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Atmospheric
Chemistry
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Discussions

Interactive comment on “Contrasting atmospheric boundary layer chemistry of methylhydroperoxide (CH_3OOH) and hydrogen peroxide (H_2O_2) above polar snow” *by* M. M. Frey et al.

Anonymous Referee #1

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The manuscript of Frey et al. describes the measurement of atmospheric hydrogen peroxide and methylhydroperoxide over both Greenland and South Pole snow. It was determined that hydrogen peroxide and methylhydroperoxide were the two most dominant hydroperoxides in the boundary layer above both South Pole and Summit. The cycling of organic peroxide is dominated by photochemistry, while hydrogen peroxide concentrations are mainly controlled by temperature dependent exchange between air and snow. At Summit, the rapid processing of methylhydroperoxide may contribute to the snowpack source of formaldehyde, measured previously at various polar sites. Authors suggested that candidates for this processing include OH reaction in the interstitial air as well as in the condensed phase in the quasi-liquid layer of snow grains.

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However, modeling results show that South Pole methylhydroperoxide levels are inconsistent with known NO concentrations and cannot be adequately explained by known photochemical sources or transport, suggesting there is a missing source of this compound. This work also illustrates the fact that models cannot simply assume methylhydroperoxide equals hydrogen peroxide (as is often done when discrete measurements are not available).

This work is an interesting and important study that should be of interest to the ACP readership. Specific measurements of both methylhydroperoxide and hydrogen peroxide are not available for Greenland, and a few studies are available from Antarctica. Comparisons of ambient and firn air concentrations of the species simultaneously are also not available. Thus, this study makes an important contribution to that general lack of measurement data that will help constrain the atmospheric HOx budget above polar snow. Additionally, the authors have made careful measurements that enable the calculation of fluxes to/from the snowpack of these species and also modeled the data (constrained by typical atmospheric parameters and species) to determine if known photochemical/deposition processes could explain the concentrations and gradients observed. The work is well described, with adequate background information and comparisons to existing data and modeling results and should certainly be published, given the few minor corrections/additions suggested below.

1.) The chemistry discussed in the introduction might better be shown with actual reactions, rather than text. I find it difficult to follow chemistry in words (page 1238 paragraph 2)

2.) In the methods section, could you also include mention of the typical air sampling flow rate?

3.) Is the air sampling line heated in any way? You discuss line losses with the firn air measurements ... could these be temperature dependent? Given that a single correction factor of 2.91 was used, it is important to discuss why it is likely the case

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(is it?) that the same correction factor would be appropriate for an entire study (or group of studies as is discussed in this manuscript). For example, could the line have initially had greater losses, but then reached an equilibrium as the surface became "inactivated" so to speak. When did the comparisons of samples taken through the two inlets occur (at the beginning, middle or end of study) and was the comparison done more than one time during the study?

4.) In discussion of the role of snowpack on ROOH (page 1251), an additional source of uncertainty in the flux calculation could be forced ventilation due to the sampling itself (hence, #2 above). You could see significant mixing of air from above/below the firn air sampling depth due to this alone ... so you could be enriching (or depleting) your measured values if the air above is higher (lower) in concentration of analyte.

5.) In the conclusions, a potential flux of HCHO is calculated based on the MHP sink. Can these flux values be compared to anything previously reported in the literature?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1235, 2009.

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