

We thank the reviewers for their reviews and recommendation to publish. We have considered every point and corrected the paper to include their points. The referees comments are in blue, responds from the authors are in black and revised text are in red.

Referee 1

(1) Atmospheric nitrate (gaseous HNO_3 + particulate nitrate) is assumed to be dominated by gaseous HNO_3 (which is supported by previous studies). In this work, the physical exchange of gaseous HNO_3 in the snow interstitial air (SIA) and the snow grains is described explicitly by different models. However, the mass exchange of HNO_3 between the SIA and air above snow (where the atmospheric nitrate is measured) is missing. Mass exchange between the SIA and air above snow is largely controlled by processes such as turbulent transport and wind pumping. How these processes would affect the bulk nitrate in the skin layer of snow needs to be clearly addressed.

It is assumed that the boundary layer was well mixed such that the surface HNO_3 concentration is same as the observation made at approximately 1 m above the surface. A table of characteristic times of different processes has now been added to the manuscript. The focus of this paper is to describe the interaction between the skin layer of the snowpack (top 4 mm) and the overlying atmosphere. The characteristic time of molecular diffusion for vertical mass transport between the SIA at 4 mm and the air above is only of the order of a second, therefore, is assumed to be in equilibrium.

The characteristic time of various processes are listed in Table. 1

Table 1. Characteristic times associated with gas-phase diffusion, mass transport and uptake of gas into ice grain

Process	Expression	Order of magnitude, s
Interfacial mass transport to a liquid surface ⁱ	$\frac{3\bar{v}\alpha_{aq}}{4R_{\text{eff}}}$	10^{-7}
Gas-phase diffusion to the surface of a spherical droplet ⁱⁱ	$\frac{3D'_a}{R_{\text{eff}}^2}$	10^{-4}
Molecular diffusion between snowpack and the atmosphere ⁱⁱⁱ	$\frac{z^2}{D'_s}$	10^0
Liquid-phase diffusion within a water droplet ^{iv}	$\frac{4R_{\text{eff}}^2}{\pi^2 k_{\text{diff(aq)}}$	10^0
Surface adsorption on ice ^v	$\frac{1}{k_{\text{des}}}$	10^3
Solid-state diffusion within a snow grain ^{vi}	$\frac{4R_{\text{eff}}^2}{\pi^2 k_{\text{diff}}}$	10^6
Photolysis at a snowpack surface ^{vii}	$\frac{1}{J}$	10^7

ⁱ Sander (1999), with an effective radius, $R_{\text{eff}} = 70 \mu\text{m}$, and accommodation coefficient on liquid water, $\alpha_{aq} = 7.5 \times 10^{-5} \exp(2100/\text{Temp})$ (Ammann et al., 2013). ⁱⁱ Sander (1999), with an effective molecular diffusivity, $D'_s = D_a/\tau_g$, where the tortuosity, $\tau_g = 2$ and molecular diffusivity in free air at 296 K, $D_a(296\text{K}) = 87 \text{ Torr cm}^2 \text{ s}^{-1}$ (Tang et al., 2014). ⁱⁱⁱ Waddington et al. (1996), with a snow layer thickness, $z = 4 \text{ mm}$. ^{iv} Finlayson-Pitts and Jr. (2000), with a diffusion coefficient in liquid water, $k_{\text{diff(aq)}} = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Yuan-Hui and Gregory, 1974). ^v Crowley et al. (2010), with an equilibrium constant for Langmuir adsorption, $K_{\text{eq}} = 2 \times 10^{-16} \text{ m}^3 \text{ molecule}^{-1}$ and adsorption coefficient, $k_{\text{ads}} = 1.7 \times 10^{-19} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^{vi} Finlayson-Pitts and Jr. (2000), with a diffusion coefficient in ice, $k_{\text{diff}} = 6 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ (Thibert et al., 1998). ^{vii} Finlayson-Pitts and Jr. (2000), with a surface NO_3^- photolysis rate, $J = 10^7 \text{ s}^{-1}$ (Thomas et al., 2011).

