The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen across Antarctica in a global chemical transport model

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Abstract
The formation and recycling of reactive nitrogen (NO, NO$_2$, HONO) at the air-snow interface has implications for air quality and the oxidation capacity of the atmosphere in snow-covered regions. Nitrate (NO$_3^-$) photolysis in snow provides a source of oxidants (e.g., hydroxyl radical) and oxidant precursors (e.g., nitrogen oxides) to the overlying boundary layer, and alters the concentration and isotopic (e.g., $\delta^{15}$N) signature of NO$_3^-$ preserved in ice cores. We have incorporated the photolysis of Antarctic snow NO$_3^-$ into a global chemical transport model (GEOS-Chem) to examine the implications of snow NO$_3^-$ photolysis for boundary layer chemistry, the recycling and redistribution of reactive nitrogen across the Antarctic continent, and the preservation of ice-core NO$_3^-$ in Antarctic ice cores. This modeling framework uses an idealized snowpack that accounts for the spatial variability in parameters that influence snow NO$_3^-$ photolysis. The goal of this research is to investigate the potential spatial variability of snow-sourced NO$_x$ fluxes along with the recycling, loss, and areal redistribution of nitrogen across Antarctica, which is an environment in which observations of these parameters over large spatial scales are difficult to obtain. The calculated potential fluxes of snow-sourced NO$_x$ in Antarctica range from $0.5 \times 10^8$ to $7.8 \times 10^8$ molec cm$^{-2}$ s$^{-1}$ and calculated e-folding depths of UV actinic flux in snowpack range from 24 to 69 cm. Snow-sourced NO$_x$ increases mean austral summer boundary layer mixing ratios of total nitrate (HNO$_3$+NO$_3^-$), NO$_x$, OH, and O$_3$ in Antarctica by a factor of up to 32, 38, 7, and 2, respectively, in the model. Model results also suggest that NO$_3^-$ can be recycled between the air and snow multiple times and that NO$_3^-$ can remain in the snow photic zone for at least 7.5 years on the East Antarctic plateau. The fraction of photolysis-driven loss of NO$_3^-$ from the snow is roughly -0.99 on the East Antarctic plateau, while areas of wind convergence (e.g., over the Ronne Ice Shelf) have a net gain of NO$_3^-$ due to redistribution of snow-sourced reactive nitrogen across the Antarctic continent. The modeled enrichment in ice-core $\delta^{15}$N(NO$_3^-$) due to photolysis-driven loss of snow NO$_3^-$ ranges from 0‰ to 363‰, with the largest enrichments on the East Antarctic plateau. There is a strong relationship between the degree of photolysis-driven loss of snow NO$_3^-$ and the degree of nitrogen recycling between the air and snow in regions of Antarctica with a snow accumulation rate greater than 85 kg m$^{-2}$ a$^{-1}$ in the present day. This modeling framework study is also used to perform a variety of sensitivity studies to highlight the largest uncertainties in our ability to model these processes in order to guide future lab and field campaigns.
1. Introduction
Nitrogen oxides (NO$_x$=NO+NO$_2$) emitted from fossil fuel combustion, biomass burning, soil microbial activity, and lightning have adverse respiratory effects, contribute to the formation of atmospheric acidity, and are a key ingredient in tropospheric oxidant cycling leading to the formation of ground-level ozone (O$_3$). Ozone also has adverse respiratory effects, is an effective greenhouse gas [UNEP, 2011], and its photolysis dominates hydroxyl radical (OH) production in much of the troposphere [Thompson, 1992]. Oxidation to form nitrate (HNO$_3$/NO$_3^-$) is the main sink for NO$_x$ in the troposphere [Logan, 1983], and the lifetime of NO$_x$ against oxidation to nitrate is 1-3 days in polar regions [Levy et al., 1999]. NO$_3^-$ is lost from the atmosphere through dry and wet deposition to the Earth’s surface, and has an atmospheric lifetime of roughly 5 days [Xu and Penner, 2012]. In Antarctica, NO$_3^-$ deposited to the snowpack originates from both the troposphere (e.g., long-range transport) [Lee et al., 2014] and stratosphere [Frey et al., 2009, Savarino et al., 2007]. In snow-covered regions, the deposition of NO$_3^-$ is not a permanent sink for NO$_x$, as the photolysis of snow NO$_3^-$ returns reactive nitrogen (N$_x$=NO$_x$, HONO) back to the atmosphere, with implications for other oxidants such as OH and ozone [Domine and Shepson, 2002].

Snow photochemistry significantly influences boundary layer chemistry and plays an important role in oxidant production and cycling, especially in pristine regions, such as Antarctica [Bloss et al., 2007, Chen et al., 2004, Grannas et al., 2007, Helmig et al., 2008]. Snow photochemistry may have more widespread impacts since up to 40% of land on Earth is snow-covered at a given time [Grannas et al., 2007]. NO$_3^-$ is not the only photochemically-active species in snow. The photolysis of nitrite (NO$_2^-$) in snow and the photolysis of snow-sourced formaldehyde (CH$_2$O), nitrous acid (HONO), and hydrogen peroxide (H$_2$O$_2$) provide additional sources of N$_x$ and OH to the boundary layer. Bromine (Br$_2$) is also produced in the snow via reactions involving bromide (Br$^-$), photochemically-active species (e.g., NO$_3^-$), and photochemically-produced species (e.g., OH) within snow grains [Pratt et al., 2013].

In snow, NO$_3^-$ photolysis likely occurs in the liquid-like region (LLR) on the surface of ice grains, in cracks between ice grains, or in brine pockets embedded within ice grains [Domine et al., 2013]. There are two channels for NO$_3^-$ photolysis at wavelengths ($\lambda$)=290-345 nm. In the aqueous phase, NO$_3^-$ can photolyze to produce NO$_2$ and OH (E1), or produce NO$_2^-$ and O(1$^3$P) (E2), but E1 is the dominant pathway [Grannas et al., 2007, Mack and Bolton, 1999, Meusinger et al., 2014].

NO$_3^-$(aq) + hv(+H$^+$) $\rightarrow$ NO$_2$(aq) + OH(aq), \hspace{1cm} E1
NO$_3^-$(aq) + hv $\rightarrow$ NO$_2$(aq) + O(1$^3$P)(aq), \hspace{1cm} E2

The aqueous phase NO$_2$ produced in E1 is can be transferred to the gas phase and subsequently transported into the interstitial air [Boxe et al., 2005] and then released to the atmosphere. The quantum yield ($\phi$) in E1 is strongly influenced by the location of NO$_3^-$ in an ice grain. Chu and Anastasio [2003] froze NO$_3^-$-doped water in the lab and measured the quantum yield for E1 (0.003 molec photon$^{-1}$ at T=253K) as frozen ice grains were exposed to ultraviolet (UV) radiation. Zhu et al. [2010] deposited HNO$_3$ on
an ice film and measured $\phi$ for E1 (0.6 molec photon$^{-1}$ at T=253K), as the frozen surface was irradiated with UV radiation. In a recent study by Meusinger et al. [2014], $\phi$=0.003-0.44 molec photon$^{-1}$ for E1, which nearly spans the full range of previously reported quantum yields. Results from Meusinger et al. [2014] suggest that $\phi$ is dependent on the length of time that snow is exposed to UV radiation, as well as the location of NO$_3^-$ in the ice grain. Meusinger et al. [2014] suggest that two photochemical domains of NO$_3^-$ exist: photolabile NO$_3^-$ and NO$_3^-$ buried within the ice grain. The NO$_x$ produced from the photolysis of photolabile NO$_3^-$ can escape the ice grain, while the NO$_x$ produced from the photolysis of buried NO$_3^-$ is likely to undergo recombination chemistry within the snow grain, thus lowering the quantum yield of NO$_x$ for NO$_3^-$ photolysis.

The NO$_3^-$ produced in E2 is quickly photolized at longer wavelengths ($\lambda$=290-390 nm) in the LLR or can react with OH or H$^+$ in the LLR to produce N$_x$ [Grannas et al., 2007]:

$$\text{NO}_2^-(aq) + \text{hv}(+,H^+, \text{aq}) \rightarrow \text{NO}(aq) + \text{OH}(aq), \quad \text{E3}$$

$$\text{NO}_2^-(aq) + \text{OH}(aq) \rightarrow \text{NO}_2(aq) + \text{OH}(aq), \quad \text{E4}$$

$$\text{NO}_2^-(aq) + H^+(\text{aq}) \rightarrow \text{HONO}(aq), \quad \text{E5}$$

HONO produced in E5 can rapidly photolize to produce NO and OH in the interstitial air or the atmospheric boundary layer [Anastasio and Chu, 2009]. Reactions involving NO$_2^-$ are intermediate reactions for NO$_3^-$ photolysis because NO$_3^-$ photolysis is required for NO$_3^-$ formation and the end products of E1-E5 are all N$_x$. Once emitted, NO$_2$ and NO are efficiently transported to the overlying atmosphere via windpumping [Zatko et al., 2013] and enter into rapid NO$_x$-cycling reactions. In the atmosphere, the relative abundance of NO and NO$_2$ will be determined by local atmospheric conditions, specifically oxidant concentrations (e.g., O$_3$, HO$_2$, RO$_2$, BrO, and ClO) [Frey et al., 2013]. The snow-sourced NO$_x$ is then re-oxidized to HNO$_3$ via E6 under sunlit conditions.

$$\text{NO}_2(g) + \text{OH}(g) \rightarrow \text{HNO}_3(g), \quad \text{E6}$$

The HNO$_3$ produced in E6 can undergo wet or dry deposition to the snow surface [Dibb et al., 2004] within a day [Slusher et al., 2002, Wang et al., 2008]. Evidence for HNO$_3$ re-deposition is seen in the snow NO$_3^-$ concentration profile at many polar locations, where NO$_3^-$ concentrations are at least an order of magnitude higher in the top two centimeters (cm) of snow compared to NO$_3^-$ concentrations below [Dibb et al., 2004, Frey et al., 2009, Mayewski and Legrand, 1990, Rothlisberger et al., 2000]. Once HNO$_3$ is deposited back to the snow, it is available for photolysis again. NO$_3^-$ can be recycled multiple times between the boundary layer and the snow before burial below the photic zone [Davis et al., 2008, Erbland et al., 2015].

