Reply to the review of Anonymous Referee #1

Replies to his/her remarks and suggestions are given below. For the sake of clarity, the reviewer's comments are in blue italics and our response is in black font.

Bock et al. use a model to examine the impacts of the physical exchange processes, adsorption, bulk diffusion and co-condensation, on the depth profiles of nitrate concentration in snow at Dome C, Antarctica. They find that bulk diffusion and co-condensation alone can explain the observed profiles.
This paper was not clearly written and thus very frustrating to read. I don't understand how one can model snow nitrate without including important processes such as atmospheric deposition and the photolysis of snow nitrate. The former is how nitrate gets to the snow in the first place, and the latter has been shown to be the dominant loss process of snow nitrate at Dome C.

Anonymous Referee #1 states that the photolysis of snow nitrate is the dominant loss process of snow nitrate at Dome C, and should be included in a modelling framework dedicated to the study of snow nitrate. We are aware that some studies concluded that the photolysis is the dominant loss process. We already highlighted these results in the submitted manuscript (L92-93). However, as explained in our paper (L50-54), the dramatic increase of nitrate concentration in surface snow during the summertime implies that uptake processes have a much stronger magnitude than sinks (which is mainly the photolysis).
In order to strengthen this point, we added a calculation of photolysis and co-condensation fluxes in the Supplementary Information (Sect. 3):
In this section, an estimation of loss and uptake fluxes is presented. Both calculations are based on the following assumptions: a skin layer thickness of 3 mm, with a snow density of 0.3 kg m^{-3}. The fluxes are calculated for an area of 1 cm^{2}.
The photolysis flux is calculated for a single nitrate concentration of 1200 ng g^{-1}, which results in 9.7 $\times 10^{14}$ molecules in the 1 cm^{2} × 3 mm volume. France et al. (2011) reported a photolysis rate for nitrate of about 1 $\times$ 10^{-7} s^{-1} in Dome C surface snow, for a solar zenith angle (SZA) of 52° which is the maximum solar elevation at Dome C. The resulting photolytic loss flux is 9.7 $\times$ 10^{7} molecules cm^{-2} s^{-1}.
The uptake flux resulting from the co-condensation process is calculated by assuming that the 1 cm^{2} × 3 mm volume is filled with ice spheres of radius 85 µm (the value used in this study) up to the prescribed density. This results in ~ 37200 spheres. In the theoretical study by Dominé and Thibert (1996), the average concentration in the condensed layer immediately before another layer condensates and isolates the previous one, is given by the integral of Eq. (15):

$$X_{average} = X_{kin} + \frac{X_{eq} - X_{kin}}{\Delta r} \int_{0}^{\Delta r} erfc\left(\frac{x}{2\sqrt{(D \cdot t)}} \right) dx$$

Using the same input data as in the model, and assuming that this average concentration multiplied by the condensed volume corresponds to the quantity of nitrate actually taken up by the snow, we calculate an average uptake flux of 5.4 $\times$ 10^{9} molecules cm^{-2} s^{-1} over the December 2009 to January 2010 period. The minimum and maximum values are 1.6 $\times$ 10^{8} molecules cm^{2} s^{-1} and 2.7 $\times$ 10^{10} molecules cm^{-2} s^{-1}, respectively.
As a conclusion, the uptake flux due to the co-condensation appears to be ? 56 times larger, on average, than the photolysis flux calculated for the highest solar elevation condition. This confirms that photolysis loss can be neglected when studying the nitrate concentration in the skin layer.
We added the following paragraph in the main text to refer to this comparison:
(L665-671)
The photolysis has not been included in this study, because the dramatic increase of summer nitrate concentration in the skin layer demonstrate

that uptake processes overtake loss processes in this specific layer. In order to refine this comparison regarding the budget of nitrate in the skin layer, an estimation of the uptake and destruction fluxes is presented in the supplementary information (Sect. 3). It appears that the uptake flux calculated with the BC3 parameterisation is 1.5 orders of magnitude larger than the maximum loss flux due to photolysis. This confirms that photolysis loss is negligible as compared to the co-condensation uptake when studying the skin layer concentration.

