Air-snow exchange of HNO_3 and NO_y at Summit, Greenland

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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.