Elevated Ozone in the Boundary-Layer at South Pole

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Abstract

Vertical profile measurements of ozone, water vapor, and meteorological conditions, as well as surface and tower measurements of these parameters during the 2003 Antarctic Tropospheric Chemistry Investigation (ANTCI) yielded their vertical (between the surface and 500 m) and temporal distribution in the boundary layer at South Pole during Dec. 13-30, 2003. Ozone in the surface and lower planetary boundary layer above South Pole was frequently enhanced over lower free tropospheric levels. During stable atmospheric conditions (which typically existed during low wind and fair sky conditions) ozone accumulated in the surface layer to reach up to twice its background concentration. These conditions were correlated with air transport from the N-SE sector, when air flowed downslope from the Antarctic plateau toward the South Pole. These data provide further insight into the impact resulting from highly elevated levels of nitrogen oxides (NO\(_x\)) that cause the vigorous photochemistry with resulting ozone production in the Antarctic surface layer.
**Key word index:** Antarctic plateau, tropospheric ozone, snowpack-atmosphere gas exchange, snow photochemistry, synoptic transport.

**Introduction**

Recent studies have revealed a previously unexpected air and snowpack chemistry in the polar environment (Domine and Shepson, 2002), and have pointed out an unusual photochemical situation at South Pole (SP) (Davis et al., 2001, 2004). Furthermore, the annual, reoccurring formation of the Antarctic stratospheric ozone hole has generated rather unnatural radiative and chemical conditions over the Antarctic continent. In 1991 Schnell et al. (1991) noted a decline in 1975-1990 surface ozone at SP and speculated that this change was driven by increased photochemical destruction of ozone in the lower troposphere caused by the increased penetration of ultraviolet radiation. Secondly, these authors noted an enhanced transport of ozone-poorer marine air to SP that may have influenced surface ozone levels. Newer analysis, incorporating later SP ozone data, have found increases in ozone during the past 15 years (Crawford et al., 2001; Jones and Wolff, 2003; Helmig et al., 2006a; Oltmans et al., 2006), which implies a surprising reversal of the earlier trend and poses questions about its interpretation.

Tropospheric ozone production and loss processes are intimately related to levels and conversion rates of nitrogen oxides. The release of the nitrogen oxide gases NO, NO$_2$, and HONO from sunlit snowpack (e.g. Dibb et al., 2002; Jones and Wolff, 2003; Davis et al., 2001, 2004; Oncley et al., 2004 and references therein) and resulting unexpected high ambient levels of NO that have been observed in ambient air at SP (Davis et al., 2001) have raised the question of how ozone is affected by the resulting photochemistry. Surface ozone at SP indeed shows anomalous features (Crawford et al., 2001; Jones and Wolff, 2003; Helmig et al., 2006a). The annual ozone cycle, with an expected minimum during the Antarctic summer months, is disturbed by the frequent occurrence of events with largely increased surface ozone levels.

The Antarctic Tropospheric Chemistry Investigation (ANTCI) during the 2003/2004 austral summer investigated linkages between snowpack photochemical processes, boundary-layer atmospheric chemistry, and transport across the Antarctic continent. The distributions of ozone and NO were studied by surface layer measurements, from a tethered balloon platform and by aircraft. The interpretation of these high resolution vertical and temporal ozone and meteoro-
logical data provide new evidence for linkages between the unique SP boundary layer stability conditions and snowpack and surface layer photochemistry that can result in the unexpected, surface layer ozone production during the Antarctic summer, suggested previously by Crawford et al. (2001) and Chen et al. (2004).

Experimental

Site Description: This experiment was conducted from Dec. 10–31, 2004 at the Amundson-Scott research station at SP. Conventions for directions at the SP identify “north” as the Greenwich meridian so that 90°E longitude becomes “east” and so forth. The tethered balloon launch site was ~300 m east from the geographic SP.

Surface Layer Ozone Measurements: Surface layer ozone was measured continuously with two UV absorption monitors (Thermo Electron Corporation Model 49C, Franklin, MA). One data set used in this analysis was from the SP station monitor, which is located in the Atmospheric Research Observatory (ARO) and collects air from an inlet on the roof of this building, at approximately 17 m above the snow surface. These data are collected at 10-second intervals and stored and reported as 5 minute and 1-hour averages. The second ozone monitor was operated in a small, temporary building near the tethered balloon launch site, approximately 150 m east of the ARO. Surface-layer air at the balloon launch site was sampled through a 10 m Teflon sampling line from an adjacent tower with an inlet at 2 m above the surface. During calendar day (CD) 350–357.2 an inlet on the roof of the balloon launch shelter (4 m above ground) was used. Both TEI instruments were calibrated against a laboratory reference instrument in the Boulder NOAA Earth System Research Laboratory. The estimated accuracy and precision of these two instruments are ~1 ppbv and 0.1 ppbv, respectively for averaged 5-min data.

