Dynamics of ozone and nitrogen oxides at Summit, Greenland: I. Multi-year observations in the snowpack

Brie Van Dam¹, Detlev Helmig^{1,*}, Claudia Toro^{2,3}, Paul Doskey⁴⁻⁶, Louisa Kramer^{2,6}, Keenan Murray⁴, Laurens Ganzeveld⁷, and Brian Seok¹

¹Institute of Arctic and Alpine Research, University of Colorado at Boulder, CO, USA

²Department of Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, MI, USA

³Department of Civil and Environmental Engineering, Washington State University, Pullman, WA

⁴Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI, USA

⁵School of Forest Resources and Environmental Science, Michigan Technological University, Houghton, MI, USA

⁶Atmospheric Sciences Program, Michigan Technological University, Houghton, MI, USA

⁷Department of Environmental Sciences, Wageningen University, Wageningen, Netherlands

*corresponding author, detlev.helmig@colorado.edu

Revised Manuscript for *Atmospheric Environment*

September 21, 2015

Abstract

A multi-year investigation of ozone (O₃) and nitrogen oxides (NO_x) in snowpack interstitial air down to a depth of 2.8 m was conducted at Summit, Greenland, to elucidate mechanisms controlling the production and destruction of these important trace gases within the snow. Snowpack O₃ values ranged from 30-40 ppbv during winter months, and dropped below 10 ppbv in summer. Wintertime NO_x levels were low at all depths in the snowpack (below 10 pptv for NO and below 25 pptv for NO₂). In the summer, NO values up to 120 pptv, and NO₂ mixing ratios up to ~ 700 pptv were observed. Ozone loss within the snowpack was observed throughout all seasons. The magnitude of the ozone loss rate tracked the seasonal and diurnal cycle of incoming short wave solar radiation. Production of NO within a shallow layer of the snowpack was recorded during the spring and summer months. Production of NO₂ also occurred, and heightened levels were measured down to 2.5 m in the snowpack. The average daily maximum in NO was observed at solar noon, and the minimum was seen during night. The daily peak in NO₂ was on average

seven hours shifted from the incoming solar radiation and NO maxima. NO_x levels in interstitial air during spring were enhanced relative to summer and fall. The influence of meteorological effects such as wind pumping on snowpack interstitial air levels of O₃ and NO_x was investigated using case study periods. Increased snowpack ventilation during high wind events, was found to yield enhancement in snowpack NO_x, with this effect being enhanced during times when ozone was elevated in ambient air. This behavior suggests that ozone is involved in NO_x production in the snowpack. This extensive set of observations is used to re-evaluate physical and chemical processes that describe the dynamic O₃ and NO_x chemistry occurring within snowpack interstitial air at Summit.

1. Introduction

Snow photochemistry has been the focus of field studies at sites in the Arctic and Antarctic following discovery of the relationship between chemistry occurring on snow and ice surfaces and polar ozone (O₃) and mercury depletion events in spring (Oltmans, 1981; Barrie et al., 1988; Oltmans et al., 1989; Foster et al., 2001; Simpson et al., 2007). Production of nitrogen oxides (NO_x [NO + NO₂]) and subsequent release from the snowpack was first measured at Summit, Greenland, in the 1990's (Honrath et al., 1999). NO_x production was hypothesized to be linked to the photolysis of deposited nitrate (NO₃⁻) in snow and suggested a photochemical NO_x source in surface snow to the Arctic boundary layer (Honrath et al., 1999; Jacobi et al., 2004).

Loss of O₃ in the snowpack has been observed at Arctic, Antarctic, and mid-latitude locations. The degree of ozone depletion with depth has been shown to be influenced by various factors, including snow physical and chemical properties, incoming solar radiation levels, meteorological conditions, and the substrate underlying the snowpack (Bocquet et al., 2007; Helmig et al.,

2007b; Seok et al., 2009). Depletion of O₃ in the Summit snowpack was first described in the early 2000's and attributed to either chemical or physical processes in the snowpack (Peterson & Honrath, 2001). In *Helmig et al. 2009*, a link between O₃ destruction in the snowpack and O₃ fluxes at the surface was demonstrated. Model sensitivity studies have demonstrated the important role of the Arctic snowpack as a sink for O₃ in the accurate representation of Arctic tropospheric O₃ budgets, particularly during winter (Helmig et al., 2007d).

Mechanisms of O₃ depletion in snowpack and effects on atmosphere-snowpack exchange are poorly understood. Reactive bromine (Br) was recently observed in the ABL at Summit, and Br and NO_x chemistry in snow has been suggested to play a role in O₃ depletion (Dibb et al., 2010; Liao et al., 2011; Stutz et al., 2011; Thomas et al., 2011). However, application of a one-dimensional snow chemistry and ABL model has not been able to accurately reproduce the magnitude of summertime O₃ depletion within snow by incorporating NO_x and Br chemistry (Seok et al., 2010; Thomas et al., 2012) alone. In the model study by *Thomas et al. (2012)* measurements of NO_x in snowpack interstitial air were cited as necessary to evaluate the accuracy of snowpack chemistry models.

At South Pole, the combination of snow photochemical production and snowpack emissions of NO, shallow and sustained atmospheric boundary layer conditions, and a long lifetime of NO_x lead to conditions that foster production of O₃ in the surface layer (Davis et al., 2001; Davis et al., 2004; Helmig et al., 2008a; Helmig et al., 2008b; Neff et al., 2008). At Summit, surface energy exchanges and boundary layer depths exhibit diurnal cycles. These diurnal variations in surface conditions is one of the reasons why accumulation of NO and O₃ production in the surface layer is much weaker at Summit than at South Pole (Dibb et al., 2002; Honrath et al., 2002; Cohen et al., 2007; Helmig et al., 2009; Van Dam et al., 2013) and elevated ozone primarily

results from transport to the site (Helmig et al., 2007a; Kramer et al., 2014). This different behavior in ozone and oxidized nitrogen chemistry between these two sites illustrates the importance and diversity of processes driving snow photochemistry, boundary layer dynamics, and oxidation chemistry in the lower polar atmosphere.

Here, we present measurements of O₃ and NO_x in the Summit snowpack from 26 June, 2008, to 22 July, 2010. The measurements were part of the first continuous, year-round study of the chemical constituents in snowpack interstitial air. Seasonal and diurnal cycles of O₃ and NO_x, the distribution of the chemical species with depth in the snowpack, and the primary physical and chemical drivers of trace gas levels in snowpack are investigated.

2. Methods

2.1. Atmospheric measurements

Summit Station, Greenland, is a research facility operating year-round near the summit of the Greenland Ice Sheet (72.6° N, 38.5° W; 3218 m above sea level). The study site included a buried laboratory facility, snow-sampling manifold, and a meteorological tower installed in the clean air sector ~650 m southwest of the main camp structures. Continuous measurements were conducted from 26 June, 2008, to 22 July, 2010, a period of 756 d. Meteorological conditions were measured on a ~9 m tower. Instrumentation included a cup anemometer to measure wind speed (Model 010C, MetOne Instruments), combined cup anemometer and wind vane to record wind speed and direction (Model 030B, MetOne Instruments), and three type-E thermocouples housed in an aspirated radiation shield for measuring ambient temperature at three heights (R.M. Young Co., Model 43408). Two pyranometers (LI-COR Biosciences Model LI-200) were mounted at ~1.25 m height on a separate tower several meters south of the meteorological tower

and measured incoming and reflected solar radiation. Instruments to record wind speed and temperature were originally installed at a height of 9 m and by the end of the sampling period were 6.2 m above the snow surface due to drifting and accumulation of snow around the tower base.

2.2. Snow interstitial air

2.2.1. Sampling system

A multi-inlet snow sampling manifold ('snow tower') for measuring trace gases at multiple depths in interstitial air was constructed for use in this study, with a similar design to that described by *Seok et al. (2009)*. A schematic and several pictures from throughout the measurement campaign are shown in Fig. 1a–d. The tower system consisted of a vertical post of square aluminum alloy (3.8 x 3.8 cm) with eight 60 cm long cross arms spaced vertically every 30 cm. To install the sampling tower, a 1 m deep hole with a $\sim 1 \text{ m}^2$ opening was carefully excavated from the snowpack at the end of May 2008. The sampling tower was placed within the hole and snow was allowed to accumulate naturally over a period of about one month. Prior research suggests that nitrate levels in the snowpack would be expected to re-equilibrate towards the original nitrate depth profiles (Burkhart et al., 2004; France et al., 2011). Thus, we make the assumption that trace gas levels measured from the sampling system are representative of the surrounding snow. Fig. 1a shows surface conditions around the snow tower in July 2008, approximately one month after the system was installed. Due to accumulating snow, an extension was installed on the snow tower on 21 August 2009, which added six additional vertical levels. By the end of the measurement period in July 2010, gas measurements were acquired at 14 levels at 30 cm intervals over a snowpack depth of 2.9 m through 1.4 m above the snow surface. Snowpack tempera-

ture at each of these sampling depths was recorded with a thermocouple wire mounted to the tower cross arm. Pairs of sampling inlets were located on each cross arm on the tower; cross arms were rotated orthogonally to the arms above and below. This design minimized flow through each inlet and reduced disturbance to the snowpack. Flow rates were 1.2 – 2.5 L min⁻¹ and were split between

Figure 0: Images of the snow interstitial air sampling tower implemented in this study from (a) July 2008, (b) November 2008, and (c) April 2010. Part (d) shows a simplified schematic of the snow tower interstitial air sampling system. Grey lines on the tower indicate thermocouples measuring snowpack temperatures, and black crosses indicate gas sampling inlets.

the inlet pairs, producing effective flow rates of 0.6 – 1.25 L min⁻¹ through each inlet. Sample

inlets were fitted with 25 mm Acrodisc® hydrophobic polytetrafluoroethylene (PTFE) syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA). Inlet pairs were connected via a Teflon perfluoroalkoxy (PFA) union tee to a 30 m x 0.64 cm OD (0.40 cm ID) Teflon PFA sampling line. Cross arms were fitted with type-E thermocouples to record temperatures at each level within and above the snow. Trace gas sampling lines and thermocouples (all ~30 m) were carried under the snow surface inside an insulated, temperature-controlled conduit with an outlet to the buried laboratory containing the instrumentation. The sampling lines were connected to a manifold with solenoid valves that allowed selection of sample inlet pairs for each layer. An automatic sampling pattern was implemented whereby each pair of inlets was measured sequentially from the uppermost to deepest level. Measurements were taken for 10 min from each inlet pair during an 80 – 140 min measurement cycle.

