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Authors: Bocquet, Florence, Helmig, Detlev, and Oltmans, Samuel J.

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Ozone in Interstitial Air of the Mid-Latitude, Seasonal Snowpack at Niwot Ridge, Colorado

*Florence Bocquet**
Detlev Helmig‡ and*
Samuel J. Oltmans†

*Institute of Arctic and Alpine Research, University of Colorado, UCB 450, Boulder, CO 80309, U.S.A.
†ESRL Global Monitoring Division, National Oceanic and Atmospheric Administration (NOAA), 325 Broadway, Boulder, CO 80305, U.S.A.
‡Corresponding author.
Detlev.Helmig@colorado.edu

Abstract

Ozone in interstitial air was studied in the seasonal, mid-latitude snowpack at a subalpine forest site at Niwot Ridge, Colorado, from January to June 2004. Sampling techniques were developed for continuous, vertical gradient measurements of ozone and temperature at four depths in the snowpack. During this time period, ozone in ambient air ranged from 15 to 80 ppbv, while in the snowpack ozone mixing ratios generally were below 5 ppbv, showed little variability, and decreased to less than 10% of ambient air levels within the first 10–20 cm below the surface. This ozone gradient (ambient air-snowpack air) appeared to be independent of solar radiation cycles. These findings are in contrast to similar studies in the polar snowpack, where a much deeper penetration of ozone into the snowpack and strong dependencies of the ozone gradient on incoming solar radiation levels has been reported. These observations imply that ozone levels in the seasonal, mid-latitude snowpack are determined by different processes, and overall are lower than in the year-round snowpack. A new question that needs to be addressed is to what degree these contrasting findings are caused by differences in the physical properties of these snowpacks (which will affect gas exchange processes), their chemical composition, and by the influence of the substrate below the snow and soil-snowpack-atmosphere gas exchange processes.

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Introduction

Seasonal snow cover, present over large areas of mid-latitude regions, is an important climate change variable that influences the energy and moisture budgets of the earth. In recent years, numerous research studies have also paid attention to the chemical interactions between air and snow-ice. Most of this research has been conducted in the polar regions, including sites with year-round snow cover in Greenland and Antarctica. This research has provided increasing evidence that photochemical production of chemical species, such as oxidized nitrogen gases, organic trace gases, and other oxidants in the snowpack, provides sufficient reactants for a rigorous chemical activity to take place in the interstitial air (e.g., Barrie and Platt, 1997; Sumner and Shepson, 1999; Zhou et al., 2001; Domine and Shepson, 2002; Shepson et al., 2003; Jacobi et al., 2004).

Measurements made at Summit, Greenland, and South Pole, Antarctica, have demonstrated that interstitial air levels of nitrogen oxides (NOx) are greatly altered by photochemical processes (Honrath et al., 1999). Production of NOx in snow was also observed in laboratory experiments (Honrath et al., 2000b; Cotter et al., 2003). This NOx formation appears to be driven by incident radiation and to be the result of photolysis of nitrate in the snow (Jones et al., 1999, 2000; Honrath et al., 2000a, 2000b; Dibb et al., 2002; Beine et al., 2002; Cotter et al., 2003). Positive fluxes of NOx coming out of the snow were measured at three polar sites: Summit (Honrath et al., 2002), Neumeyer, Antarctica (Jones et al., 2001), and South Pole (Oncley et al., 2004). The efflux of NOx can lead to substantial enrichment of nitric oxide (NO) in the lower atmosphere (Davis et al., 2001), in particular under regimes of suppressed atmospheric mixing (i.e., stable boundary layer conditions), and result in photochemical ozone production in the polar boundary layer (Crawford et al., 2001; Jones and Wolff, 2003; Chen et al., 2004).

Several recent studies have investigated the chemistry of ozone and its dependence on the nitrogen photochemistry in polar snowpack at Summit and South Pole. Peterson and Honrath (2001) were the first ones to report that ozone, at 30 cm in the snowpack, was still present at ~30–60% of the levels observed above the surface. Furthermore, over the two days of measurements that were presented, ozone in interstitial air displayed a distinct diurnal cycle with a ~10 ppbv amplitude, with ozone minima occurring shortly after solar noon and maxima shortly after midnight. The ozone diurnal signatures were anti-correlated with NO in the snowpack. A shading experiment further confirmed that ozone destruction was driven by solar radiation and coincided with photochemical NO formation (Peterson and Honrath, 2001). Ozone depletion in the snowpack was also seen by Albert et al. (2002) at Alert, Canada, though these springtime measurements resulted from somewhat different conditions. The snowpack is typically less than one meter deep and bromine-catalyzed photochemistry is a determining ozone-depletion mechanism at Alert. Ozone mixing ratios measured at 2, 5, and 10 cm below the snow surface were approximately 90, 70, and 60%, respectively, of ambient ozone during April (Albert et al., 2002) when incoming solar radiation levels were 250–500 W m^{-2} (Bottenheim et al., 2002). It appears that the ozone loss in the Alert snowpack was higher compared to Summit (Peterson and Honrath, 2001). This research was extended by several months with measurements of ozone in interstitial air at Summit (Helmig et al., 2007a) and South Pole (Helmig, unpublished results). These studies provided further evidence that, in the polar snowpack, ozone is present at significant levels (e.g., up to 90% of ambient

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levels were found at 1 m depth) during times with low levels (< 100 W m^{-2}) of incoming radiation. In contrast, during summertime, noon conditions (> 500 W m^{-2}), up to 90% of ozone was lost in the irradiated snowpack. The amplitude of this diurnal signal was dependent on wind pumping through the snowpack (e.g., during low wind conditions higher ambient-snowpack ozone gradients were found than during high winds).

The mechanism for this photochemically induced ozone destruction is not fully understood at this time. Peterson and Honrath (2001) suggested that ozone is destroyed by an unidentified, photochemically produced reactant. Reaction with NO at the observed levels could account for a mere 6% of the ozone loss rate. These authors suggested alternative reaction pathways, such as a catalytic bromine reaction cycle (e.g., triggered by photochemically formed bromine radicals).

Ozone dry deposition studies over snow-covered landscapes were recently reviewed by Helmig et al. (2007b). Reported data span a remarkably wide range of ozone deposition velocities (v_{dO3}). Overall, reported values range from $\sim -3 < v_{dO3} < 2$ cm s^{-1}, though most are within $\sim 0 < v_{dO3} < 0.2$ cm s^{-1}, which reflects a relatively small uptake rate compared to other types of landscapes (Padro, 1996; Wesely and Hicks, 2000). Interestingly, several studies report positive fluxes, indicating the release of ozone from these snow-covered environments (Galbally and Allison, 1972; Zeller and Hehn, 1994, 1996; Zeller, 2000). The tower gradient flux measurements by Zeller and Hehn (1994, 1996) were conducted at a coniferous forest site in the Snowy Range of the Medicine Bow National Forest, Wyoming, which appears to have similarities to our site (see below). Upward fluxes of 0.5 μg m^{-2} s^{-1} were routinely measured during the winter 1992 experiment. In a follow-up study, Zeller and Hehn (1995) found that "the upward (ozone) fluxes only occurred when snow completely covered the forest understory" but that ozone fluxes were downward in the absence of snow cover on the forest understory. Zeller and Hehn (1996) hypothesized that ozone may be temporarily stored in the snow base. Similarly, Galbally and Allison (1972) reported upward ozone fluxes of 1.6 μg m^{-2} s^{-1} over snow at Mount Baker in Australia. These positive ozone fluxes over seasonal snowpack in alpine environments are rather remarkable observations. Ozone is generally destroyed on surfaces, resulting in negative, downward ozone fluxes (Wesely and Hicks, 2000). These aforementioned findings differ significantly from this widely accepted principle. As already mentioned above, subsequent studies with ozone measurements in interstitial air have found lower ozone mixing ratios in the snowpack than above the surface. These positive, ambient air-snowpack ozone gradients imply a gradient flux from the atmospheric surface layer into the snowpack and contradict the hypothesis of ozone storage with subsequent release and upwards fluxes out of the snow.

