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Atmospheric Chemistry and Physics Discussions

The magnitude of the snow-sourced reactive nitrogen flux to the boundary layer in the Uintah Basin, Utah, USA

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Abstract

Reactive nitrogen (N_r=NO, NO_2, HONO) and volatile organic carbon emissions from oil and gas extraction activities play a major role in wintertime ground-level ozone exceedance events of up to 140 ppb in the Uintah Basin in eastern Utah. Such events occur only when the ground is snow covered, due to the impacts of snow on the stability and depth of the boundary layer and ultraviolet actinic flux at the surface. Recycling of reactive nitrogen from the photolysis of snow nitrate has been observed in polar and mid-latitude snow, but snow-sourced reactive nitrogen fluxes in mid-latitude regions have not yet been quantified in the field. Here we present vertical profiles of snow nitrate concentration and nitrogen isotopes ($\delta^{15}N$) collected during the Uintah Basin Winter Ozone Study 2014 (UBWOS 2014), along with observations of insoluble light-absorbing impurities, radiation equivalent mean ice grain radii, and snow density that determine snow optical properties. We use the snow optical properties and nitrate concentrations to calculate ultraviolet actinic flux in snow and the production of N_r from the photolysis of snow nitrate. The observed $\delta^{15}N(NO_3^-)$ is used to constrain modeled fractional loss of snow nitrate in a snow chemistry column model, and thus the source of snow-sourced N_r to the overlying boundary layer. Snow-surface $\delta^{15}N(NO_3^-)$ measurements range from -5‰ to 10‰ and suggest that the local nitrate burden in the Uintah Basin is dominated by primary emissions from anthropogenic sources, except during fresh snowfall events, where remote NO_x sources from beyond the basin are dominant. Modeled daily-averaged snow-sourced N_r fluxes range from 5.6-71x10^7 molec cm^{-2} s^{-1} over the course of the field campaign, with a maximum noon-time value of 3.1x10^9 molec cm^{-2} s^{-1}. The top-down emission estimate of primary, anthropogenic NO_x in the Uintah and Duchesne counties is

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at least 300 times higher than the estimated snow NO_x emissions presented in this study. Our results suggest that snow-sourced reactive nitrogen fluxes are minor contributors to the N_r boundary layer budget in the highly-polluted Uintah Basin boundary layer during winter 2014.

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1. Introduction

Ozone (O_3) has adverse respiratory effects, is an effective greenhouse gas [*UNEP*, 2011], and, through formation of the hydroxyl radical, influences the oxidizing capacity of the atmosphere [*Thompson,* 1992]. O_3 precursors include volatile organic compounds (VOCs) emitted from vegetation, biomass burning, and fossil fuel combustion [*Guenther et al*., 1995, *Warneke et al*., 2014] and nitrogen oxides (NO_x=NO+NO_2) emitted from fossil fuel combustion, biomass burning, soil microbial activity, lightning, and photochemical reactions in snow [*Delmas et al*., 1997, *Grannas et al*., 2007, *Logan et al*., 1983]. Maximum boundary layer O_3 concentrations are typically observed during the summer in major cities, where and when O_3 precursor emissions and ultraviolet (UV) radiation are highest. High O_3 concentrations in the boundary layer exceeding 100 ppbv were measured in winter 2005 in the Upper Green River Basin in rural Wyoming [*Schnell et al*., 2009], well above the current Environmental Protection Agency (EPA) National Ambient Air Quality Standard (NAAQS) 8-hour average limit of 70 ppbv. High wintertime O_3 episodes have also been observed in the Uintah Basin in rural Utah [*Martin et al*., 2011], and in both basins, these O_3 episodes only occur when the ground is snow-covered [*Oltmans et al*., 2014]. The Upper Green River Basin and the Uintah Basin are regions of major oil and gas development, and the production of oil and natural gas in the Upper Green River Basin and the Uintah Basin is expected to increase through at least 2020 [*US EIA*, 2014].

These wintertime high O_3 episodes motivated a series of field campaigns, including the Upper Green Winter O_3 Study (UGWOS 2011, UGWOS 2012) and the Uintah Basin

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Winter O_3 Study (UBWOS 2012, UBWOS 2013, UBWOS 2014). Results from these field campaigns [*Gilman et al*., 2013, *Helmig et al*., 2014, *Oltmans et al*., 2014, *Warneke et al*., 2014, *Schnell et al*., 2009] and subsequent modeling studies [*Ahmadov et al*., 2015, *Carter and Seinfeld*, 2012, *Edwards et al*., 2013, 2014, *Field et al*., 2015, *Rappengluck et al*., 2014] reveal that emissions of NO_x and VOCs from oil and gas extraction, combined with stagnant meteorological conditions, enhanced boundary layer UV radiation due to the high UV albedo of snow [*Warren et al*., 2006], and reduced O_3 loss through surface deposition due to snow cover [*Ahmadov et al*., 2015], trigger high boundary layer O_3 episodes in these basins. O_3 exceedance events occur only when the ground is snow covered because snow aids in the formation and maintenance of a stable air mass and reflects UV radiation upwards into the boundary layer. Modeling studies were used to determine whether O_3 formation in these regions is NO_x-sensitive or VOC-sensitive, which is necessary information for the enactment of effective regulations aimed to reduce boundary layer O_3 abundance. Modeling results from Edwards et al. [2014] suggest that the Uintah Basin is in an O_3 formation regime on the boundary between VOC-sensitive and NO_x-sensitive and modeling results from Ahmadov et al. [2015] suggest that the Uintah Basin regime is VOC-sensitive. Modeling results presented in Edwards et al. [2014] suggest that the dominant radical sources in the Uintah Basin are carbonyl compounds (85%), with smaller inputs from HONO, O_3, and nitryl chloride ($ClNO_2$) photolysis.

In addition to aiding in the formation and maintenance of a stable air mass with enhanced UV radiation, snow may also recycle reactive nitrogen oxides (N_r = NO_x, HONO)

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between the snow surface and the overlying atmosphere, effectively increasing the atmospheric lifetime of N_r. The major sink of N_r in the atmosphere is the formation and deposition of nitrate (particulate NO_3^- plus $HNO_3(g)$). When nitrate is deposited to snow, its photolysis serves to recycle N_r to the overlying boundary layer [*Grannas et al.,* 2007, *Honrath et al*., 2000]. This snow-sourced N_r can then be re-oxidized to nitrate and re-deposited to the snow surface. The recycling of nitrogen between the snow surface and boundary layer can occur many times, resulting in the continuous recycling of N_r during sunlit conditions.

The photolysis of nitrate occurs in the liquid-like region (LLR) in or on ice grains [*Domine et al*., 2013] in the top snow layer where UV radiation is present, which is known as the snow photic zone. Snow nitrate photolyzes at wavelengths (λ)=290-345 nm to produce aqueous-phase nitrogen dioxide (NO_2) or nitrite (NO_2^-) according to E1 and E2 [*Grannas et al*., 2007, *Mack and Bolton*, 1999, *Meusinger et al*., 2014].

$$NO_3^-(aq) + h\nu(+H^+) \rightarrow NO_2(aq) + OH(aq), \qquad \text{E1}$$

$$NO_3^-(aq) + h\nu \rightarrow NO_2^-(aq) + O(^3P)(aq), \qquad \text{E2}$$

The measured quantum yields (ϕ) for E1 range from 0.003-0.6 molec photon^{-1} at 253 K [*Chu and Anastasio*, 2003, *Meusinger et al*., 2014, *Zhu et al*., 2010], and is likely influenced by the location of nitrate within ice grains. The NO_2 produced in E1 quickly evaporates due to its low solubility and can be transported to the overlying atmosphere.

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The nitrite produced in E2 is rapidly photolyzed at longer wavelengths (λ=290-390 nm) (E3).

$$NO_2^-(aq) + h\nu(+H^+, aq) \rightarrow NO(aq) + OH(aq), \quad E3$$

Nitrite can also react with OH or H^+ in the LLR to produce aqueous-phase NO_2 and HONO [*Grannas et al*., 2007]:

$$NO_2^-(aq) + OH(aq) \rightarrow NO_2(aq) + OH^-(aq), \quad E4$$

$$NO_2^-(aq) + H^+(aq) \rightarrow HONO(aq), \quad E5$$

HONO can rapidly photolyze in the LLR to produce aqueous-phase NO and OH [*Anastasio and Chu*, 2009]; due to its short lifetime the aqueous-phase OH remains in the LLR, but the aqueous-phase NO can be transferred to the gas phase and ultimately be released into the boundary layer. Aqueous-phase HONO can also be transferred to the gas phase (HONO (aq) ←→ HONO (g)) and released into the boundary layer, where it can photolyze to produce gas-phase NO and OH [*Zhou et al*., 2001].

Snow-sourced NO_x in the boundary layer can re-oxidize to HNO_3 via E6,

$$NO_2(g) + OH(g) \rightarrow HNO_3(g), \quad E6$$

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and redeposit to the snow surface within several days [*Levy and Moxim*, 1989, *Levine et al.*, 1981], providing the snow with a recycled source of nitrate that is again available for photolysis.