2.2.2. O_3 measurement

Ozone was measured from the snowpack tower system using a UV photometric O_3 analyzer [Model 49, Thermo Environmental Instruments (TEI), Franklin, MA] with calibration traceable to the U.S. National Institute of Standards and Technology (NIST). The instrumental detection limit and precision were 1 ppbv, and the response time was 20 s. Ozone was sampled every 10 s, and the values averaged over 1 min intervals. Prior to operation the entire snow sampling system including inlet filters, sampling lines, and valve manifold were conditioned by purging at 3 L min^{-1} with air containing ~300 ppbv O_3 for 24 hrs. A measurement cycle, including variations in the mixing ratios of O_3 , line pressure, and flow rate is displayed in Fig. 2. Gas levels required ~1-2 min to stabilize after switching inlet heights. The first 3 min and last 2 min of each 10 min

sampling sequence were removed, and the mean of the 5 remaining values (5 minutes) was calculated to represent the mixing ratio for the level.

Figure 2: An example of one measurement cycle on the snow tower. Minute averages of O_3 mixing ratios (open circles), flow rate in the sampling line (filled diamonds), and pressure in the sampling line (stars) are shown as a function of time and sampling level. Each level was sampled for 10 minutes.

2.2.3. NO_x measurement

The NO_x instrument described by Honrath et al. (2002) and Beine et al. (2002) was updated to run autonomously and with an improved calibration for the subject of the subject study. Mixing ratios of NO and NO_2 were alternately measured between two inlets on the meteorological tower and inlets on the snowtower. The chemiluminescence reaction with O_3 (Ridley & Grahek, 1990) and conversion of NO_2 to NO by UV photodissociation (Kley & McFarland, 1980) were used to measure NO and NO_2 , respectively. The instrument utilized a photolytic NO_2 converter (Air

173 Quality Design Inc., Wheat Ridge, CO, USA) to reduce interferences from conversion of other
174 trace gas species to NO.

175 Calibrations to determine NO sensitivity and NO₂ conversion efficiency were performed twice
176 daily by standard addition of a small flow (10 ml min⁻¹) of NO in N₂ (several standard tanks were
177 used, ranging in mixing ratio from 0.79-0.93 ppm, ±2% accuracy; Scott Marrin and Scott Spe-
178 cialty Gases) into one of the inlets on the meteorological tower. The NO₂ conversion efficiency
179 of the photolytic converter was determined via the standard addition of NO₂ at the inlet. NO₂ was
180 generated via gas phase titration of NO and O₃ that was generated in oxygen using a low-
181 pressure mercury lamp. Automated measurements for NO and NO₂ background signals were
182 conducted every 3 d using an excess flow of zero gas (Breathing Air grade compressed air, Air-
183 gas, Radnor, PA, USA) that passed through an activated charcoal trap.

184 The 10-min measurement cycle included a 30-s average determination of photon counts in the
185 NO and NO₂ measurement mode from two inlets on the meteorological tower and one inlet on
186 the snow tower and a zero mode to measure baseline counts. Variability in the measured counts
187 was attributed to photon counting noise, which can be treated as a Poisson distribution. The 30-s
188 averaged photon counts that deviated more than 3 times greater than the expected Poisson value
189 were filtered from the dataset. High variability in the photon counts during these measurements
190 was likely to be the result of electronic noise spikes or local pollution.

191 The detection limits (DL) for NO and NO₂ were estimated from the precision of the measure-
192 ments, given as 2 times the standard error (2SE) in the 30-s averages. The median DL for the NO
193 and NO₂ measurement within the snowpack was 3.8 and 5.8 pptv respectively. The dataset was
194 filtered for measurements with very high levels (> 1000 pptv) or very large negative values. For
195 the snowpack data, 1 high NO and 11 high NO₂ measurements were removed. Thresholds for

large negative values were determined from the 99th percentile of all SE values in each snow tower inlet separately (SE₉₉) for NO and NO₂. Data points with NO or NO₂ mixing ratios below 2 SE₉₉ (~1% of the data) were excluded from further data processing. The remaining data below the detection limit were considered in statistical analyses by calculating the mixing ratio using the averaged photon count, applying the instrument response, and correcting for the background. The total uncertainty for the measurement is given by the root sum of the squares of the accuracy and the precision. Accuracy in the NO and NO₂ measurement was estimated from the root sum of the squares of the errors associated with the NO calibration gas and the mass flow controller rates, giving an estimated error of 7%. An additional contribution of the uncertainty arises from the error associated with the background correction; this correction varied throughout the campaign with upper thresholds of uncertainty in the correction of ±2.5 pptv for NO and ±5 pptv for NO₂. Considering the precision of the measurement given above results in a total relative measurement uncertainty that is highest for low values near the detection limit, reaching up to ~150%, and becomes smaller at higher mixing ratios, dropping to <10% at levels >100 pptv. NO and NO₂ can be underestimated and overestimated, respectively, due to losses from the reaction of NO and O₃ within sampling lines. The O₃ and NO mixing ratio and the residence time within the sampling line were used to correct losses as follows:

$$[\text{NO}]_t = [\text{NO}]_0 e^{-kt[\text{O}_3]} \quad (1)$$

where $[\text{NO}]_t$ is the mixing ratio of NO detected at the instrument after a lag time, t ; k is the rate constant for the reaction between O₃ and NO ($1.2 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 0 °C (Atkinson et al., 2004)), $[\text{O}_3]$ is the actual measured ozone mixing ratio, and $[\text{NO}]_0$ is the mixing ratio of NO at the inlet.

The decrease in the signal due to the loss of NO from the reaction with ambient O₃ within the sampling line was calculated using Eq. 1. The loss of NO was estimated by applying Eq. 1 to the measurements at each inlet as follows:

$$\Delta\text{NO}=[\text{NO}]_t-[\text{NO}]_0 \quad (2)$$

All the sampling lines were covered and protected from light which prevented photolysis of NO₂ to NO, and thus, the magnitude of the underestimation and overestimation in [NO] and [NO₂], respectively. We have no experimental data to estimate a possible artifact in the NO and NO₂ determination from sampling of gaseous HO₂NO₂. An estimate based on literature and theoretical considerations is provided in the Supplement.

2.2.4. Gas measurement uncertainties and data filtering

All trace gas data were filtered for northerly wind conditions that have the potential to transport polluted air from the main camp facilities into the clean air sector. This sector was classified as wind directions between 342° - 72°. This filter removed 12% of the data. Another filter was applied to remove data when there was insufficient sample flow to the instruments (as monitored by the pressure sensor in the valve manifold). Due to drastic temperature changes near the snow surface, flow in several of the near-surface sample lines during the springtime became restricted when ice accumulated in the inlets. Flow rate thresholds were different for the O₃ and the NO_x instruments and the filter removed 6% and 1% of the snowpack NO_x and O₃ data, respectively. Seasonal data were binned for winter (November through January), spring (February through April), summer (May through July), and autumn (August through October).

Figure 3: Monthly whisker plot of the incoming solar radiation through the entire measurement period. Upper and lower lines of the box correspond to the 5 and 95% levels, whiskers indicate the minimum and maximum hourly value in the given month, the line within each box corresponds to the monthly median value, and the open circles indicate the monthly mean.

3. Results

3.1. Seasonal cycles

3.1.1. Solar radiation and snow temperature

Variations in incoming solar radiation at Summit are drastic and display a strong seasonal cycle (Fig. 3). Hourly averaged wintertime solar radiation remained less than 30 W m^{-2} for the months of November, December, and January. In summer, incoming solar radiation varies on the order of a factor of 20 between night and day, with maximum daytime levels of $\sim 700 \text{ W m}^{-2}$ during clear sky conditions. Incoming shortwave radiation levels changed rapidly between the winter and summer extremes during the transitional seasons of spring and summer.

254 Snowpack temperatures exhibit very different behavior near the surface compared to deeper lev-
255 els (Fig. 4). Daily average atmospheric temperatures 20 cm above the snow surface agreed with
256 temperatures between 0 and 30 cm deep in the snowpack to within $\sim 5^{\circ}\text{C}$. The agreement indi-
257 cates that daily fluctuations in atmospheric temperature are reflected in the near-surface snow-
258 pack. Fluctuations in atmospheric temperature on a time scale of 10 d or less were not reflected
259 below 150 cm depth. Daily averages of snowpack temperatures deeper than 150 cm lagged ap-
260 proximately one month (30-32 d) behind snowpack temperatures measured within 30 cm of the
261 surface. The minimum daily averaged temperature deeper than 150 cm in the snowpack was re-
262 corded in spring (-37°C , 28 March 2009). Each level generally lagged ~ 5 d behind the level 30
263 cm above it during the spring warming period. The maximum daily average temperature below a
264 depth of 150 cm (-20°C) occurred on 27 August 2009; the seasonal amplitude below 150 cm
265 was 17°C . Temperatures during the spring seasons of 2009 and 2010 varied significantly. In
266 2009 there was an extreme cold period and the daily average temperatures 10 cm above the
267 snowpack and temperatures in the 0-60 cm deep layer dropped below -40°C for 26 consecutive
268 days. The lowest daily average temperature in snowpack during the period was -56°C . An ex-
269 treme and persistent cold period was not observed in 2010; however, a shorter intense cold pe-
270 riod of ~ 10 d in December was recorded in the 0-60 cm deep layer.

Figure 4: Snowpack temperature through the entire measurement period (July 2008 - July 2010). The vertical axis is the height or depth of the measurement relative to the snowpack surface. The horizontal axis shows the month and year.

Daily averages of O_3 , NO , and NO_2 , plotted as a function of the inlet height (or depth) relative to the snowpack surface, are shown in Figs. 5a-c. A plot of total NO_x , which, due to the $\sim 5x$ higher NO_2 , is mostly determined by the NO_2 profile, is provided as Fig. S1 in the Supplement.

Changes in snowpack depth relative to the tower inlets were measured daily during summer and 2-3 times per week during late fall, winter, and early spring. Color contours describe mixing ratios in ppbv (O_3) or pptv (NO_x). This extensive data set highlights a pronounced seasonal cycle present in O_3 , NO , and NO_2 in the snowpack interstitial air, which closely tracked the radiation cycle.

