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Impact of Photochemistry and Temperature on HCHO, H_2O_2 and HONO Mixing Ratios in Near Surface Firn Air at Summit, Greenland

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Photochemistry and temperature-driven recycling of reactive trace gases in snow can significantly alter the chemical composition of the snow, firn air (interstitial air), and the overlying atmospheric boundary layer. This has important consequences for the interpretation of ice-core records with respect to the oxidizing capacity of the atmosphere in the past and for the understanding of gas-phase photochemistry above snowpacks. A lot of progress has been achieved in the past with respect to our understanding of many aspects of the chemical exchange between the snow and the air. However, the relative importance of photochemical versus physical processes driving the observed snow-air fluxes of the different species on diurnal and seasonal time scales remains unknown.

Here we present previously unpublished HCHO, H_2O_2, and HONO data from field campaigns at Summit, Greenland, in summer 2003 and spring 2004. All three species were simultaneously measured in firn air drawn from various depths in the snowpack while a large area of the snowpack ($\approx 4m^2$) was intermittently shaded. Filters of various transmittances of UV radiation were used during the shading experiments in order to distinguish the impact of changing temperature and radiation on the firn air mixing ratios. In addition, profiles of temperature, radiation and HCHO, H_2O_2, and HONO concentrations in the snow phase were measured. These data are used to quantify the

relative importance of both, UV radiation and temperature on firn air mixing ratios and corresponding snow-air fluxes.

The results reveal much smaller firn air mixing ratios and thus snow-air fluxes in spring compared to summer for all species. The shading experiments indicate that firn air H_2O_2 was mainly driven by snow temperature and no consistent impact of UV was observed. HCHO clearly reacted to UV, however, snow temperature dominated the firn air mixing ratios throughout the day. The HONO on the other hand closely followed UV irradiation.