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# Fluxes and chemistry of nitrogen oxides in the Niwot Ridge, Colorado, snowpack

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**Abstract** The effect of snow cover on surface-atmosphere exchanges of nitrogen oxides (nitrogen oxide (NO) + nitrogen dioxide ($NO_2$); note, here '$NO_2$' is used as surrogate for a series of oxidized nitrogen gases that were detected by the used monitor in this analysis mode) was investigated at the high elevation, subalpine (3,340 m asl) Soddie site, at Niwot Ridge, Colorado. Vertical (NO + $NO_2$) concentration gradient measurements in interstitial air in the deep (up to ~2.5 m) snowpack were conducted with an automated sampling and analysis system that allowed for continuous observations throughout the snow-covered season. These measurements revealed sustained, highly elevated (NO + $NO_2$) mixing ratios inside the snow. Nitrogen oxide concentrations were highest at the bottom of the snowpack, reaching levels of up to 15 ppbv during mid-winter. Decreasing mixing ratios with increasing distance from the soil–snow interface were indicative of an upwards flux of NO from the soil through the snowpack, and out of the snow into the atmosphere, and imply that biogeochemical processes in the subnival soil are the predominant NO source. Nitrogen dioxide reached maximum levels of ~3 ppbv in the upper layers of the snowpack, i.e., ~20–40 cm below the surface. This behavior suggests that a significant fraction of NO is converted to $NO_2$ during its diffusive transport through the snowpack. Ozone showed the opposite behavior, with rapidly declining levels below the snow surface. The mirroring of vertical profiles of ozone and the $NO_2$/(NO + $NO_2$) ratio suggest that titration of ozone by NO in the snowpack contributes to the ozone reaction in the snow and to the ozone surface deposition flux. However, this surface efflux of (NO + $NO_2$) can only account for a minor fraction of ozone deposition flux over snow that has been reported at other mid-latitude sites. Neither (NO + $NO_2$) nor ozone levels in the interstitial air showed a clear dependence on incident solar irradiance, much in contrast to observations in polar snow. Comparisons with findings from polar snow studies reveal a much different (NO + $NO_2$) and ozone snow chemistry in this alpine environment. Snowpack concentration gradients and diffusion theory were applied to estimate an average, wintertime (NO + $NO_2$) flux of 0.005–0.008 nmol $m^{-2}$ $s^{-1}$, which is of similar magnitude as reported (NO + $NO_2$) fluxes

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from polar snow. While fluxes are similar, there is strong evidence that processes controlling ($NO + NO_2$) fluxes in these environments are very different, as subnivial soil at Niwot Ridge appears to be the main source of the ($NO + NO_2$) efflux, whereas in polar snow ($NO + NO_2$) has been found to be primarily produced from photochemical de-nitrification of snow nitrate.

**Keywords** Snow · Soil · Winter · Gas fluxes · Nitrogen oxides · Ozone

## Introduction

Unprecedented changes in snow and sea ice cover have been observed in recent years (Comiso and Parkinson 2004; Drobot et al. 2008). Previous research has also revealed a surprising plethora of gas exchanges occurring between snow and the overlying atmosphere (Domine and Shepson 2002; Grannas et al. 2007). An important question is how snow cover changes will affect the cryosphere-atmosphere energy and gas exchange, atmospheric composition and chemistry, and how these processes will feedback in a changing climate. To date, most snow gas exchange studies of reactive gases have focused on three unique and distinct environments, these being on top of the polar ice caps (e.g., Summit, Greenland, and South Pole, Antarctica), in polar coastal regions (e.g., Alert, Canada; Barrow, Alaska; Neumayer, Antarctica; Halley, Antarctica), and at various midlatitude sites with seasonal snow cover. These systems are extremes of a wide range of physical and chemical snowpack conditions on Earth. As findings from these various studies accumulate and are being synthesized, it has become increasingly evident that in each of these snow-covered regions transformation processes in snow chemical reservoirs are very different. While our conception of the processes in these environments has improved substantially during recent years, a comprehensive understanding of snowpack chemistry and gas exchange remains elusive. In particular, there is a lack of parameterizations that consider the variation of physical and chemical snow properties, snowpack depth, and biogeochemical properties of the substrate beneath the snow for integration in atmospheric and climate models.

In midlatitude environments, several recent experiments have shown that deep snow cover can promote respiration processes below the snowpack, resulting in the efflux of gases from the soil upward through the snow (Groffman et al. 2001). Most of this research has focused on the study of $CO_2$. These data indicate significant carbon loss due to wintertime, subnivial respiration that needs to be considered in evaluating ecosystem annual carbon exchange (Monson et al. 2006; Maljanen et al. 2007; Nobrega and Grogan 2007). While more than a dozen studies have examined snowpack $CO_2$ fluxes, comparatively little attention has been given to other snow trace gas fluxes, in particular to reactive gas species. Here, we focus on nitrogen oxides. Oxidized nitrogen inputs have increased significantly during the past century (Galloway et al. 2008). Enhancements of nitrate in atmospheric deposition have been reported in most environmental compartments, including precipitated snow. The fate of deposited nitrate in seasonally snow-covered areas is complex, with the most important sinks being uptake by vegetation, melt water runoff, and soil nitrification and denitrification (Brooks and Williams 1999). The vast majority of nitrogen cycle studies in temperate regions have been during the spring-fall season, with wintertime research focusing mostly on nitrate deposition by precipitating snow. As $CO_2$ flux studies have provided convincing evidence of respiration processes in the soil underneath the snow, it is likely that there may similarly be considerable nitrogen cycling occurring in snow-covered soils. Indeed, the few studies that have investigated soil oxidized nitrogen fluxes under snow confirmed the assumption that heterotrophic activity in the soil causes increases of $N_2O$ in soil air space and $N_2O$ fluxes underneath the snow (Brooks et al. 1997; Maljanen et al. 2007). $N_2O$ cycling dynamics was found highly sensitive to the duration and depth of the snowpack (Brooks et al. 1997; Groffman et al. 2006) as well as soil properties (Schurmann et al. 2002). This body of literature has pointed unanimously to the importance of wintertime $N_2O$ fluxes and the need for their consideration in the annual oxidized nitrogen budget. Recent research from polar sites has demonstrated the important role of snow nitrate in providing a substrate for photochemical formation of nitrogen oxides in sunlit snow (Grannas et al. 2007). Because nitrogen oxides play a crucial role in oxidation chemistry, these connections raise the questions how current wintertime soil biogeochemistry, soil fluxes, snowpack chemistry, surface fluxes, and atmospheric chemistry influences may differ from pre-industrial conditions where ($NO + NO_2$) inputs were lower than current levels (Edwards et al. 2007). To date, subnivial nitrification processes, particularly ($NO + NO_2$) production and their snowpack fluxes, have not been studied as extensively as $N_2O$ and denitrification. Most likely, this neglect is due to the fact that, while stable gases ($CO_2$, $N_2O$, $CH_4$) can be investigated by sample collection in the field with subsequent laboratory analysis, ($NO + NO_2$) flux experiments require sophisticated in-situ analytical tools that are more difficult to deploy at snow-covered field sites.

