Atmos. Chem. Phys. Discuss., 12, C3871–C3877, 2012
www.atmos-chem-phys-discuss.net/12/C3871/2012/

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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Received and published: 21 June 2012

COMMENT 1: The authors have used the MISTRA-SNOW model along with data from the GSHOX campaign of 2008 to analyze the coupled chemistry of the snowpack and the polar boundary layer at Summit, Greenland. They previously (Thomas et al., 2011) used the same model to study NOx and BrO chemistry during the same campaign. As other reviewers for this manuscript and Thomas et al. (2011) have pointed out, the MISTRA- SNOW model is a success, and a significant advance beyond previous models, in the sense that the authors have been able to reproduce the gas-phase

observations of GSHOX quite well. The paper is well-written and should be publishable in ACP after the following issues are addressed:

RESPONSE: The authors thank the reviewer for the helpful comments and for the effort to improve our study. We have addressed the specific comments below.

COMMENT 2: In this reviewer's view, the main weakness of this manuscript (really of the MISTRA- SNOW model) is that the representation in the model of the chemistry and physics of what the authors term the "liquid-like layer" (LLL) is a simplistic abstraction of many complex, and in some cases poorly understood, processes known to occur in the snow-pack. Interfacial layers on ice and snow can be categorized into two regimes: the 'quasi-liquid layer' (QLL), and brine layers (BL). The QLL is a nanoscale region of surface disorder that exists on pure ice (or at very low impurity concentrations) below the melting temperature. In contrast, a brine is a true liquid that exists in thermodynamic equilibrium with pure ice in frozen aqueous systems with higher solute content (e.g. snow with impurities). The thickness of the QLL or an interfacial brine layer depends on temperature as well as the concentration and chemical identities of the impurities present. There is mounting evidence that the QLL and brines have a dramatic impact on the interactions of ice and snow with trace gases, but a great deal of uncertainty still surrounds these issues.

RESPONSE: The reviewer points out an important issue, we have addressed this by adding the following text to section 1.2: "We use a simplified representation of the liquid-like layer (LLL) and its chemistry to represent the complex, but poorly understood, processes occuring in the snowpack. The modeled LLL is a disordered liquid-like interfacial layer on ice, which is a combination of the quasi-liquid layer (QLL) and brine layers (BL), which form for fundamentally different reasons (Kuo et al., 2011). The QLL is a disordered layer of waters at the surface of ice that forms even at very low or no impurity concentrations. On the other hand, brine pockets (BL) with high impurity concentrations form in ice with higher solute content. Both the QLL and BL should in principal grow with increased impurity concentration and temperature. Given that there is a great deal of uncertainty that surrounds how to correctly represent the LLL in models, we represent the LLL and its chemistry in a simplified way. Our representation of snow chemistry will require improvements in the future as the understanding of both LLL physics and chemistry develops."

COMMENT 3a: The authors have effectively treated the combined effects of the QLL and BL as those of a 10 nm (constant thickness) ideal aqueous solution coating 1-mm diameter spherical snow grains, with (for the most part) bulk aqueous chemistry operative in the layer. Snow-LLL partitioning coefficients for nitrate and bromide were treated as adjustable parameters. Snowpack morphology is complex and temperature dependent (see Domine et al. 2008) so the 1 mm snow grains are one simplification.

RESPONSE: The following has been added to the conclusions: "the current version of the model also contains a simplified representation of snowpack physics, which is a complex process that depends on temperature (e.g. Domine et al., 2008). In the future, work towards a more complete description of snowpack physics and chemistry in one model is needed to create a model that accurately predicts the coupling between snow chemistry and physics with the overlying atmosphere."

COMMENT 3b: The authors justify the choice of the constant 10 nm LLL thickness based on a review article about the QLL, which featured a small subset of the dozens of QLL thickness vs. T datasets available in the literature, even though the LLL resembles the BL more closely in its characteristics. Cho et al. (2002) and Kuo et al. (2011) presented models for the temperature and solute-dependent thickness of the BL. Neither the QLL nor the BL are expected to be ideal aqueous solutions, and yet the aqueous chemistry of the LLL and the gas-LLL partitioning (via Henry's Law) are treated as such. Some information is available on the solubility of trace species (HNO3, HCl, HCHO) in solid ice but it appears that it was not used for calculating the LLL-snow partitioning a priori (e.g. Kuo et al. 2011) or to check the reasonableness of the parameterized partitioning coefficient for nitrate (Thibert and Domine, 1998;Thibert and Domine, 1997;Domine et al., 1994;Barret et al., 2011).

