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

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Abstract

Ozone in interstitial air was studied in the seasonal, mid-latitude snowpack at a subalpine forest site at Niwot Ridge, Colorado during January - June 2004. Sampling techniques were developed for continuous, vertical gradient measurements of ozone and temperature at four depths in the snowpack. During this time ozone in ambient air ranged from 15–80 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 have been reported. These observations imply that ozone levels in seasonal, mid-latitude snowpack are much different (and overall lower) than in the year-round polar 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), chemical composition and possibly influences of the substrate below the snow and soil-snowpack-atmosphere gas exchange processes.

Key word index: ozone, seasonal snowpack, soil-snowpack-atmosphere gas exchange, snow-photochemistry, snow stratigraphy.

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 Earth. In recent years, numerous research studies have also paid attention to the chemical interactions between air and snow-ice. Most of this research was 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, provide 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,b; 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 (Jones et al., 2001), Antarctica and South Pole, Antarctica (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 (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 ~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

74 shading experiment further confirmed that ozone destruction was driven by solar radiation and
75 coincided with photochemical NO formation (Peterson and Honrath, 2001). Ozone depletion in
76 snowpack was also seen by Albert et al. (2002) at Alert, Canada, though these springtime
77 measurements resulted from somewhat different conditions. The snowpack is typically less than
78 one meter deep and bromine-catalyzed photochemistry is a determining ozone-depletion
79 mechanism at Alert. Ozone mixing ratios measured at 2 cm, 5 cm and 10 cm below the snow
80 surface were approximately 90, 70 and 60%, respectively of ambient ozone during April (Albert
81 et al., 2002) when incoming solar radiation levels were 250-500 W m^{-2} (Bottenheim et al., 2002).
82 It appears that the ozone loss in the Alert snowpack was higher compared to Summit (Peterson
83 and Honrath, 2001). This research was extended by several months of measurements of ozone in
84 interstitial air at Summit (Helmig et al., 2006a) and South Pole (Helmig, unpublished results).
85 These studies provided further evidence that, in the polar snowpack, ozone is present at
86 significant levels (e.g. up to 90% of ambient levels were found at 1 m depth) during times with
87 low levels (< 100 W m^{-2}) of incoming radiation. In contrast, during summertime, noon
88 conditions (> 500 W m^{-2}), up to 90% of ozone was lost in the irradiated snowpack. The
89 amplitude of this diurnal signal was dependent on wind pumping through the snowpack, e.g.
90 during low wind conditions, higher ambient-snowpack ozone gradients were found than during
91 high winds.
92 The mechanism for this photochemically induced ozone destruction is not fully
93 understood at this time. Peterson and Honrath (2001) suggested that ozone is destroyed by an
94 unidentified, photochemically produced reactant. Reaction with NO at the observed levels could
95 account for a mere 6% of the ozone loss rate. These authors suggested alternative reaction
96 pathways, such as a catalytic bromine reaction cycle (e.g. triggered by photochemically formed
97 bromine radicals).
98 Ozone fluxes and dry deposition studies to snow-covered landscapes were recently
99 reviewed by Helmig et al. (2006b). Reported data span a remarkably wide range of ozone
100 deposition velocities (v_{dO3}). Overall, reported values range from ~ $-3 < v_{dO3} < 2$ cm s^{-1}, though
101 most are within ~ $0 < v_{dO3} < 0.2$ cm s^{-1}, which reflects a relatively small uptake rate compared to
102 other types of landscapes (Padro, 1996; Wesely and Hicks, 2000). Interestingly, several studies
103 report positive fluxes, indicating the release of ozone from these snow-covered environments
104 (Galbally and Allison, 1972; Zeller and Hehn, 1994, 1996; Zeller, 2000). The tower gradient

105 flux measurements by Zeller and Hehn (1994, 1996) were conducted at a coniferous forest site in
106 the Snowy Range of the Medicine Bow National Forest, WY, which appears to have similarities
107 to our site (see below). Upward fluxes of 0.5 μg m^{-2} s^{-1} were routinely measured during the
108 winter 1992 experiment. In a later follow-up study Zeller and Hehn (1995) found that "the
109 wintertime upward ozone fluxes only occurred when snow completely covered the forest
110 understory", but that ozone fluxes were downward in the absence of snow cover (on the forest
111 understory). Zeller and Hehn (1996) hypothesized that ozone may be temporarily stored in the
112 snow base. Similarly, Galbally and Allison (1972) reported upward ozone fluxes of 1.6 μg m^{-2} s^{-1}
113 over snow at Mount Baker in Australia. These positive ozone fluxes over seasonal snowpack
114 in alpine environments are rather remarkable observations. Ozone is generally destroyed on
115 surfaces, resulting in negative, downward ozone fluxes (Wesely and Hicks, 2000). These
116 aforementioned findings differ significantly from this widely accepted principle. As already
117 mentioned above, subsequent studies with ozone measurements in interstitial air have found
118 lower ozone mixing ratios in the snowpack than above the surface. These positive, ambient air-
119 snowpack ozone gradients imply a gradient flux from the atmospheric surface layer into the
120 snowpack and contradict the hypothesis of ozone storage with subsequent release and upwards
121 fluxes out of the snow.

122 This research addressed several questions that have been raised in the aforementioned
123 literature. We examined experimental requirements for conducting automated and continuous
124 snowpack gradient gas measurements in a continental, seasonal snowpack. The topography and
125 inhomogeneous footprint of high altitude mountain sites are not amendable to direct, tower flux
126 measurements (e.g. by gradient or eddy correlation methods). Therefore, our experiments
127 examined if snowpack measurements could serve as a tool for investigating if and when the mid-
128 latitude snowpack is a net source or sink for ozone. Furthermore, by comparison with equivalent
129 measurements from high-latitude, polar snowpacks, the obtained 4-months of observations from
130 the subalpine, Rocky Mountain forest site allow a further evaluation of processes that are
131 determining snowpack-ozone gas exchange processes.

132

133 **Experimental Methods**

134 This experiment was performed at Niwot Ridge (NR, 40°03'N, 105°35'W) in the Front
135 Range of the Northern Colorado Rockies (Figure 1). This area is administrated cooperatively by

136 the U.S. Forest Service and the University of Colorado at Boulder. The Soddie site is at tree line
137 (3340 m asl) surrounded by sub-alpine tundra meadows with patches of grass and trees,
138 including Englemann spruce and sub-alpine fir. The sampling location was within a clearing,
139 approximately 10-40 m away from the surrounding trees and gently sloping (10°) to the south.
140 The snowpack sampling manifold was installed during November 2003, prior to any
141 significant snow accumulation. Subsequently, snow accumulated naturally and gradually
142 covered the sampling inlets. The early installation was expected to minimize any potential
143 disturbance to the snowpack (McDowell et al., 2000). Ozone gradient measurements were
144 performed from January 28, 2004 (calendar day (CD) 28) to June 8, 2004 (CD 160). Figure 2
145 presents the sampling manifold for measuring snowpack ozone and temperature at five levels.
146 The gas analyzer and datalogger were housed in an underground laboratory located ~10 m away
147 from the sampling tower. Air was drawn intermittently from these sampling ports through 18 m-
148 long, 6.4 mm o.d., 4.0 mm i.d. Teflon sampling lines (perfluoroalkyoxy-polymer (PFA) tubing).
149 The sampling lines had dual inlets, spaced 100 cm apart. Each inlet was equipped with a glass
150 fiber Acrodisc syringe filter (1 μm pore size, polypropylene housing, product number 4523,
151 VWR International, San Dimas, CA) to prevent the sampling of particles and ice crystals. Prior
152 to installation, all Teflon tubing and inlet filters were conditioned for 12 hours in a 2 L min^{-1}
153 flow of 250 ppbv ozone. All filters and sampling lines were tested prior to installation and ozone
154 losses during sampling through all components of the sampling system were found to be < 2%.
155 The five sampling lines were bundled together and placed inside pipe foam insulation from ~1.5
156 m distance from the tower base to near the solenoid valve sampling manifold. This section was
157 heated with water pipe heating tape to ~ 4^{o}C to minimize water accumulation and potential water
158 freeze-out in the sampling lines. The paired inlets were mounted at ground level, 30 cm, 60 cm,
159 90 cm and 245 cm above ground. The latter inlet was expected to remain above the snow
160 surface throughout the winter.
161 Unfortunately, there is no technique available that would allow measuring ozone without
162 drawing a sample aliquot from within the snowpack into a monitor. An important objective was
163 to minimize the artificial air flow through the snowpack that is induced by the air sampling
164 procedure. Secondly, air had to be sampled from five locations with one available ozone
165 monitor. Therefore, air was pulled sequentially through the five sampling lines at 1.2 L min^{-1} by
166 the ozone monitor sampling pump. The flow through each of the inlets was maintained for 12