Such information and assumptions are now included in in Sect. 4.1 (Page 12, line 359-363)

“The atmospheric boundary layer is assumed to be well mixed so that the atmospheric nitrate at the snowpack surface would be the same at 1 m. The characteristic transport time of HNO_3 from the snowpack surface to the skin layer (4 mm) is on the order of 10^0 s, which is much shorter compared to the temporal resolution of the model of 10 min (Table 1), and therefore, the HNO_3 concentration of the skin layer was assumed to be the same as above the snow.”

and Sect. 4.2 (Page 12, line 390-391)

“Again, the atmospheric boundary layer is assumed to be well mixed that the nitric acid concentration at the snowpack surface would be the same as at 7-8 m”

(2) Model 2 incorporates the micro-liquid pocket. This topic is of great interest since the brine formed by impurities may not cover the entire grain surface due to limited wettability at cold temperatures. However, instantaneous air/micro-liquid pocket equilibrium is assumed. This seems to be oversimplified. For highly soluble species such as HNO_3 in liquid water (effective Henry's law constant $> 10^{14} \text{ M atm}^{-1}$, Fig 1), interfacial transport or even gas diffusion (in this case, gas diffusion in the SIA) may well become the rate limiting steps. The timescale of the SIA/micropocket equilibrium needs to be examined before assuming equilibrium.

A table of characteristic times (Table 1) of different processes has been added to the manuscript. The characteristic times a) of interfacial mass transport across a liquid surface of a droplet with a $70 \mu\text{m}$ radius, b) gas-phase diffusion toward a droplet with $70 \mu\text{m}$ radius, and c) vertical mass transport to SIA at 4 mm depth are all significantly smaller than the characteristic time of surface adsorption, solid-state diffusion.

The following lines been change in Sect. 3.2, Line 314-320

“An instantaneous equilibrium is assumed because 1) the volume of the liquid solution is small (10^{-7} – 10^{-6} % of the total volume of the ice grain, discussed below) 2) HNO_3 is highly soluble in water; 3) the characteristic time of the interfacial mass transport across a liquid surface of a droplet with $70 \mu\text{m}$ is only $\sim 10^{-7}$ s (Table 1); and 4) the diffusion rate is faster in liquid (At 0°C , NO_3^- diffusion of NO_3^- is $9.78 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in liquid, Yuan-Hui and Gregory, 1974) than in ice (At 0°C NO_3^- diffusion rate is $3.8 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ in ice). The characteristic time of liquid-phase diffusion within a $70\mu\text{m}$ diameter water droplet is $\sim 10^0$ s (Table 1).”

(3) From the model point of view, Model 2 does not really specify or depend on the location of liquid water, i.e. whether the liquid water is covering the whole/part of the grain surface as a thin layer, or is located in grooves at grain boundaries and triple junctions. It appears mathematically that, in Eq(4) + Eq(17), only the liquid water content matters while the location of liquid water does not.

The reviewer is correct, in fact we don't know the location from the current data set; the liquid water is treated as micro-liquid pockets that can be found at an unspecified location in grooves at grain boundaries or triple junctions as stated in the Introduction (Line 101-102). The assumption implies the grain surface area being covered by liquid water is negligible and therefore mostly ice.

For clarification the following text has been added, in Sect. 3.2 (Page 10, line 302-303)

“Liquid water is assumed to be located in grooves at grain boundaries or triple junctions between grains and in the form of micropockets. This assumption implies the grain surface area being covered by liquid water is negligible.”

(4) The authors claim that the physical exchange models are based on “first principles” (what exactly are first principles btw) and hence without requiring any tuning parameters. This seems not true: some parameters involved in the models are still somewhat adjustable and/or lack direct observational support, such as max number of adsorption sites, threshold temperature T_0 , microscopic H₂O density gradient, eutectic temperature, etc.