For almost 40 years, ozone behavior over snow and ozone atmosphere-snow fluxes have raised the interest of scientists. From the review (Helmig et al. 2007b) of this previous literature, as well as from new experiments at Summit, Greenland (Helmig et al. 2007c), and South Pole, Antarctica, (Crawford et al. 2001; Oltmans et al. 2008; Helmig et al. 2008), it can be concluded that ozone chemistry in snow environments is determined by multiple chemical reactions, and that the significance of a particular chemical process varies according to coastal, polar and midlatitude locations. Ozone can completely disappear for many days during spring in the coastal Arctic surface layer, a phenomenon seen at no other place on Earth (Barrie et al. 1988; Simpson et al. 2007). The opposite is observed at South Pole, where ozone production episodes, leading to a doubling of surface ozone within a few days, have been reported (Crawford et al. 2001). A number of experiments have shown that ozone fluxes over snow may be downward, upward, or bi-directional. Important variables that have been identified in determining this confusing ozone behavior are photochemical reactions involving halogens, nitrogen oxides, and the frequently observed stable mixing conditions over snow. In particular, stable conditions and shallow mixing layer heights foster conditions where snowpack emissions can accumulate to highly elevated concentrations and their reaction times overcome the turbulent exchange rates (Neff et al. 2008).

Our previous work has shown that ozone in interstitial air of the polar snow covering the Greenland ice cap at Summit is closely linked to solar irradiation, with increases in the ozone destruction rate mirroring the seasonal and diurnal solar irradiance levels. In contrast, the high elevation snowpack at Niwot Ridge, Colorado, had much lower ozone concentrations and ozone there lacked dependency on solar irradiance (Bocquet et al. 2007). Despite the fact that this research showed that much lower ozone levels were characteristic for this seasonal snowpack, a series of other studies had shown upward ozone fluxes from sites that appear to have similar characteristics (Galbally and Allison 1972; Zeller and Hehn 1996; Zeller and Nikolov 2000). Ozone chemistry is closely tied to levels and conversion rates of ($NO + NO_2$), but unfortunately none of these previous experiments had provided concurrent monitoring and insight for the interconnection of ozone and ($NO + NO_2$) in midlatitude snow. This manuscript is the first report of snowpack ($NO + NO_2$) measurements with concurrent ozone observations and our follow-up investigation of the question how ozone and ($NO + NO_2$) concentrations and their chemistry in the snowpack are linked to their surface exchanges.

## Experimental

This experiment was conducted in a forest clearing near tree line at the high-elevation Soddie site, within the Niwot Ridge, Colorado, Long-Term Ecological Research area (40°03′N, 105°35′W, 3,340 m asl; NWT). More site information, the snowpack gradient tower, and the plumbing diagram are described in detail by Bocquet et al. (2007) and Seok et al. (2009). This snowpack gas flux research was initiated in the fall of 2003. Since then snowpack studies have been conducted at this site every winter. The experiment has been modified somewhat every season to improve the number of inlets and gas measurements. Ozone has been studied each winter since 2003/2004, carbon dioxide measurements were added in 2004/2005, and ($NO + NO_2$) and $N_2O$ measurements began in 2005/2006. Only details pertinent to the ozone and nitrogen oxides measurements are described here, please see Seok et al. (2009) for information on other gas, meteorological, and snow physical measurements.

A new sampling tower with an increased number of inlet heights was installed in fall 2006, allowing air to be sampled sequentially from paired inlets in the snow at 0, 10, 30, 60, 90, 120 at the soil surface during the 2006/2007 winter season. Air was drawn through 18 m-long (equal length), 0.64 mm o.d., 0.39 mm i.d. PFA Teflon sampling lines to gas monitors operated in an adjacent underground laboratory by the combined delivery rate of the pumps in the ozone and nitrogen oxides monitors at a total rate of ~3.2 l $min^{-1}$ (volumetric). Inlets were switched every 10 min, consequently a volume of ~32 l of air was withdrawn from the paired inlets at a given height every 80 min.

Ozone was measured with a UV absorption monitor (Model 49, Thermo Electron Corporation (TEI), Franklin, MA). A second ozone monitor (Model 49C, TEI) was used to sample air continuously from the nearby (~10 m) meteorological (MET) tower at 5 m height above the ground. Both ozone monitors were calibrated before and after each winter against a UV absorption laboratory standard (Model 49C, TEI), which was referenced against an EPA primary ozone standard at the US EPA, Region 8 (Golden, Colorado) laboratory. The continuous ozone measurements from the MET tower were compared with the 245 cm-level, 10-min measurements from the snowpack gradient tower, and these two measurements agreed within 0–2 ppbv under most conditions. The overall uncertainty in the ozone snowpack measurements is estimated at ±2 ppbv.

NO and $NO_2$ were monitored with a chemiluminescence analyzer (Model 42C-TL, Thermo Electron Corporation). This instrument has two channels, one for measurement of NO by NO + ozone chemiluminescence, and a second channel, in which air is directed first through a heated (325°C) molybdenum converter causing oxidized nitrogen compounds, including $NO_2$, to be converted to NO, and subsequently detected together with NO in the sample. $[NO_2]$ is then determined after subtracting the NO signal of the prior measurement. It is well established that there are a number of interferences in this $NO_2$ measurement (Steinbacher et al. 2007). The error in the $NO_2$ measurement increases with increasing levels of other interfering gases such as nitrous acid (HONO), peroxyacetyl nitrate (PAN), and alkyl nitrates that contribute to the $NO_2$-mode signal. In ambient air, $NO_2$ typically constitutes the largest fraction of oxidized nitrogen compounds, hence this measurement will nonetheless represent a reasonable estimate of $[NO_2]$. We have no data on other volatile oxidized nitrogen compounds in the snowpack at NWT, and it is uncertain to what degree such species may have contributed to the $NO_2$ signal in this situation. Previous ambient studies at NWT have found typical wintertime ($NO + NO_2$) values of 200–1,000 pptv (Parrish et al. 1990), and it is not unusual that the sum of oxidized nitrogen gases ($NO_y$) can exceed 1 ppbv (Fahey et al. 1986; Ridley et al. 1990). Our experiments do not allow for an evaluation of the contribution of these other species to the detected $NO_2$ signal, nor do we have measurements that allow for an assessment of the $NO_2$ to NO conversion efficiency of our TEI 42TL instrument. Consequently here we use '$NO_2$' as surrogate for the group of oxidized nitrogen species that was detected in this measurement mode. Please bear in mind that these reported quantitative data are most likely an overestimate of actual $NO_2$ levels present in these samples.

The ($NO + NO_2$) instrument was calibrated every night by running a series of dynamically diluted standards (4-point calibration, 9–36 ppbv). These calibration gases were prepared at the site by diluting a 1.023 ppmV mixture of NO in $N_2$ (Scott-Marrin, Riverside, CA) with NO-free (<1 ppbv) compressed air (Breathing Air grade, Airgas, Boulder, CO). Linear regression calibration functions gave $R^2$-values of ≥0.99. On-site calibrations during the 2005/2006 and 2006/2007 winter gave results that were within ~12 and 9% of the manufacturer's instrument calibration. Instrument drifts throughout these two seasons were ~2%. The manufacturer's detection limit at 120 s averaging time is reported as 50 pptv, our own practical experience from these winter experiments suggests a ~2–3 times higher detection limit under our operating condition (which, nonetheless was well sufficient to detect NO and $NO_2$ during all times in snowpack air). The transport time of air samples from the inlet to the gas monitors was calculated (using tubing dimensions, manifold volume, and purge rate) to ~5 s. During the transport through the tubing, in absence of light, NO will react with ozone in the sample air, according to (Atkinson et al. 2004):

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (k = 1.2 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at}\ T = 0°\mathrm{C}) \tag{R1}$$

leading to partial conversion of NO to $NO_2$. Under these conditions, in the worst case scenario, at 80 ppbv of ozone and $T = 0°C$, ~3% of the NO in the air sampled would be converted to $NO_2$ on its way to the monitor. Because snowpack ozone was usually much lower than 80 ppbv (see below), NO losses during snowpack sampling are expected to be significantly lower than this estimate; consequently we did not correct for this minor NO determination error.

