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

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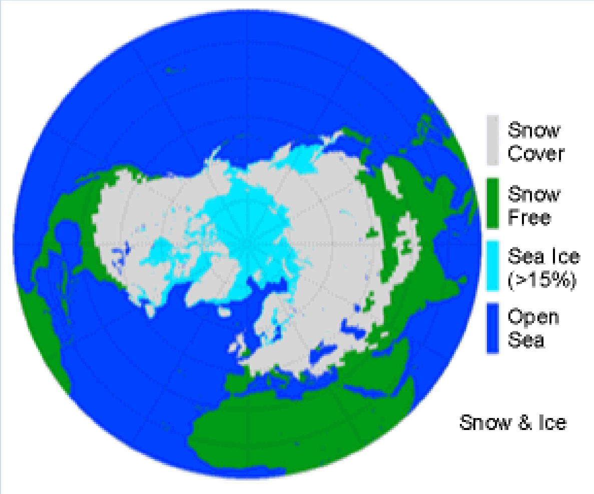
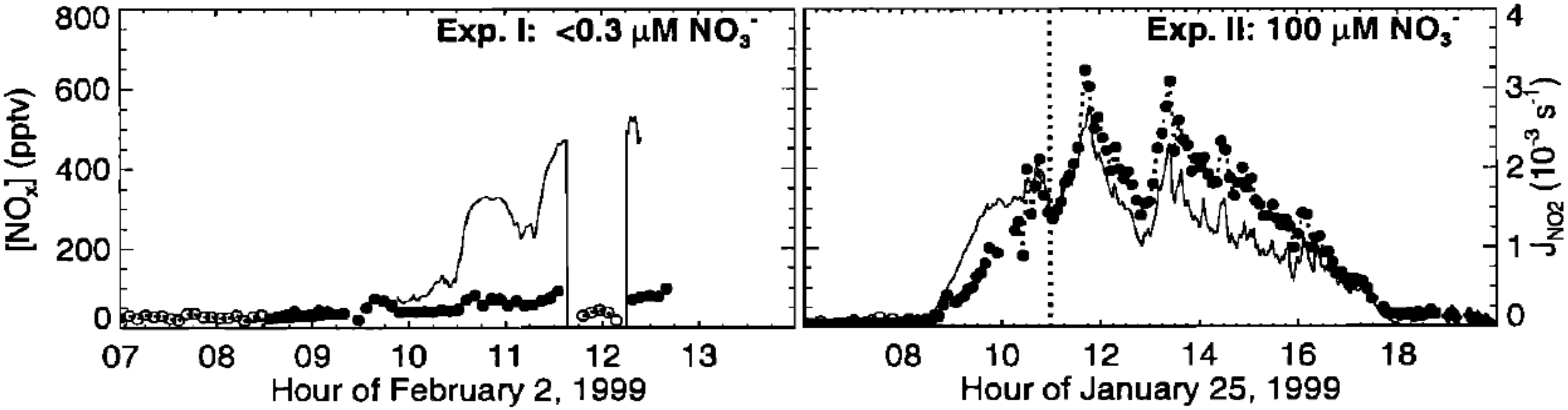
Why is the Arctic NO_x budget important?