167 min, after which the next, lower inlet line was opened (Teflon solenoid valve part #C-01367-70,
168 Cole Palmer, Vernon Hills, IL). This cycle resulted in a 12 min sampling period of each height
169 per hour (after which 48 min were allowed for air around that inlet to re-equilibrate) and an
170 effective sampling of ~14 L of air per hour from each height, respectively ~7 L hr^{-1} for each of
171 the dual inlets. This collected sample is expected to represent the composition of the air space
172 surrounding the inlet, with probably a proportionally higher amount of air pulled from the air
173 space above it. Inlets (Figure 2) were attached to horizontal cross arms. This arrangement
174 allowed the snowpack right above the inlet to remain undisturbed and compact, avoiding
175 artificial, vertically extending air spaces.
176 Ozone was measured with a UV photometric monitor (Thermo Electron Corporation
177 (TEI), Franklin, MA, Model 49). The detection limit, accuracy and precision of 1-min data from
178 these measurements are on the order of 1 ppbv. The analog signal was recorded with a
179 datalogger (Campbell Scientific, Logan, UT, Model CR10X). The ozone signal was
180 subsequently corrected for the pressure and temperature of the optical cell. A pressure
181 transducer was tee-ed into the adsorption cell, and a thermocouple measured the cell
182 temperature. The pressure signal was also used to monitor possible flow restrictions (from water
183 freeze-out) in the sampling lines and/or inlets. Pressures recorded from all five inlet lines were
184 usually within ± 5%. The ozone monitor was intercompared prior and after the field experiment
185 against a reference laboratory instrument (TEI 49C), and agreement was found to be within ± 1
186 ppbv.
187 Snowpack and ambient temperatures were recorded with thermocouples. The last 1 m of
188 the thermocouple wires were covered with white shrink tubing to minimize radiative heating
189 artifacts. Other meteorological measurements at the site provided data of air temperature and
190 humidity, wind speed and direction and incoming shortwave radiation. Data were collected
191 every second, averaged and stored at 2-minute intervals and transmitted via a radio connection
192 every two hours. Snowpack depth was measured with a probe and recorded during weekly site
193 visits. A total of 22 snow depth measurements were obtained during the study period.
194
195 **Results and Discussion**
196 *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 June 1 (CD 153). From January 28 (CD 28) to May 4 2004 (CD 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 five sampling heights. 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 (Figure 5) on the nearby (~15 m) met tower. Agreement between these two measurements was generally within ± 2^{o}C until early June when the thermocouple measurements yielded increasingly higher values, likely from an increasing radiation error, during summertime conditions. Consequently, we conclude that the snowpack thermocouple temperature measurements during the January-May period were within a 1-2^{o}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 occasionally dropping to < -20^{o}C (Figure 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 are 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 are 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 result from pulling 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 are operated 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 off the equilibrated air space surrounding the inlet. A gradual change in concentration, as would be expected as 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 (Figures 7, 8), the data from the first two minutes of each measurement interval was discarded as 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 asl) and Tundra lab (alpine tundra; 3528 m asl) sites (Figure 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 (Figure 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 (Figure 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 approaching the summer. 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 (Figures 7B and C). These sites, located on the east slope of the Colorado Rocky Mountains are 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 predominantly remain 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 asl). As the year progresses, buoyancy-driven upslope transport becomes more prominent and, particularly during the afternoon, polluted air 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, e.g. 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. CD 36, CD 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 CD 140, 141, and 143, were first encountered and typically 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 E-SE during the identified upslope occurrences. The ozone data reflect these general two ozone transport phenomena that occur at the Mountain Research Station.

290

291 *Ozone in the Niwot Ridge Snowpack*

292 The nighttime data from CD 29 (Figure 6) show the steep ozone gradients between
293 ambient air and the snowpack. Only ~3 ppbv of ozone were recorded at the 90-cm inlets, which
294 were covered by ~30 cm of snow at this time. Ozone time series with the measurements from all
295 inlet heights (except the ambient air level one) are presented in Figure 8. Gaps within the ozone
296 data represent a total of about 20 days, which resulted from the loss of the radio connection to
297 the site. While the sampling inlets were covered with snow, ozone levels were generally low,
298 e.g. < 3 ppbv and frequently below the detection limit of the ozone monitor (~1 ppbv for 1-min
299 data). From CD 128 until the end of the study period, as snow melted, inlets were one-by-one
300 uncovered of snow, at which point ambient air was sampled and ozone levels agreed with those
301 from the 245-cm inlet. Though surprisingly, first the 60-cm, followed by the 90-, 30-cm and
302 then the sampling inlets at the ground level displayed ambient ozone mixing ratios (Figure 8B).
303 After all snow had melted, we discovered that the cross arm that supported the 90-cm pair of
304 inlets had broken. The two 90-cm inlets were found aligned with the center pole and located
305 between the 30- and 60-cm cross arms, with an effective sampling height of ~40-50 cm above
306 ground. We suspect that the snow melt or creeping snow towards the later part of the experiment
307 might have been the cause of the collapse of the 90-cm inlet pairs, but we do not have an
308 accurate record when this may have occurred. January observations (Figure 6) imply that earlier
309 during the experiment, the 90-cm inlets were properly located on the sampling tower. By CD
310 146, all snow had melted and ambient air was sampled from all inlets. Ozone readings from the
311 30-, 60-, 90- and 245-cm inlets usually were within ~1 ppbv. Once exposed to ambient air,
312 ozone from the ground inlets often was 5-10 ppbv lower, which indicates the deposition of ozone
313 to the soil surface.

314 As detailed in the introduction section, several previous ozone flux measurements have
315 reported upward fluxes of ozone. The data from our experiments clearly show much lower
316 ozone levels in the snowpack compared to ambient air at NR. At every depth in the snowpack,
317 including the first few cm into the snow down from the surface, ozone levels are very much
318 reduced. These steep, positive ozone gradients between above-the-surface to within-the-
319 snowpack imply ozone destruction in the snowpack and likely transport of ozone into, but not
320 out of the snowpack. We never found any conditions with higher ozone in the snow. Therefore,

321 we conclude that for this site, ozone storage with subsequent release into the atmosphere, as
322 suggested by Galbally and Allison (1972) and Zeller and Hehn (1996) does not occur.
323
324 *Comparison of Niwot Ridge with Polar Study Sites*
325 Experiments using the same sampling and ozone monitoring technique were performed in
326 the polar at Summit (Helmig et al., 2006a) and at South Pole (Helmig, 2003, unpublished
327 results). While some uncertainties remain (due to the induced snowpack ventilation) in the
328 absolute levels of ozone at a certain depth, comparison of data from these different environments
329 reveals important insights into the different processes that determine ozone behavior in snow.
330 Distinct diurnal cycles of interstitial ozone, with minima occurring during the early
331 afternoon and recovery during nighttime were seen at Summit (Peterson and Honrath, 2001;
332 Helmig et al., 2006a). The mean amplitude of the mid-summer diurnal cycle at Summit at 50
333 cm depth was ~10 ppbv. At nighttime, ozone in the snowpack recovered to 30–50 ppbv, ~80%
334 of ambient levels. The dependence of ozone depletion on solar irradiance was further
335 exemplified by lower ozone depletion rates (higher ozone levels in the snow) during spring,
336 when incoming solar radiation was lower than during the summer months.
337 At NR, even though ambient ozone levels were similar to Summit, ozone in interstitial air
338 was much lower than at comparable depths in the Summit snowpack, both during nighttime and
339 daytime. With the much lower interstitial ozone levels any diurnal signal would be expected to
340 be much weaker at NR. In order to investigate for photochemical influences on ozone, a period
341 during which a pair of sampling inlets was close to the snow surface, was chosen. Figure 9
342 shows ozone diurnal cycles measured during CD 30-35 from the 90-cm inlets. The snowpack
343 depth during this period was between 125-147 cm, hence these inlets were ~ 35-57 cm below the
344 snow surface. Depending on cloudiness, the noontime maximum incoming solar radiation varied
345 between 100-700 W m^{-2} during these days; the mean diurnal cycle of incoming solar radiation
346 (Figure 9) peaked with average noon-afternoon radiation levels of ~450 W m^{-2}. The plotted
347 ozone data show the mean deviation from the five daily ozone means from above the surface (the
348 mean ozone mixing ratio during this period was 44.4 ppbv) in comparison to the corresponding
349 value in the snowpack (the mean ozone snowpack mixing ratio during this period was 1.5 ppbv).
350 Both data series show only a weak (statistically insignificant) diurnal cycle. Given the fact that
351 both the ambient and the snowpack diurnal cycles show a similar behavior, e.g. possibly slightly

352 decreasing ozone during the afternoon hours, it appears likely that at least some of the snowpack
353 ozone reductions are driven by the ozone changes in ambient air. This lack of a distinct diurnal
354 cycle in the snowpack contrasts the measurements at Summit (see Figures 2 and 4 in Helmig et
355 al., 2006a), where, at equivalent radiation levels, diurnal ozone cycles of 15-30 ppbv were
356 common. Furthermore, the nighttime recovery of snowpack ozone observed at Summit is absent
357 at NR. These findings imply that, in contrast to Summit, where most of the snowpack ozone loss
358 occurs during sunlit hours (resulting in diurnal snowpack ozone cycles), ozone in the interstitial
359 air of the NR snowpack remains very similar during day and night. We conclude that the ozone
360 dynamics in the NR and Summit snowpacks show two important differences: a) ozone levels in
361 the NR snowpack are much lower than at Summit, and b) the ozone loss in the NR snowpack is
362 not directly related to solar irradiance, as observed for the Summit snowpack. Low ozone
363 concentrations in the snowpack persist throughout the night, in the absence of solar radiation. In
364 the following we will investigate possible reasons for the much different ozone behavior in the
365 NR and polar snowpacks.
366
367 *What May Be Causing the Lower Ozone Levels in the Niwot Ridge Snowpack?*
368 The chemical gradients in the snowpack will depend on two processes, 1. the net of
369 chemical production and destruction rate of ozone at the surface and in the snowpack and 2. on
370 the rates at which ambient air is exchanged across the atmosphere-snow interface and on the rate
371 at which air is transported within the snowpack. In the paragraphs below a number of pertinent
372 conditions in the NR and in polar snowpack are compared and their potential roles in the
373 observed ozone dynamics are investigated.
374 The ventilation of the snowpack depends on the permeability of the snowpack, which will
375 vary with location, history and temperature of the snowpack. Snow microstructure and snow
376 density will determine the range of the snowpack porosity and tortuosity and their changes with
377 depth. These parameters are of importance for the gas transport within the snowpack. Surface
378 and interior ice and crust layers have been reported to reduce permeability and to lower the gas
379 flow (Albert and Perron, 2000). These layers may remain intact until the onset of the spring
380 snowmelt (Fortin et al., 2002). Snow stratigraphy observations for the Soddie site during the
381 2003-2004 winter are not available so it is difficult to evaluate the physical properties of the
382 snowpack in retrospect. Snow pit observations made during that same winter at the ~300 m

