

Response to Anonymous Referee #1

This manuscript focuses on the factors (mainly dynamical, with some attention to chemical processes) that contribute to large, but variable, mixing ratios of NO at South Pole (SP) during the spring to summer transition. Previously unpublished measurements of NO and NO₂ during the 2006-2007 field season are presented and discussed in context of observations made in 3 earlier campaigns (1998/99, 2000/01, and 2003/04 seasons). Several previous papers by this team have established that the surprisingly high levels of NO sometimes seen at SP are sustained by snow to air flux of NO produced by photolysis of nitrate in the snow, building up when low boundary layer height (BLH) limits vertical mixing. Low BLH resulted from low wind speeds and clear skies, with the latter also enhancing the rate of nitrate photolysis. Intervals with low BLH generally coincided with easterly winds, leading to a suggestion that some of the NO during extreme events was transported down slope to SP, with extensive recycling of redeposited nitric and pernitric acids combined with non-linear NO_x chemistry resulting in mixing ratios approaching and even exceeding 1 ppbv.

The addition of the 2006 results confirms earlier findings but does not produce any fundamental new understanding.

Response: We feel the value of 2006 data lies in the comparison of the behavior of NO over a greater portion of the seasonal cycle. These data are also useful to compare and contrast 2003 and 2006 which are similar in many aspects of their meteorology but quite different from 1998 and 2000. In addition, we now note the differences in snow accumulation rate between 2003 (lower) and 2006 (higher). Earlier papers did not examine year-to-year variability and effects on NO. In addition, the step-wise linear regression in Table A4 shows that the dominant parameters for NO vary from year to year reflecting the variability in weather regimes affecting NO at the SP. Thus, the new finding we show is that not only many variables are important but that their relative importance varies from year-to-year.

However, this manuscript does extend prior papers by exploring the links between BL dynamics at SP and synoptic and mesoscale dynamics in the upper troposphere and even into the stratosphere over Antarctica. In my opinion the key findings are that high NO at SP are most likely to occur when the flow at 300 hPa is from SE, which is found to correlate with relatively weak surface winds from the E-S quadrant and generally clear skies, factors leading to low BLH. It is also pointed out that the south-easterly flow at the surface is due to large scale pressure gradients, and not katabatic flow as had earlier been suggested.

These findings are significant enough to merit publication, but I find the manuscript overly long, repetitive at times, and hence not as accessible as it could be.

Response: Because the paper evolved over a period of time we admit there was repetition which we have hopefully reduced. As far as the length, Doug Davis and I were originally considering two papers. However, with his untimely passing, I and the other co-authors decided it was best to complete and include as much of his material as was feasible in just one paper. We appreciate the detailed reading of the manuscript and very useful comments that this reviewer provided.

In particular, I find that a lot (too much) of the discussion relies on figures in the supplemental

material, and that graphical or tabular comparisons of NO in the 4 different seasons are never provided in the main body of the manuscript. Figure S10 does provide such an overview, but I suggest it would work better as a 4 panel plot (one panel for each season) and should be moved out of the supplement to someplace early in the main text. Current version of sections 2.1 and 2.2 go into great detail about meteorological similarities and differences across the 4 sampling seasons, but rarely relate these to observed NO concentrations at SP (which seems like it should be the main point of paper). Referring (probably often) to a revised figure S10 put into section 2 would help.

Response: We appreciate this suggestion and have now included a new figure and table near the beginning of the paper that summarize the four seasons of data and highlight the differences between the observing periods. This now allows us to motivate the discussion of the meteorology in subsequent sections.

Similarly, Fig 2 would be improved by adding some kind of NO metric (e.g., season mean, or fraction of sampling hours > than some threshold (250 pptv is used elsewhere)), and the heavy black line showing average NO as function of surface wind direction in Fig 3 now averages all 4 seasons, unnecessarily obscuring interannual variations which are important and interesting.

Response: A summary of NO metrics are now included in Table1. Fig. 3 has now been revised to show individual years in terms of average NO and wind direction distributions in a two-panel display.

In the following list of detailed comments I mix purely editorial suggestions (typos, etc.) with comments related to streamlining the narrative by reducing redundancy and interesting side stories. Comments are linked to line numbers in the on-line pdf, hope these are conserved across different platforms.

Response: We very much appreciate the time and effort that this reviewer put into their review and suggestions below. They have been most helpful!

69-73 Would help to indicate the length of these weather cycles. Seems the timescales are a few days of clouds, then a few with clear skies and strong inversion based on case studies presented much later, but here the reader could assume you mean seasonal changes.

Response: Text added: "These changes occur over normal synoptic time scales of a few days and over planetary wave time scales of 10-60 days (e.g. Yasunari and Kodama 1993)."

73 I would argue that high albedo and low SZA are characteristic of most of Antarctic plateau. What is "unique" about SP is that the SZA barely changes within 24 hour day. Later on it seems the SZA is felt to be significantly lower at SP than at 75 or 80 S, but is that true averaged over a full day? Might help just to be quantitative about meaning of "low" SZA.

**Response: New text has been added:
"A detailed study of the surface energy budget and boundary layer evolution at Concordia Station (King et al., 2006) shows a convective boundary layer and positive net radiation lasting eight hours (averaged over December**

and January). This convective period developed when the solar elevation angle was greater than 25°, in contrast to the lack of thermal convection at the SP where the maximum solar elevation angle is always less than 23.5°. Frey et al. (2015) show a specific example for 9 January at Concordia when a stable boundary layer forms with large increases in NO shortly after 1800 LT when the solar elevation angle decreases to less than 20°. Similarly King et al. (2006) show a sodar record from 28 January with a stable boundary layer until 0800 and after 1730 LT when solar elevation angle less than ~22°. For these reasons air masses arriving over long distances at the SP are likely to have encountered some convective mixing enroute and may need to be considered in future model simulations of surface chemistry.”

78 “omnipresent” seems an odd description of the inversion, given you just said the really stable boundary layer reforms every weather cycle.

This text has been eliminated. One confusion lies in the distinction between a “temperature inversion” and a “stable boundary layer.” Often a very shallow stable boundary layer will form within a deeper inversion layer as might be seen in a rawinsonde temperature profile. It is only in this sublayer that vertical mixing would occur. Also, at times a very shallow convective layer can form within a deeper “inversion layer.” This typically occurs when colder air passes over a previously ‘warmed’ surface: the equilibrium state is often one with an isothermal layer with a capping inversion (Neff, 1980).

87-88 words missing here, like “Antarctica” or the Antarctic ice sheet. Does not make sense to describe storm track as pole centric, or covering so many

Response: text removed as part of the restructuring of Section 2.

95-96 Does not seem the semi-annual oscillation or the circumpolar trough are ever mentioned again, so why introduce the terms here? Are they controlling NO at SP?

Response: new text added: “Although there can be significant year-to-year variability in storminess, October can be the period of greatest snow accumulation (as measured in the stake field at the SP). The average accumulation in October from 1990 to 2015 is 3 cm whereas in November it is 1.5 cm (amrc.ssec.wisc.edu/pub/southpole/climatology). During that 25-year period, 2003 was one of the four highest accumulation years. In 2003, the snow depth increased by 6 cm in October whereas in November it decreased by 1 cm. In our other experiment years the accumulation ranged from 1.5 cm (2006) to 4.0 cm (2000) in November. The accumulation rate may be important to the fate of nitrate in the snow (e.g. Mulvaney et al. 1998) as well as the exposure of nitrate in the skin layer to photolysis and recycling (e.g. Frey et al. 2015)..”

98-100 Another interesting tidbit about large scale flow in winter that seems to have nothing to do with NO at SP in Spring/Summer

Response: Text deleted. The point was that with warm advection, clouds and higher temperatures occur (as observed in both winter and summer) with the attendant increase in boundary layer depth which is associated with low NO.

103-104 Is it fair to compare one 135 degree sector to another that is only 90 degrees? I also note that if wind direction was completely uniformly distributed the larger sector would account for 37.5% and the W to N quadrant 25%, making the quoted 43 and 31% fractions observed only slightly enhanced. Figure 1 makes the point, so consider

deleting this sentence.

Done – as pointed out by this reviewer Fig. 1 says it all with peaks in the distribution 180° apart. Wind roses have now been added in the supplemental material to provide more detail.

109-113 These last 2 sentences repeat ideas introduced earlier (in this paragraph, also in first paragraph of section 2, and in earlier papers). It is also odd to be making predictive statements about how NO should respond, rather than point to data that confirms the points discussed. Granted, the 2006 results have not yet been show, but the other 3 campaigns are published.

Response: Text removed.

114-121 Perhaps unnecessary detail, the correlation is interesting and useful for chemists on its own.

Response: We felt this was appropriate for Supplemental Material because the figure shows how synoptic pressure patterns extending over the Plateau affect surface flows which are important to boundary layer chemistry.

121 can, however, vary—! Varies

Response: corrected

124 mention 1999 and 2002 and say they coincide with a single year with sudden strat warming. Which one had the warming?

Response: 2002 is now indicated as the year with sudden stratospheric warming (in September).

125 Any decadal periodicity is not at all obvious in Fig 2. Even if it is there, is it important to understanding any differences between the 4 years (spread over 9 years) with observations at SP.

Response: The data are now shown with a five-year smoothing. As now noted in the text, 2002 was eliminated based on the unusual breakup of the vortex that spring and its potential impact on the troposphere (e.g. Charlton et al 2005). The semi-decadal variability is important for putting any particular year in a longer term context. Reference is now made to Neff (1999) for a past study of decadal variability (in that paper the focus was on decadal variability in cloud fraction).

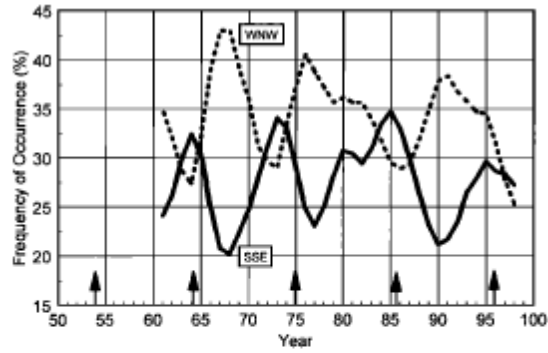


Figure 11. Frequency of occurrence (FOO) (in percent) of upper level winds from south-southeast (SSE) (summed over 90° , solid line), west-northwest (WNW) (summed over 90° , short-dashed line), together with the minima in the 10.7-cm solar radio flux (arrows) estimated from data obtained at ftp://ftp.ngdc.noaa.gov/STP/SOLARDATA/SOLAR_RADIO/FLUX.

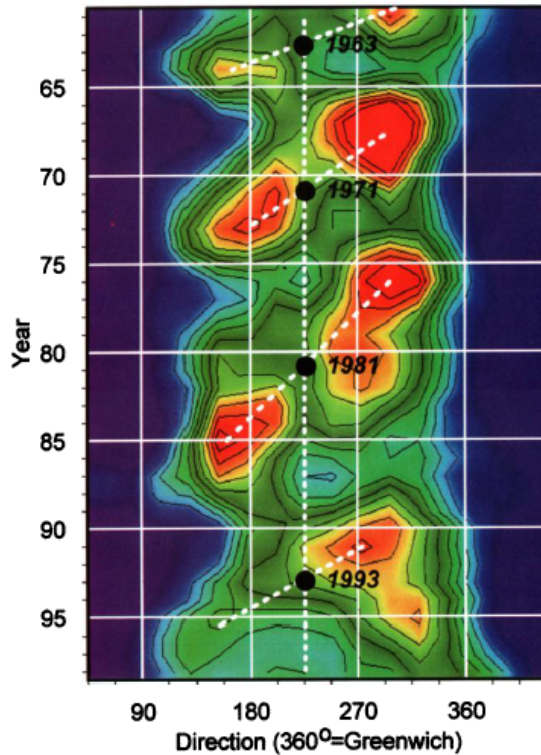


Plate 7. Frequency of occurrence (percent in each 22.5° class interval, 0.5% contour intervals from 5% to 10%) of upper level winds for the spring period shown in Plate 5. Upper level (~ 300 hPa) winds were sorted by year and by 22.5° class intervals and then smoothed with a 5-year tapered interseasonal filter and a three-point tapered class interval filter. Class intervals were centered on the directions beginning at 0° . The band of directions from 180° to 270° corresponds to the direction of maximum warm advection (Figure 7). Comparing these results with those in Plate 5 reveals that periods of maximum (minimum) cloudiness occur during maximum (minimum) frequency of occurrence of winds from this direction. Dashed lines and labels indicate the times of transition through 225° . Missing rawinsonde data from 1957 through 1960 make the first time of transition uncertain by a few years.

129-130 Is it really a new finding that NO at SP is not tightly controlled by any single parameter? Seems this has been noted in earlier papers.

Response: Earlier papers did not examine year-to-year variability and effects on NO. In addition, the step-wise linear regression in Table A4 shows that the dominant parameters for NO vary from year to year reflecting the variability in weather regimes affecting NO at the SP. Thus, the new finding we show is that not only many variables are important but that their relative importance varies from year-to-year. This has been added to the Introduction: *“However, earlier work did not examine year-to-year meteorological variability and effects on NO. In addition, the step-wise linear regression that we show later demonstrates that the dominant parameters for NO vary from year to year reflecting the variability in weather regimes affecting NO at the SP. Thus, the new finding we will show is that not only many variables are important but that their relative importance varies from year-to-year. To address some of these processes, we analyze previous data sets complemented by a new data set collected in 2006-07 that extends over much of the seasonal cycle. Past work emphasized the relationship between high NO and shallow boundary layers (Davis et al. 2008; Neff et al. 2008). Here, the primary focus is on providing a broader perspective of the origin and evolution of high NO episodes, their relationship to stable boundary layer meteorology, the unique large-scale meteorology of the high Antarctic plateau, the influence of the changes in the stratosphere in recent decades, and the effect of variability within seasons as well as from year-to-year.”*

134-170 A little confusing here, with first sentence saying SE winds aloft are associated with E winds at the surface, but figures S2 and S3 show dominant surface wind mode to be 70-210 or 60-180 which are also SE. Also note that last sentence in block mentions SE surface winds.

Response: This has been addressed with an addition to Fig. 3 that shows the relationship of 300 hPa and surface winds. New text: *“Figure 3a shows the distribution of surface wind directions for each experiment year as well as the average NO for each year as a function of surface wind direction in Fig 3b. Although the wind distributions are similar for both 2003 and 2006, the average NO is much less in 2006. In Fig. 3b, highest NO occurs with surface winds with an easterly component (between 60° and 180°.) In Fig. 3c, for the entire period 1961-2010, we show the wind distribution at 300 hPa for surface winds between 60° and 180° and the distribution of surface winds in particular when the wind at 300 hPa is between 120° and 150°. The distribution is fairly broad (with a median of 87° and the peak centered on 105°). The breadth of this distribution may be related under sampling with once- or twice-a-day rawinsondes and surface observations.”* This latter comment is relevant to Fig. 7 where we show a case where the surface wind direction shift occurs after the rawinsonde launch but before the synoptic time reported for the rawinsonde. The launch on Day 337 in Fig. 7 was at 0953Z (prior to the wind shift) but reported for 1200Z by which time the surface wind had shifted to 135° from 349° at the time of the launch.

It should be noted that in the paper we have used the corrected rawinsonde wind data rather than that reported in the GTS where wind directions from 75° to 315° were largely missing (Corrected data are available from <ftp://amrc.ssec.wisc.edu/pub/southpole/radiosonde/>). Errors in the processing software in the field produced erroneous winds (from 14 February 2005 until 16 June 2007) that were later corrected (https://amrc.ssec.wisc.edu/presentations/neff_etal_rawin.pdf).

151 Does Fig S4 need to show full annual cycle?

Response: Insofar as we are only interested in summer regimes, we do not feel it is necessary beyond showing the timing of the transition to and from summer regimes.

153-154 Statement that Fig S4 “shows” that geostrophic winds dominate katabatic forcing of surface winds in peak summer kind of has to be taken on faith (no details about calculations supporting this until discussion of Figs 7 and 8 around line 390). Can this idea be presented clearly just once in the manuscript (it does seem to be a finding authors want to stress).

Response: New text has been added. Reference to Neff 1999, Sec. 4.2 is now made where this is discussed as well as a later reference to Parrish and Cassano (2003) where a model study confirmed the result. It is also noted that Ball’s (1960) nomogram comparing horizontal pressure gradients to those due to katabatic ones was adapted by Neff (1980) in terms of geostrophic wind speeds which is the basis of the results in Fig. S4. The importance of this result is that accumulation pathways for NO in the surface flows cannot be tied to simple concepts of gravity driven flows over a sloped surface.

167-170 It is usually risky to assume transport path based on wind direction observations at a receptor site. Do trajectories follow the contours as suggested? Strictly speaking, Fig 1b suggests that air traveling from Concordia to SP along 123 would cross at least 1 contour and flow uphill for almost the last half of the trip.

Response: This text has been deleted and the discussion is now presented in the context of Figs. 5, 8, and S13 (which shows a back trajectory on 30 November 2003 from ERA-I) which suggest much more complex mesoscale circulations over the high plateau.

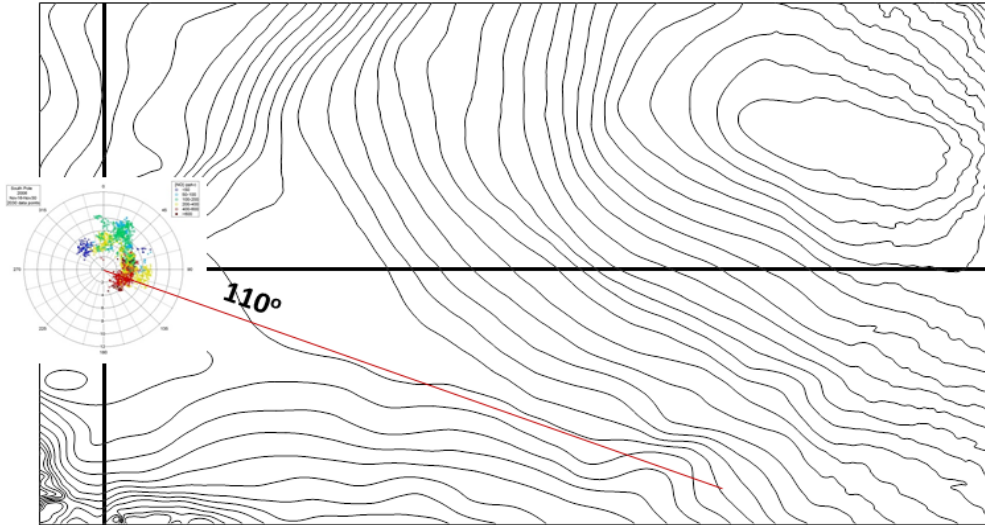
170-172 These closing sentences are problematic for at least 2 reasons. First is that heading out of SP along 110 is more “uphill” toward the central dome than just discussed, and one could imagine weak katabatic flow being influenced by the subtle topography east of SP shown in Fig 5 (and discussed later). Second is that very high NO at the same time winds and BLH are both high sort of explodes the entire conceptual model developed up to this point, so it hardly seems fair to ask the reader to take these observations as being in support of suggestion that summer time katabatic winds are over emphasized in the literature, and then dismiss them as being unusual.

Response: This case is an outlier in some respects. Initially the boundary layer was quite shallow and then as winds increased at times it became deeper with high NO. Unfortunately, we have no observations upstream to diagnose this case or to identify an accumulation area upstream. In addition, the meteorological tower data was missing from Days 333-334. The independent AWS station during this period did show consistent winds from 120° which is not a katabatic wind direction. We do point out later that an aircraft flight on 4 December (Davis et al. 2008) after the end of the event did show large NO between 100 km and 400 km from the SP along 110° even as concentrations were dropping at the SP. This suggests the possibility of inhomogeneous accumulation areas on the plateau.

Another factor that we have not discussed in this paper is the potential role of boundary layer convergence due to cross-isobar Ekman layer flow in the boundary layer of mesoscale low pressure systems. Neff (1980) calculated the e-folding time for such a stratified spin-down process at 1.1 days. Such a process could account for a deepening of the boundary layer/inversion layer without appealing to increased wind induced mixing. This

would be worth exploring with a high-resolution model and an enhanced observation network on the high plateau.

With respect to our assertion of flow relative to local topography we show below a more detailed look at the topography after a bit of smoothing. As can be seen here 110° is more aligned along the large scale terrain contours. In addition, with the Coriolis deflection to the left, any downslope flow from the high dome area would be away from the SP not towards. In our later discussion we estimate the relatively weak katabatic influence of local terrain near the SP.



184-191 Is it important to know about evolution of vortex dynamics since 1960, or are the key points the different date of breakup in the 4 study years, and the fact that the O3 hole results in higher actinic flux while the vortex is still intact?

Response: Text added in the Introduction: *“Past work (Neff, 1999) found evidence for the effect of stratospheric ozone depletion on the tropospheric circulation over the interior of Antarctica. A key question then was the potentially combined effects of changes in the radiative environment (via UV photolysis) and concomitant changes in the near-surface circulation affecting NO.”*

192-199 this paragraph mainly restates comments made earlier

Response: Text has been revised.

200-213 Of mild interest perhaps, but what is the quantitative link to NO at SP?

Response: This figure shows that the characteristics of winds in the late spring have not changed but that there has been a significant change in the early summer period that coincides with increased cloudiness (and hence deeper more well-mixed boundary layers associated with lower NO) that has been confirmed through the 1990s (Neff, 1999) and for more recent periods in Fig. S8.

215-222 Nice verbal summary of Fig 8, but no link to NO at SP

Response: Link is now made: *“The minimum in cloudiness during Julian Days 325-350, when shallow boundary development is likely due to increased clear-sky radiative cooling and coincides with increased actinic flux due to the persistent ozone hole of recent decades. This is also the period in 2003 and 2006 when the highest and most persistent NO occurred (in 1998, the field program started late and in 2000, the ozone hole filled early). Conversely, the summer period has, on the average, become cloudier, albeit subject to inter-annual and decadal variability, and hence less conducive to higher NO.”*

223-229 Another paragraph linking large scale and BL dynamics that almost makes predictions about impact on NO at SP, but does not test them with the data at hand (note that cloudiness in the 4 years mentioned in line 224 does not directly correlate with frequency and length of high NO episodes, 2003 does have high NO and few clouds, but 1998 has most clouds and second highest NO).