Nitrate nitrogen isotopes ($\delta^{15}N(NO_3^-)$) in the air and snow can provide useful information about snow photochemistry, specifically, the degree of photolysis-driven recycling and loss of nitrate from the snow. Nitrogen isotope ratios are expressed as $\delta^{15}N$, where $\delta = R_{sample}/R_{reference} - 1$, $R = {}^{15}N/{}^{14}N$, and N_2-air is the reference material. Nitrate photolysis in snow is a mass-dependent process and is associated with a large fractionation constant (ε) of -47.9‰ at wavelengths shorter than 320 nm [*Berhanu et al.*, 2014a]. Nitrate photolysis provides the boundary layer with a source of N_r that is highly depleted in ^{15}N, leaving highly enriched $\delta^{15}N(NO_3^-)$ deeper in the snow. Snow-sourced nitrate that is redeposited to the snow surface is lighter than the remaining nitrate in the snow, leading to $\delta^{15}N(NO_3^-)$ values that become more enriched with increasing depth within the snow photic zone. $\delta^{15}N(NO_3^-)$ values in the atmosphere are also influenced by the relative importance of different NO_x sources [see *Felix and Elliott,* 2014 for a summary]. For example, the atmospheric $\delta^{15}N$ signature from anthropogenic NO_x sources, such as combustion of fossil fuels, range from -19.0‰ to 25.0‰ [*Felix et al.,* 2012, *Walters et al.*, 2015]. The $\delta^{15}N$ signature from soil microbial activity is generally lower than that of anthropogenic activity and ranges from -50‰ to -20‰ [*Felix and Elliott*, 2014]. Observations of atmospheric $\delta^{15}N(NO_3^-)$ in non-polluted, mid-latitude regions range from -6 to -2‰, while $\delta^{15}N(NO_3^-)$ values measured in polluted regions range from 0 to 6‰ [*Morin et al.*, 2009]. In addition, atmospheric $\delta^{15}N(NO_3^-)$ is influenced by NO_x cycling [*Freyer et al.*,

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1993; *Walters et al*., 2016], NO_2 oxidation [*Walters and Michalski*, 2015], and the partitioning of nitrate between its gas and particulate phases [*Heaton et al*., 1997].

In this study, we investigate the importance of snow photochemistry as a source of reactive nitrogen oxides to the boundary layer in the Uintah Basin using chemical, isotopic, and optical measurements from the snow collected during the UBWOS 2014 campaign. We use these observations of snow optical properties along with observations of surface downwelling irradiance as inputs to a snow radiative transfer model to calculate photolysis frequencies in the snow. The source of snow N_r is then calculated simply by multiplying the calculated photolysis frequencies by the observed snow nitrate concentrations. The calculated photolysis frequencies in snow are also used in a snow photochemistry column model which is constrained by our observations of snow $\delta^{15}N(NO_3^-)$. In Section 2 we describe the field, laboratory, and modeling techniques used in this study. In Section 3 we present the chemical and optical measurements made during UBWOS 2014 and model-calculated fluxes of snow-sourced N_r. In Section 4 we estimate the contribution of snow-sourced N_r to the N_r burden in the Uintah Basin boundary layer.

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2. Methods

2.1. Field and Laboratory Observations

2.1.1. UBWOS 2014 Field Site Description and Meteorological Conditions

UBWOS 2014 occurred from January 17, 2014 to February 13, 2014 at the Horsepool field-intensive site (40.1°N, 109.5°W) in the Uintah Basin, roughly 35 miles south of Vernal, Utah. There are over 10,000 oil and natural gas wells in the basin connected by a series of dirt roads. The meteorological conditions were relatively constant for most of the campaign; wind speeds ranged from 1 to 3 m s^{-1} and often originated from the southwest. Sky conditions were clear, temperatures ranged from 258 to 275 K, and boundary layer heights generally ranged from 25 to 150 m. There were a few cloudy days (January 29-February 4, February 10) during the campaign and the last several days experienced temperatures above freezing. Daily maximum boundary layer O_3 mixing ratios ranged from 45 ppb to 90 ppb, and the campaign-averaged daily-maximum boundary layer O_3 mixing ratio was 61 ppb.

Snow covered the ground throughout the duration of the campaign, and ranged in depth from 10 to 30 cm, depending on how snow was redistributed by wind after deposition. The snow was deep enough to cover some of the lowest-lying vegetation, but branches from bushes were still visible. Three snow events occurred before the campaign, one event on December 4, which deposited most of the snow (19 cm), and two smaller events on December 8 and December 19, which deposited roughly 3 cm and 1 cm of snow,

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respectively. There was a distinct crust layer roughly 4 cm below the snow surface, providing evidence of surface melting between the later two snowfall events. The temperature difference between the soil and the air was at least 15 K for several weeks, allowing vapor to redistribute through the snow, leading to the formation of large hoar crystals (radiation equivalent mean ice grain radii [*Hansen and Travis*, 1974] (r_e) > 1200 μm) at all depths in the snow. There was one major snow event during the campaign on January 30 through January 31 that deposited roughly 5 cm of fresh snow (r_e ~ 100 μm). There were two smaller snow events on February 4 and February 10. On February 4 there was no measureable snow accumulation and during the early-morning hours of February 10 there was 2 cm of fresh snow that subsequently melted several hours after sunrise. Supplementary Figure 3B summarizes daily snow accumulation before and during the campaign.

2.1.2 Snowpit Measurements and Snow Sample Preparation

Twelve snowpits were dug and measured approximately every 2 to 3 days during the campaign. Snowpits were dug from the snow surface to about 1 cm above the subniveal ground and ranged in depth from 9 to 24 cm. The snowpits were dug in a variety of directions roughly 150 meters from the main Horsepool site, except for snowpit 5 (January 24), which was dug roughly 800 meters away from Horsepool. The snowpits were dug wearing clean, nitrate-free gloves using a stainless steel spatula. For each snowpit, vertical profiles (1-cm depth resolution) of snow density (ρ_{snow}), temperature, and radiation equivalent ice grain radii (r_e) were measured using a Taylor-LaChapelle snow density kit, a dial stem thermometer, and a laminated snow grid card with 1 mm

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grid spacing, respectively. Snow grains from each distinct snow layer were placed on the snow grid card and a photograph was taken. The photographs were projected onto a larger screen and the shortest dimension of each snow crystal was estimated. The shortest dimension of a snow grain is the most optically important dimension [*Grenfell and Warren*, 1999], and in this study, it is used to represent r_e. For hoar crystals, the smallest dimension is the width of the crystal wall and for freshly-fallen crystals, the smallest dimension is the radius of the rounded crystal. For each snowpit, approximately 1 kg of snow was collected at 1-cm depth intervals and placed into 'whirl-pak' plastic bags. The bags were kept covered while in the field and then immediately placed into a freezer once back at the Utah State University (USU) Uintah Basin Campus in Vernal, Utah. Supplementary section A shows detailed information on each snowpit.

2.1.3. Optical Measurements

The snow from each plastic bag was spooned into a clean glass beaker and melted in a microwave oven at USU. The meltwater was transferred to a stainless steel funnel and passed through a 0.4 μm Nuclepore filter, using an electric diaphragm vacuum pump to create a partial vacuum in a volumetric flask. The Nuclepore filter collects insoluble light absorbing impurities (LAI) in snow, including black carbon (BC) and non-black carbon (non-BC) species, the latter of which encompass brown carbon, dust, and organics. The volume of filtrate was measured, which ranged from 40 to 750 ml depending on impurity content. After the Nuclepore filters dried overnight, the filters were frozen until further analysis at the University of Washington (UW).

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The absorption spectrum of each Nuclepore filter was measured using an ISSW spectrophotometer [*Grenfell et al*., 2011] in the Arctic Snow Laboratory at UW. The Nuclepore filter is placed between two integrating spheres lined with Spectralon material to create a fully diffuse medium. An Ocean Optics USB-650 spectrophotometer is used to measure the absorption spectrum in units of optical depth, $\tau(\lambda)$ (dimensionless, e.g. cm^2 cm^{-2}), from λ=350-1000 nm in 10 nm intervals. A set of standard filters containing known loadings of black carbon (Fullerene) is used to calibrate the ISSW spectrophotometer. The spectral absorption measured by the spectrophotometer for each filter is characterized by an Ångstrom exponent ($\mathring{A}$), which represents the total absorption by both BC and non-BC LAI on the filter between two visible wavelengths. $\mathring{A}$ is calculated in E7:

$$\mathring{A}(\lambda_1 \; to \; \lambda_2) = \frac{\ln\left(\frac{\tau(\lambda_1)}{\tau(\lambda_2)}\right)}{\ln\left(\frac{\lambda_2}{\lambda_1}\right)} \; , \qquad \text{E7}$$

where λ_1=450 nm and λ_2=600 nm. The λ=450-600 nm range is chosen because the ISSW spectrophotometer signal is most stable over this wavelength range. The total absorption Ångstrom exponent on each filter along with assumed Ångstrom exponents for BC ($\mathring{A}$=1) and non-BC ($\mathring{A}$=5) are used to estimate snow BC concentrations and the fraction of ultraviolet (λ=300-350 nm) absorption by non-BC material (see *Doherty et al*., 2010, *Grenfell et al*., 2011, *Zatko et al*., 2013, and *Zatko and Warren*, 2015). Triplicate measurements were performed for all samples.

Surface upwelling and downwelling irradiance was measured using a commercial spectral radiometer equipped with a photodiode array (Metcon GMBH,

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http://www.metcon-us.com). Upwelling and downwelling UV-A and UV-B were measured with Kipp and Zonen Model UV-S-AB-T radiometers. Radiometers were placed at 2 m above ground (one up-facing and one down-facing) and were cleaned and checked weekly to ensure that the radiometers remained directly perpendicular to the ground. Detailed irradiance data is provided in the Supplemental Material.

2.1.4. Chemical Concentration and Nitrate Isotopic Measurements

In a laboratory on the USU campus in Vernal, UT, a 50 µl aliquot of snow meltwater that was passed through the Nuclepore filter was used to measure ion (Cl^-, Br^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2}, oxalate) concentrations using a Metrohm 761 Compact Ion Chromatograph Analyzer [*Quinn et al*., 1998]. The nitrate in the remaining filtrate was preconcentrated for isotopic analysis. Nitrate was preconcentrated by passing the meltwater through an anion exchange resin (BioRad AG 1-X8) using an electric diaphragm pump. The sample anions in the resin were eluted with 5x2 ml 1 M sodium chloride (NaCl/Milli-Q water) solution into a 30 ml pre-cleaned sample bottle. This method has been shown to ensure full recovery of nitrate [*Silva et al*., 2000, *Frey et al*., 2009] The solution was kept frozen in the dark until analysis in the University of Washington IsoLab (http://isolab.ess.washington.edu/isolab/).