The photolysis of snow NO$_3^-$ and subsequent recycling between the air and snow alters the concentration and isotopic (e.g., $\delta^{15}$N) signature of NO$_3^-$ that is ultimately preserved in polar ice sheets, which hampers the interpretation of ice-core NO$_3^-$ records [Wolff et al., 2008]. Such records have been sought to reconstruct the past history of the abundance of NO$_x$ in the atmosphere [Wolff, 1995]. It has also been suggested that the nitrogen ($\delta^{15}$N) and oxygen ($\Delta^{17}$O = $\delta^{17}$O – 0.52×$\delta^{18}$O) isotopic composition of ice-core NO$_3^-$ can
provide information on past variability in atmospheric NO$_x$ sources and oxidant abundances [e.g., Alexander et al., 2004, Hastings et al., 2005]. Different sources of NO$_x$ have different δ$^{15}$N signatures (~ -19% to 25‰, see summary in Geng et al., 2014a), giving ice-core δ$^{15}$N(NO$_3^-$) measurements the potential to track NO$_x$-source changes over time. The oxygen-17 excess of NO$_3^-$ ($\Delta^{17}$O(NO$_3^-$)) is determined mainly by the relative abundance of the oxidants involved in NO$_x$ cycling and conversion of NO$_2$ to NO$_3^-$ (i.e. O$_3$, HO$_2$, RO$_2$, OH), giving ice-core $\Delta^{17}$O(NO$_3^-$) measurements the potential to track variability in the relative abundance of these oxidants over time. However, δ$^{15}$N(NO$_3^-$) and $\Delta^{17}$O(NO$_3^-$) in ice cores can also be influenced by post-depositional processing of snow NO$_3^-$ initiated by photolysis. In this study we focus on the impact of snow NO$_3^-$ photolysis on ice-core δ$^{15}$N(NO$_3^-$).

Ice-core δ$^{15}$N(NO$_3^-$) values will be altered if there is photolysis-driven loss of NO$_3^-$ from the snow when snow-sourced NO$_x$ is transported away from the site of primary deposition. Nitrate photolysis in snow is associated with a large fractionation constant ($\varepsilon$) of -47.9‰ [Berhanu et al., 2014], providing the boundary layer with a source of NO$_x$ that is highly depleted in δ$^{15}$N, leaving highly enriched δ$^{15}$N(NO$_3^-$) in the snow. In the Weddell Sea, atmospheric δ$^{15}$N(NO$_3^-$) values are as low as -40‰, indicating transport of snow-sourced NO$_x$ from the continental interior [Morin et al., 2009], while on the East Antarctica plateau, snow δ$^{15}$N(NO$_3^-$) up to 480‰ has been reported [Blunier et al., 2005, Erbland et al., 2013, Frey et al., 2009, Shi et al., 2014], indicating net loss of NO$_3^-$ driven by photolysis. If snow-sourced NO$_x$ is simply re-deposited back to the snow surface at the site of emission, a vertical profile in δ$^{15}$N(NO$_3^-$) within the snow photic zone will develop due to vertical redistribution of NO$_3^-$ [Erbland et al., 2013, Frey et al., 2009]; however, the depth-integrated δ$^{15}$N(NO$_3^-$) will not be impacted, even with active photolysis-driven recycling between the atmosphere and the snow. Enrichment in δ$^{15}$N(NO$_3^-$) in ice cores requires photolysis-driven loss from snow combined with atmospheric transport of the resulting NO$_x$. In addition to photolysis, ice-core δ$^{15}$N(NO$_3^-$) values are also influenced by evaporation of HNO$_3$ [Mulvaney et al., 1998] from snow and by atmospheric processing, such as NO$_x$ cycling [Freyer et al., 1993] and gas-particle partitioning [Heaton et al., 1997, Geng et al., 2014a]; however, these impose a fractionation in δ$^{15}$N(NO$_3^-$) at least an order of magnitude smaller than photolysis, and are thus not able to explain the large enrichments in snow δ$^{15}$N(NO$_3^-$) observed on the East Antarctic plateau [Blunier et al., 2005, Erbland et al., 2013, Frey et al., 2009, Shi et al., 2014].

Here we incorporate a snowpack actinic flux parameterization used to calculate the photolysis of snow NO$_3^-$ into a global chemical transport model. The idealized Antarctic ice sheet incorporated into GEOS-Chem has similar topography, climate, and weather as the real Antarctic ice sheet, but is subject to assumptions about the chemical and physical properties of the snow. The idealized snowpack in this modeling framework accounts for the spatial variability in parameters important to snow NO$_3^-$ photolysis in order to investigate the potential spatial variability in snow-sourced NO$_x$ fluxes and associated reactive nitrogen recycling and redistribution across Antarctica, where observations of these parameters over large spatial scales are difficult to obtain. The potential impacts of nitrogen recycling between the air and snow on boundary layer chemistry as well as the
impacts of photolysis-driven loss of NO$_3^-$ from the snow on the preservation of ice-core NO$_3^-$ across Antarctica are examined in this study. A major advantage of using a global chemical transport model framework is the ability to examine the redistribution and loss of reactive nitrogen across large spatial scales due to photolysis-driven loss of snow NO$_3^-$ . Section 2 describes the inclusion of a snowpack actinic flux parameterization and NO$_3^-$ photolysis into a global chemical transport model, GEOS-Chem. Section 3 explores the implications of photolysis-driven reactive nitrogen recycling and redistribution for boundary layer chemistry and the alteration of NO$_3^-$ concentration and its isotopes ultimately archived in ice cores. We end by using our model sensitivity studies to highlight the largest uncertainties in our ability to model these processes as a guide for future laboratory and field studies.

2. Methods

2.1. Incorporating Snow NO$_3^-$ Photolysis into a Global Chemical Transport Model

Table 1 provides a glossary of the variables used throughout this paper.

2.1.1. Global Chemical Transport Model Description

GEOS-Chem is a global 3-dimensional (3-D) model of coupled aerosol-oxidant chemistry with detailed HO$_x$-NO$_x$-VOC-O$_3$-BrO$_x$ tropospheric chemistry originally described in Bey et al. [2001]. The model uses assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-5) including winds, convective mass fluxes, boundary layer depths, temperature, precipitation, and surface properties. Meteorological data have 6-hour temporal resolution (3-hour for surface variables and mixing depths). The TPCORE advection algorithm [Lin and Rood, 1996] is the transport routine in GEOS-Chem and is based on the calculation of the slopes between neighboring grid boxes. At the poles, neighboring grid boxes are used to estimate transport of chemical species into and out of the circular polar grid box. The spectral direct and diffuse downwelling surface irradiance and photolysis frequencies are calculated using the Fast-JX radiative transfer module [Wild et al., 2000, Bian and Prather, 2002, Mao et al., 2010]. In GEOS-Chem, aerosols can be wet deposited via scavenging in convective updrafts and by rainout from convective anvils and large-scale precipitation [Liu et al., 2001]. The wet deposition scheme for gases is described by Amos et al. [2012] and the scavenging of aerosol by snow and cold/mixed precipitation is described by Wang et al. [2011]. Dry-deposition velocities for coarse mode aerosols (radii between 1-10 mm) are calculated based on aerosol size and hydrosopic growth as described in Zhang et al. [2001]. Aerosol deposition to snow and ice surfaces is described by Fisher et al. [2011]. For smaller aerosols (radii less than 1 µm), dry deposition velocities are calculated with a standard resistance-in-series scheme [Wang et al., 1998, Wesely, 1989].

Anthropogenic NO$_x$ emissions are from the EDGAR 3.2-FT2000 global inventory for the year 2000 [Oliver et al., 2005], scaled by country on the basis of energy statistics as described by van Donkelaar et al. [2008]. The monthly inventory of emissions from biomass burning are from the Global Fire Emissions Database (GFED2) [van der Werf et al., 2009]. Soil NO$_x$ emissions are computed using a parameterization described in Hudman et al. [2012], which is a function of vegetation type, temperature, soil moisture,
precipitation, and fertilizer emissions. Emissions of NO\textsubscript{x} from lightning are linked to deep convection following the parameterization of Price and Rind [1992] and are scaled globally as described by Murray et al. [2012] to match OTD/LIS climatological observations of lightning flashes. The stratospheric source of NO\textsubscript{x} (=NO\textsubscript{3}+HNO\textsubscript{3}) utilizes monthly climatological 3-D production and loss rates from the Global Modeling Initiative (GMI) model [Allen et al., 2010], which captures the formation of the polar vortex and PSC sedimentation [Murray et al., 2012].

For this work, GEOS-Chem version v9-01-01 was run at 2\textdegree x2.5\textdegree horizontal resolution with 72 hybrid vertical levels using GEOS-5 meteorology from May 2009 to May 2010. The model was spun up for six months prior to May 2009. There are no sub-surface (snow) layers in GEOS-Chem and the three lowest vertical levels are each roughly 100 meters in height above Antarctica. The boundary layer in GEOS-Chem is calculated using a parameterization involving the bulk Richardson number with surface friction, a turbulent velocity scale, and non-local fluxes of heat and moisture [Holtlag and Boville, 1993] as implemented by Lin and McElroy [2010]. The mixing of emissions, dry deposition, and concentrations of individual species within the boundary layer are determined by static instability. In a stable boundary layer, the local scheme based on eddy diffusivity-theory is used, and the mixing is weak. In an unstable boundary layer, boundary layer mixing is triggered by large eddies. Average boundary layer mixing ratios (ppbv) of species reported in this study (e.g., NO\textsubscript{3}, NO\textsub{x}, OH, O\textsubscript{3}) are mixing ratios in the lowest vertical grid box (total height ~ 100 m).

Figure 1 illustrates the nitrogen recycling associated with snow NO\textsubscript{3} photolysis as included in the model. The total flux of snow-sourced NO\textsubscript{x} from the snow, \( F_{\text{NOx}} \) (molec cm\textsuperscript{-2} s\textsuperscript{-1}), is calculated using the wavelength-dependent absorption cross-section for NO\textsubscript{3} photolysis (\( \sigma_{\text{NO3}} \), cm\textsuperscript{2} molec\textsuperscript{-1}), the temperature (T)- and pH-dependent quantum yield for NO\textsubscript{3} photolysis (\( \phi \), molec photon\textsuperscript{-1}), the depth- and wavelength-dependent actinic flux in the snow photic zone (\( I \), photons cm\textsuperscript{-2} s\textsuperscript{-1} nm\textsuperscript{-1}), and the average NO\textsubscript{3} concentration (\( [\text{NO3}] \), molec cm\textsuperscript{-3}) over the depth of integration. \( F_{\text{NOx}} \) is calculated in E7 and converted into units of ng N m\textsuperscript{-2} yr\textsuperscript{-1} in E8 and E9.

\[
F_{\text{NOx}} = \int_{\lambda_0}^{\lambda_{\text{e}}} \int_{z_{\text{e}}}^{z_{\text{p}}} \sigma_{\text{NO3}}(\lambda) \cdot \phi(T, pH) \cdot I(\lambda, z) \cdot [\text{NO3}^-](z) \, d\lambda \, dz, \quad \text{E7}
\]

In E7, \( \sigma_{\text{NO3}} \) is from Burley and Johnston [1992]. The quantum yield from Chu and Anastasio [2003] assuming T=244K and pH=5 is used for the base case scenario and \( \phi \) from Zhu et al. [2010] is used for sensitivity studies. The actinic flux (\( I \)) is integrated from the snow surface (\( z_{\text{e}} \)) to the depth of the photic zone (\( z_{\text{p}} \)). The snow photic zone is defined as three times the e-folding depth of ultraviolet (UV) actinic flux in snow (\( z_{\text{e}} \)), where 1 e-folding depth is \( z_{\text{e}} \). Below \( z_{\text{e}} \), more than 95% of the radiation has been attenuated and minimal photochemistry occurs. The flux of snow-sourced NO\textsubscript{x} is integrated over several ultraviolet wavelength bands (298-307 nm, 307-312 nm, 312-320 nm, 320-345 nm), which are then summed to calculate total \( F_{\text{NOx}} \) from the photolysis of snow NO\textsubscript{3} between \( \lambda = 298-345 \) nm. We assume that all NO\textsubscript{x} formed in E7 is immediately desorbed into the gas-phase and transported from the LLR to the interstitial air and then into the overlying boundary layer [Zatko et al., 2013].
2.1.2 Calculating Radiative Transfer in Snow