Figure 5: (a) Ozone, (b) NO, and (c) NO_2 through the entire measurement period. The vertical axis reflects the height or depth of the measurement relative to the snowpack surface. The horizontal axis shows the month and year. Color contours show gas mixing ratios. White areas are due to missing data. Prior to the addition of the extension in 2009, ambient O_3 , NO, and NO_x measurements from inlets on the meteorological tower (located at ~3 m in July 2008) were used for the upper above-surface measurement level.

3.1.2. O_3

Mixing ratios of O_3 in the snowpack were less than levels in the overlying atmosphere throughout the year (Fig. 5a). Ozone in the snowpack varied from less than 10 ppbv to ~45 ppbv and the O_3 gradient changed considerably between summer and winter. Levels of O_3 within the 60-90 cm depth layer during wintertime were similar to atmospheric levels, i.e. during November - January, the minimum daily O_3 values in the same layer were on average 88% of ambient values. In contrast, from May to July, minimum daily O_3 values in that layer were only 9% of ambient levels.

Seasonally averaged depth profiles of O_3 , NO, and NO_2 are displayed in Fig. 6. Mixing ratios of the trace gases were binned by 30 cm depths, and statistics for each depth and season were calculated. The standard deviation for O_3 levels during summer is larger, indicating more dynamic behavior within the snowpack compared to winter. Summertime atmospheric O_3 levels were higher than winter, yet summer and winter median O_3 values in the 0-30 cm deep snowpack layer were within 1 ppbv of each other (38.9 ppbv and 38.2 ppbv, respectively). Summertime median O_3 values decreased rapidly in the shallow snowpack layers and remained <23 ppbv at depths below 90 cm.

3.1.3. $NO + NO_2$

Levels of NO and NO_2 within the snowpack varied from less than 10 pptv to greater than 100 pptv, and from less than 50 pptv to greater than 600 pptv, respectively (Fig. 5b,c). During winter, NO and NO_2 in the ABL and the snowpack exhibited little temporal or spatial variation (Fig. 5b,c). Mean and median NO levels were below 10 pptv in winter, with maxima not exceeding

307 50 pptv in the snowpack. Mean and median NO_2 levels were below 25 pptv during winter, with
 308 maxima not exceeding 100 pptv. Beginning in March, enhancements of NO and NO_2 were
 309

Figure 6: Seasonally averaged (a,b) O_3 , (c,d) NO , and (e,f) NO_2 as a function of depth. All data from 2008 – 2010 were filtered by season, and binned by 30 cm depth layer in the snowpack. Open circles indicate the median, upper and lower box limits are 25th and 75th percentile with the line indicating the mean, whiskers indicate 5th and 95th percentile, and the filled circles show maximum and minimum values. Two layers were used above the snow surface: a 0-30 cm layer, and all > 30 cm were combined into the “ambient” measurement. Note the different x-axis scales for NO and NO_2 during the summer. The number of measurements included in each bin is listed in Supplement Table S2.

observed in the snow, with these primarily confined to a near surface layer 0 to 60 cm deep. Enhanced NO_2 mixing ratios (higher than in ambient air) were observed down to the lowest depth that was sampled, i.e. 2.5 m in spring 2010. Seasonally averaged levels of NO and NO_2 remained below 10 pptv and 50 pptv, respectively, throughout the snowpack and in the ABL (Fig. 6c-f). Enhancements of NO occurred in a narrow range from 0 to 60 cm below the surface. Atmospheric levels of NO close to the surface exhibited a larger range in values and were slightly elevated compared to winter observations. Median NO levels beneath 60 cm in summer were 10-15 pptv and were similar to winter values. Enhanced concentrations of NO_2 were observed at all depths; the highest median mixing ratio (300 pptv) was observed within the 90-120 cm deep layer.

3.2. Spring-fall differences

If solar radiation was the primary determining variable for the snowpack ozone and NO_x dynamics, then similar behavior of these trace gases would be expected under equivalent irradiance levels in spring and fall, and highest production rates would be expected in summer. However, the comparison of the seasonal ozone and NO_x behavior shown in Figure 7 reveals some notable differences between spring and fall and nonlinearity with solar irradiance. To facilitate a more quantitative comparison, the ambient and snowpack data at each sampling depth displayed in Figure 7 were averaged for the spring and fall periods as defined above. Since the season definition does not quite space spring and fall equal distance from the summer equinox, and due to differences in cloudiness, the average solar irradiance for the spring and fall windows were different, with an average solar irradiance of 67.1 W m^{-2} during spring, and 83.9 W m^{-2} during fall (i.e. 23% higher in fall). Mean solar irradiance for the summer window was 299 W m^{-2} .

3.2.1. Ozone

Hourly-averaged daily atmospheric O₃ mixing ratios were at a maximum during the spring in agreement with previous analyses that have shown a prominent seasonal springtime O₃ maximum in surface O₃ at Summit (Helmig et al., 2007b,c). Ambient ozone mixing ratios during autumn were ~10 ppbv lower and more similar to winter observations than to spring. Similarly to ambient air, levels of O₃ in interstitial air were generally higher in spring than in fall. There was somewhat less O₃ depletion in the shallowest snowpack layer (0-30 cm depth) in spring compared to fall (Fig. 7a). However, the magnitude of the average diurnal cycle was greater in spring (on the order of 10-15 ppbv difference between daily median maximum and minimum in the layers between 30 and 120 cm depth in the snow) than in autumn (8-10 ppbv difference between daily median maximum and minimum in the same snowpack layers). These changes in the diurnal amplitude roughly scale with the seasonal differences in ozone seen in ambient air.

3.2.2. NO_x

NO was generally higher in fall than in spring, with an ambient air level of 7.3 pptv in fall, versus 5.7 pptv in spring. Higher levels were observed at all snowpack depths in the fall, with the degree of enhancement increasing with depth, i.e. NO levels below 30 cm were ~2-4 times higher in fall than in spring (Figure 7b, Supplement Table S1). The behavior of NO₂ was opposite to NO, with generally higher average levels seen in spring than in fall. NO₂ was ~80% higher in ambient air during spring and ~ 50-110% higher in the 0-0.9 m depth layer; at deeper depths NO₂ spring-fall levels were in a similar range (Figure 7c, Supplement Table S1).

3.3. Diurnal cycles

Figure 7 displays the median hourly O_3 , NO, and NO_2 values for each layer in the snowpack; panels (a)-(d) for each figure further divide the data by season. All atmospheric values are binned together in this analysis, as are measurements below 150 cm deep in the snowpack. The hourly averaged radiation cycle is included with each figure panel for reference.

3.3.1. O_3

Hourly averaged O_3 mixing ratios remained in a narrow range between 30-45 ppbv and did not exhibit a diurnal cycle during winter (Fig. 7a, panel a). Chemical dynamics in the snowpack increased as radiation increased in spring (Fig. 7a, panel b). Ozone values were below ambient at all levels within the snowpack. Maximum depletion occurred deepest in the snowpack during summer. The highest amplitude of the hourly averaged diurnal cycle (13 ppbv) occurred in the 30-60 cm deep layer during summer.

3.3.2. NO_x

Similar to O_3 , a diurnal cycle was not observed for NO and NO_2 during the winter months (Figs 7b,c). Wintertime NO remained below 10 pptv and average levels of NO_2 were less than 25 pptv. Diurnal cycles in NO and NO_2 levels developed during spring - fall. NO values at snowpack depths between 90 cm and the surface were enhanced over atmospheric values and tracked the daily solar radiation cycle. Peak NO mixing ratios at these depths occurred precisely during the peak in the incoming solar radiation cycle (Fig. 8). Median NO levels reached a maximum in the 0-30 cm layer at 14:00 GMT (12:00 local, West Greenland Time, WGT) and values in the snowpack were six times greater than median values in the overlying atmosphere during the same hour. Daily maxima of NO_2 in the snowpack below 30 cm were observed about 7 hr after peaks

in radiation and NO. The difference in timing of NO₂ enhancement has been observed in a previous controlled experiment (Honrath et al., 1999). NO₂ was higher at all levels within the snowpack than atmospheric levels during summer. NO₂ levels during springtime exhibited clear diurnal cycles at several depths and were approximately inversely related to radiation (NO₂ minima coincide with maxima in incoming solar radiation, Fig. 8c,f). The most extreme case was the 30 – 60 cm deep layer where a difference of almost 300 pptv between the average daily maximum and minimum was observed in spring. Fig. 8 summarizes the diurnal behavior of O₃, NO, and NO₂ described above, using May 2010 as an example. Particularly, this color contour plot highlights the behavior of NO₂ in different levels of the snowpack: near the snowpack surface, NO₂ levels track the radiation cycle with the peak mixing ratios observed a few hours after the hour of maximum insolation; deep in snowpack (below 30 cm), enhancement of NO₂ above ambient levels was evident during day and night, with maxima during the dark hours of the day.

3.4. Surface – snowpack gradients

Gradients in O₃, NO, and NO₂ were calculated as the mixing ratio in the overlying atmosphere minus the mixing ratio in snowpack interstitial air (Fig. 9a). ΔO_3 is defined as the O₃ gradient between the atmosphere and a mid-depth layer of 90 – 120 cm depth, ΔNO is defined to be the

Figure 7a: Hourly median values of O₃ in (a) winter (Nov, Dec, Jan), (b) spring (Feb, Mar, Apr), (c) summer (May, Jun, Jul) and (d) fall (Aug, Sep, Oct). Observations from the entire record were separated by season, then binned by depth and median hourly values are shown here to give an average diurnal cycle at each level and each season. Note the radiation scale in panel (a) is different than the other panels.

402
 403 **Figure 7b:** Hourly median values of NO in (a) winter (Nov, Dec, Jan), (b) spring (Feb, Mar, Apr), (c) summer
 404 (May, Jun, Jul) and (d) autumn (Aug, Sep, Oct). Observations from the entire record were separated by season, then
 405 binned by depth and median hourly values are shown here to give an average diurnal cycle at each level and each
 406 season. Note that the range of the vertical axis in panel (a) is 100 pptv, whilst the panels for the other three seasons
 407 extend to 400 pptv. Also note the radiation scale in panel (a) only extends to 20 W m^{-2} .