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

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

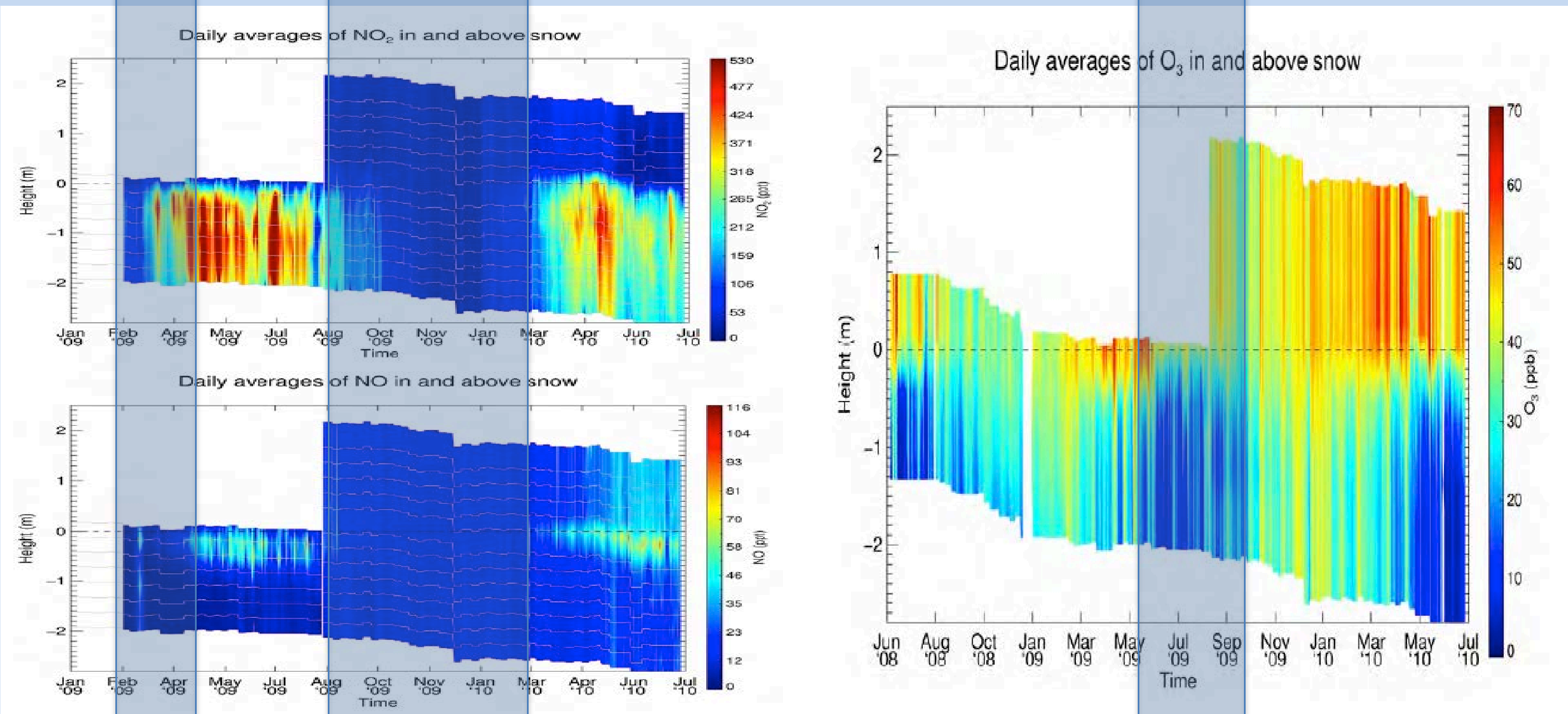
Map of Greenland depicting the location of Summit Camp.
Retrieved on 9/30/13 from maps.google.com