Response: We agree this paragraph was too general. We have eliminated much of the existing text and have added text focusing on the lack of extreme values and the importance of intermittency in conditions of high NO: *“In 1998, the late spring period was particularly cloudy compared to average conditions. However, after a late start to observations (see Fig. 1), higher NO occurred intermittently later in December during days with clear skies, light winds and higher actinic flux (due to the delay in the breakup of the ozone hole that year. The intermittency in 1998 is also reflected in the very limited values of NO in excess of 500 pptv (only 4% compared to 25% in 2003, Table 1).”*

230-247 Nice case study, and reassuring that it shows features observed in other events in the 3 earlier seasons. Just seems kind of late in the manuscript to finally be getting to NO observations at SP in any detail.

Response: This case now follows as a specific example pulling together the roles of intermittency relative to the late-spring climatological minimum in cloudiness, mesoscale eddies, and changes in total column ozone.

290-291 Pretty sure that Berhanu et al. and Frey et al. feel these sequences are not coincidental. Beside that, they must have physical/chemical explanation, even if not all the details have been nailed down.

Response: Unfortunately, these two papers as part of the OPALE program had different foci. In Berhanu et al, the interest in wind-blown snow occurred in the context of changes in isotopic composition in their samples whereas Frey et al. focused on explaining NO_x levels and effects of mixing processes as well as modeling the flux of NO_x from the snow.

Because of the typical decrease in wind speed from November to December, we were curious whether the mechanism described by Mulvaney was also at work on the high plateau. We feel this is something worth exploring in future work.

We have reworded this last section as follows: *“Recent research at Concordia Station on the high Antarctic Plateau reported a similar increase in surface nitrate in early December (Berhanu and Co-authors 2015). Wind speed had been high in late November (Frey et al. 2015, Fig. 1) followed a week later by high skin nitrate and high fluxes of NO_x from the surface consistent with the observations of Mulvaney et al. (1998) at Halley Station.”*

295-420 Please make it more clear what new insights are gained from the 2006 data set. Mostly seems to just reinforce things that were seen before.

Response: We added an overview of the four episodes in Fig. 1 to set the stage for the subsequent discussion: *“The first three field seasons have been described in some detail (Davis et al 2001, 2004, 2008) whereas a fourth more extensive observation of the seasonal cycle in NO, obtained in 2006-2007, has not yet been published. The four seasons of NO data are shown in Fig. 1 and their statistics in Table 1. In 1998, the ozone hole broke up very late as seen in Fig. 1a but the observational program was also delayed until early December. In 2000 (Fig. 1b), total column ozone increased well before the beginning of the field season and NO remained relatively low. In both 2003 (Fig. 1c) and 2006, the ozone hole broke up about the same time but higher column ozone was more persistent in 2006 until late December. In Fig. 1d, we also show the solar elevation angle ($\times 30$) increasing from 14.5° to 23.5° as well as the nitrate photolysis rate $J(\text{NO}_3^-)$ which initially follows the seasonal increase in elevation angle but responds after JD330 to shorter term variations in total column ozone and meteorology. In both 2003 and 2006, prolonged periods of high NO concentrations occur prior to Julian Day (JD) 340. In particular, in 2003, the period of JD 326-336 has a median concentration of 482 pptv whereas the sustained period in 2006, JD322-331 has a median value of 389 pptv. After JD340 the median values are 247, 91, 152, and 146 pptv for each of the four seasons respectively. Higher NO values in 1998 after JD340 presumably reflect the delay in the breakup of the ozone hole. In Table 1, we summarize the occurrence of NO concentrations in three ranges for each of the field seasons. 2003 stands out as having the highest number of NO concentrations exceeding 500 pptv, 90% of which occurred before JD 335 while 2000 had the fewest. Also 1998 saw the fewest hours of NO exceeding 500 pptv. From the perspective of Fig. 1, the first three years produced diverse results. The additional data in 2006, while more extensive, confirmed the general seasonal pattern seen in 2003.”*

The first two field seasons as we have noted were unusual with 1) a delay in starting observations in 1998 and then in 2000 a very early breakup of the ozone hole and subsequent low NO levels and few winds with an easterly component. The data in 2006 provided an opportunity to describe the full spring-summer cycle in NO.

300-302 Can't see any hash marks plotted at -20 in Fig 6.

Response: Revised the figure to only show clear sky periods as indicated by high direct radiation. Plotted every fourth data point for clarity.

324-338 A little unclear how the comparisons in the early part of this block lead to suggestion that late Dec emissions in 2006 were low due to photobleaching of the snow. In the day 305-340 block NO was 2 x higher in 2003 with similar wind/cloud statistics, but then in Dec the mean concentrations were similar despite 2003 being cloudier with deeper BL. Seems that maybe 2003 started with more nitrate in the snow for some reason, but in 2006 the lower amount available to make NO_x kept doing so longer due to favorable BL dynamics (e.g., average decreased by factor of 2.2 in 2003 in response to seasonal change, while in 2006 the early season to late season difference was only factor of 1.4)

Response: This section has been rewritten to avoid the confusion: *“Comparing these two years reveals the complexity introduced by meteorology: In 2003 NO was fairly low after JD340 during a period of higher winds and cloudy conditions but then followed by a single high NO episode near the end of the month whereas 2006 saw moderate NO concentrations intermittently throughout the period (see Fig. X). Thus the much lower average NO after JD340 in both years appear consistent with the conclusion from (Frey et al. 2015b) for the last half of December and early January at Concordia Station. Frey et al. argues, based*

on the laboratory results of (Meusinger et al., 2014) that the snow nitrate is composed of both photo-stable and photo-labile fraction and that the photo-labile fraction decreased later in December at Concordia Station. Our results would be consistent with that interpretation and show the value of multi-year and intraseasonal comparisons of NO.

351 as noted earlier, seems surface winds tend to be from SE, not E, when 300 hPa winds are SE

Response: This has been addressed by modifications to Fig. 3 and associated text.

352-353 Not very likely that much NO_x is transported in FT to SP

Response: We have softened this assertion with the following text: "Past work has indicated that the SP is not isolated from the influence from more northerly latitudes. For example, high methanesulfonate was observed from 28 November to 2 December -- an indication of marine sources (Arimoto et al. 2008). This period had the highest NO values recorded in the entire series of field programs (Davis et al. 2008) similar to those found at Concordia in a similar time frame in 2011 (Frey et al. 2015). Furthermore, as suggested in (Arimoto et al. 2008) air arriving at the South Pole may have had its origins in continental regions (due to much higher concentrations of the elements Pb, Sb, and Zn than in previous field programs) as well as in the ocean off Wilkes Land on the far side of the continent."

354-356 Just mentioned these earlier studies and suggested that maybe the link was just random.

Response: This paragraph was revised as above..

356-372 What motivates this rehash of 2003 results in a section on "Case studies and insights from new 2006 data"?

Response: Changed the title: Case studies and insights from new 2006 data in the context of past experiments. We have also pointed out the differences in seasonal snow accumulation rates between 2003 and 2006 as well as highlighting the similarities and differences in the meteorology between the two years.

385-400 Nice development of the argument against significant katabatic forcing, but it feels redundant since the finding was earlier declared (with little support first time around)

Response: Earlier discussion was expanded using Ball (1960) and Neff (1980). The rationale here was to look on potential local effects due to the terrain less than a 100 km from SP not the large-scale terrain.

403-410 Here is another example of using case study to make a solid point, that was earlier just boldly declared (lines 70-74). If this is so well established that it is in introductory remarks, does it need support here? Or should the earlier section be pulled back a little.

Response: Earlier discussion was expanded. This discussion was pulled back a bit but we still think the analogy between the rapid onset of a stable boundary layer at Concordia due to low sun elevation in the diurnal cycle and the rapid onset at SP due to increased radiative losses following clear skies is worthwhile.

420-446 Could/should these details be moved to supplement? Key point is to use the estimated BLH to estimate NO fluxes.

Response: The last paragraph has been removed as it duplicates earlier text. The discussion of Fig. 10 is useful because it provides a comparison of BLD versus NO for all four years and implies variability in source/flux terms that comes next.

455 measurements at SP

Corrected

461 associated lifetime

Corrected

513-522 Think another important aspect of these dynamical findings is that none of them, alone, had strong direct correlation with NO concentrations or fluxes at SP. This point is raised several times in the rest of manuscript, why not here?

Response: We have added the following text: "This case also reveals the difficulty in correlating peaks in NO directly with upper-level winds insofar as the peak in NO occurs in the gap between rawinsonde observations. Perhaps more important are these transitions in upper level winds that signify a direct connection to large scale dynamical changes in the atmosphere over the plateau. "

We also added in the discussion of Fig. 7 the following text: "Figure 7 also suggests limitations in correlating surface NO with wind shifts at 300 hPa: In this case the peak in NO occurs before the shift in winds aloft; by the next rawinsonde 12 hours later NO has dropped substantially."

574 because of potential collinearity

Added phrase: "such as between wind direction and temperature or wind speed and temperature"
And added: "This approach eliminates redundant variables."

647 and 649 is the "0.000 level" correct?

Response: Yes. Changed text to "highly significant at the 0.000 level (using SPSS software)"

817 the red line in 4a is not that easy to discern from black, try lighter shade
Figure S3, red diamonds in a and b seem same maroon as in Fig 4a, very close to black. Try lighter hue

Response: Done (this seems really sensitive to particular monitors/printers).

Figure S5 caption, what do you mean by "year-to-year scatter is not unreasonable"?

Response: reworded to be more explicit: : “The differences in timing determined from Harnik et al. (based on time of circumpolar stratospheric winds reversing) and the time of formation of the thermal tropopause (from the SP rawinsonde) is quite reasonable.”

Figure S6, Not sure this figure is central to the NO story, but if it stays may need to say something about what is so significant about the Breakup date. In both intervals it certainly looks like hole is filling weeks earlier. Also, why is the early interval averaged 1964-1980 (dots) but break up date averaged 1961-1980?

Response: The Dobson data only started in 1964. New text added:

“The reduction in ozone now coincides with the period most favorable to SE winds shown in Fig. 1 (with clear skies and shallow boundary layers important to high NO concentrations). In addition, changes shown in Fig. S6 suggest long term increases in actinic flux with a 30% reduction in total column ozone by the average time of vortex breakup in recent decades. In addition, the largest changes occur between JD320 and JD330 corresponding to the periods of highest NO in 2003 and 2006 as shown in Fig.1.”

Figure S9 caption. Figure 3 does not show any basin. Better callout would be Fig 5 (possibly Fig 1, but suspect 5 is better).

Response: This should be Fig. 5 – failed to update figure numbering after earlier changes in the paper.

Figure S10, as noted in text, would probably be better as 4 panels. And it should be in the main paper, not supplement.

Response: done

Response to Anonymous Referee #2

This paper describes data prescribing the boundary conditions affecting the near surface air-chemistry at the South Pole; more specifically the conditions are sought that lead to occasional episodes of surprisingly high levels of NO in the lowest 50 m or so of the atmosphere.

This is a complex discussion: NO levels may depend on large scale meteorology (advected air from the oceans), small scale mixing (boundary layer stability), sunlight, and the actual chemistry sources and sinks. The paper faces a significant challenge is presenting the reader with these processes, their importance, and the supporting data (from different campaigns) in a manner that tells the story and supports the conclusions. It is this challenge that I found wanting.

Response: We have made a number of revisions in response to RC1 including a four-season overview at the beginning of Section 2 and a figure that summarizes the NO observations for all four years and shows the variability in actinic flux, solar elevation angle and timing the breakup of the ozone hole for 2006-2007. This then sets the stage for the subsequent discussion in Section 2.

I think the paper is difficult to read: this may be in part because much of it is not my field, but I suggest that most readers will suffer similarly given the interdisciplinary nature of the discussion. The authors therefore need to help set the story better, and I suggest that two or more schematics would be most helpful. The source, mixing and ventilation of the boundary layer, with the chemical pathways (in snow, air and advected aloft) overlaid. This coupled to maps (as per figure 1, 5 and 8) with an overlay of wind roses, rather than x-y plots (figure 1 again).

Response: We have now included reference to Davis et al. (2008, esp. his Fig. 2) which outlines many of the processes at work on the high plateau. New text added in the introduction includes:

“Past work (Neff, 1999) found evidence for the effect of stratospheric ozone depletion on the tropospheric circulation in the

Austral spring over the interior of Antarctica. A key question then was the potentially combined effects of changes in the radiative environment (via UV photolysis) and concomitant changes in the near-surface meteorology affecting NO. The complexity of all the potential processes affecting NO are well captured graphically in Davis et al. (2008, Figure 2) where they identify atmosphere-surface exchange processes, plateau drainage, continental outflow, lower latitude transport, and boundary layer-free troposphere exchange as the key meteorological processes.”

As noted above we have set the stage for the discussion in Section 2 with a new figure summarizing the year-to-year differences in the four field programs. We find the x-y plots to be a good short summary of the intra-seasonal changes in the larger scale circulation but have added wind roses in the supplemental material that highlight the changes in more detail than in our new Fig. 2. This new supplemental figure also summarizes the changes in cloud fraction versus 300-hPa wind direction through the three subseasons.

The authors should think of a clearer nomenclature for wind direction, as “157.5” and “337.5” implies a very highly modal air flow, rather than, for example “the SSE and NNW sectors” (I assume this is what the authors meant). Perhaps even include a sailor’s compass for those less familiar with these terms, but emphasise that such sectors have natural angular range bin of a quarter of a right angle. These would then fit nicely with wind roses of either 8 or 16 direction bins. Finally on the topic, such schematics would stress that ‘North’ at the South Pole is nominal, and the meridian is taken.

Response: As noted above, we have added wind roses in the supplemental material and changed angular descriptions to the SSE etc nomenclature suggested by the reviewer in Fig. 1. We agree with the reviewer that wind roses reveal the angular ranges more explicitly. In the supplemental figure we have also added wind direction/cloud fraction roses. These show that low cloud fraction in the period JD310-340 can be associated with a much narrower range of directions of 300 hPa winds (SE to ESE) than might be concluded from just wind roses. These also confirm our assertion that higher cloud events are associated with winds aloft from the direction of west Antarctica while there is a major shift in cloud/wind direction in early December

The schematic of the boundary conditions would greatly assist with giving meaning (and importance) to the whole of Section 2. Each section describes some meteorological phenomenon, but not why it matters. The reader (at least this one) was left with a wealth of information dangling, without a mechanism to sift for importance for the overall Question. All of the information presented may be vital to the argument, but, I would ask the authors to check each statement here for Invasion of the Interesting Fact (which isn’t actually critical).

Response: Section 2 has been significantly revised in response to RC1 which also addresses this comment.

Perhaps (again for the non-specialist reader) the conclusions could be presented as a “recipe for a perfect NO event”, that is, High NO is likely to happen when (a) and (b) and (c) or (a) and (d) but not (d) etc.

Response: Unfortunately we have found there is no simple recipe for a perfect NO event. In fact our stepwise linear regression in Appendix A shows different variables dominate each of the four seasons that we studied. We have revised the first few paragraphs of our conclusions as follows to make this point clearer:

“Earlier work (Davis et al. 2008; Neff et al. 2008), primarily based on 2003 data which included direct sodar measurements of boundary layer depth, presented a straightforward conceptual model that linked high NO to the presence of shallow boundary layers, light winds, and stronger surface inversions. In our examination of four seasons of observations, explanation of the initiation and evolution of high NO episodes as well as intra-seasonal to interannual variability proved more challenging. Using four spring-to-summer seasons of observations, we have described the influence of the synoptic- to-mesoscale weather patterns and their seasonal cycle on stable boundary layer characteristics at the South Pole in the spring-summer period that set the stage for high NO episodes. These included

1) The relative unimportance of katabatic forcing compared to the accelerations due to synoptic and mesoscale scale pressure gradients from November through January. In fact, visualizations of near-surface airflow using ERA-I (Dee et al. 2011) revealed complex mesoscale circulations that belied any simple explanation of accumulation pathways for NO.

2) The effect of clearing skies locally that led to rapid radiative losses and the formation of very shallow inversion/boundary layers and high NO. Given observations only at the SP, the geographical extent of such radiation-driven boundary layers is unknown but worthy of further field observations. Unfortunately aircraft measurements of NO in 2003 (Davis et al. 2008) were not permitted between -40° W and 120° E (the clean air sector), an area which encompasses a large almost horizontal plane extending four hundred km east of the SP. However, the one flight along 120° E at the edge of this plateau showed NO in excess of 400 pptv between 100 and 400 km from the SP at the same time NO concentrations were dropping at the SP.

3) The three-phase transition in spring for 300-hPa winds over the SP. These three phases corresponded to a) a late winter regime of transport of moisture over west Antarctica to the interior when the circumpolar trough is at its maximum and opens the possibility for the transport of NO precursors from northerly latitudes, b) an early spring semi-bimodal regime with 300 hPa winds alternating between northwest and southeast quadrants during November and early December as part of the seasonal cycle, followed by c) an early summer regime favoring 300-hPa winds from the Weddell Sea and warmer cloudy conditions. During the second phase, 300-hPa winds from the southeast favored clear skies, light surface winds and shallow inversions conducive to high NO concentrations at the same time the total column ozone was still low allowing higher actinic fluxes. 300-hPa winds from the northwest favored warm-air advection and cloudy conditions resulting in deep boundary layers and low NO concentrations.”

The Meteorology and Chemistry of High Nitrogen Oxide Concentrations in the Stable Boundary Layer at the South Pole

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Abstract. Four summer seasons of nitrogen oxide (NO) concentrations were obtained at the South Pole during the Sulfur
Chemistry in the Antarctic Troposphere (ISCAT) program (1998 and 2000) and the Antarctic Tropospheric Chemistry
Investigation (ANTCI) in (2003, 2006-7). Together, analyses of their data here provide insight into the large-to-small scale
15 meteorology that sets the stage for high NO and the significant variability that occurs day-to-day, within seasons and year-to-
year. In addition, these observations reveal the interplay between physical and chemical processes at work in the stable
boundary layer of the high Antarctic plateau. We found a systematic evolution of the large-scale wind system over the ice
sheet from winter to summer that controls the surface boundary layer and its effect on NO: Initially in early spring (Days
280-310) the transport of warm air and clouds over West Antarctica dominates the environment over the South Pole; In late
20 spring (Days 310-340), of significance to NO, the winds at 300-hPa exhibit a bimodal behavior alternating between NW and
SE; In early summer (Days 340-375), the flow aloft is dominated by winds from the Weddell Sea. During late spring, winds
aloft from the SE are strongly associated with clear skies, shallow stable boundary layers, and light surface winds from the
east: it is under these conditions that the highest NO occurs. Examination of the winds at 300 hPa from 1961 to 2013 shows
that this seasonal pattern has not changed significantly although the last twenty years have seen an increasing trend in
25 easterly surface winds at the South Pole. What has also changed is the persistence of the ozone hole, often into early
summer. With lower total ozone column density and higher sun elevation, the highest actinic flux responsible for the
photolysis of snow nitrate now occurs in late spring under the shallow boundary layer conditions optimum for high
accumulation of NO. This may occur via the non-linear HO_x-NO_x chemistry proposed after the first ISCAT field programs
and NO_x recycling to the surface where quantum yields may be large under the low-snow-accumulation regime of the
30 Antarctic plateau. During the 2003 field program a sodar made direct measurements of the stable boundary layer depth
(BLD), a key factor in explaining the chemistry of the high NO concentrations. Because direct measurements were not
available in the other years, we developed an estimator for BLD using direct observations obtained in 2003 and step-wise
linear regression with meteorological data from a 22-m tower (that was tested against independent data obtained in 1993).
These data were then used with assumptions about the column abundance of NO to estimate surface fluxes of NO_x. These
35 results agreed in magnitude with results at Concordia Station and confirmed significant daily, intraseasonal and interannual
variability in NO and its flux from the snow surface. Finally, we found that synoptic to mesoscale eddies governed the
boundary layer circulation and accumulation pathways for NO at the South Pole rather than katabatic forcing. It was the
small scale features of the circulation including the transition from cloudy to clear conditions that set the stage for short-term
extremes in NO whereas larger-scale features were associated with more moderate concentrations.

