

## ***Interactive comment on “Contrasting atmospheric boundary layer chemistry of methylhydroperoxide (CH<sub>3</sub>OOH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) above polar snow” by M. M. Frey et al.***

**M. M. Frey et al.**

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First, we would like to thank referee No.1 for the contribution of constructive comments to this work. They are addressed below and corresponding changes will be included in a revised version of the manuscript.

1.) For clarity we added chemical reactions illustrating ROOH gas phase chemistry. Text reads now as follows (p.1238, line 13):

... The known ROOH gas phase chemistry can be summarized as follows: in the presence of sunlight, water vapor and ozone (O<sub>3</sub>), the short-lived OH radicals are

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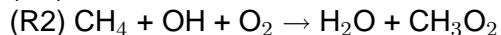
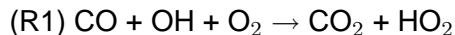
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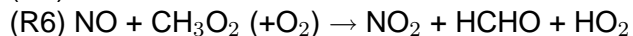
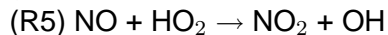
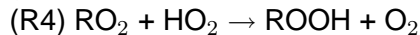
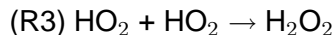
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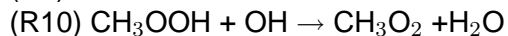
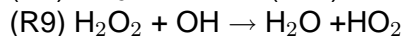
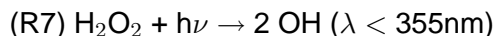
produced and then converted in the oxidation reaction with carbon monoxide (CO), methane (CH<sub>4</sub>) and other non-methane hydrocarbons to peroxyradicals (RO<sub>2</sub>).



Under low NO<sub>x</sub> conditions self and cross reactions of RO<sub>2</sub> produce H<sub>2</sub>O<sub>2</sub> and alkylperoxides (ROOH), while under high NO<sub>x</sub> conditions, ROOH formation is suppressed and production of HCHO and NO<sub>2</sub> occurs instead.



A physical snow pack source has been recognized to be important for summer BL concentrations of H<sub>2</sub>O<sub>2</sub> at Summit, Greenland, the South Pole and above the West Antarctic Ice Sheet (WAIS) between 76 and 90 degrees S. Sinks of ROOH include photolysis, attack by the OH radical, wet and dry deposition.



2.) Air sampling flow rates were always 1.5 STP-L min<sup>-1</sup>. Corrected text:

... Ambient air was pumped at 1.5 STP-L min<sup>-1</sup> through intake lines, which were heated above ambient air temperature to prevent condensation losses. ...

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3.) Intake lines were heated (see above). However, a comparison of ambient air levels of  $\text{H}_2\text{O}_2$  sampled through the intake line attaching and then removing the firn probe revealed a significant difference. As described in the text (p.1241, line 24), the test was repeated 3 times, at the start, middle and end of the season. No temporal trend was detected and therefore a single correction factor applied. The nature of the systematic loss is not known. Text changed as follows:

... They did not show any temporal trend and were independent of ambient mixing ratios. Thus, all  $\text{H}_2\text{O}_2$  firn air data were corrected using a single factor of 2.91 estimated from a linear regression between mixing ratios measured with and without the probe. ...

4.) To clarify this we expanded the existing text (p.1251, line 15) as follows and added one reference:

... It should also be noted that pumping firn air at rates of several  $\text{L min}^{-1}$  will advect air from above (or below) to the sample inlet inserted into the snow, as discussed by Albert et al. (2002). This effect was reduced by using a circular transparent disk covering snow surface adjacent to the firn probe. Any remaining mixing between sample air and air from a different depth will decrease the measured concentration gradients. Thus, it is safe to assume that our calculations yield lower limits of the true fluxes. ...

Albert et al. (2002), Processes and properties of snow-air transfer in the high Arctic with application to interstitial ozone at Alert, Canada, *Atm. Env.*, 36, 2779-2787.

5.) We expanded the conclusion as recommended.

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... Assuming a volumetric HCHO production rate of  $5.3 \text{ molec. m}^{-3}\text{s}^{-1}$  (Tab.4), which is constant over the top 0.05 m of snow yields an areal flux of  $2.7 \times 10^{10} \text{ molec. m}^{-2}\text{s}^{-1}$ . This makes only a small contribution of about 1% when compared to emission fluxes of HCHO measured previously at Summit in summer, ranging between  $1$  and  $9 \times 10^{12} \text{ molec. m}^{-2}\text{s}^{-1}$  (Grannas et al., 2007 and references therein). In spring however, the MHP loss will be more important for the HCHO budget. More detailed work on HCHO firn air photochemistry will be reported elsewhere (manuscript in preparation). ...

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

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