This research addressed several questions that have been raised in the literature. We examined experimental requirements for conducting automated and continuous snowpack gradient gas measurements in a continental, seasonal snowpack. The topography and inhomogeneous footprint of high altitude mountain sites are generally not amenable to direct, tower flux measurements (e.g., by tower gradient or eddy covariance methods). Therefore, our experiments examined whether snowpack measurements could serve as a tool for investigating if and when the mid-latitude snowpack is a net source or sink for ozone. Furthermore, for comparison with equivalent measurements from high latitude, polar snowpacks, the four months of observations obtained from our subalpine, Rocky Mountain forest site allow a further evaluation of processes that are determining snowpack-ozone gas exchange processes.

Experimental Methods

This experiment was performed at Niwot Ridge (NR, 40°03′N, 105°35′W) in the Front Range of the northern Colorado Rockies (Fig. 1). This area is administrated cooperatively by the U.S. Forest Service and the University of Colorado at Boulder. The Soddie site is at treeline (3340 m a.s.l.) surrounded by subalpine tundra meadows with patches of grass and trees, including Englemann spruce and subalpine fir. The sampling location was within a clearing approximately 10–40 m away from the surrounding trees and gently sloping (10°) to the south.

The snowpack sampling manifold was installed during November 2003, prior to any significant snow accumulation. Subsequently, snow accumulated naturally and gradually covered the sampling inlets. The early installation was expected to minimize any potential disturbance to the snowpack (McDowell et al., 2000). Ozone gradient measurements were performed from 28 January 2004 (day of year [DOY] 28) to 8 June 2004 (DOY 160). Figure 2 presents the sampling manifold for measuring snowpack ozone and temperature at five levels. The gas analyzer and datalogger were housed in an underground laboratory located ~10 m away from the sampling tower. Air was drawn intermittently from these sampling ports through 18-m long, 6.4-mm outside diameter, 4.0-mm inside diameter Teflon sampling lines (perfluoroalkyoxy-polymer [PFA] tubing). The sampling lines had dual inlets spaced 100 cm apart. Each inlet was equipped with a glass fiber Acrodisc syringe filter (1 μm pore size, polypropylene housing, product number 4523, VWR International, San Dimas, California) to prevent the sampling of particles and ice crystals into the sampling tubing. Prior to installation, all Teflon tubing and inlet filters were conditioned for 12 hours in a 2 L min^{-1} flow of 250 ppbv ozone. All filters and sampling lines were tested prior to installation, and ozone losses in all components of the sampling system were found to be $< 2\%$. The five sampling lines were bundled together and placed inside pipe foam insulation from ~1.5 m distance from the tower base to near the solenoid valve sampling manifold. This section was heated with water pipe heating tape to ~4°C to minimize water accumulation and potential water freeze-out in the sampling lines. The paired inlets were mounted at ground level, 30, 60, 90, and 245 cm above ground. The latter inlet was expected to remain above the snow surface throughout the winter.

Unfortunately, there is no technique available that would allow measuring ozone without drawing a sample aliquot from within the snowpack into a monitor. An important objective was to minimize the artificial airflow through the snowpack that is induced by the air sampling procedure. Second, air had to be sampled from five locations using one available ozone monitor. Therefore, air was pulled sequentially through the five sampling lines at 1.2 L min^{-1} by the ozone-monitor sampling pump. The flow through each of the inlets was maintained for 12 min, after which the next lower inlet line was opened (Teflon solenoid valve part #C-01367-70, Cole Palmer, Vernon Hills, Illinois). This cycle resulted in a 12 min sampling period per hour of each height (after which 48 min were allowed for air around that inlet to re-equilibrate) and an effective sampling of ~14 L of air per hour from each height, respectively, ~7 L hr^{-1} for each of the dual inlets. This collected sample is expected to represent the composition of the air space surrounding the inlet, with likely a proportionally higher amount of air pulled from the air space above it. Inlets (Fig. 2) were attached to horizontal cross arms. This arrangement allowed the snowpack right above the inlet to remain undisturbed and compact, avoiding artificial, vertically extending air spaces.

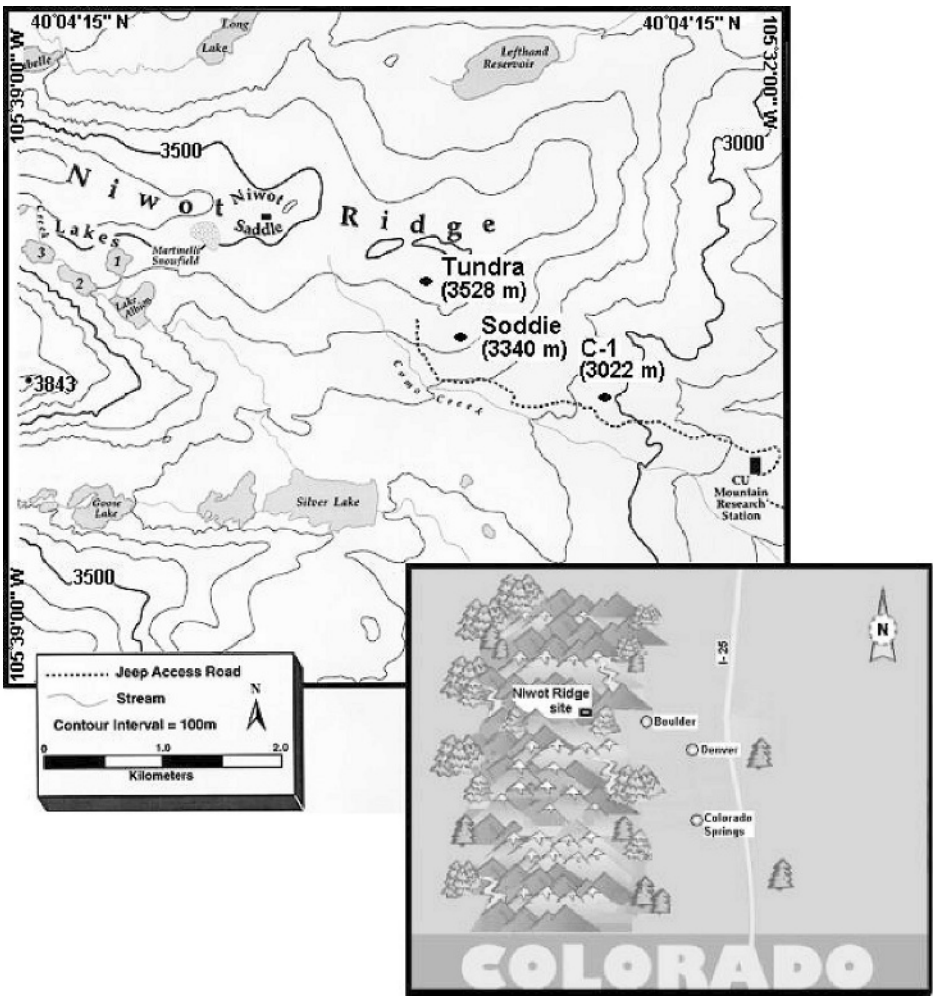

FIGURE 1. Map of the state of Colorado (bottom right) with Niwot Ridge, located ~ 40 km northwest of the Denver-Boulder metropolitan area and ~ 3 km east of the Continental Divide. The map of the Niwot Ridge long-term ecological research (LTER) study area (upper left) shows the location of the three ozone monitoring sites. The snowpack sampling experiment was performed at the Soddie site, which is at 3340 m a.s.l. Ozone data from continuous monitoring at the C-1 site (3022 m a.s.l.) and the Tundra lab site (3528 m a.s.l.) were used for comparison with the Soddie data (Niwot Ridge topographic map by Tom Davinroy, INSTAAR, University of Colorado at Boulder).

