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## ***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.***

**J. L. Thomas et al.**

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COMMENT: 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<sub>2</sub>+RO<sub>2</sub> radicals and most of the time with O<sub>3</sub>. In order to investigate impact of snow chemistry on oxidant con-

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centrations, 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<sub>x</sub> and halogens. The model indicates that NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> precursors on the respective atmospheric budget and on total oxidation capacity.

RESPONSE: The authors thank the reviewer for the helpful comments, which have improved the scientific content of the manuscript. We address the specific comments below.

COMMENT: The authors state that model predicted HO<sub>x</sub> precursors H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O compare well with observations in summer 2000. They find that H<sub>2</sub>O<sub>2</sub> snow emissions do not contribute much to a) the atmospheric budget of H<sub>2</sub>O<sub>2</sub> 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.

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(2007) showed that in summer 2003 the net snow contribution of the gross chemical production of H<sub>2</sub>O<sub>2</sub> is about 25%. Re:b) the same study showed that primary HO<sub>x</sub> sources were O(1D)+H<sub>2</sub>O (41%) and the photolysis of snow emitted precursors H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O (40%); for the latter H<sub>2</sub>O<sub>2</sub> dominated with 37% (3% from CH<sub>2</sub>O).

The conclusions regarding model performance & oxidant budget might be different had the authors not chosen to use H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O 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<sub>2</sub>O<sub>2</sub> in the 16-June 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<sub>2</sub>O 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<sub>2</sub>O<sub>2</sub>/CH<sub>2</sub>O snow-air exchange need further discussion & revision of corresponding statements.

RESPONSE: A model run with additional H<sub>2</sub>O<sub>2</sub> and HCHO in the gas and condensed phases has been completed to investigate how this changes the conclusions in the paper. For the run with higher H<sub>2</sub>O<sub>2</sub> and HCHO concentrations, we have initialized the surface HCHO equal to 230 pptv and H<sub>2</sub>O<sub>2</sub> equal to 1.4 ppbv. We also initialized the LLL concentration with the appropriate Henry's law equilibrium concentration for these higher concentrations. The OH concentrations change very little with these increased primary radical sources (shown in green in Fig. 1).

Even though the levels themselves don't change, the relative contribution of H<sub>2</sub>O<sub>2</sub> to the primary OH production does change. In the updated run, which does not sustain these high levels of HCHO or H<sub>2</sub>O<sub>2</sub> for the entire model run, we only use the first day for the purposes of constructing an OH budget. The relative importance of H<sub>2</sub>O<sub>2</sub> compared to O(1D)+H<sub>2</sub>O changes significantly as pointed out by the reviewer, and doubles the contribution of H<sub>2</sub>O<sub>2</sub> to the primary OH sources (22% in the base run compared to

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41 % in the run with more H<sub>2</sub>O<sub>2</sub> and HCHO). This does not result in significant additional OH in the boundary layer because the budget is largely dominated by recycling reactions (e.g. NO + HO<sub>2</sub>).

We have added the results from this sensitivity run into a supplementary information document that is available online and have added a discussion of these results to the manuscript.

COMMENT: 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<sub>x</sub> and BrO mixing ratios to this parameter?

RESPONSE: This is an important point because the LLL initialization and partitioning are clearly important. This is shown in the sensitivity runs included in the manuscript with varying snow nitrate and bromide concentrations. A systematic sensitivity study of different LLL initializations is out of the scope of the current paper.

COMMENT: 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).

RESPONSE: Peterson et al. 2001 shows there is significantly more ozone destruction in interstitial air than predicted in the model (Thomas et al., 2011). It is currently not known what causes rapid ozone destruction in firn air, but is likely due to catalytic destruction of ozone by halogen cycling in the snowpack. If that is the case, then the model under-predicts halogen concentrations and the corresponding ozone destruction in interstitial air. However, it is also possible there is another (currently unknown) mech-

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anism causing ozone destruction in interstitial air. To address this, the following text has been added to the manuscript: "Significant ozone destruction in firn air measured by Peterson et al. (2001) is not reproduced in the model, suggesting that the ozone destruction may not have occurred during the campaign. Alternatively, the model could under-predict halogen concentrations in interstitial air and the corresponding ozone destruction. It is also possible there is another (currently unknown) mechanism causing ozone destruction in interstitial air."

