First observations of atmospheric Hydrogen Peroxide (H_2O_2) and Methylhydroperoxide (CH_3OOH) in West Antarctica: comparison of experiment and model results

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Hydrogen peroxide (H_2O_2) and higher organic peroxides such as methylhydroperoxide MHP (CH_3OOH) are closely linked to chemical feedback mechanisms controlling the composition of the atmosphere. Recent findings in Central Greenland and at the South Pole show that a physical snowpack source is contributing significantly to boundary-layer H_2O_2. This has important implications for the current understanding of HO_x radical chemistry above extended snow and ice surfaces as well as for the quantitative interpretation of the H_2O_2 record from ice cores. Here we report atmospheric measurements of hydroperoxides from three U.S. ITASE traverses, 2000-03. The wide spatial distribution of the 21 traverse sites between 75°S and 90°S, allows investigation of the peroxide photochemistry in the summer troposphere and the impact of the upper snowpack on the boundary layer in varying depositional environments, such as up to a 5-fold change in accumulation rate (8-44 cm SWE/yr) and a 30 K difference in mean annual temperature (-21.4 to -49.3ºC). The only higher organic peroxide detected using a continuous-flow HPLC method is MHP, as expected in the remote atmosphere. Site averages of both, H_2O_2 and MHP showed a latitudinal gradient between 75°S and 90°S, decreasing from 803±150 pptv to 230±56 pptv and from 491±296 pptv to 102±41 pptv respectively. The MHP:H_2O_2 ratios varied between 0.4 and 2.5 with the higher values occuring during storm events as a consequence of the large difference in water solubility. Model runs using the NASA-Goddard Flight Center (GSFC) point photochemical model match observations of peroxides within the experimental uncertainties only by introducing source fluxes of H_2O_2 and HCHO, estimated from measured firn-ambient air ratios. The best model fits put some constraints on levels as well as snowpack fluxes of atmospheric NO_x (not measured), ranging from 20 pptv at Byrd Surface Camp (80°S) to 30-40 pptv at the South Pole.