Ozone was measured with a UV photometric monitor (Thermo Electron Corporation (TEI), Franklin, Massachusetts, Model 49). The detection limit, accuracy, and precision of 1-min data from these measurements are on the order of 1 ppbv. The analog signal was recorded with a datalogger (Campbell Scientific, Logan, Utah, Model CR10X). The ozone signal was subsequently corrected for the pressure and temperature of the optical cell. A pressure transducer was teed into the adsorption cell flow path, and a thermocouple measured the cell temperature. The pressure signal was also used to monitor possible flow restrictions (from water freeze-out) in the sampling lines and/or inlets. Pressures recorded from all five inlet lines were usually within ± 5%. The

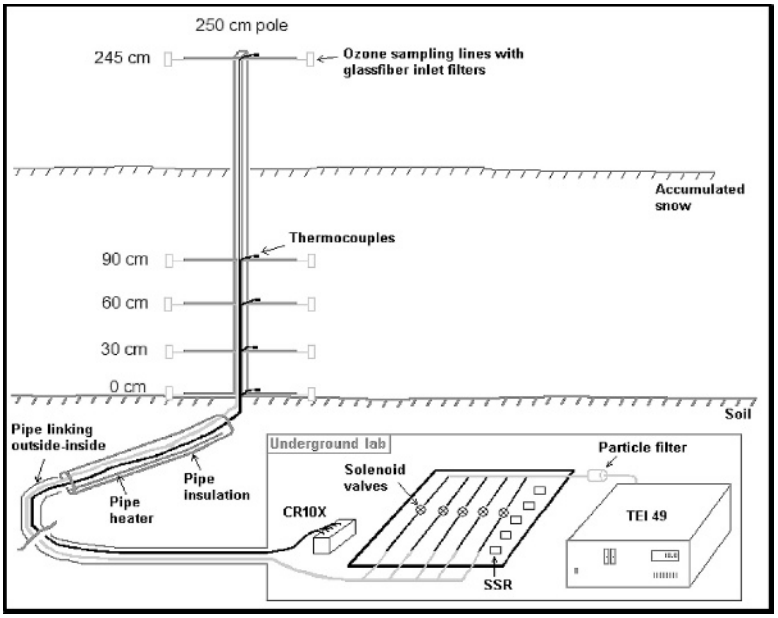

FIGURE 2. Manifold and instrumentation for snowpack sampling. The ozone sampling lines and thermocouples are fed through a conduit pipe to an underground laboratory space. The sampling manifold was installed during November 2003 before any significant snow accumulation had occurred. Temperatures, pressure, and ozone were recorded with a datalogger. This datalogger also controlled the switching of solid state relays (SSR) for activating the solenoid valves in the sampling lines.

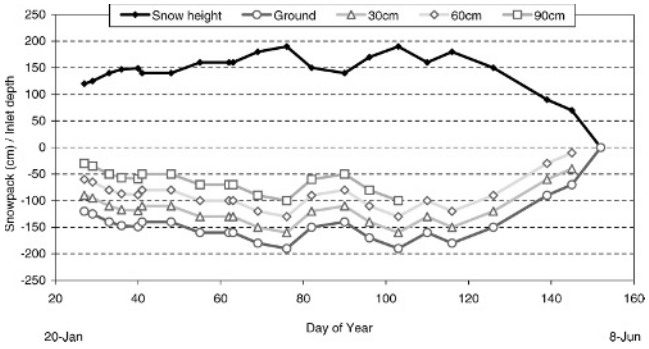

FIGURE 3. Snowpack height and sampling inlet depths at corresponding snow height during the study period (2004 year calendar day). For the 90 cm inlets, the last ~ 50 days of the study period were removed because the cross arm supporting the inlets broke at some point during the experiment and both pairs of 90 cm inlets were found at a height of ~ 40–50 cm after the snowmelt.

ozone monitor was inter-compared before and after the field experiment against a reference laboratory instrument (TEI 49C), and agreement was found to be within ± 1 ppbv.

Snowpack and ambient temperatures were recorded with thermocouples. The last 1 m of the thermocouple wires was covered with white shrink tubing to minimize radiative heating artifacts. Other meteorological measurements at the site provided data of air temperature and humidity, wind speed and direction, and incoming shortwave radiation. Data were collected every second, averaged and stored at 2 min intervals, and transmitted every two hours via a radio connection. Snowpack depth was measured with a probe and recorded during weekly site visits. A total of 22 snow depth measurements were obtained during the study period.

Results and Discussion

SEASONAL SNOWPACK DEVELOPMENT

The winter-spring 2004 NR Soddie snowpack depth record is shown in Figure 3. When the ozone measurements began in January, the snow had accumulated to a depth of ~120 cm. A snowpack depth of 150 cm was maintained continuously between February and early May, after which the snow began to melt rapidly. All snow had melted by 1 June (DOY 153). From 28 January (DOY 28) to 4 May 2004 (DOY 128), all sampling inlets, from the ground level to 90 cm, were continuously buried in the snow.

SNOWPACK TEMPERATURES

Figure 4 shows the temperatures recorded at the four sampling heights in the snowpack. We investigated possible artifacts in these measurements from radiative heating of the thermocouple wires. The record from the thermocouple wire at the 245-cm inlet height was compared with temperature measurements from a Campbell Scientific CS500 temperature/humidity probe with radiation shield model 41303 (Fig. 5) on the nearby (~15 m) met tower. Agreement between these two measurements was generally within ± 2 °C until early June when the thermocouple measurements yielded increasingly higher values likely from an increasing radiation error. Consequently, we conclude that the snowpack thermocouple temperature measurements during the January–May period were within a 1–2 °C error range. However, the error is most likely lower because of the reduced radiation in the snowpack.

The snowpack temperatures remained remarkably high with very little diurnal and seasonal changes throughout the whole winter/spring season. Even with ambient air temperatures