lower, and below-closed-canopy site C1 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 (Figure 1) (Swanson et al., 2005). Our temperature record (Figure 5) shows that above-freezing ambient air temperatures were reached on several occasions at the Soddie during the snow-covered period. From these diverse information it can be inferred that the snowpack at the Soddie undergoes thaw-freeze cycles which likely will 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 air flow by wind pumping, diffusion and thermal convection. In our experiment, air flow induced from the air sampling is another contributing effect. Wind speeds at the Soddie site, ~ 4 m above ground on the met tower near the snowpack sampling manifold, during January – 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 April 1 – August 14, 2004).

The soil temperature remained much warmer than the top of the snowpack during most of the experiment (Figure 4). Thermal gradients of 10–20^{o}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 instance, flow speeds on the order of 0.2–2 mm s^{-1} from convection were calculated for an Alaskan snowpack, although it should be 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). It should be noted that similarly to the Soddie, diurnally changing temperature profiles were seen at Summit (Helmig et al., 2006a). Also, induced gas flow from the sampling procedure would be expected to be

414 similar as the same techniques were applied. A quantitative assessment of the contribution of
415 these individual processes towards the overall snowpack ventilation is not possible with the
416 available data. It is likely that the presence of ice layers in the NR snowpack has an important
417 influence on the effective gas transfer of interstitial air with air above the surface. Crust layers
418 with reduced permeability could be responsible for a much slower exchange with ozone-richer
419 air above the surface than at Summit where transport times on the order of one hour were
420 calculated for the ventilation of the upper 1 m of the snowpack (Helmig et al., 2006a).
421 There are also notable chemical differences between polar and mid-latitude snowpacks
422 that may affect ozone chemistry. Inorganic and organic contaminant levels typically are lower in
423 the remote, polar environment. Snowpack temperatures on the glacial, polar ice caps typically
424 remain below -10 to -20^{o}C year-round. The quasi-liquid layer surrounding ice crystals
425 diminishes with lower ice crystal temperatures (Koop et al., 2000; Döppenschmidt and Butt,
426 2000; Wei et al., 2001). The predicted onset of surface melting on clean ice crystals is ~ -13^{o}C
427 (Makkonen, 1997). It is also noteworthy that the presence and the thickness of the liquid water
428 film on ice crystals varies greatly with pressure and the chemical purity of the ice crystals
429 (Ryzhkin and Petrenko, 2002; Stanley et al., 2005). A number of theoretical and experimental
430 investigations suggested that photochemical reactions occurring in the quasi-liquid layer are
431 important for snowpack chemistry (Takenaka et al., 1998; Cho et al., 2002; Dubowski, et al.,
432 2002; Hynes et al., 2002; Mossinger et al., 2002). Given the warmer conditions in the seasonal
433 snowpack, quasi-liquid layer chemistry is expected to be more important at NR which possibly
434 could have an effect on ozone reactions.
435 Other than the more favorable aqueous chemistry, the quasi-liquid layer may also favor
436 the presence of biological material. The warmer Rocky Mountain snowpack supports bacterial,
437 algae and fungal communities that affect trace gas chemistry (Sommerfeld et al., 1993; Jones et
438 al., 1999). Algal communities grow in the quasi-liquid layers present within the snowpack
439 lattice or at the snowpack-soil interface. At mid-latitude high mountain lakes, an abundant,
440 active, and very diverse microbial population was found in slush ice and snow layers (Felip et
441 al., 1995). Our temperature gradient measurements show that the NR snowpack is warm enough
442 to support these microbiological processes. Albert et al. (2002) hypothesized that crustal
443 materials, black carbon from anthropogenic combustion sources, or possibly humic and fulvic
444 acids form natural sources, deposited to the snowpack may play a role in the ozone chemistry.

445 Organic materials, in particular reactions with unsaturated organic compounds may be another
446 considerable ozone loss pathway.
447 As enumerated in the introduction section, several recent experiments have shown that
448 oxidized nitrogen gases are formed in illuminated snow. Formation rates of nitrous acid
449 (HONO), NO and NO_2 were found to increase with increasing nitrate levels. Theoretical and
450 actinometry experiments showed that most of this photochemistry is expected to occur in the
451 upper ~10 cm of the snowpack. Light scattering enhances photolysis rates in the near-surface
452 layer (approximately fourfold), and quickly drops to lower levels deeper in the snowpack. E-
453 folding depths increase with wavelength, and are in the 5-25 cm range for near-UV and visible
454 radiation (Peterson et al., 2002; Philips and Simpson, 2005). Qiu et al. (2002) measured e-
455 folding depths for nitrate photolysis in the Summit snowpack of 10-20 cm.
456 Nitrate concentrations in seasonal snow at the NR saddle site have generally ranged from
457 5-15 nmol g^{-1} (or μEq L^{-1}) (Brooks et al., 1996, 1997; Williams et al., 1998a,b) which is
458 consistent with reports from other areas of the Colorado Rocky Mountains (Heuer et al., 2000;
459 Turk et al., 2001; Nanus et al., 2003). Nitrate levels in the polar snowpack are lower, typically
460 on the order of 1-5 nmol g^{-1} with mean values of 2-3 nmol g^{-1} (Heaton et al., 2004; Hastings et
461 al., 2004; Burkhart et al., 2004). Given the enhanced levels of nitrate in the NR snowpack,
462 higher NO production rates resulting in higher NO concentrations in interstitial air appear
463 plausible. These conditions may speed up a possible ozone loss via ozone-NO reaction in
464 comparison to the polar sites. This chemistry, which is directly driven by photodinitrification,
465 would exhibit strong diurnal cycles (as observed at Summit). Ozone in the NR snowpack clearly
466 is depleted during day and night, which contradicts the theory that this process is driven by
467 photochemistry (e.g. by photo-dinitrification). Similarly, catalytic destruction of ozone via
468 halogen (e.g. bromine) radical chemistry, as hypothesized by Honrath et al. (2002) for Summit
469 conditions, appears to be an unlikely cause for the effective ozone destruction at NR. Again, this
470 process would imply a dependency on incoming solar radiation, which is not supported by our
471 NR data.
472 Another, obvious difference that may impact snowpack trace gas chemistry in the
473 temperate environment is the underlying soil, which represents a much more complex and
474 dynamic system than the glacial ice under the Greenland or Antarctic snow. It is well known
475 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) through the winter snowpack were caused by microbial activity in relatively warm (within ~1^oC of freezing) soil 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 subnivial (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 air flow through the permeable snowpack (Takagi et al., 2005). In contrast to CO_2, little research has been reported on wintertime fluxes of NOx. It appears likely that, similar to CO_2, bacterial subnivial nitrification and dinitrification processes results 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 further investigated 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

Interstitial ozone levels in deep, seasonal, mid-latitude snowpack are 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 midlatitude and the polar snowpack may be due to one or a combination of processes: microphysical snowpack properties, warmer snowpack temperatures and quasi-liquid layer chemistry 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 the ozone-snow

chemistry should include experiments for the study of these aforementioned physical, chemical and biological parameters and conditions.

Positive, upward ozone fluxes that were reported in the literature from other, but similar study sites, can not 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 upwards 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 under stable atmospheric conditions accumulation of NO and ozone production of several ppbv per day above the polar snowpack were reported (Crawford et al., 2001; Helmig et al., 2006c,d). Ozone production right above the snow surface will result in bi-directional ozone fluxes, downwards into the snow as well as upwards, into the atmosphere. Similar processes may have caused the upwards ozone fluxes that were described in the earlier tower flux experiments (Galbally and Allison, 1972; Zeller and Hehn, 1994, 1996; Zeller, 2000).

It has previously been assumed that snow-covered landscapes do not contribute significantly to ozone exchange in the tropospheric ozone budget. Our data infer that ozone uptake to snow-covered landscapes (i.e., positive ozone deposition velocity to snow) probably differ 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 infer that ozone deposition rates may be different in this environment than to 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 in order to achieve a better understanding of the geographical sink strength of snow-covered landscapes in the tropospheric ozone cycle.

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References

Albert M.F., and Perron F.E. Jr., 2000: Ice layer and Surface Crust Permeability in a Seasonal Snow Pack. *Hydrological Processes*, **14**, 3207-3214.

Albert, M. R., Grannas, A. M., Bottenheim, J. W., Shepson, P. B., and Perron F. E., 2002: Processes and Properties of Snow-Air Transfer in the High Arctic with Application to Interstitial Ozone at Alert, Canada. *Atmos. Envir.*, **36**, 2779-2787.