A 2-stream, plane parallel snowpack actinic flux parameterization based on a 4-stream radiative transfer model [Grenfell, 1991] was developed and described in detail in Zatko et al. [2013] and has been implemented into GEOS-Chem for the purposes of this study. The parameterization is simple, broadly applicable, and allows for variation in snow and sky properties (e.g., solar zenith angle, cloud fraction) over time. Ice grains are assumed to be spherical in shape and light-absorbing impurities (LAI), including black carbon, brown carbon, dust, and organics, are assumed to be homogeneously distributed throughout the snow and always external to the ice grain. The snowpack actinic flux parameterization is used to calculate the UV actinic flux (photons cm\(^{-2}\) s\(^{-1}\) nm\(^{-1}\)) and the mean austral summer (DJF) e-folding depths (cm) across Antarctica (Figure 3a), which are both needed to calculate \(F_{NOx}\). The snowpack actinic flux parameterization is most sensitive to radiation equivalent mean ice grain radii \(r_e\) and insoluble LAI in snow [Zatko et al., 2013]; higher concentrations of LAI in the snow and smaller \(r_e\) lead to shallower e-folding depths \(z_e\). Field and satellite measurements suggest significant increases in surface \(r_e\) throughout austral summer in Antarctica [Jin et al., 2008, Klein, 2014]. The \(r_e\) and snow density values used in this study are from observations reported in Gallet et al. [2011] and Klein [2014] and range from 86-360 \(\mu\)m and 260-360 kg m\(^{-3}\), respectively. The mean Dome C vertical \(r_e\) profile from Gallet et al. [2011] is applied across Antarctica for all seasons except austral summer. During austral summer, larger surface \(r_e\) values are incorporated across all of Antarctica to simulate the rapid surface \(r_e\) growth reported in Klein [2014].

The concentration of black carbon (BC) in the model (Figure 3b) is calculated by scaling observed BC concentrations \(C_{BC}\) at Vostok [Grenfell et al., 1994] by the modeled annual average snow accumulation rates (kg m\(^{-2}\) yr\(^{-1}\)) from GEOS-Chem. However, high accumulation rates in coastal regions (700 kg m\(^{-2}\) yr\(^{-1}\)) lead to unrealistically low \(C_{BC}\). The minimum \(C_{BC}\) values used in the model are 0.08 ng g\(^{-1}\), which is comparable to the \(C_{BC}\) values measured in high snow accumulation rate regions in Antarctica, such as in the East Antarctic sea ice zone (0.1 ng g\(^{-1}\)) [Bisiaux et al., 2012, Zatko and Warren, 2015]. Insoluble non-black carbon species (nonBC) including dust, brown carbon, and organics, are responsible for the majority (up to 89% at \(\lambda=305\) nm) of the absorption of radiation at UV wavelengths [Zatko et al., 2013] in snow. These nonBC species and their concentrations have not been well quantified in snow. Based on observations reported in Zatko et al. [2013], we scale UV-absorption by insoluble nonBC to the absorption by insoluble black carbon in snow by assuming that at \(\lambda=650-700\) nm, which is a wavelength range where black carbon dominates absorption, insoluble black carbon is responsible for 70% of the particulate absorption. We also assume that nonBC material has an absorption Ångstrom exponent of 5 [Doherty et al., 2010].

We neglect the influence of soluble light absorbers in the snow and only consider the influence of insoluble LAI on calculations of actinic flux profiles in snow. To determine whether soluble LAI contribute significantly to light-absorption in the snow, we calculate the total extinction coefficient for insoluble BC, insoluble nonBC, and soluble LAI following section 2.1 of Zatko et al. [2013] and using the absorption coefficients for
soluble material in snow reported in Beine et al., [2011] in northern Alaska. To our knowledge, observations of soluble light-absorbing impurities in Antarctic snow are unavailable. We use soluble LAI observations from the Arctic to provide a general estimate of the importance of soluble LAI in polar snow. The absorption coefficients (0.028 m$^{-1}$ at $\lambda=307$ nm) from Beine et al. [2011] are identical to the extinction coefficients because it is assumed that there is no scattering by soluble species. Insoluble $C_{BC}$ (9 ng g$^{-1}$) from Barrow, Alaska [Doherty et al., 2010] were used to calculate extinction coefficients for BC and nonBC material and therefore the amount of nonBC absorption in the UV and near-visible wavelengths following Zatko et al. [2013]. Insoluble nonBC material is responsible for 9-14 times more absorption than soluble material in the wavelength range $\lambda=298-345$ nm. Insoluble BC material is responsible for 1.5-10 times more absorption than soluble material in the wavelength range $\lambda=298-345$ nm. The extinction coefficient is not influenced by the addition of a soluble absorber because scattering by snow grains dominates the extinction in snow. The effective albedo of single scattering is increased by 6-15% when soluble absorbers are included. The resulting change in $z_e$ is at most 0.5 cm, which represents an increase of 4-9% in the wavelength region $\lambda=298-345$ nm.

### 2.1.3. Calculating NO$_3^-$ Concentrations in Snow

The median value of sub-surface (varied depth resolution) snow NO$_3^-$ concentrations from the ITASE campaign (60 ng g$^{-1}$) [Bertler et al., 2005] is used for modeled sub-surface (from 2-cm depth to the depth of the snow photic zone, $z_{ph}$) snow NO$_3^-$ concentrations ($[NO_3^-]_{bot}$) across all of Antarctica. Although there is a large variation in snow NO$_3^-$ concentrations from observations collected during the ITASE campaign (Figure 3d), there is no clear spatial pattern. Since NO$_3^-$ concentrations in the top 2 cm of snow are up to 10 times higher than NO$_3^-$ concentrations below 2-cm depth, the NO$_3^-$ concentrations in the top 2 cm of snow ($[NO_3^-]_{top}$) are calculated by enhancing $[NO_3^-]_{bot}$ by a factor of 6, the median of observed NO$_3^-$ enhancement factors ($EF$) in the top 2 cm of snowpack [Dibb et al., 2004, Erbland et al., 2013, Frey et al., 2009, Mayewski and Legrand, 1990, Rothlisberger et al., 2000]. Since NO$_3^-$ concentrations are enhanced by a factor of 6 in the top 2 cm of snow, an equal amount of NO$_3^-$ has been removed from the remainder of the photic-zone depth to maintain mass balance of nitrate within the snow column.

As mentioned in the introduction, the measured quantum yields for the dominant NO$_3^-$ photolysis pathway (E1) range from 0.003 molec photon$^{-1}$ [Chu and Anastasio, 2003] to 0.6 molec photon$^{-1}$ [Zhu et al., 2010] at T=253K. A higher fraction of NO$_3^-$ was likely present on ice surfaces in the Zhu et al. [2010] study compared to the Chu and Anastasio [2003] study due to the different sample preparation methods, and likely explains the 3 order-of-magnitude difference in quantum yields. This interpretation suggests NO$_3^-$ on the surface of ice grains is much more photolabile compared to NO$_3^-$ embedded within ice grains, consistent with results from Meusinger et al. [2014]. In this study, we assume that NO$_3^-$ that is wet deposited to the snow surface is more likely to be embedded in the interior of a snow grain compared to NO$_3^-$ that is dry deposited to the surface of the snow grain, which is a simplistic scheme designed to take nitrate recombination chemistry into account. To simulate this effect in an idealized snowpack, we scale snow NO$_3^-$ concentrations by the fraction of dry deposition relative to total (wet + dry) deposition to
the Antarctic snow surface, assuming that only the fraction of dry deposited NO$_3^-$ is photolabile ($F_p$). The degree of migration of NO$_3^-$ within a snow grain after deposition due to snow metamorphism is unknown, which may influence the photolability of NO$_3^-$ [Domine and Shepson, 2002]. Snow NO$_3^-$ concentrations scaled by $F_p$ are shown in Figure 3d.

Other modeling studies have attempted to calculate the fraction of photolabile NO$_3^-$ in snow by estimating the concentration of NO$_3^-$ contained within the liquid-like region (LLR) on the surface of ice grains (e.g., Thomas et al., 2012). In this work, we do not explicitly calculate NO$_3^-$ photolysis within the LLR because there are still many unknowns about the LLR [Domine et al., 2013], including the distribution of NO$_3^-$ between the bulk snow and the LLR. This distribution is better understood for some species, such as chloride [Cho et al., 2002], but it is unclear if NO$_3^-$ behaves similarly. In this study, we have assumed that all NO$_3^-$ formed in the LLR is transferred to the boundary layer, which may lead to overestimates in the modeled $F_{NOx}$ values presented in this study. The quantum yield for NO$_3^-$ photolysis is dependent on the location of NO$_3^-$ in snow, and although there are uncertainties surrounding the location of NO$_3^-$ in snow, in this study we use the full range of measured quantum yields to provide bounds for the amount of NO$_3^-$ produced from snow NO$_3^-$ photolysis.

**2.2. Model Sensitivity Studies**

Due to uncertainties in our understanding of snow photochemistry [Domine et al., 2013], we perform a variety of model sensitivity studies, as shown in Table 3. The quantum yield is varied from 0.002 molec photon$^{-1}$ (corresponding to $T=244$ K) [Chu and Anastasio, 2003] to 0.6 molec photon$^{-1}$ [Zhu et al., 2010]. Snow NO$_3^-$ concentrations below 2 cm ($[NO_3^-]_{bot}$) are halved and doubled with respect to the base case scenario and the impact of scaling NO$_3^-$ concentrations by the fraction of photolabile NO$_3^-$ ($F_p$) is investigated. The NO$_3^-$ enhancement factor in the top 2 cm of snowpack is varied from 1 to 10, based upon a range of reported observations [Dibb et al., 2004, Frey et al., 2009, Mayewski and Legrand, 1990, Rothlisberger et al., 2000]. $C_{BC}$ is halved and doubled with respect to the base case scenario. The $r_e$ profiles are varied in three sensitivity studies to examine the influence of $r_e$ on the model-calculated mean austral summer (DJF) flux of snow-sourced NO$_x$ ($F_{NOX}$). The bulk extinction coefficient for snow ($K_{ext,\text{snow}}$) is increased and decreased by 20% with respect to the base case scenario because Libois et al. [2013] suggest that the spherical snow grain assumption overestimates e-folding depths by a factor of 1.2. These sensitivity studies are used to provide estimates of the influence of these parameters on $F_{NOX}$ throughout the Antarctic continent.