408

409 **Figure 7c:** Hourly median values of NO₂ in (a) winter (Nov, Dec, Jan), (b) spring (Feb, Mar, Apr), (c) summer
 410 (May, Jun, Jul) and (d) autumn (Aug, Sep, Oct). Observations from the entire record were separated by season, then
 411 binned by depth and median hourly values are shown here to give an average diurnal cycle at each level and each
 412 season. Note that the range of the vertical axis in panel (a) in winter is 100 pptv, in panel (b) and 400 pptv for the
 413 other seasons. Also note the radiation scale in panel (a) only extends to 20 W m⁻².

Figure 8: Hourly mean chemical data for the month of May 2010 shown in two different ways. Panels (a), (b), and (c) show O_3 , NO, and NO_2 mixing ratios plotted as color contours against snowpack depth. Panels (d), (e), and (f) show the same constituents plotted as a single line for each depth with the mixing ratio on the vertical axis. Hourly averaged radiation for the month is also shown as a yellow line in the figures on the right column.

NO gradient between the atmosphere and the near-surface snowpack level of 0 – 30 cm depth, ΔNO_{2_15} is the NO_2 gradient between the atmosphere and the 0 – 30 cm snowpack depth layer, and ΔNO_{2_45} is the NO_2 gradient between the atmosphere and the 30 – 60 cm depth layer. ΔO_3 is a 4-hr average, while the NO and NO_2 gradients are daily averages. T_a , T_{s_30} , and T_{s_90} are the atmospheric temperature, and temperatures at 30 and 90 cm depth, respectively. Time series of these data shown in Figure 9 indicate the relationship between the snowpack chemical observa-

tions and the seasonal snow and physical data. These graphs clearly depict the seasonal cycles, particularly the summer maximum of the atmosphere-snowpack gradients due to the production and destruction of NO_x , and O_3 , respectively, in the snowpack. These graphs also show a ~ 1 month time lag between the solar irradiance and atmospheric temperature, and ~ 2 months time lag between solar irradiance and snowpack temperature (at -90 cm) during the summer. A simple linear regression analysis of gas gradients versus individual physical variables using the entire measurement period, and disregarding these time lags, resulted in R^2 values of ≤ 0.4 between chemical gradients and radiation, atmospheric temperature, or snowpack temperature. The highest R^2 -value overall (0.4) was observed for the correlation between ΔO_3 and incoming solar radiation. Higher R^2 -values were calculated for spring and fall, with the highest value yielding an R^2 of 0.5 between ΔNO_{2_45} and T_{s_30} value in spring. These findings indicate that only a fraction of the variation in the chemical gradients during summer and winter can be explained solely by diurnal and seasonal changes of one of the considered variables (incoming solar radiation, atmospheric temperature, or snowpack temperature). This points towards multiple physical conditions, and possibly additional variables affecting both the ozone and NO_x snowpack chemical processes.

3.5. Effect of wind speed on snowpack chemistry

Interesting dynamics occurred when wind speeds exceeded 10 m s^{-1} between 5 May and 24 May, 2009 (Fig. 10). During this period, O_3 mixing ratio in snowpack interstitial air increased and were within 5 – 10 ppbv of atmospheric values when wind speeds were highest (day of year (DOY) 133-136). NO mixing ratios in snowpack interstitial air were unaffected during the pe-

449 riod; however, interestingly, there was an overall increase in NO₂ levels. Aside from the period

450 of

455

464 **Figure 9:** Time series plots showing chemical gradients between the atmosphere and snowpack along with relevant meteorological parameters for the entire measurement period. In all legend text, “A” designates “Atmospheric.” Panel (a) shows the daily average NO gradient between the atmosphere and the 0 – 30 cm layer in the snowpack in green circles, the daily average NO₂ gradient between the atmosphere and the 0 – 30 cm snowpack layer in dark red circles, the daily average NO₂ gradient between the atmosphere and the 30 – 60 cm snowpack layer in pink circles, and the blue line designates the 4-hr average O₃ gradient between the atmosphere and the 90 – 120 cm layer in the snowpack. Panel (b) shows the incoming solar radiation in light orange, the atmospheric temperature measured at ~7 m height from the meteorological tower, and the snow temperature averaged from the 60 – 120 cm depth layer in the snowpack from thermocouples on the snowpack air sampling manifold. Solar radiation and temperatures are 4-hr average values.

Figure 10: Time series plots of (a) wind speed and incoming solar radiation, (b) O_3 above the surface and at all levels within the snowpack, (c) NO above the surface and at all levels within the snowpack, and (d) NO_2 above the surface and at all levels within the snowpack. Data span the period from May 5, 2009, through May 24, 2009.

464
465

465
466 high wind, O₃, NO, and NO₂ exhibited diurnal cycles as described above, and NO₂ in the 0 – 30
467 cm layer displayed a diurnal cycle that was out of phase with the rest of the snowpack layers (i.e.
468 values in the near-surface layer peaked at 16:00 – 17:00 GMT whereas values in the layers below
469 30 cm peaked at 23:00 – 03:00 GMT). These observations are consistent with a second case
470 study shown in Fig. 11 when surface wind speeds increased to $\geq 10 \text{ m s}^{-1}$ on April 16 (DOY 106)
471 and remained above this level until increasing again and peaking at nearly 25 m s^{-1} by the end of
472 the day on April 17 (DOY 107) (Fig. 11). During this period air with enhanced ozone was trans-
473 ported to Summit, possibly due to a stratospheric intrusion event. Ambient air O₃ mixing ratios
474 increased to levels close to 80 ppbv (Fig. 11), which are close to the highest surface ozone levels
475 that have been observed at Summit (Helmig et al., 2007a). Ozone levels in the snowpack in-
476 creased to 70 ppbv, which were the highest recorded during the experimental period. NO levels
477 appear to be unaffected by the high surface winds and O₃ transport into the snow. However,
478 NO₂ levels increased during the increased snowpack ventilation period and remained enhanced,
479 and high levels protruded deeper into the snowpack for several days following. The relationship
480 between snowpack NO_x production and surface winds is also evident in the multi-month spring
481 record (Figure 12; a time series figure showing this period is also included as Figure S2 in the
482 Supplemental Materials). There were three to five major NO_x production events during this time
483 window, lasting on the order of 1-5 d. This record shows that the three most prominent events
484 all coincided with or succeeded periods with elevated surface winds.

Figure 11: Wind speed at 8 m height, ambient ozone at 2 m above the surface, and color contour plot of (a) O_3 , (b) NO, and (c) NO_2 in the snowpack for the time period of 14-20 April 2009. Snowpack mixing ratio data are 4-hr averages plotted by depth relative to the snow surface. Colors indicate mixing ratios of each constituent in

488
489

490

Figure 12: Wind speed at 8 m height (top), and NO₂ in the snowpack during spring 2009 (bottom). Daily mean data were used for generation of the color contour plot.

Figure 13: Panels (a) – (g) show regression analyses using a 2nd order polynomial fit between wind speed at ~7 m and O₃ values at binned 30 cm layers within the snowpack down to 2.1 m. Data are from 1 June – 30 June 2009. Snowpack data were filtered to include only time periods when the incoming solar radiation was greater than 300 W m⁻² in order to remove some of the variability attributed to diurnal changes in solar radiation. Data points are color contoured by the hour of the day simply to illustrate that remaining dependency.

4. Discussion

4.1. Snowpack ventilation

Each 30 cm depth within the snowpack exhibits maximum depletion in O₃ ~1-hr later than the layer above throughout the afternoon. Recovery following depletion also occurs at ~1-hr inter-

vals between each 30 cm snowpack level. An effective diffusion coefficient of O₃ in snowpack (0.0407 cm² s⁻¹) was estimated using the reported diffusivity of O₃ in air [0.1444 cm² s⁻¹; (Massman, 1998)] and estimates of porosity and tortuosity in the Summit, Greenland snowpack (Albert and Shultz, 2002). The characteristic gas diffusion time (Seinfeld and Pandis, 2006) for O₃ to traverse a 30 cm layer of snowpack is 1.5 hr. *Helmig et al. (2007)* used mean time shifts of the minima and maxima at progressively deeper snowpack levels to estimate a mean transport time of 55 minutes between 50 and 80 cm depth in snow, and 48 minutes between 80 and 100 cm depth, which is slightly faster than the estimate based purely on diffusion.

A regression analysis was performed using a second order polynomial fit between wind speed (at ~7 m above the snowpack) and O₃ mixing ratios in 30-cm layers down to a depth of 2.1 m (Fig. 13). Coefficients in the polynomial equation are interpreted according to *Seok et al. (2009)*: *a* is the expected O₃ value in the layer when the wind speed drops to zero; *b* is the strength of the effect of winds on the O₃ mixing ratios at each level; and *c* represents the degree of curvature relative to a linear fit. The analysis of these June 2009 data indicates that O₃ in the shallowest layer in the snowpack (0-30 cm, Fig. 12a) is influenced to the greatest extent by wind. The influence of wind decreases with depth in the snowpack. In the deepest layers *c* becomes small and the fit is nearly linear. Values of R² between wind speed and O₃ mixing ratios in all snowpack levels are 0.5 except for the 30-60 cm level (R² = 0.4). Thus, changes in wind speed could explain up to ~50% of the variation in O₃ concentrations from the surface to at least 2 m deep. This is slightly higher than previously reported by *Helmig et al. (2007b)*, who found a weak linear correlation (R² = 0.3) between wind speed and the gradient of O₃ down to 30 cm deep in snowpack for high radiation conditions. Analysis of the data from two high wind events shows that wind pumping

can significantly ventilate the snowpack, resulting in fast transport within the snowpack, on short time scales to depths in excess of 2 m (Fig. 10 and 11).

4.2. NO_x production

Several features of the NO_x dynamics in snowpack interstitial air provide new insight into NO_x snowpack chemistry. Profiles of NO closely follow diurnal changes in irradiance and NO is observed exclusively in the uppermost snowpack layers, which implies nearly instantaneous production and a short lifetime in the snowpack (Fig. 5b). Production of NO₂ appears to be higher in spring compared to fall under equivalent light levels (Fig. 5c and section 4.4). Mixing ratios of NO₂ in the 0-30 cm layer exhibit a daily peak coincident with the timing of the maxima in incoming solar radiation, NO mixing ratios, and maximum depletion of O₃. However, from mid-March through mid-September deeper layers of the snowpack typically show a maximum in NO₂ shifted approximately 6-12 h from that of the 0-30 cm layer, during the time of day when lowest light levels were present (Fig. 10, 11). Temperatures in the deepest layer of the snowpack warmed from about -40°C to -15°C during the spring to summer (Fig. 4). For much of the mid-March to July period, transport of high levels of O₃ (> 60 ppbv) deep into the snowpack (Fig. 5a) was coincident with elevated levels of NO₂ in the deep snowpack. However, from July to mid-September O₃ levels diminished to about 45 ppbv above the snowpack and elevated levels of NO₂ were occasionally observed in the absence of deep intrusion of O₃ into the snowpack.