Albert, M. R., and Shultz, E. F., 2002: Snow and Firn Properties and Air-Snow Transport Processes at Summit, Greenland. *Atmos. Env.*, **36**, 2789-2797.

Barrie, L. A., and Platt, U., 1997: Arctic Tropospheric Chemistry: An Overview. *Tellus*, **49B**, 450-454.

Beine, H. J., Domine, F., Simpson, W., Honrath, R. E., Sparapani, R., Zhou, X., and King, M., 2002: Snow-Pile and Chamber Experiments during the Polar Sunrise Experiment 'Alert 2000': Exploration of Nitrogen Chemistry. *Atmos. Env.*, **36**, 2707-2720.

Bottenheim J. W., Fuentes, J. D., Tarasick, D. H., and Anlauf, K. G., 2002: Ozone in the Arctic Lower Troposphere during Winter and Spring 2000 (ALERT 2000). *Atmos. Envir.*, **36**, 2535-2544.

Brooks, P. D., Williams M.W., and Schmidt S.K., 1996: Microbial activity under alpine snowpacks, Niwot Ridge, Colorado, *Biogeochemistry* **32**, 93-113.

Brooks, P. D., Schmidt S.K., and Williams M.W., 1997: Winter Production of CO_2 and N2O from Alpine Tundra; Environmental Controls and Relationship to Inter-System C and N Fluxes, *Oecologia* **110**, 403-413.

Burkhart, J. F., Hutterli, M., Bales, R. C., and McConnell, J. R., 2004: Seasonal Accumulation Timing and Preservation of Nitrate in Firn at Summit, Greenland. *J. Geophys. Res.*, **109**, D19302, doi:10.1029/2004CD004658.

Chen G., Davis D., Crawford J., Hutterli L.M., Huey L.G., Slusher D., Mauldin L., Eisele F., Tanner D., Dibb J., Buhr M., McConnell J., Lefer B., Shetter R., Blake D., Song C.H., Lombardi K. and Arnoldy J., 2004: A Reassessment of HOx South Pole Chemistry Based on Observations Recorded During ISCAT 2000. *Atmos. Environ.*, **38**, 5451-5461.

Cho, H., Shepson, P. B., Barrie, L. A., Cowin, J. P., and Zaveri, R., 2002: NMR Investigation of the Quasi-Brine Layer in Ice/Brine Mixtures. *J. Phys. Chem. B*,

Cotter, E. S. N., Jones, A. E., Wolf, E. W., and Baugitte, S. J-B., 2003: What Controls Photochemical NO and NO_2 production from Antarctic Snow? Laboratory Investigation Assessing the Wavelength and Temperature Dependence. *J. Geophys. Res.*, **108**, 4147.

Crawford J.H., Davis D.D., Chen G., Buhr M., Oltmans S., Weller R., Mauldin L., Eisele F., Shetter R., Lefer B., Arimoto R., and Hogan A: 2001: Evidence for Photochemical Production of Ozone at the South Pole Surface. *Geophys. Res. Let*. **28**, 3641-3644.

Davis D., Nowak J.B., Chen G., Buhr M., Arimoto R., Hogan A., Eisele F., Mauldin L., Tanner D., Shetter R., Lefer B., and McMurry P.: 2001: Unexpected High levels of NO Observed at South Pole. *Geophys. Res. Let*. **28**, 3625-3628.

Dibb, J. E., Arsenault, M., Peterson, M. C., and Honrath, R. E., 2002: Fast Nitrogen Oxide Photochemistry in Summit, Greenland. *Atmos. Envir.*, **36**, 2501-2511.

Döppenschmidt, A., and Butt, H.-J., 2000: Measuring the Thickness of the Liquid-like Layer on Ice Surfaces with Atomic Force Microscopy. *Langmuir,* **16**, 6709-6714.

Domine, F. and Shepson, P. B., 2002: Air-Snow Interactions and Atmospheric Chemistry. *Science*, **297**, 1506-1510.

Dubowski, Y., Colussi, A. J., Boxe, C., and Hoffmann, M. R., 2002: Monotonic Increase of Nitrate Yields in the Photolysis of Nitrate in Ice and Water between 238 and 294K. *J. Phys. Chem.*, **106**, 6967-6971.

584 Felip, M., Sattler, B., Psenner, R., and Catalan, J., 1995: Highly Active Microbial Communities in the Ice
585 and Snow Cover of High Mountain Lakes. *Applied and Envir. Microbiology*, **61**, 2394-2401.
586 Fortin, G., Jones, G.H., Bernier, M., and Schneeblei, M., 2002: Changes in the Structure and Permeability
587 of Artificial Ice Layers Containing Fluorescent Tracer in Cold and Wet Snow Cover. 59th Eastern
588 Snow Conference, Stowe, Vermont, Conference Proceedings pp. 257-266.
589 Galbally, I. E., and Allison, I., 1972: Ozone Fluxes over Snow Surfaces. *J. Geophys. Res.*, **77**, 3946-3949.
590 Hastings, M. G., Steig, E. J., and Sigman, D. M., 2004: Seasonal Variations in N and O Isotopes of
591 Nitrate in Snow at Summit, Greenland: Implications for the Study of Nitrate in Snow and Ice
592 Cores. *J. Geophys. Res.*, **109**, D20306, doi:10.1029/2004CD004991.
593 Heaton, T. H. E., Wynn, P., and Tye, A. M., 2004: Low $^{15}N/^{14}N$ Ratios for Nitrate in Snow in the High
594 Arctic (79°N). *Atmos. Envir.*, **38**, 5611-5621.
595 Helmig, D., Bocquet, F., Cohen, L., and Oltmans, S., 2006a: Ozone Uptake to the Summit, Greenland
596 Snowpack. *Atmos. Envir.*, in press.
597 Helmig, D., Ganzeveld, L., Butler, T., and Oltmans, S., 2006b: Ozone Snow-Atmosphere Gas Exchange.
598 *Atmos. Chem. Phys. Discus.* **6**, 1-40.
599 Helmig, D., Johnson, B., Oltmans, S.J., Neff, W., Eisele, F., and Davis, D.D., 2006c: Elevated Ozone in
600 the Boundary-Layer at South Pole, *Atmos. Environ*., submitted for publication.
601 Helmig, D., Johnson, B., Warshawsky, M., Morse, T., Eisele, F., and Davis, D.D., 2006d: Nitric Oxide in
602 the Boundary Layer at South Pole during the Antarctic Tropospheric Chemistry Investigation
603 (ANTCI), *Atmos. Environ*., submitted for publication.
604 Heuer, K., Tonnessen, K. A., and Ingersoll, G. P., 2000: Comparison of Precipitation Chemistry in the
605 Central Rocky Mountains, Colorado, USA. *Atmos. Envir.*, **34**, 1713-1722.
606 Hirano, T., 2005: Seasonal and Diurnal Variations in Topsoil and Subsoil Respiration under Snowpack in
607 a Temperate Deciduous Forest. *Global Biogeochem. Cycles*, **19**, GB2011,
608 doi:10.1029/2004GB002259.
609 Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B., and Campbell, B., 1999: Evidence of
610 NOx Production Within or Upon Ice Particles in the Greenland Snowpack. *Geophys. Res. Lett.*,
611 **26**, 695-698.
612 Honrath, R. E., Peterson, M. C., Dziobak, M. P., Dibb, J. E., Arsenault, M. A., and Green, S. A., 2000a:
613 Release of NOx From Sunlight-Irradiated Midlatitude Snow. *Geophys. Res. Lett.*, **27**(15), 2237-
614 2240.
615 Honrath, R. E., Guo, S., Peterson, M. C., Dziobak, M. P., Dibb, J. E., and Arsenault, M. A., 2000b:
616 Photochemical Production of Gas Phase NOx from Ice Crystal NO_3^-. *J. Geophys. Res.*, **105**,
617 24183-24190.
618 Honrath, R. E., Lu, Y., Peterson, M. C., Dibb, J. E., Arsenault, M. A., Cullen, N. J., and Steffen, K., 2002:
619 Vertical Fluxes of NOx, HONO, and HNO_3 Above the Snowpack at Summit, Greenland. *Atmos.*
620 *Envir.*, **36**, 2629-2640.
621 Hynes, R. G., Fernandez, M. A., and Cox, R. A., 2002: Uptake of HNO_3 on Water-Ice and Coadsorption
622 of HNO_3 and HCl in Temperature Range 210-235K. *J. Geophys. Res.*, **107**, 4797-4807.
623 Jacobi, H.-W., Bales, R. C., Honrath, R. E., Peterson, M. C., Dibb, J. E., Swanson, A. L., and Albert. M.
624 R., 2004: Reactive Trace Gases Measured in the Interstitial Air of Surface Snow at Summit,
625 Greenland. *Atmos. Envir.*, **38**, 1687-1697.
626 Jones, H.G.: The ecology of snow-covered systems: a brief overview of nutrient cycling and life in the
627 cold. *Hydrological Processes* **13**, 2135-2147.
628 Jones, A. E., Weller, R., Minikin, A., Wolff, E. W., Sturges, W. T., McIntyre, H. P., Leonard, S. R.,
629 Schrems, O., and Bauguitte, S., 1999: Oxidized Nitrogen Chemistry and Speciation in the
630 Antarctic Troposphere. *J. Geophys. Res.*, **104**, 21355-21366.