Met and Snow Towers

MET Tower

Snow Tower

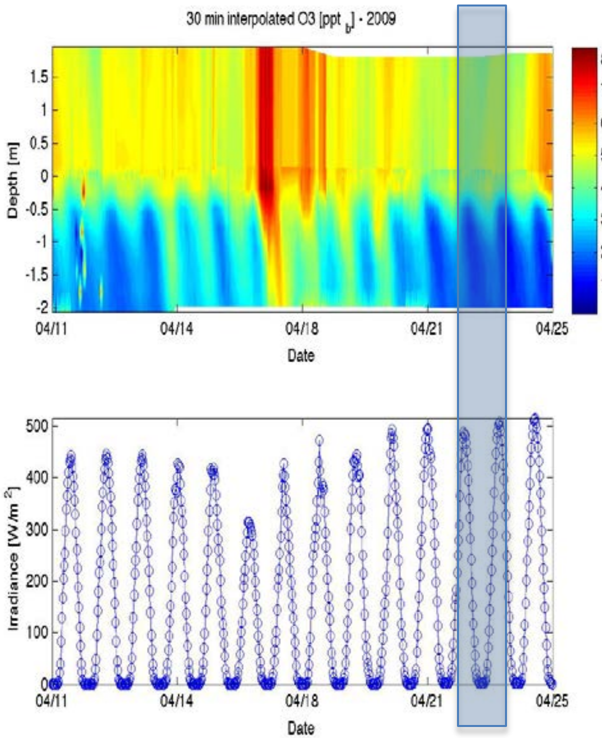
Seasonal Trends in the Measurements

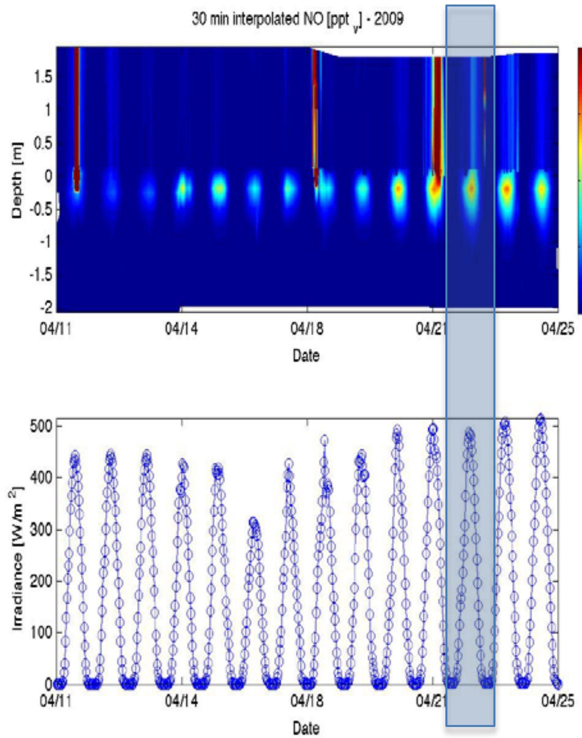


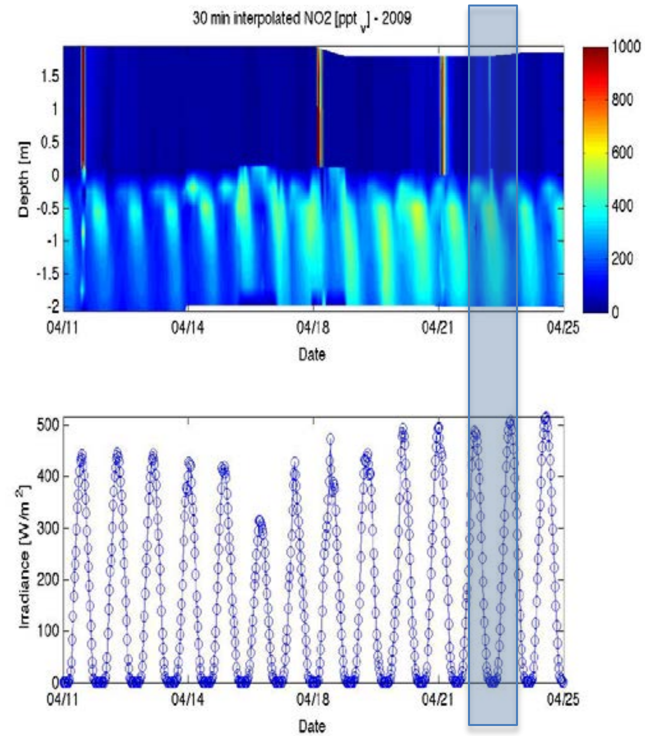
Toro, Michigan Technological University, 2011