**2.3. Estimating the Impact of Snow NO$_3^-$ Photolysis on Boundary Layer Chemistry and Ice-Core NO$_3^-$ Records**

Nitrate photolysis, followed by oxidation, recycling, and redistribution of snow-sourced NO$_x$, influences both boundary layer chemistry and the concentration and isotopic signature of NO$_3^-$ that is ultimately preserved in ice-core records. The preservation of NO$_3^-$ in ice cores is most dependent on the amount of NO$_3^-$ lost from the snow through photolysis via transport of snow-sourced NO$_x$ away from the site of primary deposition.
The methods used to explore and quantify nitrogen recycling and photolysis-driven loss of \( \text{NO}_3^- \) in snow are described in the following sections.

### 2.3.1. Reactive Nitrogen Recycling Between the Air and Snow

The Nitrogen Recycling Factor (\( \text{NRF} \)) is a metric originally proposed by Davis et al. [2008] to quantify the degree of reactive nitrogen recycling in snow over 1 year. The \( \text{NRF} \) is calculated in E8:

\[
\text{NRF} = \frac{f_{\text{NO}_x}}{f_{\text{PRI}}} \quad \text{E8}
\]

In E8, \( f_{\text{NO}_x} \) (ng N m\(^{-2}\) yr\(^{-1}\)) is the annual sum of \( \text{NO}_x \) released from the snow and \( f_{\text{PRI}} \) (ng N m\(^{-2}\) yr\(^{-1}\)) is the annual sum of primary \( \text{NO}_3^- \) deposited to the snow. Davis et al. [2008] use the \( \text{NRF} \) to describe nitrogen recycling on both macro-scale (e.g., across the East Antarctic plateau) and micro-scale (e.g., the number of times one molecule of \( \text{NO}_3^- \) is recycled) levels. An \( \text{NRF} \) greater than 1 suggests that multiple nitrogen recycling events occur in the snow. \( \text{NRF} \) represents the average, or “bulk” degree of nitrogen recycling in snow because this global modeling study cannot resolve the degree of nitrogen recycling on a molecular level in the snow; some \( \text{NO}_3^- \) molecules may never be photolysed while other \( \text{NO}_3^- \) molecules may be photolysed and recycled many times greater than \( \text{NRF} \).

The \( \text{NRF} \) has implications for boundary layer chemistry because the continual re-emission of \( \text{NO}_x \) enhances the effective concentration of \( \text{NO}_x \) in the boundary layer [Davis et al., 2008]. Additionally, nitrogen recycling between the air and snow may alter the preservation of \( \text{NO}_3^- \) in ice-core records.

### 2.3.2. Export of Snow-sourced Nitrate Away from the Original Site of Photolysis

Once snow-sourced \( \text{NO}_x \) is emitted to the atmosphere, it is subject to transport away from the original site of photolysis. If snow-sourced \( \text{NO}_x \) is oxidized to \( \text{HNO}_3 \) and re-deposited back to the snow surface, then there is no net photolysis-driven loss of \( \text{NO}_3^- \) from the snow. However, if some of the snow-sourced \( \text{NO}_x \) is transported away from the site of primary deposition, there is a net photolysis-driven loss of \( \text{NO}_3^- \) from the snow. The fraction of total \( \text{NO}_3^- \) (photolabile + non-photolabile) lost from the snow driven by photolysis (\( f \)) is calculated in E9:

\[
f = \left( \frac{F_R}{F_{\text{NO}_x}} \right) \tau_2 - 1 \right) \cdot F_p \quad \text{E9}
\]

In E9, negative values of \( f \) represent loss of \( \text{NO}_3^- \) from the snow and positive values of \( f \) represent gain of \( \text{NO}_3^- \) to the snow. In E9, \( F_R \) (ng N m\(^{-2}\) yr\(^{-1}\)) is the total annual flux of recycled \( \text{NO}_3^- \) to the snow surface and \( F_{\text{NO}_x} \) (ng N m\(^{-2}\) yr\(^{-1}\)) is the total annual flux of \( \text{NO}_x \) released from the snow. \( F_R \) is calculated by subtracting the depositional flux of \( \text{NO}_3^- \) from a model run without snow photochemistry from the depositional flux of \( \text{NO}_3^- \) from a model run with snow photochemistry. The ratio of \( F_R \) to \( F_{\text{NO}_x} \) represents the fraction of photolabile \( \text{NO}_3^- \) remaining in the snow after 1 year. As long as \( \text{NO}_3^- \) remains in the photic zone, \( \text{NO}_3^- \) can continually be lost from the snow by photolysis-driven processes.

The preservation of \( \text{NO}_3^- \) in ice cores is dependent on the fraction of \( \text{NO}_3^- \) lost from the snow through photolysis during the entire time that \( \text{NO}_3^- \) remains in the photic zone.
Provided that there are no major changes in parameters that influence snow photochemistry (e.g., LAI, overhead ozone abundance) from year to year, the fraction of photolabile NO$_3^-$ lost from the snow over 1 year will be stable from year to year.

\[ \tau_z (E10) \text{ represents the number of years that NO}_3^- \text{ remains in the photic zone (} \tau_z \text{, years)} \]

and in E9, \( \tau_z \) accounts for the loss of NO$_3^-$ that occurs during the entire time that it remains in the photic zone. When NO$_3^-$ remains in the photic zone for less than a year (\( \tau_z < 1 \)), \( \tau_z \) in E9 is set equal to 1. \( \tau_z \) is calculated according to E10, where both the depth of the photic zone (cm) and the total annual snow accumulation (\( \alpha_r \) cm yr$^{-1}$) are considered.

\[ \tau_z = \frac{ze}{\alpha_r}, \quad \text{E10} \]

In E10, \( \tau_z \) (cm) is 1 e-folding depth of UV actinic flux and is used instead of \( z_{3e} \) because 87-91% of snow-sourced NO$_x$ is produced within the top 1 e-folding depth. To convert total annual snow accumulation rate from kg m$^{-2}$ yr$^{-1}$ to cm, a typical snow density for Antarctica (0.36 g cm$^{-3}$) [Grenfell et al., 1994] is assumed. \( \tau_z \) is the minimum number of years on average that NO$_3^-$ remains in the top one-third of the snow photic zone before burial beneath because nitrogen recycling, which effectively redistributes NO$_3^-$ upwards in the snow, is not factored into E10. \( \tau_z \) thus represents the lifetime of NO$_3^-$ in snow in an average sense and does not resolve photolysis and recycling of individual NO$_3^-$ molecules.

In E9, \( \left( \frac{F_R}{F_{NOx}} \right)^{\tau_z} - 1 \) represents the fraction of photolabile NO$_3^-$ lost from the snow through photolysis. This fraction is multiplied by \( F_p \) to calculate the fraction of total (photolabile + non-photolabile) NO$_3^-$ lost from the snow through photolysis (f). If \( f \) is 0, then all snow-sourced NO$_x$ is redeposited to the snow and there is no net loss of NO$_3^-$. \( f \) is also 0 if the net export of snow-sourced NO$_x$ away from the site of original photolysis is balanced by net import of snow-sourced NO$_x$ from other Antarctic locations. If \( f \) is between -1 and 0, the export of local snow-sourced NO$_x$ is higher than the deposition of snow-sourced NO$_x$ from elsewhere in Antarctica, resulting in net photolysis-driven loss of NO$_3^-$ from the snow. If \( f \) is greater than 0, the export of local snow-sourced NO$_x$ is lower than the deposition of snow-sourced NO$_x$ from elsewhere in Antarctica, resulting in net photolysis-driven gain of NO$_3^-$ to the snow.

\( f \) is used to calculate the enrichment in ice-core \( ^{15}\text{N(NO}_3^-) \) due solely to the impact of photolysis-driven loss of NO$_3^-$ in snow. We use a Rayleigh fractionation equation used to calculate \( ^{15}\text{N(NO}_3^-) \) [Blunier et al., 2005]:

\[ ^{15}\text{N(NO}_3^-) = ^{15}\text{N(NO}_3^-)_{air} \cdot (1 + f)^\epsilon - 1 \quad \text{E11} \]

In E11, \( ^{15}\text{N(NO}_3^-)_{air} \) is the annual-averaged \( ^{15}\text{N} \) value of boundary layer NO$_3^-$ and \( \epsilon \) is the fractionation constant (-47.9‰ [Berhanu et al., 2014]). In this work, we set \( ^{15}\text{N(NO}_3^-)_{air} \) equal to 0‰ to investigate the enrichment in \( ^{15}\text{N(NO}_3^-) \) only from photolysis-driven loss of NO$_3^-$ from snow.
3. Results and Discussion

3.1. Parameters that Influence $F_{NOX}$ and its Spatial Redistribution

Figure 2a shows modeled total annual snow accumulation rates from GEOS-Chem (kg m$^{-2}$ yr$^{-1}$) along with estimated total annual snow accumulation rates (kg m$^{-2}$ yr$^{-1}$) in Antarctica [Erbland et al., 2013, Fegyveresi et al., 2011, Grenfell et al., 1994], ranging from 10-700 kg m$^{-2}$ yr$^{-1}$. The rapid decrease in snow accumulation rate from the coast to the top of the East Antarctic plateau is attributed to increased distance from the ocean (moisture source) and increased elevation. Figure 2b shows modeled annual mean surface wind divergence from May 2009 to May 2010. Figure 2b and Antarctic Mesoscale Prediction System surface wind output [Figure 3 in Parish and Bromwich, 2007] indicate that the large-scale airflow pattern in Antarctica flows from the East Antarctic plateau downslope towards the coast. There are three major regions of wind convergence in Antarctica, located near the Ross, Ronne, and Amery ice shelves.

Figure 3a shows the mean austral summer (DJF) e-folding depth of UV actinic flux in snow ($z_e$). $z_e$ ranges from 24 to 69 cm, with the shallowest depths on the East Antarctic plateau, due to the relatively high $C_{BC}$ values (Figure 3b). Higher $C_{BC}$ in snow results in a shallower $z_e$ because UV absorption in snow is enhanced as the concentration of LAI increases [Zatko et al., 2013]. In this study, coastal grid boxes are a mixture of water, sea ice, and snow-covered surfaces, and since actinic flux profiles are only calculated for snow-covered surfaces, the average $z_e$ in coastal grid boxes are artificially shallow. Observations of e-folding depths across Antarctica are limited. France et al. [2011] report $z_e$ from near-station snow at Dome C ranging from 9-20 cm at 350 nm, which agree well with our modeled $z_e$ [Zatko et al., 2013]. There are no $z_e$ observations in Antarctica from snow without station contamination, which is representative of the majority of snow in Antarctica. Zatko et al. [2013] calculate $z_e$ of 38 cm ($\lambda=298-345$ nm) for remote Dome C snow due to lower $C_{BC}$ far away from station contamination. The $z_e$ for remote Dome C snow in this study (48 cm) is a factor of 1.3 larger than reported in Zatko et al. [2013] because larger radiation equivalent ice grain radii ($r_e$) are used during austral summer (based on Klein [2014]), and larger $r_e$ grains lead to deeper $z_e$.

