Investigating the Impact of Snowpack Photodenitrification on Polar Atmospheric Chemistry Utilizing Results from a Snowpack Radiative Transfer Model in GEOS-Chem

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Abstract

The photolysis of nitrate (NO_3^-) in snowpack is a source of NO_x to the overlying atmosphere, with implications for the oxidizing capacity of polar atmospheres and the preservation of chemicals in the ice core record. We have developed a parameterization for the vertical profile of actinic flux $I_o(\lambda,z)$ in snowpack (E1-10) based on the δ-Eddington formulation [*Wiscombe and Warren*, 1980] modified by a correction factor from a 4-stream DOM model [*Grenfell*, 1991] that will be incorporated into GEOS-Chem. Based on updated optical properties in the UV, we calculate e-folding depths of actinic flux in snowpack of 30 cm in Antarctica and 15 cm in Greenland. Since NO_x production can occur tens of centimeters deeper in the snowpack than previously determined, we compare the ventilation lifetime of NO_x out of the snowpack by diffusion and wind pumping to the chemical lifetime of NO_x against conversion to HNO_3, $BrNO_3$, and INO_3 in the snowpack to determine the NO_x ventilation depth (z_{vent}) in snowpack. Below z_{vent}, the NO_x produced through NO_3^- photolysis does not escape into the atmosphere. The range of NO_x fluxes from South Pole, Neumayer, Halley, and Summit snowpacks computed in this study are an order of magnitude larger than observed NO_x fluxes in Antarctica and Greenland. Our $I_o(\lambda,z)$ parameterizations will be used in GEOS-Chem to estimate the impacts of snowpack photodenitrification on polar nitrogen and oxidant budgets.

I. Introduction

Description of Nitrate Photolysis

$NO_3^- + hv(+H^+) \rightarrow NO_2 + OH$ Reaction 1

Nitrate photolysis occurs at wavelengths from 300-350nm and is centered on 320 nm [*Wolff et al.*, 2002].

$NO_2 + OH \rightarrow HNO_3$ Reaction 2

NO_x created during NO_3^- photolysis can escape into the atmosphere, convert to HNO_3, and redeposit to the snowpack as NO_3^-.

Figure 1. Map of Antarctica And Greenland

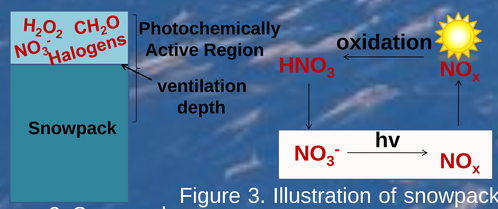

Figure 2. Snowpack photochemistry.

Figure 3. Illustration of snowpack photodenitrification and post-depositional processing.

II. Snowpack Radiative Transfer Model

Calculation of $I_o(\lambda,z)$ in the snow is based on calculations using a snowpack radiative transfer model [*Grenfell*, 1991] with updated optical properties in the UV [*Warren and Brandt*, 2008]. Updated optical properties of ice indicate much greater UV transmission, leading to an e-folding depth of actinic flux in snowpack of 30 cm in Antarctica and 15 cm in Greenland.

Impact of soot concentration on actinic flux profile

Impact of dust on actinic flux profile

Wavelength dependence of actinic flux profile

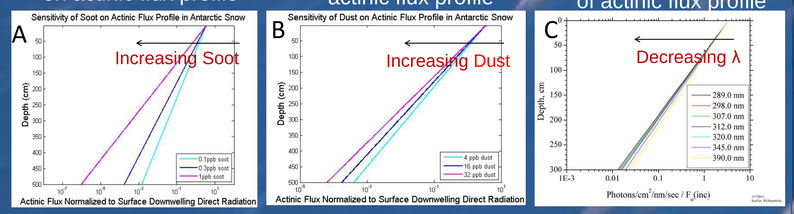

Figure 4. Results of sensitivity studies performed to determine the dependence of soot (A) , dust (B), and wavelength (C) on the attenuation of actinic flux with increasing depth in the snowpack. The attenuation of actinic flux is highly dependent on soot and dust, but weakly dependent on wavelength within the UV-region, although the absolute magnitude $I_o(\lambda,z)$ depends on wavelength.

In order to represent spatio-temporal variations in the properties of the snowpack and ambient lighting conditions, we have developed a simple and broadly applicable parameterization of $I_o(\lambda,z)$ (E1-10). These equations retain full capability to vary the properties of the snow to represent actinic flux accurately over a wide range of snow conditions present in the Antarctic and Greenland.

