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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxy radicals in the summer free troposphere: seasonality and heterogeneous loss" *by* A. E. Parker et al.

A. E. Parker et al.

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1. The reason for setting RH=76% for "snowy" is unclear to me. Is it an arbitrary number in a certain range or based on some supporting evidence? How about the temperature conditions during these snowy days?

The choice of 76% is essentially arbitrary based on visual observations during the campaign. Temperature was lower on "snowy" days an average of 1.8 deg C on not snowy days vs -1.6 deg C on snowy days.

2. The conclusion of the heterogeneous losses to snow particles is based on the derived negative gamma values. The uncertainty of the calculated gamma values needs to be provided. To support the conclusion, these gamma values need to be proven statistically significant for being negative or positive.

For an alpha of 0.25, the median gamma becomes -0.55738, compared to a median gamma of 0.49208 for an alpha of 0.5 - a change of 13.3%. Likewise, for an alpha of 0.75 the median gamma becomes -0.42647 - also a change of 13.3%. So gamma is still going to be negative regardless of the alpha however the calculated loss rate will change. We have added a note to the paper saying:

"It is worth reiterating here that alpha has been set to 0.5. Altering alpha by ś0.25 results in the value of gamma changing by ś13%, but not its sign. This clearly results in a change in the magnitude of kex, but not its existence."

3. In section 3.3, the authors should also include the contribution from the photolysis of H2O2. According to Ren et al. (2008), this is a bigger contribution for HOx than HCHO at this altitude. If this measurement was not available, some typical values should be used to investigate its contribution.

This referee raises a good point. Walker et al (2006) measured 206 +/- 261 pptv in Febuary/March 2003 at JFJ. If we take a value for 500 pptV, then we can produce the remaining 0.05 missing gamma and close the peroxy radical production term, which is not out of the bounds of possibilities. The following text has been added:

"Ren et al., 2008 have reported that the photolysis of H2O2 can be a bigger contributor to HOx than HCHO at these altitudes. H2O2 was not measured during this campaign, however a concentration of 500 pptv H2O2 is sufficient to generate the remaining 0.05 of the total gamma. H2O2 measurements at the Jungfraujoch are scarce, but the mean H2O2 of 206 ś 261 pptv measured by Walker et al., 2006 during February and March 2003 suggests that this is not out of the question."

4. In equation (9) about net ozone production, the reaction OH+NO2 should also be subtracted. More recently E. Wood (http://www.cosis.net/copernicus/EGU/acpd/8/S5350/acpd-8-S5350.pdf) suggested that, only the portion that was formed by HO2 oxidation of NO should be subtracted. Nonetheless, the contribution from this reaction could be insignificant but this term

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should be mentioned at least in the context.

If the correction is calculated as per (http://www.cosis.net/copernicus/EGU/acpd/8/S5350/acpd-8-S5350.pdf) then the daytime correction factor is >˜0.997. Therefore we have mentioned it in the text as follows, but not changed any graphs or conclusions.

"It has recently been suggested by Wood (2008) that the ozone production term should be corrected to account for the fraction of NO2 that reacts with OH rather than photolyses. For this dataset with an OH concentration of 10ˆ6 molecules cm-3 the daytime correction factor is greater than approximately 0.997 and thus has been neglected."

5. I am also wondering how long did the snowfall generally last. Since the authors attribute the extra losses to heterogeneous losses(and it looks like a big loss), the measurements should be able to show the difference of peroxy radicals during and after snowfall, if the snowfall stops in the daytime and the radical sources do not change much during and after snowfall. Was this investigated?

Unfortunately, we have no supporting data to be able to investigate this point.

6. What is possibly driving the seasonal trends of peroxy radicals? This needs further discussion.

In the main the seasonal trend in peroxy radicals will be driven by the production terms (j(O1D), T, O3, H2O, CO, CH4). This topic is dealt with in Zanis et al. (2003). We have added the following to the text:

"The main driving force for the seasonal trend in peroxy radicals are the production terms, with jO1D being the dominant factor (as discussed in Zanis et al., 2003)."

Minor comments:

7. In Fig.10, the filter1 and filter2 should be described instead of referring to other papers.

Done

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8. P17845 L14: some references should be included here about the calibration set-up of the instrument.

Done

9. Fig.2 should be merged with Fig.1.

Done

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17841, 2008.

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