

Interactive comment on “Modeling the Physical Multi-Phase Interactions of HNO₃ Between Snow and Air on the Antarctic Plateau (Dome C) and coast (Halley)” by Hoi Ga Chan et al.

T. Bartels-Rausch (Editor)

thorsten.bartels-rausch@psi.ch

Received and published: 19 December 2017

With this editorial comment, I'd like to summarize the discussion between me and the authors that continued via email after the referee comments have been received.

The work by Chan et al. describes field measurements and snow-chemistry modelling of HNO₃ in Antarctic surface snow and the overlaying air. The performance of 2 model approaches to capture measurement at 2 sites that are distinct in ambient temperature –among other factors- are compared. One model introduces a liquid brine fraction to parameterize snow-chemistry, while the other model built on the quasi-liquid layer.

C1

I find the comparison of these two concepts – liquid and liquid-like – ability to capture trends in a valuable data set most interesting for the general audience of ACP. As with any snow chemistry model, also the approaches presented here include parameters some of which are strictly not physically based or have a large uncertainty. This is not per se a disadvantage. The importance is to present enough details and to acknowledge that the models are not built on first principals alone, which is now the case throughout the manuscript. Further similarities to previous models are now acknowledged. Along with this came a change in tone of the manuscript and achievements in previous work are now acknowledged. While I remain very skeptical about de-facto parameterizing the QLL as a layer with a thickness in the μm range, I leave it to the reader to judge.

To ensure transparency, please find a copy of the email exchange with the authors here:

Question: Thanks for the revised version. I'm still a little confused about one aspect that a referee has previously raised as major concern. It is related to the volume of the DI. Actually, also to the volume of the [HNO₃ (surf)] in general. I still have difficulties to understand 1) how you can get a mass balance if the DI has a volume of 0 and 2) how can define U(REff) without a volume of the DI? Answer: All surface or boundary concentrations actually refer to the volume of the outermost concentric model shell of the snow grain. In particular, at $T > T_0$ the outermost model shell of the snow grain becomes essentially a DI, with Henry's Law describing air-DI exchange and defining its NO₃- concentration. The outermost model shell thickness varies with grain size, which in turn is constrained by the observed seasonal cycle of SSA. The thickness ranges between 0.5 in winter and 1.5 μm in summer. To clarify we have updated the model description (P7, Ål97-226) as well as the assumptions made regarding the DI in Model 1

Changes to text: "3 Modelling Approach The aim of this paper is to focus on the physical exchange mechanisms of HNO₃ between air and snow to predict the concentration

C2

of nitrate in the skin layer of the snowpack, as a first step towards a full snowpack model. The two models are constrained by the observed atmospheric concentration of HNO₃, air temperature, skin layer temperature, atmospheric pressure and humidity. The loss or gain in the atmospheric HNO₃ due to the mass exchange between air and snow are included implicitly by constraining the models with the observed atmospheric concentration of HNO₃. The following assumptions were made in both Model 1 & 2: 1) the concentration of HNO₃ in snow interstitial air is the same as in the overlying atmosphere justified by a short characteristic time scale for gas-phase diffusion of $\hat{\Delta}L_{ij}$ 1 s (Table 1); 2) the physical properties of the skin layer are homogeneous and include density and specific surface area (SSA); and 3) the snow grain is assumed to be a radially symmetrical sphere with an effective radius, R_{eff} , which is estimated from the SSA as follows:

Eq.6

where ρ_{ice} is the density of ice. Snow metamorphism and resulting changes in snow grain size are not modeled explicitly, but are approximated instead by prescribing temporal changes in SSA. Here an annual cycle of SSA is included based on observations at Dome C (Picard et al., 2016), ranging from 25 m²kg⁻¹ in summer to 90 m²kg⁻¹ in winter (details in Sect. 4.3 and Fig. A4a), and yielding a R_{eff} of $\hat{\Delta}L_{ij}$ 130 μ m in the summer, which gradually reduces to $\hat{\Delta}L_{ij}$ 30 μ m in the winter (Fig. A4b). Modeled co-condensation (Eq. 9 & 10) does not change model snow grain size, since the involved ice volumes are relatively small compared to the volume of the snow grain. The model set up implies also that the snow grain size remains constant during each model time step of $\Delta t = 10$ min. For the calculation of solid-state diffusion the snow grain is divided into N concentric shells of equal thickness. To optimise model performance and computational cost, the number of concentric shells is fixed to N = 85, yielding a model shell thickness Δr of $\hat{\Delta}L_{ij}$ 1.5 μ m in summer and $\hat{\Delta}L_{ij}$ 0.5 μ m in winter due to seasonal change in grain size. Δr remains at all times smaller than the minimum typical length-scale, $\langle x \rangle$, a molecule diffuses over a finite time, Δt , and described by the root-mean

C3

square displacement, $\langle x \rangle = \sqrt{6\Delta t k_{diff}}$. Minimum typical length-scales occur in winter when air temperatures are lowest, and for a modeling time step, $\Delta t = 10$ min, they range between 1.5 μ m at Dome C and 5.5 μ m at Halley."