Chemical measurements

O_3	NO	NO_2

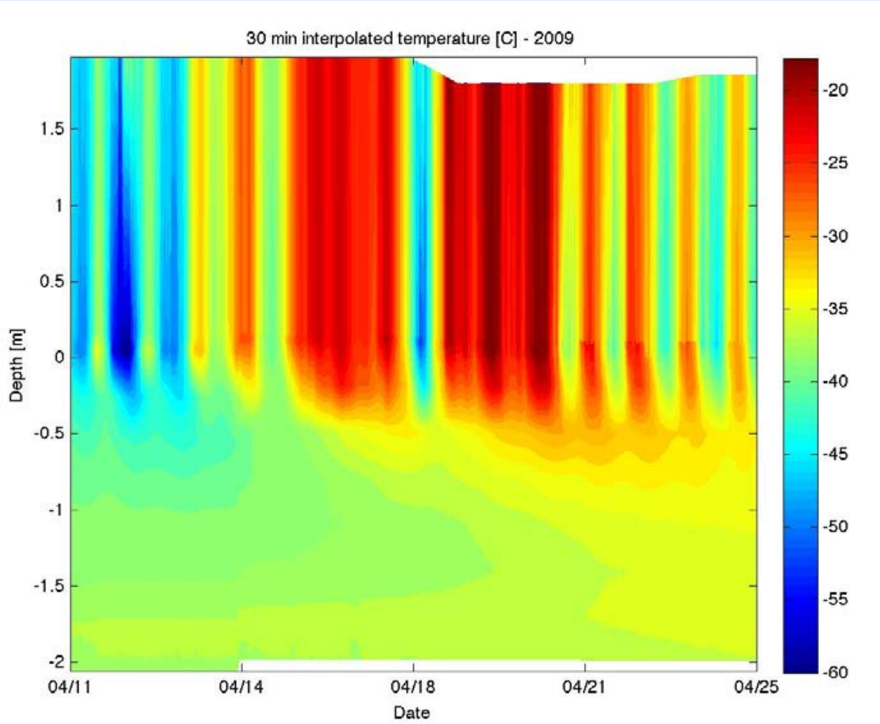




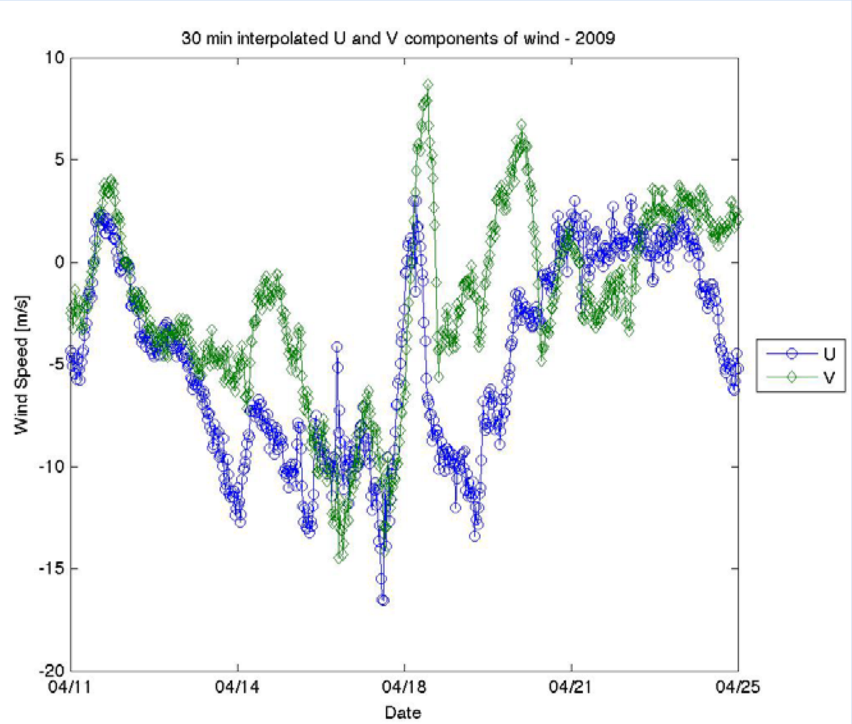


Physical measurements

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_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

