Abstract

Ice core records of NO$_3^-$ to polar glaciers could provide unrivaled information on past photochemical status and N cycling dynamics of the troposphere, if the ice core records could be inverted to yield concentrations of reactive N oxides in the atmosphere at past times. Limited previous investigations at Summit, Greenland, have suggested that this inversion may be difficult, since the levels of HNO$_3$ and aerosol-associated NO$_3^-$ over the snow are very low in comparison with those of NO$_3^-$ in the snow. In addition, it appears that some fraction of the NO$_3^-$ in snow may be re-emitted to the atmosphere after deposition. Here we report on extensive measurements of HNO$_3$, including vertical gradients between 1.5m and 7 m above the snow, made during the summers of 1994 and 1995 at Summit. These HNO$_3$ data are compared with NO$_3^-$ concentrations in surface snow and the first measurements of the concentrations and fluxes of total reactive nitrogen oxides (NO$_y$) on a polar glacier. Our results confirm that HNO$_3$ concentrations are quite low (mean 0.5 nmol m$^{-3}$) during the summer while NO$_3^-$ is the dominant ion in snow. Daytime peaks in HNO$_3$ appear to be due at least partly to emissions from the snow, an assertion supported by gradients indicating a surface source for HNO$_3$ on many days. Observed short-term increases in NO$_3^-$ inventory in the snow can be too large to be readily attributed to deposition of HNO$_3$, suggesting that deposition of one or more other N oxides must be considered. We found that the apparent fluxes of HNO$_3$ and NO$_y$ were in opposite directions during about half of the intervals when both were measured, with more cases of HNO$_3$ leaving the snow, against a NO$_y$ flux into the snow, than the reverse. The concentrations of NO$_y$ are generally about 2 orders of magnitude greater than those of HNO$_3$, hence deposition of only a small non-HNO$_3$ fraction of this pool could dominate NO$_3^-$ in snow, if the depositing species converted to NO$_3^-$, either in the snowpack or upon melting for analysis.