

Interactive comment on “Air–snow exchange of nitrate: a modelling approach to investigate physicochemical processes in surface snow at Dome C, Antarctica” by Josué Bock et al.

Anonymous Referee #2

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My sincere apologies to the authors and the editor for the delayed submission of my referee comments.

[Summary]

In this paper, Bock et al. develop numerical models to analyze physical mechanisms behind the incorporation of nitrate from ambient air into surface snow at Dome C, Antarctica. Four different types of the models are developed, each of which is applied to simulate the evolution of nitrate concentrations in a single grain of the surface snow over one annual cycle. Each model is constrained by measured concentrations of total nitrate (gaseous + particulate, but assumed with some rationales to be predominated by the gaseous component) in ambient air, invariant grain size and specific

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surface area assumed on the basis of previous field measurements, and simulated snow temperatures by using a 1-D snow physics model previously developed by one of the authors. The first model assumes that the uptake of nitrate occurs entirely via surface adsorption on the snow grain. The second model (“BC1 model”) assumes that the solid-state diffusion and thermodynamic equilibrium solubility of HNO₃ in bulk ice determines the uptake of HNO₃ from ambient air. The third and fourth models (“BC2 model” and “BC3 model”, respectively) assume that the co-condensation of HNO₃ and H₂O (associated especially with snow-grain metamorphism in the summer) augments the uptake of HNO₃ from that predicted by the process of solid-state diffusion and thermodynamic equilibrium represented in the BC1 model. The difference between the BC2 and BC3 models is that the former parameterizes the co-condensation process in a diagnostic fashion where empirical parameters are adjusted to match the model with the measurements of nitrate in the snow at Dome C whereas the latter formulates the physical processes involved in the co-condensation in a relatively simple and yet prognostic fashion.

The first model, which accounts only for the surface adsorption of HNO₃, over-predicts the measured concentrations of nitrate in the surface snow almost all the time over the annual cycle and particularly from September to mid-November when the model over-prediction reaches a factor of eight. Uncertainties in the gaseous HNO₃ concentrations in ambient air and in the model input of snow temperature and specific surface area all appear to be contradictory and/or insufficient to bring the simulated concentrations of nitrate in the snow down satisfactorily to the measured ones. The authors then elaborate on the existence of major pitfalls in the laboratory experimental data for the surface adsorption of HNO₃ on ice, which I think is very useful and compelling. Hence, by using the other three models (BC1, BC2 and BC3), the authors seek possibilities for reproducing the measured nitrate concentrations by neglecting the surface adsorption. This endeavor seems to have worked out quite well. The reasonable success of all the BC1 to BC3 models during the wintertime indicates the key role of solid-state diffusion and thermodynamic equilibrium solubility of HNO₃ in bulk ice during that time of the

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year at Dome C. On the other hand, the failure of the BC1 model and the success of the BC2 and BC3 models during the summertime indicate the co-condensation as a major process leading to the summertime peak of nitrate concentrations in the surface snow at Dome C. The bulk incorporation models (BC1, BC2 and BC3) all have a difficulty in capturing the relatively high concentrations of surface snow nitrate from September to mid-November, which the authors interpret as an indication for the involvement of surface adsorption neglected in these models.

Overall, I find the paper very interesting and support its publication in ACP once the following problems are addressed. My biggest complaint to the current state of the manuscript is the insufficient detail of the BC3 model provided in the model description section and of its behavior in terms of water vapor condensation in the discussion section, as I mention below in the specific comments. I am also puzzled by the formulation of the BC2 model as currently described, which I wish the authors to clarify. The quality of English should be improved to catch up with the quality of science presented in the paper. To some extent, this problem may be addressed by an English copy-editor assigned by the editorial office at the final production of the manuscript. But, according to my own experience with publication process for ACP, the authors themselves should put some efforts beforehand because the copy-editor can often misinterpret loosely written sentences.