1. Introduction

40 The Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) field programs in the austral summers of 1998 and again in 2000 (Davis et al. 2004a; Davis et al. 2001) discovered unexpectedly high atmospheric nitrogen oxide (NO) concentrations at the South Pole (SP). These early investigations suggested that the high NO levels were associated with continuous sunlight, shallow stable boundary layers, downslope flow from the east Antarctic plateau, and associated non-linear NO_x-HO_x chemistry that resulted in long NO_x lifetimes, (Davis et al. 2004a; Davis et al. 2008)). It was also argued that the high levels of NO at the SP, compared to other polar sites, were partly due to the long fetches for air parcels in the katabatic flow from the Antarctic high plateau and the lack of a diurnal cycle, thus allowing continuous photolysis of snow nitrate. A major field program followed in 2003 to re-examine this phenomenon, the Antarctic Tropospheric Chemistry Investigation (ANTCI). This new study involved ground-based measurements at SP as well as aircraft probing over more extensive areas of the Antarctic Plateau in 2003 (Davis et al. 2008) and then again in 2005 (Slusher et al. 2010). These field studies reinforced the earlier ISCAT results and introduced evidence suggesting that fast recycling mechanisms for redeposited nitrate could be important given that photolysis of buried nitrate appeared inadequate to explain the sustained levels of atmospheric NO_x. In combination with meteorological factors, this recycling enabled NO_x levels which routinely reached and/or exceeded several hundred pptv. Because of significant daily, seasonal, and inter-annual variability in NO observed in the previous field studies this paper will examine in greater detail the influence of large- to small-scale meteorological circulations on the boundary layer and associated chemical factors that set the stage for high NO episodes. A key feature of the boundary layer at the South Pole is that it is statically stable throughout most of the year and often very shallow which leads to the confinement of surface chemical emissions near the surface except during higher-wind events and cloudy periods when a deeper internally well-mixed inversion layer is often present. Important factors also influencing the near-surface chemical environment include the winter-to-summer seasonal cycle in wind and temperature as well as inter-annual variability and synoptic variability in cloudiness (important to the surface energy budget and the boundary layer structure), low snow accumulation, and total column ozone and the radiative changes associated with the breakup of the stratospheric polar vortex and ozone hole in the spring. Past work (Neff, 1999) found evidence for the effect of stratospheric ozone depletion on the tropospheric circulation in the Austral spring over the interior of Antarctica. A key question then was the potentially combined effects of changes in the radiative environment (via UV photolysis) and concomitant changes in the near-surface meteorology affecting NO. The complexity of the potential processes affecting NO are well captured graphically in Davis et al. (2008, Figure 2) where they identify atmosphere-surface exchange processes, plateau drainage, loss mechanisms associated with continental outflow, lower latitude transport into the continent, and boundary layer-free troposphere exchange as key meteorological processes. However, earlier work did not examine year-to-year meteorological variability and effects on NO. In addition, the step-wise linear regression that we show later demonstrates that the dominant parameters for NO vary from year to year reflecting the variability in weather regimes affecting NO at the SP. Thus, the new finding we will show is that not only many variables are important but that their relative importance varies from year-to-year. To address some of these processes, we analyze previous data sets complemented by a new data set collected in 2006-07 that extends over much of the seasonal cycle. Past work emphasized the relationship between high NO and shallow boundary layers (Davis et al. 2008; Neff et al. 2008). Here, the primary focus is on providing a broader perspective of the origin and evolution of high NO episodes, their relationship to stable boundary layer meteorology, the unique large-scale meteorology

of the high Antarctic plateau, the influence of the changes in the stratosphere in recent decades, and the effect of variability within seasons as well as from year-to-year. ~~se, effort uses analyses of previous data sets complemented by a new unreported data set collected in 2006-07 that extends over much of the seasonal cycle. The foci here are the origin of high NO episodes and their relationship to stable boundary layer meteorology, meteorological variability within seasons as well as from year-to-year~~

2. ~~Boundary layer meteorology, NO, and the seasonal cycle, and boundary layer meteorology~~

In this section, we examine the meteorological factors controlling boundary layer depth (BLD) and NO variability, over hourly, ~~intra~~seasonal and interannual time scales, using the summer field program data from 1998, 2000, 2003, and 2006-07. Because NO was the one species measured consistently in all field studies cited, it will be used in most of the follow-on discussions (NO and NO₂ were both measured in 2006-2007). This analysis benefits from a repeatable weather cycle at SP and the lack of a diurnal solar insolation cycle. The weather cycle typically includes a period of advection of warm air, higher wind speeds, and clouds with a deep boundary layer followed by clearing skies, strong radiative surface cooling and formation of shallow statically stable boundary layers (Neff, 1999). ~~These changes occur over normal synoptic time scales of a few days and over planetary wave time scales of 10-60 days (Yasunari and Kodama 1993). During periods of warm air advection and cloudy conditions, the surface inversion can be fairly deep and well-mixed as the warm air adjusts to a colder ice surface. In these cases the boundary layer is often several hundred meters deep (Neff, 1980). This is in contrast to clear sky conditions:~~ A unique aspect of the SP includes a high snow albedo and low sun elevation angle (~23.5° at solstice). Because of this combination the surface typically suffers a net loss of energy under clear-sky conditions (Stone and Kahl 1991) even at the summer solstice. This effect is in contrast with summer observations at Concordia Station (~75°S, 3233 m ASL: ~~diurnal solar elevation at solstice 8.5° to 38.5°~~) and Dome Argus (~80°S, 4093 m ASL: ~~diurnal solar elevation at solstice 13.5° to 33.8~~) that show a diurnal cycle of thermal convection followed by the formation of a stable boundary layer during the “evening (low sun elevation)” period (Frey et al. 2015a) (Bonner 2015; Bonner et al. 2010). ~~A detailed study of the surface energy budget and boundary layer evolution at Concordia Station (King et al., 2006) shows a convective boundary layer and positive net radiation lasting eight hours (averaged over December and January). This convective period developed when the solar elevation angle was greater than 25°, in contrast to the lack of thermal convection at the SP where the maximum solar elevation angle is always less than this. Frey et al. (2015) show a specific example for 9 January at Concordia when a stable boundary layer forms with large increases in NO shortly after 1800 LT when the solar elevation angle decreases to less than 20°. Similarly King et al. (2006) show a sodar record from 28 January with a stable boundary layer until 0800 and after 1730 LT when solar elevation angle less than ~22°. For these reasons air masses arriving over long distances at the SP are likely to have encountered some convective mixing enroute and may need to be considered in future model simulations of surface chemistry.~~

~~The synoptic weather variability at SP occurs in the context of a strong seasonal cycle from early spring to summer as the sun rises and the omnipresent surface inversion weakens to less than 10% of its winter value (Neff 1999) implying only weak katabatic influence during the Austral summer (discussed in more detail below).—Also of~~

~~Of particular interest in our analyses are the major shifts in large scale weather patterns that occur from early October to mid or late December, coincident with the weakening of the circumpolar trough, warming of the stratosphere and breakup of~~

the polar vortex and the stratospheric ozone hole. The dynamical consequences of these transitions also affect boundary layer behavior that is dependent on cloud fraction, surface radiative balance, inversion strength, as well as upper level winds and associated surface pressure gradients. In our discussions we will use the grid direction convention at SP where grid north is aligned with the Greenwich Meridian (Fig. 1).

2.1 Overview of the four field seasons

The first three field seasons have been described in some detail (Davis et al 2001, 2004, 2008) whereas a fourth more extensive observation of the seasonal cycle in NO, obtained in 2006-2007, has not yet been published. The four seasons of NO data are shown in Fig. X1 and their statistics in Table X1. In 1998, the ozone hole broke up very late as seen in Fig. 1a but the observational program was also delayed until early December. In 2000 (Fig. 1b), total column ozone increased well before the beginning of the field season and NO remained relatively low. In both 2003 (Fig. 1c) and 2006, the ozone hole broke up about the same time but higher column ozone was more persistent in 2006 until late December. In Fig. 1d for 2006, we also show the solar elevation angle ($\times 30$) increasing from 14.5° to 23.5° as well as the nitrate photolysis rate $J(\text{NO}_3)$ which initially follows the seasonal increase in elevation angle but responds after JD330 to shorter term variations in total column ozone and meteorology. In both 2003 and 2006, prolonged periods of high NO concentrations occur prior to Julian Day (JD) 340. In particular, in 2003, the period of JD 326-336 has a median concentration of 482 pptv whereas the sustained period in 2006, JD322-331 has a median value of 389 pptv, $\sim 25\%$ lower than in 2003. After JD340 the median values are 247, 91, 152, and 146 pptv for each of the four seasons respectively. Higher NO values in 1998 after JD340 presumably reflect the delay in the breakup of the ozone hole. In Table 1, we summarize the occurrence of NO concentrations in three ranges for each of the field seasons. 2003 stands out as having the highest number of NO concentrations exceeding 500 pptv, 90% of which occurred before JD 335 while 2000 had the fewest. Also 1998 saw the fewest hours of NO exceeding 500 pptv. From the perspective of Fig. 1, the first three years produced diverse results. The additional data in 2006, while more extensive, confirmed the general seasonal pattern seen in 2003 with the most persistent high NO occurring in November.

2.2 The seasonal cycle, upper-level winds and their influence on surface flows

As the stratosphere over Antarctica begins warming around the time of the spring equinox, prevailing winds at the height of the summer tropopause over the South Pole (~ 300 hPa) evolve in three stages as shown in Fig. 4-2 (based on rawinsonde data for the period 1990 to 2013). In Fig. S1 we provide more detailed wind-rose plots for each subseason as well as cloud fraction as a function of 300-hPa wind direction for extremes in daily cloud fraction of 8-10 tenths and 0-2 tenths.

In **Early Spring** (JD280-310), 300-hPa winds are largely from the direction of west Antarctica and associated with high cloud fraction and advection of warmer air at the South Pole (Neff 1999). This period coincides with the maximum in the semi-annual oscillation when the circumpolar trough is most intense (Meehl 1991). Although there can be significant year-to-year variability in storminess, October can be the period of greatest snow accumulation (as measured in the stake field at the SP). The average accumulation in October from 1990 to 2015 is 3 cm whereas in November it is 1.5 cm (amrc.ssec.wisc.edu/pub/southpole/climatology). During that 25-year period, 2003 was one of the four highest accumulation years. In 2003, the snow depth increased by 6 cm in October whereas in November it decreased by 1 cm. In our other experiment years the accumulation ranged from 1.5 cm (2006) to 4.0 cm (2000) in November. The accumulation rate may be important to the fate of nitrate in the snow (e.g. Mulvaney et al. 1998) as well as the exposure of nitrate in the skin layer to

photolysis and recycling (e.g. Frey et al. 2015).

~~The increase in synoptic weather activity at this time suggests increased likelihoodthe possibility of transport of NO precursors from the ocean, surrounding sea ice and more northerly latitudes to the interior of the continent. The increase in synoptic weather activity at this time suggests the possibility of transport of NO precursors from the ocean, surrounding sea ice and more northerly latitudes to the interior of the continent. During this period it has been noted that atmospheric nitrate typically increases in mid-October whereas surface nitrate increases later in mid-November although this may reflect higher fluxes of reactive nitrogen early in the season compared subsequent nitrate deposition rates (Erbland et al. 2013). Erbland et al (2015) also suggest, as an estimate, that half of the annual average nitrate comes from stratospheric sources and half from long-range transport (although there are no measurements of this). Meanwhile, it has been suggested that increased surface nitrate at Concordia Station in 2006 has stratospheric origins (Traversi et al. 2014). In fact, back trajectories for this period show them passing just to the east of SP in early November 2006 with higher nitrate observed on 13 November at Concordia Station whereas during our last observational field program we observed higher NO on 18 November at SP. For austral winters Neff (1999) calculated isobaric geostrophic temperature advection at the SP from averaged rawinsonde profiles and found advective warming associated with NW to SW winds aloft and cooling associated with SE winds aloft.~~

As the season evolves during the **Late Spring** (JD310-340), the winds become semi-bimodal as shown in Fig. 4-2 where percentages in 45°-bins have peaks centered about 180° apart at 157.5°SSE and 337.5°NW. The most significant aspect of this semi-bimodal distribution is the much diminished transport of warm air from west Antarctica and lower cloud fraction at SP. During the Late Spring period 43% of the 300 hPa winds lie between 90° and 225° whereas 31% lie between 270° and 360°. As reported in Neff (1999), this Late Spring period also has the lowest average cloudiness (see also Fig. S8 for more recent data). Furthermore, for winds greater than 10 ms⁻¹ at 300 hPa, between 1990 and 2010, in the 45° intervals centered on 157.5°SSE and 337.5°NW, the average surface inversion strength (from rawinsonde soundings) and surface wind speed are 6.3°C and 3.5 ms⁻¹ and 2.5°C and 5.4 ms⁻¹, respectively. Thus, in addition to reduced cloudiness during this period, surface wind speeds are less and surface-based inversion strengths are larger for 300-hPa winds from the SE. As seen in Fig. S1, clear-sky conditions byare most likely with winds aloft from ESE to SE.

In **Early Summer**, the occurrence of SSE winds decrease while the frequency of winds from the NNW increases. (For the Early Summer period, the results are similar at 2.2°C and 3.1 ms⁻¹ and 0.3°C and 5.9 ms⁻¹, respectively). With the higher frequency of winds from the northwest in early summer with increased cloudiness, low static stability and higher surface wind speeds, high NO should be less likely on the average, after mid-December. Conversely, periods of low cloud fraction are consistent with increased radiative cooling of the surface and the stronger surface temperature inversions that result are consistent with higher NO.

The difference in surface wind speed and inversion strength for the NW and SE modes can be explained in terms of the 300 hPa geopotential height (GPH) patterns corresponding to the NW-SE-two modes of upper level winds (Fig. S1+S2). For NW winds, low GPH lies between the Ross and Weddell Seas over West Antarctica with higher GPH over the continental

interior. For SE winds, lower GPH lies in the eastern hemisphere extending over most of the high Plateau. Although somewhat different than the winter pattern in Neff (1999) where for SE winds aloft a strong ridge of high pressure extended from the Ross Sea over portions of east Antarctica, the large scale pressure gradient force still reveals either an on-shore or off-shore orientation in the two cases. In the case with low pressure centered mostly over high terrain, downslope flows would be less likely likely be weaker whereas the inverse would be true for off-shore pressure gradient forces.

The frequency of occurrence of SE winds at 300 hPa can, however, vary varies from year to year and from decade to decade as reported in (Neff 1999).—Figure 2-3 shows the year-to-year variability in the occurrence of SE winds for the more recent period 1990-2013, which except for outliers in 1999 and 2002 (where the year 2002 has been eliminated as it was the year of the only sudden stratospheric warming observed over Antarctica and may have subsequently affected the tropospheric circulation (Charlton et al. 2005). follows the almost Figure 23 shows the semi-decadal variability discovered earlier documented previously for the period 1961-1998 (Neff, 1999). For each of the four observational periods (approximately mid-November through December for consistency) the frequencies of occurrence of winds at 300 hPa from the SE were as follows: 27% in 1998, 2% in 2000, 24% in 2003, and 42% in 2006. For each of these periods when NO was recorded at SP, the number of hours of NO>250 pptv were as follows: 42% in 1998, 4% in 2000, 56% in 2003, and 29% in 2006. The lack of a one-to-one relationship between the occurrence of SE winds and NO concentrations suggest additional year-to-year variability in chemical source terms and the details of the synoptic weather conditions favorable to high NO. What does stand out in 2000, with very low frequency of winds from the SE quadrant is the limited number of hours when NO exceeded 250 pptv, thus indicating the seasonal dependence of NO concentrations on the large scale weather patterns over the Antarctic.

~~Winds aloft from the SE quadrant often coincide with a transition to easterly winds at the surface. Figure 3 shows that these easterly surface winds were most prevalent in 2003 and 2006, intermediate in 1998, and minimal in 2000.—Also, averaged over the four field seasons, highest NO occurred when surface winds were from the east to southeast in concert with winds aloft from the SE. Figure S2 shows the distribution of winds at 300 hPa when surface winds are greater than 2 ms⁻¹ and lie between 70° and 210° during November and December, from 1961 to 2010. 67% of the winds at 300 hPa are between 90° and 180° for these surface wind directions implicating SE winds at tropopause level as a major determinant for easterly winds at the surface and extreme NO concentrations.~~

Figure 34a shows the distribution of surface wind directions for each experiment year as well as the average NO for each year as a function of surface wind direction in Fig 34b. Although the wind distributions are similar for both 2003 and 2006, the average NO is less in 2006 for surface wind directions greater than 90°. In Fig. 34b, highest NO occurs with surface winds with an easterly component (between 60° and 180°.) In Fig. 34c (for 1961-2010) we show the wind distribution at 300 hPa for surface winds between 60° and 180° and the distribution of surface winds in particular when the wind at 300 hPa is between 120° and 150° showing a 30° offset between peaks aloft and at the surface. The distribution is also fairly broad (with a median of 87° and the peak centered on 105°). The breadth of this distribution may be related to discrete sampling with once- or twice-a-day rawinsondes and surface observations. Figure S3 explores, in more detail, the relationship of winds aloft to surface wind behavior for average surface wind directions (60° to 180°) associated with average NO greater than 200 pptv for Late Spring (Days 310-340) and for the full period of rawinsonde data starting in 1961. Figure S3a reveals strong

interannual variability in the occurrence of surface winds with an easterly component as well as an upward trend exceeding 10% beginning in the late 1990s. In this case, we are only looking at the period of Late Spring whereas in Fig. 2, the data extended to the end of December. Figure S3b shows similar interannual variability in SE winds at 300-hPa as well as multi-decadal variability but no systematic trend. In Fig. S3c, we show that extremes in the frequency of occurrence of winds from the SE at 300 hPa correspond to extremes in the occurrence of surface winds from the SE with $r^2=0.4$. Comparing Fig. S3 with Fig.2 which spanned the period mid-November to the end of December, shows that easterly surface winds occurred primarily after mid-December in 1998: However, in that year, the ozone hole breakup was delayed until the end of December and hence optimum boundary layer conditions favorable for high NO occurred with still-high actinic flux as seen in Fig. 1 where the 1998 field study started later in the seasonal cycle.

The surface inversion strength also varies strongly with the season as shown in Fig. S4a where we have plotted the average inversion strength from 1961 to 1998 (Neff 1999) as well as daily data for 2006 showing typical short-term variability. (The inversion strength was determined from the daily or twice-daily rawinsonde temperature profile, measuring the difference from the 2-m tower temperature to that at the first relative maximum in the rawinsonde profile). Because of the common assumption that the winds over Antarctic are largely katabatic in nature, motivated mainly by wintertime observations in coastal areas, we also show in Fig. S4a the geostrophic wind equivalent of inversion strengths of 4°C (1 ms^{-1}) and 18°C (5 ms^{-1}) assuming a terrain slope of 0.001, characteristic of the interior of the ice sheet and derived from (Ball 1960) by Neff (1980). From the figure, geostrophic winds aloft of only 1 ms^{-1} will dominate over katabatic forcing from mid-December to mid-January. In Fig. S4b we show the distribution of wind speeds at 300 hPa for December, averaged from 1998 to 2014. This figure shows that almost all synoptic scale winds in December at 300 hPa imply surface synoptic pressure gradients substantially greater than the katabatic ones associated with summer inversion strengths (Neff, 1980; Neff, 1999, Sec. 4.2; Parish and Cassano, 2003). The conclusion from the previous figures is that synoptic and mesoscale pressure gradients at the surface dominate over those driving katabatic flows over the interior of Antarctica, especially in the period November-January and that 300-hPa winds from the SE provide a significant control over the boundary layer depth important to high NO. Past work has suggested that katabatic trajectories may have been responsible for long fetches over which NO could accumulate (Davis et al. 2004a). However, from these arguments it appears more likely that meso- to synoptic-scale circulations define accumulation pathways over the interior of Antarctica in the late spring and summer and that these pathways vary significantly on intraseasonal to interannual time scales. Furthermore, as can be seen comparing surface wind directions for maximum observed NO in Fig. 3 with the large scale topography in Fig. 1b, the surface flows align largely along constant topographic contours between South Pole and Concordia Station (along 123°E) rather than downslope. Of note, high NO, up to 400 pptv, along 110°E was found for several hundred km from the SP on 4 December 2003 in aircraft measurements (Davis et al. 2008). However, this was an unusual period starting in late November with a deep boundary layer, high winds as well as high NO, in particular, on 30 November (Neff et al. 2008). At the same time high filterable nitrate occurred with high methanesulfonate (MSA) suggesting marine origins (Arimoto et al., 2007). Also, Arimoto et al. found trace elements normally associated with continental origins and thus could not rule out external influences during this period (although for most of the experimental period the preponderance of evidence pointed to recycling of NO from the surface (Davis et al. 2008).

2.3 The Changes associated with the spring breakup of the polar stratospheric vortex

The warming of the stratosphere between October and December is important for changes in the large scale circulation as well as to boundary layer behavior at the South Pole (Neff 1999). It has been noted by others that the final warming of the southern stratosphere has a significant influence on the tropospheric circumpolar circulation (Black and McDaniel 2007) and over the interior of the continent (Neff 1999). Furthermore, with the final warming, downward coupling (at Wave-One scales) from the stratosphere to the troposphere ceases (Harnik et al. 2011) although the subsequent impact on the circumpolar storm track has not been explored. The timing of this final warming varies from year to year and is marked initially as the time the zonal wind in the polar vortex between 30–10 hPa and 54°S–75°S first goes to zero. From the work of Harnik et al. (2011) this occurred very late in 1998 and very early in 2000; 2003 and 2006 followed the long-term trend toward a later warming. Of primary importance in the delay of the vortex breakup is the persistent low total column ozone and resulting increase in actinic flux later into spring (as in 1998) responsible for increased photolysis of snow nitrate.

In Fig. 4-2 we looked at the period 1990-2010, the decades following the onset of rapid stratospheric ozone depletion beginning in the 1980s. This depletion resulted in a 30-day delay in the formation of the thermal tropopause over the South Pole as documented in Fig. S5. Prior to 1980, the tropopause formed, on the average, around Julian Day 306 (November 2). After 1990, the average time is Julian Day 336 (December 2), a delay of 30 days. Past analyses calculated the covariance of fluctuations in the easterly component of the surface wind and temperature (essentially the easterly flux of cold air: $v'T'$) from 1961 to 1997 (Neff 1999) finding a persistence of about 20 days later between 1961-1970 and 1988-1997 commensurate with the delay in the breakup of the polar vortex. This suggests that a delay in the breakup of the vortex leads to an increase in easterly-E to S surface flows associated with higher NO later in the spring which is not inconsistent with the results in Fig. S3a.

Figure S6 compares the seasonal change in total column ozone between 1964-1980 (these data are only available starting in 1964) and 1990-2010 (measured with a Dobson Ozone spectrophotometer – available from www.esrl.noaa.gov/gmd/ozwv/dobson/) showing reductions of about 30% in early December. The reduction in ozone now coincides with the period most favorable to SE winds shown in Fig. 4-2 (with clear skies and shallow boundary layers important to high NO concentrations). In addition, changes shown in Fig. S6 suggest long term increases in actinic flux with a 30% reduction in total column ozone by the average time of vortex breakup in recent decades. In addition, the largest changes occur between JD320 and JD330 corresponding to the periods of highest NO in 2003 and 2006 as shown in Fig. 1. A consequence of delays in recent decades, the actinic flux has increased in the spring as a result of a persisting ozone depleted column coupled with a higher sun elevation angle. Figure 1 suggested that during the late spring/early summer period of higher sun elevation angle and thus higher potential actinic flux, the late spring period had an almost 50% higher occurrence of SE winds compared to early summer. A question remains, however, is whether the distribution of winds aloft in Fig. 4-2 is an artifact of coincidental changes in the timing of the vortex breakup and the normal seasonal cycle in the circumpolar circulation or has, perhaps, been influenced the effect of ozone depletion on the tropospheric circulation. Figure S7 explores this question in more detail where we examined winds at both 200 hPa and 300 hPa. In Fig. S7 a,b for Days 270-305 (~October), the wind distributions are very similar to those of Fig. 1 for both 1960-1980 and as well as 1990-2010. In Fig. S7 c,d for Days 305-340 (~November) the bimodal distribution seen in Fig. 1 appear at both 200 and 300 hPa as well as in both time periods although the trend is toward a more bimodal distribution at 200 hPa. This suggests that the wind aloft becoming bimodal in November is an artifact of the seasonal cycle rather than resulting from the breakup of the polar vortex. What is

different in the most recent decades is the increase in actinic flux at the same time that the seasonal cycle in boundary layer meteorology is more conducive to high NO levels. In Fig. S7 e,f for Days 341-365 (~December), winds at 300 hPa from the northwest are favored as in Fig. 1 with the effect a bit more evident in 1990-2010 compared to 1960-1980. However, at 200 hPa the wind direction distributions are significantly different with a reversal of the distributions between the two 20-year periods. At both 200 and 300 hPa, winds aloft favor the NW to N directions which are associated with increased cloudiness: This implies even less favorable conditions for high NO during the summer period. This change in the circulation may be due associated with the stronger tropopause strength in the 1960s and 1970s (average difference of 6.7°C between 300 hPa and 200 hPa) versus recent decades (1.6°C). that allows winds in the lowermost stratosphere to be less isolated from those in the upper troposphere.

