



The Meteorology and Chemistry of High Nitric-Acid Episodes at the South Pole

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Between 1998 and 2007, a series of field experiments carried out at the South Pole and with aircraft over a wider area revealed a very chemically active boundary layer overlying the east Antarctic ice sheet during the Austral summer. An early discovery was unexpectedly high concentrations of nitric acid (NO) at the South Pole. These were argued to be a result of the UV photolysis of reactive nitrogen in surface and/or near-surface snow followed by subsequent confinement and non-linear HO_x/NO_x chemistry within a thin stable atmospheric boundary layer. The concentrations of NO also demonstrated daily, intraseasonal, as well as interannual variability as seen in the four field programs. This paper seeks to elucidate the interplay of large-to-small scale meteorology and chemistry at the South Pole that leads to highly variable NO concentrations and to examine boundary layer depth effects on NO in years when no direct measurements were available, in particular during the latest field program in 2006-2007.

The importance of the South Pole is that it, unlike other high-latitude sites, has no diurnal cycle to disturb the evolution of the mostly stable boundary layer and its physics and chemistry. In the spring, as the solar elevation angle increases, nitrate photolysis rates increase. At the same time, the stratospheric vortex warms and with its breakup, the total column ozone increases leading to decreased photolysis rates. In addition, following the formation of the thermal tropopause in early spring, the tropospheric circulation over Antarctica changes dramatically, affecting the transport and dominant source regions for warm air and clouds arriving at the South Pole. The timing of the final warming ranged from early-November to mid-December for the four field experiment years. During the 30 days prior to the final increase in column ozone, as the thermal tropopause forms (~100 hPa), the winds at 300 hPa become bimodal, either along the eastern side of the Weddell Sea (cloudy, windy, and warmer with deeper boundary layers) or southeast, along the continent above the Ross Sea (clear skies, light winds, colder with shallow boundary layers). The latter situation sets the stage for higher NO concentrations. Following the breakup of the ozone hole, 300 hPa winds favor directions from the Weddell Sea, typically providing warming events. With the surface warming, we found limited katabatic influence for the period of late November-January period as the inversion strength decreased to near zero, on average. As a consequence we found that synoptic and mesoscale weather patterns dominated surface boundary layer flow characteristics during the summer months. We found that year-to-year changes in the large scale circulation accounted for some of the differences in the average concentrations of NO during the four field programs: However, the same seasonal meteorological changes may affect the concentration of surface nitrate as a result of changes in transport, deposition, recycling, and/or stratospheric-tropospheric exchanges of nitrate precursors.

Past work implicated the pivotal role of the boundary layer depth (BLD) on NO concentrations. However, direct measurements were only available in 2003. To overcome this limitation, we used multiple-linear-regression with routine observations of wind speed, direction, temperature and static stability in 2003 to develop a regression equation for BLD to apply to other years. This application confirmed the general inverse BLD dependence of NO concentrations: When NO was binned in 100 pptv bins, regression with 1/BLD yielded r² from 0.87 to 0.98 for each of the four years. Looking at the regression slopes based on our BLD calculations, we found for deeper boundary layers (~100m) there was little difference in average NO from year to year whereas when confined to shallow boundary layers (~25m) concentrations varied by factors of 4 or 5 suggesting major differences in source terms for NO from year to year.