Beyersdorf et al. (2007) showed using hydrocarbon gas ratios in a transparent flow chamber with undisturbed surface snow that the lower limit to peak OH radical concentration on 10–12 July 2003 was  $\sim 3.0 \times 10^6$  (lower than ambient concentrations reported in Sjostedt et al. (2007)). Beyersdorf et al. calculated OH radical concentrations using an inlet placed below the snow surface at a depth of 5 cm with a sample flow rate of  $0.5 \text{ L min}^{-1}$ . The values shown from the model in the paper at a depth of 10 cm are higher than the values suggested by Beyersdorf et al. (2007). There are two factors that determine interstitial air OH concentrations. First, there is decreasing sunlight with depth, which should decrease the OH concentration. Second, the additional NO<sub>x</sub> and bromine in interstitial air should increase the concentrations of OH significantly. We have shown earlier in the paper that even a small amount of NO ( $\sim 10 \text{ pptv}$ ) increases the OH in the boundary layer by a factor of 2. So, it is not surprising that in the interstitial air, the large NO<sub>x</sub> concentrations overwhelm the decrease in sunlight and that the model calculated OH concentrations are higher than in the boundary layer. There are several possibilities to explain the discrepancy, the first is that the model NO<sub>x</sub> concentrations are not representative interstitial air NO<sub>x</sub> concentrations during the campaign. The second is that in sampling NMHC Beyersdorf et al. (2007) sampled concentrations at multiple depths, therefore there may be a contribution from interstitial air with very low OH concentrations deeper in the snowpack. Beyersdorf et al. (2007) also state that their measurement is a lower limit, so the model may not be inconsistent with the measurements.

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To address this we have added the following text to the manuscript: "In an initial study, Beyersdorf et al. (2007) showed using hydrocarbon gas ratios in a transparent flow chamber with undisturbed surface snow that the lower limit to peak OH radical concentration on 10-12 July 2003 was  $3.0 \times 10^6$  molec cm<sup>-3</sup>. Given that their measurement was a lower limit, this may not be inconsistent with the model predicted OH concentrations.

There are several potential explanations for the discrepancy between Beyersdorf et al. (2007) and the present study. The model may over predicting OH, due to over prediction of the NO<sub>x</sub> concentrations in the interstitial air. But, without measurements to compare with it is difficult to determine if this is the cause of the discrepancy. It is also possible that during sampling Beyersdorf et al. (2007) also sampled hydrocarbons from deeper in firn air, which contained lower OH concentrations."

Frey et al. (2009) compared measurements of organic peroxides from different years at Summit. We have added a short discussion of the variability of observations by adding the following to the paper: "Frey et al. (2009) presented H<sub>2</sub>O<sub>2</sub> measurements at Summit from 2003 and 2004 which ranged from 1.4 ppbv in June/July to 100-300 pptv in March-early May. Summer 2000 H<sub>2</sub>O<sub>2</sub> levels were lower, as shown by Jacobi et al. (2004). Suggesting both seasonal and inter-annual variability in radical sources may be important. But, given that H<sub>2</sub>O<sub>2</sub> and HCHO were not measured during GSHOX the comparison with prior years can only be considered qualitative."

COMMENT: Abstract: I16-19 The impact of BrO is a lot smaller than that of NO<sub>x</sub>. It would be instructive to include the fractional contributions of NO<sub>x</sub> 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<sub>x</sub> budget above snow at Summit, although not with a coupled snow-air model and with different conclusions (see above).

RESPONSE: We have added to the abstract: "Bromine chemistry increases the OH concentration by between 10-18% (10% at noon), while snow sourced NO<sub>x</sub> increases

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OH concentrations by 20-50% (27% at noon).

We have added to the discussion of prior work: "Prior modeling work using a constrained box model showed the importance of these species for OH budget at Summit (Chen et al., 2007)."

COMMENT: I24-25: but not with typical summer levels of H<sub>2</sub>O<sub>2</sub> & CH<sub>2</sub>O measured in other campaigns (e.g. 1996 and 2003, see above)

RESPONSE: To clarify this point we modified the abstract to read: "Other model predicted HO<sub>x</sub> precursors, H<sub>2</sub>O<sub>2</sub> and HCHO, compare well with measurements taken in summer 2000, which had lower levels than other years."

COMMENT: p5560, I16-23: A brief note would be helpful regarding H<sub>2</sub>O<sub>2</sub> & CH<sub>2</sub>O snow grain distribution and initial snow profiles.

RESPONSE: The text has been updated to address this: "The base case model run is initialized with gas and aqueous phase concentrations as described in Thomas et al. (2011), Table 2. Briefly, the initial gas phase mixing ratios in the interstitial air are vertically uniform for species with long atmospheric lifetimes (for example CO) and decay with snow depth for reactive species (for example O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HCHO)."