Photolysis of nitrate (NO₃⁻), nitrite (NO₂⁻), and nitrous acid (HONO) in a quasi-liquid layer (QLL) on the surface of snow grains has been proposed to explain production of NO_x in sunlit snow (Warneck & Wurzinger, 1988; Honrath et al., 2000; Jacobi and Hilker, 2007; Bock and Jacobi, 2010; Jacobi et al., 2014). Thomas et al. (2011) incorporated detailed snowpack chemis-

try in a 1-D model that coupled the atmospheric boundary layer and snowpack to simulate the dynamics of O₃ and NO_x within and above snowpack. In contrast to their modeling results, we observed NO₂ maxima shortly after solar noon in the upper snowpack layers and enhancements deep in the snowpack during night. The latter feature was not simulated by their 1-D model and might be explained by dark chemical reactions that produce NO₂ such as:

The NO_x reservoir species [i.e., CH₃C(O)OONO₂ (PAN), N₂O₅ (dinitrogen pentoxide), HO₂NO₂ (peroxynitric acid)] are sensitive to thermal dissociation; however, the reactions are reversible and reformation can occur when mixing ratios of decomposition species increase above equilibrium levels.

Ford et al. (2002) found PAN mixing ratios of approximately 200 pptv at a depth of 25 cm in snowpack interstitial air, which are about half the levels of NO₂ observed during spring (Fig. 5c). However, the lifetime of PAN in snowpack is estimated to be ~23 d, and thus, production of NO₂ deep in the snowpack on a diurnal timescale via transport and thermal dissociation of PAN is unlikely. Levels of N₂O₅ above the surface of snowpack near Fairbanks, AK, were reported to be about 20-80 pptv (Apodaca et al., 2008; Huff et al., 2011). Thermal dissociation of N₂O₅ is a source of NO₂; however, heterogeneous hydrolysis of N₂O₅ on ice surfaces produces HNO₃ (Apodaca et al., 2008). On a diurnal timescale, N₂O₅ might be a minor source of NO₂ in the photic zone via thermal dissociation and photolysis of NO₃⁻; however, levels of N₂O₅ are likely

564 too low to explain the levels of NO₂ deep in the snowpack. Median levels of the mixing ratios of
565 HO₂NO₂ between 0-50 m above the surface during summer in the Antarctic when temperatures
566 were -15 to -30 °C were about 25-65 pptv (Slusher et al. 2002, 2010; Davis et al., 2004; Eisele et
567 al., 2008). Levels of HO₂NO₂ in the Antarctic during winter are much lower (0.4-5 pptv) and
568 reflect diminished photochemical activity (Jones et al., 2014). Murphy et al. (2004) found 300
569 pptv of HO₂NO₂ in the mid- and high-latitude upper troposphere over continental North America
570 in July when temperatures were below -30°C. Partitioning of HO₂NO₂ to ice is nearly complete
571 between -40°C and -20°C and is a reversible process (Ulrich et al., 2012). Thus, HO₂NO₂, which
572 is formed in snowpack during the sunlit season and is not ventilated from the snowpack, will re-
573 partition to the snow over winter and replenish the NO_x reservoir below about 30 cm.

574 The temperature dependence and reversibility of Reaction (R5) and the effects of temperature on
575 diffusion of HO₂NO₂ through the interstitial air of snowpack might explain the diurnal and sea-
576 sonal behavior of NO₂ below the photic zone. Temperatures in snowpack over winter 2008 into
577 mid-April of 2009 varied between -35°C and -45°C, which would favor adsorption of HO₂NO₂
578 to ice and an increase in the NO_x reservoir. Diffusion of HO₂NO₂ in snowpack interstitial air is
579 slowed by about 900 times relative to diffusion in air within this temperature range due to the
580 high surface area density of snow (Ulrich et al., 2012). Levels of NO₂ in snowpack interstitial air
581 in layers deeper than about 30 cm appear to initially increase in late March 2009 when a slight
582 elevation of surface snowpack temperature to about -25°C might have initiated desorption of
583 HO₂NO₂ from snow, thermal dissociation, and downward transport of NO₂. Intrusions of O₃
584 deep into the snowpack were observed during the same period when surface winds were greater
585 than about 4 m s⁻¹. Production of HO₂NO₂ would reach a maximum during the day concomitant
586 with increases in NO_x and HO_x production at solar noon. Depending on the level of HO₂NO₂ in

snowpack interstitial air deep in the snowpack, HO₂NO₂ might diffuse into the deeper, colder layers of the snowpack and into the QLL during the day. At night HO₂ levels diminish, which promotes dissociation of HO₂NO₂ and release of NO₂ from the QLL into the snowpack interstitial air, causing the nighttime NO₂ maxima seen in the data.

Ventilation of the snowpack with air containing elevated levels of O₃ might accelerate HO₂ production via the aqueous-phase reaction of O₃ with formic acid (HCOOH) as follows (Hoigne et al., 1983):

Measurements of HCOOH in snowpack interstitial air at Summit indicate levels increase with depth and are about 2500 and 4000 ppt_v at 10 and 30 cm, respectively, below the surface (Jacobi et al., 2004). Reformation of HO₂NO₂ in snowpack interstitial air or in the QLL via Reaction (R5) might occur as NO₂ and HO₂ increase above equilibrium levels. However, maxima in NO₂ were typically observed deep in the snowpack 6-12 h following ventilation with ambient air containing elevated O₃, which indicates Reaction (R6) might not be an important source of HO₂ deep in snowpack. Instead, downward transport of HO₂NO₂ from the photolytic zone and dissociation due to diminishing levels of HO₂ during the night might be the source of NO₂ deep in the snowpack following ventilation with air containing elevated levels of O₃.

Temperatures of the deep snowpack warmed from -30 °C to -25 °C from late April to July and NO₂ maxima were observed deeper in the snowpack after mid-April and were coincident with times of snowpack ventilation with air containing elevated O₃. Increases in temperature of the deep snowpack would promote thermal dissociation of HO₂NO₂ and production of NO₂. Diffu-

sion of HO_2NO_2 is slowed by about 600 times compared to ambient air within the temperature range, which would not deplete the NO_x reservoir despite warming of the deep snowpack. From July to mid-September, the deepest snowpack layer warmed from -25°C to about -15°C . Levels of O_3 in the air above the snowpack were lower than during the period before July and transport of elevated levels of O_3 into the deep snowpack was diminished. However, NO_2 maxima were still observed, but, notably constrained to deeper in the snowpack (Fig. 5). During mid-summer the upper snowpack warms up to temperatures on the order of -10°C (Helmig et al., 2007b), and thus, ventilation of the deep snowpack with air depleted in HO_2NO_2 might have promoted desorption from the snowpack and thermal dissociation that was favored by the higher mid-summer temperatures deep in the snowpack. Considering the chemistry and physical transport discussed above, model results for an episode in April compared well with the observations, both in terms of absolute NO_x mixing ratios, depth profiles, and the timing of observed NO and NO_2 maxima (Murray et al., 2015).

Measurements for the subject study did not include HO_2NO_2 . Thermal dissociation of HO_2NO_2 in the sampling lines and photolytic NO_2 converter of the NO_x instrument via Reaction (R5) produces a positive artifact in the NO_2 measurements (Frey et al., 2014). The lifetime of HO_2NO_2 in the photolytic converter (30°C ; residence time ~ 1 s) and sampling lines (-6°C ; residence time ~ 15 s) with respect to thermal dissociation was calculated at the mean ambient pressure (~ 670 hPa) using the rate coefficient reported by Sander et al. (2011) (Supplement). According to these calculations up to $\sim 12\%$ of all HO_2NO_2 may potentially be converted to NO_2 in the snowtower sampling system. A much smaller conversion rate ($\sim 0.1\%$) is calculated for PAN decomposition (Supplement). However, correcting the NO_2 measurements for the positive artifact is problematic due to unknown HO_2NO_2 snowpack mixing ratios and the complex dynamics of HO_2NO_2 in

a warming snowpack during the spring and summer periods. Temperatures in the deep snowpack increased from -40 °C in early March to -15 °C in early September, and thus, HO₂NO₂ levels in the deep snowpack will vary seasonally as HO₂NO₂ desorbs and thermally dissociates forming NO₂.

4.3. Depletion of O₃ within the snowpack

Peterson & Honrath (2001) postulated that O₃ loss due to reaction with NO_x or HO_x could only explain ~6% of the observed O₃ loss rate. Modeling studies have been unable to reproduce the observed depletion (Thomas et al., 2011; Thomas et al., 2012). Simulations with a single-column chemistry-climate model, which included a representation of atmosphere-snowpack exchange, accounted for ~10% of the observed snowpack O₃ gradient with gas-phase NO_x-O₃ chemistry (Seok et al., 2010). Predicted levels of BrO in interstitial air are too low and the rate of mixing between the atmosphere and snowpack too slow to account for the observed O₃ dynamics in interstitial air (Thomas et al., 2011). The reaction of NO₂⁻ with O₃:

and O₃ reaction with HCOOH (Eq. 6) are alternative O₃ sinks (Murray et al., 2015), however we hypothesize that these pathways are too small based on predicted NO₂⁻ and HCOOH levels to provide a significant O₃ sink. Considering the known chemical and physical processes Murray et al. (2015) were able to yield good model representation of O₃ gradients with depth and ozone transport into the snowpack from wind pumping, but the model fell short of representing the diurnal dynamics of O₃ in the snowpack. This implies that important contributions to the intersti-

tial O₃ depletion remain unexplained in terms of established chemical mechanisms, and that currently unidentified additional or alternative chemical or physical sinks must be considered to account for the observed dynamics of the O₃ destruction in the snowpack.