## Results and discussion

### Snowpack levels of $(NO + NO_2)$ and ozone

Here we focus on data from the 2006/2007 measurements. Observations from this season were in qualitative agreement with the three previous year ozone measurements as well as with one previous year of nitrogen oxides data. The 2006/2007 experiment yielded the most complete and highest vertically resolved (highest number of inlets) gas measurements, and the most frequent snow depth and snow density profile sampling conducted thus far. An example of time series data for NO, $NO_2$, $(NO + NO_2)$, and ozone is illustrated in Fig. 1. These data are from one sampling cycle through the eight inlets, with measurements starting above the snow surface (sampling height 245 cm, ~59 cm above the snow surface). This measurement is on the order of ~1 ppbv of NO and 1 ppbv of $NO_2$ [2 ppbv of $(NO + NO_2)$], which is common for this site, where wintertime ambient $(NO + NO_2)$ typically remains ≤1–2 ppbv. Levels of $(NO + NO_2)$ increased steadily as the sampling sequence progressed downwards into the snowpack,

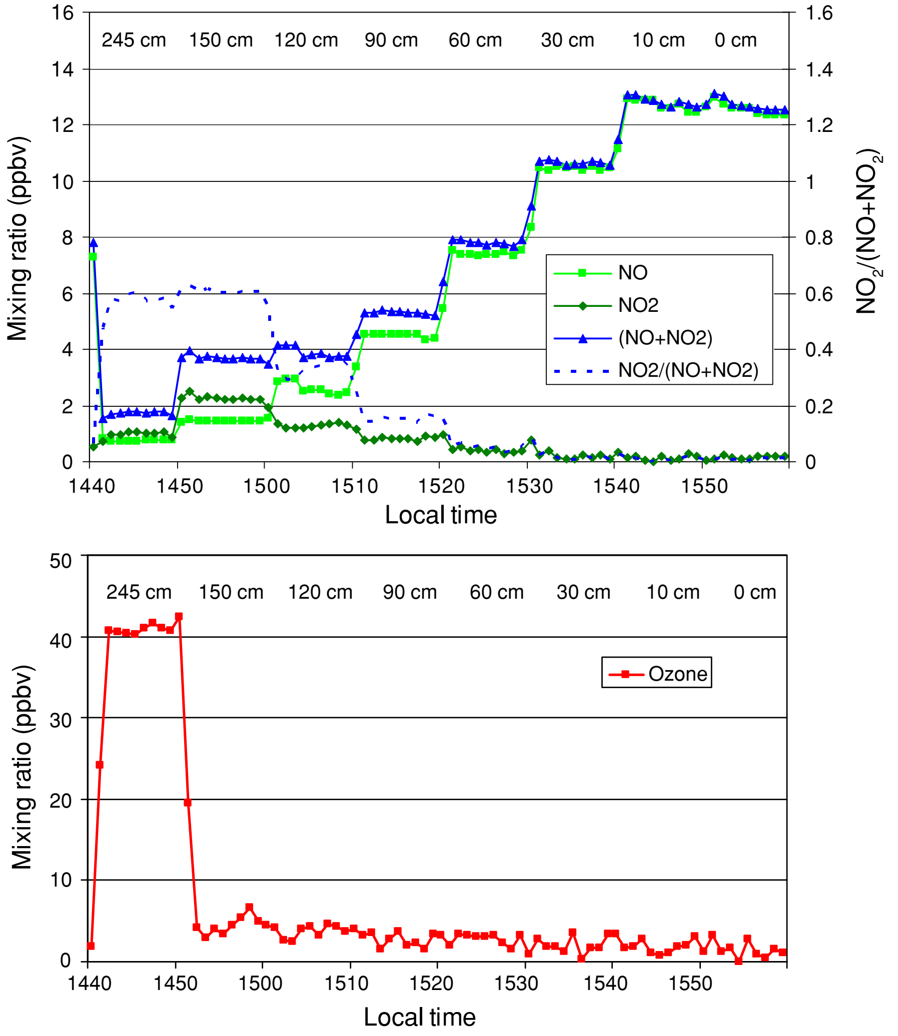

**Fig. 1** Time series of 1-min mean data from snowpack gradient sampling of NO, $NO_2$, $(NO + NO_2)$ (*upper graphs*) and ozone (*lower graph*) on March 12, 2007, when the snowpack was 186 cm deep. This 100-min sampling sequence starts out with 10 min of measurements above the snow, and from there moves downward in 10-min intervals towards the bottom of the snowpack at the height intervals (above the ground surface) shown in the graphs

usually by 1–3 ppbv with each depth interval. After switching to a new inlet pair, measurements stabilized after a 1–2 min transition period (Fig. 1). This result indicates that sampling flows, instrument response time, and data logging frequency were sufficient to yield at least 7–8 representative 1-min data points from each level. Furthermore, there is little change in signal during the 10 min-sampling period at each height. From this behavior, we conclude that the snowpack ventilation that is caused by the sample withdrawal itself has relatively little influence on the (NO + $NO_2$) and ozone snowpack gradients, because otherwise steeper concentration changes would be expected while air surrounding the inlets is replaced from other nearby locations/heights in the snowpack (see Seok et al. (2009) for a more in depth discussion of the effect of air sampling on snowpack ventilation).

The increase of (NO + $NO_2$) concentration toward the bottom of the snowpack is evidence for (NO + $NO_2$) emissions from the subnival soil, with transport of (NO + $NO_2$) and eventual release from the snowpack surface into the much lower-concentration atmosphere (see below). An interesting and consistent feature in the NO and $NO_2$ profiles is that $NO_2$ is at its highest concentration at the uppermost inlet within both ambient air as well as compared to deeper in the snowpack. [$NO_2$] dropped steadily with depth while [NO] increased, resulting in lower and lower $NO_2$/(NO + $NO_2$) ratios toward the snowpack base (Fig. 1). The ratio of $NO_2$/(NO + $NO_2$) approaches zero at the bottom of the snowpack. This behavior indicates that NO is likely the principle result of soil emission. As NO is transported up through the snowpack, an increasing NO fraction is converted to $NO_2$; by the time that (NO + $NO_2$) leaves the snowpack, most of the NO has been converted, making $NO_2$ the primary species released from the snow surface.

A much different behavior was found for ozone, which was always measured at lower levels in the snow and at highest concentration in air above the snowpack (lower graph in Fig. 1). In this case, less than 10% of ambient levels were observed just below the snowpack surface in the air pulled from the ~36 cm deep inlet. Deeper inside the snowpack, ozone levels were close or below the instrument detection levels (~2 ppbv). These data, while at higher resolution using eight sampling heights rather than four, are in agreement with the earlier measurements from Bocquet et al. (2007), who also showed little remaining ozone with increasing depth in the snowpack.