The denitrifier method [*Casciotti et al*., 2002, *Kaiser et al*., 2007, *Sigman et al*., 2001] was used to determine the nitrogen isotopic signature ($\delta^{15}N$) in each snow sample. Denitrifying bacteria, *Pseudomonas aureofaciens,* convert nitrate to nitrous oxide (N_2O) gas in anaerobic conditions [*Casciotti et al*., 2002, *Sigman et al*., 2001] and N_2O is

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transported via helium gas through a heated gold tube (800°C), where it thermally decomposes into O_2 and N_2. After separation by gas chromatography, the O_2 and N_2 are run through a Thermo Finnigan™ DeltaPlus Advantage isotope ratio mass spectrometer (IRMS), equipped with a Precon and GasBench II™. The $\delta^{15}N$ values were calculated with respect to N_2 (air) via two international reference materials USGS32 ($\delta^{15}N$ =180‰) and USGS34 ($\delta^{15}N$ =-1.8‰), with IAEA ($\delta^{15}N$ =4.7‰) as a quality control standard. For many samples, the $NaCl/NO_3^-$ solution was diluted with Milli-Q water to obtain the optimal nitrate concentration (200 nmol in 2 ml) for each sample run on the IRMS. Triplicate measurements were performed for all samples. The analytical uncertainty of $\delta^{15}N(NO_3^-)$ (1σ) was 0.75‰ based on repeated measurements of the quality control standard.

Aerosol nitrate was collected throughout the campaign in 12-hour intervals. Aerosol nitrate was sampled from an inlet 13 meters above ground and drawn through a heated (283K) pipe, where it was then collected on a two-stage, multi-jet cascade impactor. The impactor tedlar films separates aerosols with diameters less than 2.5 μm from those with diameters between 2.5 to 12.5μm. The aerosols were extracted from the filters and analyzed using ion chromatography, following methods described in Quinn et al. [2000]. Gas-phase nitric acid was measured using an Acetate HR-ToF-CIMS instrument throughout the campaign with 1-minute time resolution, as described in Yuan et al. [2016].

2.2. Calculations

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2.2.1. Snow Radiative Transfer Model

A 4-stream, plane-parallel radiative transfer model using the discrete ordinates method with a δ-M transformation originally described in Grenfell et al. [1991] was used to calculate vertical profiles of UV actinic flux in each snowpit. This model properly treats layers with differing refractive indices and the 4-stream model produces albedo and absorptivity results that agree to within 1% of higher-order models representative of snow [*Wiscombe*, 1977], including DISORT [*Stamnes et al*., 1988]. Vertical profiles of the ρ_{snow}, r_e, and LAI absorption are used to calculate vertical profiles of inherent optical properties (IOPs) in snow at the wavelengths relevant for photochemistry (UV). These wavelength-dependent IOPs include the bulk extinction coefficient in snow ($Kext_{tot}$) and the co-albedo of single scattering ($c\varpi_{eff}$); see Zatko et al. [2013] for more details about the IOP calculations. $Kext_{tot}$ and $c\varpi_{eff}$, along with observations of downwelling surface UV irradiance, solar zenith angle, cloud fraction, and soil albedo (0.1) [*Markvart et al*., 2003, *Matthias et al*., 2000] are used to calculate 1-cm resolution vertical profiles of UV actinic flux for each snowpit, following methods described in Zatko et al. [2013]. The UV actinic flux profiles are used to calculate depth-dependent photolysis rate constants for nitrate photolysis in snow as described below.

2.2.2. Snow-Sourced Reactive Nitrogen Flux Calculations

The modeled vertical profiles of actinic flux and observed snow nitrate concentrations are used to calculate daily-average fluxes of snow-sourced N_r from each snowpit according to E8.

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$$F_{Nr}(z) = \int_{\lambda_0}^{\lambda_1} \sigma_{NO_3^-}(\lambda) \cdot \phi(T,pH) \cdot I(\lambda, z) \cdot [NO_3^-]\, d\lambda, \qquad \text{E8}$$

$F_{Nr}(z)$ is the flux of snow-sourced N_r (molec cm^{-2} s^{-1}) at 1-cm depth (z) increments in the snow, $\sigma_{NO_3^-}$ is the wavelength (λ)-dependent absorption cross-section for nitrate photolysis (cm^2) from Berhanu et al. [2014], ϕ is the temperature- and pH-dependent quantum yield for nitrate photolysis (ϕ, molec $photon^{-1}$) from Chu and Anastasio [2003] (4.6×10^{-3} molec $photon^{-1}$ at T=267 K), I is the depth (z)- and λ-dependent actinic flux in the snow photic zone (photons cm^{-2} s^{-1} nm^{-1}), and $[NO_3^-]$ is the observed nitrate concentration (ng g^{-1}) in each snow layer. E8 is integrated over the UV wavelength region (λ=298-345 nm). The snow photic zone is defined as three times the e-folding depth of UV actinic flux in snow [*Zatko et al.*, 2016]. The total flux of Nr to the boundary layer, F_{Nr}, is calculated according to E9.

$$F_{Nr} = \sum_{z_0}^{z_{3e}} F_{Nr}(z) \qquad \text{E9}$$

Observed surface downwelling irradiance values for a solar zenith angle of 65°, the average SZA from mid-December to mid-February, are used for calculation of $I(\lambda,z)$ in E8. Therefore the calculated F_{Nr} values represent daily-averaged F_{Nr} values. It is assumed that all N_r escapes into the boundary layer due to its low solubility.

2.2.3. Snow Photochemistry Column Model (TRANSITS)

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The flux of snow-sourced N_r from each snowpit is also calculated using a snow photochemistry column model, TRansfer of Atmospheric Nitrate Stable Isotopes To the Snow (TRANSITS) model [*Erbland et al*., 2015]. TRANSITS is a multilayer, one-dimensional model that simulates nitrate photochemistry in the snow and allows for chemical exchange between the air and snow and calculates the isotopic composition of snow nitrate. The model was originally developed to simulate snow nitrate photolysis and subsequent nitrogen recycling at the air-snow interface on the East Antarctic plateau (Dome C), and has been adapted to mid-latitude, shallow-snowpack conditions for this study. The model has a well-mixed, atmospheric boundary layer with a height of 50 m and a snow compartment containing up to 50 1-cm thick layers. In the atmosphere and in each snow layer, the model solves a general mass-balance equation for nitrate concentration and isotopic composition [*Erbland et al*., 2015] at each time step (1 hour).

In TRANSITS, nitrate is deposited to the snow surface via dry deposition. Nitrate dry-deposition is calculated using the campaign-averaged observed boundary layer mixing ratios for HNO_3 (5784 ng m^{-3}) and NO_3^- (5777 ng m^{-3}) and an assumed dry-deposition velocity of 0.03 cm s^{-1}, which is similar to the dry-deposition velocity used in Edwards et al. [2013, 2014] (0.02 cm s^{-1}) (see Supplementary Table 1B for nitrate dry-deposition fluxes). Nitrate diffuses through the snowpack based on a diffusion coefficient that is dependent on temperature, pressure, snow specific surface area, snow density, and tortuosity [*Crowley et al*., 2010, *Durham et al*., 1986, *Massmann*, 1998].

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We include only the major channel for the production of N_r from nitrate photolysis (E1) in TRANSITS. The minor channels, E2-E5, all consist of chemistry of the intermediate in nitrate photolysis, nitrite, which will photolyze or react rapidly once produced to form N_r. We assume no export of snow-sourced N_r out of the atmospheric box, which is consistent with the low wind speeds and stable boundary layer conditions observed during the campaign. In this way there is no net loss of nitrate from the snow; however, vertical redistribution of snow nitrate can occur which would result in distinctive vertical profiles of nitrate concentration and $\delta^{15}N(NO_3^-)$ in the snow column. In addition to calculating the flux of snow-sourced N_r, TRANSITS calculates vertical profiles of nitrate concentration and isotopes ($\delta^{15}N(NO_3^-)$) in the snow. To calculate $\delta^{15}N(NO_3^-)$ in the snow, the nitrate photolysis fractionation factor ($^{15}\varepsilon_{pho}$) is calculated at each time step and is dependent upon the spectral distribution of the UV irradiance at the snow surface [*Bernhau et al*., 2014, *Erbland et al*., 2015]. Calculated $^{15}\varepsilon_{pho}$ values range from -88 to -35‰ between the snowpits and are constant with snow depth.

In this study, TRANSITS is run at hourly resolution and is spun up beginning 27 days before the start of the campaign using available atmospheric chemical (boundary layer gas-phase and aerosol-phase nitrate) and meteorological data (air temperature and pressure). A constant model boundary layer height of 50 m is assumed, which is a rough estimate of daily-averaged boundary layer heights based on sodar facsimile data from NOAA. The campaign-averaged observed boundary layer total nitrate (HNO_3+ NO_3^-) mixing ratio (11,560 ng m^{-3}) was used to spin up the model. We collected and measured atmospheric $\delta^{15}N(NO_3^-)$ throughout the campaign using a high volume air sampler with

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Nylasorb filters. However, comparison with the nitrate (HNO_3+ NO_3^-) concentration measurements from the PMEL two-stage, multi-jet cascade impactor measurements revealed incomplete trapping. Since non-quantitative collection of nitrate may influence the observed $\delta^{15}N(NO_3^-)$ values, the data was not used in this study. We instead use surface snow $\delta^{15}N(NO_3^-)$ observations to represent atmospheric $\delta^{15}N(NO_3^-)$ (Figure 1a). The TRANSITS snowpack is initialized by setting the snow height equal to 50 cm, the snow photic zone to 6 cm (average photic zone depth for all snowpits), and using the measured snow nitrate concentration and $\delta^{15}N(NO_3^-)$ vertical profiles from the first snowpit of the campaign (January 15). The snowfall event on January 31 is simulated in the model, but the other smaller events are not included. As the model evolves, "snapshots" of the top 25-cm of snow are taken on days corresponding to each snowpit and modeled profiles of nitrate concentration and $\delta^{15}N(NO_3^-)$ are compared to observed profiles for each snowpit. Since vertical profiles of snow $\delta^{15}N(NO_3^-)$ are highly sensitive to photochemical-driven redistribution of N_r in the snowpack [*Erbland et al.*, 2013, 2015], observed $\delta^{15}N(NO_3^-)$ provides a metric to assess model-calculated F_{Nr}.