4.4. Elevated NO_x during spring

Differences in the spring-fall behavior of O₃ and NO_x add some new insight to the chemistry of these gases. The higher levels of O₃ in the snowpack during the spring can be explained by transport of O₃ from above the surface and the seasonal O₃ maximum in ambient air. During April-May surface ozone is ~15 ppbv higher than at the end of the summer (Helmig et al., 2007c; Kramer et al., 2014). The most striking feature in the seasonal comparison are the higher NO₂ levels in spring, despite the fact that average solar radiation was ~19% lower in spring, compared to fall. Secondly, despite the summer months having an average irradiance of ~4.5x that of spring (299 versus 67 W m⁻², for the data plotted in Fig. 7), NO_x values during summer exceed the springtime values only by ~20-40%. These analyses indicate that NO_x levels in ambient air do not linearly respond to available irradiance and that other snow physical or chemical variables significantly affect the degree of the NO_x production.

There are a number of other conditions that can provide explanation for the elevated springtime NO_x observations: Year-round monitoring of ambient nitrogen oxides has shown a seasonal maximum of reactive nitrogen compounds in spring, with NO_x, NO_y, and PAN all peaking during the month of April, and with the springtime NO_y maximum peaking at approximately 2x its seasonal minimum in late summer (Kramer et al., 2014). The Kramer et al. (2014) study presents an analysis of factors contributing to the spring maximum, including accumulation of NO_y species during the dark and cold winter months in the arctic troposphere, increased transport

from the stratosphere, and increased pollution from lower latitudes, which due to the lower southern location of the Arctic Polar Front, have a stronger influence during the winter months. Hastings et al. (2004) suggested an increased transport during spring-summer from biomass burning, biogenic soil emissions, and lightning based on higher $\delta^{15}\text{N}$ in snow nitrate. Measurements of nitrate in surface snow showed a peak in June, followed by a substantial decline (to $\sim 1/3$ of peak values) of NO_3^- towards the fall (Dibb et al., 2007). Other studies have shown evidence for two NO_3^- peaks in some post-1900 snowpack layers (Yang et al., 1995; Burkhardt et al., 2006). The additional peak was seen to occur in late winter/early spring, and was suggested to be associated with pollution transport (Burkhardt et al., 2006). Geng et al. (2014), utilizing NO_3^- firn and ice core data, sulfate as a pollution tracer, isotopic signatures, and ozone column measurements, argue that observed spring peaks in the snow NO_3^- records are linked to increased photochemical formation due to increases in surface UV radiation from a weakened stratospheric ozone layer.

Similar to NO_x , ambient surface O_3 peaks during spring (April-May), with O_3 $\sim 25\%$ higher than during mid-summer (Helmig et al., 2007; Kramer et al., 2014). The wind pumping - O_3/NO_x dependencies seen in the data (Figures 10-12) and the chemistry detailed in Section 4.2 suggest that ozone interplays with NO_x production; consequently, this relationship would promote enhanced NO_x production during spring, when O_3 is highest.

Declining NO_x production in late spring-summer might also suggest that the snowpack NO_x reservoir is gradually depleted during the spring-summer, with NO_x loss possibly occurring through volatilization from the snowpack. Honrath et al. (2002) reported that the summer NO_x production in the snowpack is associated with a NO_x and HONO emission flux out of the snow and that the emission flux of NO_x and HONO was larger than HNO_3 uptake to the snowpack. This would

be consistent with a loss of oxidized nitrogen from the snowpack through the summer. Recent snow chamber measurements at Dome C, Antarctica, indicate a decrease in NO_x production without a measureable change in the snow NO_3^- content (unpublished data; Helmig et al., manuscript in preparation). These observations are consistent with (1) the reservoir species for NO_x production being partitioned with a minor part readily available for NO_x production, and (2) equilibration between NO_3^- bound in the bulk snow with NO_3^- in an active layer (most likely the QLL) being slower than the rate of photochemical NO_x production. Davis et al. (2008), in their treatise of NO_3^- chemistry in the Antarctic snow, noted that HNO_3 appeared to be contained in two different sites, one of which is weakly bonded and readily available for QLL – gas phase exchanges, and the other portion exhibiting a stronger bonding with the partitioning dependent on snowpack temperature. Cho et al. (2002) described relationships whereby increases in the temperature of the QLL lead to decreases in the concentration of the solute in the QLL. According to these elaborations, lower NO_x production rates may be a consequence of changes in the NO_3^- partitioning from the warming of the snowpack that is occurring during the polar summer months. In summary, the elevated NO_x levels seen in the firn air during spring are likely a reflection of several causes, including more frequent transport of air containing elevated NO_x , elevated photochemical production rates from increased UV, and higher snowpack NO_3^- concentrations, and higher NO_3^- enhancement in the QLL at lower springtime snowpack temperatures. In contrast to NO_2 , NO production rates surprisingly seem to be favored in fall, also yielding higher NO/NO_2 ratios compared to spring. The ~24% higher mean irradiance during the fall window appears too low to account for all of this difference. Consequently, there must be other contributing processes. The plausible explanation from available data is a dependency of NO production on snowpack temperature, which during the fall was ~10-15 °C warmer than during spring.

5. Summary

Seasonal and diurnal trends in mixing ratios of O_3 , NO, NO_2 , and temperature in interstitial air of snowpack over glacial ice from the surface to 210 cm deep were presented for the period June 2008 to July 2010. Significant removal of O_3 in snowpack interstitial air was observed from spring through fall. Removal of O_3 also exhibited a diurnal cycle with peak depletion in the snow occurring several hours following the peak in solar radiation. Enhancements of NO and NO_2 were observed during spring, summer, and fall. Enhancements of NO were constrained to a layer between the surface and a depth of 60 cm; however, NO_2 levels were elevated at all depths. Daily maxima in NO_2 within the 0-30 cm deep layer tracked the diurnal cycle in solar radiation; however, daily NO_2 maxima in layers deeper than 30 cm were offset from the solar radiation cycle by an average of 7 hours. NO_x production rates are not linearly related to solar irradiance. Relatively enhanced NO_2 production was observed in spring, whereas NO appeared to be enhanced in fall. NO and NO_2 in the 0-30 cm deep layer were attributed to production via NO_3^- photolysis. We propose that daytime production of HO_2NO_2 with downward diffusion of HO_2NO_2 and nighttime reversal of this reaction to NO_2 as a potential source of NO_2 deeper in the snow.

Depletion of O_3 in deep layers of the snowpack could not be attributed to halogen chemistry, and thus, reaction of O_3 with NO_2^- that produces NO_2 was presented as a potential explanation for depletion of O_3 in deep layers of the snowpack and the offset of NO_2 enhancements. Year-round measurements of NO_2^- within various depth levels in the snowpack would be valuable to advance this hypothesis. Interpretation of the extensive data set indicates that snowpack ventilation processes and photochemical and heterogeneous chemistry influence levels of reactive compounds

such as NO_x and O_3 in snow interstitial air and exchange at the atmosphere-snowpack interface. Results suggest that HO_2NO_2 might play a key role in the diurnal and seasonal dynamics of NO_2 in sunlit snowpack. Other NO_y species such as PAN and N_2O_5 cannot explain the behavior of NO_x on diurnal timescales; however, the species might contribute to the NO_x reservoir in snowpack. Future efforts should focus on better speciation of NO_y , which contributes to storage of NO_2 in the deep snowpack. An in depth analysis of chemical and physical processes reflecting these data using a process-based 1-D model is presented in Murray et al. (2015).

Acknowledgements

The research was funded through the National Science Foundation grant NSF-OPP-07-13992. M. Dziobak, J. Hueber, and P. Boylan assisted with instrumental set-up and measurements in the field. We would like to acknowledge C. Anastasio for helpful discussions. During the winter the Summit Station science technicians were of invaluable help, assisting with regular measurements and instrumental issues. Richard Honrath was a co-investigator and integral in the implementation of this experiment, but sadly passed away during the beginning phase of the study. Two reviewers provided constructive feedback that was essential in improving sections of the manuscript. The authors thank the 109th Air National Guard and CH2MHill Polar Services for logistical support. We are also grateful to the Danish Commission for Scientific Research for providing access to GEOSummit Station.

References

Albert, M. R., & Shultz, E. F. (2002). Snow and firn properties and air-snow transport processes at Summit, Greenland. *Atmospheric Environment*, 36(15-16), 2789-2797. doi: 10.1016/s1352-2310(02)00119-x.

772 Apodaca, R.L., Huff, D.M., Simpson, W.R., 2008. The role of ice in N₂O₅ heterogeneous hy-
 773 drolysis at high latitudes. *Atmos. Chem. Phys.* 8, 7451-7463.

774 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin,
 775 M.E., Rossi, M.J., Troe, J. (2004). Evaluated kinetic and photochemical data for
 776 atmospheric chemistry: Volume I - gas phase reactions of O-x, HOx, NOx and SOx
 777 species. *Atmospheric Chemistry and Physics*, 4, 1461-1738.

778 Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., & Rasmussen, R. A. (1988).
 779 Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic
 780 atmosphere. *Nature*, 334(6178), 138-141. doi: 10.1038/334138a0

781 Beine, H. J., Honrath, R. E., Domine, F., Simpson, W. R., & Fuentes, J. D. (2002). NO_x during
 782 background and ozone depletion periods at Alert: Fluxes above the snow surface. *Journal*
 783 *of Geophysical Research-Atmospheres*, 107(D21). doi: 458410.1029/2002jd002082

784 Bock, J., & Jacobi, H. W. (2010). Development of a mechanism for nitrate photochemistry in
 785 Snow. *Journal of Physical Chemistry A*, 114(4), 1790-1796. doi: 10.1021/jp909205e

786 Bocquet, F., Helmig, D., & Oltmans, S. J. (2007). Ozone in interstitial air of the mid-latitude,
 787 seasonal snowpack at Niwot Ridge, Colorado. *Arctic Antarctic and Alpine Research*,
 788 39(3), 375-387. doi: 10.1657/1523-0430(06-027)

789 Boxe, C. S., & Saiz-Lopez, A. (2008). Multiphase modeling of nitrate photochemistry in the
 790 quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal
 791 Antarctic snowpack. *Atmospheric Chemistry and Physics Discussions*, 8(16), 4855-4864.

792 Burkhardt J.F., Hutterli M., Bales R.C., and McConnell J.R. (2004) Seasonal accumulation timing
 793 and preservation of nitrate in firn at Summit, Greenland. *J. Geophys. Res.* 109, D19302.