Figure 3b shows snow $C_{BC}$, ranging from 0.08 to 0.6 ng g$^{-1}$. Black carbon observations at WAIS-Divide [Bisiaux et al. 2012], Siple Dome [Chylek et al., 1992], Vostok [Grenfell et al., 1994], South Pole [Warren and Clarke, 1990], and Dome C [Warren et al., 2006] are included in Figure 3b. The highest $C_{BC}$ values in Antarctica are found on the East Antarctic plateau (0.6 ng g$^{-1}$) and the spatial pattern of $C_{BC}$ is governed by the snow accumulation rate; higher snow accumulation rates dilute $C_{BC}$ [Doherty et al., 2013]. The modeled boundary layer black carbon concentrations are relatively uniform across Antarctica (0.1-0.6 pptv) because the majority of black carbon reaches Antarctica through long-range transport (with the exception of local production from Antarctic research stations).

Figure 3c shows the fraction of dry-deposited NO$_3^-$ compared to total deposited NO$_3^-$ across Antarctica. The ratio of dry deposition to total deposition ranges from 0 to 0.2 in coastal Antarctica and from 0.95 to 0.99 on the East Antarctic plateau. Figure 3d shows...
the modeled annual mean sub-surface (from 2-cm depth to the bottom of the photic zone, 
z_{\text{sub}}) snow NO$_3^-$ concentrations ([NO$_3^-$]$_{\text{sub}}=60$ ng g$^{-1}$) scaled by $F_p$ compared to averaged multi-year NO$_3^-$ observations from the ITASE campaign [Bertler et al., 2005] and mean asymptotic (sub-photic zone) NO$_3^-$ mixing ratios from Erbland et al. [2013] and Shi et al. [2014].

3.2. Model Sensitivity Studies

Table 3 shows the dependence of mean austral summer (DJF) $\overline{F_{\text{NOX}}}$ on $\phi$, [NO$_3^-$]$_{\text{bot}}$, $C_{BC}$, $F_p$, $K_{\text{ext,0t}}$, $r_e$. The sensitivity study results are compared to $\overline{F_{\text{NOX}}}$ from the base case scenario, which is also described in Table 3. $\overline{F_{\text{NOX}}}$ is most sensitive to $\phi$, which increases $\overline{F_{\text{NOX}}}$ by up to a factor of 330 compared to the base case scenario. The second most influential parameter is the concentration of photolabile NO$_3^-$ ([NO$_3^-$]$_{\text{bot}}$ and $F_p$). Assuming that all NO$_3^-$ is photolabile ($F_p=1$) increases $\overline{F_{\text{NOX}}}$ by up to a factor of 7.4 (at the coasts) with respect to the base case scenario. Variations in $r_e$, $K_{\text{ext,0t}}$, $EF$, and $C_{BC}$ influence $\overline{F_{\text{NOX}}}$ by up to a factor of 1.3 compared to the base case scenario. Appendix A shows model-calculated mean austral summer (DJF) $\overline{F_{\text{NOX}}}$ throughout Antarctica for the sensitivity studies described in Table 3. The quantum yield for NO$_3^-$ photolysis and the concentration of photolabile NO$_3^-$ are likely related to one another. This highlights the need for field, laboratory, and modeling studies to investigate factors influencing these parameters, such as the location of NO$_3^-$ in ice grains.

Figure 4 shows model-calculated mean austral summer (DJF) $\overline{F_{\text{NOX}}}$ for several sensitivity studies compared to previously reported $F_{\text{NOX}}$ at Neumayer [Jones et al., 2001], Halley [Bauguitte et al., 2012, Jones et al., 2011], South Pole [Onceley et al., 2004, Wang et al., 2008, Zatko et al., 2013], Dome C [Frey et al., 2013, Zatko et al., 2013], and WAIS-Divide [Masclin et al., 2013]. The flux of snow-sourced NO$_x$ is overestimated by three orders of magnitude compared to observations when $\phi$ from Zhu et al. [2010] is used to calculate $\overline{F_{\text{NOX}}}$. In contrast, model-calculated $\overline{F_{\text{NOX}}}$ using $\phi$ from Chu and Anastasio [2003] provides better agreement with the observations, but is lower than the observations by 14-78%. Use of the fraction of dry-deposited NO$_3^-$ ($F_p$) to scale the concentration of photolabile NO$_3^-$ lowers $\overline{F_{\text{NOX}}}$ by up to 85% along the coast, but has little impact on the East Antarctic plateau due to the high fraction of dry deposited NO$_3^-$ (Figure 3c). The spatial patterns of $\overline{F_{\text{NOX}}}$ in Figure 4 are largely governed by the depth of the photic zone ($z_{\text{v}}$) across Antarctica (Figure 3a), which are inversely related to LAI concentrations. The spatial patterns of $\overline{F_{\text{NOX}}}$ are also influenced by the fraction of photolabile NO$_3^-$, which is lowest at the coast in the model.

Previously reported $F_{\text{NOX}}$ values are calculated from measurements of NO$_x$ concentration gradients and turbulent diffusivity [Jones et al., 2001, 2011, Frey et al., 2013] or calculated based on observed NO gradients and assuming photochemical steady-state [Onceley et al., 2004], by incorporating observations into 1-D multi-phase chemistry models [Bauguitte et al., 2012, Boxe and Saiz-Lopez., 2008, Wang et al., 2008], or by using depth-integrated $F_{\text{NOX}}$ calculations similar to E7 [France et al., 2011, Masclin et al., 2013, Zatko et al., 2013]. Observations of $F_{\text{NOX}}$ represent either noontime maxima [Bauguitte et al., 2012, Frey et al., 2013, Jones et al., 2001, Zatko et al., 2013], daily averages [Jones et al., 2011, Masclin et al., 2013], or averages over the duration of the
field campaign [Onceley et al., 2004, Wang et al., 2008] (see Table 4 in Masclín et al., [2013]). There is a wide range of reported $F_{\text{NOx}}$ at many of these locations; 2.4-17x10$^8$ molec cm$^{-2}$ s$^{-1}$ at Dome C [France et al., 2011, Frey et al., 2013, Zatko et al., 2013], 3.2-22x10$^8$ molec cm$^{-2}$ s$^{-1}$ at South Pole [Onceley et al., 2004, Wang et al., 2008, Zatko et al., 2013], 2.4-12.6x10$^8$ molec cm$^{-2}$ s$^{-1}$ at Halley [Bauguitte et al., 2012, Jones et al., 2011], 2.1-3.3x10$^8$ molec cm$^{-2}$ s$^{-1}$ at Neumayer [Jones et al., 2001], 42.5x10$^8$ molec cm$^{-2}$ s$^{-1}$ at WAIS-Divide [Masclín et al., 2013].

Regardless of the time period that the $F_{\text{NOx}}$ observations represent, all $F_{\text{NOx}}$ values for each location are averaged together and presented in Figure 4c and Figure 4d. Unfortunately, the actinic flux parameterization used here [Zatko et al., 2013] is unable to resolve $F_{\text{NOx}}$ directly at the coast because coastal grid boxes are a mixture of ocean, sea ice, and land, which prevents direct comparison of $F_{\text{NOx}}$ at Halley and Neumayer. Since the flux of snow-sourced NO$_x$ is overestimated by three orders of magnitude compared to observations when the quantum yield from Zhu et al. [2010] is used, all following results (Figures 5-10) are calculated using the Chu and Anastasio [2003] quantum yield ($\phi = 1.3x10^{-3}$). Additionally, to approximate the potential spatial variability in the fraction of NO$_3^-$ that is photolabile, we scale snow NO$_3^-$ by $F_\phi$ in Figures 5-10. Figure 4d shows the $F_{\text{NOx}}$ values, ranging from 0.5-7.8x10$^8$ molec cm$^{-2}$ s$^{-1}$, used in Figures 5-10. All the other parameters used to calculate $F_{\text{NOx}}$ in following sections and in Figures 5-10 are described in the base-case scenario in Table 3.

### 3.3. Redistribution and Recycling of Reactive Nitrogen Across Antarctica

Figure 5a shows the total annual depositional flux of primary NO$_3^-$ ($F_{\text{PRI}}$), which ranges from 0.9-35x10$^5$ ng N m$^{-2}$ yr$^{-1}$ and is highest at the coasts due to its relative proximity to NO$_x$-source regions in lower latitudes. An adjoint modeling study by Lee et al. [2014] suggests that boundary layer NO$_3^-$ abundance in Antarctica is dominated by NO$_3^-$ transport to Antarctica originating from NO$_x$ emissions from 25-65°S during austral winter and by thermal decomposition of peroxyacetyl nitrate (PAN) as it descends from the free troposphere in all other seasons. Figure 5b shows the total annual depositional flux of recycled NO$_3^-$ ($F_R$), which ranges from 0.7-31x10$^5$ ng N m$^{-2}$ yr$^{-1}$ and is also highest at the coasts due to transport from the Antarctic interior by katabatic winds. $F_{\text{PRI}}$ and $F_R$ are comparable in magnitude to the total annual flux of snow-sourced NO$_x$ to the atmosphere ($F_{\text{NOX}}$), which ranges from 2-23x10$^5$ ng N m$^{-2}$ yr$^{-1}$ (Figure 4d). Figure 5c shows that recycled nitrogen ($F_R$) is the dominant form of NO$_3^-$ deposition across Antarctica, except along the coastline where it represents as little as 11% of the deposition flux, and is most important in regions of wind convergence such as the Ronne, Ross, and Amery ice shelves.

To further investigate the role that wind patterns have on the redistribution of NO$_3^-$ across Antarctica, we alternately turn off the upward $F_{\text{NOx}}$ in East Antarctica and in West Antarctica to examine the influence of each region on NO$_3^-$ redistribution across Antarctica. Figure 6 compares $F_R$ in these sensitivity studies to $F_R$ in the base case scenario. The large reduction in $F_R$ when $F_{\text{NOx}}$ is separately turned off in East and West Antarctica demonstrates that little snow-sourced NO$_3^-$ is transported between East and West Antarctica, likely due to the influence of the trans-Antarctic mountains on
atmospheric transport. However, recycled NO$_3^-$ is present in West Antarctica where $F_{NOx}$ has been turned off, suggesting that some snow-sourced NO$_3^-$ from East Antarctica is transported across the trans-Antarctic mountains likely due to the influence of katabatic winds originating from the East Antarctic plateau.