3. Results and Discussion

3.1. Observations

3.1. 1. Nitrate Concentrations and $\delta^{15}N(NO_3^-)$ in the Surface Snow

Figure 1a shows mean surface snow $\delta^{15}N(NO_3^-)$ values for each snowpit, which range from -5.5 to 11.1‰. The lowest observed surface snow $\delta^{15}N(NO_3^-)$ occurred immediately

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after the only significant fresh snowfall event on Jan. 30 – 31 (-5.5‰). All other surface snow samples were over 10‰ higher (5.2 to 11.1‰).

Figure 1b shows surface snow nitrate concentration measurements for each snowpit, which range from 800 to 18,000 ng g^{-1}. Similar to $\delta^{15}N(NO_3^-)$, surface-snow nitrate concentrations are lowest during the snowfall event on January 30 through January 31, with the exception of February 11 when the snow was rapidly melting. Similarly, boundary layer gas (HNO_3) and aerosol-phase (NO_3^-) nitrate mixing ratios decrease by a factor of 6 between January 30 and January 31 (Supplementary Figure 1B) compared to the rest of the field campaign.

Generally, the surface-snow $\delta^{15}N(NO_3^-)$ values fall within the range of primary anthropogenic $\delta^{15}N$ values (4-25‰) [*Felix and Elliott*, 2014, *Walters et al.*, 2015]. During snow events the boundary layer is less stable, possibly allowing for the transport of nitrate from remote sources outside the basin. In unpolluted, mid-latitude environments, background atmospheric $\delta^{15}N(NO_3^-)$ ranges from -6 to -2‰ [*Morin et al.*, 2009]. During the major snowfall event on January 30 - 31, surface-snow $\delta^{15}N$ values are ~10‰ lower compared to the rest of the campaign, suggesting that nitrate from beyond the basin deposits to the snow surface.

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3.1.2. Snow Depth Profiles of Snow Optical Properties, Nitrate Concentrations, and $\delta^{15}N(NO_3^-)$

In this section and the following sections, we focus on three snowpits (January 22, January 31, February 4) as being representative of the time period before, during, and after the largest snow event. The other 9 snowpits will not be discussed in detail, but observed and modeled vertical profiles of chemical and optical measurements for all 12 snowpits can be found in Supplementary section A.

Figures 2a and 2b show vertical profiles of snow optical properties from an 18-cm deep snowpit dug on January 22, which represents typical profiles from the beginning of the field campaign until before the first snow event. Black carbon concentrations (C_{BC}, ng g^{-1}) range from 3 to 100 ng g^{-1} with the highest concentrations in the top several centimeters of snow. Below 3 cm snow depth, C_{BC} decreases dramatically. Figure 2b shows the average absorption Ångstrom exponent ($\mathring{A}$) from λ=450-600 nm. Over this wavelength range, the dominant absorber at the snow surface is non-BC material ($\mathring{A}$ is nearly 5), and both BC and non-BC contribute to absorption in sub-surface snow layers ($\mathring{A}$ ranges from 2 to 2.7). Although BC and non-BC material are both responsible for the absorption of radiation at λ=450-600 nm, non-BC material is responsible for between 99.6 and 100% of UV (λ=300-350 nm) absorption at all depths in this and in all snowpits measured during the field campaign. The top 3 cm of snow contains the highest concentration of both BC and non-BC material; we define this layer as the "dusty layer" and this layer is represented as a brown shaded region in Figure 2.

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Figures 2c and 2d show vertical profiles of snow optical properties from a 14-cm deep snowpit dug on January 31. It snowed 5 cm between the afternoon of January 30 and morning of January 31, and this new snow layer is evident in Figures 2c and 2d because the dusty layer is now located roughly 5 cm below the snow surface. Figure 2c shows that C_{BC} ranges from 5 to 100 ng g^{-1}; the maximum C_{BC} value has been buried deeper into the snow. Figure 2d shows that $\mathring{A}$ is close to 1 at the snow surface, indicating that BC material dominates visible absorption at the snow surface immediately following the fresh snowfall event. Figures 2e and 2f show vertical profiles of snow optical properties from a 24-cm deep snowpit dug on February 4, 5 days after the snow event. In this snowpit, C_{BC} ranges from 4 to 100 ng g^{-1} and $\mathring{A}$ ranges from 1.7 to 3.4. Figures 2e and 2f show that the original dusty layer is still located roughly 5 cm below the snow surface and that a new dusty layer has formed at the snow surface.

Figure 3 shows observed vertical profiles of nitrate concentration and nitrogen isotopes ($\delta^{15}N(NO_3^-)$) in snow from snowpits dug on January 22, January 31, and February 4. Prior to the fresh snowfall event, snow nitrate concentrations are highest at the surface (13,900 ng g^{-1}), and decrease exponentially in the top 10 cm to a low of 90 ng g^{-1} at 18 cm depth (Figure 3a). Immediately following the fresh snowfall event, the highest nitrate concentrations (12,200 ng g^{-1}) are buried below 5 cm of fresh snow within the dusty layer at 5 – 7 cm depth. The measured nitrate concentrations in the fresh snow layer range from 1,280 to 4,640 ng g^{-1}, which is up to 10 times lower than nitrate concentrations in the dusty layer (Figure 3b). Five days after the fresh snowfall event, the highest nitrate concentrations are still located roughly 7 cm below the snow surface within the dusty

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layer, but surface nitrate concentrations are a factor of 2 higher compared to immediately after the fresh snowfall event (Figure 3c).

Figure 3 shows measured snow $\delta^{15}N(NO_3^-)$ in each of the snowpits, which ranges from -5.5‰ to 13‰. In the Jan. 22 snowpit, measured $\delta^{15}N(NO_3^-)$ is highest near the top and bottom of the snowpit and lowest from 12-cm to 16-cm depth (Figure 3d). Following the fresh snowfall event on Jan. 30 – 31, snow $\delta^{15}N(NO_3^-)$ values are lightest at the snow surface and increase with depth in the fresh snow layer until the top of the dusty layer, below which they decrease to -3.5‰ (Figure 3e). Five days after the fresh snowfall event, measured $\delta^{15}N(NO_3^-)$ is most enriched in the dusty layer and at the snow surface (Figure 3f).

The last snowfall event prior to the start of the campaign occurred on December 19 and resulted in roughly 1 cm of snow accumulation (Supplementary Figure 5A). The high concentrations of LAI and nitrate in surface snow on January 22, combined with the prolonged lack of snowfall, suggest continual dry-deposition of LAI to the surface snow. We speculate that the major source of LAI originates from truck traffic on the dirt roads in the area of the field site due to high values of $\mathring{A}$ (Figure 2). The factor of 150 and 17 decrease in nitrate and black carbon concentrations, respectively, from the surface to 18-cm depth on January 22 suggests that minimal nitrate and LAI are transported (via e.g., diffusion or meltwater transport) from upper to lower snow layers. Immediately after the snowfall event on January 31, nitrate and black carbon concentrations are 10 and 3 times lower, respectively, in the surface snow layers compared to earlier in January, because

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the fresh snow has lower concentrations of these species. Even just five days after the snowfall event on January 30 - 31, concentrations of nitrate and the Ångstrom exponent (*Å*) in the snow surface layer have increased by a factor of 2, likely due to dry deposition of these species to the surface in the absence of snowfall.

The $\delta^{15}N(NO_3^-)$ profiles in snow do not immediately suggest significant photolysis-driven redistribution of nitrate in the snowpack, which would result in the lightest values at the surface, increasing exponentially with depth as observed in Antarctica [*Erbland et al*., 2013]. Prior to the first snowfall event on January 30-31, the surface dusty layer contains the highest values of measured $\delta^{15}N(NO_3^-)$, which are similar to that expected from primary emission of NO_x from anthropogenic sources [*Felix and Elliott*, 2014, *Walters et al*., 2015]. We speculate that the depleted $\delta^{15}N(NO_3^-)$ values towards the bottom of the snowpit correspond to remote-sourced atmospheric nitrate that was deposited during the large snow event (~20 cm of snow) on December 4. On January 31, depleted $\delta^{15}N(NO_3^-)$ measurements at the snow surface suggest that there is deposition of nitrate from less polluted regions surrounding the basin during the snow event. The increase in surface snow $\delta^{15}N(NO_3^-)$ values after January 31 is likely due to deposition of primary-sourced nitrate from anthropogenic NO_x sources in the basin. In the following section, we examine the influence of photolysis of snow nitrate on the profiles of $\delta^{15}N(NO_3^-)$ in snow.