COMMENT: p5562 I.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)?

RESPONSE: Our primary goal is to model snowpack-boundary layer chemistry. Due the uncertainties in modeling boundary layer physics, we use the measured wind speeds for calculation of the snowpack ventilation via wind pumping. There is a discussion of this as part of the response to H. W. Jacobi's review of the model description (<http://www.atmos-chem-phys-discuss.net/10/C13159/2011/acpd-10-C13159-2011.pdf>). We refer the reviewer to this discussion online to ad-

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dress this comment (<http://www.atmos-chem-phys-discuss.net/10/C14978/2011/acpd-10-C14978-2011.pdf>).

COMMENT: 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).

RESPONSE: A summary table would duplicate Table 2 in Thomas et al. (2011). A full error analysis of how the input parameters impact the output of the model is outside the scope of the present manuscript.

COMMENT: p5570, I14-21 & Fig.6: The differences in O3 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?

RESPONSE: The answer to this question is not known. Either the model underpredicts halogen concentrations in the interstitial air, or there is another process involved in ozone destruction (as discussed in an earlier comment). A measurement of BrO concentrations in firn air is needed to evaluate if the model is reasonable, but is currently unavailable. The following has been added to address this: "The model does not predict strong ozone depletion in the snowpack, which has been observed at Summit (Peterson and Honrath, 2001). This is because of the relatively small halogen concentrations in interstitial and ozone production from NO<sub>x</sub> in the interstitial air offsets most ozone destruction that does occur. Measurements of halogens and NO<sub>x</sub> in the interstitial air are needed to compare with the model. However, measurements of undisturbed interstitial chemical concentrations are difficult and will likely require developments in measurement techniques."

COMMENT: p5571 I15-16: See above. In addition, the model underestimate of CH<sub>2</sub>O in firn air might be even more significant due to a low bias in measured CH<sub>2</sub>O from

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ventilation effects during sampling. RESPONSE: We have updated the text to: " In addition, the measurements are likely a lower limit of interstitial air concentrations due to dilution while sampling. In the future, model improvements will be needed to fully represent this chemistry. "

COMMENT: p5572,18: see above, choice of H<sub>2</sub>O<sub>2</sub> data set for comparison p5572,115: not Jacobi 2002,2004, the correct citation would be Hutterli et al., 2001, where June 1996 H<sub>2</sub>O<sub>2</sub> data were first described and interpreted

RESPONSE: We have changed the text to read: "Snow sourced hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, can contribute to the OH budget and the boundary layer oxidizing capacity over snow upon photolysis. Multiple years of measurements of hydrogen peroxide have been made at Summit, Greenland (e.g. Hutterli et al., 2001). As no H<sub>2</sub>O<sub>2</sub> measurements were made during GSHOX we also compare H<sub>2</sub>O<sub>2</sub> modeled in the base case with prior measurements during summer 2000 (Jacobi et al., 2004)."

"Measured H<sub>2</sub>O<sub>2</sub> fluxes in June 1996 suggested a daytime H<sub>2</sub>O<sub>2</sub> release from the surface snow and redeposition at night (Hutterli et al., 2001)"

COMMENT: p5572, 118-19: here most of ambient H<sub>2</sub>O<sub>2</sub> production is from HO<sub>2</sub> self reaction; however, the model seems to underestimate the H<sub>2</sub>O<sub>2</sub> snow source if typical Summit values are taken into account and the budget would change accordingly.

RESPONSE: This has been addressed via the sensitivity runs now included in the supplementary information provided with the manuscript, which contains an OH/HO<sub>x</sub> budget for a run with higher H<sub>2</sub>O<sub>2</sub> concentrations.

COMMENT: p5572, 120-22: needs revision with above comments

RESPONSE: We have updated the text to: "gas phase chemistry in the boundary layer can largely explain H<sub>2</sub>O<sub>2</sub> levels measured in summer 2000."

COMMENT: p5572, 127: to avoid confusion define oxidation capacity, e.g. as the sum of HO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> or similar.

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RESPONSE: We have updated the text to: "boundary layer oxidation capacity, which for the purposes of this study we define as the sum of OH, HO<sub>2</sub>, and RO<sub>2</sub>."

COMMENT: p5574, I21-24: in contrast to the SUM03 model study (Chen et al., 2007), see previous comments.