‘First principles’ are based on physical laws and relationship. The “tuning parameters” are referred to scaling factors that use to fit the model to observations. However, some of the physical parameter used in the current work have ill defined values which merited a study of the model sensitivity against some of the parameterisations and inputs were analyzed. The results of model sensitivity are now listed in Table 4.

Table 4. Sensitivity Test for Model 1 and 2 based on the coefficient of variation of RMSE, $C_v(\text{RMSE})$, the metric used as goodness of fit. Note that column one is not fitted to the observation and the values are only varying to show the sensitivity of the models against inputs and parameterisation.

Parameter	Model 1						Model 2						
	Dome C			Halley			Dome C			Halley			
	Whole year	Winter-Spring	Summer	Whole year	Winter	Spring-Summer	Whole year	Winter-Spring	Summer	Whole year	Winter	Spring-Summer	
Control	1.34	0.73	1.11	89.28	27.78	87.15	0.84	0.73	0.67	0.84	1.08	0.65	
[HNO ₃]	-20%	0.98	0.60	0.81	71.19	22.12	69.5	0.80	0.62	0.64	0.77	1.10	0.56
	+20%	1.73	0.90	1.45	107.36	33.43	104.80	0.95	0.88	0.76	0.92	1.07	0.75
SSA	-10%	1.06	0.63	0.88	79.35	24.79	77.46	0.83	0.67	0.67	0.84	1.10	0.65
	+10%	1.63	0.84	1.36	99.22	30.75	96.86	0.84	0.78	0.67	0.83	1.07	0.65
α	-10%	1.34	0.73	1.11	79.35	24.78	77.46	0.83	0.73	0.67	0.83	1.08	0.65
	+10%	1.34	0.73	1.11	79.35	24.80	77.46	0.83	0.73	0.67	0.83	1.08	0.65
N_{max}	-10%	1.32	0.67	1.10	89.27	27.77	87.15	0.83	0.69	0.67	0.84	1.09	0.65
	+10%	1.36	0.80	1.13	89.29	27.78	87.15	0.84	0.77	0.67	0.84	1.07	0.65
T_o (Model 1) or	-2 K	3.53	0.91	3.00	90.45	42.54	87.31	0.95	0.92	0.75	0.85	1.12	0.65
T_e (Model 2)	+2 K	0.50	0.64	0.36	67.49	25.33	65.62	0.73	0.65	0.58	0.86	1.07	0.65
	+4 K	0.61	0.65	0.47	50.76	23.86	49.00	0.72	0.65	0.57	0.88	1.06	0.67
pH	-0.4	1.34	0.73	1.11	89.28	27.78	87.15	-	-	-	-	-	-
	+0.4	1.34	0.73	1.11	89.28	27.78	87.15	-	-	-	-	-	-
	+0.8	1.34	0.73	1.11	89.28	27.78	87.15	-	-	-	-	-	-
[NO ₃ ⁻]	-20%	1.85	0.98	1.54	111.87	34.84	109.2	0.99	0.96	0.79	1.09	1.08	0.93
	+20%	1.04	0.61	0.86	74.22	23.07	72.45	0.80	0.64	0.64	0.74	1.10	0.51

(5) Comparison between models and measurements needs to be discussed in the context of their respective uncertainty ranges. What is the measurement uncertainty of skin layer nitrate concentration? What is the model uncertainty propagated from the inputs and parameters?

Results of the sensitivity tests on atmospheric nitrate concentration, accommodation coefficient, maximum number of adsorption sites, threshold temperature or eutectic temperature and skin layer snow nitrate concentration are listed in Table 4 (See the comment above).

(6) The quality of English could use some polish.

In addition, the authors claim that the photochemistry of snow nitrate can be ignored due to slow photolysis in this region. Well, “what goes up must come down” and vice versa. What processes are then responsible for the loss of snow nitrate? And what is driving the seasonal variations of snow nitrate in this region? Snow nitrate can’t cannot always accumulate. This is perhaps not the main focus of this work, but the fact that only snow nitrate sources are included in the model may be quite confusing.