Figure 7 shows the Nitrogen Recycling Factor ($NRF$). Across Antarctica, $NRF$ ranges from 0 to 16, indicating that nitrogen is recycled multiple times over the course of 1 year across most of Antarctica, with the exception of the coasts. The spatial pattern of $NRF$ is governed by the flux of snow-sourced NO$_x$ to the atmosphere ($F_{NOx}$, Figure 4d), which is influenced by the depth of the photic zone ($z_p$) and the concentration of photolabile nitrate. The spatial pattern of $NRF$ is also dependent on $F_{PRI}$, which is highest at the coast and lowest on the East Antarctica plateau. $NRF$ values are lowest near the coast because the fraction of photolabile NO$_3^-$ is small and $F_{PRI}$ values are high. The maximum $NRF$ values occur partway up the plateau, corresponding to maximum $F_{NOx}$ values. Erbland et al. [2015] use a multi-layer snow chemistry column model along with snow and atmospheric NO$_3^-$ concentration and isotopic measurements to estimate the $NRF$ at Dome C. The difference in model-estimates of nitrogen recycling at Dome C in Erbland et al. [2015] (4 recycling events) and in this study (9 recycling events) is at least partially due to the assumption in Erbland et al. that 20% of snow-sourced NO$_3^-$ is transported away from Dome C via katabatic winds. We use our global chemical transport modeling framework to calculate that 25% of snow-sourced NO$_3^-$ is transported away at Dome C, which is slightly larger than the assumption in Erbland et al. [2015]. Larger NO$_3^-$ export fractions will lead to larger loss of snow nitrate, which may also lead to a larger number of recycling events via transport and redeposition of snow-sourced NO$_x$ throughout East Antarctica. Davis et al. [2008] use estimates of atmospheric NO$_x$ overhead-column burdens and average NO$_x$ atmospheric lifetimes along with primary nitrogen deposition measurements from Legrand and Kirchner [1990] to estimate the $NRF$ in East Antarctica. Davis et al. [2008] estimate an $NRF$ of 1.8, which is roughly 3 to 6 times lower than the modeled East Antarctic $NRF$ values in this study ($NRF=5-10$), although Davis et al. state that their estimated $NRF$ value could be factors of 3 to 5 times higher due to uncertainties in primary nitrogen deposition estimates.

3.4. Impact of Reactive Nitrogen Recycling on Boundary Layer Chemistry

The height of the boundary layer will strongly influence the abundance of NO$_3^-$, reactive nitrogen oxides, and oxidants emitted or formed at or near the surface. At many Antarctic stations (e.g., Neumayer, South Pole, Dome C, Halley, Kohnen) there is a wide range of observed boundary layer heights during austral summer (10-600 m [Casasanta et al., 2014, Davis et al., 2004, Handorf, 1996, Jones et al., 2006, 2008, King et al., 2006, Kodama et al., 1985, Konig-Langlo et al., 1998, Neff et al., 2008, Oncley et al., 2004, Travouillon et al., 2008, Weller et al., 1999]), and although modeled boundary layer heights are not systematically biased in one direction compared to observations, they often do not agree well. Therefore, only the relative impacts of snow photochemistry on reactive nitrogen and oxidant abundances are compared in this study. The impact of snow photochemistry on boundary layer chemistry can be examined by considering factor changes in boundary layer NO$_x$, NO$_3^-$, OH, and O$_3$ mixing ratios between simulations with and without snow NO$_3^-$ photolysis. As shown in Figure 8, the inclusion of a snow
NO$_3$ source leads to factor increases in boundary layer mixing ratios of NO$_x$ from 7.0-31.6, gas-plus aerosol-phase nitrate from 3.9-38.1, OH from 3.6-6.7, and O$_3$ from 1.3-2.0. The largest factor increases are in West Antarctica, particularly near the Ross and Ronne ice shelves, where winds carrying photo-produced species converge. The surface transport pattern is especially important for the redistribution of the longer-lived species NO$_3^-$ and O$_3$. Other snow photochemical reactions mentioned in the introduction but not included in this modeling study will also impact oxidant abundances, but the effects of each photochemical reaction are not be additive due to the highly non-linear nature of oxidant cycling.

### 3.5. Implications for Ice-Core Records of Nitrate Concentrations and Isotopes

Figure 9a shows the minimum number of years that snow NO$_3^-$ remains in the photic zone on average, $\tau_z$ (E9). NO$_3^-$ remains in photic zone for 3 months near the Antarctic coasts and up to 7.5 years on the East Antarctic plateau before burial below the photic zone. The spatial pattern of $\tau_z$ is governed by the snow accumulation rate, both directly and indirectly through its influence on $C_{BC}$. The spatial pattern of $\tau_z$ is in agreement with the expectation that NO$_3^-$ remains in the photic zone the longest in areas with low snow accumulation rates.

Figure 9b shows the fraction of NO$_3^-$ gained or lost from the snow through photolysis ($f_{E11}$), which ranges from -0.99 to 0.21. The positive $f$ values indicate regions with net gain of NO$_3^-$ to the snow resulting from the spatial redistribution of NO$_3^-$ driven by snow photochemistry. In regions of convergence, such as over the Ronne Ice Shelf, and parts of the coast, there is a net gain of snow-sourced NO$_3^-$. There is a sharp gradient in $f$ between the plateau and the coast, with the largest loss of snow NO$_3^-$ on the East Antarctic plateau. On the East Antarctic plateau, most photolyzed NO$_3^-$ is transported away by katabatic winds, but along the coast, the photolysis-driven loss of NO$_3^-$ from the snow is minimal due to high snow accumulation rates and transport of snow-sourced NO$_3^-$ from the continental interior. The spatial pattern of $f$ is largely influenced by the number of years that NO$_3^-$ remains in the photolytic zone ($\tau_z$), the concentration of photolabile NO$_3^-$ ($F_{P}$), and wind patterns across Antarctica.

Figure 9c shows modeled enrichments in ice-core $\delta^{15}$N(NO$_3^-$) from photolysis-driven loss of NO$_3^-$ in snow, compared to sub-photonic zone $\delta^{15}$N(NO$_3^-$) observations from Erbland et al. [2013], Frey et al. [2009], Jarvis, [2008], Shi et al., [2014], and Sofen et al. [2014]. The $\delta^{15}$N(NO$_3^-$) values at Dome C and along the transect from Dumont d’Urville to Dome C are calculated asymptotic $\delta^{15}$N(NO$_3^-$) values from Erbland et al. [2013] and Frey et al. [2009], which are representative of snow depths well below the photic zone at Dome C. The $\delta^{15}$N(NO$_3^-$) values along the transect from Dome A towards Zhongshan are asymptotic $\delta^{15}$N(NO$_3^-$) values calculated in Shi et al. [2014]. The $\delta^{15}$N(NO$_3^-$) values at WAIS-Divide [Sofen et al., 2014] and South Pole [Jarvis, 2008] are average ice-core $\delta^{15}$N(NO$_3^-$) measurements from 1900-2000 CE, which are also representative of $\delta^{15}$N(NO$_3^-$) values well below the snow photonic zone. Model-calculated ice-core $\delta^{15}$N(NO$_3^-$) values range from 0$\%$ to 363$\%$. The modeled enrichments in ice-core $\delta^{15}$N(NO$_3^-$) values are generally higher than the sub-photonic zone $\delta^{15}$N(NO$_3^-$) observations presented in Figure 9c, however, boundary layer $\delta^{15}$N(NO$_3^-$) observations are negative in
both coastal [Morin et al., 2009, Savarino et al., 2007, Wagenbach et al., 1998] and continental [Erbland et al., 2013, Frey et al., 2009] Antarctica, making modeled δ\(^{15}\)N(NO\(_3^-\)) values biased high by up to ~40\% since we assume that the δ\(^{15}\)N of atmospheric nitrate (NO\(_3^-\) and HNO\(_3\)) deposited to the snow surface is always equal to 0\%. The modeled ice-core δ\(^{15}\)N(NO\(_3^-\)) values resulting from the photolysis-driven loss of snow nitrate are sensitive to the fractionation constant (ε). The fractionation constant is varied over the full range of values reported in Erbland et al [2013], Frey et al., [2009], and Shi et al. [2014]; an ε of ~90\% increases modeled ice-core δ\(^{15}\)N(NO\(_3^-\)) by a factor of 2 and an ε of ~10\% decreases modeled ice-core δ\(^{15}\)N(NO\(_3^-\)) by a factor of 5 across Antarctica. Both the modeled and observed δ\(^{15}\)N(NO\(_3^-\)) values show that δ\(^{15}\)N(NO\(_3^-\)) is most enriched on the East Antarctic plateau, where the fraction of NO\(_3^-\) lost from the snow through photolysis is highest.

3.6. Relationship Between Nitrogen Recycling and Photolytic-loss of NO\(_3^-\) in Snow

The degree of photolysis-driven loss of snow NO\(_3^-\) is determined by both rates of photolysis and transport patterns across the Antarctic continent. The spatial patterns of recycling (NRF, Figure 7) and loss (f, Figure 9b) differ across Antarctica and Figure 10 shows the relationship between f and NRF across Antarctica. The magnitude of nitrogen recycling and degree of photolysis-driven loss of snow NO\(_3^-\) are well correlated (r\(^2\) > 0.8, p< 0.001) in regions where NO\(_3^-\) remains in the photic zone for less than 3 years (τ\(_z\) < 3) (Figure 10a). The relationship between recycling and loss breaks down in locations where NO\(_3^-\) remains in the photic zone for more than 3 years (Figure 10b). The relationship between recycling and loss weakens with increasing τ\(_z\) because recycling of reactive nitrogen occurs at or near the surface only, while loss of NO\(_3^-\) occurs throughout the depth of snow photic zone. The number of years that NO\(_3^-\) remains in the snow photic zone (τ\(_z\), E10) is mainly dependent on snow accumulation rates and the concentrations of light-absorbing impurities in snow, which are partially governed by snow accumulation rates. In the present climate, τ\(_z\) less than 3 years corresponds to snow accumulation rates higher than 85 kg m\(^{-2}\) a\(^{-1}\).

4. Conclusions

We have incorporated the photolysis of snow NO\(_3^-\) into a global chemical transport model (GEOS-Chem) for the first time in order to calculate the flux and redistribution of nitrogen in Antarctic snowpack. An important goal of this study is to investigate the impact of snowpack NO\(_3^-\) photolysis on boundary layer chemistry and the preservation of NO\(_3^-\) concentration and isotopes in Antarctic ice cores.