2.4 Seasonal variation in cloudiness

Shallow boundary layers occur most often with clear skies. With cloudy conditions the boundary layer is usually deep and well mixed (Neff et al. 2008). It has been noted that cloudiness has generally increased over Antarctic in recent decades (Neff 1999; Schnell et al. 1991). Figure S8 shows an updated version of Plate 5 in Neff (1999) from 1957 to 2013 of average cloud fraction at the South Pole from winter to summer. The figure shows a continued increase in cloudiness in late winter and summer after 1980 and, a somewhat decadal periodicity, a mid-summer/late spring minimum generally during Julian Days 325-350 as well as a late winter increase in cloud fraction in the most recent decade. The minimum in cloudiness during Julian Days 325-350, when shallow boundary development is more likely due to increased clear-sky radiative cooling and also coincides with increased actinic flux due to the persistent ozone hole of recent decades. This is also the period in 2003 and 2006 when the highest and most persistent NO occurred (in 1998, the field program started late and in 2000, the ozone hole filled early). Conversely, the summer period has, on the average, become cloudier, albeit subject to interannual and decadal variability, and hence less conducive to higher NO.

However, the average cloud fraction can vary within a season and from year to year. For example, the average cloudiness for days 310-340 (late spring) was 6.5, 5.1, 3.9, 5.1 for 1998, 2000, 2003, and 2006 respectively. In 1998, the late spring period was particularly cloudy compared to average conditions. However, after a late start to observations (see Fig. 1), higher NO occurred intermittently later in December during days with clear skies, light winds and higher actinic flux (due to the delay in the breakup of the ozone hole that year). The intermittency in 1998 is also reflected in the very limited values of NO in excess of 500 pptv (only 4% compared to 25% in 2003, Table 1) -The relative minimum in cloudiness marks the transition in the dynamical regime favoring transport of clouds from West Antarctica to one favoring transport from the area of the Weddell Sea. Following this minimum, cloudiness again increases in concert with decreasing inversion strength. This period also occurs at the time of the sea ice minimum implying a shorter moisture transport path from the open ocean to the interior. Because the total column ozone increases at the same time, the lower actinic flux coupled with higher cloud fraction and its effect on the boundary layer will not be as favorable for high NO concentrations. Figure 4-5 shows an example of this behavior of the importance of short-term variability in creating high NO episodes using an example from 2006 when a minimum in cloudiness occurred around JD 337 (3 December 2006) just before the photolysis rate for nitrate, $j(\text{NO}_3^-)$ started decreasing by 40%. This decrease was associated with the breakdown of the winter stratospheric vortex and the attendant increase in ozone which results in decreased UV flux due to absorption in the stratosphere. Figure 4a-5a summarizes the

330 consistent timing of this cloud minimum showing the 2000-2010 average observer-based cloud-fraction compared to that in
2006 (using 14-day running averages). Figure 4b5b, using three-day running averages, shows the timing of the cloud-
fraction minimum in 2006 relative to the start of rapid warming and ozone increases in the lowermost stratosphere: the
maximum in nitrate photolysis rate occurs just prior to the stratospheric warming as shown in the figure as well as in Fig.
4e5c. Figure 4e-5c shows the direct solar irradiance for JD 335-340 (December 1-5) where decreases indicate the presence of
335 clouds which affect the surface radiation balance. The daily average cloud fraction (green bars - from the SP climatological
record) shows close inverse agreement with the average direct solar irradiance. Starting on JD 337, skies clear, leading to the
rapid formation of a surface temperature inversion below 10m as seen on the 22-m tower. Several hours after the cooling
starts, the winds shift from N to SE (winds not shown), the inversion strengthens and hourly NO increases to nearly 800 pptv
(1200 pptv in 10-min averages) despite a modest decrease in actinic flux. What is interesting in this case is the fact that even
340 though the photolysis rate is decreasing, NO is increasing locally. What is unknown is whether high NO was generated
earlier away from the SP and then transported into the site. This will be discussed more fully in Section 3.2. These results
still suggest the dominant role of a strong surface inversion, shallow boundary layer and potential non-linear NO_x chemistry
as suggested by Davis et al. (2004).

2.5 The role of local topography

345 Figure 5-6 shows the local terrain within several hundred km of the South Pole as well as the location of the clean air sector
(340° to 110° - where no potential contamination sources are allowed) and other areas of potential anthropogenic NO_x
sources (210° to 340°) that depend on wind direction. As noted in the figure, the station power plant lies almost due west of
the Atmospheric Research Observatory (ARO) whereas runways and aircraft taxiways and parking areas encompass much of
the 210° to 340° sector. To avoid potential contamination, data from this sector were removed from the analysis. Except for
the power plant, other anthropogenic NO_x sources are likely to be intermittent and show up as large outliers and were also
350 removed.

Although discussions of the slope flows at the SP generally assume an idealized sloped plane of great fetch, the local
topography is much more complex as seen in Fig. 56. In fact, the terrain rises 250 m in the first 150 km to the east of the SP
(slope~0.002) just adjacent to an extensive plateau (slope~0.0003) that begins 150 km east of the SP and extends 200 km to
the foot of the relative steep central Antarctic dome that rises to 4 km ASL to the northeast. In addition, a small “air
355 drainage” basin about 100 km in extent lies to the southeast. The average surface wind direction from the northeast follows
terrain isopleths for several hundred km rather than flowing down a slope as is normally envisioned. However, while the
average surface wind direction at SP is from the northeast along the terrain, the wind direction actually fluctuates between
north (with warmer temperatures) and east (with colder temperatures). In the winter, the difference in the centers of the wind
direction distributions for warming- and cooling-events is 90° (Neff 1999). The distribution for our summer experimental
360 periods is narrower with maxima at 20° and 70° and a relative minimum at 40°. Figure S9 shows an example of the
distribution of 10-min NO concentrations as a function of wind speed and azimuth for November 16 -30, 2006. In this case
surface wind directions between 50° and 150° and speeds less than 5 ms⁻¹ account for most of the high NO concentrations,
consistent with Fig.34. These directions align closely with the shallow basin to the east-northeast and southeast of the South
Pole (Fig. 56).

365 2.6 Possible meteorological precursors to high NO

We have shown the dependence of NO on 10-m wind speed and direction (Figs. 3-4 and S9). However, in both 2003 and 2006, prolonged and high NO occurred in the last half of November (Fig. S401). This raises the question of whether antecedent conditions set the stage for high NO. In particular, past studies (Mahesh et al. 2003) have noted the systematic change in wind speed between November and December and also concluded that blowing snow was prevalent at the South Pole when the wind exceeded about 7.5 ms^{-1} which was more likely in November. Figure S11-S10 shows the 1-min wind speed distributions between November and December for the four ANTCI seasons revealing the much higher prevalence of winds in excess of 7.5 ms^{-1} in November. Table S1 shows a more detailed breakdown of the number of hours of winds exceeding 7.5 ms^{-1} for October, November, and December for each of 1998, 2000, 2003, and 2006. Unlike the other field experiment years, 2003 saw the fewest high winds in November and the greatest number in December (although light winds only prevailed after 10 November). Snow stake-field depth data in 2003 showed an increase in snow depth of 6.1 cm in October whereas November showed a decrease of 1 cm (from Local Climatological Data records - <ftp://amrc.ssec.wisc.edu/pub/southpole/climatology/>). A coincidence between blowing snow and increased surface nitrate has been observed at Halley Station (Mulvaney et al. 1998) where high wind events in November coincided with increased accumulation followed by a lowering of the snow surface though processes such as sublimation and metamorphosis such as also observed in 2003 at the SP. Following the high wind period at Halley Station, a factor-of-four increase in surface snow nitrate concentrations was seen (followed by significant losses over the subsequent 10 days). They suggested one possibility for this increase was scavenging by wind-blown snow crystals of air rich in nitric acid during the high wind period followed by the loss of water vapor via sublimation resulting in higher concentrations of nitrate on the surface. Recent research at Concordia Station on the high Antarctic Plateau reported a similar increase in surface nitrate in early December (Berhanu and Co-authors 2015). Wind speed had been high in late November (Frey et al. 2015a) followed a week later by high skin nitrate and high fluxes of NO_x from the surface consistent with the observations of Mulvaney et al. (1998) at Halley Station.

380 3. Case studies and insights from new 2006 data in the context of past experiments

Figure 1 provided a summary of all four field programs. Here we focus on events that reflect the coupling of boundary layer meteorology and chemistry using the unpublished data set obtained from 2006 to early 2007 and compare with previous field studies. Of the four field periods, 2006-2007 was the only one to capture the early spring to summer transition in meteorology and chemistry. To provide an overview of the seasonal evolution and short-term weather events on near-surface NO concentrations in 2006, Fig. 6-7 shows the time series of NO, wind direction, wind speed, and temperature from 1 November 2006 (Day 305) through 13 January 2007 (Day 378) with eight events highlighted and labeled “A” through “H”. In addition, hours of relatively clear skies (direct irradiance $>80\%$ of maximum) are indicated on the temperature plot with hash marks plotted at -20 C . and daily cloud fraction less than $6/10^{\text{ths}}$ at -15 C on the temperature time series panel. In general, high direct irradiance associated with a lack of clouds, implies a net loss of radiation from the surface because of the cold dry atmosphere that prevails over the SP, high albedo, and the lower sun angle compared to other polar sites. In each of these cases in 2006, higher NO follows the clock-wise rotation of the wind past 60° together with slight-to-moderate drops in temperature (see Fig. 4). The duration in each case ranges from less than a day to multiday periods. Episodes “A to C” follow high wind episodes by 2 to 3 days. Episode A in Fig. 6-7 reveals a rapid increase in NO as the

wind shifts to the east and weakens, followed by a rapid decrease as the wind increases to 10 ms^{-1} and shifts to northerly. Episode “B” follows several periods of winds reaching 10 ms^{-1} until JD320 (16 November) followed by lighter winds from easterly directions and persistently high NO for almost ten days. During the period of high NO in “B”, winds at 300 hPa were consistently from the SE, an artifact of a persistent, elongated trough of low pressure over the higher terrain grid NE of the South Pole (see also Fig. S4S2). Episode “C” was explored in the example shown in Fig. 4-5 and will be discussed more fully below. Episodes “D-G” represent short excursions of NO and all occur with lower wind speeds and occasional easterly directions. Episode “H” is included because of its contrast with early periods and its occurrence as one of the few “events” available during the summer period: “H” begins with the temperature exceeding -20 C and then dropping to between -30 C and -25 C with the arrival of a cold front and clear skies. The highest temperatures, above -20°C , occurred during totally overcast skies, a weak inversion, and NO concentrations less than 100 pptv. Later, there were periodic wind shifts to the east, clear skies, light winds and colder temperatures, and higher but modest levels of NO (200-300 pptv). In this case, NO levels remained only moderate despite weak easterly winds, increased inversion strength, a shallow boundary layer, and a longer potential fetch.

3.1 NO levels before and after the final warming of the stratosphere

Of particular interest in 2006 is the fact that Episode ‘C’ occurred just prior to the final warming of stratosphere (Fig. 45). As noted earlier, from 1990 to 2010, this warming occurs on the average on Day 336 and coincides with the transition in the seasonal cycle as summarized in Fig. 42. Comparing NO levels for 20 days before and after Episode “C”, 20% of hourly NO levels >400 pptv occur before (JD305-340) and only 6% occur after (JD340-360). Similarly, in 2003, 43% of hourly NO levels >400 pptv occur before (JD326-335) and only 10% occur after (JD340-360). In both 2006 and 2003 high NO events were typically associated with periods of SE winds aloft. Table S2 shows the breakdown of SE (45° - 225°) and NW (225° - 360°) winds at 300 hPa. For both 2003 and 2006 the distributions of wind directions for $\text{JD}<340$ are very similar but the average NO differs by a factor of two (2003: 445 pptv; 2006: 247pptv). For $\text{JD}>340$, 2003 has many more NW winds than 2006 but similar average NO (200 pptv in 2003 and 175 pptv in 2006). In 2003, 300-hPa wind distributions were consistent with long-term averages (1990-2014) whereas 2006 was an anomaly in early summer with many fewer NW winds aloft and many more from the SE (see Fig. 23). Comparing these two years reveals the complexity introduced by meteorology: In 2003 NO was fairly low after JD340 during a period of higher winds and cloudy conditions but then followed by a single high NO episode near the end of the month whereas 2006 saw sustained moderate NO concentrations throughout the period (see Fig. 1). An implication from the 2006 data is that despite meteorological conditions (wind speed and direction) conducive to high NO in both November and December, Thus the much lower average NO after JD340 in both years emission fluxes from the snow are likely lower in December, appear consistent with the results-conclusion from (Frey et al. 2015b) for the last half of December and early January at Concordia Station. Frey et al. argues, based on the laboratory results of (Meusinger et al. 2014) that the snow nitrate is composed of both photo-stable and photo-labile fraction and that the photo-labile fraction decreased later in December at Concordia Station. Our results would be consistent with that interpretation-although one would also need to consider the effect of warmer and cloudier conditions with deeper boundary layers later in the summer as the seasonal cycle progresses- and show the value of multi-year and intraseasonal comparisons of NO.

It should be noted that we did not consider 1998 or 2000: in 1998, the breakup of the vortex was much delayed whereas in 2000 it was very early (Harnik et al. 2011; Neff 1999). Figure S10 1 summarized the spring cycle in NO levels and extremes showing hourly NO concentrations for all four years as well as the day on which total column ozone at the South Pole first exceeds 300 DU. The figure showed that 2003 and 2006 are similar in sustained high NO in late November with a few isolated peaks in late December (typically with light winds, strong surface inversions, and clear skies). It should be noted that the 2003 peaks in NO in late November stand out as the highest in all four years. As noted earlier, this was also a period of lowest cloud fraction and light winds. In 2000, the ozone hole filled in early November coincident with the breakup of the polar stratospheric vortex: NO concentrations stayed very low through the entire observing period. In 1998, the ozone hole filled briefly near the end of December followed by a very delayed (until the end of January 1999) formation of the thermal tropopause due to a cooler than normal lowermost stratosphere. In addition, as noted in Section 2.2, 2003 was unusual with a reduction in snow heights in November whereas 2006 saw continuous increases in snow depth through November which may have reduced the exposure of surface nitrate to photolysis and recycling.

3.2 Meteorological and other potential local and external influences on NO concentrations

Figures 1-42-5 revealed that there were well defined meteorological regimes that favored high NO concentrations that involved wind directions aloft from the southeast, surface winds from the east, and a surface energy balance that was strongly influenced by clear sky conditions. Past work has indicated that the SP is not isolated from the influence from more northerly latitudes. For example, high methanesulfonate was observed from 28 November to 2 December -- an indication of marine sources (Arimoto et al. 2008). This period had the highest NO values recorded in the entire series of field programs (Davis et al. 2008) similar to those found at Concordia in a similar time frame in 2011 (Frey et al. 2015). Furthermore, as suggested in (Arimoto et al. 2008) air arriving at the South Pole may have had its origins in continental regions (due to much higher concentrations of the elements Pb, Sb, and Zn than in previous field programs) as well as in the ocean off Wilkes Land on the far side of the continent.

~~Other antecedents may include transport of NO_x in the free troposphere that then mixes to the surface supplying nitrate or alternatively, that air previously in contact with the surface was enriched from snowpack emissions upwind of the station (Huey et al. 2004). As an example, Concordia Station in early December 2011 (Berhanu and Co authors 2015) showed large increases in surface nitrate following a period of high wind in late November (Frey et al. 2015a). Similarly at the South Pole in 2003 particularly high filterable nitrate was observed in the period JD328-338 (24 November to 4 December) as well as high methanesulfonate from 28 November to 2 December — an indication of marine sources (Arimoto et al. 2008). This period had the highest NO values recorded in the entire series of field programs (Davis et al. 2008) similar to those found at Concordia in a similar time frame in 2011 (Frey et al. 2015a). Furthermore, as suggested in (Arimoto et al. 2008) air arriving at the South Pole may have had its origins in continental regions (due to much higher concentrations of the elements Pb, Sb, and Zn than in previous field programs) as well as in the ocean off Wilkes Land on the far side of the continent.~~

The conceptual description of Arimoto et al. depended on the December 2003 mean geopotential pattern which reflected a large high pressure region over east Antarctica and its large scale counter clockwise circulation. However, the pattern for the

ten days prior to December 4, 2003, when NO was the highest, was much more complex as shown in Fig. S112, with lower
GPH over most of the continent and deep lows over the southern Weddell Sea, Enderby Land and Victoria Land all in
475 position to provide transport of air from more northerly latitudes. Figure S13-S12 shows the ERA-I trajectory for air at 700
hPa arriving near the South Pole at 12Z on 30 November 2003 from the vicinity of Wilkes Lake which extends between
about 100° E and 140° E. The period after December 4 was consistent with the pattern described by (Arimoto et al. 2008)
with much higher GPH over East Antarctica. This leaves open the question of the origins of high snow nitrate in late
winter/early spring insofar as October-early November is a period of vigorous transport from latitudes north of Antarctica
480 following the maximum in the semi-annual oscillation and as evidenced by high cloud fraction (Neff 1999).

Episode “C” is quite interesting insofar as it is preceded by a period of high winds and a rapid surface wind shift from north
to southeast following the winds at 300 hPa. Figure 7-8 shows this case in more detail using wind data from the South Pole
and AWS stations Henry (100 km along 0° E) and Nico (100 km along 90° E) as seen in Fig. 5. These data show that as the
wind speed aloft drops, the surface wind speed also drops to less than 0.5 ms⁻¹ albeit sequentially first at Henry, then Nico,
485 and finally at the South Pole. The increase in NO follows a surface wind direction shift and increase in speed from the SE
that appears first at Henry and then four hours later at the South Pole. These shifts are quite abrupt whereas that at Nico is
more gradual. The increase in NO at the South Pole does not coincide with the drop in wind speed to 0.5 ms⁻¹ (which would
have implied local accumulation or local sources) but rather follows during an increase in wind speed with the wind direction
shift to the SE (from the basin shown in Fig. 56.) This suggests a hypothesis that this basin to the SE is an accumulation area
490 for high NO that is exhausted after an hour or two (see Fig. 78: with wind speeds of 2-4 ms⁻¹, transport distances of 7 to 14 km
per hour might be inferred).

Tracing the progression of the event through the AWS and the South Pole, suggests that the event is triggered by a mesoscale
disturbance propagating from the NE that leads to boundary layer changes. However, referring to Fig. 7d8d, it appears that
clearing skies quickly result in a low-level radiation inversion and associated shallow BL in which NO can accumulate. The
495 22-m tower data show that most of the radiative cooling is felt below 10 m. Of interest in this case is the greater contribution
of mesoscale processes relative to the potential influence of katabatic forcing. Figure 8-9 shows geopotential and wind field
at 650 hPa from ERA-I (~300-400 m above the surface at the SP) during this event at 12Z, JD 337 (3 December) between 90°
S and 75° S. In this case a small mesolow formed to the west of the SP and ~~migrated-rotated~~ **migrated-rotated cyclonically** to just north of the
SP over 24 hours. It then intensified further north bringing air over longer distances from the E to NE back to the station but
500 with a reduction of NO to about 200 pptv over the following day. The rawinsonde at 1048Z on Day 337 recorded winds from
the NE at 8 ms⁻¹ below 100 m. By 2120Z the rawinsonde showed winds increasing in the lowest 100 m approaching 10 ms⁻¹.
It is instructive to compare these winds to those estimated from katabatic arguments. An estimate of the katabatic
acceleration can be obtained from: $\text{acceleration} = 9.8 \text{ ms}^{-2} * \Delta T/T * \sin(\alpha)$. With $\Delta T=2C$, $T=250C$, and terrain slope,
 $\sin(\alpha)=0.002$ (from Fig. 56), the acceleration is $\sim 0.5 \text{ ms}^{-1}$ per hour. Four hours at this acceleration rate would lead to a wind
505 speed of 2 ms⁻¹ and a transport distance of several tens of km. In this case katabatic effects can account for only a small
portion of the local circulation and Fig. 8-9 shows the dominance of meso-to-synoptic scale eddies in producing transport
across the ice sheet. In particular, the small meso-low moved clockwise around SP until at 18Z it was in position to
accelerate easterly flow at the surface. With NO decreasing to 200 pptv following the initial peak of 800 pptv in the
prolonged NE flow, one might reasonably assume that the initial extreme in this case resulted from short-term boundary layer

510 effects but that prolonged levels of 200 pptv are fetch related and reflect accumulation and/or dilution upstream or transport from longer distances.