631 Jones, A. E., Weller, R., Wolf, E. W., and Jacobi, H-W., 2000: Speciation and Rate of Photochemical NO
632 and NO_2 Production in Antarctic Snow. *Geophys. Res. Lett.*, **27**, 345-348.
633 Jones, A. E., Weller, R., Anderson, P. S., Jacobi, H-W., Wolf, E. W., Schrems, O., and Miller, H, 2001:
634 Measurements of NOx Emissions From the Antarctic Snowpack. *Geophys. Res. Lett.*, **28**, 1499-
635 1502.
636 Jones, A.E., and Wolff, E.W., 2003: An Analysis of the Oxidation Potential of the South Pole Boundary
637 Layer and the Influence of Stratospheric Ozone Depletion. *J. Geophys. Res.*, 108, 4565,
638 doi:10.1029/2003JD003379.
639 Koop, T., Kapilashrami, A., Molina, L. T., and Molina, M. J., 2000: Phase Transitions of Sea-Salt/Water
640 Mixtures at Low Temperatures: Implications for Ozone Chemistry in the Polar Marine Boundary
641 Layer. *J. Geophys. Res.*, **105**, 26393-26402.
642 Losleben, M., and Pepin, N., 2000: Thermal Wind Frequency on the East Slope of the Colorado Front
643 Range. *Eos. Trans. AGU*, **81**(48), Fall Meeting Suppl., Abstract U22A-03.
644 Makkonen, L., 1997: Surface Melting of Ice. *J. Phys. Chem. B*, **101**, 6196-6200.
645 McDowell, N. G., Marshall, J. D., Hooker, T. D. and Musselman, R., 2000: Estimating CO_2 Flux from
646 Snowpacks at Three Sites in the Rocky Mountains. *Tree Physiol.*, **20**, 745-753.
647 Mossinger, J. C., Hynes, R. G., and Cox, R. A., 2002: Interaction of HOBr and HCl on Ice Surfaces in the
648 Temperature range 205-227K. *J. Geophys. Res.*, **107**, 4740-4753.
649 Nanus, L., Campbell, D. H., Ingersoll, G. P., Clow, D. W., and Mast, A., 2003: Atmospheric Deposition
650 Maps for the Rocky Mountains. *Atmos. Envir.*, **37**, 4881-4892.
651 Oncley, S. P., Buhr, M., Lenschow, D. H., Davis, D., and Semmer, S. R., 2004: Observations of
652 Summertime NO Fluxes and Boundary-Layer Height at the South Pole During ISCAT 2000
653 Using Scalar Similarities. *Atmos. Envir.*, **38**, 5389-5398.
654 Padro, J., 1996: Summary of Ozone Dry Deposition Velocity Measurements and Model Estimates over
655 Vineyard, Cotton, Grass and Deciduous Forest in Summer. *Atmos. Envir.*, **30**, 2363-2369.
656 Parrish, D. D., Hahn, C. H., Fahey, D. W., Williams, E. J., Bollinger, M. J., Hubler, G., Buhr, M. P.,
657 Murphy, P. C., Trainer, M., Hsie, E. Y., Liu, S. C., and Fehsenfeld, F. C., 1990: Systematic
658 Variations in the Concentration of NOx (NO + NO_2) at Niwot Ridge, CO. *J. Geophys. Res.*, **95**,
659 1817-1836.
660 Peterson, M. C., and Honrath, R. E., 2001: Observations of Rapid Photochemical Destruction of Ozone in
661 Snowpack Interstitial Air. *Geophys. Res. Letters*, **28**, 511-514.
662 Peterson, M. C., Barber, D., and Green, S., 2002: Monte Carlo Modeling and Measurements of Actinic
663 Flux Levels in Summit, Greenland Snowpack. *Atmos. Envir.*, **36**, 2545-2552.
664 Philips, G. J., and Simpson, W. R., 2005: Verification of Snowpack Radiation Transfer Models Using
665 Actinometry. *J. Geophys. Res.*, **110**, D08306, doi:10.1029/2004CD005552.
666 Powers, D., O'Neill, K., and Colbeck, S.C., 1985: Theory of Natural Convection in Snow. *J. Geophys.*
667 *Res*. **90**, 10,641-10,649.
668 Qiu, R. Green, S. A., Honrath, R. E., Peterson, M. C., Lu, Y., and Dziobak, M., 2002: Measurements of
669 J_{NO3}- in Snow by Nitrate-Based Actinometry. *Atmos. Envir.*, **36**, 2563-2572.
670 Ryzhkin, I. A. and Petrenko, V. F., 2002: Violation of Ice Rules near the Surface: a Theory for the Quasi-
671 Liquid Layer. *Phys. Rev. B*, **65**, doi:10.1103/PhysRevB.65.012205.
672 Shepson, P. B., Matrai, P., Barrie, L. A., and Bottenheim, J. W., 2003: Ocean-Atmosphere-Sea-Ice-
673 Snowpack Interactions in the Arctic, and Global Change. *Eos*, **84**, 349-355.
674 Sommerfeld, R. A., Mosier, A. R., and Musselman, R. C., 1993: CO_2, CH_4 and N_2O Flux Through a
675 Wyoming Snowpack and Implications for Global Budgets. *Nature*, **361**, 140-142.
676 Stanley, H. E., Buldyrev, S. V., Franzese, G., Giovambattista, N., and Starr, F. W., 2005: Static and
677 Dynamic Heterogeneities in Water. *Phil. Trans. R. Soc. A*, **363**, 509-523.

678 Sturm, M., and Johnson J.B., 1991: Natural Convection in the Subarctic Snow Cover. *J. Geophys. Res.*
679 **96**, 11,657-11,671.
680 Sumner, A. L. and Shepson, P. B., 1999: Snowpack Production of Formaldehyde and its Impact on the
681 Arctic Troposphere, *Nature*, **398**, 230-233.
682 Swanson, A.L., Lefer, B.L., Stroud V., and Atlas E., 2005: Trace gas emissions through a winter
683 snowpack in the subalpine ecosystem at Niwot Ridge, Colorado. *Geophys. Res. Let.* **32**,
684 doi:10.1029/2004GL21809.
685 Tagaki, K., Nomura, M., Ashiya, D., Takahashi, H., Sasa, K., Fujinuma, Y., Shibata, H., Akibayashi, Y.,
686 and Koike, T., 2005: Dynamic Carbon Dioxide Exchange Through Snowpack by Wind-Driven
687 Mass Transfer in a Conifer-Broadleaf Mixed Forest in Northernmost Japan. *Global Biogeochem.*
688 *Cycles*, **19**, GB2012, doi:10.1029/2004GB002272.
689 Takenaka, N., Daimon, T. Ueda, A., Sato, K., Kitano, M., Bandow, H, and Maeda, Y., 1998: Fast
690 Oxidation Reaction of Nitrite by Dissolved Oxygen in the Freezing Process in the Tropospheric
691 Aqueous Phase. *J. Atmos. Chem.*, **29**, 135-150.
692 Turk, J. T., Taylor, H. E, Ingersoll, G. P., Tonnessen, K. A., Clow, D. W., Alisa Mast, M., Campbell, D.
693 H., and Melack, J. M., 2001: Major-ion chemistry of the Rocky Mountain Snowpack, USA.
694 *Atmos. Envir.*, **35**, 3957-3966.
695 Wei, X. Miranda, P. B., and Shen, Y. R., 2001: Surface Vibrational Spectroscopic Study of Surface
696 Melting of Ice. *Phys. Rev. Lett.*, **86**, 1554-1557.
697 Wesely, M. L., and Hicks, B. B., 2000: A Review of the Current Status of Knowledge on Dry Deposition.
698 *Atmos. Envir.*, **34**, 2261-2282.
699 Williams, M. W., Bardsley, T., and Rikkers, M.,1998a: Oversampling of Snow and Overestimation of
700 Inorganic Nitrogen Wetfall Using NADP Data, Niwot Ridge, Colorado, *Atmospheric*
701 *Environment* **32**, 3827-3833.
702 Williams, M. W., Brooks, P.D., and Seastedt, T., 1998b: Nitrogen and Carbon Soil Dynamics in
703 Response to Climate Change in a High-Elevation Ecosystem in the Rocky Mountains, *Arctic and*
704 *Alpine Research* **30**, 25-29.
705 Zeller, K., and Hehn, T., 1994: Wintertime Anomalies in Ozone Deposition above a Subalpine Spruce-Fir
706 Forest. Research and Applications of Chemical Sciences in Forestry. Proceedings of the 4th
707 Southern Station Chemical Sciences Meeting. New Orleans, *General Technical Report,* **SO-104**,
708 131-138.
709 Zeller, K. F., and Hehn, T., 1995: Ozone Deposition in a Snow-Covered Subsapline Spruce-Fir Forest
710 Environment. *Biochemistry of Seasonally Snow-Covered Catchments.* Proceedings of a Boulder
711 Symposium, July 1995.
712 Zeller, K. F., and Hehn, T., 1996: Measurements of Upward Turbulent Ozone Fluxes above a Subalpine
713 Spruce-Fir Forest. *Geophys. Res. Lett.*, **23**, 841-844.
714 Zeller, K. F., 2000: Wintertime Ozone Fluxes and Profiles above a Subalpine Spruce-Fir Forest. *J. Appl.*
715 *Meteorol.*, **39**, 92-101.
716 Zhou, X., Beine, H. J., Honrath, R. E., Fuentes, J. D., Simpson, W., Shepson, W., and Bottenheim, J. W.,
717 2001: Snowpack Photochemical Production of HONO: a Major Source of OH in the arctic
718 Boundary Layer in Springtime. *Geophys. Res. Lett.*, **28**, 4087-4090.