Surface Layer Meteorological Measurements: Surface layer meteorological measurements were also made at the 2-m tower, 10 m west of the balloon launch site. Instruments mounted on this tower included a wind speed/wind direction cup anemometer with wind vane (Model 034B, Met One Instruments, Grants Pass, OR), an aspirated type E thermocouple for air temperature, and a incident solar radiation sensor (LI200X pyranometer, Campbell Scientific, Logan, UT). Data were recorded every second and averaged and stored in 1-min intervals. Atmospheric turbulence was measured with a 3D sonic anemometer (CSAT-3, Campbell) at 60 Hz and averaged to 20 Hz
data. Data analysis procedures for the sonic anemometer data were presented by Cohen et al. (2006).

**Tethered Balloon Platform:** Depending on wind conditions and payload two helium-filled SkyDoc tethered balloons (one 14-feet diameter two-ply and one 18-feet single ply, Floatograph Technologies, Marion, IN) (Helmig et al., 2002) were alternated for the vertical profile experiments. Balloon ascent and descent were controlled with a hydraulic winch. Two types of profile observations were conducted. Profiles with the lightweight, battery-operated instruments (ECC ozone, tethersonde) were done to a target altitude of 500 m. Ascent and descent rates typically were 0.2–0.3 m s\(^{-1}\), resulting in 1–1.5 hour duration experiments. The long sampling line experiments (see below) were performed to the height of the maximum length of the sampling line, i.e. ~120 m. Tethersonde and ECC-radiosonde combinations were deployed together with the long sampling line for concurrent meteorological and ECC ozone measurements. The instantaneous balloon geopotential height was calculated from the barometric pressure and temperature measurement of the radiosonde and tethersonde using the hypsometric relationship. All flight data, including launch time, apex time, touchdown time and maximum altitude are graphically displayed in Figure 1. Overall 64 profile flights were conducted, yielding a maximum of 178 vertical profile data sets (one flight typically yields two profiles, some parameters were measured with multiple instruments). The continuous data series from the two tower measurements are also displayed in this figure. Besides the tethered balloon vertical profiles, four ECC/radiosonde release balloons were launched from SP at times coinciding with tethered balloon profiles on CD 352.23, 357.27, 360.28, 363.28.

**Electrochemical Ozone Sondes:** EN-SCI Model 2Z (EN-SCI Corporation, Boulder, CO) electrochemical concentration cell (ECC) sondes were used for the vertical ozone profile measurements. These measurements and evaluation and intercomparison data are presented by Johnson et al. (2006, this issue). The ECC sondes were interfaced to RS-80 radiosondes (Vaisala, Helsinki, Finland) for remote data transfer.

**Vertical Profile Meteorological Measurements:** TSP-5A-SP Vaisala tethersondes were used for the measurement of meteorological conditions during the balloon profiling. Data were transmitted to a ground receiving station. The tethersonde measures temperature, relative humidity, wind
speed, wind direction and barometric pressure. The RS-80 radiosonde records temperature, relative humidity and barometric pressure.

Long Sampling Line Experiments: In a second series of experiments the surface layer was probed with a long sampling line with an air inlet that was mounted to the balloon. This tubing was made of PFA Teflon (0.78 cm o.d, 0.64 cm i.d., 135 m length, McCoy, Fort Collins, CO) with an PFA inlet funnel (Sallivex Corp., Minnetonka, MN) which housed a PTFE (polytetrafluoroethylene) membrane filter (Millipore Corp., Bellerica, MA). Prior to the field trip, this tubing was conditioned in the laboratory by purging it with 250 ppbv of ozone-enriched air for two days. The inlet was mounted to the tether line, approximately 6 m below the balloon. Air was pulled through the line continuously while the balloon raised and lowered the sampling line inlet to a maximum height of ~120 m. The surface end of this line ran into the balloon launch building and was connected to a sampling manifold that allowed sampling of air with either the TEI ozone monitor or an NO chemiluminescence instrument or both simultaneously. The sampling flow rate was determined by the sampling pumps of these two analyzers and was ~ 1.2 l min\(^{-1}\) (TEI) or 2.4 l min\(^{-1}\) (both instruments combined). Under these conditions the sample residence time in the sampling line was 4.2 min and 2.1 min, respectively. Between balloon flights a short sampling line (~10 m) and the long line inlet were placed side by side on the 2-m tower and sample air was alternated between these two inlets every 5 min. The ozone loss rate in the long line was determined by comparing these two data series. This loss rate fluctuated slightly over the nine days while this sampling line was used. A 6-hour running mean was calculated and applied for correcting all long sampling line data. The mean ozone loss rate in the long sampling line over the nine-day period was 1.9 +/- 0.8 %. A thorough intercomparison between the long sampling line data and concurrent ECC sonde measurements is presented by Johnson et al. (2006); further analytical details on the tethered balloon NO measurements are provided in Helmig et al. (2006b).