Sect 3.1, line 241-259:

'The physical properties of the DI are still poorly known, and currently there are no physical parameterizations available to estimate DI thickness, partitioning coefficients or diffusivities. Hence, for the DI in Model 1 the following four assumptions are made: 1) the partitioning between air and the DI follows Henry's law, similar to previous models (e.g. Thomas et al., 2011 & Toyota et al., 2014); 2) the model geometry described above implies that the DI, i.e. the outermost model shell of the snow grain, follows the seasonal cycle of snow grain specific surface area and has a thickness of 1.5 μ m in summer decreasing to 0.5 μ m in winter. A seasonal cycle is qualitatively consistent with laboratory measurements, which show that DI thickness increases with temperature (Bartels-Rausch et al., 2014). But the absolute model values are larger than previous lab measurements on pure ice, which range from the thickness of a monolayer of water (0.3 nm) to 100 nm, depending on the measurement technique (e.g. Bartels-Rausch et al., 2014), or values adopted in previous model studies (range 10-30 nm) (e.g. Thomas et al., 2011, Toyota et al., 2014, Murray et al., 2015). However, DI thickness is also sensitive to the type and concentration of impurities, and generally increases with ion concentration (e.g. Dash et al., 2006; Bartels-Rausch et al., 2014); 3) the DI is interacting with the bulk ice, i.e. solvated nitrate ions diffuse into the interior of snow grain and the mass transport is determined by the solid-state diffusion coefficient of ice, k_{diff} , and the concentration gradient across the snow grain; and 4) the solid-state concentration of nitrate in the bulk is limited by the thermodynamic equilibrium solubility of ice (e.g. by Thibert et al., 1998 as shown in Eq. 19), except the outermost model shell of the snow grain.'

Question: (The nitrate concentration at the centre is set to $U(0) = 0$ and at the grain boundary $U(R_{eff}) = [HNO_3(\text{surf})]$, which is defined by surface adsorption and co-

C4

condensation at temperatures below T_0 (Eq. 7) or by solvation into the infinitesimal DI at temperature above T_0 (Eq. 13).) Wouldn't then the concentration gradient and thus the diffusivity not also depend on the choice of the layer thickness in the diffusion parameterisation?

Answer: At $T > T_0$ the concentration in the outermost model shell is determined by Henry's law and is independent of model shell thickness and grain size. At $T < T_0$ the concentration in the outermost model shell depends on grain size, because it depends on number of surface sites (Eq.3). But the concentration gradients and associated mass flux depend on the current snow grain size, which is not freely chosen but constrained by observed SSA. However, the absolute number of molecules in the outermost model shell depends on the choice of shell thickness, and influences the NO_3^- bulk concentration. This model uncertainty is clarified and discussed in a short paragraph in Sect 6.3 line 680-694:

Changes to text: 'The onset and thickness of the DI not only depend on temperature, but also the speciation and concentration of impurities present within the snow grain (McNeill et al., 2012; Dash et al., 2006). Different impurities have different impacts on the hydrogen bonding network at the ice surface and hence have a different impact on the thickness of the DI, leading in general to a thickening compared to pure ice (Bartels-Rausch et al., 2014). However no accepted model parameterisation is available. In this model imposing a seasonal cycle of SSA and therefore grain size causes the thickness of the outermost model shell to vary between $1.5 \mu\text{m}$ in summer and $0.5 \mu\text{m}$ in winter (Sect. 3.1), relatively large values and potentially contributing to the positive bias in Model 1. This is explained as follows: the bulk concentration of NO_3^- is calculated as the sum of number of molecules in each model shell divided by the total volume of the snow grain (Eq. 17). At $T > T_0$ the outermost model shell is equivalent to a DI and its concentration is determined by Henry's Law (Eq. 13), which is independent of grain size and thus model shell thickness Δr . However, the absolute number of molecules in each model shell including the DI, increases with Δr yielding a larger bulk

C5

concentration in summer. Choosing a thinner outermost model shell may reduce the Model 1 bias at Halley.'

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2016-1069>, 2016.

C6