Because (NO + $NO_2$) and ozone profiles did not show diurnal dependencies (see discussion below), all 18 profiles from the same day as the data in Fig. 1 were combined to better illustrate the vertical gradient in the snowpack of NO, $NO_2$, (NO + $NO_2$), and ozone, including their variability, within a 24-h period (Fig. 2). The gradual increase of (NO + $NO_2$) going down into the snowpack contrasts with the abrupt loss of ozone below the snow surface. Furthermore, the data for this particular day show that the variability (1 $\sigma$) that was calculated at a given sampling height had a similar magnitude to that of the (NO + $NO_2$) vertical concentration gradients over a 30-cm height interval. Data in Figs. 1 and 2 show that the two lower inlet pairs at 0 cm (located right on the soil surface), and at 10 cm height deviate from this general behavior, and that there is no clear concentration difference between these two heights. Similar observations were made throughout the study, hence we conclude that these two measurement heights, which are only 10 cm apart in height and ~40 cm in distance, were sampling air with similar composition. We suspect that the slightly sloped terrain and

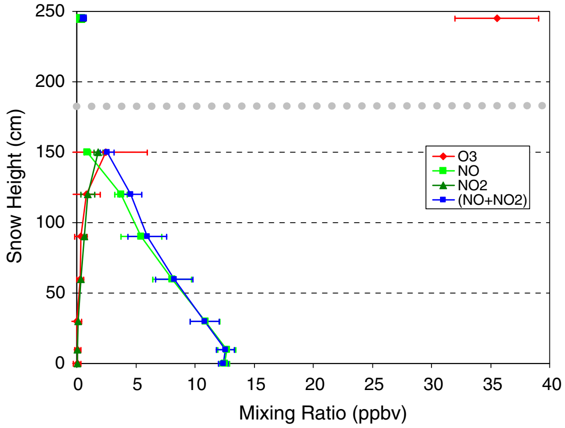

**Fig. 2** Mean concentration profile of NO, $NO_2$, and (NO + $NO_2$) during March 12, 2007, from a total of 18 10-min means at each inlet height with error bars indicating the variability (standard deviation) of the 10-min means at each height. Snowpack depth, indicated by the grey dotted line, was 186 cm during this period. Measurements from above the snow surface; i.e. at 245 cm during this period are also indicated for comparison

vegetation cover cause distinct vertical concentration gradients to develop only above a surface boundary layer; these data imply that for this site this layer is on the order of 10 cm deep and of similar scale as the vegetation height.

The continuous 8-height data (with 7 of these measurements from within the snowpack during the time with maximum snow depth), with ~18 measurements at each level per day, were combined in color contour graphics that show both the spatial and temporal evolution of these gases in the snowpack (Fig. 3). NO buildup is related to the snowpack depth, with progressively higher NO levels developing as the snowpack depth increases, with a reverse pattern near the end of the winter as the snowpack diminishes (Fig. 3a). While there are fluctuations of

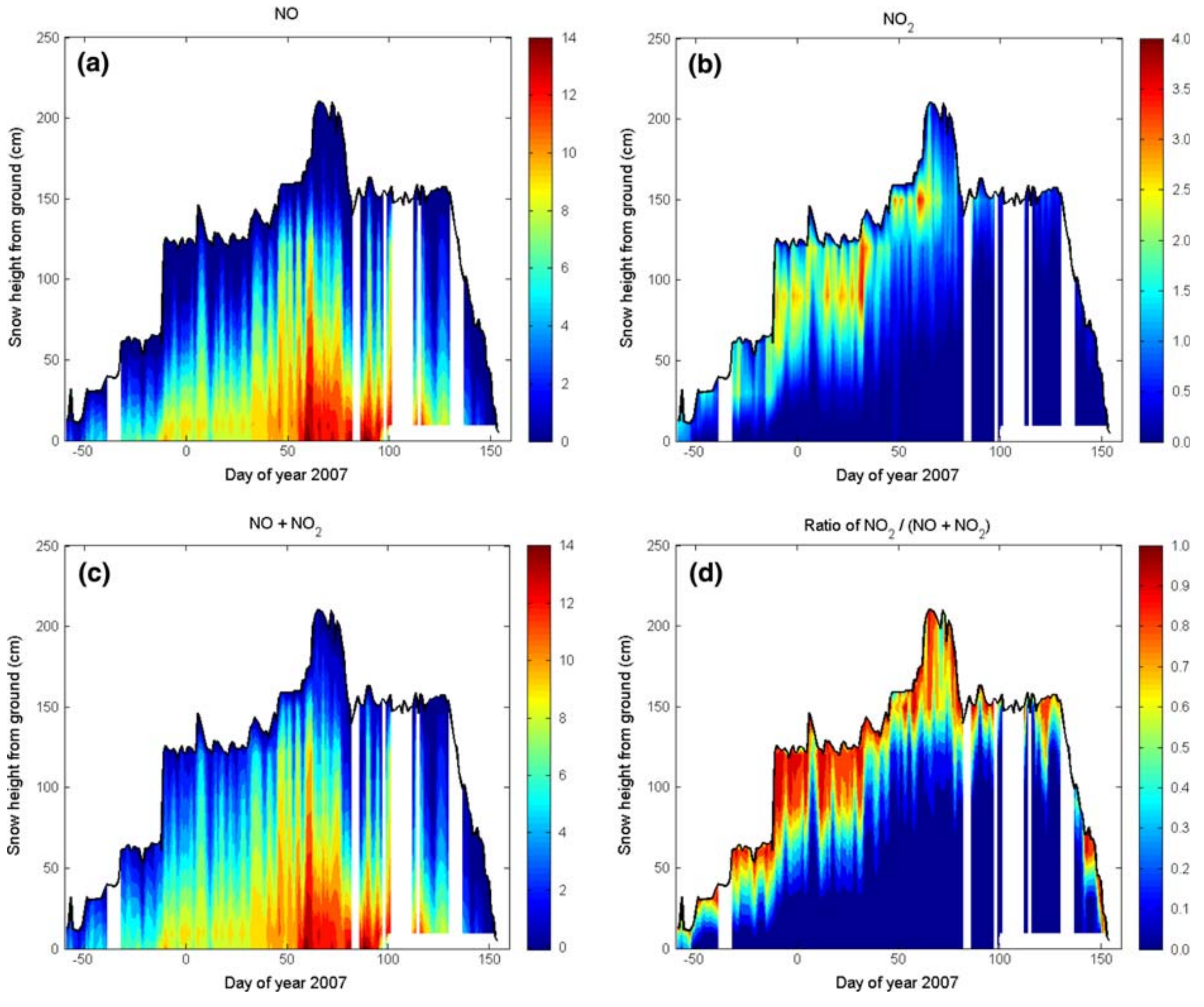

**Fig. 3** **a–d** Color contour plots of NO, $NO_2$, NO + $NO_2$, and $NO_2$/(NO + $NO_2$). The upper edge of the colored area indicates the snowpack height, the *x*-axis the day of year 2007 (with negative values indicating the day prior to Jan. 1, 2007), and the color scale shows the mixing ratio of the respective gases shown. Please note that for $NO_2$ the color contour plot may not be an accurate depiction of the $NO_2$ behavior right below the snow surface, as the interpolation routine uses the ambient (245 cm) concentration as the snowpack border value, and the limited resolution of data between the height of maximum [$NO_2$] and the snowpack border poses a larger degree of uncertainty in this area. [NO] and [$NO_2$] in air collected from the 245-cm inlet above the snow surface remained below 1 and 2 ppbv, respectively, during all times. Therefore, data from above the snow surface were not included in these figures for better clarity of this presentation. Sampling from the lowest inlet was stopped after DOY 100 to avoid pulling liquid water into the manifold during the snowmelt period