Anonymous Referee #1 states that atmospheric deposition is an important process which should be taken into account. We are not sure of the exact processes he/she is referring to. However, we emphasise that our study focuses on air – snow exchanges processes on the scale of a snow grain. The study of atmospheric processes is much beyond the scope of our work. However, we also stress that the air-snow uptake processes studied here are able to explain "how nitrate gets to the snow in the first place".

Although I agree that their study is important, as such physical processes will influence the distribution of nitrate in the snow column and the snow grain, the latter of which may influence e.g., how photolabile snow nitrate is, I don't see how they can ignore these other important processes. It seems that it would be better to use their model to examine the results in a laboratory, where the processes they ignore can be controlled. Since the manuscript is not clearly written, it is possible that I am misunderstanding something important about their modeling framework

We agree with Anonymous Referee #1 that the developed modelling framework allows us to infer the distribution of nitrate inside the snow grain, which is likely to influence how photolabile snow nitrate is. We emphasised this aspect in the conclusion by adding the following sentence:
(L743-749)
In this study focused on skin layer snow, nitrate photolysis inside the snow grain has not been implemented since nitrate loss is much weaker than uptake for this specific layer, as demonstrated by the dramatic increase of nitrate concentration during summer. This is not true for the whole snowpack, and photolysis should be included in a 1-D snow chemistry model. For that purpose, the description of a snow grain as a layered medium will enable using different quantum yields, after some studies suggested that it span more than 2 orders of magnitude depending on the availability of nitrate inside the ice matrix (Zhu et al. 2010, Meusinger et al, 2014).

Cited Papers:

Dominé, F. and Thibert, E.: Mechanism of incorporation of trace gases in ice grown from the gas phase, Geophysical Research Letters, 23, 3627–3630, doi:10.1029/96GL03290, 1996.

France, J. L., King, M. D., Frey, M. M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A., and Savarino, J.: Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, Atmospheric Chemistry and Physics, 11, 9787–9801, doi:10.5194/acp-11-9787-2011, 2011.

Meusinger, C., Berhanu, T. A., Erbland, J., Savarino, J., and Johnson, M. S.: Laboratory study of nitrate photolysis in Antarctic snow. I. Observed quantum yield, domain of photolysis, and secondary chemistry, The Journal of Chemical Physics, 140, 244 305, doi:10.1063/1.4882898, 2014.

Zhu, C., Xiang, B., Chu, L. T., and Zhu, L.: 308 nm photolysis of nitric acid in the gas phase, on aluminum surfaces, and on ice films, The Journal of Physical Chemistry A, 114, 2561–2568, doi:10.1021/jp909867a, 2010.

Reply to the review of Anonymous Referee #2

We thank Reviewer #2 for his/her positive appreciation of this work and especially his/her detailed comments regarding the model description and the discussion of the co-condensation process and parameterisation.
Replies to his/her remarks and suggestions are given below. For the sake of clarity, the reviewer's comments are in blue italics and our response is in black font.

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 clarity. 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.

We asked native English speakers to proofread the manuscript. We think that the quality of English now match the requirements for a publication in ACP.

[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 HNO_3 (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 HNO_3 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 HNO_3 are controlled by the co-condensation, which seems inappropriate. Judging from the initial "spin-up" behavior 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.

The second configuration of the model describes the snow grain as a layered sphere. Solid state diffusion is the only exchange process occurring between adjacent layers. Lying at the interface, the outermost layer undergoes both air – snow exchange processes and solid state diffusion with the inner layer. We developed three parameterisations to describe the air – snow partitioning and prescribe the nitrate concentration in the outermost layer. It is the boundary condition (BC) of the diffusion scheme, and this is why we choose to label the different parameterisations BC1 to BC3. This was stated in the introduction of section 3.3 (L289-294).
The entire volume of the snow grain is thus never constrained, it only "feels the impact" of the outermost layer concentration through solid state diffusion.

To clarify the description of these parameterisations, we changed the text as follows:
- we split section 3.3.1 ("Diffusion scheme and equilibrium boundary condition (BC1)") into 2 sections ("3.3.1 Diffusion scheme"; "3.3.2 Equilibrium boundary condition (BC1)"), and we stressed that the diffusion scheme applies to any of the chosen boundary conditions.
- we slightly rephrased the description of BC2 to emphasise that the developed parameterisation only changes the outermost layer concentration, as compared to BC1:

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[old text] Thus, in order to test these hypotheses, a first simple
diagnostic parameterisation of cocondensation
process was implemented by adding an adjustable term in the boundary
condition definition of the concentration:
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→

[new text] Thus, in order to test these hypotheses, a first simple diagnostic parameterisation of co-condensation process was implemented by adding an adjustable term to prescribe the outermost layer concentration (BC2):

(…)

Solid state diffusion within the layered snow grain then proceeds as previously described (Sect. 3.3.1).