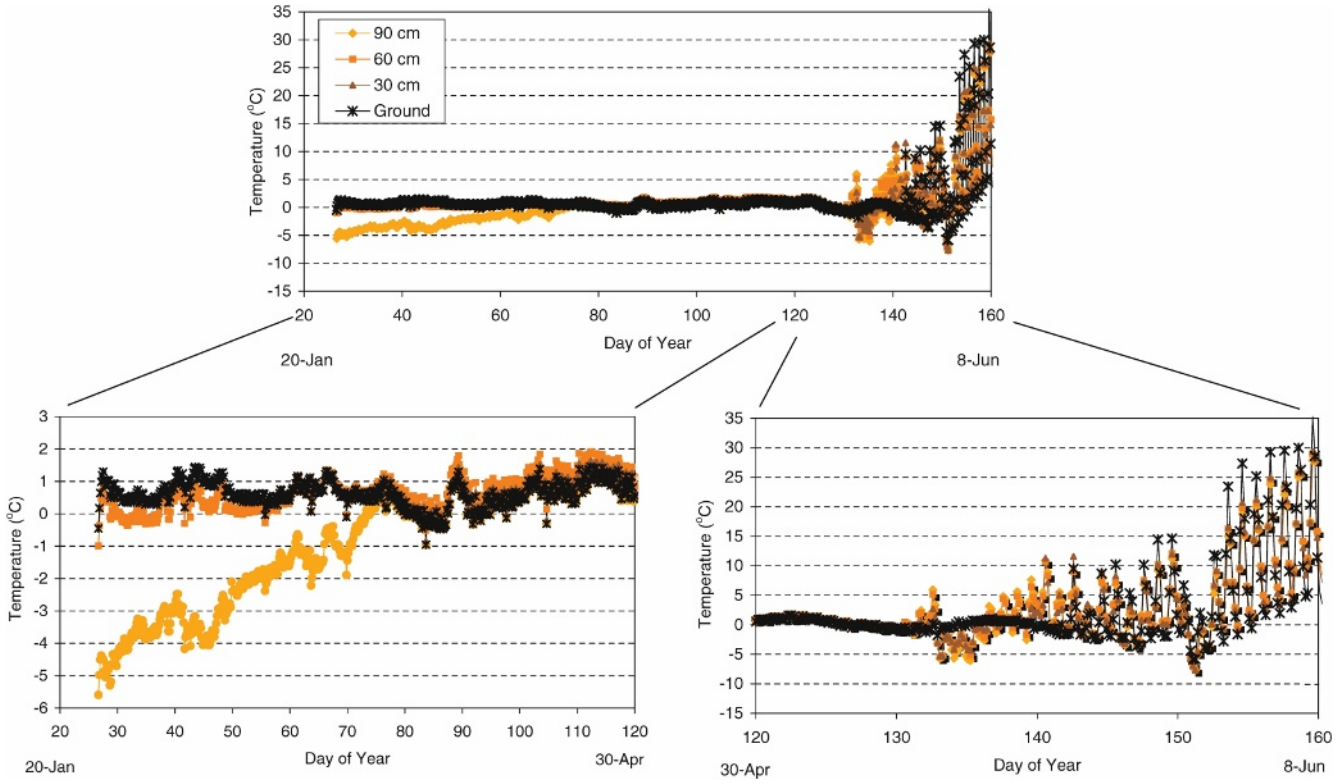

FIGURE 4. (A) Snowpack temperatures at ground level, 30, 60, and 90 cm above ground for the entire experiment, (B) enlargement of the period before, and (C) enlargement of the period during snowmelt. (Note that this figure is illustrated in color in the online version of this manuscript.)

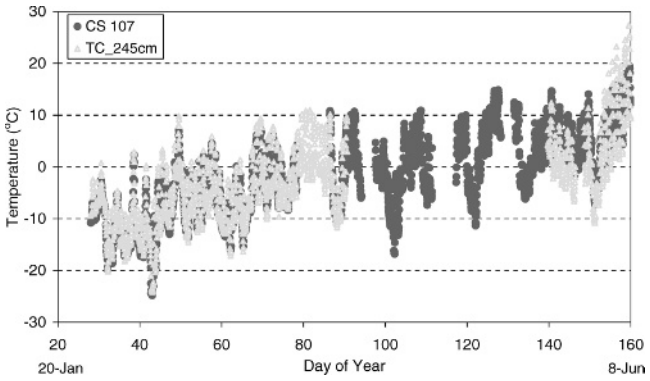

FIGURE 5. Comparison of temperature data from the thermocouple wire on the sampling tower (at 245 cm, remaining above the snowpack all the time) with the concurrent measurements from a nearby (~ 15 m) temperature/humidity probe (Campbell Scientific CS500 with radiation shield) on a met tower during 2004.

occasionally dropping to < -20°C (Fig. 5), snowpack temperatures remained close to the freezing point. The 90 cm snowpack temperature gradually warmed up with increasing snow accumulation as the season progressed. Clearly, the snowpack acted as an effective insulation between the colder air and the warmer, vegetated soil. Diurnal ambient temperature fluctuations were very much suppressed in the upper snowpack and completely absent at depths in excess of ~50 cm. As soon as the thermocouples were no longer covered by snow, temperatures displayed a distinct diurnal cycle. The temperature measurements were therefore a valuable indicator for gauging the time when inlet pairs were covered by snow or exposed to ambient air.

EVALUATION OF OZONE MEASUREMENT TECHNIQUE AND OZONE IN AMBIENT AIR AT NIWOT RIDGE

It is desirable to analyze interstitial gas concentrations without drawing any sample air out of the snowpack, as the induced sampling flow will disturb the natural snowpack ventilation interstitial air composition. Experiments and modeling studies (Albert et al., 2002) have shown that air sampled from a firn air inlet will over-proportionally pull ambient air downwards through the snow from right above the inlet. Our experiment attempted to determine ozone concentrations and gradients in the snowpack air from the smallest possible air sample.

Typically, ozone monitors operate by continuously sampling air from one sampling inlet, which assures a continuous purging and equilibration of the inlet and sampling tubing. The rotating, sequential sampling that was applied here raised the question of possible biases resulting from this intermittent line purge and sample delivery to the monitor. A three-hour time series with three cycles of ozone measurements from the five inlets is shown in Figure 6. These data show that equilibrium and stable ozone readings were achieved within ~2 min after switching to a new inlet height. From these data we concluded that re-equilibration times were short on the time scale of the data acquisition rate. Also, little change in ozone concentration was seen after the first 1–2 minutes, which implies that over the 12 min sampling period the sample taken remained representative of the equilibrated air space surrounding the inlet. A gradual change in concentration, as would be expected when air withdrawn from the inlet area is increasingly replenished with air from above (which would be expected to have a different composition), was not observed. For representation of ozone time series from individual inlet heights (Figs. 7 and 8), the data from the first two minutes of each measurement interval was discarded because the first sample point was suspected to have readings from the transition period between two inlets.

For further quality control, the data from the highest inlet, which remained above the snow surface at all times, was compared with the hourly data from continuous ozone measurements (TEI model 49C) at the C-1 (coniferous forest; 3022 m a.s.l.) and Tundra lab (alpine tundra; 3528 m a.s.l.) sites (Fig. 1). Ozone in ambient air showed a high variability during the study period, ranging from minimum values of 15 ppbv to a maximum of 81 ppbv (Fig. 7). The 25-percentile/median/75-percentile values were 47.3/51.5/55.4 ppbv. Even though these sites are spread over a ~500 m elevation difference, good agreement in ozone levels was found (Fig. 7). During winter and early spring, hourly and diurnal ozone at the three sites are similar and at most times agree within the accuracy range of the measurements. The deviation between the three data sets increased slightly as summer approached. This is possibly the result of a stronger vertical ozone altitude gradient as the snow melts and the lower sites become subject to greater ozone deposition loss to exposed soils and vegetation. As detailed above, the Soddie data are 12 min of measurements during every hour, while at the two other locations air is sampled continuously. The agreement between these measurements confirms that the data from the intermittent and reduced volume sampling with the snowpack tower manifold results in a good representation of actual ozone concentrations.

OZONE TRANSPORT TO NIWOT RIDGE

These ozone measurements also provide some insight into ozone transport to the Soddie site. During several occasions, typically lasting 3–6 hours, the data from the three sites show a somewhat higher disagreement (Figs. 7B and 7C). These sites, located on the east slope of the Colorado Rocky Mountains, are

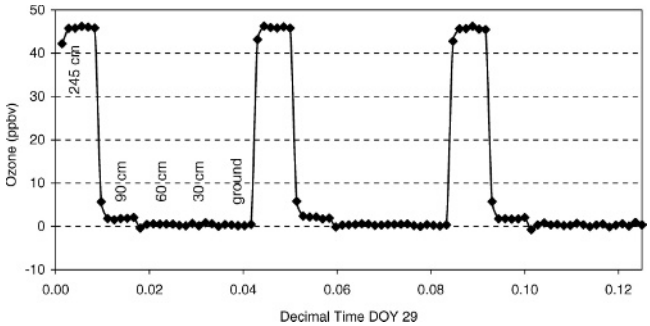

FIGURE 6. Three cycles of raw data from ozone measurements taken from the five inlet levels early in the experiment (CD 29). Each inlet samples air for 12 min; data are averaged over 2 min intervals yielding six data points for each measurement height.

