Atmos. Chem. Phys. Discuss., 12, C1228–C1232, 2012
www.atmos-chem-phys-discuss.net/12/C1228/2012/

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.

Anonymous Referee #1

Received and published: 2 April 2012

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:

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 snowpack. 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.

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. 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

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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).

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. Specific suggestions follow:

- 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.

- 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

- 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.

- 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.

- 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.

- 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.

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

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