RESPONSE: The text has been updated to: "only a small portion of this is a primary OH source (from snow emissions of H<sub>2</sub>O<sub>2</sub>). In the sensitivity run presented in the supplementary information shows that for a case with higher hydrogen peroxide concentrations the contribution of H<sub>2</sub>O<sub>2</sub> to primary OH is consistent with the study of Chen et al. (2007). These higher concentrations likely result from snowpack emissions of hydrogen peroxide."

COMMENT: p5575, I24-27: An important terminal loss of HO<sub>2</sub> 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).

RESPONSE: We believe this comparison is best left for a separate model study.

COMMENT: p5579, I11-22: revision according to comments above.

RESPONSE: We have updated the text to: "Model predicted HCHO and H<sub>2</sub>O<sub>2</sub> are in agreement with prior measurements taken in 2000 at Summit. However, measurements during this year were lower than other campaign measurements (Hutterli et al., 2001, Frey et al., 2009)."

COMMENT: TECHNICAL CORRECTIONS Figure 12d. title should be 'HO<sub>2</sub> destruction'

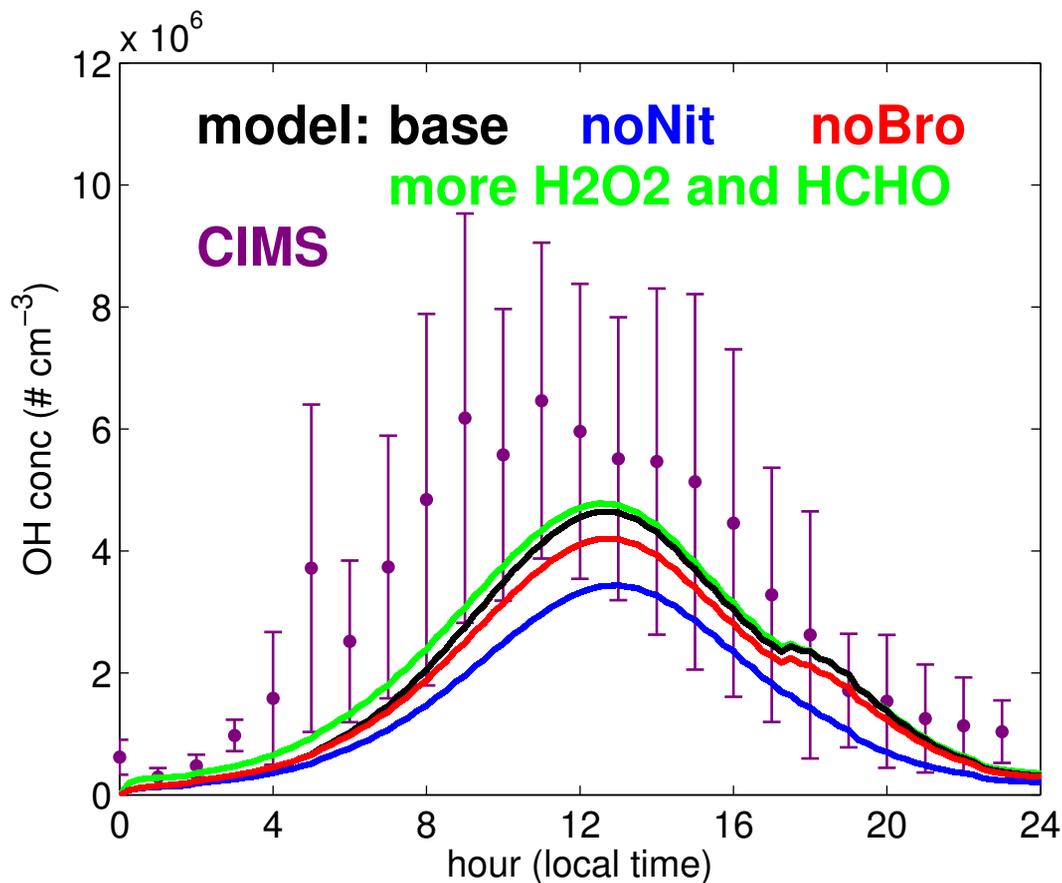
RESPONSE: This figure has been updated to show only the first 24 hours of the model run so that it's clear what dominates HO<sub>x</sub> cycling. The label has also been corrected.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5551, 2012.

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**Fig. 1.** Model predicted OH for the base case and for the sensitivity run with higher HCHO and H<sub>2</sub>O<sub>2</sub>. Model results show that the additional primary radical sources have a small impact on OH concentrations.

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