Balloon Data Analysis: Ascent balloon heights were calculated by the radiosonde change in pressure referenced to the average “before launch” pressure, while descent balloon height calculations were referenced to the surface pressure measured after completion of the descent profile. All raw data were averaged to 1-m height intervals. Missing data points (fewer than ~2 % of 1-m interval data) at selected heights were interpolated from adjacent height measurements. The temporal and spatial distribution of atmospheric stability was determined by calculating 5-m
interval bulk Richardson numbers using the vertical gradient temperature, wind speed and wind
direction data from 2 m above and below the reference height. The averaged balloon and the
time series surface data were combined for the color contour analysis plots.

Back Trajectories: The back trajectories to SP were computed from the NCEP/NCAR Reanalysis Data Set (Kalnay et al., 1996). The trajectory model (Harris et al., 2005) determines the vertical position of the air parcel explicitly using the vertical wind field in the analyzed data set (three-dimensional trajectories).

Results and Discussion

Surface Ozone

Data from the two continuous ozone surface measurements (ARO and balloon launch site) are shown in Figure 2. During the period of this experiment, surface ozone at SP showed large variations, between minima of 18 ppbv (CD 354) and maxima of 50 ppbv on CD 358. Both measurements, even though 130 m separated by distance and 15 m by height show excellent agreement, typically within 1 ppbv during the first phase. A striking feature of the observations is that during the later part of CD 354, a significant increase in surface ozone (almost doubling) of ozone was observed and that thereafter both measurements showed a 3-4 ppbv disagreement until ozone levels dropped back to below 30 ppbv on CD 359. Upon closer inspection it becomes apparent that generally high agreement between these two data series is seen at lower ozone levels and that the disagreement scales with the absolute ozone levels. The vertical balloon profile data, to be discussed in the following paragraphs, show that the differences in these two measurements do not stem from an analytical bias, but instead represent vertical ozone gradients in the shallow SP surface layer.

Vertical Ozone Profiles

The vertical ozone distribution at SP showed strong variations during Dec. 2003. Two examples that illustrate the extremes of these conditions are presented in Figure 3. On Dec. 24 a strong variability in ozone was seen in the lowest 500 m of the atmosphere. Near the surface, ozone mixing ratios were approaching 50 ppbv. Ozone concentrations declined steeply with altitude, dropping to 22 ppbv at 180 m. Several layers with 2-4 ppbv enhanced ozone were seen between 200 m and 500 m height. Data from the balloon ascent and descent show a high degree
of agreement, indicative that ozone profiles changed very little during the 58-min flight duration. It should be noted that due to the 25–30 s response time of the ECC sonde, the ozone readings are somewhat delayed causing a slight upwards/downwards shift of the ozone profile during ascent and descent, respectively (by ~10 m at the 0.3 m s\(^{-1}\) ascent/descent rate). Correcting for this effect would further improve the agreement between the ascent and descent ozone profiles. Ozone mixing ratios measured near the surface generally agreed within 1 ppbv with the concurrent ARO and tower observations (Fig. 2) (Johnson et al., 2006). Much different conditions were encountered two days later, as shown in the pair of profiles on the right in Figure 3. Ozone was homogenously distributed in the surface and boundary layer, showing less than a 2 ppbv gradient between the surface and 500 m. Again, both ascent and descent data follow each other closely and ozone data from the balloon instruments near the surface are in excellent agreement with the continuous surface measurements at this time (19–20 ppbv, Fig. 2).

The temporal behavior of the observed surface layer ozone gradient was investigated in another balloon experiment on Dec. 21 where the long sampling line was raised and ‘parked’ for three hours at 110 m. During this experiment ambient air was sampled from two lines/inlets alternated every 5 min and analyzed with the TEI monitor (Fig. 4). First, the short and long sampling line inlets were both near the surface (balloon line inlet at 2 m, short sampling line inlet at 4 m). Ozone in air from both inlets showed no discernable difference, both samples agreed within better than ~ 0.5 ppbv. Next, the long line inlet was raised with the balloon in 7 min to 110 m. Ozone in air collected from the balloon during the ascent dropped instantaneously from 45 ppbv to 40 ppbv. Over the next 3 three hours ozone at 110 m remained lower, approximately 5 ppbv below the surface readings. During this time surface ozone increased by 1 ppbv. Similarly, a slight increase in ozone at 110 m was observed; towards the end of this experiment, the gradient decreased slightly. After three hours the balloon was brought back down, and another, more rapid up and down profile (~25 min) was measured with continuous sampling through the long balloon sampling line. These data confirm the results from the previous intermittent sampling and that the ozone gradient between the surface and 110 m had declined to 3 ppbv.