794 Burkhardt J.F., Bales, R.C., McConnell, J.R., and Hutterli, M.A. (2006) Influence of North
 795 Atlantic Oscillation on anthropogenic transport recorded in northwest Greenland ice
 796 cores, *J. Geophys. Res.*, 111, D22309, doi:10.1029/2005jd006771.

797 Cho, H., Shepson, P.B., Barrie, L.A., Cowin, J.P., Zaveri, R. (2002). NMR investigation of the
 798 quasi-brine layer in ice/brine mixtures, *J. Phys. Chem.*, 106, 11226-11232.

799 Chu, L., & Anastasio, C. (2007). Temperature and wavelength dependence of nitrite photolysis
 800 in frozen and aqueous solutions. *Environmental Science & Technology*, 41(10), 3626-
 801 3632. doi: 10.1021/es062731q

802 Cohen, L., Helmig, D., Neff, W. D., Grachev, A. A., & Fairall, C. W. (2007). Boundary-layer
 803 dynamics and its influence on atmospheric chemistry at Summit, Greenland. *Atmospheric*
 804 *Environment*, 41(24), 5044-5060. doi: 10.1016/j.atmosenv.2006.06.068

805 Davis, D., Nowak, J. B., Chen, G., Buhr, M., Arimoto, R., Hogan, A., . . . McMurtry, P. (2001).
 806 Unexpected high levels of NO observed at South Pole. *Geophysical Research Letters*,
 807 28(19), 3625-3628.

808 Davis, D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F.,
 809 Mauldin, L., Hogan, A. (2004). South Pole NO_x chemistry: an assessment of factors
 810 controlling variability and absolute levels. *Atmospheric Environment*, 38(32), 5375-5388.

- 811 Davis, D., Seelig, J., Huey, G., Crawford, J., Chen, G., Want, Y., Buhr, M., Helmig, D., Neff,
812 W., Blake, D., Arimoto, R., Eisele, F. (2008). A reassessment of Antarctic plateau
813 reactive nitrogen based on ANTCI 2003 airborne and ground based measurements.
814 *Atmospheric Environment*, 42, 2831-2848.
- 815 Dibb, J. E., Arsenault, M., Peterson, M. C., & Honrath, R. E. (2002). Fast nitrogen oxide
816 photochemistry in Summit, Greenland snow. *Atmospheric Environment*, 36(15-16), 2501-
817 2511. doi: 10.1016/s1352-2310(02)00130-9
- 818 Dibb, J. E., Ziemba, L. D., Luxford, J., & Beckman, P. (2010). Bromide and other ions in the
819 snow, firn air, and atmospheric boundary layer at Summit during GSHOX. *Atmospheric*
820 *Chemistry and Physics*, 10(20), 9931-9942. doi: 10.5194/acp-10-9931-2010
- 821 Dubowski, Y., Colussi, A. J., & Hoffmann, M. R. (2001). Nitrogen dioxide release in the 302 nm
822 band photolysis of spray-frozen aqueous nitrate solutions. Atmospheric implications.
823 *Journal of Physical Chemistry A*, 105(20), 4928-4932. doi: 10.1021/jp0042009
- 824 Eisele, F., Davis, D., Helmig, D., Oltmans, S., Neff, W., Huey, G., Tanner, D., Chen, G., Craw-
825 ford, J., Arimoto, R., Buhr, M., Mauldin, L., Hutterli, M., Dibb, J., Blake, D., Brooks,
826 S.B., Johnson, B., Roberts, J., Wang, Y., Tan, D., Flocke, F., 2008. Antarctic tropo-
827 spheric chemistry investigation (ANTCI) 2003 overview. *Atmos. Environ.* 42, 2749-
828 2761.
- 829 Finlayson-Pitts, B. J., & Pitts, J. N. (2000). *Chemistry of the Upper and Lower Atmosphere:*
830 *Theory, Experiments, and Applications* (Vol. 1): Academic Press.
- 831 Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D., & Ramazan, K. A. (2003). The
832 heterogeneous hydrolysis of NO₂ in laboratory systems and in outdoor and indoor
833 atmospheres: An integrated mechanism. *Physical Chemistry Chemical Physics*, 5(2), 223-
834 242. doi: 10.1039/b208564j
- 835 Ford, K.M., Campbell, B.M., Shepson, P.B., Bertman, S.B., Honrath, R.E., Peterson, M., Dibb,
836 J.E., 2002. Studies of peroxyacetyl nitrate (PAN) and its interaction with the snowpack at
837 Summit, Greenland, *J. Geophys. Res.* 107, D10, 4102, doi:10.1029/2001JD000547.
- 838 Foster, K. L., Plastringe, R. A., Bottenheim, J. W., Shepson, P. B., Finlayson-Pitts, B. J., &
839 Spicer, C. W. (2001). The role of Br₂ and BrCl in surface ozone destruction at polar
840 sunrise. *Science*, 291(5503), 471-474. doi: 10.1126/science.291.5503.471
- 841 Frey, M.M., Roscoe, H.K., Kukul, A., Savarino, J., France, J.L., King, M.D., Legrand, M., Pre-
842 unkert, S., 2014. Atmospheric nitrogen oxides (NO and NO₂) at Dome C, East Antarc-
843 tica, during the OPAL campaign. *Atmos. Chem. Phys. Discuss.* 14, 31,281-31,317.
- 844 Galbavy, E. S., Anastasio, C., Lefer, B., & Hall, S. (2007a). Light penetration in the snowpack at
845 Summit, Greenland: Part 2 nitrate photolysis. *Atmospheric Environment*, 41(24), 5091-
846 5100. doi: 10.1016/j.atmosenv.2006.01.066
- 847 Galbavy, E. S., Anastasio, C., Lefer, B. L., & Hall, S. R. (2007b). Light penetration in the
848 snowpack at Summit, Greenland: Part I - Nitrite and hydrogen peroxide photolysis.
849 *Atmospheric Environment*, 41(24), 5077-5090. doi: 10.1016/j.atmosenv.2006.04.072
- 850 Geng, L., Cole-Dai, J., Alexander, B., Erbland, J., Savarino, J., Schauer, A.J., Steig, E.J., Lin, P.,
851 Fu, Q., and Zatzko, M.C. (2014) On the origin of the occasional spring nitrate peak in

852 Greenland snow, *Atmos. Chem. Phys.*, 14, 13361-13376, doi:10.5194/acp-14-13361-
853 2014, 2014.

854 Helmig, D., Oltmans, S. J., Morse, T. O., Dibb, J. E. (2007a). What is causing high ozone at
855 Summit, Greenland? *Atmospheric Environment*, 41(24), 5031-5043. doi:
856 10.1016/j.atmosenv.2006.05.084

857 Helmig, D., Bocquet, F., Cohen, L., & Oltmans, S. J. (2007b). Ozone uptake to the polar
858 snowpack at Summit, Greenland. *Atmospheric Environment*, 41(24), 5061-5076. doi:
859 10.1016/j.atmosenv.2006.06.064

860 Helmig, D., Oltmans, S. J., Carlson, D., Lamarque, J. F., Jones, A., Labuschagne, C., Anlauf, K.,
861 Hayden, K. (2007c). A review of surface ozone in the polar regions. *Atmospheric*
862 *Environment*, 41(24), 5138-5161. doi: 10.1016/j.atmosenv.2006.09.053

863 Helmig, D., Ganzeveld, L., Butler, T., & Oltmans, S. J. (2007d). The role of ozone atmosphere-
864 snow gas exchange on polar, boundary-layer tropospheric ozone - a review and
865 sensitivity analysis. *Atmospheric Chemistry and Physics*, 7.

866 Helmig, D., Cohen, L. D., Bocquet, F., Oltmans, S., Grachev, A., & Neff, W. (2009). Spring and
867 summertime diurnal surface ozone fluxes over the polar snow at Summit, Greenland.
868 *Geophysical Research Letters*, 36. doi: L0880910.1029/2008gl036549

869 Helmig, D., Johnson, B. J., Warshawsky, M., Morse, T., Neff, W. D., Eisele, F., & Davis, D. D.
870 (2008a). Nitric oxide in the boundary-layer at South Pole during the Antarctic
871 Tropospheric Chemistry Investigation (ANTCI). *Atmospheric Environment*, 42(12),
872 2817-2830.

873 Helmig, D., Johnson, B., Oltmans, S. J., Neff, W., Eisele, F., & Davis, D. D. (2008b). Elevated
874 ozone in the boundary layer at South Pole. *Atmospheric Environment*, 42(12), 2788-2803.
875 doi: 10.1016/j.atmosenv.2006.12.032

876 Hoigne, J., Bader, H. (1983). Rate constants of reactions of ozone with organic and inorganic
877 compounds in water. 2 Dissociating organic compounds. *Water Research*, 17, 185-194.

878 Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B., & Campbell, B. (1999).
879 Evidence of NO_x production within or upon ice particles in the Greenland snowpack.
880 *Geophysical Research Letters*, 26(6), 695-698. doi: 10.1029/1999gl900077

881 Honrath, R. E., Guo, S., Peterson, M. C., Dziobak, M. P., Dibb, J. E., & Arsenault, M. A. (2000).
882 Photochemical production of gas phase NO_x from ice crystal NO₃. *Journal of*
883 *Geophysical Research-Atmospheres*, 105(D19), 24183-24190. doi:
884 10.1029/2000jd900361

885 Honrath, R. E., Lu, Y., Peterson, M. C., Dibb, J. E., Arsenault, M. A., Cullen, N. J., & Steffen,
886 K. (2002). Vertical fluxes of NO_x, HONO, and HNO₃ above the snowpack at Summit,
887 Greenland. *Atmospheric Environment*, 36(15-16), 2629-2640. doi: 10.1016/s1352-
888 2310(02)00132-2

889 Huff, D.M., Joyce, P.L., Fochesatto, G.J., Simpson, W.R., 2011. Deposition of dinitrogen pen-
890 toxide, N₂O₅, to the snowpack at high latitudes. *Atmos. Chem. Phys.* 11, 4929-4938.

891 Jacobi, H. W., Bales, R. C., Honrath, R. E., Peterson, M. C., Dibb, J. E., Swanson, A. L., &
892 Albert, M. R. (2004). Reactive trace gases measured in the interstitial air of surface snow

893 at Summit, Greenland. *Atmospheric Environment*, 38(12), 1687-1697. doi:
894 10.1016/j.atmosenv.2004.01.004

895 Jacobi, H. W., & Hilker, B. (2007). A mechanism for the photochemical transformation of nitrate
896 in snow. *Journal of Photochemistry and Photobiology a-Chemistry*, 185(2-3), 371-382.