The calculated flux of snow-sourced NO\(_3^-\) from Antarctic snow (0.5-7.8x10\(^8\) molec cm\(^2\) s\(^{-1}\)) is in general agreement with snow NO\(_3^-\)-flux observations when using a quantum yield for snow NO\(_3^-\) photolysis on the order of 10\(^{-3}\) molec photon\(^{-1}\) [Chu and Anastasio, 2003]. The flux of snow-sourced NO\(_3^-\) is overestimated by 2-3 orders of magnitude when the quantum yield from Zhu et al. [2010] is used along with various assumptions for the amount of photolabile NO\(_3^-\). The modeled spatial pattern of the flux of snow-sourced NO\(_3^-\) is determined by the patterns of light-absorbing impurity concentrations in snow and the fraction of photolabile NO\(_3^-\) across Antarctica. In the model, the spatial pattern of light-absorbing impurities is strongly influenced by snow accumulation rates and the
The Nitrogen Recycling Factor (NRF) ranges from 0.07 to 15.8, suggesting that nitrogen is recycled multiple times on average over the course of one year across all of Antarctica, except at the coasts where snow accumulation rates are high. Nitrate can remain in the photic zone for up to 7.5 years in Antarctic snow and is recycled multiple times (up to 57, on average) before burial beneath the photic zone in Antarctica. The fraction of NO$_3^-$ lost from the snow through photolysis ranges from -0.99 to 0.21, where negative values indicate net loss of NO$_3^-$ from the snow. Photolysis of snow NO$_3^-$ results in a net gain of NO$_3^-$ in parts of West Antarctica, such as near the Ronne Ice Shelf where winds converge. The fraction of NO$_3^-$ lost from the snow through photolysis is highest on the East Antarctic plateau (up to -0.99). The fraction of NO$_3^-$ lost from the snow through photolysis is used to calculate the enrichment in ice-core $\delta^{15}$N(NO$_3^-$) solely from photolysis-driven NO$_3^-$ loss in snow. The modeled enrichment in ice-core $\delta^{15}$N(NO$_3^-$) ranges from 0‰ to 363‰ and are in agreement with the broad-scale spatial patterns of observed sub-photonic zone $\delta^{15}$N(NO$_3^-$) observations. A significant relationship exists between nitrogen recycling and photolysis-driven loss of snow NO$_3^-$ when NO$_3^-$ remains in the photic zone for less than 3 years ($\tau_s < 3$), corresponding to a snow accumulation rate greater than 85 kg m$^{-2}$ a$^{-1}$ in the present day. Since the spatial variability of Antarctic ice-core $\delta^{15}$N(NO$_3^-$) is mainly determined by the fractional loss of snow NO$_3^-$, observations of $\delta^{15}$N(NO$_3^-$) in snow and ice can be used to estimate both the degree of recycling and loss of snow NO$_3^-$ in Antarctica as long as this condition is met. The relationship between recycling and loss can be useful for the interpretation of the oxygen isotopic composition of ice-core NO$_3^-$ (e.g., Sofen et al. [2014]). We note that the relationship between $\tau_s$ and snow accumulation rate may vary in different climates depending on the concentrations of light-absorbing impurities in snow [Geng et al., 2015].
shown here are broadly consistent with observations of the flux of NO\textsubscript{x} from the Antarctic snowpack and snow δ\textsubscript{15}N(NO\textsubscript{3}−), suggesting that the model captures the large-scale features of nitrogen recycling and loss across the Antarctic continent. Model sensitivity studies suggest that the flux of snow-sourced NO\textsubscript{x} and loss of snow NO\textsubscript{3}− is most sensitive to the quantum yield for NO\textsubscript{3}− photolysis and the concentration of photolabile NO\textsubscript{3}−, which are likely related to one another. We suggest that future field, laboratory, and modeling studies continue to focus on gaining a better understanding of the quantum yield for NO\textsubscript{3}− photolysis and the concentration of photolabile NO\textsubscript{3}−. Updated information about the quantum yield for NO\textsubscript{3}− photolysis and the concentration of photolabile NO\textsubscript{3}− in snow along with additional snow photochemical reactions can be incorporated into this modeling framework in the future, which will continue to improve our understanding of the impacts of snow photochemistry on boundary layer chemistry and the preservation of NO\textsubscript{3}− and other photochemically-active species in ice cores.

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Table 1. Glossary of variables used in this paper.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>nm</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\phi$</td>
<td>molec photon$^{-1}$</td>
<td>Quantum yield for NO$_3^-$ photolysis</td>
</tr>
<tr>
<td>$\sigma_{NO_3}$</td>
<td>cm$^2$</td>
<td>Absorption cross-section for NO$_3^-$ photolysis</td>
</tr>
<tr>
<td>$I$</td>
<td>photons cm$^{-2}$ s$^{-1}$ nm$^{-1}$</td>
<td>Actinic flux of UV radiation</td>
</tr>
<tr>
<td>$z_e$</td>
<td>cm</td>
<td>e-folding depth of UV actinic flux in snow</td>
</tr>
<tr>
<td>$z_{3e}$</td>
<td>cm</td>
<td>Depth of snow photic zone</td>
</tr>
<tr>
<td>$\alpha_r$</td>
<td>kg m$^{-2}$ yr$^{-1}$</td>
<td>Total annual snow accumulation rate</td>
</tr>
<tr>
<td>$C_{BC}$</td>
<td>ng g$^{-1}$</td>
<td>Annual mean snow black carbon concentration</td>
</tr>
<tr>
<td>$r_e$</td>
<td>$\mu$m</td>
<td>Radiation equivalent mean ice grain radii</td>
</tr>
<tr>
<td>$K_{ext_{bot}}$</td>
<td>cm$^{-1}$</td>
<td>Bulk extinction coefficient for snow</td>
</tr>
<tr>
<td>$[NO_3^+]_{top}$</td>
<td>ng g$^{-1}$</td>
<td>Mean NO$_3^-$ concentration in top 2 cm of snow</td>
</tr>
<tr>
<td>$[NO_3^+]_{bot}$</td>
<td>ng g$^{-1}$</td>
<td>Mean NO$_3^-$ concentration from 2-cm depth to the bottom of the snow photic zone</td>
</tr>
<tr>
<td>$EF$</td>
<td>unitless</td>
<td>NO$_3^-$ enhancement factor in top 2 cm of snow</td>
</tr>
<tr>
<td>$F_p$</td>
<td>fraction</td>
<td>Fraction of photolabile NO$_3^-$ in snow</td>
</tr>
<tr>
<td>$\Delta^{17}O(NO_3^-)$</td>
<td>%o</td>
<td>Oxygen isotopic composition of NO$_3^-$</td>
</tr>
<tr>
<td>$\delta^{15}N(NO_3^-)$</td>
<td>%o</td>
<td>Nitrogen isotopic composition of NO$_3^-$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>%o</td>
<td>Fractionation constant for NO$_3^-$ photolysis</td>
</tr>
<tr>
<td>$F_{NOX}$</td>
<td>molec cm$^{-2}$ s$^{-1}$</td>
<td>Mean austral summer flux of snow-sourced NO$_x$</td>
</tr>
<tr>
<td>$F_{NOx}$</td>
<td>ng N m$^{-2}$ yr$^{-1}$</td>
<td>Annual sum of snow-sourced NO$_x$ flux</td>
</tr>
<tr>
<td>$F_{PRI}$</td>
<td>ng N m$^{-2}$ yr$^{-1}$</td>
<td>Annual sum of primary NO$_3^-$ deposited to snow</td>
</tr>
<tr>
<td>$F_R$</td>
<td>ng N m$^{-2}$ yr$^{-1}$</td>
<td>Annual sum of recycled NO$_3^-$ to snow</td>
</tr>
<tr>
<td>$NRF_{yr}$</td>
<td>unitless</td>
<td>Metric to assess degree of nitrogen recycling in 1 year</td>
</tr>
<tr>
<td>$NRF_{\tau_z}$</td>
<td>unitless</td>
<td>Metric to assess degree of nitrogen recycling before NO$_3^-$ burial below snow photic zone</td>
</tr>
<tr>
<td>$\tau_z$</td>
<td>years</td>
<td>Years NO$_3^-$ remains in snow photic zone</td>
</tr>
<tr>
<td>$f$</td>
<td>fraction</td>
<td>Fraction of photolysis-driven loss of NO$_3^-$ from snow</td>
</tr>
</tbody>
</table>
Table 2. Value(s) of parameters used in the model.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value(s) used in model</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>0.002 molec photon$^{-1}$a</td>
<td>Chu and Anastasio [2003]</td>
</tr>
</tbody>
</table>
| $\sigma_{NO_3}^-$ | 2.7x10$^{-20}$ cm$^2$ ($\lambda$=298-307 nm)
                       2.4x10$^{-20}$ cm$^2$ ($\lambda$=307-312 nm)
                       1.9x10$^{-20}$ cm$^2$ ($\lambda$=312-320 nm)
                       2.3x10$^{-21}$ cm$^2$ ($\lambda$=320-345 nm) | Sander et al. [2006]            |
| $\varepsilon$ | -47.9‰                                                                           | Berhanu et al. [2014]           |
| $r_e$        | Jan: 332.0 µm$^{b}$
                       Dec-Feb: 198-332.0 µm$^b$
                       Mar-Nov: 86.0-332.0 µm$^b$     | Gallet et al. [2011]
                       Klein [2014]                   |
| $\rho_{\text{snow}}$ | 260-360 kg m$^{-3c}$                                                              | Gallet et al. [2011]            |
| $EF^d$       | 6$^a$                                                                               | Dibb et al. [2004]
                       Erbland et al. [2013]
                       Frey et al. [2009]
                       Mayewski and Legrand [1990]
                       Rothlisberger et al. [2000]    |
| $[NO_3^-]_{\text{bot}}$ | 60 ng g$^{-1c}$                                                                     | Bertler et al. [2005]           |

---

$^a$At temperature (T) = 244K

$b$ $r_e$ is varied vertically and temporally, but uniformly across Antarctica based on Gallet et al. [2011] and Klein [2014]. In January, $r_e$ is constant with depth (332 µm), in December and February, $r_e$ ranges from 198 µm at the snow surface to 332 µm at 300 cm depth, and from March to November, $r_e$ ranges from 86 µm at the surface to 360 µm at 300 cm depth.

$c$The mean vertical $\rho_{\text{snow}}$ profile from several Dome C snowpits are used in this study (see Figure 11 in Gallet et al. [2011]).

$d$Median of observed NO$_3^-$ enhancement factors.

$^e$Median of observed sub-surface snow NO$_3^-$ mixing ratios from the ITASE campaign.
Table 3. Dependence of mean austral summer (DJF) flux of snow-sourced NO$_x$ ($\overline{F}_{NOx}$) on quantum yield ($\phi$), the fraction of photolabile NO$_3^-$ ($F_p$), snow NO$_3^-$ concentrations below 2 cm ([NO$_3^-$]$_{bot}$), the radiation equivalent ice grain radius ($r_e$), the bulk snow extinction coefficient ($K_{ext_{bot}}$), the NO$_3^-$ concentration enhancement factor in the top 2 cm (EF), and snow black carbon concentration ($C_{BC}$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base case values$^a$</th>
<th>Values used in sensitivity studies</th>
<th>$\overline{F}_{NOx}$ range in sensitivity studies $(x10^8$ molec cm$^{-2}$ s$^{-1}$)</th>
<th>Corresponding Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantum yield ($\phi$)</td>
<td>0.002 molec photon$^{-1}$ $^b$</td>
<td>0.6 molec photon$^{-1}$</td>
<td>5-2600</td>
<td>Fig. 4a, b, c, d</td>
</tr>
<tr>
<td>Fraction of photolabile NO$_3^-$ ($F_p$)</td>
<td>0.01-0.99</td>
<td>Set to 1 everywhere</td>
<td>3.7-9.6</td>
<td>Fig. 4c, d</td>
</tr>
<tr>
<td>Sub-surface snow NO$_3^-$ ([NO$<em>3^-$]$</em>{bot}$)</td>
<td>60.0 ng g$^{-1}e$</td>
<td>30-120 ng g$^{-1}$</td>
<td>0.3-15.8</td>
<td>Fig. 1Ab</td>
</tr>
<tr>
<td>Radiation equivalent mean ice grain radii ($r_e$)</td>
<td>Jan: 332.0 µm$^e$</td>
<td>Study 1: 332.0 µm$^e$ Study 2: 198-332.0 µm$^e$ Study 3: 86.0-332.0 µm$^e$</td>
<td>0.5-10.2</td>
<td>Fig. 1Aj</td>
</tr>
<tr>
<td>Bulk snow extinction coefficient ($K_{ext_{bot}}$)</td>
<td>1.7-6.9x10$^4$ m$^{-1}$ (spatial variation)</td>
<td>± 20% with respect to base case values</td>
<td>0.5-9.4</td>
<td>Fig. 1A</td>
</tr>
<tr>
<td>NO$_3^-$ enhancement factor in top 2 cm (EF)</td>
<td>6.0$^f$</td>
<td>1-10</td>
<td>0.5-9.3</td>
<td>Fig. 1A</td>
</tr>
<tr>
<td>Snow black carbon ($C_{BC}$)</td>
<td>0.08-0.6 ng g$^{-1}$ (spatial variation, Figure 3b)</td>
<td>± factor of 2 with respect to base case values</td>
<td>0.5-8.6</td>
<td>Fig. 1A</td>
</tr>
</tbody>
</table>

$^a$base case $F_{NOx}$=0.5-7.8x10$^8$ molec cm$^{-2}$ s$^{-1}$ (Figure 4d)

$^b$from Chu and Anastasio [2003] at T=244K

$^c$median of ITASE campaign [Bertler et al., 2005]

$^d$in $r_e$ sensitivity study 1, the base-case ‘January’ $r_e$ profile is applied for every month. In $r_e$ sensitivity study 2, the base-case ‘December and February’ $r_e$ profile is applied for every month. In $r_e$ sensitivity study 3, the base-case ‘March-November’ $r_e$ profile is applied for every month.