~~This case also highlights a unique feature of the South Pole, namely the low sun angle through the summer that allows a net loss of radiation from the surface in non-cloudy conditions (Carroll 1982). This is unlike the situation at sites at 75°S and 80°S where a convective boundary forms during the “daytime” such as Concordia Station (King et al. 2006) or Dome Argus (Bonner 2015).~~ The above example of the role of the rapid onset of surface radiative cooling as clouds clear is analogous to observations from Concordia Station (Frey et al. 2015a), which is subject to a strong diurnal cycle and show a similar rapid collapse in BLD in the late afternoon as the surface cools through long-wave radiation. Even though the actinic flux decreases dramatically relative to its value at local noon at Concordia, the BLD collapses even more rapidly as the production of NO into the BL continues, leading to increases in NO to 0.3 to 1.0 ppbv (Frey et al. 2015). It was also concluded by Frey et al. (2015) that the rapid increase in NO with the collapse of the boundary layer in the early evening suggests that nonlinear HO_x-NO_x chemistry need not be invoked in these cases. The case in Fig. 7-9 suggests that smaller enhancements of NO (say, less than 200 pptv) occur with longer fetches when NO can accumulate but large excursions such as those in Fig. 7-8 respond to rapid changes in the surface energy budget that lead to very shallow inversion layers. The subsequent evolution of NO would then depend on chemical processes as well as changes in boundary layer mixing, such as those due to increased wind speeds. Figure 8 also suggests limitations in correlating surface NO with wind shifts at 300 hPa: In this case the peak in NO occurs before the shift in winds aloft; by the next rawinsonde 12 hours later NO has dropped substantially. Given the apparent sensitivity to surface cooling under clear sky conditions, Fig. 9-10 shows the relationship between the magnitude of direct solar irradiance, NO, and surface wind direction. In Fig. 9a-10a, NO > 400 pptv only occurs when skies are essentially cloud-free whereas in Fig. 9b-10b, wind directions > 45 degrees are associated with clear skies. Conversely, more persistent cloudy conditions and surface winds from the west to NNW are associated with lower NO. The few outliers for wind azimuths > 45° indicate the presence of occasional scattered clouds (in hourly data).

530 3.3 BLD calculated for 1998, 2000, 2003, and 2006 data

Given the success of the multiple linear regression technique described in Appendix A which used 22-m meteorological tower data with 2003 sodar data to develop regression equations which were then tested against independent data from 1993, we computed hourly BLD for each of the four years during which NO measurements were recorded. The main time period addressed by these estimates was from mid-November (or somewhat later if data collection started later) to the end of December (for consistency). The next step was to test these data for the inverse relationship between NO and BLD as was found for 2003 (Davis et al. 2004a; Neff et al. 2008). If one bins the data to average out short-term fluctuations (Davis et al. 2004a; Neff et al. 2008) one finds a close inverse relation as shown in Fig. 10-11. Here we averaged BLD for 100 pptv bins of NO. Earlier results (Davis et al. 2004a; Oncley et al. 2004) applied empirical surface-layer similarity relations to observations of turbulence scales in the surface-flux layer to determine BLDs in the 2000 data set. In their results they found BLD between ~80m and ~500m (Davis et al. 2004a) when they binned NO and BLD in sequential 30-point averages. In Fig. 10-11, for 2000, our binned BLD data fell between 28 m and 100 m, a factor of ~3 less in total range. A key argument for high NO at the SP has been the presence of shallow boundary layers which Fig. 10-11 confirms. However, in contrast, direct measurements of BLD at Summit Station Greenland (3216m ASL, 72.6°N, 38.5°W) show values of NO in the range of only

10-30 pptv with BLD on the order of 5 m (Van Dam et al. 2013). One potential explanation for this difference is the high snow accumulation rate in the summer at Summit Station of 5.0 to 7.5 cm per month in the summer, maximizing in July (Castellani et al. 2015).

550 ~~Results from 2003 stand out in Fig. 10. Recapping the findings of Neff et al. (2008), an unusual period of high NO and/or deeper BLD occurred from 24 November to 4 December. This period was unusual in that strong winds from the east extended from the boundary layer to several kilometers aloft. As described in (Neff et al. 2008) the boundary layer was well mixed up to a capping inversion at about 100 m after an initial shallow phase. This was also a period of high methanesulfonate (MSA) and filterable nitrate that were likely of marine origin either from the Weddell Sea or from across the high eastern ice sheet from Wilkes Land and/or continental regions (Arimoto et al. 2008). During this period there were~~
555 ~~three bursts each lasting 30 to 50 hours of easterly wind and decreasing levels of NO with each burst (765 pptv, 512 pptv, 290 pptv, respectively). The first burst had NO > 900 pptv coincident with high nitrate (0.5 $\mu\text{g m}^{-3}$) and high MSA (0.046 $\mu\text{g m}^{-3}$). The highest MSA occurred toward the end of the first easterly burst (Arimoto et al. 2008).~~

4. Estimating seasonal NO_x emission fluxes for the SP region

560 The development of a robust method for estimating BLD opens the door to estimating seasonal NO_x emission fluxes. This is based on the assumption that the surface flux is in balance with the photochemical loss of NO_x in the overlying BL column. These flux estimates require several factors to be considered. First, the total BL NO_x must be extrapolated from the near-surface measurement of NO. While only NO was measured in previous years, the 2006 measurements included both NO and NO₂. Based on those measurements, NO/NO_x was found to be 0.65 +/- 0.08. This is consistent with NO_x estimates derived from model calculations in previous years (Chen et al. 2001; Chen et al. 2004). Those calculations also indicate that the NO_x
565 lifetime exhibits nonlinear behavior increasing from ~7.5 hours when NO_x is less than 200 pptv to more than 20 hours when NO_x exceeds 600 pptv (Davis et al. 2004a). Along with these effects, tethered balloon measurements at SP during ANTCI 2003 show that the exponential roll off in NO concentrations from the surface to the top of the boundary layer can often be as much as a factor of five for very shallow boundary layers (Helmig et al. 2008; Neff et al. 2008). Using these vertical profiles, the BL column NO_x abundance can be derived from surface NO observations. Given that the roll off in NO may not always
570 be as severe as a factor of five, these are considered to be conservative estimates of the total BL NO_x.

Seasonal NO_x emission fluxes are generated by taking daily average values of NO measurements and BLD estimates (based on Appendix A). Then based on the assumptions listed above, a total BL NO_x and associated lifetime are estimated. The flux is then equivalent to the total BL NO_x divided by the lifetime. It is important to do this calculation daily since changes in BLD can cause total BL NO_x and lifetime to vary in different ways. Results for the four seasons as summarized in Table 4-11
575 are 12.5, 6.3, 13.7, and 9.1 × 10⁸ molec cm⁻² s⁻¹ for 1998, 2000, 2003, and 2006, respectively, assuming a fall-off factor of five. These values are commensurate with expectations from Figure 4-11, with the highest seasonal flux in 2003 and the lowest in 2000. As can be seen in Fig. 4-12, NO concentrations at BLD⁻¹ = 0.03 m⁻¹ (from Fig. 4-11) scale almost linearly with the seasonal average flux (r² = 0.7).

580 Each year shows similar variability in daily flux estimates with standard deviations of 0.4-0.5 (10⁸ molec cm⁻² s⁻¹). These estimates are generally consistent with other published flux estimates for the Antarctic plateau. (Oncley et al. 2004) estimated a flux of 3.9 × 10⁸ molec cm⁻² s⁻¹ at SP in 2000 over several days at the end of November 1998, which is essentially in

agreement with the seasonal estimate for this work. Likewise, flux observations at Dome C have been found to range from 8.2×10^8 to $\text{molec cm}^{-2} \text{ s}^{-1}$ in 2009-2010 to 1.6×10^9 $\text{molec cm}^{-2} \text{ s}^{-1}$ in 2011-2012 (Frey et al. 2015b; Frey et al. 2013). These larger values also exhibit a larger range of temporal variability due to the diurnal cycle at Dome C.

585 | The range of seasonal flux values and daily variability is smaller than might be expected based on Fig. 4011, but it is important to note that under shallow BL conditions, nonlinear growth in NO_x abundance can occur as radical concentrations become suppressed and NO_x lifetime increases (Davis et al. 2004b). Nevertheless, the differences between years are significant and point to other potential factors affecting the seasonal NO_x emission flux. One factor that has already been discussed at some length is the interannual difference in the breakup of the polar stratospheric vortex and associated ozone
590 | hole. With regard to nitrate photolysis, this is particularly important to determining the available UV actinic flux in the early Austral spring over the Antarctic plateau. As shown in Fig. S401, this breakup happened much earlier in 2000, the year with the smallest seasonal flux. A second related factor has to do with the potential for recycling of NO_x between the firm and atmosphere. As described in the following paragraph, secondary NO_x emissions due to recycling are likely to grow in importance throughout the season and are likely influenced by primary emissions in the early spring.

595 | The NO_x emissions flux represents contributions from both primary and secondary release of nitrogen from the snow. Primary release represents the photolysis and ventilation of NO_x from nitrate initially deposited through snowfall. This nitrate can be much harder to release due to cage effects (Noyes 1956) associated with incorporation into the bulk ice phase. By contrast, secondary release of redeposited nitrate should recycle through the atmosphere much faster due to several factors. First, the redeposited nitrate is at the snow surface where higher actinic fluxes are available. Second, being adsorbed to the
600 | surface of ice crystals, redeposited nitrate should be more easily photolyzed. In a laboratory experiment by (Marcotte et al. 2015), photolysis of nitrate on the ice surface was enhanced by a factor of three over nitrate in the bulk ice phase. Finally, redeposition of reactive nitrogen is in the form of both nitric and pernitric acid (Slusher et al. 2002). Pernitric acid would be even more readily photolysed than nitric acid and its relative importance would also increase at lower temperatures. While representing these effects with any realism is beyond the scope of this analysis, more detailed modeling and representation of
605 | the factors influence NO_x emissions are being investigated by other groups such as in (Bock et al. 2016; Frey et al. 2015b). Future laboratory and field studies are needed to further illustrate the complex mechanisms controlling snow NO_x emissions and the chemistry above snow surface.

610 **5. Conclusions**

Earlier work (Davis et al. 2008; Neff et al. 2008), primarily based on 2003 data which included direct sodar measurements of boundary layer depth presented a straightforward conceptual model that linked high NO to shallow boundary layers, light winds, and stronger surface inversions. In our examination of four seasons of observations, explanation of the initiation and evolution of high NO episodes as well as intra-seasonal to interannual variability proved more challenging. Using four
615 spring-to-summer seasons of observations, ~~We~~ we have described the influence of the synoptic- to-mesoscale weather patterns and their seasonal cycle on stable boundary layer characteristics at the South Pole in the spring-summer period that set the stage for high NO episodes ~~on the Antarctic plateau~~. These included

1) The relative unimportance of katabatic forcing compared to the accelerations due to synoptic and mesoscale scale pressure gradients from November through January. In fact, visualizations of near-surface airflow using ERA-I (Dee et al. 2011)
620 revealed complex mesoscale circulations that belied any simple explanation of accumulation pathways for NO.

2) The effect of clearing skies locally that lead to rapid radiative losses and the ~~rapid~~ formation of very shallow inversion/boundary layers and high NO. Given observations only at the SP, the geographical extent of such radiatively driven boundary layers is unknown but worthy of further field observations. Unfortunately aircraft measurements of NO in 2003 (Davis et al. 2008) were not permitted between -40°W and 120° E (the clean air sector). However, the one flight along
625 120°E showed NO in excess of 400 pptv between 100 and 400 km from the SP as NO concentrations were dropping at the SP.

3) The three-phase transition in spring for 300-hPa winds over the SP. These three phases corresponded to ~~4a~~ a late winter regime of transport of moisture over west Antarctica to the interior when the circumpolar trough is at its maximum and opens the possibility for the transport of NO precursors from northerly latitudes, ~~2b~~ a semi-bimodal regime with 300 hPa winds
630 alternating between northwest and southeast quadrants during November and early December as part of the seasonal cycle, followed by ~~3c~~ a summer regime favoring 300-hPa winds from the Weddell Sea and warmer cloudy conditions. During the second phase, 300-hPa winds from the southeast favored clear skies, light surface winds and shallow inversions conducive to high NO concentrations at the same time the total column ozone was still low allowing higher actinic fluxes. 300-hPa winds from the northwest favored warm--air advection and cloudy conditions resulting in deep boundary layers and low NO
635 concentrations. ~~Because these boundary layer characteristics follow the same seasonal cycle as temperature, it is difficult to separate out the temperature dependence of nitrate photolysis rates from December into January.~~

Because of the importance of SE winds aloft to high NO episodes ~~We~~ we examined the frequency of their occurrence of SE winds at 300-hPa ~~and~~ as well as winds at the surface from the east to south during late spring (Days 310-340) from 1961 to 2013 and found strong interannual variability. At 300 hPa the interannual variance was significant but modulated on decadal time scales with a maximum in the period 1995-2010. At the surface, the interannual variance doubled with an upward trend
640 of 30% in the mean in the last 30 years. We also found that extremes in the frequency of occurrence of SE winds at 300 hPa correlated well with extremes in easterly surface winds at the surface ($r^2=0.4$). This suggests that continuous multi-year monitoring may be advisable to avoid sampling bias in the interpretation of the chemical environment over the high Antarctic

645 plateau. We also examined wind distributions aloft between the periods 1961-1980 and 1990-2010 and found no systematic change except that related to the weakening of the tropopause and increased coupling of winds between 300- and 200-hPa. We concluded that the delay in the breakup of the ozone hole in recent decades has allowed higher actinic fluxes to coincide with the optimum time in spring when boundary layer conditions are conducive to high NO concentrations.

650 We also examined NO data collected in 2006 confirming the systematic relationship between NO concentrations and wind direction shifts to easterly with lower temperatures, lower wind speeds, and shallow boundary layers. In comparing 2006-07 with other years, we found similar frequencies of easterly surface winds in 2003, fewer in 1998, and the lowest in 2000. We carried out a case study from 2006 that occurred just prior to the final stratospheric warming. It was at this time that a minimum in cloudiness occurred, a minimum that is persistent in the long-term climatology over 50 years although subject to some synoptic “noise.” Over a few hours in this case study, winds aloft rotated 180° from northerly to southerly (in a grid sense), a mesoscale cool front moved from the northeast (observed in two AWS stations 100 km from the Pole and captured by ERA-I reanalysis) and skies cleared. With a clearing sky, a surface inversion formed below 10 m and NO climbed in 10-min averages of up to 1200 pptv with light surface winds from the southeast. NO>400pptv lasted only eight hours in this case with sustained moderate NO (150-400 pptv) lasting for another 48 hours in a sustained northeasterly flow (see Fig. 8).
655 This case also reveals the difficulty in correlating peaks in NO directly with upper-level winds insofar as the peak in NO occurs in the gap between rawinsonde observations. Perhaps more important are these transitions in upper level winds that signify a direct connection to large scale dynamical changes in the atmosphere over the plateau. In addition,

660 We argued that the source area for extreme NO concentrations was a shallow basin that extended about 100 km from the South Pole to the southeast. In this case we hypothesize that the short-term peak in NO occurred, not from transport in a long-range katabatic circulation but rather originated from local, subtle terrain accumulation areas in the vicinity of the South Pole. This was coupled with rapid radiative losses from the snow surface that created a strong surface inversion below 10 m. In some respects, this situation is similar to the peaks in NO that occur at more northerly sites such as Concordia Station where an evening peak in NO occurs with the collapse of the daytime convective boundary layer into a shallow stable boundary layer. In such cases long fetches are not necessary to achieve extremes in the concentrations of NO. However, in 2006, only 15% of the hourly NO data exceeded 400 pptv whereas 53% lay between 100 and 200 pptv. It is in this latter range that accumulation in long fetches associated with stable boundary layers and meso- and synoptic-scale circulations may be most relevant. However, without observations further away for the SP, we can't rule the possibility that high NO is first generated in a larger area of light winds and shallow boundary layers- upstream of the SP and then with increases in wind speed and boundary layer depth undergoes dilution. In addition, further away from the SP where convective mixing is possible during part of the diurnal cycle, further dilution is also possible. These results suggest further studies of chemical and boundary layer processes along pathways more complicated than predicted by katabatic flow arguments, particularly with the subtle topography to the east and southeast of the SP.

675 We developed a method to estimate boundary layer depth using 20-m meteorological tower data together with direct depth measurements in 2003 and tested against an independent data set collected in 1993. Step-wise linear regression using wind speed and direction, temperature and the 2-to-20 m tower temperature difference produced regression equations that accounted for about 70% of the variance with direct observations. These equations were applied to all four seasons of NO

680 data and confirmed the inverse depth relationships found in earlier studies. However, we also found significant year to year
differences in magnitude of these inverse relationships that suggested interannual variability in the surface fluxes of NO. To
calculate NO_x fluxes, the BLD data were used to obtain an estimate of the BL column NO_x abundance (based on 2006 data
where NO/NO_x ~0.7). The abundance was derived from surface NO observations using a range of values of fall-off with
height obtained from tethersonde profiles in 2003 and calculated using the increased lifetime of NO_x for very shallow
685 boundary layers. For each season, we found the average NO (scaled at 33.3 m from a least-squares fitting of NO versus
BLD⁻¹ for each of four seasons) which followed a nearly linear relationship with the seasonally averaged fluxes of NO_x
confirming the consistency of our analysis. The source of the year-to-year variability in fluxes was not ~~fully~~-resolved but the
variability was consistent with similar results at Concordia Station.

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695 Appendix A Boundary Layer Depth Estimation

In the main sections of the paper we discussed the large- and meso-scale influences on local micrometeorology and chemistry that can set the stage for enhanced levels of NO. Past work has implicated shallow boundary layers as a key ingredient in high NO episodes (Davis et al. 2004a). These shallow boundary layers were associated with lower wind speed, changes in wind direction, colder temperatures and greater static stability as indicated by the temperature difference between 2 and 22 m on a nearby tower (Fig. 4). Although a shallow BLD was proposed as a major factor underlying high-NO episodes, the only direct BLD measurements were those carried out in 2003 using a sodar in combination with surface turbulence measurements and balloon profiling (Neff et al. 2008). However, such supporting measurements were not available for other field seasons.

700 With this background, we examined regression analysis of NO and BLD against the various meteorological variables available to us for all four field seasons including the more recent data from 2006. This establishes some of the basic relationships between NO and BLD for the routine meteorological variables. However, because potential collinearity between a number of the variables, we also pursued step-wise linear regression to find a subset of the variables that best account for NO and BLD for each observational period. This approach eliminates redundant variables. This approach then identified a simple subset of variables to develop prediction equations for BLD through multiple linear regression (MLR). Establishing a relationship between NO and BLD, it then becomes possible to explore the unique chemical mechanisms which might be responsible for the high concentrations of NO at SP as compared with other sites and with the here-to-for under prediction by chemical models (Davis et al. 2008; Frey et al. 2015b).

710 The most routine hourly variables available at SP include wind speed (WS) and direction (WD), temperature (T), and temperature difference across a 20-m tower (ΔT). We also considered hourly direct solar irradiance (DR), net long-wave irradiance NIR, and solar zenith angle (SZA). (The variables DR, NIR, and SZA were available from www.esrl.noaa.gov/gmd.) Cloud fraction (CF) was available as a daily average from station climatological records whereas bulk stability (ΔT_B) was obtained from the twice daily rawinsonde in summer. Sodar data gathered in 1993 (Neff 1994) provided an additional test data set with which to evaluate the effectiveness of the 2003 MLR results. These data were stored as facsimile records rather than digitally [unlike the 2003 data where automated processing was used (Neff et al. 2008)]. Also the sodar in 1993 was operating in a Doppler wind measuring mode so the pulse resolution was coarser (~30 m) so echo layers and hence BLD appeared to extend higher by one half the pulse length or 15 m. To correct for this effect 15 m was subtracted from the BLD estimates.

720 Linear regression results are shown in Table A1 for NO in each of the four field seasons along with results for measured BLD given in Table A2 for 2003. In all four years, the dependence of NO on near surface stability ΔT is consistent. In 2003 and 2006, NO depended primarily on WD, T, and ΔT ; WS was more important in 2003 than 2006. In Table A2, we show overall regression results for BLD in 2003 as well as a breakdown into two periods corresponding to the dynamical changes around JD340 (6 December). The early period, JD326-340, is dominated by WS, T, SZA, and net radiation. The change in the impact of bulk temperature difference in this period ΔT_B , from the rawinsonde, marks the change due to the seasonal cycle as in Fig. S4a. However, based on Fig. S4a, katabatic forcing will be small compared to that due to large scale weather systems. During the later period, JD340-361, WS, WD, ΔT , and cloud fraction CF play bigger roles.

730 In general, NO and 2-m temperature have robust seasonal trends from October to late November except in the year 2000
when the polar vortex broke up a month earlier than normal and the temperature showed no trend after early November and
in 2003 when the trend persisted into early December. In 2003, the dependence of NO on SZA is quite clear with moderate
dependence on direct solar irradiance whose variability depends to some degree on cloudiness (see Figs. 4 and 9: With
respect to Fig. 9a, the simple linear regression between NO and DR in Table I does not capture the threshold effect evident in
735 the figure. (Cases with high DR in Fig. 9a and low NO usually occur under high wind conditions with deep boundary
layers.) The dependence of BLD on tower-measured ΔT is greater than on the bulk inversion temperature difference ΔT_B
which is typically measured over several hundred meters: This is consistent with the fact that the BLD is usually much
shallower than the background temperature inversion and more consistent with the ΔT measured on the 22-m tower. When
 ΔT is dominant over ΔT_B it indicates that the shallow temperature inversion is likely due to surface radiative cooling (with
740 clearing skies) rather than synoptic weather changes. Comparison of these correlations with those from the more extended
data in 1993 sheds some insight into the appropriate variables to use in our MLR analyses (Table III).

From Table A3 (1993 Data), the dependence of BLD on wind speed increases significantly from October to
December while the dependence on ΔT is remarkably consistent; after October, there is little dependence on either cloud
fraction or bulk inversion strength. The increased dependence on WS in December is consistent with changes following the
745 breakup of the polar vortex and the progression of the seasonal cycle. Comparing monthly averaged ΔT with ΔT_B yields the
result: October (1.44/16.5 °C), November (0.34/8.3 °C), and December (0.47/0.10 °C). Typical bulk inversion strength was
obtained over average depths of 542m, 579m, and 622m for each month respectively. This demonstrates the strong seasonal
cycle in inversion strength and the changing seasonal impact on katabatic forcing of surface winds (see Fig. S2a). In
December the near-surface (2-22m) inversion is much stronger than the bulk value from the rawinsonde suggesting that any
750 slope effects will reflect nearby terrain variations such as those shown in Fig. 5. It should be noted that the effect of WD on
BLD is greatest in the transition month of November. With a weaker inversion strength in the summer, those winds
(December) respond mostly to meso- and synoptic scale weather influences such as cloudy versus clear skies and/or high
versus low wind speeds (Neff 1999) rather than katabatic forcing.