897 Jacobi, H.W., Kleffmann J., Villena G., Woese P., King M., France J., Anastasio C., and
898 Staebler R. (2014) Role of nitrite in the photochemical formation of radicals in the snow.
899 *Environ. Sci. Technol.* 48, 165-172.

900 Jones, A.E., Brough, N., Anderson, P.S., Wolff, E.W., 2014. HO₂NO₂ and HNO₃ in the coastal
901 Antarctic winter night: a “lab-in-the-field” experiment. *Atmos. Chem. Phys.* 14, 11,843-
902 11,851.

903 Kim, S.-K., & Kang, H. (2010). Efficient conversion of nitrogen dioxide into nitrous acid on ice
904 surfaces. *Journal of Physical Chemistry Letters*, 1(20), 3085-3089. doi:
905 10.1021/jz1011669

906 Kley, D., & McFarland, M. (1980). Chemiluminescence detector for NO and NO₂. *Atmos. Tech.*,
907 12, 62-69.

908 Kramer L.J., Helmig D., Burkhardt J.F., Stohl A., Oltmans S., and Honrath R.E. (2014) Seasonal
909 variability of atmospheric nitrogen oxides and non-methane hydrocarbons at the GEO-
910 Summit station, Greenland. *Atmos. Chem. Phys. Discuss.* 13817-13867.

911 Liao, J., Sihler, H., Huey, L. G., Neuman, J. A., Tanner, D. J., Friess, U., . . . Ullmann, K.
912 (2011). A comparison of Arctic BrO measurements by chemical ionization mass
913 spectrometry and long path-differential optical absorption spectroscopy. *Journal of*
914 *Geophysical Research-Atmospheres*, 116. doi: D00r02 10.1029/2010jd014788

915 Massman, W. J. (1998). A review of the molecular diffusivities of H₂O, CO₂, CH₄, CO, O₃, SO₂,
916 NH₃, N₂O, NO, and NO₂ in air, O₂, and N₂ near STP. *Atmospheric Environment*, 32(6),
917 1111-1127.

918 Murray, K.A., Kramer, L.J., Doskey P.V, Ganzeveld L., Seok B., Van Dam B., and Helmig D.
919 (2015) Dynamics of ozone and nitrogen oxides at Summit, Greenland . II. Simulating
920 snowpack chemistry during a spring high ozone event with a 1-D process-scale model.
921 *Atmos. Environ.*, in press.

922 Murphy, J.G., Thornton, J.A., Woldridge, P.J., Day, D.A., Rosen, R.S., Cantrell, C., Shetter,
923 R.E., Lefer, B., Cohen, R.C., 2004, Measurements of the sum of HO₂NO₂ and CH₃O₂NO₂
924 in the remote troposphere. *Atmos. Chem. Phys.* 4, 377-384.

925 Neff, W., Helmig, D., Grachev, A., & Davis, D. (2008). A study of boundary layer behavior
926 associated with high NO concentrations at the South Pole using a minisodar, tethered
927 balloon, and sonic anemometer. *Atmospheric Environment*, 42(12), 2762-2779.

928 Oltmans, S. J. (1981). Surface ozone measurements in clean-air. *Journal of Geophysical*
929 *Research-Oceans and Atmospheres*, 86(NC2), 1174-1180. doi:
930 10.1029/JC086iC02p01174

931 Oltmans, S. J., Schnell, R. C., Sheridan, P. J., Peterson, R. E., Li, S. M., Winchester, J. W., . . .
932 Barrie, L. A. (1989). Seasonal surface ozone and filterable bromine relationship in the

933 high Arctic. *Atmospheric Environment*, 23(11), 2431-2441. doi: 10.1016/0004-
 934 6981(89)90254-0

935 Peterson, M. C., & Honrath, R. E. (2001). Observations of rapid photochemical destruction of
 936 ozone in snowpack interstitial air. *Geophysical Research Letters*, 28(3), 511-514. doi:
 937 10.1029/2000gl012129

938 Ridley, B. A., & Grahek, F. E. (1990). A small, low flow, high sensitivity reaction vessel for NO
 939 chemiluminescence detectors. *Journal of Atmospheric and Oceanic Technology*, 7(2),
 940 307-311.

941 Sander, S. P., Abbatt, J., Barker, J.R., Burkholder, J.B., Friedl, R.R., Golden, D.M., Huie, R.E.,
 942 Kolb, C.E., Kurylo, M.J., Moortgat, G.K., Orkin, V.L., Wine, P.H., 2011. *Chemical Ki-*
 943 *netics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17*, JPL
 944 Publication 10-6, <http://jpldataeval.jpl.nasa.gov/>, Jet Propulsion Laboratory, Pasadena,
 945 CA.

946 Seinfeld, J. H. and Pandis S. N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution*
 947 *to Climate Change*. New Jersey: John Wiley & Sons, Inc.

948 Seok, B., Helmig, D., Williams, M. W., Liptzin, D., Chowanski, K., & Hueber, J. (2009). An
 949 automated system for continuous measurements of trace gas fluxes through snow: an
 950 evaluation of the gas diffusion method at a subalpine forest site, Niwot Ridge, Colorado.
 951 *Biogeochemistry*, 95(1), 95-113. doi: 10.1007/s10533-009-9302-3

952 Seok, B., Ganzeveld, L., Helmig, D., Honrath, R., Van Dam, B., Hueber, J., Kramer, L. (2010).
 953 Evaluation of snowpack ozone and nitrogen oxide exchange at Summit, Greenland, in a
 954 single-column chemistry-climate model. Paper presented at the *State of the Arctic*
 955 *Meeting*, Miami, FL, USA. [http://soa.arcus.org/abstracts/evaluation-snowpack-o3-and-](http://soa.arcus.org/abstracts/evaluation-snowpack-o3-and-nox-exchange-summit-greenland-single-column-chemistry-climate-m)
 956 [nox-exchange-summit-greenland-single-column-chemistry-climate-m](http://soa.arcus.org/abstracts/evaluation-snowpack-o3-and-nox-exchange-summit-greenland-single-column-chemistry-climate-m)

957 Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows,
 958 J., Carpenter, L.J., Friess, U., Goodsite, M.E., Heard, D., Hutterli, M., Jacobi, H.W.,
 959 Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson,
 960 P., Sodeau, J., Steffen, A., Wegner, T., Wolff, E. (2007). Halogens and their role in polar
 961 boundary-layer ozone depletion. *Atmospheric Chemistry and Physics*, 7(16), 4375-4418.

962 Slusher, D.L., Huey, G., Tanner, D.J., Chen, G., Davis, D.D., Buhr, M., Nowak, J.B., Eisele,
 963 F.L., Kosciuch, E., Mauldin, R.L., Lefer, B.L., Shetter, R.E., Dibb, J.E., 2002. Measure-
 964 ments of pernitric acid at the South Pole during ISCAT 2000. *Geophys. Res. Lett.* 29, 21,
 965 2011, doi:10.1029/2002GL015703.

966 Slusher, D.L., Neff, W.D., Kim, S., Huey, L.G., Wang, Y., Zeng, T., Tanner, D.J., Blake, D.R.,
 967 Beyersdorf, A., Lefer, B.L., Crawford, J.H., Eisele, F.L., Mauldin, R.L., Kosciuch, E.,
 968 Buhr, M.P., Wallace, H.W., Davis, D.D., 2010. Atmospheric chemistry results from the
 969 ANTCI 2005 Antarctic plateau airborne study. *J. Geophys. Res.* 115, DO7304,
 970 doi:10.1029/2009JD012605.

971 Stutz, J., Thomas, J. L., Hurlock, S. C., Schneider, M., von Glasow, R., Piot, M., Gorham, K.,
 972 Burkhardt, J.F., Ziemba, L., Dibb, J.E., Lefer, B. L. (2011). Longpath DOAS observations
 973 of surface BrO at Summit, Greenland. *Atmospheric Chemistry and Physics*, 11(18), 9899-
 974 9910. doi: 10.5194/acp-11-9899-2011

- 975 Takenaka, N., Ueda, A., & Maeda, Y. (1992). Acceleration of the rate of nitrite oxidation by
976 freezing in aqueous solution. *Nature*, 358(6389), 736-738. doi: 10.1038/358736a0
- 977 Thomas, J. L., Stutz, J., Lefer, B., Huey, L. G., Toyota, K., Dibb, J. E., von Glasow, R. (2011).
978 Modeling chemistry in and above snow at Summit, Greenland - Part 1: Model description
979 and results. *Atmospheric Chemistry and Physics*, 11(10), 4899-4914. doi: 10.5194/acp-
980 11-4899-2011
- 981 Thomas, J. L., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., von Glasow, R., Stutz, J.
982 (2012). Modeling chemistry in and above snow at Summit, Greenland - Part 2: Impact of
983 snowpack chemistry on the oxidation capacity of the boundary layer. *Atmospheric*
984 *Chemistry and Physics*, 12(14), 6537-6554. doi: 10.5194/acp-12-6537-2012
- 985 Ulrich, T., Ammann, M., Leutwyler, S., Bartels-Rausch, T., 2012. The adsorption of peroxyxynitric
986 acid on ice between 230 K and 253 K. *Atmos. Chem. Phys.* 12, 1833-1845.
- 987 Van Dam, B., Helmig, D., Neff, W., & Kramer, L. (2013). Evaluation of boundary layer depth
988 estimates at Summit Station, Greenland. *Journal of Applied Meteorology and*
989 *Climatology*, 52(10), 2356-2362, doi:10.1175/JAMC-D-13-055.1.
- 990 Warneck, P., & Wurzinger, C. (1988). Product quantum yields for the 305-nm
991 photodecomposition of NO_3^- in aqueous solution. *Journal of Physical Chemistry*, 92(22),
992 6278-6283. doi: 10.1021/j100333a022
- 993 Yang, Q.Z., Mayewski, P.A., Whitlow, S., Twickler, M., Morrison, M., Talbot, R., Dibb, J., and
994 Linder, E. (1995) Global perspective of nitrate flux in ice cores, *J. Geophys. Res.*, 100,
995 5113-5121, doi: 10.1029/94JD03115.