**Vertical and Temporal Ozone Distribution**

The vertical and temporal (Dec. 13-31) distribution of ozone shown in the 3D contour plot in Figure 5 combines the data from all ECC sonde profiles, the continuous monitoring at the
ARO at 17 m, the continuous monitoring at the tethered balloon launch site (at 2/4 m) and from the long sampling line profile measurements. The results of this analysis reemphasize the conditions with enhanced and variable boundary layer ozone at SP. During most times ozone near the surface (e.g. in the 0-300 m layer) was elevated compared to air aloft. The observed gradients varied widely. During two isolated conditions with overall low ozone concentrations (CD 354, 361) ozone showed a homogenous distribution (also see Fig. 2). During all other times, ozone near the surface was enhanced, with gradients of typically 5–25 ppbv higher ozone near the surface. During a four-day period from CD 355–359, sustained conditions with 20-25 ppbv enhanced ozone in the surface layer were observed. The depth of this enhanced ozone layer varied from 60–200 m. In the following section we will analyze the meteorological and boundary layer conditions that fostered the ozone buildup in the SP surface layer.

**Boundary-Layer Conditions**

The contour plots of potential temperature (Fig. 5b), wind speed (Fig. 5c), and wind direction (Fig. 5d) illustrate the sustained, stable boundary layer conditions during the period with increased surface ozone. The potential temperature gradient between the surface and 300 m was on the order of 10°C during CD 355–359. These conditions were accompanied by low winds (< 2 m s⁻¹) from the surface to 500 m. The low wind speeds and lack of wind shear with altitude creates conditions with minimal vertical mixing. The water vapor partial pressure distribution (Fig. 5e) further underlines the strongly stratified conditions. The warmer air aloft remained much drier than surface air, indicating the lack of vertical mixing and, consequently, the lack of gas exchange throughout this period. Air within the lowest 50 m shows a positive water vapor gradient, which suggests drying of the lowest air layers possibility through condensation/freezeout of atmospheric water vapor to the surface, which during December remains ~10 degrees colder than the average air temperature at SP. The time series with the incident solar radiation data (Fig. 6) illustrate the clear sky conditions during this time. South Pole, lacking a diurnal solar cycle is expected to have no diurnal changes in incoming radiation. Deviations from this behavior in the data are from the slight distance of our measurement site from the geographic pole and a slight tilt of the radiation sensor (some of which has been corrected in the data analysis). Occasionally the balloon was casting a shadow on the sensor, causing a few, artificially lowered readings. Prior to and after the enhanced ozone episode, incident radiation fluctuated highly, with values ranging between 250–550 Wm⁻². These fluctuations were due to
the varying degree of cloud cover and height. In contrast, during the clear sky conditions on CD 355-359, incident radiation levels were much less variable, averaging about 460 W m$^{-2}$. It is well known, that over snow, due to the high reflection of radiation from the snowpack and backscatter from clouds, incoming radiation to the surface during times with overhead cloud cover can be significantly higher than during clear sky conditions. Conversely, clear-sky conditions over the snowpack lead to net radiative losses and stable stratification (Ambach, 1974), as observed during the period of maximum ozone production during CD 355-359.

The sonic anemometer turbulence data and soundings from a SODAR system (Neff et al., 2006) were used to develop a continuous record of mixed boundary layer depth. Mixed boundary layer heights fluctuated between 40-200 m during CD 347–354 and 359–365, but during the CD 354–359 period, an uninterrupted, shallow boundary layer height of 15–50 m was observed. The contour plot analysis of the bulk gradient Richardson number from the tethered balloon soundings further solidifies this analysis. Above a shallow, neutrally stable 20 m-deep surface layer, the atmosphere was consistently stable (Richardson numbers > 0.5) in both the temporal (CD 355–359) as well as the vertical (50–500 m) domain.

**Air Transport during Conditions with Ozone Enhancements**

On CD 354 surface ozone rose from 19 ppbv to 41 ppbv in 10 hours and to 44 ppbv after 22 hours. This increase (2.2 ppbv hr$^{-1}$) is larger than calculated ozone production rates for SP, which were estimated to be 0.09–0.15/0.25 ppbv hr$^{-1}$ (Crawford et al., 2001) and 0.13–0.2/0.27 ppbv and hr$^{-1}$ (Chen et al., 2004) (interquartile range/maximum), respectively (see more discussions on ozone production below). Thus, the rapid increase in ozone on CD 354 cannot be explained by local ozone production alone, but transport of air with elevated ozone to SP must be another determining factor. Surface wind data and trajectory analyses were used to investigate the air flows associated with the transitions and periods of enhanced ozone levels.

In Figure 7, the ozone record from the 17 m inlet on the ARO is plotted with the wind speed and wind direction data from the NOAA tower (at 13 m) and $u^*$ (from the sonic anemometer turbulence measurements). This figure also includes selected 10-day back trajectories from the NCEP reanalysis. It should be noted that the reanalysis data is coarse in resolution and may not reflect the flow within the shallow inversions that occur over the icepack. Rather, trajectories derived from the reanalysis data should be seen as indicating the synoptic-scale origins of air
above the surface inversion. A further limitation lies in the absence of a surface observing network over the high plateau that might give more insight into the origins of the air near the surface.