3.2. Calculations

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3.2.1. Calculations of Snow Actinic Flux Profiles and Flux of Snow-Sourced N_r

Figure 4 shows calculated vertical profiles of UV actinic flux normalized to surface downwelling irradiance for the three snowpits. The non-normalized actinic flux values and surface downwelling irradiance values for all snowpits are presented in the supplementary material. On January 22, the normalized actinic flux ratio is nearly 4 at the snow surface because actinic flux is calculated by integrating irradiance over a sphere (surface area of $4\pi r^2$) and also because scattering in snow dominates over absorption. In Figure 4a, the actinic flux decreases to 2.9 within the top centimeter of snow due mainly to UV absorption by non-BC in the surface snow layer. The actinic flux is rapidly extinguished in the dusty layer and continues to decrease with increasing depth in the snow, reaching a value of 0.01 at 18-cm depth. The blue shaded region represents the snow photic zone (top 5 cm of snow) on January 22. The snow photic zones calculated in this study (4-7 cm) are much shallower compared to calculated snow photic zones in polar regions (72-207 cm in Antarctica, 6-51 cm in Greenland) [*Zatko et al*., 2016] because concentrations of LAI in the snow photic zone are at least five orders of magnitude higher in Utah compared to Antarctica and Greenland.

In the snowpits following the fresh snowfall event, the existence of the dusty layer deeper into the snow influences the vertical actinic flux profile and increases the photic zone depth from 5 to 7 cm. The fresh snow at the surface contains less LAI compared to the dusty layer, therefore actinic flux values are higher in the top several centimeters of snow compared to actinic flux values measured before the snowfall event even though r_e values in the new snow are a factor of 3.3-8.3 times smaller than the underlying depth hoar

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grains. Smaller r_e values lead to more scattering in the snow, which increases the probability of absorption by LAI. Although actinic flux values are highest at the surface on January 31, Figure 4b illustrates that UV radiation is rapidly attenuated below the fresh snow layer because radiation is forward-scattered into the highly-absorbing dusty layer. As a result, there is roughly an order of magnitude less actinic flux at 14-cm depth on January 31 compared to January 22.

The presence of a new dusty layer on the snow surface five days after the fresh snowfall event does not significantly alter the vertical profile of normalized UV actinic flux likely because the LAI concentrations in surface layer are at least 5 times lower than LAI concentrations in the original dusty layer (surface snow from January 22 snowpit). Surface snow UV albedo is strongly influenced by the presence of LAI, and Supplemental Figure 2B shows that snow UV albedo is lowest right before the snowfall event on January 30-31 and highest immediately afterwards.

We use these actinic flux profiles (Figure 4) and the observed snow nitrate concentrations (Figure 3a-c) to calculate daily-averaged $F_{Nr}(z)$ and F_{Nr} according to E8 and E9 for each of the three snowpits. Prior to the fresh snowfall event, $F_{Nr}(z)$ decreases exponentially with depth in the photic zone (Figure 5a). $F_{Nr}(z)$ is highest at the snow surface because both actinic flux and snow nitrate concentrations are highest near the snow surface. Daily average F_{Nr} summed over the snow photic zone is 5.6 x 10^8 molec cm^{-2} s^{-1} on January 22 (Figure 5a and Table 1). Immediately following the fresh snowfall event, $F_{Nr}(z)$ decreases by a factor of 3 at the surface because of the factor of 4 decrease in surface

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snow nitrate concentrations, which is partially compensated by the higher UV actinic flux in the top of the snow photic zone (Figure 4b). The daily-averaged F_{Nr} on January 31 is 1.9×10^8 molec cm^{-2} s^{-1}, which is a factor of 3 lower than total F_{Nr} on January 22. Five days later, $F_{Nr}(z)$ has increased by a factor of 2 at the surface due to the factor of 2 increase in surface nitrate concentrations (Figure 3c and 5c). The daily-averaged F_{Nr} on February 4 is 3.2×10^8 molec cm^{-2} s^{-1}, which is a factor of 1.7 higher than total F_{Nr} on January 31.

3.2.2. Snow Photochemistry Column Model

The snow chemistry column model is used to calculate the time-dependent flux of snow-sourced N_r (F_{Nr}) and the depth profile of nitrate concentration and $\delta^{15}N(NO_3^-)$. Figure 6 shows the diurnal F_{Nr} values on January 22, January 31, and February 4. The daily-averaged snow F_{Nr} on January 22 is 6.3×10^8 molec cm^{-2} s^{-1}. Immediately following the snow event, the daily-averaged snow F_{Nr} decreases by a factor of 11 compared to January 22 (5.6×10^7 molec cm^{-2} s^{-1}). The dramatic difference in F_{Nr} is due to the differences in nitrate concentrations in the top several centimeters of snow. Modeled snow nitrate concentrations in the fresh snow layer on January 31 are between 30 and 300 times lower compared to nitrate concentrations in the dusty layer. Five days after the snow event, the daily-averaged snow F_{Nr} has increased by a factor of 2 (1.2×10^8 molec cm^{-2} s^{-1}) because deposition of nitrate to the snow surface layer enhances surface nitrate concentrations and thus F_{Nr}. Calculated daily average F_{Nr} using observed (section 3.2.1) and modeled (TRANSITS) snow nitrate concentrations agree within a factor of ~2 (Table 1); modeled

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F_{Nr} tends to be lower because modeled snow nitrate concentrations are lower than observed (Figure 8).

Figure 7 shows hourly F_{Nr} values calculated for the entire UBWOS2014 campaign using TRANSITS. From the start of the campaign until the fresh snow event on January 31, the daily maximum F_{Nr} values increase as surface snow nitrate concentrations increase due to continual dry-deposition of atmospheric nitrate to the snow surface. Immediately after the snow event on January 31, daily maximum F_{Nr} values are lowered by more than a factor of 10 due to decreased nitrate concentrations in the snow photic zone. Following the snow event, the flux of snow-sourced N_r gradually increases again due to dry-deposition of nitrate to the surface layer, although daily maximum F_{Nr} values remain lower compared to values before the snow event throughout the remainder of the field campaign.

Observed snow nitrate concentration and $\delta^{15}N(NO_3^-)$ values are used to assess results from TRANSITS. $\delta^{15}N(NO_3^-)$ observations are particularly useful as a metric to assess the F_{Nr} values calculated in TRANSITS because $\delta^{15}N(NO_3^-)$ vertical profiles are highly sensitive to photolytic recycling and photolysis-driven loss of nitrate from snow. Figure 8 shows modeled snow nitrate concentrations and $\delta^{15}N(NO_3^-)$ from TRANSITS compared to the observations. The general shapes of the modeled and measured vertical profiles of nitrate concentration are in agreement for all three snowpits; both modeled and measured nitrate concentrations are highest in the dusty layer and lowest near the bottom of the snowpit (Figure 8a-c). Both the model and the observations show increased snow

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nitrate concentrations at the surface following the fresh snowfall event, but the model tends to underestimate surface snow nitrate concentrations after the snow event.

Modeled $\delta^{15}N(NO_3^-)$ is also within the range of observations (Figure 8d-f). Modeled $\delta^{15}N(NO_3^-)$ at the top surface snow layer becomes more depleted from the January 22 to the January 31 snowpit reflecting the decrease in atmospheric $\delta^{15}N(NO_3^-)$ in the model based on surface snow observations (Figure 1a). Without additional snowfall between January 31 and February 4, surface snow $\delta^{15}N(NO_3^-)$ becomes more enriched in the model over this time period because model atmospheric $\delta^{15}N(NO_3^-)$ becomes more enriched (Figure 1a). In contrast, the observations retain this light $\delta^{15}N(NO_3^-)$ at a depth of ~2 cm until the February 11 snowpit (see supplement A). The difference between modeled and observed $\delta^{15}N(NO_3^-)$ at 2 cm depth after January 31 may be due to the redistribution of surface snow by wind, and the fact that each snowpit was dug in a slightly different location. Blowing snow will bury the surface snow with light $\delta^{15}N(NO_3^-)$, and subsequent atmospheric deposition of more enriched $\delta^{15}N(NO_3^-)$ will occur onto this new, wind-blown snow surface, retaining the light $\delta^{15}N(NO_3^-)$ at 2 cm depth. In contrast to the observations, the model does not account for windblown redistribution of snow, and calculates the time-evolution of nitrate concentration and $\delta^{15}N(NO_3^-)$ gradients of a single snowpit.

As discussed in the introduction, laboratory-based quantum yield measurements range from 0.003 to 0.6 [*Chu and Anastasio*, 2003, *Meusinger et al.*, 2014, *Zhu et al.*, 2010]. We use ϕ from Chu and Anastasio (4.6×10^{-3} at T=267 K, which is the average daytime

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temperature during the campaign) in our base case simulation discussed above as it results in calculated values of F_{Nr} in Antarctica and Greenland that are the same order of magnitude as observations [*Zatko et al.*, 2016]. In a sensitivity study, we turn off photolysis of snow nitrate in the model by setting $\phi = 0$. When snow nitrate photolysis is turned off, snow nitrate concentrations change by less than 0.5% in all snowpits, resulting in relatively little sensitivity of modeled snow nitrate concentration to snow photochemistry because only this small fraction (< 0.5%) of nitrate is lost via photolysis at all depths. Despite the large nitrogen isotope fractionation (ε = -88 to -35‰) resulting from the photolysis of snow nitrate, the difference in modeled $\delta^{15}N(NO_3^-)$ when snow nitrate is turned on ($\phi = 4.6\text{x}10^{-3}$) and off ($\phi = 0$) is small because of the very small fraction of nitrate photolyzed. When photolysis is turned on, snow $\delta^{15}N$ values are slightly lower in the top several centimeters due to deposition of isotopically light, snow-sourced nitrate and $\delta^{15}N$ values are slightly more enriched at depth. On January 22, the $\delta^{15}N(NO_3^-)$ profiles in the snow photic zone with and without snow nitrate photolysis differ by vary by ≤ 0.1‰ , on January 31 by ≤ 1.3‰, and on February 4 by ≤ 0.3‰. Snow nitrate photolysis influences both the magnitude and gradient of the snow $\delta^{15}N(NO_3^-)$ profiles on January 31 and February 4 more than January 22, likely because light-absorbing concentrations are lower in the fresh snow layer.