A.1 Linear regression

755 Because of the potential covariance of meteorological variables (e.g., often when the wind direction shifts to the SE,
wind speed, ΔT and temperature all decrease: see Fig. 6), we used stepwise linear regression (using SPSS) of NO and BLD
with principal meteorological data as summarized in Table A4. The value of stepwise regression is that it orders the results
by magnitude of the importance of variables to the regression. In Table A4, step-wise regression reveals year-to-year
variability in important variables depending on the year-to-year variability of dominant meteorological regimes. It should
760 also be noted that the step-wise regression process can produce a different sequence of regression coefficients than those
obtained from individual regressions as can be seen in comparing Table A1 and Table A4. The process also excludes
variables that are collinear with other variables in the time series. In this case, results with at least an improvement of 0.02 in
 r^2 are presented as shaded. For BLD in 2003 the principal predictors are WS (56%), T (10% improvement), and WD (7%
improvement). Including ΔT adds little (0.01) because it is significantly correlated with both WS and WD ($r^2=0.3$ for both).
765 When the stepwise regression is applied to only JD340-361, the ordering is WS, WD, and ΔT with T being dropped because
there is no temperature trend. When examining the results for NO, the year-to-year differences in meteorology can be seen in

the dominant independent variable for each year: 1998: WS, 2000: ΔT , 2003:T, 2006:WD. For the most part, meteorology can account for about 50% of the variance in NO leaving unknowns in the emission source terms unaccounted for. 2003 was an exception with 78% of the variance for which meteorology provided the explanation for the variability in NO.

770 Given the dependence of BLD and NO on WS, WD, T, and ΔT for various periods we used these four variables to obtain regression equations for 2003 and 1993 using sodar derived BLD. For testing purposes the regression equation from 2003 was applied to both 2003 and 1993 as well as the regression equation from 1993 to both 1993 and 2003. The equations used were:

775 2003: $BLD=66.9+18.8*WS+0.23*WD+2.9*T-16.0*\Delta T$ (A1)

1993: $BLD=68.3+16.1*WS-0.04*WD+2.3*T-10.0*\Delta T$ (A2)

780 For 2003, $r^2=0.74$ with all the variables highly significant at the 0.000 level (using SPSS software); for 1993, $r^2=0.64$ with all the variables, except WD, significant at 0.000 (WD was at 0.080). Shifting the time series 10 days earlier made all variables highly significant showing the importance of changing weather regimes each year and sensitivity to the length of the time series. The major difference between 2003 and 1993 lies in the relative weights given to WD and ΔT : In 1993 they are of the same sign (reducing BLD) whereas in 2003 they are opposite in sign and partially cancelling. Figure A1 a,b,c shows the results of applying the MLR technique (using WS, WD, ΔT , and T) to 2003 data while Fig. A1 d,e,f shows comparisons using 1993 data. As can be seen in the figures the regression equations capture the transitions between shallow and more deeply mixing boundary layers quite nicely. Because the minimum range for the sodar observations was about 15 m, we set all MLR estimated BLD values less than 15 m (some were negative) to that value. For deeper observed BLD in 2003, the MLR for both 2003 and 1993 regression equations underestimate the depth; for shallow BLD, the MLR overestimates the depth. Overall the MLR method captures about 70% of the variance for both 2003 and 1993. It is also of note that the 2003 MLR, based on observations only to 160 m, does capture the deeper observed BLD in 1993 (Fig. A1) suggesting that wind speed dominates the regression fit in those cases. Figure 10c provides a scatterplot for 2003 data using 1993 and 2003 regression fits with $r^2=0.96$. For 1993, the data appear to have two modes perhaps because of a weather regime shift not captured by the MLR method using just a few meteorological variables (e.g., there was a major change in bulk inversion strength ΔT_B around mid-December). In this case the two equations still agree quite well with $r^2=0.93$.

795 A.2 Results

795 We have extended the past analysis of boundary-layer depth (BLD) effects on NO concentrations from data collected at SP in 2003 to new data collected in 2006-07 as well as past field programs carried out in 1998 and 2000-2001. Stepwise linear regression showed that the principal variables affecting both NO and BLD were wind speed and direction, temperature, and low-level static stability as measured on a 22 m tower. We then used these variables to develop a multiple linear regression equation for BLD using sodar data from 2003 and simple meteorological tower measurements. When we 800 tested the regression equation derived from 2003 data against independent sodar data collected in 1993, we accounted for 60-70 percent of the variance in estimating BLD. We then applied these equations to each year of NO data to examine the NO response to BLD. When the data were binned in 100 pptv bins (Fig. 10), we found a linear fit between NO and 1/BLD with regression fits accounting for 88% to 97% of the variance confirming past results. When we looked at the binned data for

BLD=100 m, all four years converged with NO levels of about 50-100 pptv. However, at BLD=25m there was a systematic
805 spread in NO according to observation year resulting in NO that ranged from 200 to 1000 pptv. In looking at the results of
step-wise linear regression for NO we found a different primary variable in the regression for each year: 1998: wind speed,
2000: ΔT , 2003: T, and 2006: WD. This primarily reflects the different weather regimes for each year and the need for
multi-year observations to fully understand the various factors leading to high NO concentrations.

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Tables

Table X Percentage of hourly NO values in three ranges compared over the four experiment years shown in Fig. X1.

	1998	2000	2003	2006
<i>Total hours</i>	438	806	516	1601
<i>NO < 200 pptv</i>	28%	89%	31%	68%
<i>200 pptv < NO < 500 pptv</i>	68%	10%	44%	29%
<i>NO > 500 pptv</i>	4%	1%	25%	3%

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Table 1 Assessment of ISCAT/ANTCI NO_x flux at SP for BL concentration fall-off of factor of 5

<i>Year^a Time-period</i>	<i>10m-NO_x^b molec/cm³</i>	<i>Avg-NO_x^c molec/cm³</i>	<i>BLD_{avg}^d cm</i>	<i>NO_xCD_{f5}^e molec/cm²</i>	<i>τ_{NO_x}^f s</i>	<i>Estimated NO_x Flux^g molec/cm²/s</i>
<u>2006</u> 11/15-12/31	6.8 x 10 ⁹	4.7 x 10 ⁹	6.1 x 10 ³	2.9 x 10 ¹³	3.2 x 10 ⁴	9.06 x 10⁸
<u>2003</u> 11/22-12/27	10 x 10 ⁹	6.5 x 10 ⁹	8.1 x 10 ³	5.2 x 10 ¹³	3.8 x 10 ⁴	1.37 x 10⁹
<u>2000</u> 11/15-12/31	3.2 x 10 ⁹	2.1 x 10 ⁹	8.3 x 10 ³	1.7 x 10 ¹³	2.7 x 10 ⁴	6.30 x 10⁸
1998 12/1-12/31	7.8 x 10 ⁹	5.4 x 10 ⁹	7.5 x 10 ³	4 x 10 ¹³	3.2 x 10 ⁴	1.25 x 10⁹

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(a) Year of NO or NO_x measurement and time period (Year-time period); (b) average NO_x or NO measured at 10m - NO converted to NO_x as discussed in text; (c) average NO_x concentration within BLD; (d) average BLD; (e) average NO_x column density, given BL concentration fall-off factor of 5; (f) average NO_x lifetime; (g) Estimated NO_x flux – derived from average column density divided by the average NO_x lifetime.

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Table A1 Regression (r²) of Meteorological Variables with NO. r² > 0.2 in bold. No trends were removed.

WS	WD	T	ΔT	CF	ΔT _B	SZA	DR
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NO 1998 (JD 335-365)	0.15	0.07	0.26	0.26	0.15	0.00	0.11	n/a
NO 2000 (JD 320-366)	0.14	0.16	0.11	0.41	0.08	0.01	0.00	n/a
NO 2003 (JD 326-361)	0.29	0.45	0.51	0.25	0.18	0.34	0.37	0.14
NO 2006 (JD 320-379)	0.18	0.25	0.56	0.36	0.06	0.34	0.07	0.15

935 Table A2 Linear Regression of BLD with observed meteorological variables in 2003

	WS	WD	T	ΔT	CF	ΔT_B	SZA	DR	NIR
BLD 2003 (JD 326-361)	0.56	0.10	0.25	0.32	0.03	0.14	0.13	0.07	0.00
JD 326-340	0.48	0.01	0.73	0.15	0.21	0.23	0.72	0.02	0.58
JD 340-361	0.67	0.46	0.06	0.53	0.32	0.10	0.19	0.16	0.14

Table A3 Regression (r^2) of Meteorological Variables with BLD, October-December, 1993(no radiation data in 1993)

	WS	WD	T	ΔT	CF	ΔT_B
OCT	0.33	0.07	0.20	0.23	0.02	0.17
NOV	0.37	0.20	0.02	0.27	0.06	0.00
DEC	0.64	0.01	0.15	0.24	0.01	0.00
JD 326-361	0.61	0.04	0.17	0.24	0.00	0.00

940

Table A4 Stepwise linear regression analysis (r^2) for BLD and NO (mid-November-December.)
 Stepwise improvements of 0.02 or better are highlighted.

BLD	2003(all)	0.56	0.66	0.73	0.74
	Variable	WS	+T	+WD	+ΔT
	2003 (Days 340-361)	0.67	0.72	0.74	Excluded
	Variable	WS	+ΔT	+WD	T
	1993	0.60	0.63	0.64	Excluded
	Variable	WS	+T	+ΔT	WD
NO	1998	0.25	0.40	0.43	0.47
	Variable	WS	+ΔT	+T	+WD
	2000	0.42	0.51	0.54	0.55
	Variable	ΔT	+WS	+T	+WD
	2003	0.51	0.76	0.78	0.79
	Variable	T	+WD	+WS	+ΔT
	2006	0.32	0.48	0.53	0.59
	Variable	WD	+ΔT	+T	+WS

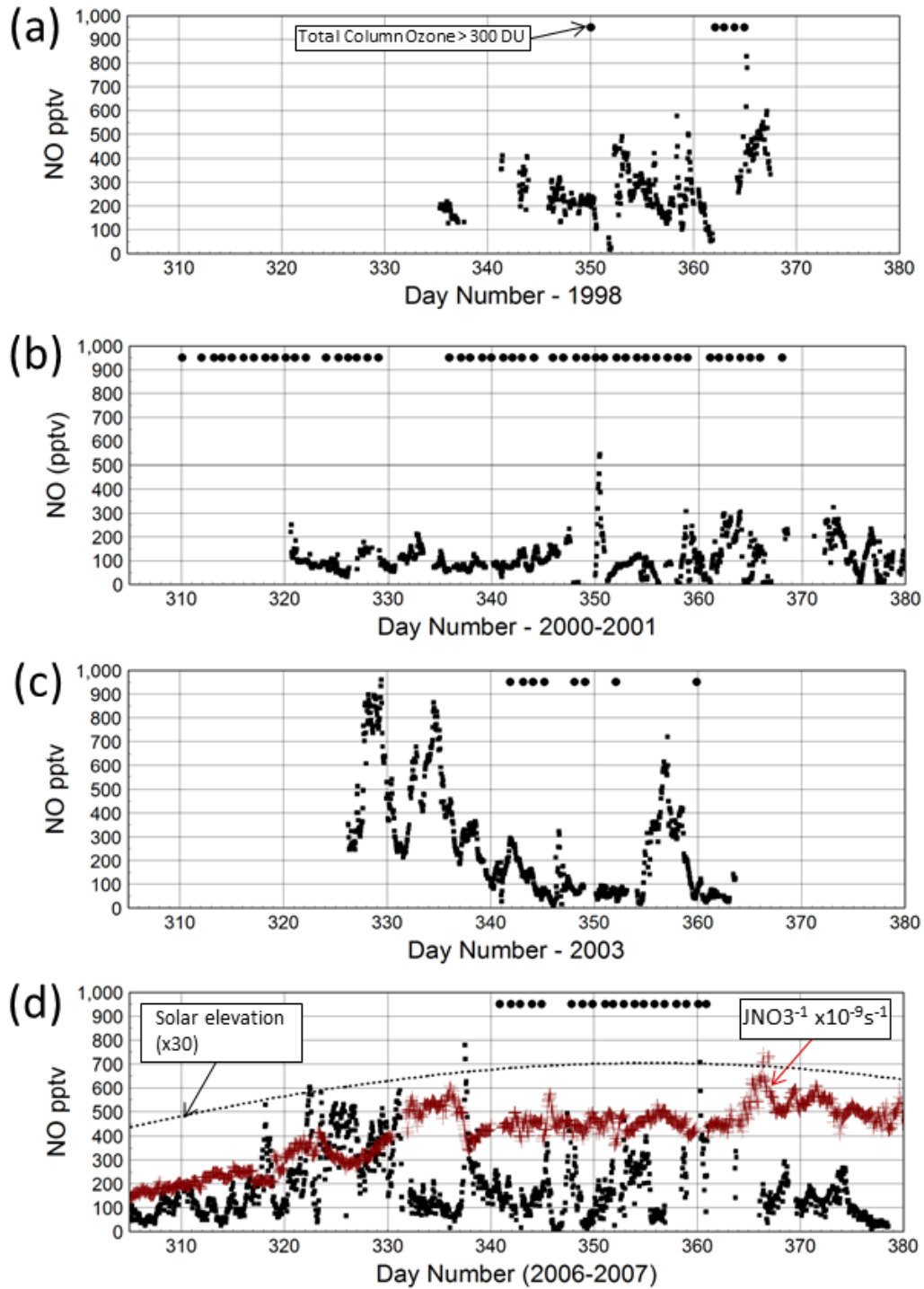


Figure X. Primary periods of data collection used in our analysis for a) 1998, b) 2000-2001, c) 2003, and d) 2006-2007. Periods of daily total column ozone in excess of 300 DU appear at the top of each panel. In d) the seasonal change in solar elevation angle (x30) is shown together with the nitrate photolysis rate (JNO_3^{-1}).

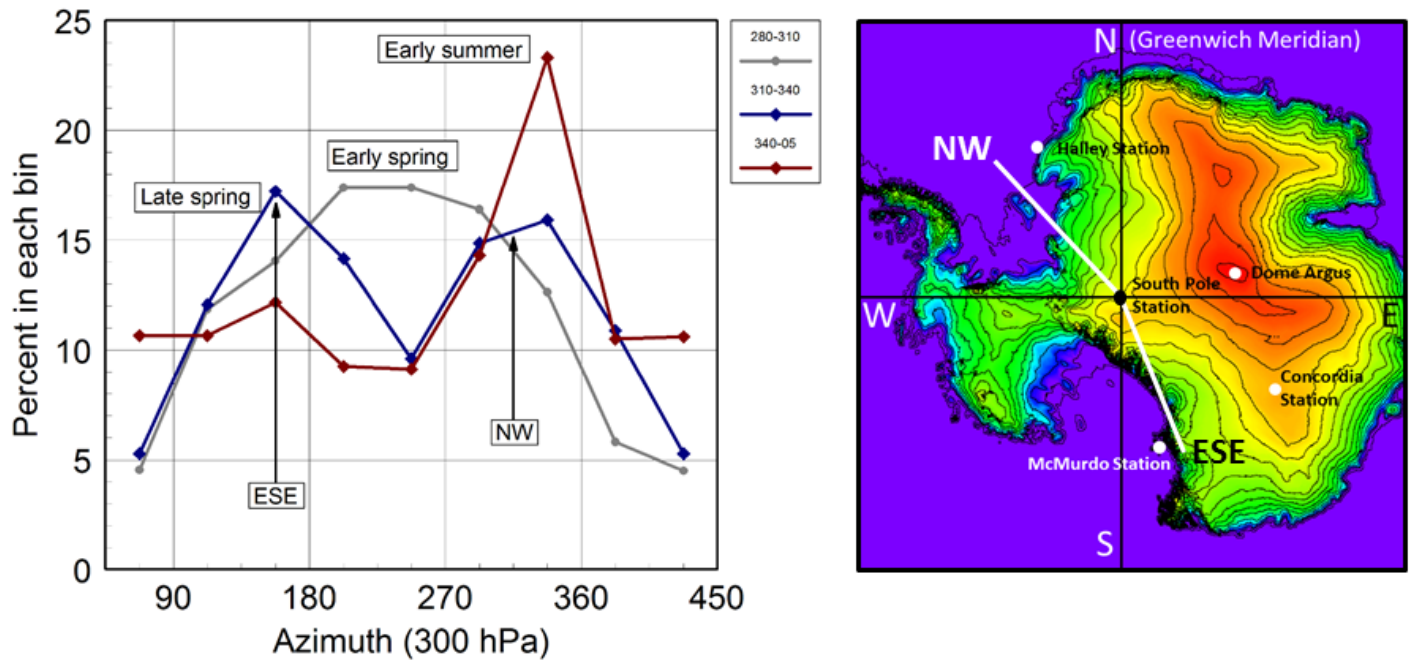
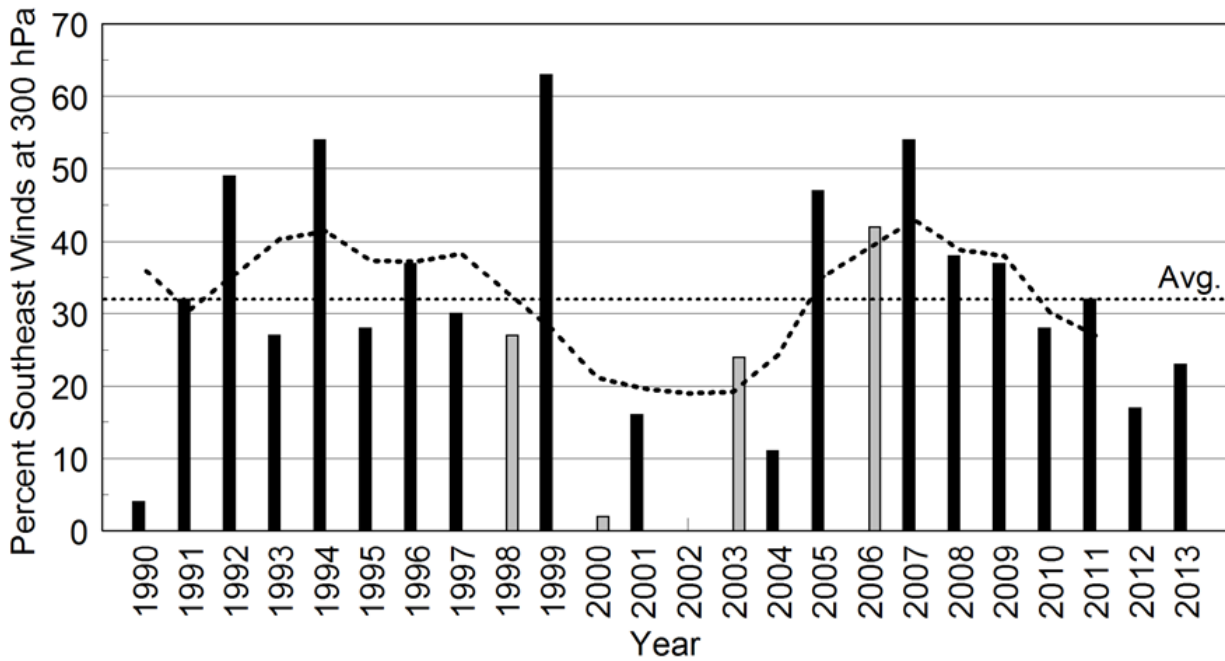
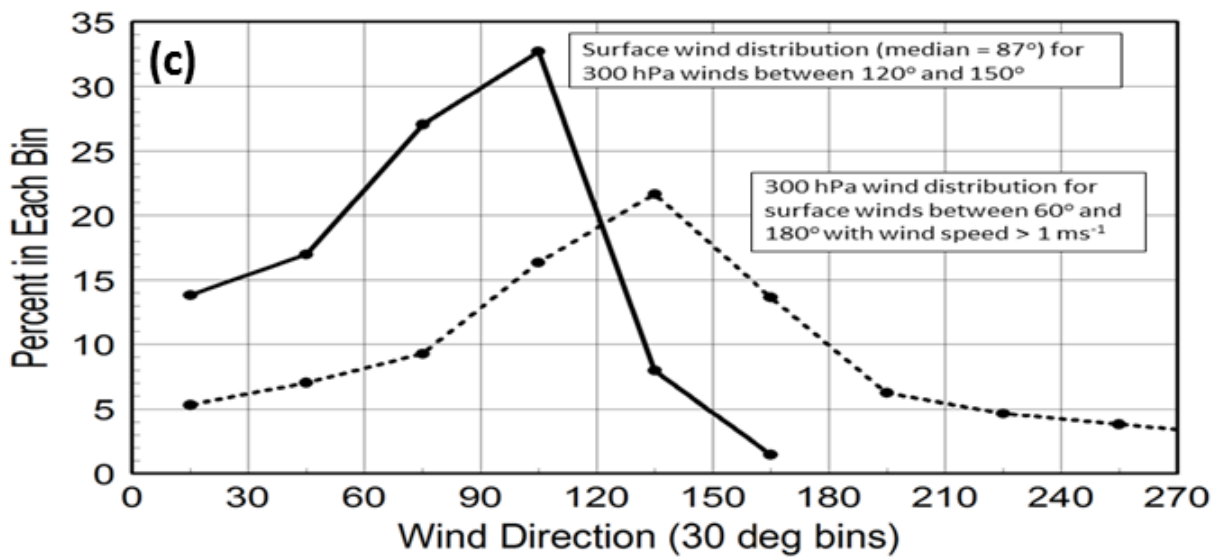
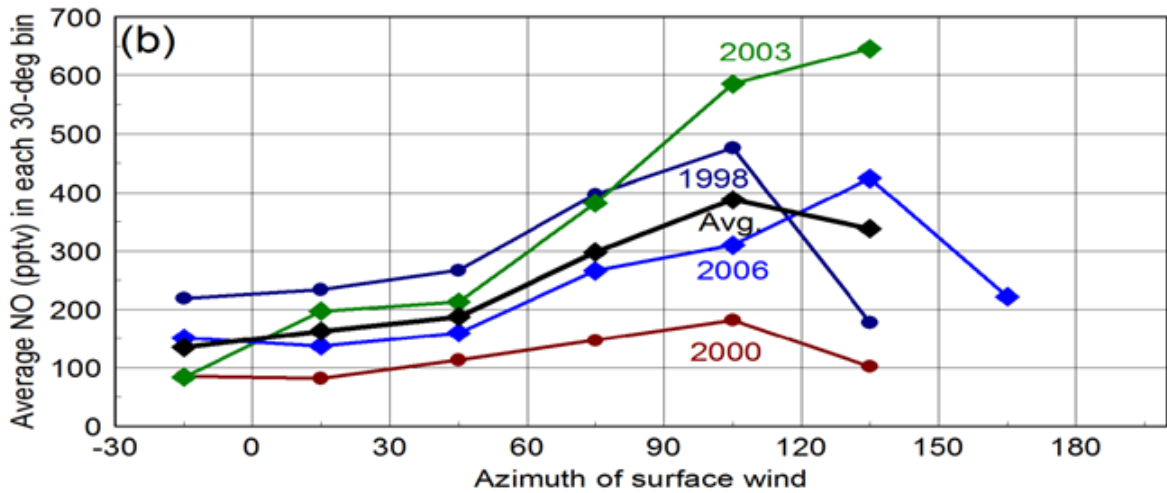
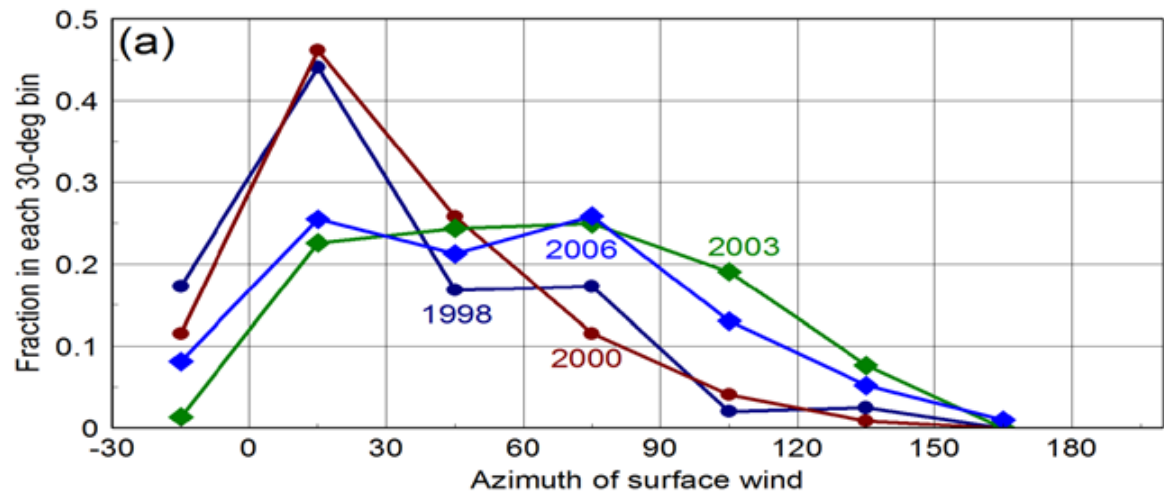