$$SSA = -308.2 * LOG(\rho_{snow}) - 205.96$$

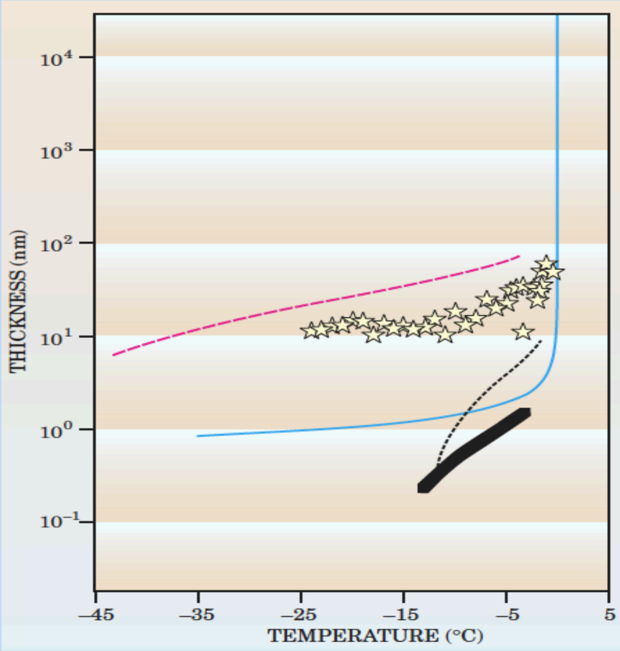
$$r = \frac{3}{SSA * \rho_{ice}}$$

$$por = 1 - \frac{\rho_{snow}}{\rho_{ice}}$$

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

Domine, Atmos. Chem. Phys ,2008

QLL thickness vs. temperature



Rosenberg, Physics Today , 2005

Chemistry

Aqueous Light Reactions

$$NO_3^- + h\nu \rightarrow NO_2 + OH$$

$$NO_2^- + h\nu \rightarrow NO + OH$$

$$NO_3^- + h\nu \rightarrow NO_2^- + O$$

Aqueous Dark Reactions

$$O_3 + NO_2^- \xrightarrow{H^+} NO_2 + OH + O_2$$

$$NO + NO_2 \rightarrow 2NO_2^- + 2H^+$$

$$NO_2 + NO_2 \rightarrow HNO_3 + HONO$$

- Photolysis rates calculated with Fast-JX
- Chemistry calculated with Kinetic Pre-Processor (KPP)

Physical Transport Part1
Wind pumping and Diffusion

$$\frac{\partial c_g}{\partial t} = -\nabla \cdot \left(U_{firn} c_g\right) + \nabla \cdot \left(D_g \nabla c_g\right)$$

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

$$\delta = \frac{1}{2} \frac{\alpha}{\sqrt{\alpha^2+1}} \frac{\lambda_{surf}}{\pi}$$

- U_{firn} – vertical wind speed in snow
- u_{10} – wind speed 10 meters high
- k – permeability of snow
- μ – dynamic viscosity of air
- λ_{surf} – relief wavelength
- h – relief amplitude
- ρ_{air} – density of air
- α – 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