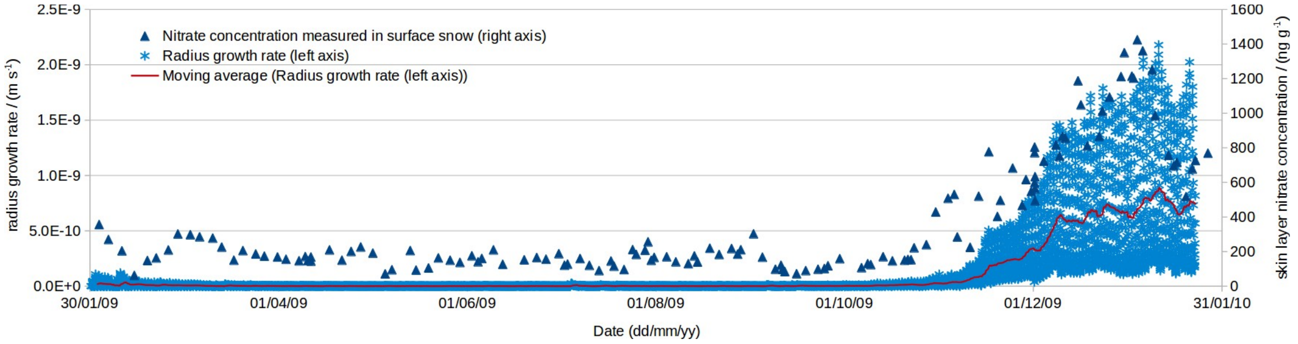
2. The authors should also provide further details of how they formulate the BC3 model and how it behaves in terms of the condensation of water vapor and its impact on the radius growth (Δr) of the snow grain. Without these pieces of information, one cannot really make sense of why this model is so successful 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?;

Following the request of Anonymous Reviewer #2, we added a new figure (reproduced below) showing the time series of the radius growth rate. We decided to include it in the main text since it clearly shows that this time series feature similar yearly pattern that the skin layer nitrate concentration. This is another evidence that the skin layer concentration is driven by temperature gradient metamorphism, and co-condensation. We also added the following paragraphs in the discussion about BC3 results (Sect. 5.3).

(L630-642)

The radius growth rate $\Delta r/\Delta t$ as derived from Eq. (14) is presented in Fig. 5. It spans roughly three orders of magnitude over the year, from about 10^{-12} m s^{-1} in winter to ~8 10^{-10} m s^{-1} in summer. The explanation of this behaviour is twofold. First, the diurnal temperature cycle has a larger amplitude in summer, which enhances the temperature gradient close to the surface. Second, the vapour pressure over ice increases exponentially with temperature. As a consequence, with a given temperature gradient, the gradient of water vapour concentration used in Eq. (12) is larger if temperatures are higher. This also explains the diurnal variation of the grain radius growth. The most striking feature of the radius growth rate is that it peaks during the same period of the year that the peak of nitrate concentration in the skin layer. The yearly pattern of the radius growth rate predicted by our model is also consistent with independent studies focused on snow physical properties (Picard et al, 2012, Libois et al 2015). This comes as another evidence that snow metamorphism, and co-condensation, have a major influence over the snow chemical concentration.



(L645-650)

A diurnal variation of the modelled concentration is observed, as a consequence of the diurnal variation of the radius growth rate. However, the diurnal variation of the concentration is much smoother because solid state diffusion in the whole snow grain softens the large diurnal `variations in the outermost layer of the snow grain. The modelled diurnal variation of the concentration is smaller than 20 %, which is similar to the measurements uncertainty due to spatial heterogeneity.`

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+Δt). 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;

In model configuration 2 (handling solid state diffusion), the outermost layer concentration is first prescribed according to one of the three different boundary conditions (BCs) developed in this study. Then solid state diffusion proceeds as described in the relevant section (Sect. 3.3.1). Whatever the BC, the concentration is thus never "locked into" the outermost layer.
We expect that the improved description of the model configuration 2 (see our answer to Major comment 1) also addresses this comment regarding the clarity of the description for BC3.
We also added a sentence at the end of the section describing BC3 to clarify the role of the radius increase calculation:
(L429-432)
`We emphasise that the radius of the modelled snow grain is kept unchanged along the whole simulation. The calculation of the radius increase due to the condensation of water vapour is only used to compute the concentration (Eq. 15) at the surface of the modelled snow grain (BC).`

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?