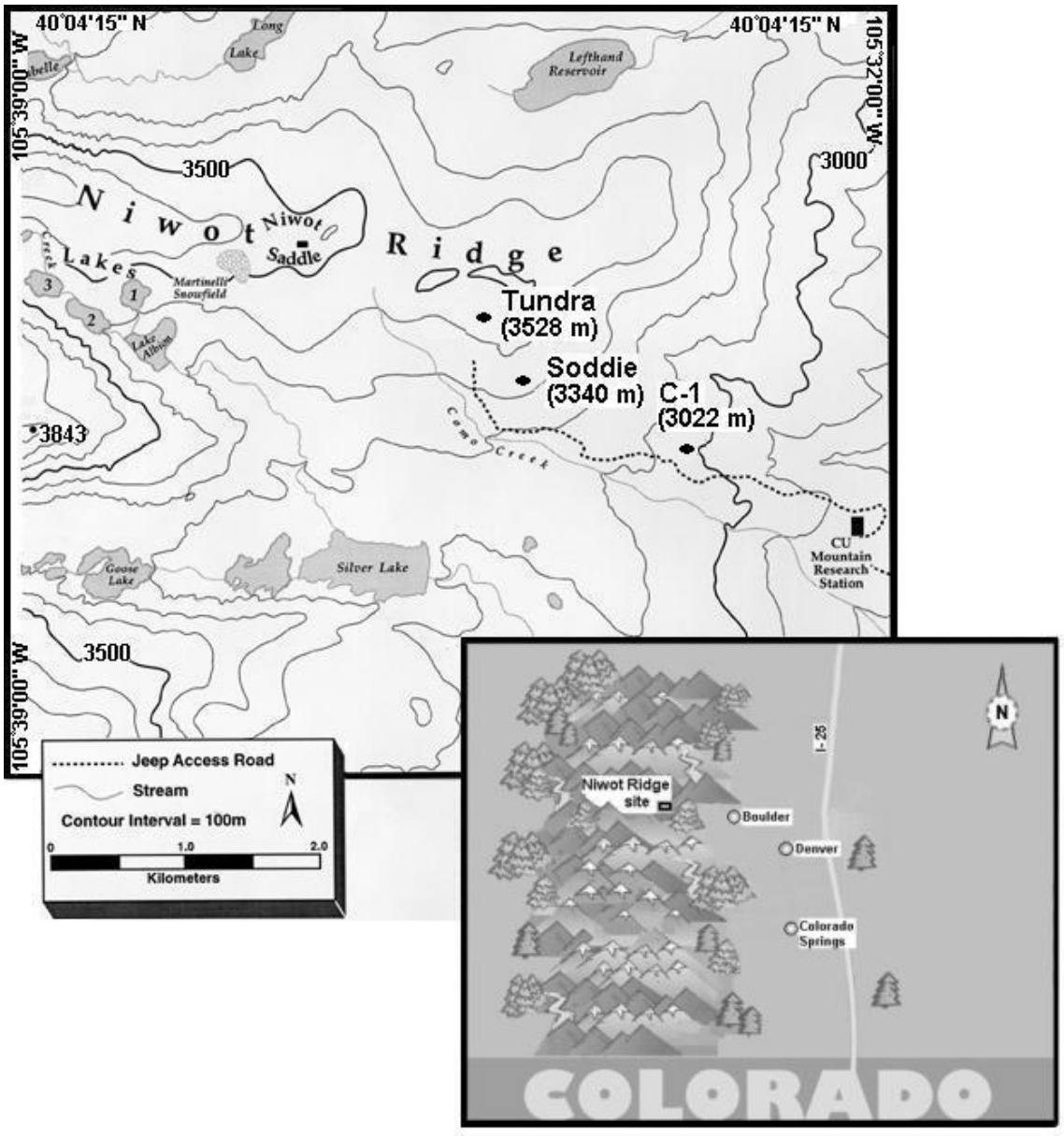
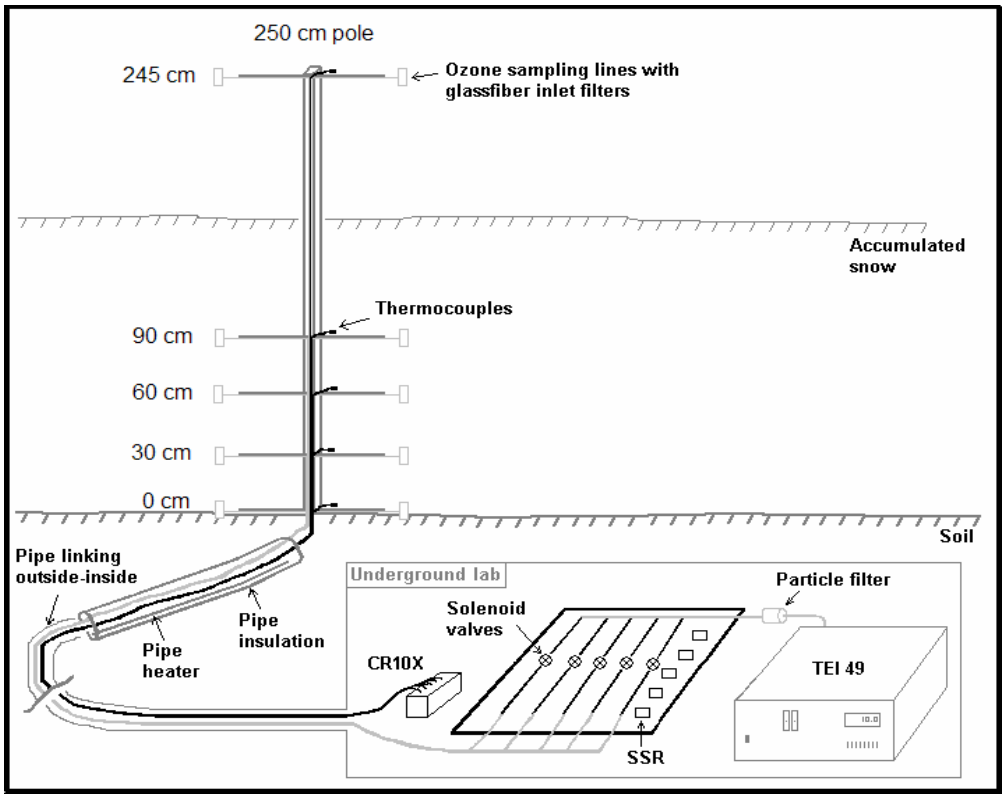


Figure 1

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 asl. Ozone data from continuous monitoring at the C-1 site (3022 m asl) and the Tundra lab site (3528 m asl) were used for comparison with the Soddie data (Niwot Ridge topographic map by Tom Davinroy, INSTAAR, University of Colorado at Boulder).



729

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

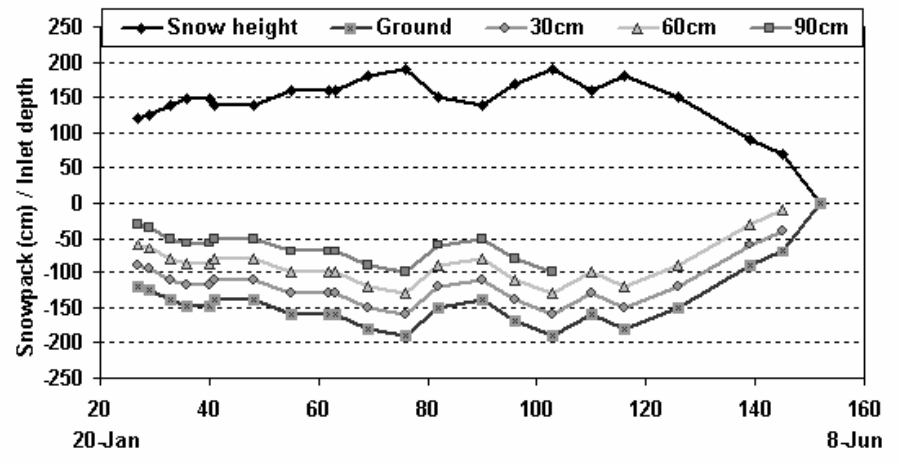


Figure 3

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 pair of 90-cm inlets were found at a height of ~ 40-50 cm after the snowmelt.