E1 - For direct radiation at the surface:

$$\left[\frac{I_o(\lambda, z=0)}{F_{inc}(\lambda_\downarrow)}\right]_{direct} = \left[\frac{0.577 + \mu_o}{0.577 \cdot \mu_o}\right] \cdot Corr(\mu_o)$$

E2 - For direct radiation below z_{ref}:

$$\left[\frac{I_o(\lambda, z \geq z_{ref})}{F_{inc}(\lambda_\downarrow)}\right]_{direct} = G(z_{ref}, \mu_o) \cdot e^{-0.60 \cdot c\varpi_{eff}^{\frac{1}{2}} \cdot Kext_{tot} \cdot (z - z_{ref})}$$

where, $G(z_{ref}, \mu_o) = 3(0.577 + \mu_o) \cdot e^{-0.60 \cdot c\varpi_{eff}^{\frac{1}{2}} \cdot Kext_{tot} \cdot z_{ref}} \cdot Corr(\mu_o)$

E4 - For diffuse radiation:

$$\left[\frac{I_o(\lambda,z)}{F_{inc}(\lambda_\downarrow)}\right]_{diffuse} = 3.831 \cdot e^{-0.60 \cdot c\varpi_{eff}^{\frac{1}{2}} \cdot Kext_{tot} \cdot z}$$

E5- Extinction coefficient for snow

$$Kext_{snow} = \frac{3\, Qext \cdot \rho_{snow}}{4\, r_e \cdot \rho_{ice}}$$

E6 - Extinction coefficient for dust

$$Kext_{soot} = \frac{\beta_{soot} \cdot L_{soot} \cdot \rho_{snow}}{c\varpi_{soot}}$$

E7 - Extinction coefficient for soot

$$Kext_{dust} = \frac{\beta_{dust} \cdot L_{dust} \cdot \rho_{dust}}{c\varpi_{dust}}$$

E8 – Total extinction coefficient

$$Kext_{tot} = [Kext_{snow} + Kext_{soot} + Kext_{dust}]$$

E9 – co-albedo for single scattering

$$c\varpi_{eff} = \frac{[c\varpi_{snow} \cdot Kext_{snow} + c\varpi_{soot} \cdot Kext_{soot} + c\varpi_{dust} \cdot Kext_{dust}]}{Kext_{tot}}$$

E10 – Actinic Flux

$$I_{o_{combined}}(\lambda, z) = \left\{\left[\frac{I_o(\lambda,z)}{F_{inc}(\lambda_\downarrow)}\right]_{diffuse} \cdot (f_{dif}) + \left[\frac{I_o(\lambda,z)}{F_{inc}(\lambda_\downarrow)}\right]_{direct} \cdot (1 - f_{dif})\right\} \cdot [F_{inc}(\lambda_\downarrow)]_{tot}$$

E1-10 can be integrated over wavelength and depth (0-z_{vent}) to obtain the total actinic flux available for NO_x production and release to the atmosphere.

III. Depth Dependent Lifetime of NO_x in Snowpack

$\tau_{chemical}$ - NO_x produced through NO_3^- photolysis can convert to HNO_3, $BrNO_3$, and INO_3 in the snowpack.

$\tau_{ventilation}$ - NO_x produced through NO_3^- photolysis can escape from the snowpack through diffusion and wind pumping.

Compare $\tau_{chemical}$ and $\tau_{ventilation}$ to determine ventilation depth. Ventilation Depth is depth below which NO_x produced cannot escape to atmosphere

$\tau_{diffusion} = z^2/D_s$	$Ds = D_a\phi^m$
$\tau_{wind\ pumping} = (a^{-1})(\phi\lambda\delta K^{-1})(C^{-1})(Re^{-1})(\lambda U^{-1})e^{z/b}$	$\delta=\lambda/2\pi$, a=h/λ
$\tau_{NO2+X} = (k_x[X])^{-1} + (1+[NO]/[NO_2])$	where X = OH, BrO, IO

Table 1. Equations used to calculate the NO_x lifetimes with respect to diffusion [*Albert and Shultz, 2002*], wind pumping [*Waddington et al., 1996*], and conversion to HNO_3, $BrNO_3$, and INO_3.

Chemical Lifetime of NO_x:

$\tau_{chemical} = (\tau_{conv.\ to\ HNO3}^{-1} + \tau_{conv.\ to\ BrNO3}^{-1} + \tau_{conv.\ to\ INO3}^{-1})^{-1}$

Ventilation Lifetime of NO_x:

$\tau_{ventilation} = (\tau_{diffusion}^{-1} + \tau_{windpumping}^{-1})^{-1}$

Conversion of NO_x into HNO_3, $BrNO_3$, and INO_3 via reactions 3-5 in snowpack prevents NO_x ventilation to atmosphere.

