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Atmospheric Chemistry and Physics 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.

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First, we would like to thank reviewer No.2 for providing constructive comments, which helped to further strengthen this manuscript. They are addressed below and corresponding changes will be included in the revised version.

1.) Regarding the observed sudden H_2O_2 enhancement at Summit from Apr-19 through Apr-25 2004 we find that some of the numerous chemical species measured in parallel by other researchers showed a similar increase. Text is changed as follows (p.1251 l.24):

Thus, H_2O_2 was likely formed in situ above the snow or regionally in a newly arriving air mass. Advective transport is supported by concurrent increases of specific humidity, O_3 and CO (data not shown). On the other hand, the radionuclide ^{210}Pb, the daughter product of the continental tracer ^{222}Rn, did not show any unusual excursions during the same time period (Dibb et al., 2007).

2.) As stated in section 3.1 MHP was the only organic peroxide observed. Thus the correction applied to the continuous channel for all hydroperoxides was done accordingly. Text (p.1241, l.7) was changed as follows:

To account for the interference of the fluorescence detection method to all hydroperoxides, a correction term in pptv H_2O_2-equivalent was calculated based on a 24-point running mean of the difference between HPLC derived signals of total observed peroxides (H_2O_2+MHP) and H_2O_2 and then subtracted from the continuous measurements in channel 1.

3.) No gas calibration source for hydroperoxides was available in the field. However, the firn air probe was tested as follows: ambient air levels of H_2O_2 sampled through the intake line attaching and then removing the firn probe were compared. The test was repeated 1-2 times daily, before and after the firn air measurements. No temporal trend was detected and therefore a single correction factor applied. The nature of the systematic loss is not known. The corresponding paragraph in the method section was changed as follows, including further details of the firn probe design:

Firn interstitial air was sampled during SUM04 by switching the instrument for 10 min each hour to a second intake line attached to a firn air probe used by all investigators participating in the Greenland Photochemistry Experiment (Dibb et al., 2007). Firn air experiments included depth profiles as well as shading experiments. All tubing connected to the PTFE firn air probe head was made of PFA. For protection the probe was placed into another tube made of plexiglass down to 0.5m depth and of aluminium below. The heated inlets and the firn probe were tested regularly for systematic bias. ROOH ambient mixing ratios at 1m above the snow surface were measured in parallel through both heated inlets for up to 12 h at a time. The comparison of 29 subsequent 10-min intervals from 5 April, 14 April and 2 May using parametric (two-sample t-test) and non-parametric (Wilcoxon signed rank test) statistics showed no significant difference between the two inlets at a 95% confidence level. However, the 1-2 times daily comparison of ambient ROOH levels sampled through the inlet, with and then without the firn air probe attached, revealed systematic losses of H_2O_2 but not for MHP. If condensation (deposition) of water vapor had taken place in the unheated firn air probe head, one might expect removal of H_2O_2 followed by release later on from evaporation (sublimation) of potential water droplets (ice crystals). However, losses did not show any temporal trend, were independent of ambient mixing ratios and no icing up of the probe was observed. In conclusion, the nature of the loss process remains uncertain. All H_2O_2 firn air data were therefore corrected using a single factor of 2.91 estimated from a linear regression between mixing ratios measured with and without the probe.

REFERENCES

Dibb, J. E.: Vertical mixing above Summit, Greenland: Insights into seasonal and high frequency variability from the radionuclide tracers ^{7}Be and ^{210}Pb, Atmos. Environ., 41, 5020–5030, 2007.

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