In another sensitivity study, we calculate the maximum possible F_{Nr} in the Uintah Basin by increasing the value of ϕ until modeled snow $\delta^{15}N(NO_3^-)$ falls outside the full range of observations. Above $\phi = 0.2$, there is significant disagreement (when the maximum change in $\delta^{15}N(NO_3^-)$ is > 1σ of the mean $\delta^{15}N(NO_3^-)$ in all snowpits) between modeled

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and measured $\delta^{15}N(NO_3^-)$ values. Using ϕ = 0.2 results in more enriched $\delta^{15}N(NO_3^-)$ at depth due to enhanced photolytic loss, and more depleted $\delta^{15}N(NO_3^-)$ at the snow surface due to the deposition of isotopically light snow-sourced nitrate. Using ϕ = 0.2 results in a maximum possible F_{Nr} at least 45 times larger than when using ϕ = 4.6x10^{-3} for all snowpits (see Table 1).

4. Impact of Snow-Sourced N_r on the Boundary Layer Reactive Nitrogen Budget

4.1. NO_x

We first assume that all N_r is NO_x and use F_{Nr} values calculated using the snow photochemistry column model to estimate the impact of F_{NOx} on the reactive nitrogen budget in the Uintah Basin. Using the best estimate for the quantum yield of nitrate photolysis (ϕ=4.6x10^{-3}), the modeled daily-averaged flux of snow-sourced NO_x ranges from 5.6x10^7 to 7.2x10^8 molec cm^{-2} s^{-1} and the maximum F_{Nr} value is 3.1x10^9 molec cm^{-2} s^{-1} for the entire campaign (Supplementary Table 4B). The top-down NO_x emission inventory for oil, gas, and all other sources excluding the Bonanza power plant in Duchesne and Uintah counties is 6.5x10^6 kg NO_x yr^{-1} [*Ahmandov et al.*, 2015]. The power plant is excluded because its smokestack emissions are above the boundary layer. Assuming a constant NO_x emission rate and using the area of Duchesne (8433 km^2) and Uintah counties (11658 km^2), the top-down NO_x emission estimate for the Uintah and Duchesne counties is 1.2x10^{12} molec cm^{-2} s^{-1}. The emission of primary NO_x in these two counties is thus at least 300 times higher than the estimated snow NO_x emissions,

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implying that snow-sourced NO_x fluxes likely do not influence the NO_x boundary layer budget in the highly-polluted Uintah Basin. If the upper limit of ϕ = 0.2 is used, snow-sourced NO_x emissions are still at least 7 times smaller than primary NO_x emissions. Although reactive nitrogen is likely being emitted from the snow into the boundary layer, the snow-sourced NO_x signal is swamped by emissions from primary anthropogenic sources in the Uintah Basin.

4.2. HONO

Only the major channel for snow nitrate photolysis (E1) is simulated in the TRANSITS model, although nitrate can also photolyze via E2 and form both NO_x and HONO (E3-E5). We estimate the maximum possible influence of snow-sourced N_r for boundary layer HONO mixing ratios by assuming that all snow-sourced N_r is in the form of HONO. If we assume that the campaign-maximum F_{Nr} value (3.1×10^9 molec cm^{-2} s^{-1}) is all HONO that escapes from the snow into the boundary layer, a boundary layer height of 50 m, and a lifetime of HONO of 18 minutes (at solar noon) [*Edwards et al*., 2013], snow nitrate photolysis would contribute a maximum of 25 pptv of HONO to the boundary layer at solar noon. The modeled and observed Uintah Basin boundary layer HONO mixing ratios presented in Edwards et al. [2014] range from ~20 pptv at night to up to 150 pptv during the day, which suggests that the daytime fluxes of reactive nitrogen are not a significant source of HONO to the boundary layer compared to other HONO sources in the basin. Our estimated maximum HONO flux is comparable to snow-sourced HONO fluxes measured at another polluted, mid-latitude location (Paris, France), estimates of which ranged from $0.7\text{-}3.1 \times 10^{10}$ molec cm^{-2} s^{-1} (assuming a snow density of 0.36 g cm^{-3} and

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snow photic zone depth of 6 cm) [*Michoud et al*., 2015]. If the upper limit of ϕ = 0.2 is used (campaign-maximum F_{Nr}=1.4x10^{11} molec cm^{-2} s^{-1}), the maximum boundary layer HONO mixing ratio calculated using this approach is 1.1 ppbv at solar noon, which would significantly impact boundary layer HONO mixing ratios in the Uintah Basin. Given that HONO is thought to be only a minor fraction of total N_r emitted from snow [*Beine et al*., 2008], we consider this to be an overestimate.

5. Conclusions

This study estimates the influence of snow nitrate photolysis on the boundary layer reactive nitrogen budget in the Uintah Basin, which is a region with heavy oil and natural gas extraction processes. Observations of snow optical properties, including ultraviolet (UV) light-absorbing impurities (e.g., black carbon, dust, organics), radiation equivalent ice grain radii, and snow density from 12 snowpits measured during the Uintah Basin Winter Ozone Study (UBWOS) 2014 are incorporated into a snowpack radiative transfer model to calculate vertical profiles of UV actinic flux at 1-cm depth intervals in 12 snowpits dug during the campaign. The vertical UV actinic flux profiles along with measurements of nitrate concentration are used to calculate snow-sourced reactive nitrogen (N_r) fluxes associated with snow nitrate photolysis using both a simple equation (E8) and a more complex snow photochemistry column model. Snow nitrate photolysis in the column model is constrained by 1-cm depth resolved observations of $\delta^{15}N(NO_3^-)$ in the snowpits, which is highly sensitive to UV photolysis [*Erbland et al*., 2015].

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Atmospheric Chemistry and Physics Discussions

Observations of UV light-absorbing impurities (LAI) reveal the highest concentrations in the top several centimeters of all snowpits dug before the snowfall event on January 30 through January 31. This "dusty" layer experienced continual dry deposition for over a month due to lack of snowfall, and UV radiation is rapidly attenuated in this snow layer. Nitrate concentrations are up to a factor of 151 times higher in the surface, dusty layer compared to other snow layers, suggesting that much of the nitrate in snow is also dry-deposited to the snow surface. The LAI and nitrate concentrations in the 5 cm of fresh snow that fell on January 30 through January 31 are a factor of 5 and 36 lower, respectively, compared to dusty layer LAI and nitrate concentrations. The highest $\delta^{15}N(NO_3^-)$ values in snow are generally located in the dusty layer, suggesting that much of deposited nitrate is associated with primary NO_x emissions from anthropogenic sources. Snow-surface $\delta^{15}N(NO_3^-)$ measurements range from -5.5‰ to 11.1‰ and suggest that the local nitrate burden at Horsepool is dominated by primary emissions from local anthropogenic sources, except during fresh snowfall, when nitrate formed outside of the basin is an additional source of nitrate to the snow surface.

The snow-sourced N_r fluxes calculated using calculated UV actinic flux profiles and observed snow nitrate concentrations are similar in magnitude to the daily-averaged fluxes of snow-sourced N_r calculated using the more complex snow photochemistry column model. The daily-averaged flux snow-sourced N_r (F_{Nr}) to the boundary layer ranges from 5.6×10^7 to 7.2×10^8 molec cm^{-2} s^{-1} and the modeled campaign-maximum F_{Nr} is 3.1×10^9 molec cm^{-2} s^{-1}. Snow-sourced NO_x fluxes are highly dependent on nitrate concentrations in the top several centimeters of snow; F_{Nr} values are roughly an order of

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magnitude higher in snowpits with a surface dusty layer compared to a buried dusty layer. The top-down emission estimate of primary NO_x in the Uintah and Duchesne counties reported in Ahmadov et al. [2015] is at least 300 times higher than estimated snow NO_x emissions, assuming that all N_r is emitted as NO_x. This suggests that snow-sourced NO_x fluxes likely have little influence on the boundary layer NO_x budget in the highly-polluted Uintah Basin. Assuming that all N_r is emitted as HONO also suggests that the snow-sourced reactive nitrogen fluxes associated with snow nitrate photolysis also likely do not significantly contribute to boundary layer HONO mixing ratios in the Uintah Basin. The relative importance of the flux of NO_x and HONO will influence the impact of the recycling of reactive nitrogen in snow on the chemistry of the boundary layer in snow-covered regions, but is unknown. Knowledge of the chemical speciation of snow-source N_r is required for a better understanding of the full impact of snow on local oxidant budgets. However, in the Uintah Basin, we conclude that air quality models can safely neglect the recycling of reactive nitrogen in snow when identifying the most effective strategies for reducing wintertime ozone abundances.

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Table 1. Snow photic zone depth and daily-averaged modeled F_{Nr} calculated using E8 and the TRANSITS model on January 22, January 31, and February 4.