See the comment above

The observed atmospheric concentration HNO_3 is used as a model constrain, which implicitly included change in atmospheric HNO_3 concentration due to air-snow exchange.

In this particular region of the snowpack the loss of nitrate by photolysis is slow compared to the physical uptake of nitrate by adsorption and co-condensation.

The following text has been added to Sect. 3, Line 187-193

“The loss or gain in the atmospheric HNO_3 due to the mass exchange between air and snow are included implicitly by constraining the models with the observed HNO_3 concentration. The aim of this paper is to focus on the exchange mechanisms between air-snow, and by limiting the working layer to the skin layer, the following assumptions can be made, 1) homogenous physical properties across the skin layer, such as snow density and SSA. 2) the HNO_3 concentration in SIA is in equilibrium with the overlying atmosphere due to a short characteristic time (Table 1).”

Specific comments:

Page 3, Line 61: the characteristic times of surface adsorption and solid-state diffusion for HNO_3 ... please provide more details (either literature or point to later sections).

Details are now listed in Table 1 (See above comment)

Page 3, Line 83: define skin layer. What is the thickness of this skin layer in the model and why this value is chosen? Or is it simply the layer in which the bulk ion concentrations are measured?

Information regarding to the skin layer been added to Page 2, Line 52-54

“Here in this paper, the skin layer is defined as the top 4 mm of the snowpack, which is the depth of which the surface snow nitrate samples were collected at Dome C (Sect. 4.1).”

Since the model is limited to the skin layer, it seems that there is no exchange between the skin layer and the deeper snow. However, previous studies(e.g. Traversi et al 2014) indicated that temperature gradients and wind pumping exist in the snowpack, therefore nitrate could be mobilized by physical processes reaching much deeper than the “skin layer” in this model (a few mm?).

The aim of this paper is to demonstrate the interaction between skin layer nitrate and atmospheric HNO_3 with a simple physical model without a scaling factor. Atmospheric nitrate can reach deeper than the skin layer via wind pumping and temperature gradient, however, to reproduce nitrate concentration in deeper snow requires a complicated multi-layer model. Developing a multi-layer model is an extremely large undertaking and is being performed at the time of writing. The conclusion highlighted the referee's point and further work will address this.

Within the Conclusion, Line 704-716

“Despite the simplified parameterisation of processes in Model 2, such as the impurities content in snow, liquid pockets located in different locations were treated as one and had the same chemical properties as bulk liquid, it is a promising step towards parameterising the interactions between air and snow. The models presented here are describing the exchange between air and the skin layer that the uptake processes are much quicker than the photochemical loss, and therefore, can be modelled by physical only processes. Atmospheric nitrate can reach deeper than the skin layer via wind pumping and temperature gradient, however, the nitric acid concentration in SIA is expected to be small compared to the overlying atmosphere due to the high uptake of nitrate near the surface of the snowpack. A lower HNO_3 concentration in SIA implies a smaller uptake in deeper snow, and hence the photochemical loss cannot be assumed to be negligible in deeper snow. Therefore, a more complex multi-layer model including both physical and chemical processes is required to reproduce the nitrate concentration in deeper snow and being implement in regional and global atmospheric chemistry model..”

Page 5, Line 141: the solid-state diffusivity is introduced here, and hence characteristic time can be calculated. Please compare to other processes, e.g. surface accommodation and gas-phase diffusion

The characteristic times of other processes are now listed in Table 1 (See the comment above)

Page 6, Line 178: what is the size of snow grain?

The sentence is now written as (Line 194-195)

“For simplicity, the snow grain is assumed to be a radially symmetrical sphere with a radius, R_{eff} , which is estimated from the specific surface area (SSA) with the follow equation:

(... Eq. 6) ”

Eq. 14 is now Eq. 6 and moved to Sect. 3.