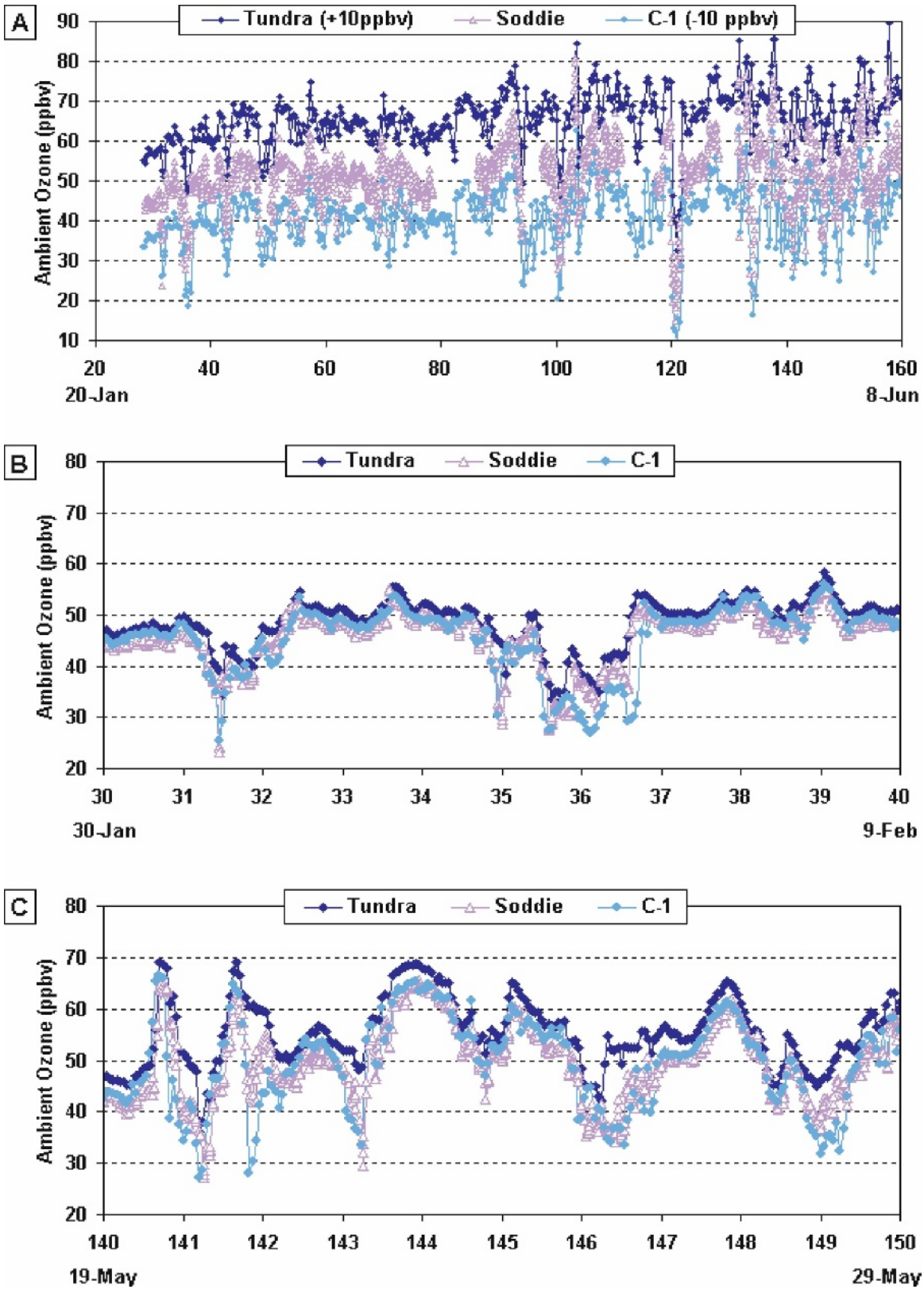

FIGURE 7. (A) Comparison of ambient ozone measurements from the C-1, Soddie, and Tundra lab sites for the entire period, (B) for 10 days during the early phase, and (C) for 10 days during the late phase of the year 2004 experiment. Note that in panel A, for better readability, 10 ppbv were added to the Tundra data series, 10 ppbv were subtracted from the C-1 data, and hourly data were averaged to 6 hr means. (Note that this figure is illustrated in color in the online version of this manuscript.)

subject to upslope/downslope flow events that will impact air composition, in particular ozone. Previously, Losleben and Pepin (2000) have shown that during winter, all NR sites remain predominantly well above the mixed boundary layer height of the Boulder/Denver area, and upslope events are too weak to reach the Mountain Research Station (2850 m a.s.l.). As the year progresses, buoyancy-driven upslope transport becomes more prominent and, particularly during the afternoon, polluted air