The wind speed and $u^*$ data further exemplify the strong correlation of high ozone with low wind speed and limited mixing, as already pointed out in the discussion above and by the data in Fig. 5. Prior to CD 354, winds were from the N to NW at wind speeds of 4-6 m s$^{-1}$. Back trajectories for this period (not shown) show a counterclockwise flow pattern, with air arriving at SP that had been transported over the center and N-NE part of the continent for the previous 1-10 days. During the time of rapid ozone increase on CD 354 the wind data reveal a distinct change in air flow and wind speed, as measured surface winds shifted from 320° to 90° and dropped from ~6 to 2 m s$^{-1}$. The back trajectory analyses for this transition period are inconclusive as they show only a small shift of NW flow prior to CD 354 to a somewhat more northeasterly and slower transport between CD 354.5–357.5. During the enhanced ozone period, winds remained calm with continuing easterly flow near the surface. Interestingly, during the tail end of the increased ozone period, while the wind direction shifted back from easterly to northerly winds and wind speeds increased gradually, ozone increased by another ~5 ppbv and remained elevated at this level for about a day. Here, the trajectories show that during CD 358 transport shifted for about one day from the previously prevailing northerly flow towards a circular pattern where air that reached SP had resided in the area to the SE of SP for 2-4 days. On CD 360.5 trajectories shift back towards the previously dominating northerly flow. Inspection of the rawinsonde data during this period reveals that the wind veers with height from easterly to northerly over the first 100 to 500 m: For this reason, the trajectory analysis should be treated with some caution because the reanalysis data may not reflect this fine structure in the boundary layer wind field.

The entire December 2003 wind direction and ozone records were used for a statistical analysis of the relationship between ozone and wind direction. Hourly ozone enhancement values were calculated by subtracting the inferred December ozone background (25.6 ppbv, Oltmans et al., 2006). Note that this inferred background ozone mixing ratio was derived from a smoothing analysis of the seasonal ozone cycle and that on occasion surface ozone levels at SP during December will be below this value. Results of this analysis in Figure 8 illustrate that in general significantly higher ozone levels were observed with air being transported from the NE to SE sector while winds from W-NW brought in air with much lower ozone. Air that was trans
ported upslope (with winds from the lower elevation sectors at W/NW) typically was below or right at the inferred seasonal ozone background level.

The contour map in Figure 9 shows how the landscape N to SE of SP is much more homogeneous, sloping gradually uphill for 500 km or 1000 km, respectively, whereas to the S, SW, W and NW the Antarctic terrain drops rapidly in altitude. The MBL wind speeds of 2 m s\(^{-1}\) that were observed during the ozone enhancement period would result in a horizontal transport distance of ~170 km per day, near the surface. At this wind speed, with the sustained stable conditions during CD 355–359, and with the flow patterns as indicated by the trajectories, air would have been transported over high-altitude (> 3000 m), relatively gently sloping snowpack for several days before it reached SP.

**Chemical Conditions that are Causing Ozone Enhancements**

A combination of a series of unique meteorological and chemical conditions have been shown to contribute towards the surprising ozone production in the Antarctic boundary layer. A critical and determining parameter are the enhanced NO levels that build up in the shallow surface layer above the cold Antarctic snowpack. Previous surface and tower gradient measurements have shown that NO originated from surface emissions and that surface layer concentrations were highest during times with low boundary layer depths (Davis et al., 2001, 2004). During ANTCI, measurements of NO were extended to higher in the atmosphere by vertical NO profile measurements from the tethered balloon (Helmig et al., 2006b) as well as by aircraft observations (Davis et al., 2006). Both experiments showed large increases of NO in the surface layer. During the stable conditions on CD 354–359, the balloon NO observations showed gradually increasing NO near the surface, with NO eventually exceeding 500 pptv on CD 356-357. Concentrations dropped rapidly with increasing height, typically to less than 1/5 at 50 m.

Collectively several factors are responsible for the buildup of high NO surface concentrations at SP (Davis et al., 2004). Twenty-four hour continuous radiation, stable atmospheric conditions, and accumulation resulting from surface-advected air parcels are critical for achieving high NO levels. Another important factor is the non-linear lifetime of NO\(_x\) (NO\(_x\) = NO + NO\(_2\)) as at higher NO\(_x\) levels (> 200 pptv) the NO\(_x\) lifetime increases steadily. This is due to the fact that above 200 pptv of NO\(_x\), NO\(_2\) reduces both the levels of OH and HO\(_2\), which define the major sinks for NO\(_x\), resulting in an overall increase in the NO\(_x\) lifetime (Davis et al., 2004). NO
to NO₂ conversion via reaction with is mostly facilitated by high levels of peroxy radicals (HO₂ and RO₂) which, in turn, are facilitated by H₂O₂, CH₂O and CH₄ oxidation. This conversion will subsequently result in ozone production as NO₂ + hν → NO + O, followed by O + O₂ → O₃. Similar to OH levels and NOₓ lifetime, ozone production is expected to have a non-linear dependence upon NO concentration, i.e. maximum production rates were calculated for NO mixing ratios in the 100–300 pptv range (Crawford et al., 2001; Chen et al., 2004). Given the very steep vertical NO gradients observed in the balloon profiles, ozone production is expected to be strongly dependent on the height above the surface, with highest production rates at a distinct height in the 0–50 m layer and with smaller production rates above and below (Helmig et al., 2006b).