NO concentrations at a given height over 1–5 day periods, overall these data show the consistent, all-winter long enrichment of NO in the snowpack. Seok et al. (2009) present a detailed investigation of effects contributing to the variability of trace gas concentrations on hourly and several day time scales and conclude that variable ventilation of the snowpack from wind pumping is a major source of observed day-to-day concentration changes. $NO_2$, as already seen in Figs. 1 and 2, reaches its highest concentration near the top of the snowpack, and then drops again to lower levels right at the snowpack-atmosphere interface (Fig. 3b). The graph with the $NO_2/(NO + NO_2)$ ratio (Fig. 3d) shows that the behavior seen in Fig. 1 is consistent throughout the season, i.e., near the bottom of the snowpack most of the $(NO + NO_2)$ is present as NO while near the snow surface this ratio is reversed. Given the uncertainty in the accuracy of the graphical contour plot representation of the $NO_2$ behavior right below the snow surface, we examined the $NO_2$ vertical profile data in a number of selected cases where we had high accuracy measurements of snowpack depth. For those situations we found that absolute $NO_2$ mixing ratios were indeed highest ~20–40 cm below the snow surface, and were declining both towards the bottom of the snowpack and towards the surface. The pattern of the $NO_2$ profile is indicative of the source of $NO_2$ being underneath the snow surface in the upper layers of the snowpack, with a resulting upward flux and loss of this gas from the snow surface (into the much lower concentration ambient air). The $(NO + NO_2)$ profile contour plot (Fig. 3c) shows that there is gradual, monotonic $(NO + NO_2)$ decline with distance from the soil surface, and that despite increased $NO_2$, $(NO + NO_2)$ never reaches its maximum in this same region. This pattern contradicts the hypothesis of a $NO_2$ source that is decoupled from NO, but suggests that the $NO_2$ increase is caused by conversion of NO into $NO_2$ during the migration of NO from the soil to the snowpack surface. Please note that due to the measurement limitations of the $NO_2$ determination there is also the possibility that one or several other $NO_y$ compounds may have contributed to the '$NO_2$' signal. Consequently, the question of the source of the '$NO_2$' can not be unequivocally answered until a more selective $NO_2$ measurement will be applied for this experiment.

## Source of $(NO + NO_2)$

Recent research at polar sites has shown that the concentration and chemistry of many important atmospheric gases is determined by photochemical reactions, and increasing evidence suggests that these reactions evolve around heterogeneous processes with snow trace constituents on ice crystals and in the quasi-liquid layer of the snowpack (Domine and Shepson 2002; Grannas et al. 2007). Furthermore, photochemical reactions can lead to significant formation rates of nitrogen oxides at polar sites. At Summit, Greenland, peak $(NO + NO_2)$ values 10–30 cm deep in the snowpack were between 500–600 pptv in July during times of maximum solar radiation. At night and during shading experiments $(NO + NO_2)$ mixing ratios dropped markedly, with nighttime values at 150–200 pptv (Peterson and Honrath 2001; Jacobi et al. 2004). In a similar experiment at South Pole, $(NO + NO_2)$ levels at 20 cm depth in the snow were ~1,500 pptv, with ~40–50% of the $(NO + NO_2)$ in the form of NO (Davis et al. 2004). All studies in the polar snow have found an unequivocal dependency of $(NO + NO_2)$ levels on incident radiation, and this dependency has supported the conclusion that $(NO + NO_2)$ formation is driven by photodenitrification of trace amounts of nitrate present in the snow.

Our results from NWT show snowpack $(NO + NO_2)$ enrichment at much higher levels than ever recorded for polar sites. During the time with the deepest snowpack, the highest snowpack $(NO + NO_2)$ mixing ratios were 15 ppbv, which is ~10 times higher than the maximum $(NO + NO_2)$ mixing ratios that have been reported in snow at polar sites.

Nitrate levels in the NWT snow average at ~11 $\mu M\ l^{-1}$ (Williams et al. 2009), ~4 times higher than the 2.9 μM mean snow nitrate concentration at Summit (Burkhart et al. 2004). The annual nitrate loading in the snowpack at the Soddie site in 2006 was 1.4 kg N $ha^{-1}$ (Williams et al. 2009). Conversion of this amount of nitrate to gaseous $(NO + NO_2)$ over a 180-day snow-covered period would result in a flux of ~0.7 nmol N $m^{-2}\ s^{-1}$. This flux is ~100 times larger than the actual $(NO + NO_2)$ surface flux estimate (see below). Consequently, in theory, the oxidized N-loading of the NWT snowpack is well sufficient to sustain the snowpack $(NO + NO_2)$ fluxes that were observed in these measurements. These considerations suggest that the nitrate levels in the snow would not limit the potential photochemical ($NO + NO_2$) production route as reported in the polar literature.

The question of whether ($NO + NO_2$) is formed photochemically from nitrate in the snow or from the underlying soil was further investigated by analyzing the 10-day record of ($NO + NO_2$) and ozone during a period with constant snowpack depth during DOY 47–57. The data investigated were from the bottom (near the soil surface) and the highest pair of inlets (150 cm), which during this time were covered by approximately 10 cm of snow. The averaged concentration plots show only small changes in NO, $NO_2$, ($NO + NO_2$), and ozone (Fig. 4), with the discernable diurnal changes being well within the overall variability seen in these data (expressed by the error bars in this graph). The slight decrease in NO and $NO_2$, mirrored by an increase in ozone, during the morning to mid-day hours could possibly be related to increased snowpack advection during that time of day. Seok et al. (2009), using snowpack $CO_2$ data, show that wind speed at NWT has a diurnal cycle, and argue that higher winds in the morning are the cause for reduced snowpack levels (and derived fluxes of snowpack emissions calculated by the diffusion method) during that time window. The fact that ozone, a gas being destroyed in the snow, shows the opposite behavior adds more credence to the explanation of this increased ventilation effect.

The lack of a clear dependency on incident irradiance in our data is a surprise because snow chamber studies in Northern Michigan (Honrath et al. 2000) using natural snow had shown that irradiation with UV-light triggered ($NO + NO_2$) production. However, the maximum ($NO + NO_2$) levels seen in these irradiation experiments (300 pptv) were lower than [($NO + NO_2$)] in the NWT snowpack, so it is possible that while photochemical ($NO + NO_2$) production in the snow at NWT may be occurring, it is too small to be discernable against the high background [($NO + NO_2$)] caused by the soil fluxes. The important point to note is that the diurnal dynamics of ($NO + NO_2$) in the NWT snowpack is strikingly different than at polar sites. At Summit during July, snowpack [($NO + NO_2$)] displayed large daytime–nighttime concentration changes with an amplitude on the order of a factor of 4–5 (Peterson and Honrath 2001), and these changes were attributed to the diurnal changes in levels of incident radiation at this site. The lack of any such diurnal changes at NWT is particularly remarkable because at 40°3′N latitude day-nighttime changes in solar irradiance conditions at Summit.

## Are ($NO + NO_2$) soil emissions a source of snow nitrate?

Photochemical reaction and product studies have shown that NO and $NO_2$ in interstitial snowpack air can react with oxidants in the quasi-liquid layer or interstitial air to yield nitrite ($NO_2^-$) and nitrate ($NO_3^-$). Possible reaction pathways for production of these anions are (Jacobi and Hilker 2007):

$$NO + OH \rightarrow NO_2^- + H^+ \tag{R2}$$

$$NO_2 + OH \rightarrow NO_3^- + H^+ \tag{R3}$$

$$NO + NO_2 + H_2O \rightarrow 2\ NO_2^- + 2\ H^+ \tag{R4}$$

as well as hydrolysis of the $NO_2$ dimer,

$$2\ NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2\ H^+. \tag{R5}$$

Measurements in snow have provided evidence for the formation of OH on snow grains, which would provide the reactant for the NO and $NO_2$ conversion in R2 and R3. OH in snow is formed by photochemical mechanisms, with HOOH likely being the primary precursor, and most of the OH production (90%) occurring in the top 10 cm of the snowpack (Chu and Anastasio 2005; Anastasio et al. 2007; France et al. 2007). Since the NWT snowpack sustains elevated concentrations of ($NO + NO_2$), an interesting question warranting further investigation is whether these gases may potentially be a secondary source for snowpack $NO_2^-$ and $NO_3^-$ via R2–R5?