$^e$median of observed EF [Dibb et al., 2004, Frey et al., 2009, Mayewski and Legrand, 1990, Rothlisberger et al., 2000].

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Figure 1. Schematic showing the nitrogen recycling associated with NO$_3^-$ photolysis as included in the model. $F_{PRI}$ (ng N m$^{-2}$ yr$^{-1}$) is the downward, primary flux of NO$_3^-$ to Antarctica originating from long-range transport and the stratosphere, $F_{NOx}$ (ng N m$^{-2}$ yr$^{-1}$) is the upward flux of snow-sourced NO$_x$ to the boundary layer, and $F_R$ (ng N m$^{-2}$ yr$^{-1}$) is downward, recycled flux of HNO$_3$ to the snow surface. The surface snow layer (top 2 cm) is distinguished from the rest of the photic zone because 30-65% of snow-sourced NO$_x$ is produced in the top 2 cm of snowpack [Zatko et al., 2013], and because both NO$_3^-$ concentrations and actinic flux are much higher in the top surface layer compared to deeper layers.
Figure 2. (a) Annual total snow accumulation rate (kg m$^{-2}$ yr$^{-1}$) in GEOS-Chem from May 2009 to May 2010 with annual snow accumulation rates (circles) estimated in Erbland et al. [2013], Fegyveresi et al. [2011], and Grenfell et al. [1994]. (b) Annual mean surface wind divergence (s$^{-1}$) in GEOS-Chem from May 2009 to May 2010. Blue regions indicate regions of convergence.
Figure 3. (a) Calculated mean austral summer (DJF) UV e-folding depth ($z_e$). (b) Modeled and observed (circles) annual mean snow black carbon concentrations ($C_{BC}$), with observations from WAIS-Divide and Law Dome [Bisiaux et al., 2013], Siple Dome [Chylek et al., 1992], Vostok [Grenfell et al., 1994], South Pole [Warren and Clarke, 1990], and Dome C [Warren et al., 2006]. (c) Ratio of annual dry-deposited NO$_3^-$ to annual total deposited NO$_3^-$, $F_P$. (d) Annual sub-surface snow NO$_3^-$ concentrations ($[\text{NO}_3^-]_{bot}$) from 2-cm depth to the bottom of the snow photic zone ($z_{ph}$) used in the model scaled by $F_P$. Mean sub-surface multi-year NO$_3^-$ observations from the ITASE campaign along with mean asymptotic (sub-photic zone) NO$_3^-$ mixing ratios from Erbland et al. [2013] and Shi et al. [2014] (circles) are also included in Figure 3d [Bertler et al., 2005].
Figure 4. Mean austral summer (DJF) flux of snow-sourced NO\textsubscript{x} from the snow ($\overline{F}_{\text{NOx}}$) with previously reported $F_{\text{NOx}}$ observations from Neumayer [Jones et al., 2001], Halley [Jones et al., 2011, Bauguitte et al., 2012], South Pole [Oncley et al., 2004, Wang et al., 2008, Zatko et al., 2013], WAIS-Divide [Masclin et al., 2013], and Dome C [Frey et al., 2013, Zatko et al., 2013]. (a) $\overline{F}_{\text{NOx}}$ calculated using $\phi$ from Zhu et al. [2010] and uniform snow NO\textsubscript{3}\textsuperscript{-} concentrations ($[NO\textsubscript{3}\textsuperscript{-}]_{\text{top}}=360$ ng g\textsuperscript{-1}, $[NO\textsubscript{3}\textsuperscript{-}]_{\text{bot}}=60$ ng g\textsuperscript{-1}). (b) $\overline{F}_{\text{NOx}}$ calculated using $\phi$ from Zhu et al. [2010] and uniform snow NO\textsubscript{3}\textsuperscript{-} concentrations ($[NO\textsubscript{3}\textsuperscript{-}]_{\text{top}}=360$ ng g\textsuperscript{-1}, $[NO\textsubscript{3}\textsuperscript{-}]_{\text{bot}}=60$ ng g\textsuperscript{-1}) scaled by the ratio of annual dry-deposited NO\textsubscript{3}\textsuperscript{-} to annual total deposited NO\textsubscript{3}\textsuperscript{-} ($F_p$, Figure 3c) (c) $\overline{F}_{\text{NOx}}$ calculated using $\phi$ from Chu and Anastasio [2003] and uniform snow NO\textsubscript{3}\textsuperscript{-} concentrations ($[NO\textsubscript{3}\textsuperscript{-}]_{\text{top}}=360$ ng g\textsuperscript{-1}, $[NO\textsubscript{3}\textsuperscript{-}]_{\text{bot}}=60$ ng g\textsuperscript{-1}). (d) Base case: $\overline{F}_{\text{NOx}}$ calculated using $\phi$ from Chu and Anastasio [2003] and uniform snow NO\textsubscript{3}\textsuperscript{-} concentrations ($[NO\textsubscript{3}\textsuperscript{-}]_{\text{top}}=360$ ng g\textsuperscript{-1}, $[NO\textsubscript{3}\textsuperscript{-}]_{\text{bot}}=60$ ng g\textsuperscript{-1}) scaled by the ratio of annual dry-deposited NO\textsubscript{3}\textsuperscript{-} to annual total deposited NO\textsubscript{3}\textsuperscript{-} ($F_p$).
Figure 5. (a) Annual wet plus dry deposition flux of primary NO$_3^-$ to the snow ($F_{PRI}$). (b) Annual wet plus dry deposition flux of recycled NO$_3^-$ to the snow ($F_R$). (c) Ratio of $F_R$ to the total downward NO$_3^-$ flux ($\frac{F_R}{F_{PRI}+F_R}$) for the base case scenario.
Figure 6. Sensitivity studies examining transport of snow-sourced NO$_x$ across Antarctica. Mean austral summer (DJF) $F_{NOx}$ across Antarctica when $F_{NOx}$ set to 0 (a) in East Antarctica and (b) in West Antarctica. Ratio of recycled NO$_3$ flux ($F_R$) to $F_R$ in the base case scenario when $F_{NOx}$=0 in (c) East Antarctica and (d) in West Antarctica.
Figure 7. Nitrogen recycling factor (NRF, E8).
Figure 8. Factor increase in mean austral summer (DJF) boundary layer (a) NO$_x$, (b) gas+aerosol phase nitrate, (c) OH, and (d) O$_3$ mixing ratios between model runs with $F_{NOx}$ compared to without $F_{NOx}$.
Figure 9. (a) Minimum years NO$_3^-$ remains in photolytic zone ($\tau_z$, years, E10). (b) Fraction of NO$_3^-$ gained (positive values) or lost (negative values) from the snow through photolysis ($f$, E9). (c) Modeled enrichment in ice-core $\delta^{15}$N(NO$_3^-$) (E11) due to photolysis-driven loss of NO$_3^-$ in snow compared to sub-photic zone $\delta^{15}$N(NO$_3^-$) observations [Erbland et al., 2013, Frey et al., 2009, Jarvis, 2008, Shi et al., 2014, Sofen et al., 2014].
Figure 10. NRF versus $f$ values across Antarctica. (a) Regions where NO$_3^-$ remains in the photic zone for 3 years or less. (b) Regions where NO$_3^-$ remains in the photic zone for more than 3 years. The color scale represents the number of years NO$_3^-$ remains in the photic zone ($\tau_z$). Note the different x-axis range for (a) and (b).
Figure 1A. Results of sensitivity studies that show how the average austral summer (DJF) flux of snow-sourced NO$_x$ ($\overline{F}_{\text{NO}_x}$) in Antarctic snowpacks is altered by changes in variables relevant to snow NO$_3^-$ photolysis. The standard set of variables in the above figures are quantum yield ($\phi$) = 0.002 molec photon$^{-1}$, fraction of photolabile NO$_3^-$ ($F_p$) = 1, annual mean sub-surface snow NO$_3^-$ ([NO$_3^-$]$_{\text{bot}}$) = 60 ng g$^{-1}$, radiation equivalent mean ice grain radii ($r_e$) = 332 $\mu$m, NO$_3^-$ enhancement factor ($EF$) = 6, bulk snow extinction coefficient ($K_{\text{ext tot}}$) = 1.7x10$^{-3}$ to 6.9x10$^{-3}$ (spatial variability), and annual mean snow black carbon ($C_{BC}$) = 0.08 to 0.6 ng g$^{-1}$ (spatial variability). Observed $\overline{F}_{\text{NO}_x}$ values are overplotted (see Figure 4 for references). In (a), for the top centimeter of snow, the Zhu et al. [2010] $\phi$ is applied to all dry-deposited NO$_3^-$ and the Chu and Anastasio [2003] $\phi$ is applied to all wet-deposited NO$_3^-$ Below 1 cm, the Chu and Anastasio [2003] $\phi$ is applied to all NO$_3^-$. In (b), [NO$_3^-$]$_{\text{bot}}$ is doubled from the base case value and in (c), [NO$_3^-$]$_{\text{bot}}$ is halved from the base case value. In (d), the C$_{BC}$ is doubled from base case values and in (e) the C$_{BC}$ is halved from base case values. In (f), EF=1 and in (g), EF=10. In (h), $K_{\text{ext tot}}$ is a factor of 1.2 higher than the base case value. In (i), $K_{\text{ext tot}}$ is a factor of 0.8 than the base case value. In (j), $r_e$ is representative of austral mid-summer (January) conditions is used (see Table 3 footnote). In (k), $r_e$ is representative of austral spring, fall, and winter (March-November) conditions. In (l), $r_e$ is representative of austral early summer and late summer (December, February) conditions. Note different color scales.