$NO_2 + OH \rightarrow HNO_3$ Reaction 3

$NO_2 + BrO \rightarrow BrNO_3$ Reaction 4

$NO_2 + IO \rightarrow INO_3$ Reaction 5

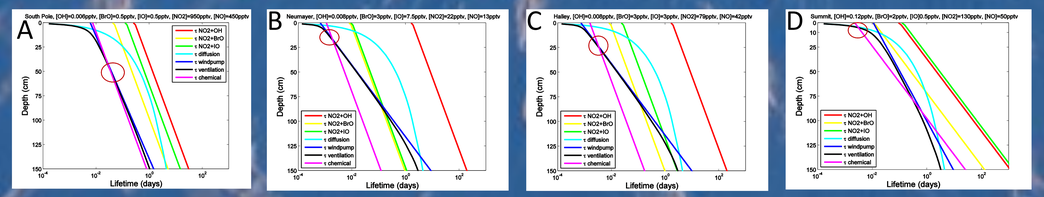

Figure 6. Comparison of the escape lifetimes to the decay lifetimes at South Pole (A), Neumayer (B), Halley (C), and Summit (D) using typical [BrO], [IO], [OH], [NO_x], sastrugi dimensions, and austral summer wind speeds for each location. NO_2 produced from NO_3^- photolysis can escape into the atmosphere by diffusion and wind pumping before being converted to HNO_3, $BrNO_3$, or INO_3 in the snowpack above 58 ± 41 cm (1σ) at South Pole, 19 ± 13 cm (1σ) at Neumayer, 26 ± 11 cm (1σ) at Halley, and 5 ± 8 cm (1σ) at Summit.

Figure 5. Location of dominant ventilation and chemical processes.

IV. Flux of NO_x to overlying atmosphere

The photolysis rate constant is described in Equation 12 and is the product of the absorption cross section (σ) [*Burley and Johnston*, 1992], the quantum yield (ϕ) [*Chu and Anastasio*, 2003], and the actinic flux ($I_o(\lambda,z)$) [*Grenfell*, 1991, *Wild et al*., 2000] over specific wavelength bins from λ=298.25-345 nm at a given depth.

$J = \int \sigma(\lambda)\phi(T,pH)I_o(\lambda,z)d\lambda dz$ E12

The flux of NO_x out of the snowpack is calculated in Equation 13,

$F_{NOx} = J_{NO3^-}[NO_3^-]$ E13

where J_{NO3^-} is the photolysis rate constant (E12) and $[NO_3^-]$ is the snowpack nitrate concentration. NO_x fluxes are calculated using E13 with a range of nitrate concentrations; 200-800 μg kg^{-1} for 0-1 cm and 20-150 μg kg^{-1} for 1 cm - z_{vent} [*Dibb et al., 2004*, *Rothlisberger et al*., 2000]

Polar NO_x Flux Comparisons		
Locations	**NO_x Flux (molecules cm^{-2} s^{-1})**	**Reference**
Neumayer (coastal)	$2.5x10^8$	Jones et al., 2000
Neumayer (coastal)	$1.3x10^8$	Jones et al., 2001
South Pole (continental)	$2.2x10^8$	Davis et al., 2004
South Pole (continental)	$3.8x10^8$	Oncley et al., 2004
Halley (coastal)	$1.9x10^8$	Jones et al., 2007
Halley (coastal)	$1.7\text{-}3.8x10^8$	Baguitte et al., 2009
Summit (continental)	$2.5x10^8$	Honrath et al., 2002
Our Calculations	**NO_x flux (molecules cm^{-2} s^{-1})**	**Reference**
Neumayer (coastal)	$1.1\text{-}8.5x10^9$	This Study
South Pole (continental)	$8.0x10^8\text{-}6.1x10^9$	This Study
Halley (coastal)	$1.3\text{-}9.8x10^9$	This Study
Summit (continental)	$2.5x10^8\text{-}2.0x10^9$	This Study

Table 2. NO_x fluxes calculated in this study are compared to observed NO_x fluxes at Neumayer, South Pole, and Halley, and Summit.

V. Conclusions and Future Directions

•The calculated e-folding depth of actinic flux is 30 cm in Antarctic snowpack and 15 cm in Greenland snowpack.

•We have developed simple and broadly applicable equations to calculate depth dependent actinic flux in snowpack. These equations can be incorporated into global models and adjusted to represent all snowpack types by varying relevant parameters (e.g. soot, dust, snow density).

•Large error bars in the ventilation depth result from the numerous combinations of chemical concentrations, sastrugi dimensions, and wind speeds possible at South Pole, Neumayer, Halley, and Summit. Ventilation depths are most sensitive to sastrugi dimensions and [BrO].

•Our calculated NO_x fluxes are roughly an order of magnitude larger than observed NO_x fluxes in Antarctica and Greenland, but we have assumed that all nitrate in snowpack is available for photolysis. Next we will develop an efficiency factor to account for this overestimate.

•Our next step is to incorporate our methods and results into the GEOS-Chem global chemical transport model to investigate the impacts on polar nitrogen and oxidant budgets.

References

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Acknowledgements Funding provided by NSF ANT 0944537. We thank Oliver Wild, Steve Warren, Ed Waddington, and Eric Wolff for useful discussions.