless]
\[ r \] – radius of snowflake
\[ D_g \] – Gas phase diffusion coefficient
\[ \alpha \] – accommodation coefficient
\[ v \] – molecular velocity

Sander, Surveys in Geophysics, 1999
Comparison of Model to Measurements

- Date of comparison is 4/11/09-4/25/09
  - Ozone intrusion event
- Model nudged with surface measurements of NO$_x$, O$_3$, temperature, and wind speed
Model vs. Measurements

$O_3$

Interpolated 30-minute measurements of $O_3 \text{ [ppb$_v$]}$

Model spin-up

Modeled $O_3 \text{ [ppb$_v$]}$
Model vs. Measurements

$\text{NO}_2$

Interpolated 30-minute measurements of $\text{NO}_2$ [ppt$_v$]

Modeled $\text{NC}_2$ [ppt$_v$]
Model vs. Measurements

NO

Interpolated 30-minute measurements of NO [ppt]$

Modeled NO [ppt]$

Model spin-up
Conclusion

• Model results
  – Over predication of O3
  – Over/under prediction of NO
  – Trend of NO₂ present, but not identical

• Major uncertainties in model
  – Does the QLL really behave as an aqueous phase?
  – What is the sensitivity of wind pumping to micro-topography parameters?
  – Is it acceptable to model snowflakes as spherical?

• Looking forward
  – Identify major chemical pathways
    • New laboratory experiments reveal relative humidity could significantly affect release of HONO from QLL [Finlayson-Pitts, UC Irvine, 2013]
  – Calculate NOₓ fluxes from snowpack
  – Combine major components into simplified model for possible integration into global models.
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References


7) Finlayson-Pitts, B. Personal Correspondence and Seminar. UC Irvine, 2013

Questions?

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