We agree with Reviewer #2 that sublimation of water is an important process regarding the mass balance of a snow grain. Despite many efforts to integrate this process in our model, we have not found a satisfactory way to implement it. However, we stress that in the current hypothesis, the snow grain has a constant radius. The mass growth calculated with Eq. (12) in order to estimate the thickness Δr of a virtually condensed layer (Eq. 14) is only used to calculate the theoretical concentration in the condensed layer according to Eq. (15). We have stated this feature more clearly, as presented previously (answer to major comment 2b).
A model able to describe both the condensation and the sublimation, with a varying radius of the snow grain, would obviously be a better way to proceed. To the best of our knowledge, only 2-D or 3-D studies, using either modelling or microtomography, are currently able to provide a satisfactory description of these processes inside the snowpack. This requires knowing the temperature field within both the snow grains and the interstitial air, in order to calculate both condensation and sublimation (see for instance Fig. 5 in Calonne et al 2015, or the studies by Calonne et al 2014 and Ebner et al 2016). Such accurate modelling is even more difficult when considering the skin layer, since the processes governing the water vapour exchange with the lower troposphere are different than those occurring only in the porous snowpack. We are not aware of any study extending the domain to the interface with the atmosphere.

We also agree with Anonymous Reviewer #2 that not taking into account the sublimation might lead to important errors if supersaturated layers buried inside the ice matrix become exposed to the interstitial air and sublimate. This would indeed lead to an important loss regarding the overall snow concentration. However, this does not happen in our model, since the radius is kept unchanged. In other words, the supersaturated condensed layer is virtually condensed at the beginning of each timestep, and virtually removed at the end of each timestep. During the timestep, the surface of the snow grain sees the concentration as calculated with Eq. (15), and exchanges with the core of the snow grain through solid state diffusion.

The comparison of BC1 and BC3 (Fig. 4 and 5) also reveals that winter concentration is mostly unchanged between these two parameterisations. In wintertime, the radius increase calculated with Eq. (14) is so small compared to the typical diffusion length that the argument of the erfc function in Eq. (15) tends towards 0, thus the prescribed concentration tends towards X_{eq}. We believe that the consistent behaviour of the model throughout the year of simulation also demonstrates that there is no undue accumulation when using BC3, which would necessary lead to a long term drift if this was not the case.

[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 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}.

We added the following statement after Eq. 8 (numbered 7 in the revised manuscript):

(L302-309)

The modelled snow surface temperature ranges from 198 K to 253 K (average 222 K) during the studied period. The diffusion coefficient thus ranges from 8.9×10^{-18} m^2 s^{-1} to 6.4×10^{-15} m^2 s^{-1} (average 7.1×10^{-16} m^2 s^{-1}). A characteristic time for diffusion, τ, can be estimated as $\tau = l^2 / D$ where l is a characteristic diffusion length. Considering the assumed spherical geometry of the snow grain, when diffusion reaches $0.21\times R$, 50 % of the volume is affected; and when diffusion reaches $0.37\times R$, 75 % of the volume is affected. Using these values as characteristic diffusion length and the average diffusion coefficient, the characteristic times for diffusion are $\tau_{.50}\simeq5$ days and $\tau_{.75}\simeq16$ days.

We rephrased the end of the sentence in Sect. 5.1 to refer to this characteristic diffusion time:

(L578-580)

The time needed to re-equilibrate the snow grain concentration, roughly 2 weeks, compares well with the characteristic diffusion time (see Sect. 3.3.1).

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.