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

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

Physical Transport Part2
Mass Transfer

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

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

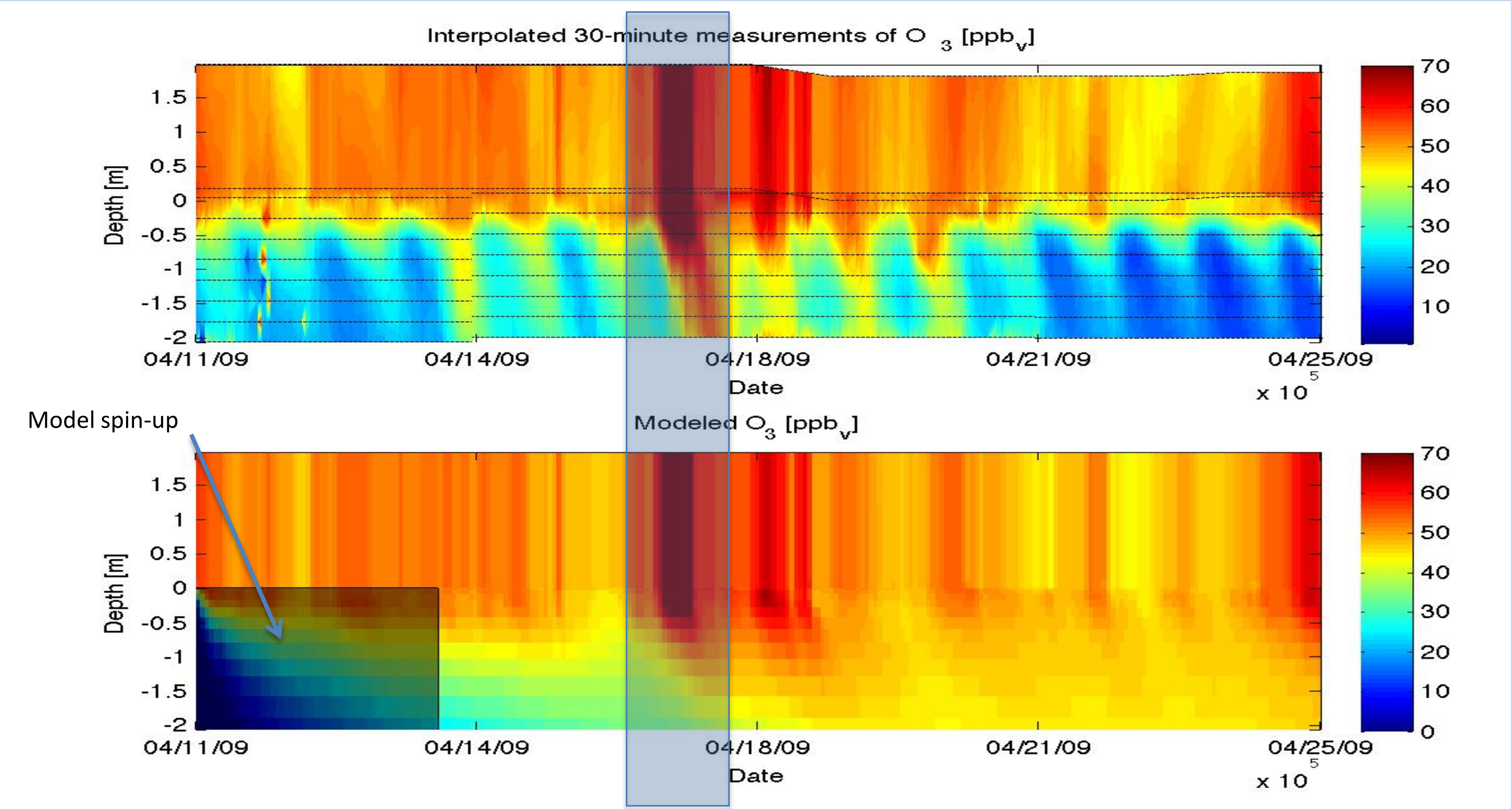
c_g – Gas phase concentration
c_a – Aqueous phase concentration
L – Volumetric ratio aqueous/gas phases
k_{mt} – Mass transfer coefficient
K_H – Henry's Law constant [dimensionless]
r – radius of snowflake
D_g – Gas phase diffusion coefficient
α – accommodation coefficient
v – molecular velocity