Nitrogen cycling in the NWT snowpack was further evaluated by Williams et al. (2009) using data from the Soddie site. They compared the volume–weighted mean (VWM) concentrations of nitrate for the winter and spring seasons at the NWT Saddle national atmospheric deposition program (NADP) site, which were 14 $\mu M\ l^{-1}$ in 2006 and 16.5 $\mu M\ l^{-1}$ in 2007; almost exactly the same as for the NADP site at the lower elevation C1 site. The nitrate concentrations in the seasonal snowpack were similar to or slightly lower than those recorded in wetfall for the same time period by nearby NADP stations, suggesting little loss or gain of nitrate from internal transformations or from dry deposition.

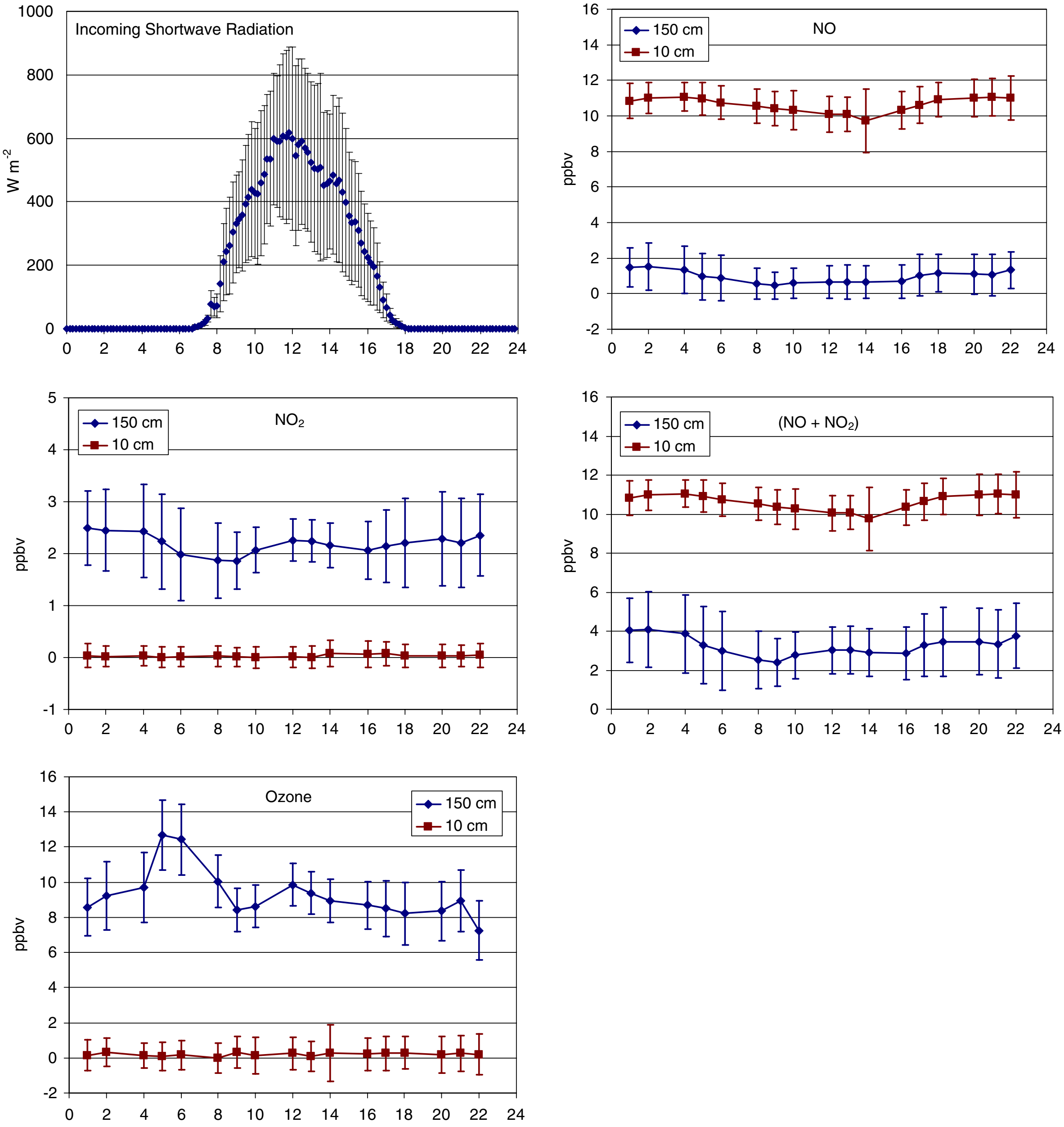

**Fig. 4** Mean diurnal cycle (*x*-axis scale in hours local time) for incoming shortwave radiation, NO, $NO_2$, ($NO + NO_2$), and ozone during DOY 47–57, 2007, at 10 cm and 150 m above the soil surface (covered by ~150 cm and 10 cm of snow, respectively) with error bars indicating the variability (standard deviation) of the 10 min-means for data that were included in these calculations

These findings are consistent with those reported by Williams et al. (1996) for an alpine location near the Saddle NADP site. This study also evaluated potential transformations of dissolved inorganic nitrate by adding isotopically-labeled ammonium and nitrate to separate snowpack plots, and reported no evidence for nitrification of ammonium or reduction of nitrate. These results show no evidence for snow nitrate being formed from photochemical production. In summary, these data do not point towards significant secondary formation of oxidized nitrogen gases in the NWT snow, nor do they support the theory of snow nitrate levels being altered by the soil ($NO + NO_2$) emissions.

## Fluxes of ($NO + NO_2$)

Given the demonstrated monotonic ($NO + NO_2$) concentration gradient in the snowpack, and the absence of any obvious diurnal (photochemical) dependency, it is reasonable to propose that at NWT subnival soil is the predominant source of ($NO + NO_2$). Neither the concentration profile data nor other chemical considerations enumerated above imply ($NO + NO_2$) sinks other than the emission flux from the snow surface. These assumptions allow application of Fick's Law for calculating ($NO + NO_2$) snowpack fluxes from the snowpack gradients. With our current understanding of ($NO + NO_2$) sources and chemistry within the snow, it is justified to assume that these results should then reasonably well represent the soil-snowpack and the snowpack-atmosphere ($NO + NO_2$) flux.

Seok et al. (2009), Liptzin et al. (2009), and Filippa et al. (2008) evaluate how Fick's Law diffusion theory can be applied to derive trace gas fluxes of ($NO + NO_2$), $CO_2$, and $N_2O$ from the snowpack concentration gradients of these gases. This method relies on the assumption of a constant flux through the gradient layer. As enumerated in detail by Seok et al. (2009) there are a number of limitations in using the diffusion method for this flux estimation, with the most important ones including snowpack density gradients, ice layers (which may lower the gas diffusivity in the snowpack), and snowpack ventilation from wind pumping. Nonetheless, this method is the most straightforward approach and was therefore applied and further evaluated for obtaining a first order gas flux estimate using our available gas gradient observations.

Using different combinations of gradient data from the 8-inlet snowpack tower allows for calculation of diffusion fluxes from 36 inlet pairs. The variability in these results offers an opportunity for evaluating the applicability, and associated errors in this approach. The ($NO + NO_2$) flux calculations in Fig. 5 show that results from different inlet combinations may vary at times by up to an order of magnitude, but that under most conditions individual gradient fluxes fall within a ±50% error window of the overall mean value. The mean ($NO + NO_2$) flux during the early snow-covered season, at 0.004–0.007 nmol $m^{-2}$ $s^{-1}$, gradually declined to lower values in late spring, but during the middle of the snow-covered season the ($NO + NO_2$) flux was relatively constant with typical values of 0.002–0.003 nmol $m^{-2}$ $s^{-1}$. This finding further illustrates that the increased NO mixing ratios that are seen at the bottom of the snowpack in the middle of the winter season (i.e., DOY 50–100, Fig. 3a) are not caused by major changes in the soil emission flux during that period but are primarily due to the overall slower NO transport to the surface through the deeper snowpack, which causes concentration levels to increase to higher levels.