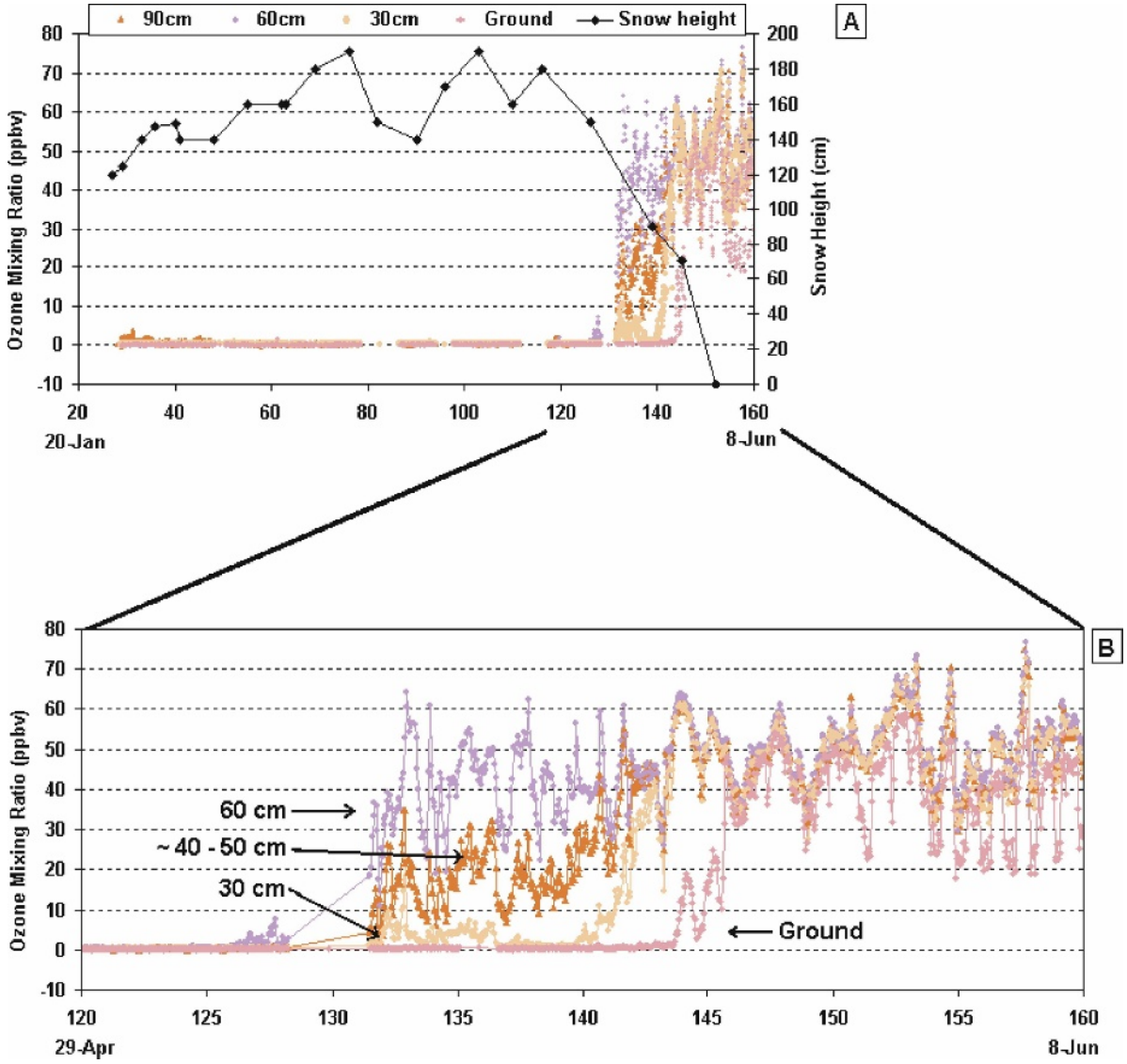

FIGURE 8. Ozone mixing ratio time series for the four lower pairs of inlets (ground, 30, 60, and 90 cm). Four minutes of data from the transition periods (switching between inlets, Fig. 6) were removed and the remaining 8 min data were averaged and plotted as individual data points. (A) Shows the entire study period. During CD 28 to 128, snow covered all pairs of inlets. During that period, ozone mixing ratios lower than ~ 1 ppbv were measured. (B) Shows the last 40 days of the experiment. From CD 127 to 160, the 60 cm inlet pair was the first exposed to ambient air. The 90 cm inlets had collapsed within the snowpack and were found below the 60 cm inlets (at ~ 40–50 cm). As the snow melted, the next lower inlet was exposed to ambient air (i.e., 90 cm, 30 cm, and, finally, ground pair of inlets). (Note that these figures are illustrated in color in the online version of this manuscript.)

with elevated levels of NOx and photochemically produced ozone is more frequently encountered at the station (Parrish et al., 1990). Upslope events have been found to increase in frequency towards the summer (i.e., the percentage occurrence of upslope hours at the Tundra lab station was found to rise from ~3% in January to ~12% during May–June) (Losleben and Pepin, 2000). The comparison of the three ozone data series show both upslope and downslope events during which air with elevated ozone was transported to the Soddie. During several occasions (e.g., DOY 36, DOY 146), it appears that downslope air with elevated ozone was first encountered at the higher Tundra site and subsequently, 2–6 hours later, at the lower elevation Soddie and C-1 sites. In contrast, the increases in ozone on DOY 140, 141, and 143 were first encountered, and typically were relatively larger, at the lower elevation stations. This analysis is further supported by wind direction data that show westerly winds during the downslope events and winds from ESE during the identified upslope occurrences.

OZONE IN THE NIWOT RIDGE SNOWPACK

The nighttime data from DOY 29 (Fig. 6) show the steep ozone gradients between ambient air and the snowpack. Only ~3 ppbv of ozone were recorded at the 90 cm inlets, which were covered by ~30 cm of snow at this time. Ozone time series showing the measurements from all snowpack inlet heights are presented in Figure 8. Gaps within the ozone data represent a total of about 20 days, which resulted from the loss of the radio connection to the site. While the sampling inlets were covered with snow, ozone levels were generally low (e.g., < 3 ppbv) and frequently below the detection limit of the ozone monitor (~1 ppbv for 1 min data). From DOY 128 until the end of the

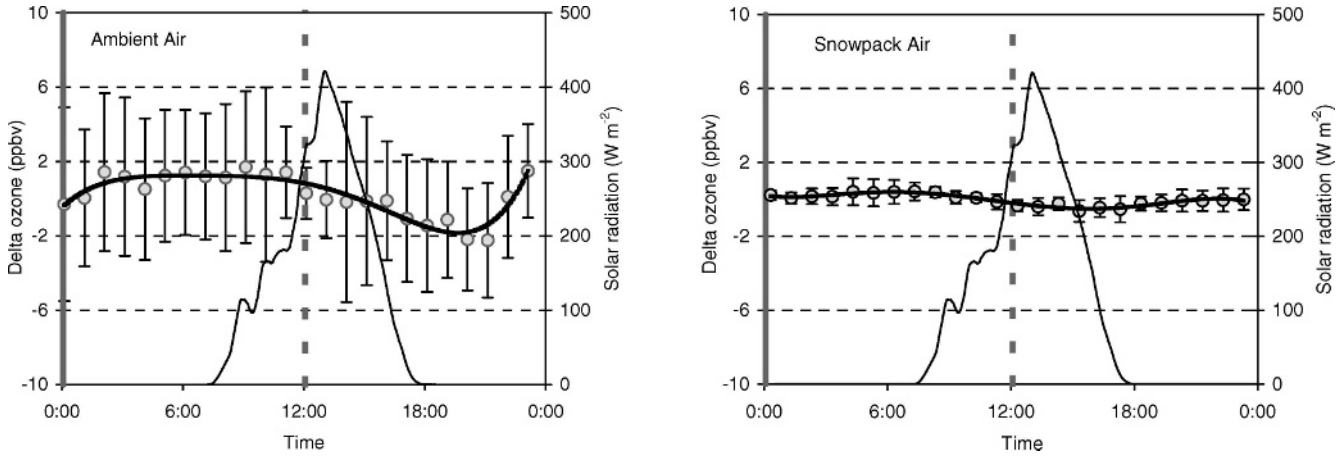

FIGURE 9. Mean diurnal change for ambient air ozone (left graph) and ozone in the snowpack (right graph) during the period DOY 30–35 plotted against local time. Error bars represent the standard deviation of the mean, hourly data points for the six days. A fifth-order polynomial fit curve was calculated through the means. Solar noon and midnight are indicated by the vertical staggered and solid line, respectively. The mean diurnal cycle of incoming solar radiation during these six days is shown by the dark gray data series. The ozone data are presented in the same format as results for Summit (see Fig. 4, Helmig et al., 2007a).

study period, as the snow melted, inlets were one by one uncovered of snow, at which point ambient air was sampled and ozone levels agreed with those from the 245 cm inlet. Surprisingly, first the inlets at 60 cm followed by the 90 and 30 cm and then the sampling inlets at the ground level displayed ambient ozone mixing ratios (Fig. 8B). After all snow had melted, we discovered that the cross arm that supported the 90 cm pair of inlets had broken. The two 90 cm inlets were found aligned with the center pole and located between the 30 and 60 cm cross arms, with an effective sampling height of ~40–50 cm above ground. We suspect that the snowmelt or creeping snow towards the later part of the experiment might have been the cause of the collapse of the 90 cm inlet pairs, but we do not have an accurate record of when this may have occurred. January observations (Fig. 6) imply that earlier in the experiment the 90-cm inlets were properly located on the sampling tower. By DOY 146, all snow had melted and ambient air was sampled from all inlets. Ozone readings from the 30, 60, 90, and 245 cm inlets usually were within ~1 ppbv. Once exposed to ambient air, ozone from the ground inlets often was 5–10 ppbv lower, which indicates the deposition of ozone to the soil and resulting lower ozone mixing ratios near the surface.

As detailed in the introduction, several previous ozone flux measurements have reported upward fluxes of ozone. The data from our experiments clearly show much lower ozone levels in the snowpack compared to ambient air at NR. At every depth in the snowpack, including the first few cm down into the snow from the surface, ozone levels are very much reduced. These steep, positive ozone gradients between above-the-surface and within-the-snowpack indicate ozone destruction in the snowpack and imply transport of ozone into but not out of the snowpack. We never found any situation in which there was higher ozone in the snow. Therefore, we conclude that for this site, ozone storage with subsequent release into the atmosphere (as suggested by Galbally and Allison, 1972, and Zeller and Hehn, 1996), does not occur.

COMPARISON OF RESULTS FROM NIWOT RIDGE WITH POLAR STUDY SITES

Experiments using the same sampling and ozone monitoring technique were performed in the polar regions at Summit (Helmig et al., 2007a) and at South Pole (Helmig, 2003, unpublished results). Although some uncertainties remain (due to the induced snowpack ventilation) in the absolute levels of ozone at a certain depth, comparison of data from these different environments reveals important insights into the different processes that determine ozone behavior in snow.