Pit Date	Photic zone depth (cm)	Daily-averaged F_{Nr} (molec cm^{-2} s^{-1})		
		E8	TRANSITS (ϕ = 4.6 x 10^{-3})	TRANSITS (ϕ = 0.2)
January 22	5.0	5.6x10^{8}	6.3x10^{8}	2.9x10^{10}
January 31	7.0	1.9x10^{8}	5.6x10^{7}	2.7x10^{9}
February 4	7.0	3.2x10^{8}	1.2x10^{8}	5.6x10^{9}

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Atmospheric Chemistry and Physics
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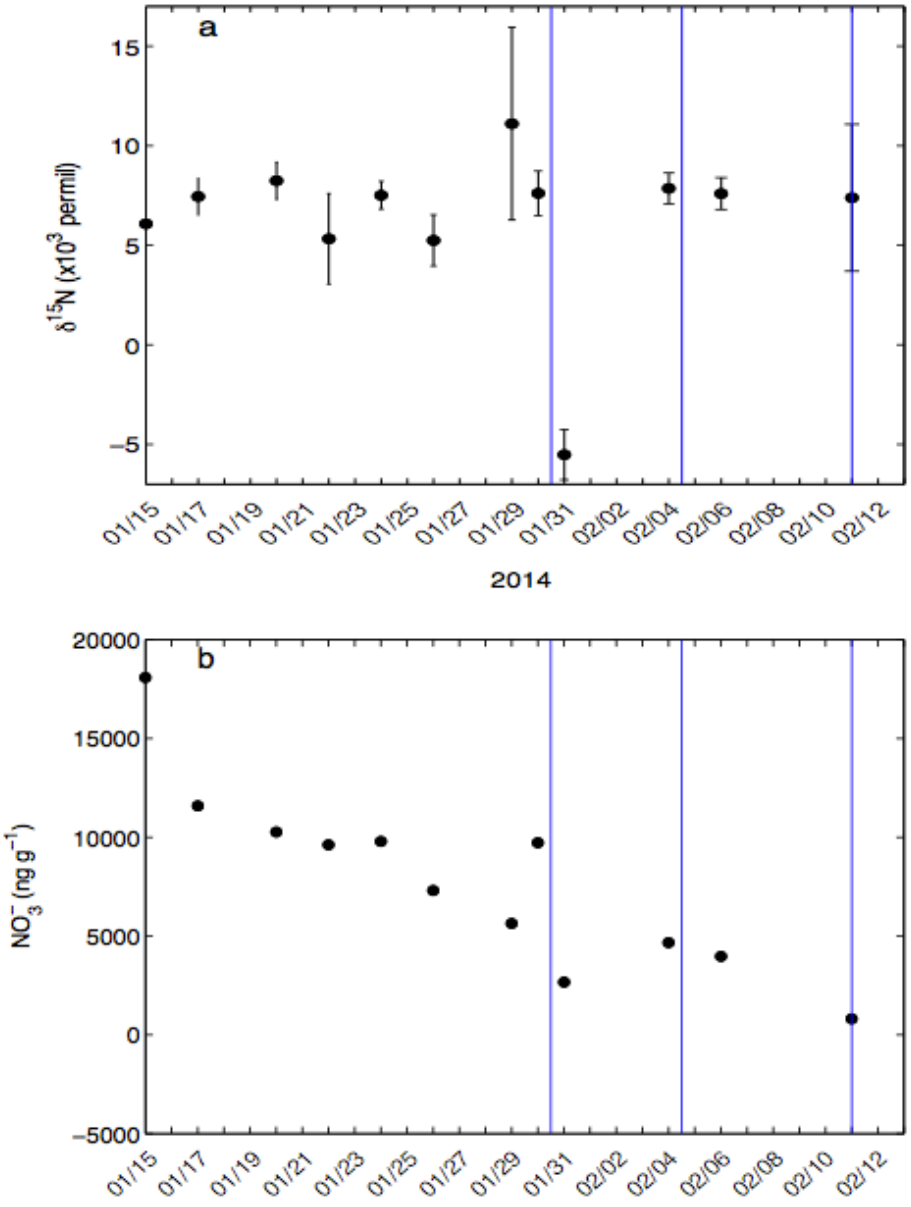

Figure 1. (a) Mean surface snow (top 1 cm) $\delta^{15}N(NO_3^-)$ observations (‰) for triplicate measurements from each snowpit (close circles). The full range of triplicate measured surface snow $\delta^{15}N(NO_3^-)$ for each snowpit is also indicated (vertical black lines). (b) Surface snow nitrate concentration measurements (ng g^{-1}) for each snowpit. The uncertainty in the concentration measurements is 0.75‰. The vertical blue lines indicate snowfall events.

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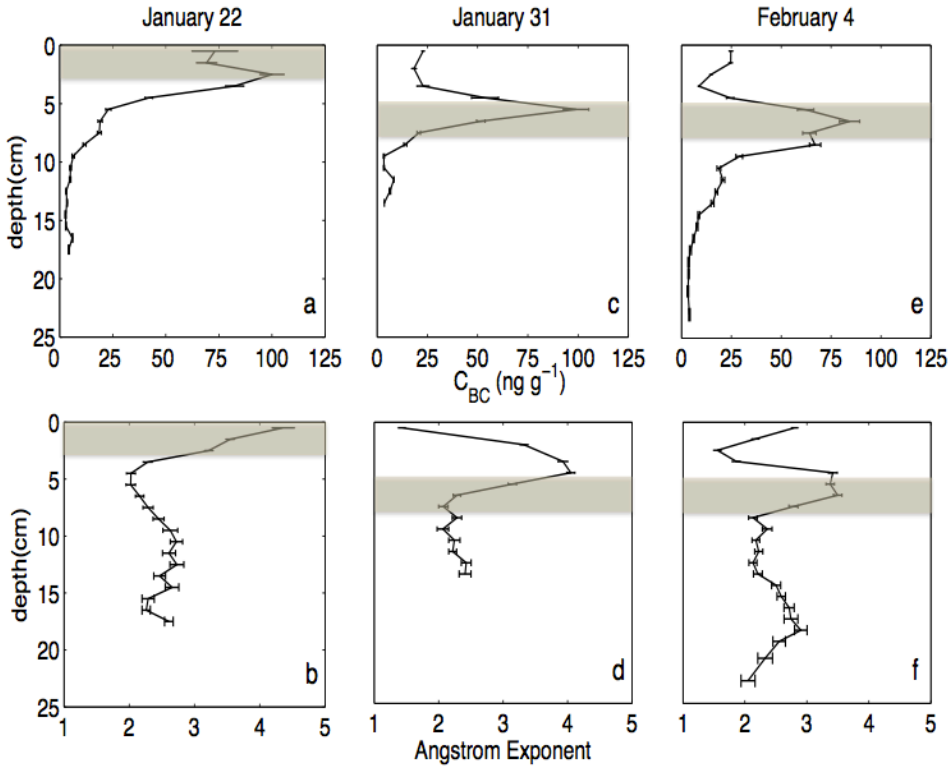

Figure 2. Snow optical properties measured on January 22 (top), January 31 (middle), and February 4 (bottom). (top) Vertical profiles of mean snow black carbon (C_{BC}, ng g^{-1}) measurements and the full range of C_{BC} measured at each depth (horizontal black lines), (bottom) mean Ångstrom exponent (Å, unitless) measurements and the full range of Å measured at each depth (horizontal black lines). The brown shaded region represents the dusty layer as defined in the text.

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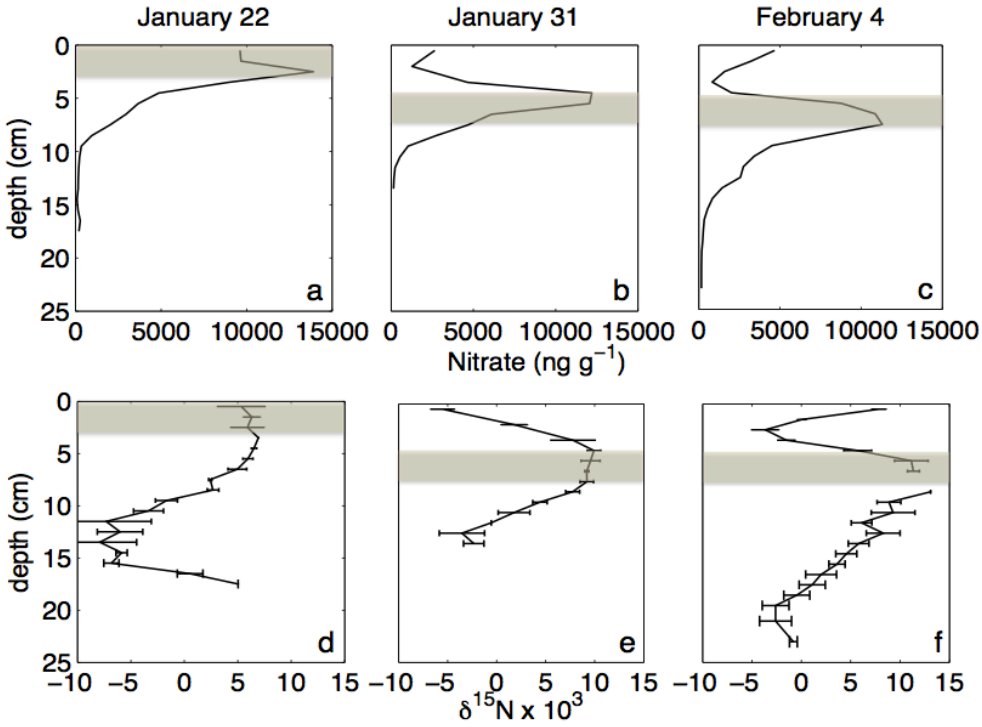

Figure 3. Observed vertical profiles of nitrate concentration (top) and its nitrogen isotopes (bottom) in snow on January 22 (left), January 31 (center), and February 4 (right). The brown shaded region represents the dusty layer.

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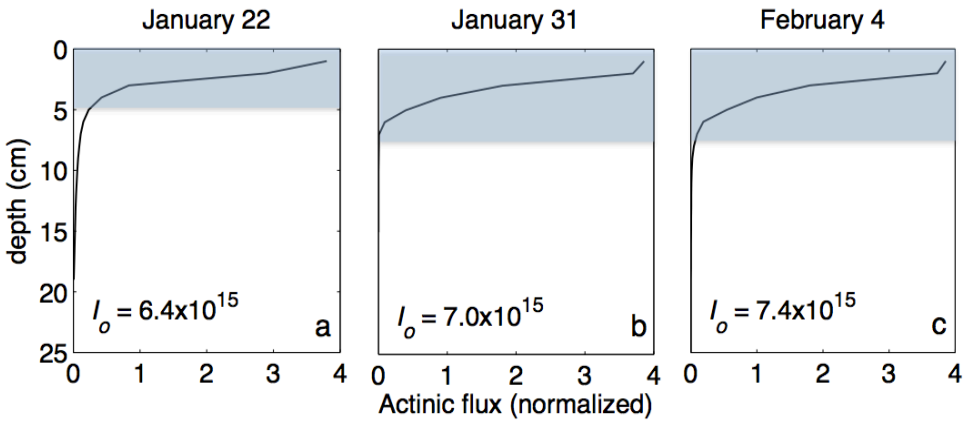

Figure 4. Modeled vertical profiles of UV actinic flux (I, photons cm^{-2} s^{-1}) normalized to surface downwelling irradiance (I_o, photons cm^{-2} s^{-1}). Also presented is measured total UV I_o (λ=300-350 nm) for a solar zenith angle of 60° on each day. The blue shaded region represents the snow photic zone.