Analysis of the 2004–2005, and 2005–2006 winter data, which resulted from measurements at only five sampling heights and during overall fewer days (due to a larger fraction of instrument downtime, leaving 41 and 136 available measurement days, respectively), gave median flux values (median of all calculated daily mean fluxes from all height intervals with standard deviation) of $0.012 \pm 0.010$ nmol $m^{-2}$ $s^{-1}$ for the 2004–2005, and of $0.004 \pm 0.008$ nmol $m^{-2}$ $s^{-1}$ for the 2005–2006 winters.

These flux analyses were based on the assumption that gas transport through the snowpack is determined solely by diffusion processes. As shown elsewhere (Seok et al. 2009), wind pumping will reduce the gas gradient and fluxes calculated by Fick's law. Using observations from a selected time window with steady-state snowpack depth, it was estimated that the diffusion calculation underestimates actual fluxes on average by ~50%. Please note that data in Fig. 5 were not corrected for this negative flux bias. Consequently, our best estimate for the average ($NO + NO_2$) flux through the NR snowpack during 2006–2007, corrected by the effect from wind pumping, would be higher, and be more on the order of 0.003–0.005 nmol $m^{-2}$ $s^{-1}$. Incorporating the somewhat higher flux results from the two previous seasons yields an average best ($NO + NO_2$) flux estimate on the order of 0.005–0.008 nmol $m^{-2}$ $s^{-1}$.

($NO + NO_2$) emissions from snow-covered areas have been reported by several other investigators. Three studies in polar regions, all using above-surface flux-gradient techniques, found average ($NO + NO_2$) fluxes of 0.002, 0.004, and 0.006 nmol $m^{-2}$ $s^{-1}$ in coastal Antarctica (Jones et al. 2000), at Summit (Peterson and Honrath 2001), and at South Pole (Davis et al. 2004),

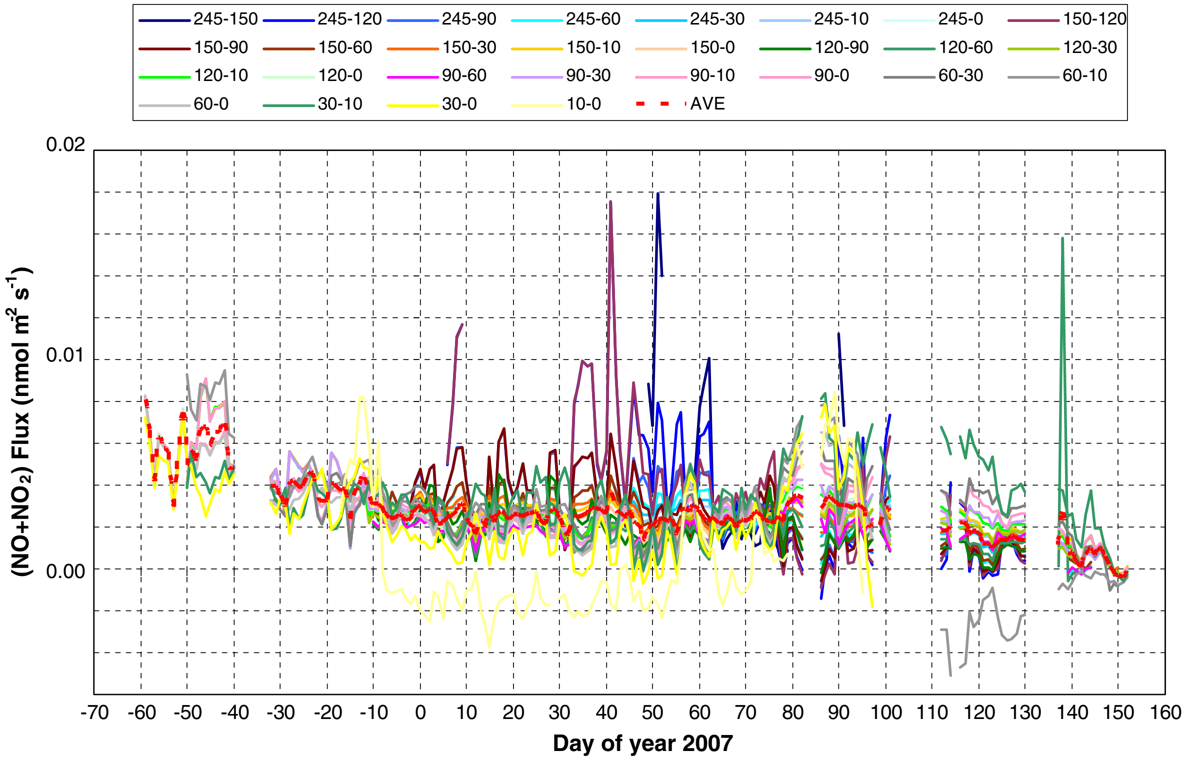

**Fig. 5** Fluxes of ($NO + NO_2$) calculated from each possible gradient interval using data from the eight sampling heights, as well as the mean of all data combined. The displayed data are the mean values of 18 individual daily flux determinations. Please note that these diffusion flux data were not corrected for the negative flux bias caused by snowpack ventilation from wind pumping, which was estimated to result in a ~50% underestimation of the actual snowpack gas fluxes (Seok et al. 2009)

respectively. These comparisons show that the ($NO + NO_2$) flux at NWT is on the same order of magnitude as observations over polar snow, which is surprising given the different formation routes enumerated in the preceding section.

Reported soil NO fluxes span more than three orders of magnitude (Ludwig et al. 2001). This body of research shows that NO soil flux depends on many different parameters, with soil type, vegetation cover, water content and temperature being the most important ones. The comparison with these previous studies shows that our measured NWT snow fluxes fall in the lower range (~20%) of the reported NO soil flux data in most of these other environments. The NWT ($NO + NO_2$) wintertime fluxes fall into a similar range as reported fluxes for swamps and marshes, tundra and temperate forests (Ludwig et al. 2001). Literature with wintertime ($NO + NO_2$) flux studies is too scarce for a worthwhile comparison with our data from NWT. Therefore, the NWT wintertime ($NO + NO_2$) flux data provide new insight into the magnitude of ($NO + NO_2$) fluxes from natural snow-covered landscapes, which previously have been neglected in assessing oxidized nitrogen cycling and/or as an oxidized nitrogen source for atmospheric chemistry. Filippa et al. (2008) provide a more in depth analysis of the soil nitrification and denitrification processes at NWT and the relative contribution of winter and summertime fluxes to the annual oxidized nitrogen exchange at this site.