Distinct diurnal cycles of interstitial ozone, with minima occurring during the early afternoon and recovery during nighttime, were seen at Summit (Peterson and Honrath, 2001; Helmig et al., 2007a). The mean amplitude of the mid-summer diurnal cycle at Summit at 50 cm depth was ~10 ppbv. At nighttime, ozone in the snowpack recovered to 30–50 ppbv, ~80% of ambient levels. The dependence of ozone depletion on solar irradiance was further exemplified by lower ozone depletion rates (higher ozone levels in the snow) during spring, when incoming solar radiation was lower than during the summer months.

At NR, even though ambient ozone levels were similar to Summit, ozone in interstitial air was much lower than at comparable depths in the Summit snowpack, both during nighttime and daytime. With the much lower interstitial ozone levels, any diurnal signal would be expected to be much weaker at NR. To investigate for photochemical influences on ozone, a period during which a pair of sampling inlets was close to the snow surface was chosen. Figure 9 shows ozone diurnal cycles measured during DOY 30–35 from the 90 cm inlets. The snowpack depth during this period was between 125–147 cm; therefore, these inlets were ~35–57 cm below the snow surface. Depending on cloudiness, the noontime maximum incoming solar radiation varied between 100 and 700 W m^{-2} during these days; the mean diurnal cycle of incoming solar radiation (Fig. 9) peaked with average noon-afternoon radiation levels of ~450 W m^{-2}. The plotted ozone data show the mean deviation from the five daily ozone means from above the surface (the mean ozone mixing ratio during this period was 44.4 ppbv) and the corresponding values in the snowpack (the mean ozone snowpack mixing ratio during this period was 1.5 ppbv). Both data series show only a weak, statistically insignificant diurnal cycle. Given the fact that both the ambient and the snowpack diurnal cycles show a similar behavior (i.e., possibly a slight decrease in ozone during the afternoon hours), it appears likely that at least some of the snowpack ozone reductions are driven by the ozone changes in

ambient air. This lack of a distinct diurnal cycle in the snowpack contrasts with the measurements at Summit (see Figs. 2 and 4 in Helmig et al., 2007a), where, at equivalent radiation levels, diurnal ozone cycles of 15–30 ppbv were common. Furthermore, the nighttime recovery of snowpack ozone observed at Summit is absent at NR. These findings imply that, in contrast to Summit where most of the snowpack ozone loss occurs during sunlit hours (resulting in diurnal snowpack ozone cycles), ozone in the interstitial air of the NR snowpack remains very similar during day and night. We conclude that the ozone dynamics in the NR and Summit snowpacks show two important differences: 1) ozone levels in the NR snowpack are much lower than at Summit, and 2) the ozone loss in the NR snowpack is not directly related to solar irradiance (as observed for the Summit snowpack), and low ozone concentrations in the snowpack persist throughout the night. In the following section, we will investigate possible reasons for the very different ozone behavior in the NR and polar snowpacks.

WHAT MAY BE CAUSING THE LOWER OZONE LEVELS IN THE NIWOT RIDGE SNOWPACK?

The chemical gradients in the snowpack will depend on two processes: 1) the net chemical production and destruction rate of ozone at the surface and in the snowpack, and 2) the rate at which ambient air is exchanged across the atmosphere-snow interface and the rate at which air is transported within the snowpack. In the paragraphs below, a number of pertinent conditions in the NR and in polar snowpack are compared and their potential roles in the observed ozone dynamics are investigated.

The ventilation of the snowpack depends on the permeability of the snowpack, which will vary with the location, history, and temperature of the snowpack. Snow microstructure and snow density will determine the range, and changes with depth, of the snowpack porosity and tortuosity. These parameters are important to gas transport within the snowpack. Surface and interior ice and crust layers have been reported to reduce the snowpack permeability and to lower the gas flow (Albert and Perron, 2000). These layers may remain intact until the onset of the spring snowmelt (Fortin et al., 2002). Snow stratigraphy observations for the Soddie site during the 2003–2004 winter are not available, so it is difficult to evaluate the physical properties of the snowpack in retrospect. Snow pit observations made during that same winter at the C-1 site, which is ~300 m lower and below the closed canopy, showed several ice and crust layers in the late winter and spring snowpack. Similarly, several ice layers were seen in spring 2003 snowpack at the CU Mountain Research Station (Swanson et al., 2005). Our temperature record (Fig. 5) shows that above freezing ambient air temperatures were reached on several occasions at the Soddie during the snow-covered period. From this information, it can be inferred that the snowpack at the Soddie undergoes thaw-freeze cycles that likely result in the formation of ice layers, which would restrict the ventilation of the snowpack and the gas exchange between the snowpack and the overlying atmosphere. Ice layers were not identified in the snow at Summit; the snowpack permeability generally increased with depth (up to 3 m depth) and snowpack profiles did not show pronounced layers that would restrict gas transfer (Albert and Shultz, 2002).

The rate of air exchange is driven by several components, including forced airflow by wind pumping, diffusion, and thermal convection. In our experiment, airflow induced from the air sampling is another contributing effect. Wind speeds at the Soddie site at ~4 m above ground on the met tower near the snowpack sampling manifold from January to June 2004 were 1.0/1.8/3.1 m s^{-1} (25/50/75 percentiles). These winds are, on average, lower than at Summit, where the corresponding wind speeds at ~2 m above ground were 2.2/3.4/5.3 m s^{-1} (during 1 April–14 August 2004).

The soil temperature remained much warmer than the top of the snowpack during most of the experiment (Fig. 4). Thermal gradients of 10–20 °C between the snowpack and the snow surface were not uncommon (with the highest extremes occurring at night, when ambient air temperatures were the lowest). Most of the temperature gradient was observed in the upper 30 cm of the snowpack. Under these conditions thermal convection (upwelling of warm air from the soil and the downwelling of colder air from the upper layer in the snowpack) can be another contributing factor to the gas transfer (Powers et al., 1985). For example, for an Alaskan snowpack transport from convection was calculated to be on the order of 0.2–2 mm s^{-1}. It was also noted that vertical temperature gradients were higher than those in a Colorado snowpack, and that under such conditions pronounced kinetic metamorphism caused a coarse grain texture and high air permeability (Sturm and Johnson, 1991). Similar to the NR, diurnally changing temperature gradients were seen at Summit (Helmig et al., 2007a), with nighttime snowpack temperature gradients on the same order as for the Soddie site. Also, induced gas flow from the sampling procedure would be expected to be similar, as the same air sampling techniques were applied. A quantitative assessment of the contribution of these individual processes to the overall snowpack ventilation is not possible with the available data. From these comparisons it appears unlikely that differences in wind conditions or thermal convection would have caused the stark differences in ozone behavior seen in these two studies. It is conceivable that the presence of ice layers in the NR snowpack has an important influence on the effective gas transfer of interstitial air with air above the surface. At Summit transport times on the order of one hour were calcualted for the ventilation of the upper 1 m of the snowpack (Helmig et al., 2007a). At NR the presence of crust layers with reduced permeabilitly could possibly be responsible for a slower exchange of snowpack air with ozone-richer air above the surface.

There are also notable chemical differences between polar and mid-latitude snowpacks that may affect ozone chemistry. Inorganic and organic contaminant levels typically are lower in the remote, polar environment. Snowpack temperatures on the glacial, polar ice caps typically remain below −10 to −20°C year round. The quasi-liquid layer surrounding ice crystals diminishes with lower ice crystal temperatures (Koop et al., 2000; Döppenschmidt and Butt, 2000; Wei et al., 2001). The predicted onset of surface melting on clean ice crystals is ~−13°C (Makkonen, 1997). It is also noteworthy that the presence and the thickness of the liquid water film on ice crystals varies greatly with pressure and the chemical purity of the ice crystals (Ryzhkin and Petrenko, 2002; Stanley et al., 2005). A number of theoretical and experimental investigations suggested that photochemical reactions occurring in the quasi-liquid layer are important for snowpack chemistry (Takenaka et al., 1998; Cho et al., 2002; Dubowski, et al., 2002; Hynes et al., 2002; Mossinger et al., 2002). Given the warmer conditions in the seasonal snowpack, quasi-liquid layer chemistry is expected to be more important at NR, where it could possibly have an effect on ozone reactions.