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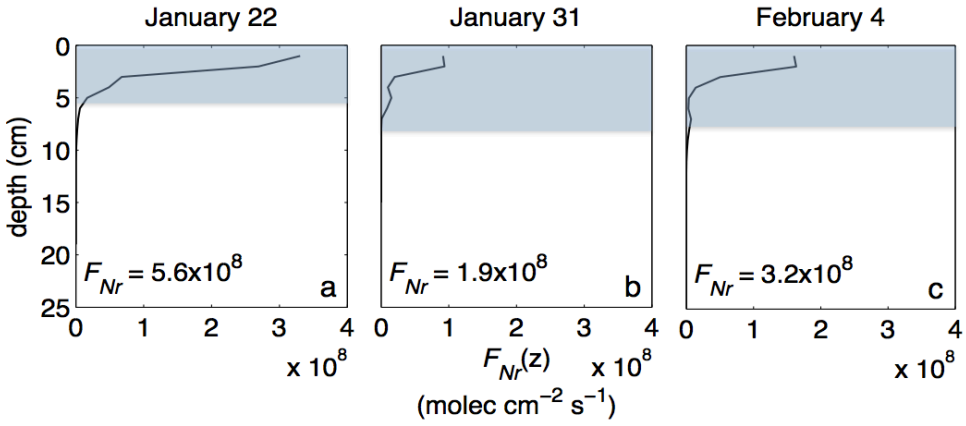

Figure 5. Modeled vertical profiles of snow-sourced N_r fluxes (F_{Nr}, molec cm^{-2} s^{-1}) calculated using E8. Also shown is total F_{Nr}, which is the depth-integrated F_{Nr} over the photic zone. The blue shaded region represents the snow photic zone.

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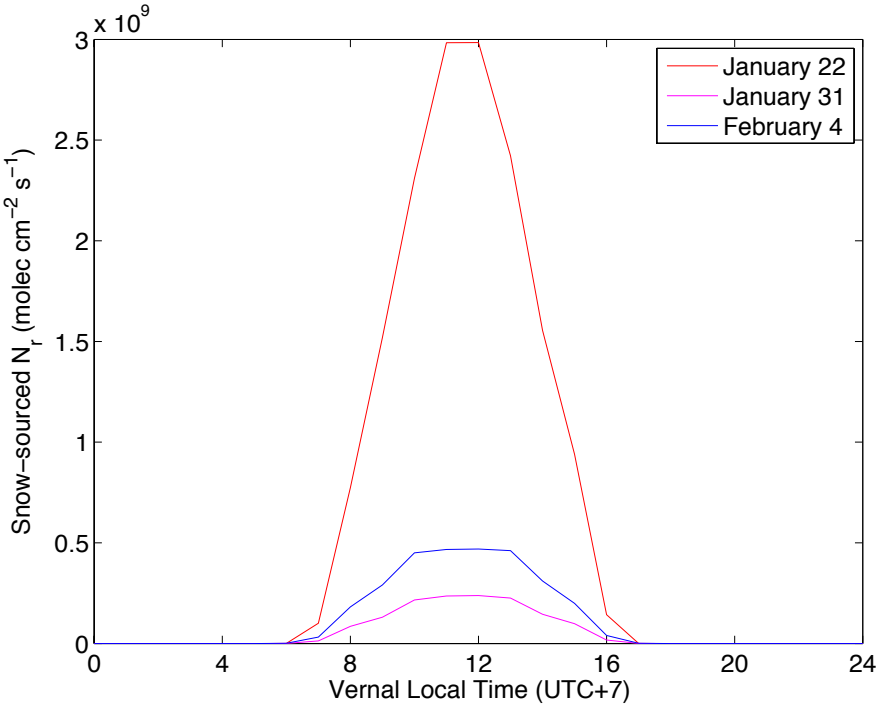

Figure 6. Modeled diurnal profiles of snow-sourced N_r fluxes (F_{Nr}, molec cm^{-2} s^{-1}) calculated using TRANSITS on January 22 (red), January 31 (magenta), and February 4 (blue).

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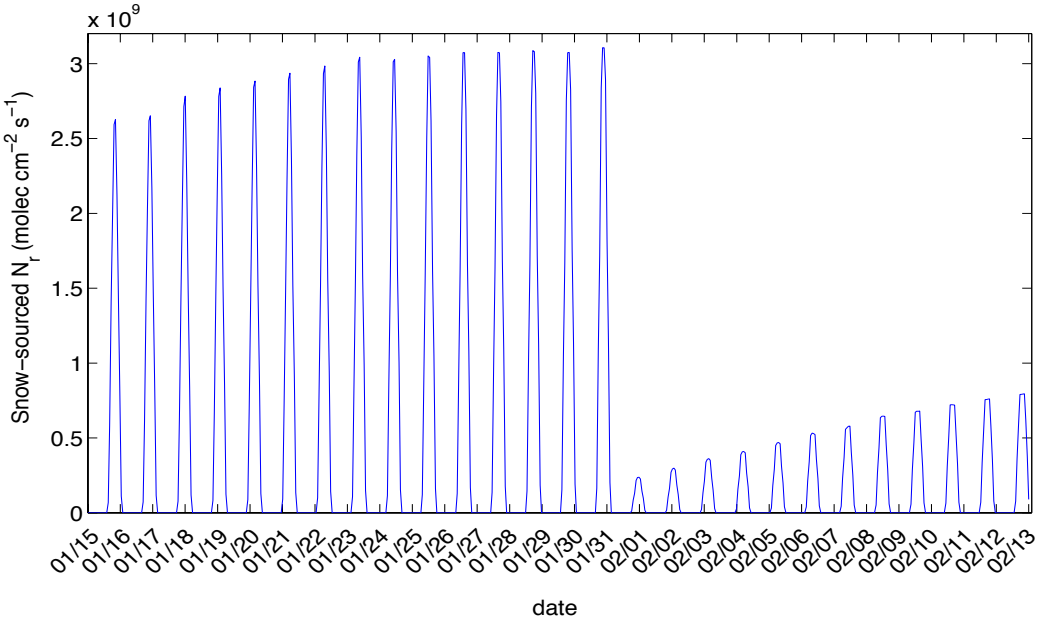

Figure 7: Modeled snow-sourced N_r fluxes (molec cm^{-2} s^{-1}) for each hour during the campaign from January 15 to February 11.

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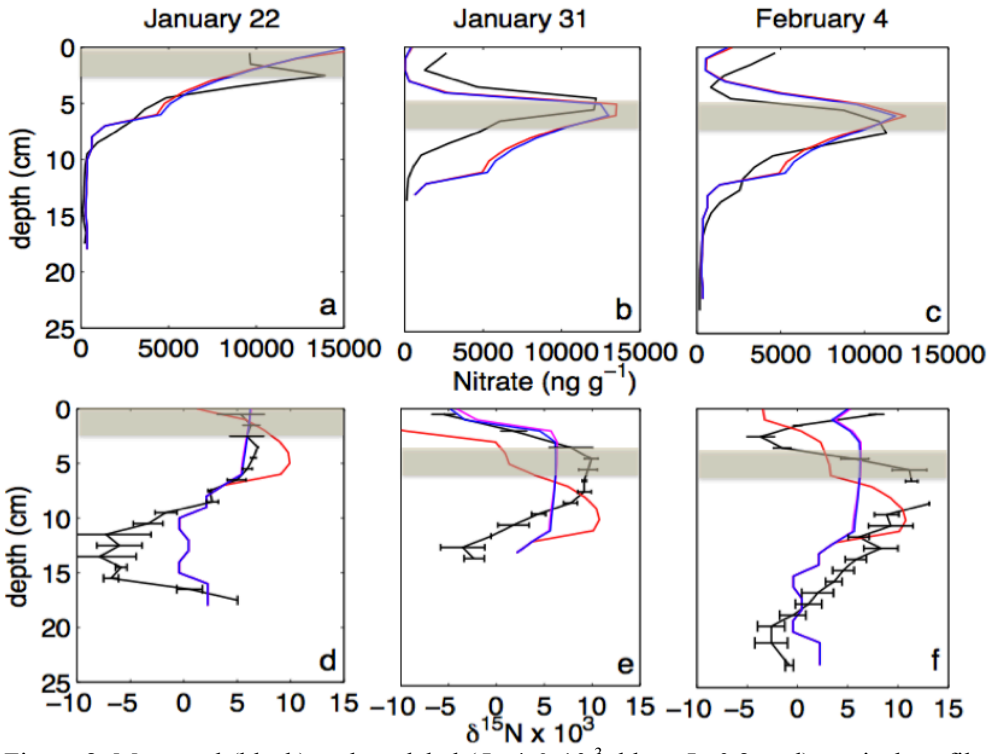

Figure 8. Measured (black) and modeled (Φ=4.6x10^{-3}, blue; Φ=0.2, red) vertical profiles of snow nitrate concentration (top) and $\delta^{15}N(NO_3^-)$ (bottom) on January 22 (left), January 31 (center), and February 4 (right). Modeled $\delta^{15}N(NO_3^-)$ profiles are calculated using variable quantum yields (Φ=4.6x10^{-3}, blue; Φ=0.2, red, Φ=0, magenta). The brown shaded region represents the dusty layer.