[Major comments]

1. I am puzzled by the formulation of the BC2 model as currently described. Section 3.3.2 states that equation (11) is used to diagnose the concentration of HNO₃ (X_{HNO_3}) according to its thermodynamic equilibrium solubility into ice and enhanced uptake due to co-condensation with water vapor. Does this equation apply to the concentration of HNO₃ in the entire volume of the snow grain? If this is the case, the model assumes that the entire volume of the snow grain instantly feels the impact of the near-surface domain of the grain where the concentrations of HNO₃ are controlled by the co-condensation, which seems inappropriate. Judging from the initial “spin-up” behav-

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ior of the BC1 model (section 5.1 and figure 4), I presume that the relevant timescale of solid-state diffusion within the bulk ice volume is on the order of a week to a month. Please clarify.

2. The authors should also provide further details of how they formulate the BC3 model and how it behaves in terms of the condensation of water vapor and its impact on the radius growth (Δr) of the snow grain. Without these pieces of information, one cannot really make sense of why this model is so successful in reproducing the summertime peak of nitrate concentrations at Dome C and are unable to discuss their potential future studies in light of the present model results. So I would like the authors to clarify the following aspects in the formulation of the model and its behavior: a) what is the magnitude of $\Delta r/\Delta t$ prescribed in the model? The authors should provide this information in a time series over the entire annual cycle in the supplement. Does $\Delta r/\Delta t$ also vary diurnally to a significant degree?; b) From the description in section 3.3.3, it seems that equation (15) is applied to prescribe the concentration of nitrate only within the outermost layer of the depth of Δr in the snow grain. If this is the case, the model seems to be assuming that the high concentration of nitrate due to the co-condensation is locked into that layer after the model proceeds to the next time step ($t + \Delta t$). How is the solid-state diffusion in the deeper layers of the snow grain handled in this model? This aspect of the model formulation should be properly described, perhaps with additional equations in section 3.3.3; and c) as currently formulated in the model, it appears that the evaporation of water from the snow grain does nothing to nitrate in it. But I wonder if it is appropriate to assume that such an evaporation of water may expose the layer of ice once buried with supersaturated HNO₃, leading to the volatilization of HNO₃ to ambient air. Is it not feasible at all to consider this possibility in the present model framework?

[Minor comments]

1. After introducing equation (8), it may be useful state the relevant timescale of solid-state diffusion with the spherical snow gain with the radius of 85 micrometers. This

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information can then be restated in section 5.1, where the authors refer the initial drop of nitrate concentrations in the BC1 model from 500 ng g^{-1} .

2. L625-626: This statement on indication for the involvement of surface adsorption in the spring should be stressed more clearly in the abstract and conclusions.

3. L645-651: What happens to the BC1 model if you decrease the solid-state diffusivity of HNO_3 by 72%?

4. Table 1: Is it useful to show mean model biases as well here?

[Editorial suggestions]

L51: features -> exhibits

L53: shows -> implies

L60-61: affinity TO

L62-63: "small chemical species" -> "small molecules"

L71: "consists in" -> is

L100: IN the late 1990's

L106: In THAT study

L167: "further accounting for" -> "a more extensive characterization of"

L171: features -> shows

L192: "Indeed, the ..." -> "The ..."

L196-198: Sounds awkward to me. Please consider rephrasing.

L349: adjusted -> adjustable

L352: "submitted to" -> "in accordance with"

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L409: during -> over

L423: the AVERAGE modelled concentration

L425: "till end" -> "toward the end of"

L447: compelling -> forcing

L531: "the SSA value is relevant to summertime" -> "the SSA value adopted in our model is comparable to summertime observations"

L585: It is not clear to me what is meant by the statement "features similar shape".

L609: supposed TO BE constant

L625-626: "another clue to say" -> "another indication"

L681: "getting rid of" -> ignoring

L692: "1-D," -> "one-dimensional (1-D)"

Supplement line 5: ARE not straightforward

Supplement line 18: WAS applied to

Supplement line 20: Drop "at total"

Supplement line 22: feature -> shows

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-133, 2016.

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