Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Modeling chemistry in and above snow at Summit, Greenland – Part 2: Impact of snowpack chemistry on the oxidation capacity of the boundary layer" *by* J. L. Thomas et al.

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GENERAL COMMENTS

The coupled 1-D snow chemistry and atmospheric boundary layer model MISTRA-SNOW is used to study the impact of snow chemistry on the oxidising capacity of the boundary layer at Summit/Greenland. Model output is compared with observations in ambient and partially also in firn air over a three day period in summer 2008 (GSHOX campaign). Within the measurement uncertainties the model agrees well with observed oxidant levels, i.e. OH and the sum of HO_2+RO_2 radicals and most of the time with O_3. In order to investigate impact of snow chemistry on oxidant concentrations,

runs without snow bromide and without snow nitrate are compared to the base case. The main result is that OH levels can only be matched by including snow emissions of NO_x and halogens. The model indicates that NO_x emissions contribute to ozone production, which is reduced but not offset by catalytic destruction via snow sourced bromine chemistry. The mismatch with HONO is interpreted as a potential missing HONO source.

This is a nice model study investigating the coupled snow-atmosphere system in order to understand better the chemical composition of air above snow. The finding that snow photochemistry influences the HO_x radical budget at Summit is not a novelty as such, as this has been shown previously by Chen et al. (2007). However, difficulties in that study remained in reproducing radical levels. The present work is clearly a step forward in that it employs a truly coupled approach and matches observations of hydroxyl radicals with only temperature as a constraint. In addition, links and feedbacks between NO_x and halogen chemistry and how they relate to the oxidant budget above snow are illustrated. The MISTRA-SNOW appears to be a valuable tool for the interpretation of atmospheric chemistry studies above snow.

The main concern, which needs to be addressed/discussed further before going ahead in ACP, is that the model probably underestimates the impact of snow emissions of HO_x precursors on the respective atmospheric budget and on total oxidation capacity.

SPECIFIC COMMENTS

The authors state that model predicted HO_x precursors H_2O_2 and CH_2O compare well with observations in summer 2000. They find that H_2O_2 snow emissions do not contribute much to a) the atmospheric budget of H_2O_2 and b) to primary production of OH radicals. Both statements are quite different to what has been found previously at the same site or other polar sites. For example, regarding a) Chen et al. (2007) showed that in summer 2003 the net snow contribution of the gross chemical produc-

tion of H_2O_2 is about 25%. Re:b) the same study showed that primary HO_x sources were $O(^1D)+H_2O$ (41%) and the photolysis of snow emitted precursors H_2O_2 and CH_2O (40%); for the latter H_2O_2 dominated with 37% (3% from CH_2O).

The conclusions regarding model performance & oxidant budget might be different had the authors not chosen to use H_2O_2 and CH_2O from summer 2000 (due to lack of measurement during GSHOX). This was a summer with atypically low concentrations of both species at Summit, e.g. mean H_2O_2 in the 16-Jun to 7-July 2000 period was 0.65 ppbv (Jacobi 2002) whereas average levels measured in 4-20 June 1996 (Hutterli, 2001) and 27-June to 12-July 2003 (Frey, 2009) were with 1.4 ppbv about twice as high. The same applies to CH_2O with 0.12 ppbv in summer 2000 (Jacobi et al., 2002) compared to 0.23 ppbv in June 1996 (Hutterli et al., 1999) or >0.15 ppbv in July 2003 (Chen et al., 2007).

Thus, uncertainties in modelled oxidant levels & production/loss pathways from less accurate model description of H_2O_2/CH_2O snow-air exchange need further discussion & revision of corresponding statements.

As acknowledged by the authors, the model has some shortcomings such as lack of organic snow chemistry or still rather simplistic snow physics, e.g. the representation of the liquid-like layer (LLL). The main tuning parameter is the bulk-LLL ratio of nitrate and bromide and is adjusted to match NO and BrO in ambient air. How sensitive are modelled NO_x and BrO mixing ratios to this parameter?

And finally, a more detailed comparison between modelled and observed firn air concentrations would be beneficial for model validation, but certainly another study in its own right. However, discussing some more of the published firn air data at Summit would yield insight into where the model needs development, e.g. firn air concentrations of ozone (Peterson et al., 2001), OH radicals (Beyersdorf et al., 2007) or possibly organic peroxides (Frey et al., 2009).

Further comments:

Abstract: l16-19 The impact of BrO is a lot smaller than that of NO_x. It would be instructive to include the fractional contributions of NO_x and BrO to the OH increase at noon. Credit should be given (here or in the summary of previous model work) that Chen et al. (2007) demonstrated previously the impact of snow chemistry on the HO_x budget above snow at Summit, although not with a coupled snow-air model and with different conclusions (see above).

l24-25: but not with typical summer levels of H_2O_2 & CH_2O measured in other campaigns (e.g. 1996 and 2003, see above)

p5560, l16-23: A brief note would be helpful regarding H_2O_2 & CH_2O snow grain distribution and initial snow profiles.

p5562 l.12-15: BL physics seemingly well modelled as suggested by the match of observed vs. modelled T-profiles. So does this imply that wind-shear driven mixing plays a lesser role at Summit (during the model period)? How do wind speeds compare to observations (important for snowpack ventilation e.g. via wind pumping)?

p5564-5566 (section 3): A summary table would be helpful, e.g. parameter (mean, range), uncertainty & reference and also including a quantitative measure of model performance such as the rms error for each parameter & run (base, noNO, noBr).

p5570, l14-21 & Fig.6: The differences in O_3 mixing ratios between base case and noBro are surprisingly small and would not explain a difference of >15 ppbv between firn and ambient air previously observed by Peterson et al., (2001). Is this due to model inconsistencies or are perhaps other halogens at play?

p5571 l15-16: See above. In addition, the model underestimate of CH_2O in firn air might be even more significant due to a low bias in measured CH_2O from ventilation effects during sampling.

p5572,l8: see above, choice of H_2O_2 data set for comparison

p5572,l15: not Jacobi 2002,2004, the correct citation would be Hutterli et al., 2001, where June 1996 H_2O_2 data were first described and interpreted

p5572, l18-19: here most of ambient H_2O_2 production is from HO_2 self reaction; however, the model seems to underestimate the H_2O_2 snow source if typical Summit values are taken into account and the budget would change accordingly.

p5572, l20-22: needs revision with above comments

p5572, l27: to avoid confusion define oxidation capacity, e.g. as the sum of HO_x, H_2O_2 and O_3 or similar.

p5574, l21-24: in contrast to the SUM03 model study (Chen et al., 2007), see previous comments.

p5575,l24-27: An important terminal loss of HO_2 radicals identified by the model is the formation of organic peroxides (see also Fig.13). This could be further supported/evaluated by comparison with existing observations of ROOH at Summit (Frey et al., 2009).

p5579,l11-22: revision according to comments above.

TECHNICAL CORRECTIONS

Figure 12d. title should be 'HO_2 destruction'

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