Impacts of snowpack emissions on deduced levels of OH and peroxy radicals at Summit, Greenland


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Abstract

Levels of OH and peroxy radicals in the atmospheric boundary layer at Summit, Greenland, a location surrounded by snow from which HOX radical precursors are known to be emitted, were deduced using steady-state analyses applied to (OH + HO2 + CH3O2), (OH + HO2), and OH–HO2 cycling. The results indicate that HOX levels at Summit are significantly increased over those that would result from O3 photolysis alone, as a result of elevated concentrations of HONO, HCHO, H2O2, and other compounds. Estimated midday levels of (HO2 + CH3O2) reached 30–40 pptv during two summer seasons. Calculated OH concentrations averaged between 05:00 and 20:00 (or 21:00) exceeded 4 × 106 molecules cm−3, comparable to (or higher than) levels expected in the tropical marine boundary layer. These findings imply rapid photochemical cycling within the boundary layer at Summit, as well as in the upper pore spaces of the surface snowpack. The photolysis rate constants and OH levels calculated here imply that gas-phase photochemistry plays a significant role in the budgets of NO3, HCHO, H2O2, HONO, and O3, compounds that are also directly affected by processes within the snowpack. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A series of studies over the past several years have demonstrated that processes within surface snowpacks result in the release (and in some cases, the uptake) of a variety of photochemically active compounds. It appears that these effects are largely driven by three processes: photodissociation of nitrate ion present within the surface layer of ice crystals in the snowpack (Honrath et al., 2000), temperature-dependent adsorption or cocondensation onto, and desorption from, ice surfaces (e.g. Bales et al., 1995), and autocatalytic release of halogen compounds, resulting from reactions on ice surfaces (Tang and McConnell, 1996). (The latter process has been clearly documented only near the marine boundary layer and is not considered in detail here.)

It is likely that these processes significantly alter levels of HOX (OH + HO2) in the atmospheric boundary layer above snowpacks. Photodissociation of nitrate ion near the surface of ice crystals is believed to be the source of NO3 release observed from sunlight-irradiated snow (e.g. Honrath et al., 1999), and, if so, results in the production of OH radicals at the site of photodissociation. The fate of this OH is not known, but in the