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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An overview of snow photochemistry: evidence, mechanisms and impacts" *by* A. M. Grannas et al.

A. M. Grannas et al.

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We thank the reviewer for consideration of this manuscript and the useful comments provided. The manuscript has been amended in the following ways to address the reviewer comments:

Point 1: "Discussion of snowpack metamorphism ought to make more of a distinction between changes to the state of individual ice grains, which do not affect the bulk composition as opposed to transformations of the total snowpack, which do alter the bulk composition..."

The snowpack changes because individual grains change. Even in the case of isothermal metamorphism, where it might be argued that there is no grain to grain exchange of matter, the composition of snow changes, if only because the specific surface area of

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snow changes and therefore its concentration of adsorbed species changes. Moreover, species forming a solid solution with ice, such as HCHO, can diffuse out of snow grains in the absence of vigorous metamorphism, resulting in snow compositional changes. This is for example what was observed at Alert (see the Perrier et al., 2002 paper in the Atmospheric Environment special issue). We feel the reviewer is mistaken in the suggestion that it is necessary to separate the tightly interconnected processes of grain metamorphism and snowpack metamorphism and thus see no reason to modify the text.

Point 2: "Should lower wavelengths be considered for the Antarctic spring when the ozone layer is significantly thinned for a period of time?"

Indeed this is an important point to consider and could also potentially impact the Arctic as well, as an Arctic ozone hole has also recently been discovered. We have added the following sentence to reflect this at page 4179 line 8. "...In addition to the aforementioned albedo effect at very high latitudes, there can also be a substantial influence at these latitudes from having 24 h of continuous photolysis and thus continuous photochemistry in summer. Additionally, the loss of stratospheric ozone in both the Antarctic and Arctic will allow for greater penetration of shorter wavelength (and more photochemically reactive) UV radiation to the surface, albeit at a time of year when solar irradiance is reduced compared with the summer."

Point 3: "In the discussion of HOx concentrations relative to model predictions it might be helpful to have figures comparing the observed and predicted values, along with some quantification of measurement uncertainty. From the text it is not immediately clear what is the significance of differences and similarities being described. Are the disparities entirely with predictions and models, or are there possible measurement artifacts?"

OH observed is nearly always $>$ 2X predicted, and can be even higher in high wind events. These differences are not likely to be due to measurement artifacts, as the

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typical uncertainty of OH measurements are about 40% and calibration methods are relatively well established. We have added additional text to explicitly state OH measurement uncertainties in section 4.2.4. ...“These levels were more than a factor of two higher than model predictions constrained to a full set of photochemical precursors. Typical HOx measurement uncertainties of 40% are reported, so it is unlikely that the disparity is due to measurement error. Conversely, levels of HO2 + RO2 were found to be in excellent agreement with predictions, indicating that peroxy radical sources and sinks were well understood but that the ratio of (RO2 + HO2) to OH was perturbed.”... We feel the additional text is sufficient to explain such observations and does not warrant an additional figure.

Point 4: "What is the geographic range of snow algae?"

Snow algae has been identified in widespread areas - from the Arctic, Antarctic, Greenland, U.S., Canada, Europe, Japan, etc. We have included an additional sentence with references to reflect the widespread distribution of snow algae populations at page 4216 line 21. “Snow algae have been identified globally at a variety of sites, including the Arctic, Antarctic, Greenland, U.S., Canada, Europe and Japan (Gerrath and Nicholls, 1974; Cota, 1985; Felip et al., 1995; Duval et al., 1999; Painter et al., 2001; Yamamoto et al., 2004; Edwards et al., 2004).”

Point 5: "Fluxes and gradients are related by an exchange velocity, and the magnitude of flux need not track the magnitude of gradient. Large positive gradient may be observed precisely because there is negligible exchange (very small flux) and the compound is simply accumulating or has been left behind in the stagnant layer..."

We have added additional text that more explicitly describes the relationship of fluxes and gradients, as well as the cautionary note suggested by the reviewer (page 4220 line 21). We also have pointed out explicitly the companion boundary layer meteorology paper that also will appear in this special issue of ACP, as this will provide much more detail than what could be described in this snow photochemistry review.

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“It should be noted that fluxes and gradients are related by an exchange velocity and measured concentration gradients may not directly relate to the magnitude of the flux. To quantitatively determine the surface-air flux, and the magnitude of the vertical impact of snowpack emissions/sinks, it is necessary to understand the dynamics above the snow surface, as discussed in section 5.1 and in greater detail in the accompanying boundary layer physics review (Anderson and Neff, 2007).”

Point 6: Table 1 "How do the sums of individual components compare to total NOy measurements during those campaigns or other campaigns at same place but different times?"

As an example using data from Neumayer, Summer 1999:

Measurements were made of individual components as well as a targeted NOy measurement. There were 5 occasions for which data could be compared; the data were averaged over the HNO3 sampling period (24 hours), while alkyl nitrate data corresponded to sampling periods of roughly 30 minutes, i.e. there is an inherent discrepancy, although there was no assessment of its influence.

From 1999:

Date, Integrated sum(pptv), Targeted NOy measurement(pptv)

8 Feb, 30.6 +/- 5.1, 35.1 +/- 12

17 Feb, 28.6 +/- 4.8, 45.1 +/- 16

18 Feb, 28.1 +/- 4.0, 42.2 +/- 15

19 Feb, 33.1 +/- 4.4, 24.7 +/- 8.6

20 Feb, 32.2 +/- 3.6, 16.0 +/- 5.6

Conclusion - there is no consistency in the comparison between the measured and the integrated sum, with differences varying both in magnitude and sign.

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Direct measurements of NOy are highly controversial. This paper focuses on snow photochemistry, not polar boundary layer chemistry. In the paper, we discuss the budget of NOy within the context of which NOy component species are likely depositing to the snow surface and are therefore contributing to nitrate in the surface snow. There is a relevance to considering the relative dominance of NOy species, but no benefit to the paper in getting into a discussion about the validity of NOy measurements (which are not referred to in the paper). For these reasons, we prefer not to alter the paper to cover this topic.

Additionally:

Two typographical errors pointed out by the reviewer have now been corrected.

Where applicable, we have updated references that were previously in review, in press or submitted.

During the review process, co-authors pointed out a few corrections to make including:

4171 line 13: "...but little is known of the chemical form that they take (for example as CH2O or H2C(OH)2).."

4181 line 8: added Fisher et al., 2005 as reference.

4190 line 26: added Jacobi and Hilker, 2006 as reference.

4205 line 5: “However, this idea of the photochemical formation of H2O2 on snow grains is in its infancy (Chu and Anastasio, 2005). Indeed, Jacobi et al. (2006) have identified the photochemical decomposition of H2O2 in snow. More work is needed to quantify the snow grain budget of H2O2.”

Table 4: We have noticed that table 4 in the online version did not print correctly. Specifically: at the top of page 4271 (table 4 continued) it should read CH2O rather than H2O2. At the top of page 4272 (table 4 continued) it should read CH3CHO rather than H2O2. Also, a space between the line beginning 47N, 88W and the line beginning

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CH3C(O)CH3 was added to help better separate those two table entries.

We have amended the acknowledgments section.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4165, 2007.