An extra sub-plot of the effective grain radius has been added to the Appendix, Fig A3

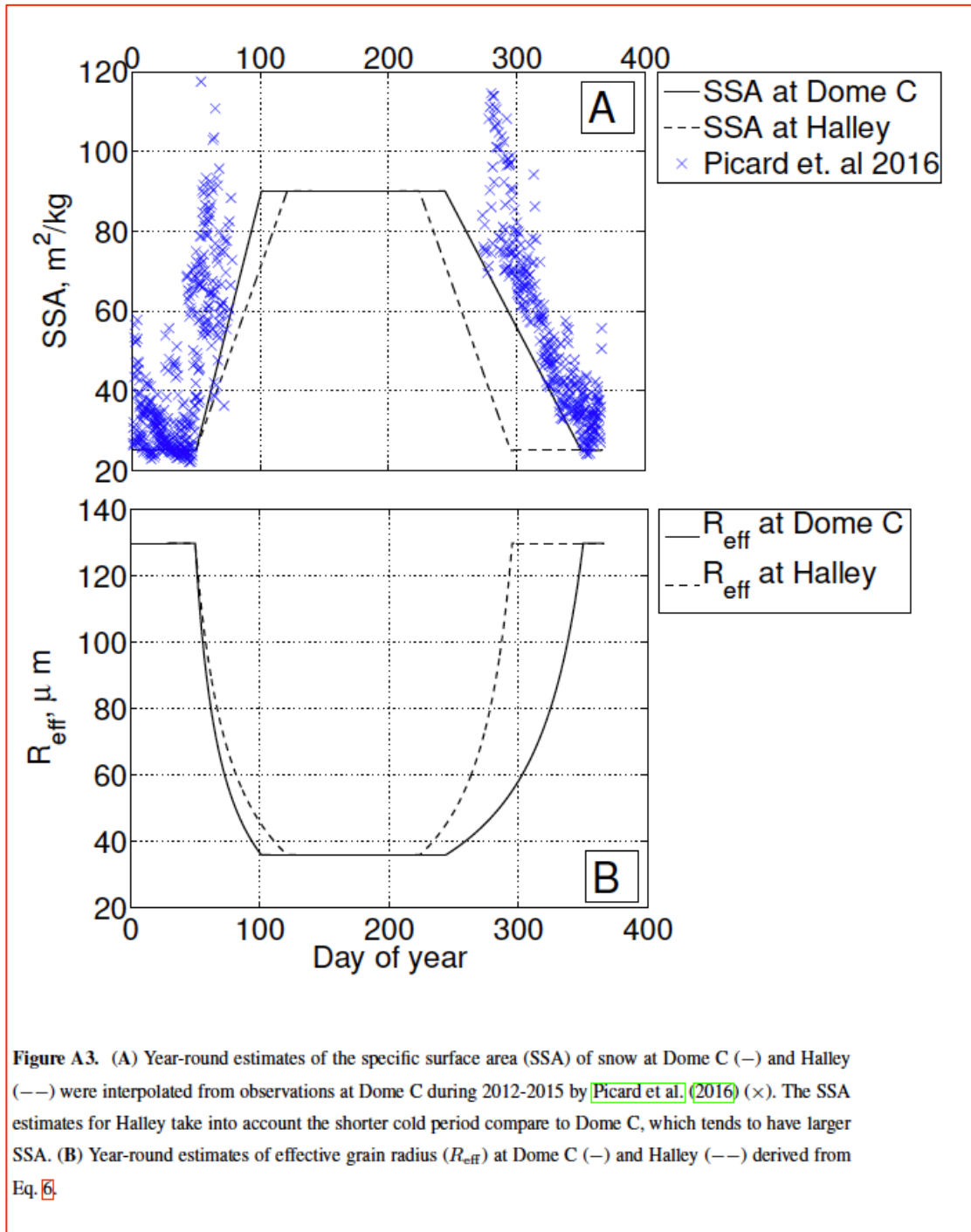


Figure A3. (A) Year-round estimates of the specific surface area (SSA) of snow at Dome C (—) and Halley (---) were interpolated from observations at Dome C during 2012-2015 by Picard et al. (2016) (x). The SSA estimates for Halley take into account the shorter cold period compare to Dome C, which tends to have larger SSA. (B) Year-round estimates of effective grain radius (R_{eff}) at Dome C (—) and Halley (---) derived from Eq. 6.