Figure 1. Left: Histograms of wind directions sorted in 45° bins ($>5\text{ms}^{-1}$) at 300 hPa for early spring (Days 280-310, gray line) and late spring (Days 310-340) and early summer (Days 340-370) over the period 1990-2013. Right: Topographic map of Antarctica. In late winter/early spring winds aloft are primarily from the direction of West Antarctica and the Amundsen Sea ($\sim 270^\circ$). In late spring, 300-hPa winds become bimodal in direction, with higher probabilities from $\sim 157.5^\circ$ and $\sim 337.5^\circ$ and fewer from the west. Past work has indicated that winds from 157.5° bring cooler temperatures and lighter wind speeds to the South Pole: this direction corresponds to an inland directed synoptic scale pressure gradient. Conversely, 300-hPa winds centered on 337.5° are typically associated with higher surface winds, increased cloudiness, and warmer temperatures: this direction reflects an off-shore directed synoptic pressure gradient. In early summer, winds at 300 hPa increasingly favor a north-northwest direction from the Weddell Sea.



965 Figure 2. Percent of 300 hPa wind directions between 67.5° and 202.5° for each year 1990 to 2010 for mid-November through December. Experiment years are shaded gray and the longer term variability shown using a 5-yr smoothing. The year 2002 was eliminated because of the never-before seen sudden stratospheric warming that year. The average over 20 years is shown by the dashed line.

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975 Figure 3. a) Comparison of surface wind direction distributions for 1998, 2000, 2003, and 2006, b) the
average NO over ~~four~~ each years as a function of wind azimuth in 30° bins. Wind directions between
210° and 340° (-20°) are not included because of potential contamination from the station and aircraft
operations. A total of 3300 hourly values of NO were averaged in 20°-30° wind-direction bins. c)
980 Distribution of 300 hPa wind directions when the surface wind is between 60° and 180° and greater than
1 ms⁻¹. Also shown is the distribution of surface winds when the 300 hPa wind directions are between
120° and 150°. Median values are 87° and 134° respectively showing that surface winds tend to be
easterly when winds aloft are from the SE.

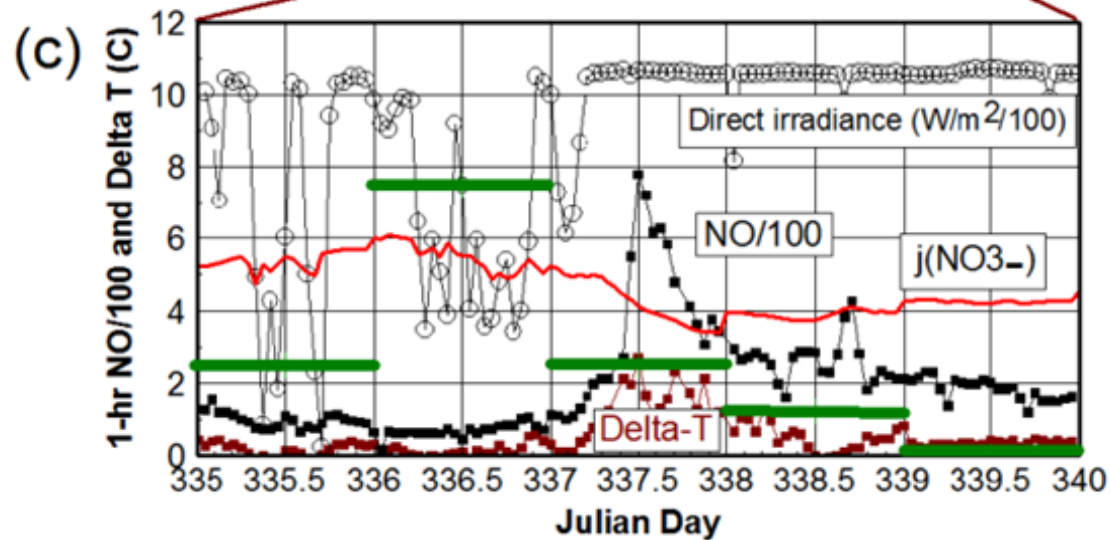
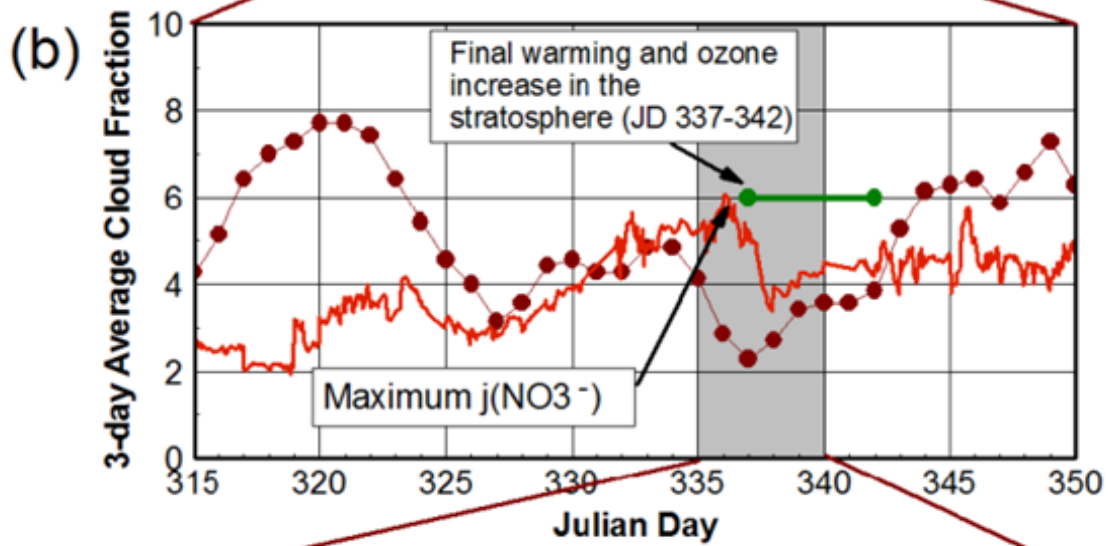
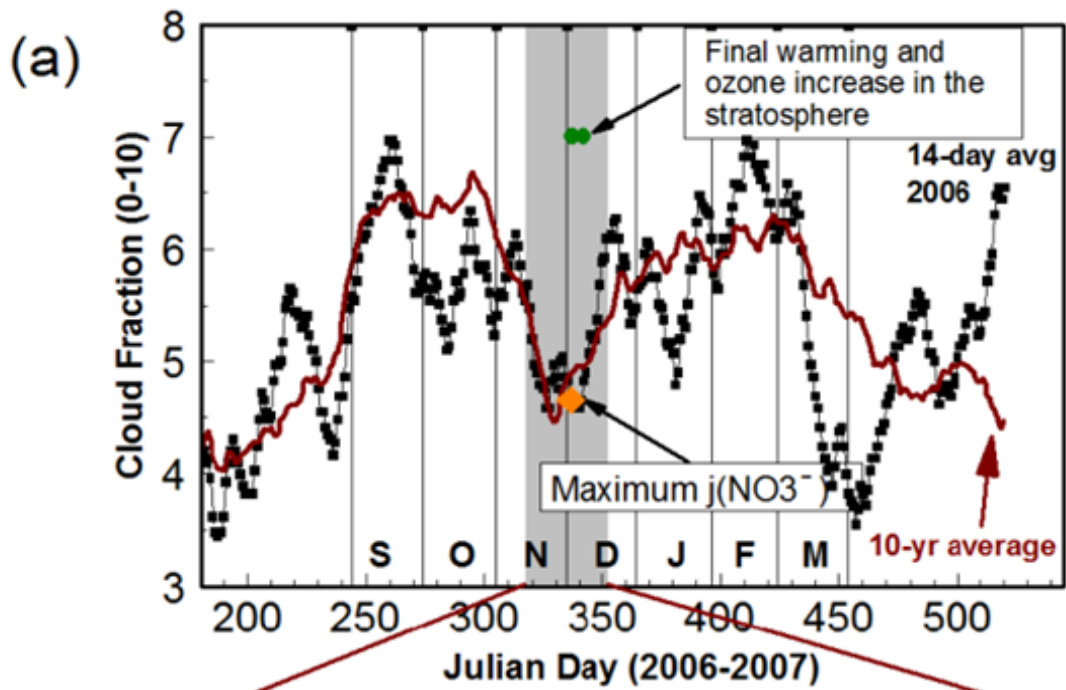


Figure 4. (a) Time series of observer-derived cloud fraction averaged for 2000-2010 (red line) at the South Pole and the field season of 2006-07 (black line) showing the consistency of individual years with the long-term average. A 14-day running average (red line) was used. The period of final warming of the stratosphere in 2006 ($t_{200\text{hPa}} - t_{300\text{hPa}} > 0$) and the period of rapid increase in total column ozone are indicated symbolically for JD 337-342. The date of the maximum in $j(\text{NO}_3^-)$ is indicated by an orange diamond (Day 336) from (Davis et al. 2010). (b) The expanded time series of cloud fraction for JD 316-350 showing relative minima on JD327 and JD337 as well as the timing for the breakdown of the ozone hole (as seen in $J_{\text{NO}_3^-}$ nitrate photolysis rate coefficients scaled for plotting) and stratospheric warming. (c) Expanded view of NO, Delta T (2-10 m), $J_{\text{NO}_3^-}$ (scaled), and direct radiance time series for JD 335-340. Daily cloud fraction, derived from climatological observer records, is shown using green bars. Note the decrease in $J_{\text{NO}_3^-}$ prior to the increase in NO.

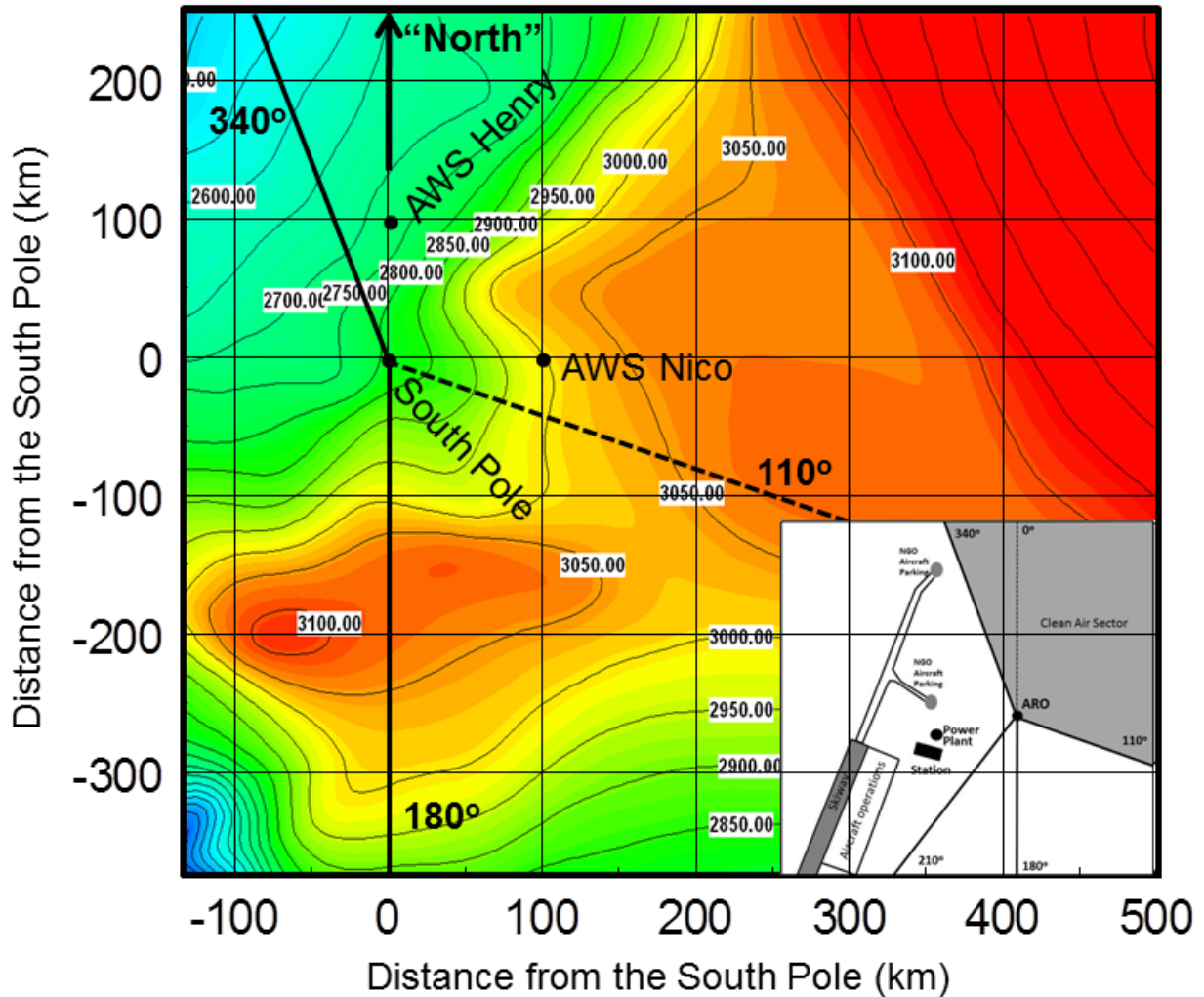


Figure 5. Local terrain around the South Pole and the location of station facilities and the clean air sector (insert). Contour interval is 50 m. The clean air sector extends from 340° to 110° whereas the major station activity is located between 340° and 210°. Note that the prevailing surface wind (northeasterly) is actually along terrain isopleths upstream of the station except for the last 50 km. “Downslope winds” come from directions generally between east and south. Automatic Weather Stations (AWS) Nico and Henry which have been operating since 1993 are also indicated lying about 100 km from the South Pole. Highest NO is observed when the wind directions are from the direction of the terrain “gap” to the southeast of the Station.

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A B C D E F G H

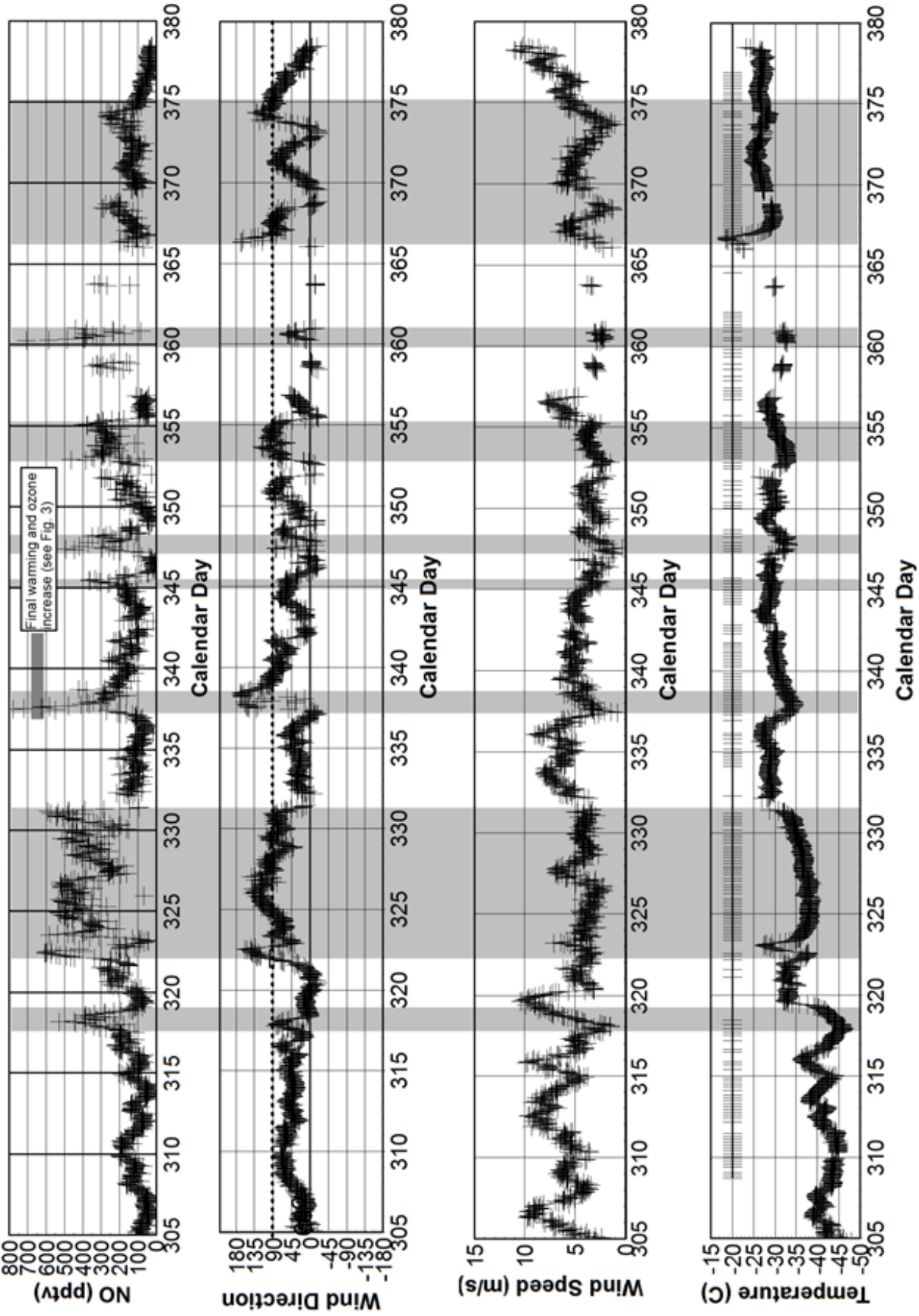
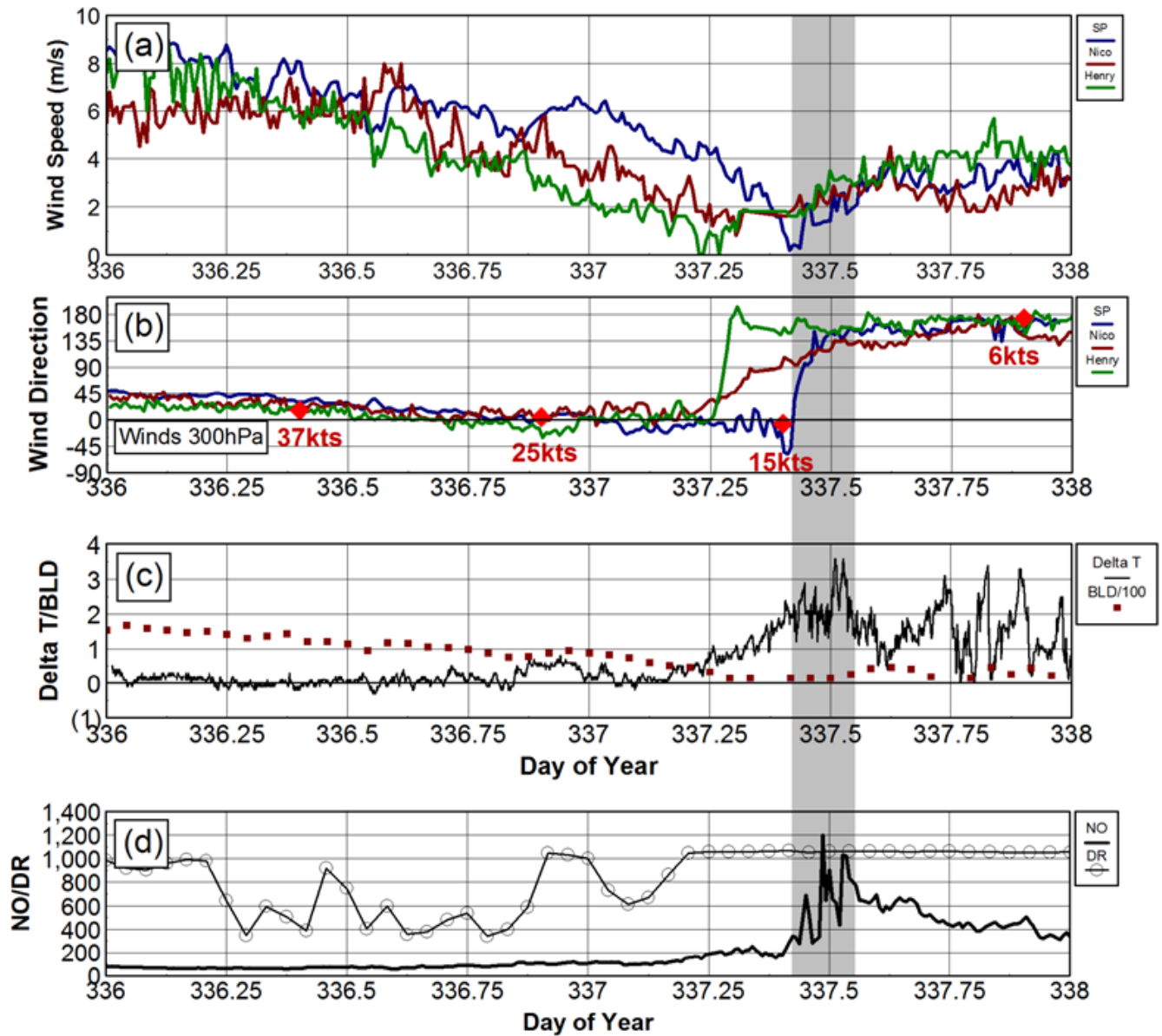