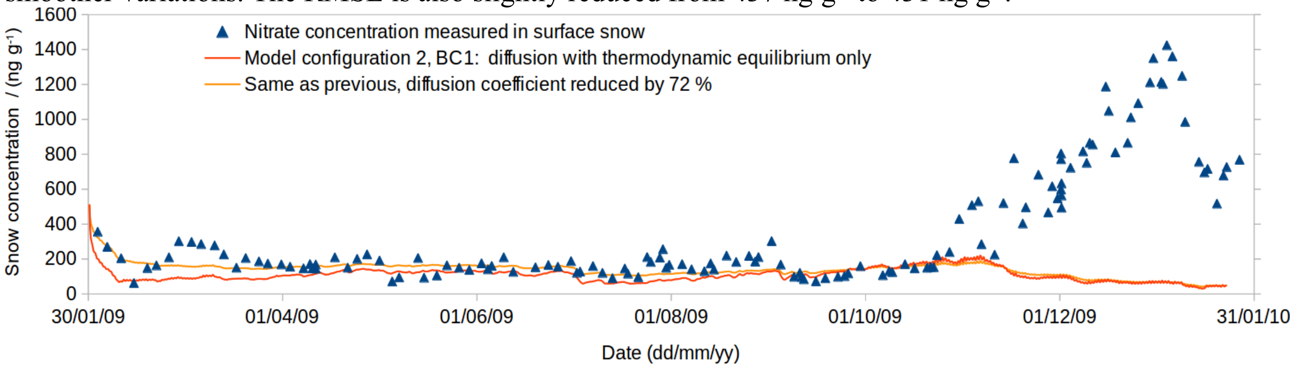
The analysis provided in conclusion of Sect. 4.2 (L551-565 of the original manuscript) is intended to give a rough estimation of the error when ignoring the adsorption process, given the inability of the current parameterisation to fit the measurements. However, we stressed that assuming a constant overestimation factor is a strong hypothesis, and the conclusion of this analysis should be used with caution. We thus only mentioned it in the conclusion in the revised manuscript:

(L725-729)

Assuming that the adsorption parameterisation is flawed by a constant overestimation factor which would leave the yearly pattern unchanged, the maximum featured by the modelled adsorbed concentration in September and October suggests that adsorbed nitrate might account for roughly 30 % of snow nitrate during these 2 months. As for the rest of the year and based on the same hypothesis, adsorbed nitrate should account for less than 10 % of snow nitrate.

3. L645-651: What happens to the BC1 model if you decrease the solid-state diffusivity of HNO3 by 72%?

When reducing the diffusion coefficient by 72 % in BC1 configuration, the modelled concentration features smoother variations. The RMSE is also slightly reduced from 437 ng g^{-1} to 431 ng g^{-1}.



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

The numerical values of the RMSE for the various runs are only shown in Table 1, and not mentioned in the main text. We believe that it can help the reader to appreciate the improvements in the reproduction of the measurements along with the various runs. We also think that it could be useful to compare with forthcoming studies based on similar datasets, and/or using similar modelling framework.

However, if the Anonymous Reviewer #2 and/or the Editor want this information to be removed from Table 1, we agree it is not essential.

[Editorial suggestions]

All editorial suggestions have been modified accordingly.

Cited Papers:

Calonne, N., Flin, F., Geindreau, C., Lesaffre, B. & Rolland du Roscoat, S. Study of a temperature gradient metamorphism of snow from 3-D images: time evolution of microstructures, physical properties and their associated anisotropy. *The Cryosphere* **8,** 2255–2274 (2014).

Calonne, N., Geindreau, C. & Flin, F. Macroscopic modeling of heat and water vapor transfer with phase change in dry snow based on an upscaling method: Influence of air convection. *Journal of Geophysical Research: Earth Surface* **120,** 2476–2497 (2015).

Dominé, F. & Thibert, E. Mechanism of incorporation of trace gases in ice grown from the gas phase. *Geophys. Res. Lett.* **23,** 3627–3630 (1996).

Ebner, P. P., Schneebeli, M. & Steinfeld, A. Metamorphism during temperature gradient with undersaturated advective airflow in a snow sample. *The Cryosphere* **10,** 791–797 (2016).

Gallet, J.-C., Domine, F., Savarino, J., Dumont, M. & Brun, E. The growth of sublimation crystals and surface hoar on the Antarctic plateau. *The Cryosphere* **8,** 1205–1215 (2014).