Page 7, Eq 7: both adsorption and co-condensation contribute to surface HNO_3 . Is co-condensed HNO_3 available for desorption? Judging from Eq 6 it seems the answer is yes, yet in Eq 7 it seems co-condensed HNO_3 is not included. Also, will the cocondensed HNO_3 molecules undergo solid diffusion?

Yes, the grain surface HNO_3 concentration has contributions from the sum of adsorption, desorption and co-condensation or co-sublimation. Condensation or sublimation depends on the sign of the water vapour gradient and hence the sign of the rate of volume change (Eq. 10)

The grain surface concentration of HNO_3 is then treated as the boundary concentration for solid grain diffusion driven by concentration gradient of the grain surface and the centre of grain.

For clarification the following text has been added, in Page 7, Line 215-217

“where $[\text{HNO}_3(\text{ads})]$ is the concentration contributed from the sum of surface adsorption and desorption (Eq. 8), and $[\text{HNO}_3(\text{cc})]$ is the concentration contributed from the co-condensation or co-sublimation (Eq. 9).”

and Page 8, Line 238-240

“The temperature gradient and relative humidity gradient between the surface of the snowpack and the skin layer create a gradient in water vapour pressure, which drives condensation or sublimation of snow, depending on the sign of the gradient.”

Page 8, Line 248: what is the thickness of this DI covering the entire grain surface?

The DI is treated as the boundary of the snow grain, of which the concentration of DI is used as the boundary condition for the diffusion into the snow grain. Therefore, no thickness is assigned to the DI.

For clarification, the following lines (Page 9, line 275-277) are now included in the manuscript.

“Note that in this model the DI is treated as the boundary between the air and bulk ice. The concentration of the DI is used as the outermost boundary condition for solid-state diffusion within the grain, therefore, the DI has no thickness.”

Also, Eq 13 describes $d[\text{HNO}_3(\text{DI})]/dt$, and there should be another equation for $d[\text{HNO}_3(\text{g})]/dt$ accordingly. Please provide this. Finally, I may be wrong but shouldn't mass transfer (Eq 13 and $d[\text{HNO}_3(\text{g})]/dt$) depend on liquid water content of some sort?

Both models presented here are constrained by the observed gas phase HNO_3 concentration with time, therefore, the loss of $\text{HNO}_3(\text{g})$ due to mass transfer is included implicitly.

Page 8, Eq 8: this equation describes co-condensation. How about H_2O sublimation? Does HNO_3 undergo co-sublimation (or whatever the term should be) as well?

Both co-condensation or co-sublimation occur depending on the sign in Eq. 10.

Page 10, Line 294: again, for highly soluble species in liquid, interfacial transport or gas diffusion may be limiting (Schwartz, 1986). Please calculate the equilibrium timescale and discuss in the context of other mass transfer processes.

Details are now listed in Table 1.

Page 13, Line 399: define winter (and other seasons too). The Northerners would appreciate this.

Has been added to Page 11, Line 336-340. It reads

“... in summer (mid November till end of January) and down to -80°C in the winter (April to mid September). The diurnal temperature variation is ~ 10 K in summer, spring (mid September till mid November) and autumn (February to March).”

Page 14, Line 432: "However, Model 1... overestimated concentration by a factor of 1.5-5 in December". Which model 1? With 238 K or 242 K?

Now (Line 448-449) written as “However, Model 1 (with $T_0 = 238$ K) did not capture the peak in early February and overestimated concentration by a factor of 1.5-5 in December.”

Page 15, Line 476: "the combination of larger temperatures and a larger diurnal temperature range" this sentence is confusing.

The sentence (Line 491-192) has been corrected and now reads

“... the combination of warmer temperatures and a larger range of diurnal temperature causes ...”