In addition to the more favorable aqueous chemistry, the quasi-liquid layer may also favor the presence of biological material. The warmer Rocky Mountain snowpack supports bacterial, algal, and fungal communities that affect trace gas chemistry (Sommerfeld et al., 1993; Jones, 1999). Algal communities grow in the quasi-liquid layers present within the snowpack

lattice or at the snowpack-soil interface. At mid-latitude high mountain lakes, an abundant, active, and very diverse microbial population was found in slush ice and snow layers (Felip et al., 1995). Our temperature gradient measurements show that the NR snowpack is warm enough to support these microbiological processes. Albert et al. (2002) hypothesized that crustal materials, black carbon from anthropogenic combustion sources, or possibly humic and fulvic acids form natural sources deposited to the snowpack may play a role in the ozone chemistry. Reactions with organic materials, in particular unsaturated organic compounds, may be another considerable ozone loss pathway.

As enumerated in the introduction, several recent experiments have shown that oxidized nitrogen gases are formed in illuminated snow. Formation rates of nitrous acid (HONO), NO, and NO_2 were found to increase with increasing nitrate levels. Theoretical and actinometry experiments showed that most of this photochemistry is expected to occur in the upper ~10 cm of the snowpack. Light scattering enhances photolysis rates in the near-surface layer (approximately fourfold), and quickly drops to lower levels deeper in the snowpack. E-folding depths increase with wavelength and are in the 5–25 cm range for near-UV and visible radiation (Peterson et al., 2002; Philips and Simpson, 2005). Qiu et al. (2002) measured e-folding depths for nitrate photolysis in the Summit snowpack at 10–20 cm.

Nitrate concentrations in seasonal snow at the NR saddle site have generally ranged from 5–15 nmol g^{-1} (or μEq L^{-1}) (Brooks et al., 1996, 1997; Williams et al., 1998a, 1998b), which is consistent with reports from other areas of the Colorado Rocky Mountains (Heuer et al., 2000; Turk et al., 2001; Nanus et al., 2003). Nitrate levels in the polar snowpack are lower, typically on the order of 1–5 nmol g^{-1} with mean values of 2–3 nmol g^{-1} (Heaton et al., 2004; Hastings et al., 2004; Burkhart et al., 2004). Given the enhanced levels of nitrate in the NR snowpack, higher NO production rates resulting in higher NO concentrations in interstitial air appear plausible. These conditions may speed up a possible ozone loss via ozone-NO reaction, in comparison to the polar sites. This chemistry, which is directly driven by photodinitrification, would exhibit strong diurnal cycles (as observed at Summit). Ozone in the NR snowpack clearly is depleted during the day and night, which contradicts the theory that this process is driven by photochemistry. Similarly, catalytic destruction of ozone via halogen (e.g., bromine) radical chemistry, as hypothesized by Honrath et al. (2002) for Summit conditions, appears to be an unlikely cause for the lower snowpack ozone levels at NR. Again, this process would imply a dependency on incoming solar radiation, which is not supported by our NR data.

Another obvious difference that may impact snowpack trace gas chemistry in the temperate environment is the underlying soil, which represents a much more complex and dynamic system than the glacial ice under the Greenland or Antarctic snow. It is well known that trace gases (e.g., CO_2) are rigorously exchanged through snowpack (Sommerfeld et al., 1993; McDowell et al., 2000; Tagaki et al., 2005). At the nearby Saddle site, elevated fluxes of CO_2 and nitrous oxide (N_2O) throughout the winter snowpack were caused by microbial activity in relatively warm soil (within ~1 °C of freezing) underlying the seasonal snowpack (Brooks et al., 1996, 1997; Williams et al., 1998b). The wintertime CO_2 flux has been shown to be a significant carbon loss process in temperate forest ecosystems (Sommerfeld et al., 1993; McDowell et al., 2000), with subnival (under the snowpack) soil respiration fluxes reaching 0.1–1.1 μmol m^{-2} s^{-1} (Hirano, 2005). It was also found that the CO_2 flux was larger than the estimated diffusive transfer velocities and was fostered by wind-driven airflow through the permeable snowpack (Takagi et al., 2005). In contrast to CO_2, there has been little reported research on wintertime fluxes of NOx. It appears likely that, similar to CO_2, bacterial subnival nitrification and dinitrification processes result in significant production and upward fluxes of NO. These fluxes would cause elevated NO mixing ratios in interstitial air. Such enhanced NO levels, under the low radiation levels in the snowpack, are expected to be an ozone sink via the ozone + NO titration reaction. Subsequent research at the Soddie site has indeed provided new evidence that levels of NO in the snowpack are enhanced over ambient air concentrations. The role of NO in the ozone chemistry in the NR snowpack is currently being investigated further and will be presented in more detail in a future publication. In summary, the snow at NR is expected to have higher concentrations of a series of gas, particle, and liquid-phase contaminants, which potentially could provide a substrate for enhanced ozone depletion reactions.

Conclusions

Mixing ratios of ozone in the interstitial air in the deep, seasonal, mid-latitude snowpack at NR were much lower than those that have been reported in polar snowpacks. Ozone levels have, at most, a very weak diurnal signal and consequently do not appear to be directly dependant on solar radiation cycles, as observed at Summit, Greenland. It is hypothesized that the observed differences in the ozone dynamics between the mid-latitude and the polar snowpack may be due to one or a combination of processes: microphysical snowpack properties, warmer snowpack temperatures, which leads to higher levels of snow impurities, and soil-snowpack-atmosphere gas exchange processes. It appears likely that, in contrast to the polar snowpack, the determining mechanism of ozone depletion is light independent. Future investigations of ozone-snow chemistry should include experiments to study these aforementioned physical, chemical, and biological parameters and conditions.

The positive, upward ozone fluxes that were reported in the literature from other, similar study sites cannot be explained by our snowpack observations—the NR snowpack is clearly an ozone sink and not a source for ozone. A possible explanation for previously reported upward ozone fluxes may be the photochemical formation of ozone in a shallow air layer right above the snow surface. A similar phenomenon has recently been discovered in the Antarctic environment, where accumulation of NO and ozone production of several ppbv per day above the polar snowpack were reported during stable atmospheric conditions (Crawford et al., 2001; Helmig et al., 2007c; Helmig et al., 2007d). Ozone production right above the snow surface will result in bidirectional ozone fluxes, downward into the snow as well as upward, into the atmosphere. Similar processes may have caused the upward ozone fluxes that were described in the earlier tower flux experiments (Galbally and Allison, 1972; Zeller and Hehn, 1994, 1996; Zeller, 2000).

Previously, it has been assumed that snow covered landscapes do not significantly contribute to ozone exchange in the tropospheric ozone budget. From our data, we infer that ozone uptake to snow-covered landscapes (i.e., positive ozone deposition velocity to snow) probably differs significantly depending on chemical and physical snow properties, snowpack depth, and the nature of the substrate underneath the snow. The comparatively lower ozone levels in the deep, seasonal snowpack show that ozone deposition rates may be different in this environment than in year-round polar snow and that, globally,

ozone deposition to snow-covered landscapes may be more complex than previously believed. These dependencies warrant further investigations to achieve a better understanding of the geographical sink strength of snow covered landscapes in the tropospheric ozone cycle.

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