Coincident with the ~25 ppbv increase in ozone on CD 355-356, surface NO rose from about 20 pptv to over 200 pptv. Sodar and balloon data show that during that time the mixing-layer depth decreased from over 150 m to less than 30 m. Of note was the fact that the enhanced ozone extended above 300 m whereas the NO enhancement was confined to the lowest few tens of meters. This observation suggests that the NO enhancement represents a short-term response to confining surface emissions into a thin boundary layer whereas the deeper ozone enhancement implicates a much longer history of transport and mixing. Using the maximum modeled ozone production rates a minimum time of 3-4 days would be required to generate 44 ppbv ozone from a 25 (seasonal background) or 19 ppbv (CD 354) starting level. While the meteorological data suggest a period of 5 days with sustained, sunny and stable boundary layer conditions during Dec. 2003, an inspection of records from other years has shown that most ozone enhancement episodes (which yield similar maximum ozone levels) are shorter, typically lasting 2-3 days. If this ozone production would occur locally, this comparison would suggest that actual ozone production rates are likely in the upper range of the modeled values (5-7 ppbv d⁻¹). Another possibility is that stable boundary layer conditions in regions upwind of SP prevail for longer periods than at SP itself and allow ozone levels to build up to these high levels that then are transported to SP and cause these sudden increases in surface ozone. However, sustained stable boundary layer conditions become less likely with increasing distance from the poles (Cohen et al., 2006; King et al., 2006), as the increasing diurnal radiation cycle drives diurnally changing sensible heat fluxes and stability regimes, which will cause increased boundary layer mixing (King et al., 2006). This suggests that this observed boundary layer ozone production will be
increasingly pronounced with decreasing distance to the SP. These arguments therefore point towards an efficient ozone production in the vicinity of SP, with net ozone production rates likely being in the upper range, or possibly even higher than the previously modeled data.

Note that here we have given only a brief summary of the most important conditions that are fostering enhanced ozone at SP as the focus of this manuscript is on the data and interpretations of the tethered balloon experiment. More in depth treatment of the SP oxidation chemistry has been presented in previous publications (Crawford et al., 2001; Davis et al., 2004, Chen et al., 2004); newer findings, including measurements from other concurrent experiments, are discussed in several other contributions to this special ANTCI issue (Helmig et al., 2006d; Davis et al., 2006; Wang et al., 2006).

**Upwards Ozone Fluxes?**

The frequent negative ozone gradients (higher ozone near the surface) are indicative of conditions where ozone will be transported upwards out of the height layer where maximum ozone production and buildup of ozone occurs. At SP (Helmig, unpublished results), at Summit (Helmig et al., 2006d) and in midlatitude seasonal snow (Bocquet et al., 2006), ozone concentrations in air pulled from within the snowpack were always lower than above the surface. Since ozone is destroyed in the snowpack, there must also be a downward ozone flux close to the surface. With the limited resolution of the ozone profile data near the surface and given the high uncertainty of published ozone deposition rates (Helmig et al., 2006e), it is not possible to accurately determine the exact height at which ozone fluxes diverge. However, the significant ozone enhancements seen at the inlet height (2 m) of the balloon building site compared to the 17-m inlet at the ARO, and the fact that ozone mixing ratios always declined with height above the ~2 m balloon launch reference height, suggests that the ozone flux divergence height should be below the 2-17 m range. Hence, positive (upwards) ozone fluxes are expected at heights close to the surface, likely upwards from no more than a few meters height.

Depending on the height of observation, these positive ozone fluxes may be interpreted as ozone coming out of the snow. Such a surprising phenomenon has previously been described for midlatitude sites in Wyoming (Zeller and Hehn, 1994, 1996; Zeller, 2000) and Australia (Galbally and Allison, 1972); but hitherto has lacked a plausible explanation. Interpretations of these earlier studies suggested that ozone may be stored and released out of the snowpack (Galbally
and Allison, 1972; Zeller and Hehn, 1994). However, as mentioned above, measurements of ozone in interstitial air, during most times, have shown much lower ozone in the snow than above the surface (Bocquet et al., 2006; Helmig et al., 2006d). Of course, while both environments share the condition of snow cover, there are a number of important differences between the polar and the midlatitude environments where these upwards ozone fluxes were reported. Most importantly, for the Wyoming and Australia studies are the presence of soil underneath the snow. Microbial activity in the soil underneath the snow has been shown to significantly contribute to gas exchange through the snow. Most likely, soil fluxes (including NO) are the determining process for gas fluxes through the snow surface in snow-covered, extra-polar environments. Additionally, it should be noted that snow-contaminant levels typically are several factors higher in midlatitudes than at polar locations, which provides a larger substrate for activation of gases by photochemistry (Bocquet et al., 2006 and references therein). Given the available observations and with our current understanding we speculate that NO\textsubscript{x} fluxes out of the seasonal snowpack are likely to be higher than in the polar environment. One recent study in the Colorado Rocky Mountains has also shown that volatile organic compounds within, and likely fluxes out of the snowpack, are significant (Swanson et al., 2005). Since, similar to SP, stable atmospheric conditions will also be enhanced over gently sloped and flat terrain with seasonal snowpack, and given the aforementioned sources of RO\textsubscript{2} and NO\textsubscript{x}, similar ozone production is expected for snow-covered, extra-polar environments during times of high actinic fluxes (daytime, sunny conditions). It is therefore possible that the aforementioned earlier observations of positive ozone fluxes (Zeller and Hehn, 1994, 1996; Zeller, 2000; Galbally and Allison, 1972) may have resulted from atmospheric, gas-phase ozone production in a shallow layer right above the snow surface. This ozone production will result in upward fluxes, which, during tower gradient flux measurements (as applied in the referenced literature), depending on the inlet height, may be interpreted as ozone being released out of the snowpack.