Page 16, Line 493: "it is possible that the snow NO_3^- concentration measured from Halley might be 'diluted' from deeper snow layer..." then can you extend your model to cover deeper layers, or simply increase the skin layer thickness? Also, as shown in Fig 11, Model 2 underestimated nitrate for the majority of the time (Line 458-459). If measured snow NO_3^- was indeed diluted, would this mean the model underestimates even more?

The models presented here would lose their physical meaning by increasing the thickness, of which is assumed to be homogenous as well as in equilibrium with the atmosphere above. A multi-layer model is required to cover deeper layers.

Moreover, Model 2 underestimates the concentration of nitrate at Halley mainly in the winter period where new snowfall events were accounted for the large surface snow nitrate.

Page 16, Line 497: what do you mean by "fixed by sea salt, ammonium or terrestrial dust"?

The sentence (Line 511-512) was rewritten as “ Thirdly, atmospheric nitrate can be in a more stable forms of NO_3^- , i.e. associated with Na^+ , Ca^{2+} or Mg^{2+} (Beine et al., 2003)”

Page 16, Line 502: "the increase in sea salt concentration decreases the ratio of concentration of gaseous HNO_3 to total atmospheric nitrate". Please provide evidence.

A reference, Dasgupta et al., 2007, has been added.

Page 16, Line 503: "A possible explanation for the overestimation of NO_3^- concentration in both Model 1 and 2 in November at Dome C" this is not a complete sentence.

The sentence has been removed.

Page 17, Line 546: "In the summer, other processes are replaced..." this sentence is ill-formed. What are you trying to say?

The sentence (Line 562-564) is rewritten as “In the summer, the dominant process in Model 1 is solvation in DI (See Sect. 6.3) while in Model 2 the dominant process is partitioning in the micropockets (See Sect. 6.4), hence the contribution from co-condensation to the skin nitrate concentration is insignificant.”

Page 19, Line 605: there is no purple on Fig 7.

Corrected. The sensitivity analysis is now moved to Sect. 6.5. The results from Model 1 at Halley are now in Fig. 8A. The purple line (on the right axis) is the results when $T_0 = 242$ K and the text has been adjusted to demonstrate it.

Page 19, Line 628: Again this is only true if gas diffusion and interfacial transport are not limiting. Also, Model 1 output is quite sensitive to T_0 . How sensitive is Model 2 to the eutectic temperature?

A set of sensitivity tests have been run against inputs such as nitric acid concentration, SSA, accommodation coefficient (α), maximum number of adsorption site (N_{max}), and either the threshold temperature in Model 1 (T_0) or the eutectic temperature in Model 2 (T_e). The coefficient of variation of RMSE ($Cv(RMSE)$) is used as a metric of the goodness of fit and is listed in Table 4.

Fig 1: Please include units for the effective Henry's law constant. Also I feel this belongs in the Supplementary Information. The temperature and pH dependencies of effective Henry's law constant, although are important, do not deserve the spot of the very first figure of this particular paper.

The plot of the temperature and pH dependencies of effective Henry's law constant (Figure 1) is now moved to the Appendix

Fig 4, Fig 6-11: dates on the bottom axis are difficult to read, i.e. it is hard to identify "early Feb" or "early May", ... Please set date tick labels to the first day of each month. If not enough space, rotate 90 degrees.

Figures are now has the first day of each month on the bottom axis and day of year (DOY) on the top of the graph to make it easier to read.

Fig 5: figure legend very unclear. What exactly are the scatter points? And what are "Head 1 1213", "Head 2, 1213", ...?

The figure (now Fig. 4) had been re-plotted and legend been clarified.

Fig 7 & Fig 8: I think these two figures can be combined. Easier to tell the difference between Model 1 and Model 2. Same for Fig 10 & Fig 11.

Fig 7 and Fig 8 are now combined as Fig 6, and, Fig 10 and Fig 11 are now combined as Fig 8

Table A1: temperature dependent Henry's law constant: standard temperature in 258K?

The standard temperature for the calculation of temperature-dependent Henry's law is now corrected to 298K