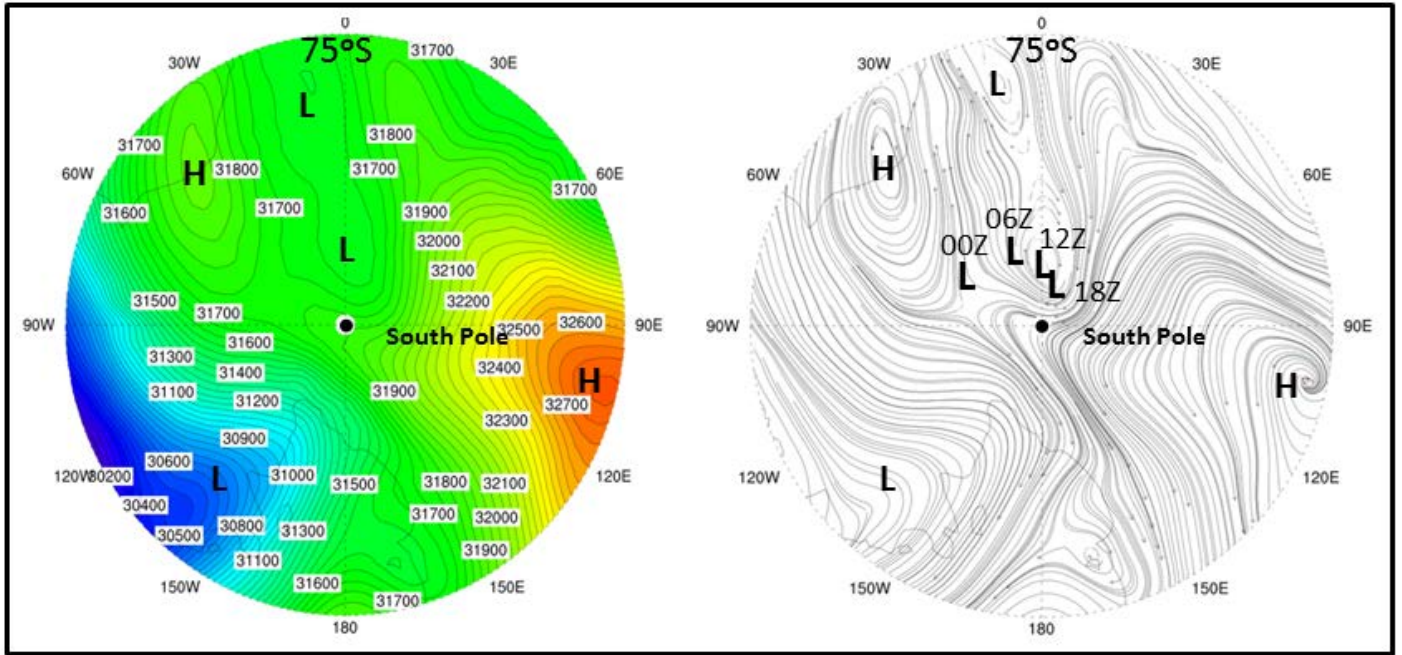
Figure 6. Time series of NO, wind direction, speed and 2-m temperature for November 2006 through mid-January 2007 (Days 305-380). Data gaps at the end of December are due to either missing NO and/or meteorological data. Shaded areas and labels A-H are cases where NO >300 pptv. Case “C” is that highlighted in Fig. 4 which occurs at the time of stratospheric warming and total column ozone increase. The wind azimuth of 60° is also noted (corresponding to Fig. 3 for directions associated with higher NO). Periods of clear skies are indicated on an hourly basis by hash marks at -20 C on the temperature plot: Note the increase in temperature around JD 320 associated with cloudy skies, increase in wind speed, and shift in wind direction.



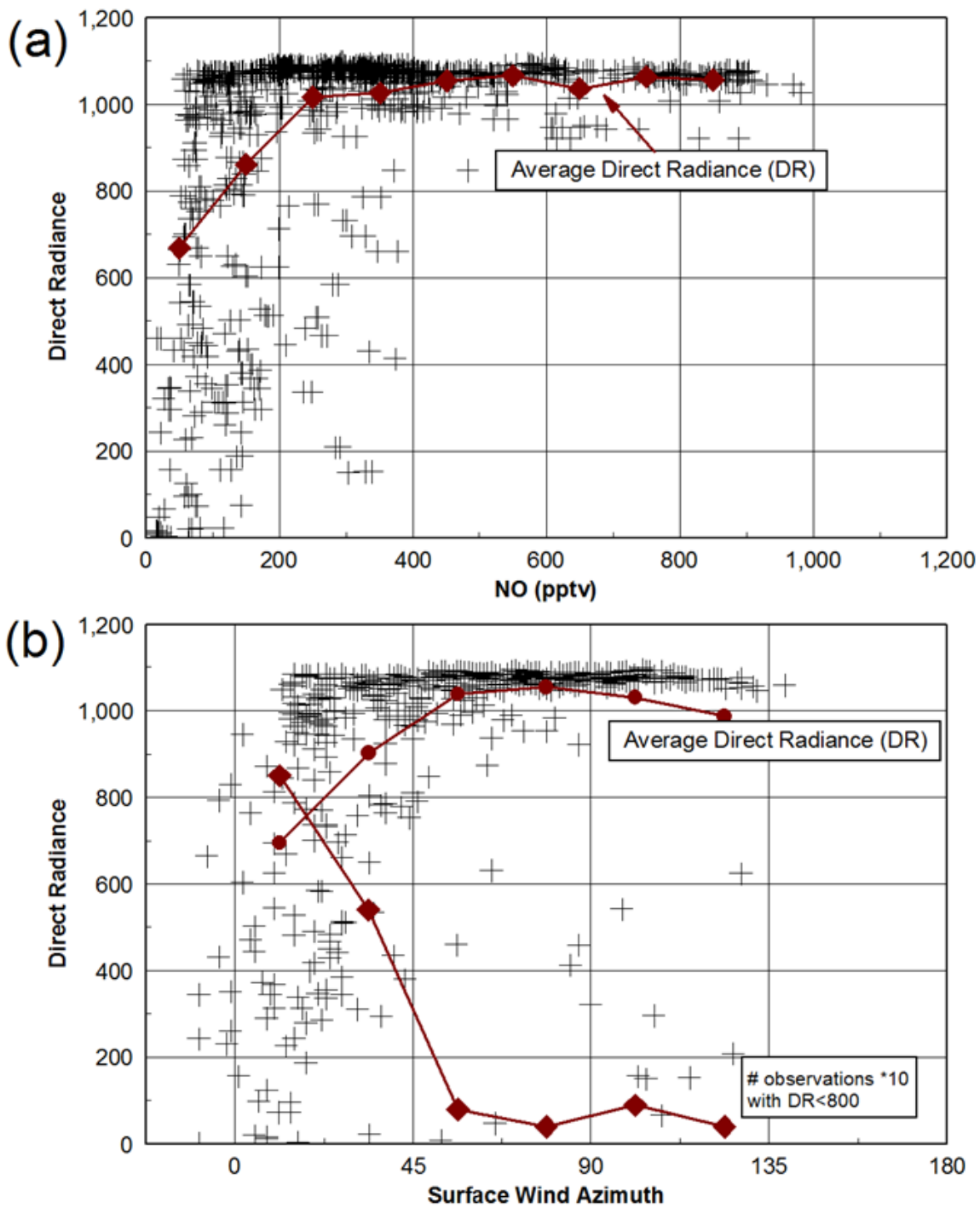
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Figure 7. Time series of (a) Wind Speed, (b) Direction (c) Delta T and BLD and (d) NO and direct radiance (DR) for Days 336-338, 2006 (Case C in Figure 6). In (b) we indicate wind speed and direction at 300 hPa (red diamonds) at the actual launch times of the rawinsondes (2-3 hours prior to reporting times of 00Z and 12Z). Of note is the decrease in surface wind speeds from over 8 ms^{-1} (sufficient for blowing snow) that follow the same trend as at 300 hPa. We have also indicated the BLD calculated later in Section 4.3 that shows the rapid decrease in BLD.

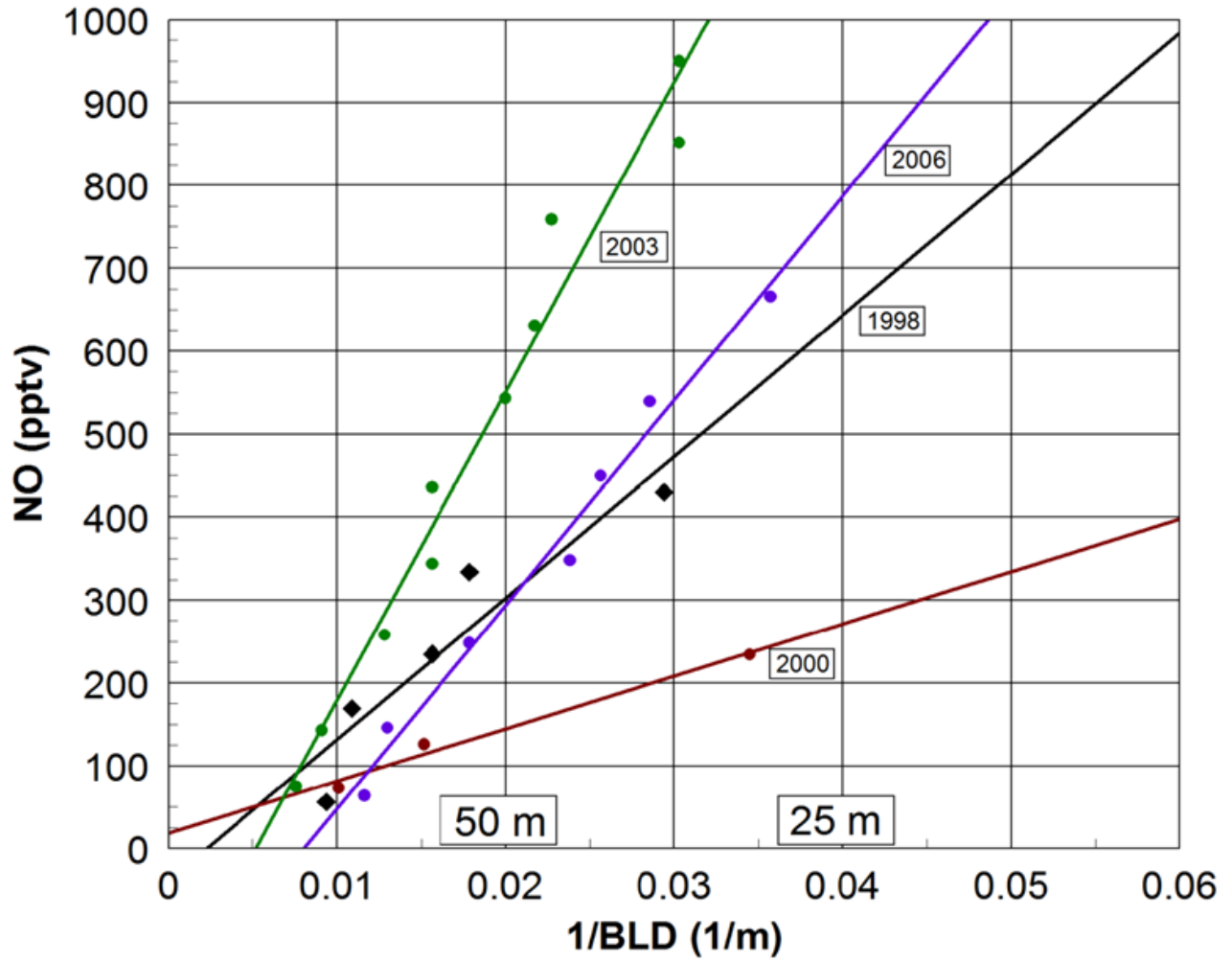
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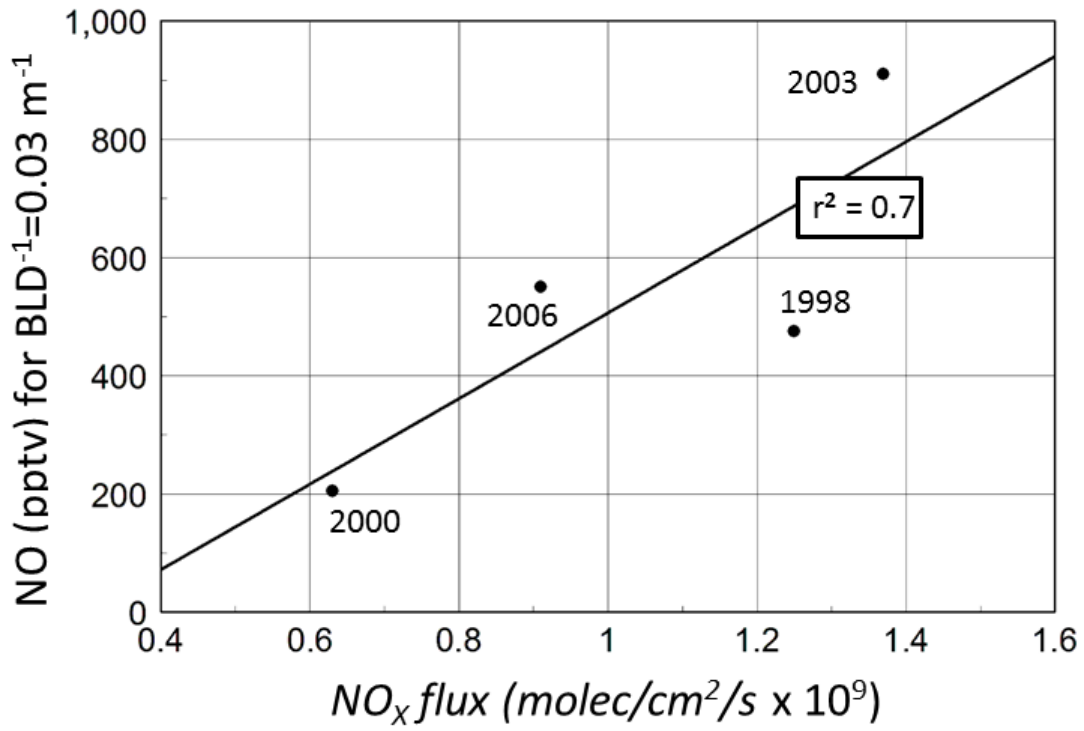
1025 Figure 8. Geopotential at 650 hPa at 12Z on JD 337 (3 December 2006) and wind field (using curly vector representation) from ERA-I. A trough of low geopotential lies along 0° with higher geopotential and anticyclonic winds over the high plateau. Lows and highs are indicated and the location of a small cyclonic circulation at 6-hr intervals on JD337 that brought easterly winds to SP. By 12Z on JD 338, the low to the NNE had intensified and produced a consistent NE winds to SP



1030 Figure 9. (a) Direct radiance (DR) versus NO (hourly) for 2003 showing that values of NO > 400 pptv occur with virtually clear skies (DR > 80% of the maximum). (b) Direct radiance versus surface wind direction (hourly) for 2003 with average DR and number of observations in 45-deg bins, showing cloudy to partly-cloudy conditions prevail with surface wind directions less than 45 degrees.

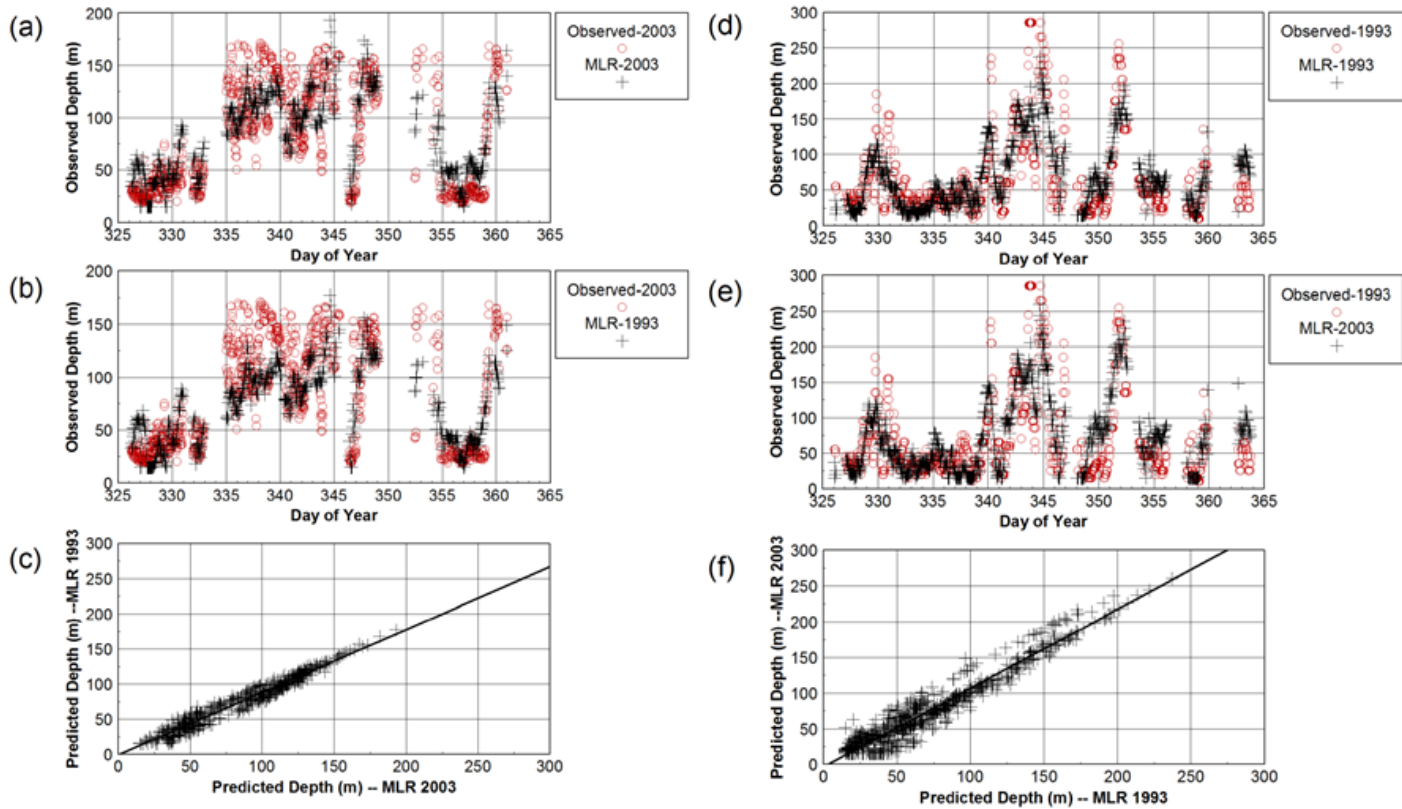


1035 Figure 10. NO versus 1/BLD for BLD averaged for each 100 pptv bin of NO. r^2 is as follows: 1998: 0.88; 2000: 0.98; 2003:0.97; 2006: 0.98.



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Figure 11. NO (BLD = 33.3m) versus seasonally averaged NO_x flux from Table 1 using a fall-off factor of five (more typical of shallow boundary layers).



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Figure A1. a) Comparison of 2003 observed BLD with that predicted by the 2003 MLR equation with $r^2=0.71$, b) Comparison of 2003 observed BLD with that predicted by the 1993 MLR equation with $r^2=0.67$, c) least-squares fit for MLR1993 versus MLR 2003 with $r^2=0.96$, d) Comparison of 1993 observed BLD with that predicted by the 1993 MLR equation with $r^2=0.65$, e) Comparison of 1993 observed BLD with that predicted by the 2003 MLR equation with $r^2=0.61$, f) least-squares fit for MLR2003 versus MLR 1993 with $r^2=0.93$.

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