**Implications for SP Ozone Trends**

At SP ozone gradients up to 5 ppbv between the surface and the 17 m-high inlet of the ARO can be encountered. Hence, the inlet height will be of importance when comparing the SP ozone record, in particular summertime measurements, with data from other sites, or with older SP records where measurements were taken at a different height above the surface (note that from 1977 onward the SP surface ozone measurements were made at a comparable height to...
what they are now except for the variation associated with the drifting of the snow around the building).

Decadal time scale trends and variability have been evident in the Antarctic tropospheric circulation, particularly in the Austral spring during the period of maximum ozone loss in the stratosphere. It has been argued that photochemical ozone depletion in the stratosphere has caused a longer-lived polar vortex, an increasing strength of the Antarctic Oscillation (AAO) and colder temperatures over the Antarctic plateau (Thompson and Solomon, 2002). Lower surface winds and temperatures were observed at SP, following a long-term trend toward increased inversion strength in the 1990s (Neff, 1999), a period when the AAO was in its positive index state. Thus, increases in the AAO as reported by Thompson and Solomon (2002), if they continue, should lead to more frequent episodes of light winds and stagnation in the SP region. Our data show the strong dependency of ozone production on boundary layer stability. It is noteworthy that the increasing surface ozone trend in the 1990 to 2004 has exclusively resulted from an increase in ozone during November–January (Helmig et al., 2006a; Oltmans et al., 2006), when surface layer photochemical ozone production chemistry is expected to be most important. Therefore, we hypothesize that a stronger AAO, by fostering more stable boundary layer conditions, may have influenced ozone production in the surface layer and has contributed to the observed recent increases in the SP surface ozone record.

Comparison of SP with other Polar Sites

The ozone enhancements in the SP surface layer are unique compared to other polar research sites. For instance, at Summit, Greenland, ozone chemistry has been noted to be much different. Summit is at similar elevation and with similar year-round snowpack. However, being at 72°N Summit experiences significant diurnal radiation cycles. The snowpack remains at sub-freezing temperatures year-round, although is some 10-15 degrees warmer during the summer than at SP, with daytime snow surface temperatures regularly warming up to -10 to -5°C (Helmig et al., 2006d). Episodes with increased ozone at Summit are related to transport events (Helmig et al., 2002; 2006c) with a frequent occurrence of transport from the higher troposphere/lower stratosphere as well as occasional upslope flow with polluted air from lower latitudes (Helmig et al., 2006c). Our ANTCI data and earlier studies (Crawford et al., 2001) have shown that high ozone at SP originates near the surface and is not transported from higher alti-
tudes (Oltmans and Komhyr, 1976). Furthermore, there is no indication for polluted, anthropoge-
nically-influenced air reaching SP. Summit, in contrast to SP, during summer is subject to
substantial diurnal radiation and temperature cycles and the MBL is much more dynamic; e.g.
stability regimes change frequently and are inhomogeneous with altitude (Cohen et al., 2006).
Snowpack temperatures at Summit are higher and surface heating during sunny daytime condi-
tions results in convective heating, which contributes to boundary layer growth and increased
vertical mixing. Stable atmospheric conditions at Summit mostly occur during night, when there
is very little sunlight to drive photochemistry. Air reaching Summit is mostly representative of
NH, lower tropospheric composition, rather than being transported upslope over the Greenland
glacial ice shield. Consequently, the effective footprint and residence time of air in contact with
the snow surface on average is much shorter and sustained residence of air in a shallow surface
layer, as at SP, is not encountered at Summit. Under the found at Summit, NO concentrations
and ozone production in the surface layer do not build up to the high levels observed at SP
(Davis et al., 2004).

Conclusions

Enhanced ozone concentrations are a frequent phenomenon in the summertime surface
and lower boundary layer at SP. Ozone is predominantly produced and transported from the
high altitude Antarctic plateau in the area surrounding SP from the N to SE. Ozone production
occurs by photochemical processes in a shallow surface layer, 20-200 m deep, during stable,
light wind, strongly stratified boundary layer conditions.