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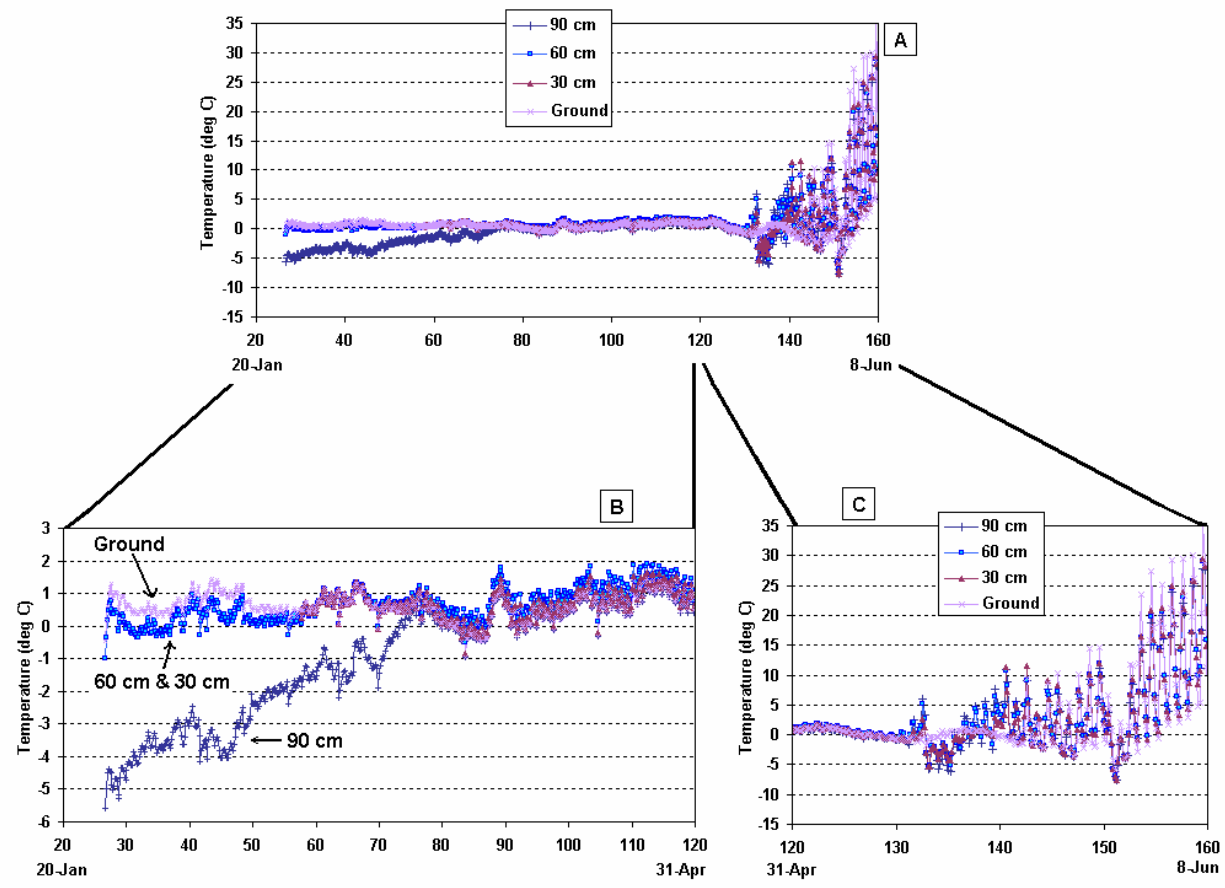

745

746 **Figure 4**
747 Snowpack temperatures at ground level, 30, 60 and 90 cm above ground for the entire experiment (A) with
748 enlargements of the period before (B) and during snowmelt (C). (Note that this figure is illustrated in color in the
749 online version of this manuscript.)
750

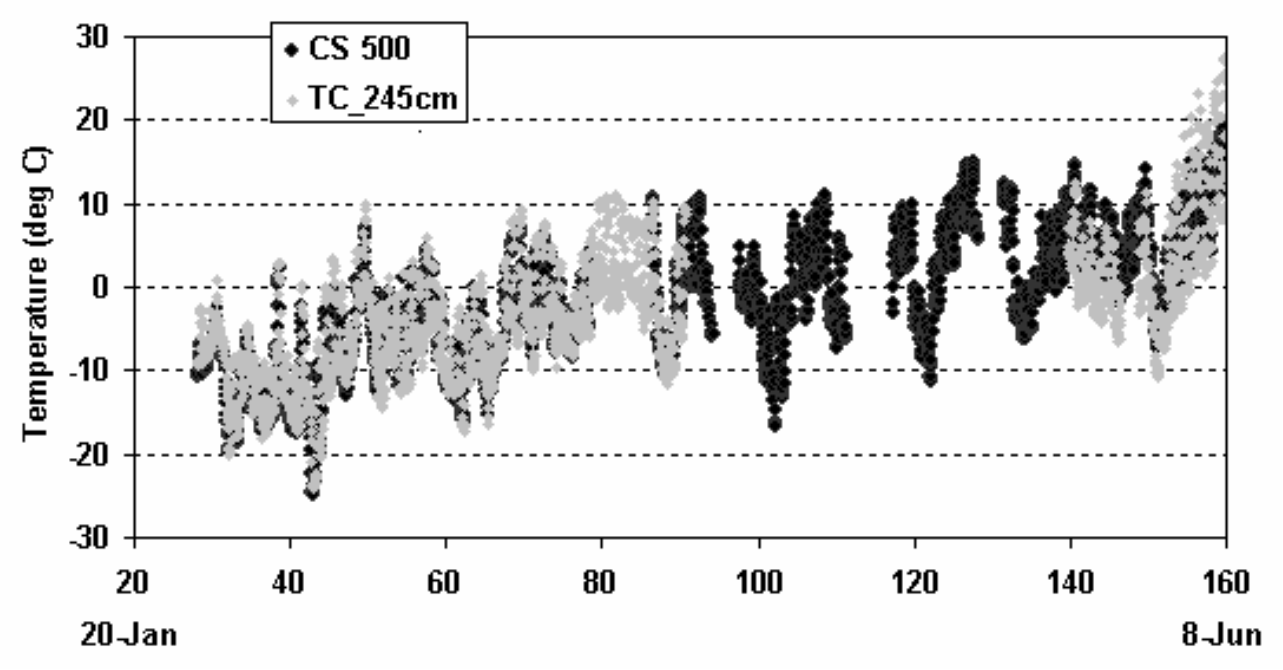

Figure 5
Comparison of temperature data from the thermocouple wire on the sampling tower (at 245 cm, remaining above the snowpack all the time) with the concurrent measurements from a nearby (~15 m) temperature/humidity probe (Campbell Scientific CS500 with radiation shield) on a met tower during 2004.

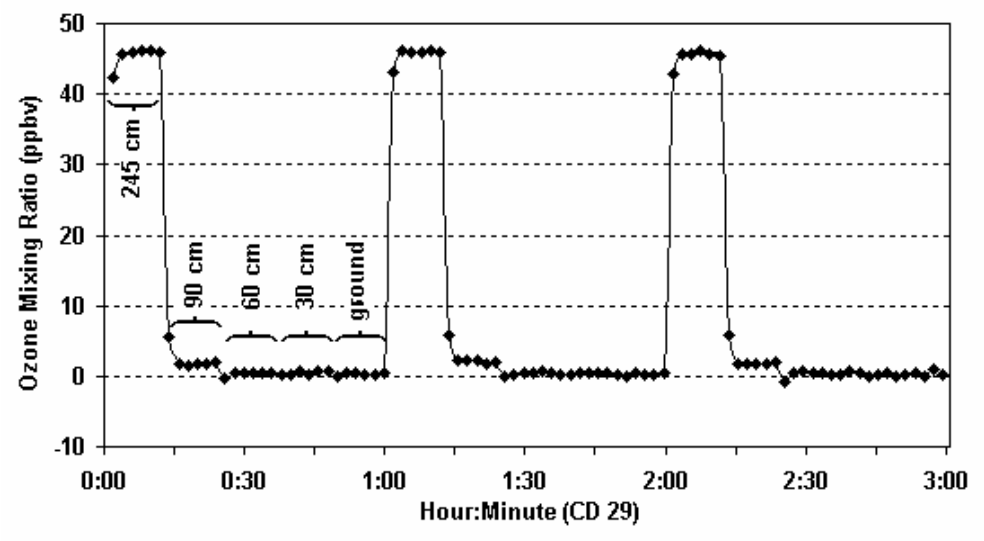

Figure 6

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.