## Relationship between ($NO + NO_2$) and ozone

In contrast to the nitrogen gases, the concentration of ozone was always reduced in the snow (Fig. 1, 2). The color contour plot of the full season record (Fig. 6) shows the consistency of this behavior; ozone levels in the NWT snowpack always declined sharply below the snow surface throughout the entire snow period. This behavior and the lack of a diurnal dependency contrasts with observations in polar snow, where ozone in the snowpack is correlated inversely with the incident solar irradiance cycle (Helmig et al. 2007a). The opposite behavior in absolute levels of ($NO + NO_2$) and ozone (i.e. lower [($NO + NO_2$)] and high [ozone] in the polar snowpack and high [($NO + NO_2$)] and low [ozone] at NWT), as well as their dependencies on radiation (in polar snow), suggests that ozone chemistry is linked to the snowpack ($NO + NO_2$) levels. As ozone does not react with frozen water itself, a number of ozone reaction mechanisms, involving primary snow contaminants as well as photochemically-formed radicals, have been proposed (see discussions in Bocquet et al. 2007; Helmig et al. 2007a). Our data support the hypothesis of a close linkage of ozone with ($NO + NO_2$) chemistry, where ozone may be destroyed in the upper layer of the snowpack by NO according to R1. This ozone depletion is reversible, because photolysis of $NO_2$.

$$NO_2 + hv \rightarrow NO + O(^3P), \qquad (R6)$$

is followed by

$$O(^3P) + O_2 \rightarrow O_3. \qquad (R7)$$

$NO \rightarrow NO_2$ recycling provided by reaction with $HO_2$ and $RO_2$ radicals, followed by R6–R7, constitutes the main ozone production mechanism in the troposphere. Radiation at $\lambda < 420$ nm is required for R6; consequently, in the absence of light, R1 will be inhibited once all of the NO has been converted to $NO_2$. Solar radiation is attenuated exponentially with increasing snowpack depth, where the e-folding depth (depth at which radiation drops to 1/e of levels above the surface) is used to describe this behavior. The e-folding depth depends on multiple parameters, including solar zenith angle, snow chemical and physical properties, and the particular wavelength. For the UV-B to visible wavelength range where $NO_2$ photolysis takes place, e-folding depths are commonly 5–25 cm (Grannas et al. 2007, and references therein). These findings imply that in the snowpack regeneration of NO via R6 will be much less than above the snow surface. Also, the photolysis of $NO_2$, i.e. $J_{NO_2}$, will be very low deep inside the snowpack, and from there will steadily increase towards the snow surface.

Data for NO, $NO_2$, and ozone (Fig. 1,2, 3), and the fast rate of R1, suggest that R1 is a mechanism for ozone destruction in the snowpack, and that this reaction may constitute a chemical ozone sink that contributes to the deposition of ozone to the snow surface. Hence it is possible to estimate a lower threshold for the ozone deposition flux from the NO flux and the conversion ratio seen in the upper snowpack. Taking the mean NO flux of 0.005–0.008 nmol $m^{-2}$ $s^{-1}$ , assuming that all $NO - NO_2$

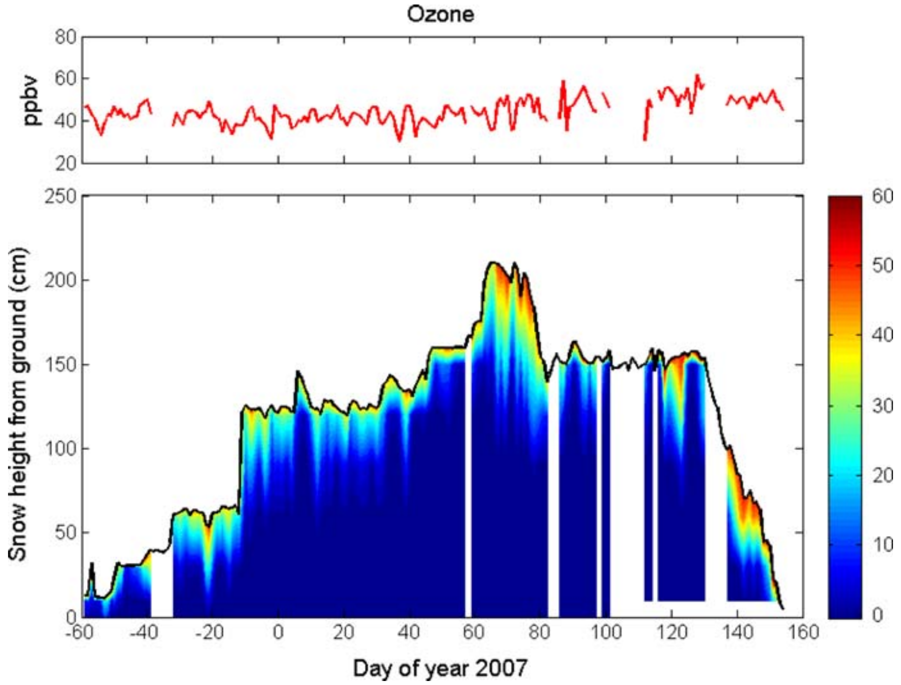

**Fig. 6** Color contour plot of ozone using same criteria as in Fig. 3, with the color bar showing the ozone mixing ratio scale in ppbv. The top part of the figure shows the time series of ozone from the 245-cm inlet above the snow surface

conversion is from reaction with ozone, and applying the maximum value of the $NO_2/(NO + NO_2)$ ratio in the snowpack of 0.8, we infer an ozone flux of 0.004–0.006 nmol $m^{-2}$ $s^{-1}$. At 50 ppbv of ozone and typical pressure and temperature conditions at NWT, this would correspond to an ozone deposition velocity in the range of 0.0002–0.0004 cm $s^{-1}$. This value is very low ($\sim$less than a few %) compared to most previous reports of ozone deposition rates from seasonal snow (Helmig et al. 2007b). Consequently, titration of ozone by NO can only be a minor contributing ozone sink; therefore other chemical and physical processes must be determining factors in the ozone destruction in the snow. It is important to note that this ozone deposition velocity will represent only the ozone downward flux, right at the surface. Several other recent studies (Crawford et al. 2001; Jones and Wolff 2003; Helmig et al. 2008) have pointed out that ozone production can occur in the atmospheric layers right above the snow surface, and that the degree of ozone production is dependent on the $(NO + NO_2)$ flux out of the snow, solar irradiance, and atmospheric stability above the snow. Consequently, the net ozone flux at a given height will depend on the controls and magnitude of these contributing ozone source and sink processes (Helmig et al. 2009).

## Conclusions

The snowpack at Niwot Ridge is ‘soaked’ with nitrogen oxides, with concentrations being one to two orders of magnitude higher than in the ambient air above the snow. These $(NO + NO_2)$ snowpack concentrations are $\sim$10–25 times greater than the available observations in polar snow. Production from biogeochemical soil nitrification processes that occur in moist, relatively warm, constant temperature soil below the snowpack are the most obvious source for the elevated $[(NO + NO_2)]$. Given the importance of $(NO + NO_2)$ in chemical oxidation processes, it is likely that elevated $(NO + NO_2)$ influences chemical reaction rates and cycles. Consideration of $(NO + NO_2)$ reaction pathways in snow suggest the potential for production of snow nitrite and nitrate from enhanced gas phase $(NO + NO_2)$ in the snowpack air, however, there is no direct evidence in support of this reaction route in these data.

The changes in $NO/NO_2$ partitioning over the vertical scale of the snowpack show that snowpack chemistry has a strong gradient and that $NO - NO_2$ conversion is only occuring in the layer just below the snow surface. The contrasting profiles of ozone and $(NO + NO_2)$ suggest that ozone either plays a role in determining the $NO - NO_2$ conversion near the snowpack surface, or that both $NO \rightarrow NO_2$ conversion and ozone destruction are influenced by similar processes.

These are the first quantitative wintertime $(NO + NO_2)$ flux determinations from an all-winter snow-covered site. Seasonally averaged $(NO + NO_2)$ fluxes of 0.005–0.008 nmol $m^{-2}$ $s^{-1}$, determined by applying diffusion law principles, are of the same order of magnitude as NO fluxes seen from polar sites, although $(NO + NO_2)$ fluxes in these two environments result form different sources and display much different behavior. It is uncertain how representative the NWT findings are for the highly variable conditions of snow cover depth, length of the snow-covered season, and properties of the subnival substrate. In particular, the biogeochemical soil conditions are expected to have a determining role in the wintertime $(NO + NO_2)$ production. Consequently, care should be exercised in extrapolating the NWT data to other snow-covered environments. These findings call for comparison studies at other snow-covered sites and process-oriented research in order to develop a better conceptual understanding of biogeochemical, physical, and chemical reaction processes in the subnival soil and within the snowpack.

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