Sander , Surveys in Geophysics ,1999

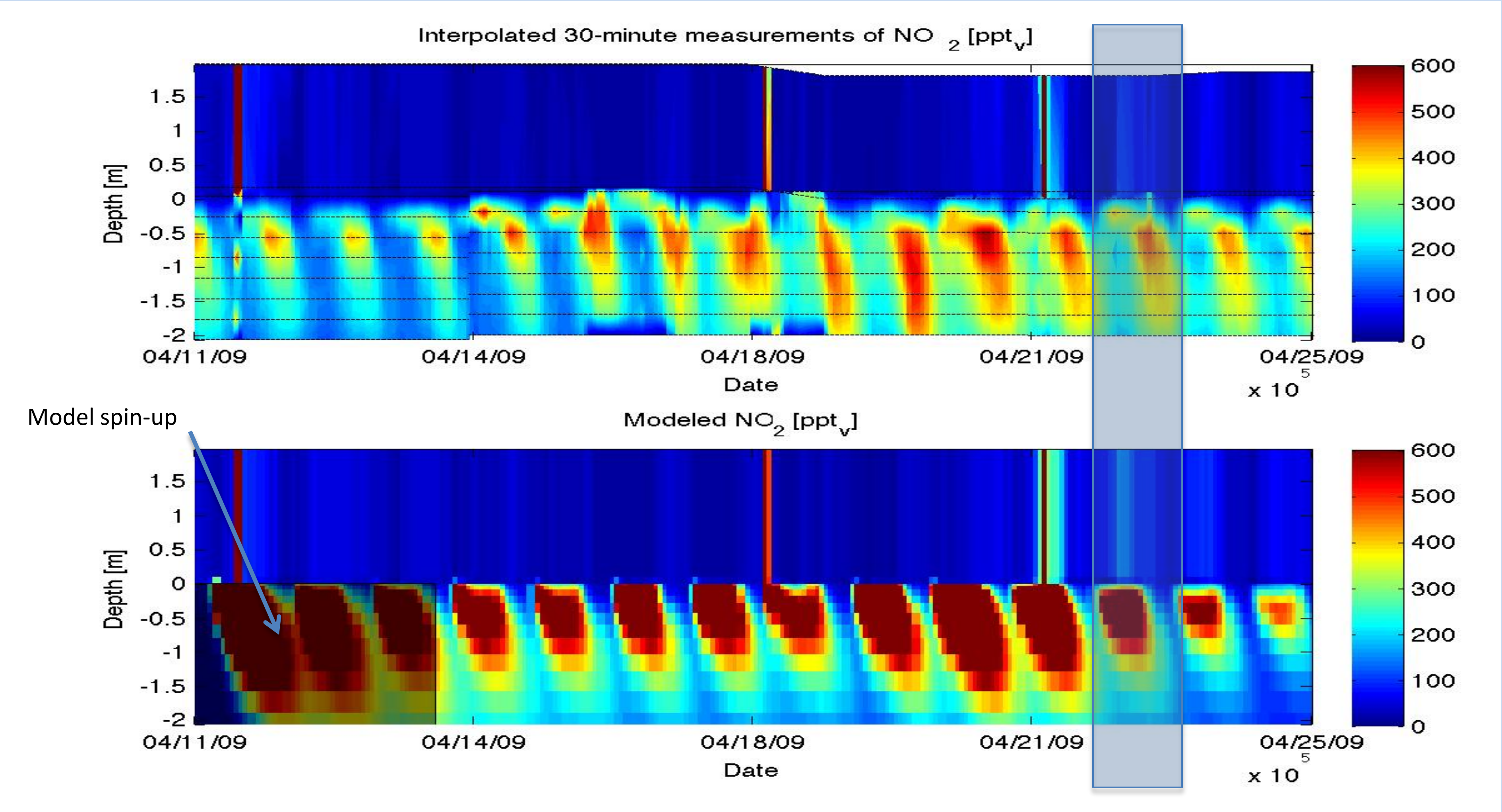
Comparison of Model to Measurements

- 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

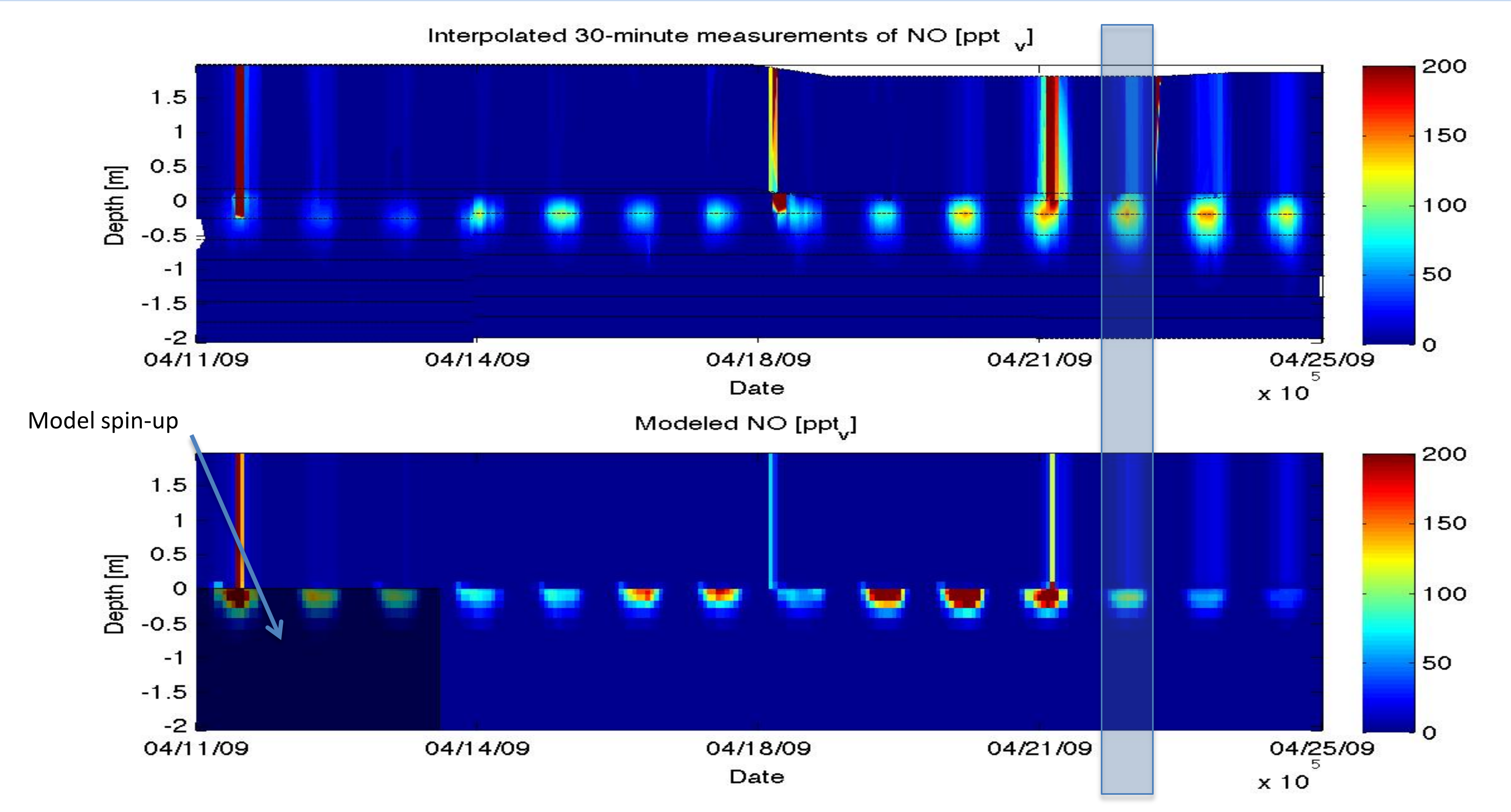
Model vs. Measurements O_3



Model vs. Measurements
NO_2



Model vs. Measurements
NO



Conclusion

- Model results
  - Over predication of O3
  - Over/under prediction of NO
  - Trend of NO_2 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 NO_x fluxes from snowpack
  - Combine major components into simplified model for possible integration into global models.

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References

1) Honrath, R. E., Guo, S., Peterson, M.C., Dziobak, M.P. (2000). "Photochemical producation of gas phase NOx from ice crystal NO3-." J. Geophys. Res. 105: 24183-24190.

2) Domine, F., et al. (2008). "Snow physics as relevant to snow photochemistry." Atmos. Chem. Phys. 8(2): 171-208.

3) Liao, W., Tan, D. (2008). "1-D Air-snowpack modeling of atmospheric nitrous acid at South pole during ANTCI 2003." Atmos. Chem. Phys. 8: 7087-7099.

4) Sander, R. (1999). "Modeling Atmospheric Chemistry: Interactions between Gas-Phase Species and Liquid Cloud/Aerosol Particles." Surveys in Geophysics 20(1): 1-31.

5) Rosenberg, R. (2005). "Why Is Ice Slippery?" Physics Today 58(12): 50-55.

6) Toro, C. (2011). Masters Thesis " Nitrogen Oxides in the Firn Air at Summit, Greenland". Michigan Technological University

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

Questions?

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