



Boundary Layer Chemistry of Hydroperoxides (H_2O_2 and CH_3OOH) in Greenland (Summit) and Antarctica (South Pole): Links to Atmospheric Oxidation Capacity

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Hydroperoxides (ROOH) influence the oxidizing capacity of the troposphere, defined as the total burden of ozone (O_3), HO_x radicals and hydrogen peroxide (H_2O_2), and they also constitute an important radical reservoir. Recent observations have shown that methylhydroperoxide (CH_3OOH) is the only other important peroxide next to H_2O_2 occurring in the summer boundary layer above the West Antarctic Ice Sheet (WAIS) and the South Pole. Both chemical species are, as photochemical box model calculations suggested, tightly linked to the tropospheric NO_x - HO_x budget and thus provide a quantitative tool to constrain the current and, using ice cores, past oxidation capacity of the remote atmosphere. However, concurrent measurements of ROOH and NO_x - HO_x species have been lacking so far to test the model. Here we present atmospheric ROOH measurements from the Snow Photochemistry Experiment in the Arctic (Summit, Greenland) and from the Antarctic Tropospheric Chemistry Investigation (ANTCI) in the Antarctic (South Pole). These include new H_2O_2 data and first-time quantitative observations of CH_3OOH in Greenland, the only higher organic peroxide detected at both sites using a continuous-flow HPLC method. Atmospheric CH_3OOH levels were 582 ± 393 pptv and 156 ± 96 pptv at Summit during summer 2003 and spring 2004, respectively, and 150 ± 272 pptv at the South Pole during summer 2003. CH_3OOH mixing ratios exhibit low frequency changes at both locations, while H_2O_2 shows diurnal cycles at Summit due to the temperature-driven exchange with surface snow. Comparisons with available measurements of formaldehyde (HCHO), NO and

the OH radical confirm the modeled relationship between ROOH and the budget of photo oxidants: as NO and OH concentrations increase more HCHO is produced at the expense of H₂O₂ and CH₃OOH, which both decline rapidly during episodes of elevated NO. Therefore, we suggest that a combination of H₂O₂, CH₃OOH and HCHO measurements allows constraining the oxidative power of the atmosphere quantitatively.