These experiments show that strong vertical ozone gradients which result from a buildup
of ozone in the surface layer are a common, summertime condition at SP. Our data further illust-
rate that even between the surface and the 17 m-high inlet of the ARO observatory up to 5 ppbv
ozone gradients can be encountered. Hence, the inlet height for the station ozone measurements
will affect and will be of importance when evaluating and comparing the SP ozone record with
data from other sites. Previously reported upwards ozone fluxes out of snow in other environ-
ments may have resulted from similar conditions of photochemical ozone production in a shal-
low atmospheric layer above the snow surface.

These new observations solidify the previous analyses and estimates of summertime
ozone production chemistry at SP. Our measurements point towards ozone production rates that
are in the upper range of previous calculations. These data provide new evidence that polar
surface ozone concentrations are tied to photochemical processes in the sunlit snowpack, chemi-
cal reactions in the atmospheric surface layer and boundary layer dynamics.

These comparisons denote the remarkable conditions at SP. In contrast to the pre-ISCAT
understanding, it is likely that the lower boundary layer of large areas of Antarctica should be
considered a spring-summertime source of surface ozone as has been shown in the 3-D modeling
results of Wang et al. (2006). The Antarctic plateau represents a unique situation on this planet,
where, the combination of snowpack emissions, the sustained prevalence of stable boundary
layer conditions, and the presence of 24-hour unmodulated sunlight will be found. The resulting
conditions of sustained and vigorous ozone production chemistry that occur above the snowpack
at SP have hitherto not been reported from any other polar or clean-air environment on Earth.
Natural ozone production in the lower troposphere has been known to occur mostly in air af-
fected by biomass burning plumes and in areas that are subjected to high NOx levels from light-
ning. SP surface chemistry can be added to the list of natural systems that causes significant
ozone production in an environment that is virtually devoid of human impacts.

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Guard for providing excellent logistical support and the South Pole staff for an extraordinary
effort in accommodating the tethered balloon experiment.
Figure 1
Distribution of tethered balloon profiles during the December 2003 profiling experiment at South Pole. Balloon apex height is plotted against calendar day 2003 (Dec. 13–31). High profiles (to ~500 m) were conducted using the balloon-borne radiosonde instruments (ECC, tethersonde), profiles to ~100 m were done with the long Teflon sampling line attached to the balloon. The launch times of ECC release sondes and the continuous data from the surface monitoring are also illustrated.
Ozone during calendar day 2003 measured from the roof (~17 m) of the ARO building (hourly mean data, black solid line) in comparison to surface ozone (1-min data) measured from the roof (~4 m above the surface, CD 350.0 – 357.2) and a 2-m tower inlet (CD 348 – 350, 357.2 – 364) adjacent of the balloon launch shelter.

Two examples of vertical ozone distribution at South Pole during December 2003. The profiles on the left were measured on December 24 (launch time CD 358.82, flight duration 57 min). The profile on the right was obtained on Dec. 26 (launch time CD 360.89, flight duration 47 min).
Figure 4

Approximately 4 hours of ozone measurements from two surface inlets and from ~110 m. First, two inlet lines were sampled side-by-side near the surface. Next the long sampling line inlet was lifted to 110 m and air was alternated between the raised balloon inlet and the tower inlet every 5 min. After 3 hours, the balloon was brought back to the surface, equipped with a new pressure sensor and another vertical profile was measured with continuous sampling from the balloon inlet.
Figure 5
Ozone (A), potential temperature (B), wind speed (C), wind direction (D) and water vapor partial pressure (E) at South Pole (in ppbv) between the surface and 500 m during Calendar Day 2003 (December 13–30) with data from all available balloon (up to 179 vertical profile data series) and surface measurements. The black dots indicate the distribution of data points that went into this contour plot analysis.
Figure 6

Incoming solar radiation at South Pole during calendar day 2003 measured adjacent to the balloon launch site. Shading by the balloon caused a few occasional artificially reduced radiation readings.
Figure 7
Ozone (ARO at 17 m), wind speed and wind direction (NOAA tower at 13 m), and $u^*$ (from turbulence eddy correlation measurements at 2 m near the balloon launch site) during calendar day 2003 at SP. 10-day back trajectories during four selected times and at 36 hours spacing (356.0; 357.5, 359.0; 360.5), and as indicated by the arrows, are shown in the upper part of the figure. Numbers along the trajectories indicate transport time in days.
Figure 8
Ozone enhancement in the SP surface layer ([25.6 ppbv] (Oltmans et al., 2006)) with mean and standard deviation for 10 degree wind sectors. The frequency of the occurrence of wind direction from the 10 degree sectors during December 2003 is also indicated.

Figure 9
Location of South Pole with wind direction sectors and elevation contours on the Antarctic continent. Black dots indicate location of other Antarctic research sites.
References


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