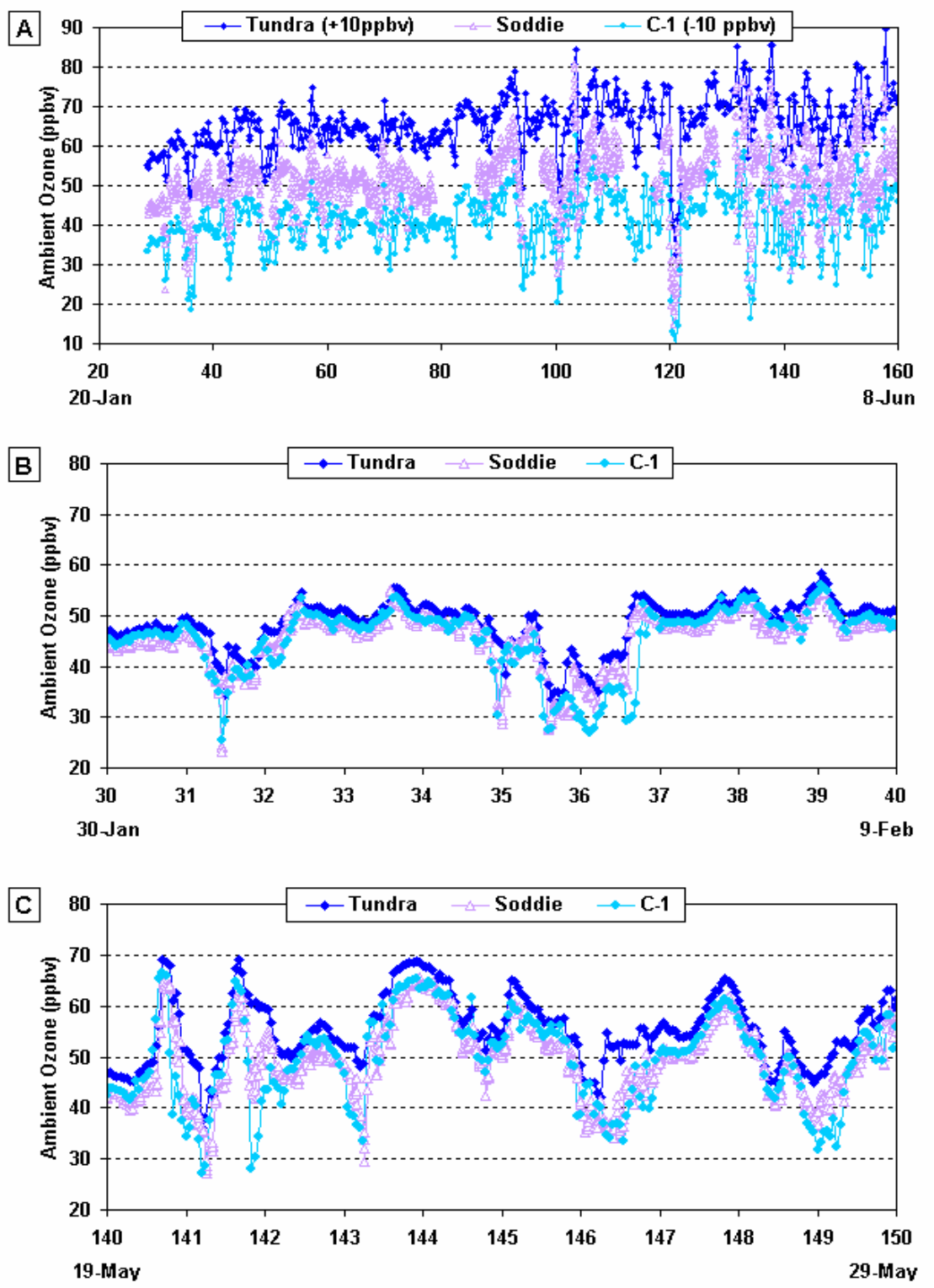

Figure 7

Comparison of ambient ozone measurements from the C-1, Soddie and Tundra lab sites for the entire period (A), as well as for 10 days during the early phase (B) and late phase of the year 2004 experiment (C). 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.)

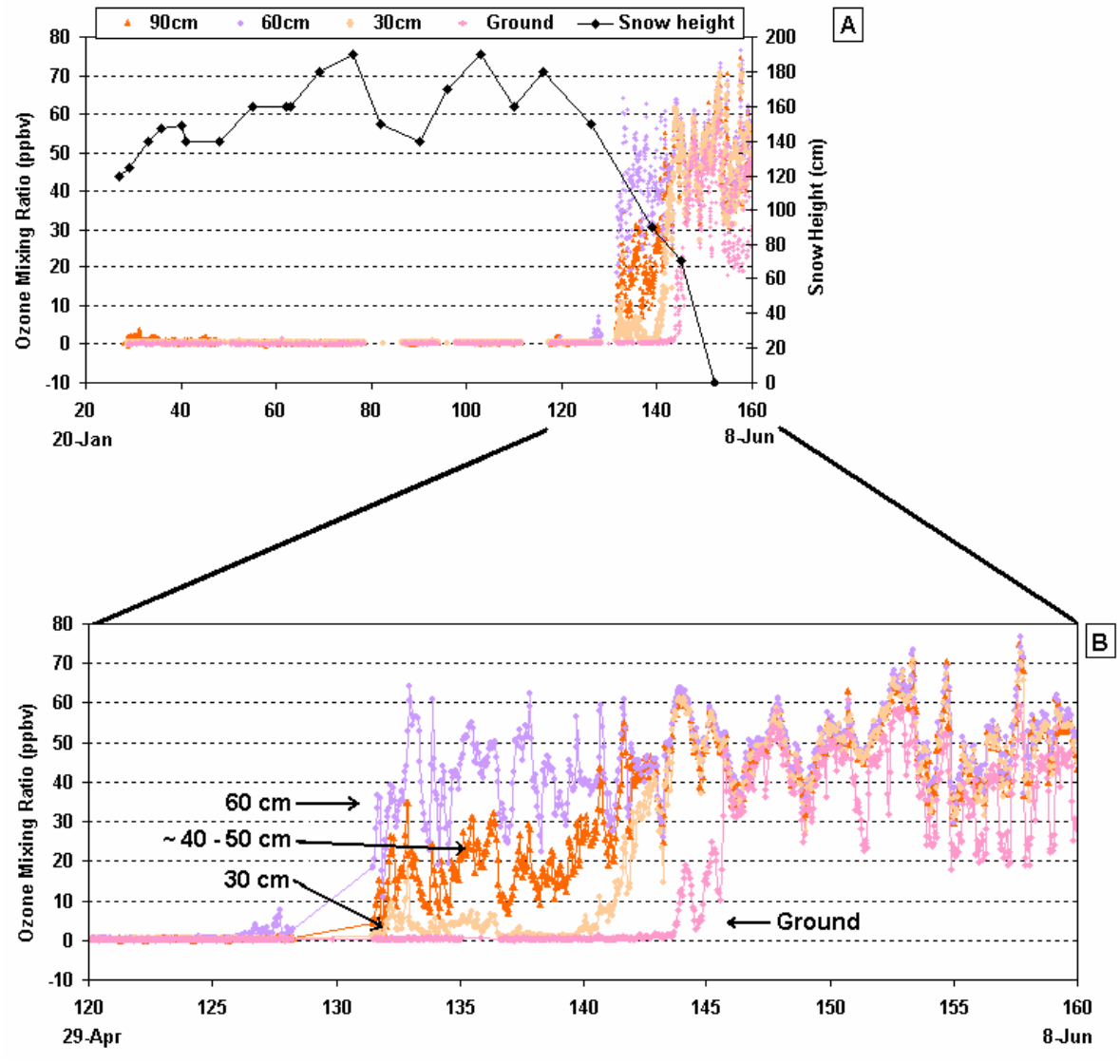

Figure 8

Ozone mixing ratio time series for the 4 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. Figure 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. Figure B shows the last 40 days of the experiment. From CD 127 to 160, first the 60-cm inlet pair was 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 this figure is illustrated in color in the online version of this manuscript.)

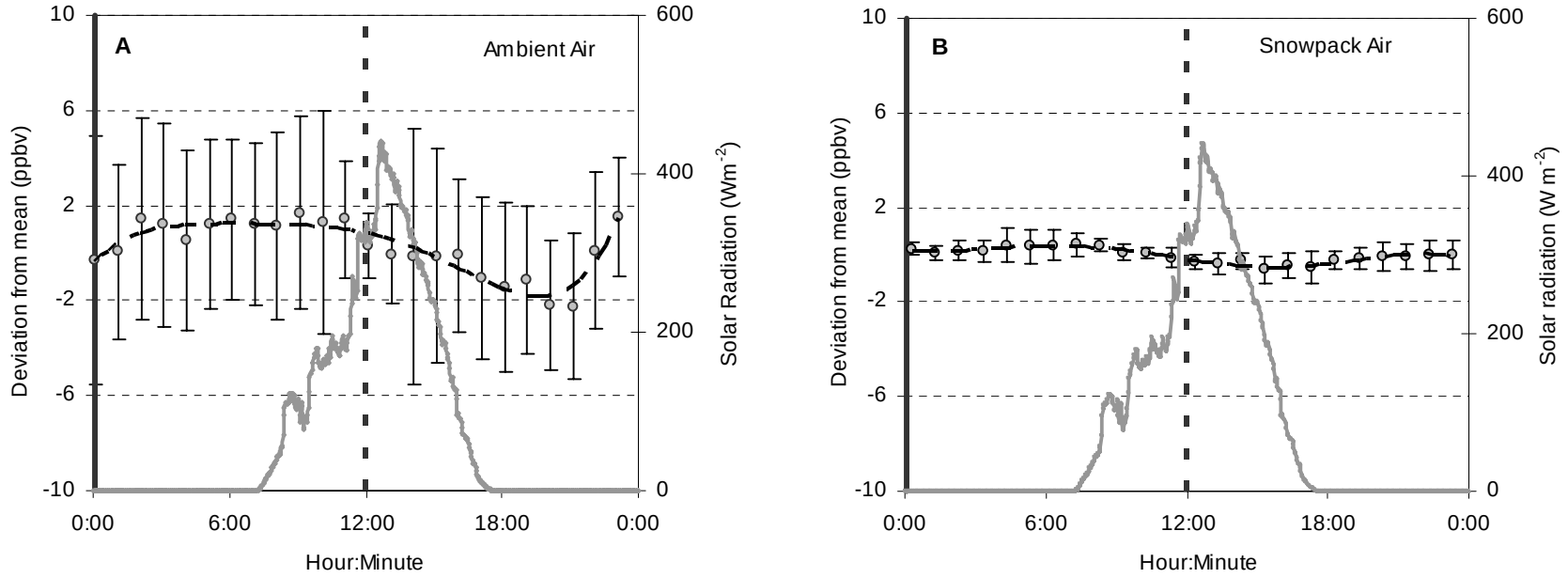

Figure 9

Mean diurnal change for ambient air ozone (left graph) and ozone in the snowpack (right graph) during the period CD 30-35 plotted against local time. Error bars represent the standard deviation over the mean, hourly data points for the 6-days. A 5th 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 grey data series. The ozone data are presented in the same format as results for Summit (see Figure 4, Helmig et al., 2006a).