RESPONSE: How the QLL and BL should be represented in models of snow chemistry (via a LLL with chemistry) is still under discussion. According to the model of Cho et al. 2002 (similar to what is shown in Fig. 2 in Kuo et al 2011), the volume fraction for the brine layer for frozen seawater is significant (~0.2 volume fraction of brine layer at T=263K). However, for the lower ion concentrations at Summit, it's not clear if a true BL forms. According to Kuo et al. (2011) for a known melt concentration, very little or no brine formation is predicted for solute concentrations between 3-10 μM at T<268 (see table 1, Scenario 1b, using a cutoff for the brine volume fraction of φv<3x10-5). At Summit, during the campaign the melt concentration of nitrate in surface snow (the dominant ion) was ~3.5 μM. Our model LLL volume fraction is 8.7x10-5, which fits the definition of very little or no brine layer formation. To address this the following text has been added to the paper: "We have chosen a liquid layer thickness in the mid-range of QLL measurements for pure ice in the temperature range of the model. Exactly how to represent the QLL and BL in models of snow chemistry is still under discussion, despite recent progress (Kuo et al. 2011). For the low ion concentrations at Summit, it's not clear if a true BL forms. According to Kuo et al. (2011) for a known melt concentration very little or no brine formation is predicted for the solute concentrations measured in surface snow at Summit, which is consistent with the model initialization."

COMMENT 4: I acknowledge that, in the face of the many uncertainties surrounding snowpack chemistry and physics at this time, simplification and parameterization is necessary to model this system. In the case of this GSHOX modeling exercise, where a fairly complete dataset was available for tuning, the simplified approach taken by the authors seems to have worked well enough. However, the lack of fundamental underpinning means that the predictive capability of the model for other scenarios, where less data may be available, is in question. My discussion here points to future model development work which is probably outside the scope of this manuscript. However, for this manuscript to be suitable for publication in ACP, the authors at least need to refine the language they use in discussing the model and add some additional explanation to make the issues clear to the reader.

RESPONSE: Fundamental process level understanding will undoubtedly only come from analysis of other datasets and conditions. It is clear that other similarly complete datasets must be modeled in order to further our understanding and develop appropriate model descriptions of these processes. We have modified the final paragraph of the paper to address this comment.

COMMENT 5: - A passage should be added discussing the LLL as an abstract representation of the QLL and BL, and the fundamental differences between what is known about QLL and BL behavior and the way the LLL is represented in the model.

RESPONSE: See response to Comment 2 above.

COMMENT 6: - It should be mentioned that the ability of MISTRA-SNOW to predict coupled snowpack-PBL chemistry in scenarios other than the GSHOX environment is potentially limited by the current simplified representation of snowpack chemistry and physics

RESPONSE: We have added: " Additional modeling studies, backed up by field observations as well as new laboratory studies, are needed to confirm that our results are representative for other snow covered locations. This in-depth research is needed to provide complete understanding, which can used to develop predictive modeling capabilities and parameterizations of these processes for inclusion in regional and global atmospheric chemistry models. Despite the simplified parameterization of processes, such as LLL physics and chemistry, air transport in and out of snow, etc., our study shows that photochemical processing in snow is essential to accurately describe the mechanisms controlling boundary layer ozone chemistry and oxidation capacity."

COMMENT 7: - A discussion of possible future model developments which could allow a more fundamental representation of snowpack chemistry and physics should be included. This could include a list of data not currently available which would be necessary for this to happen.

RESPONSE: Unfortunately, it's not possible to make a complete list of the missing available data necessary to create a predictive modeling system without first using the model to understand other datasets. We have added text to address this comment (see above, Comment 6).

COMMENT 8: - Page 5577 line 22: I may be misunderstanding what is meant by the term, but I am not certain that it is appropriate to call this model "unconstrained," since the model is tuned using the snow-LLL partitioning coefficients for nitrate and bromide.

RESPONSE: The modeling as part of GSHOX is just a first step, as the reviewer points out. However, a model framework that correctly describes many of the behaviors of the coupled snow-atmosphere system without constraining the gas phase concentrations in the model to measurements is already a significant advance. We have changed the wording from "results using an unconstrained coupled air-snow chemistry" to "results using a coupled air-snow chemistry".

COMMENT 9: - Page 5577 line 27-28: based on the discussion here, "we conclude that the model represents accurately the coupled air-snow system" should be rephrased. The model does not accurately represent the chemistry and physics of the snowpack, but it does accurately reproduce the GSHOX observations.

RESPONSE: This has been changed to: "we conclude that the model represents accurately the influence of the snowpack on boundary layer chemistry during GSHOX"

COMMENT 10: - Page 5579, lines 23-27: The authors suggest in this concluding sentence that the MISTRA-SNOW model and the conclusions derived using it are a) general for Summit and b) could be extended to other snow covered locations. This is in question for the reasons I mentioned earlier, so some caveat needs to be included here.

RESPONSE: This sentence has been removed and the concluding paragraph has been rewritten (see Comment 6).

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