Response to the referees

We appreciate the two anonymous reviewers and Prof. Savarino (the handling editor) for their time in reviewing our manuscript. Below, we give a point-by-point response to the comments and suggestions of the three reviewers, in the order of (1) comments from Referees, (2) author's response, and (3) author's changes in manuscript (referee comments in black; author's response and changes in manuscript in blue).

Reviewer #1

We thank the reviewer very much for the careful read of our manuscript. The constructive comments and suggestions have greatly improved the quality of this manuscript. Below, we give a point-by-point response to the comments and suggestions of the reviewer, in the order of (1) comments from Referees, (2) author's response, and (3) author's changes in manuscript (referee comments in black; author's response and changes in manuscript in blue).

(1) comments from Referees

General comments

This study reports new measurements of nitrate in a large number of Antarctic surface snow and pit samples collected over several years on a transect between the coast and Dome A. Based on a linear model it is concluded that on the coast nitrate flux to the snowpack is dominated by wet deposition illustrated by a positive correlation with accumulation rates, dry deposition contributing up to 44% and atmospheric nitrate being quite homogeneous. Further inland on the Antarctic Plateau a positive correlation between concentration and acculumlation rate is found suggestive of post-depositional loss. Contrary to a previous coastal study no association between nitrate and sodium in snow was found, but rather with nss-so4 suggesting a role of small sized aerosol in nitrate scavenging and deposition.

This study contributes a large number of new observations from remote areas, which involved careful sampling on locations along the traverse, sample handling and analysis, and they clearly merit publication. The finding that no3 correlates with nss-so4 but not with na is very interesting and new. The main weakness is the discussion on no3 deposition processes, which needs significant improvement before I can recommend publication. In particular, a more thorough comparison with other studies and a critical discussion of model choice and interpretation are required.

(1) author's response

We greatly appreciate the reviewer for the general positive comments of our work. We have revised the discussion on NO_3^- deposition process. In addition, we have expanded the discussion on the potential association between NO_3^- and co-existing ions in the surface snow, and the possible connections.

In the model section, we now present a detailed description of the model choice and results (please also see the comments from Referee #2).

(1) author's changes in manuscript

Following the reviewer's comments, we substantially revised the discussion section. Please see the revised manuscript, sections **4.1.1 NO_3^- in coastal snowpack, 4.1.2 NO_3^- in inland snowpack and 4.2 Effects of coexisting ions on NO_3^-**

(2) comments from Referees

SPECIFIC COMMENTS - The authors apply a linear model to interpret their data. Contrary to their description Eq. 4-6 are esentially the same model, i.e. inserting Eq.4 into Eq.6 yields Eq.5. I strongly suggest to simplify (use maybe the notation of Alley et al, 1995), explain model assumptions, parameters and limitations. Note this model is the simplest plausible model to relate chemical flux and concentration in snow to atmospheric concentrations introduced more than 20yr ago (Legrand, M., 1987; Alley et al., 1995) and is a gross over-simplification of the complex nature of air-snow exchange of nitrate. It's probably ok near the coast, but fails inland due to post-depositional redistribution and loss of nitrate. Negative dry deposition rates can be interpreted as losses and should also be compared to other studies in the regions, e.g. Pasteris et al. (2014) and Weller et al. (2004, 2007). I suspect that precise values for dry deposition rates and fresh snow values depend which and how many locations are included in the regression analysis (and also to a minor extent if you use regression parameters from eq4 or eq5). The discussion on inland snowpack (Section 4.1.2) should be expanded accordingly; e.g. take a closer look at losses shown in Fig 4, how do they compare to loss rate from the regressions, how do they depend on environmental factors?

(2) author's response

We thank the reviewer for the very helpful comments. We agree with the reviewer that the Eqs. 4-6 represent essentially the same model and can be consolidated. In addition, the parameters and limitations of the model should be clarified. We also agree that the model in this work was introduced 20 years ago (Legrand, 1987; Alley et al., 1995) and is a gross over-simplification of the complicated snow-air exchange of NO_3^- in Antarctica, especially in the inland Antarctica (Erbland et al., 2015; Shi et al., 2015; Bock et al., 2016; Zatko et al., 2016). Although a simple model, it provides a simple approach to compare the processes occurring on the coast versus those inland. In addition, this model can provides useful parameter values in modeling NO_3^- deposition/preservation at large scale, considering that observations remain sparse across Antarctica (e.g., Zatko, et al., 2016).

Yes, the negative slope of the linear regression between NO_3^- concentration and inverse snow accumulation rate, i.e., the negative dry deposition rates, can be interpreted as losses of NO_3^-. The emission rates of NO_3^- in this investigation can be compared with other reports, e.g., the observations of DML and the Kohnen Station (Weller et al., 2004; Weller and Wagenbach, 2007; Pasteris et al., 2014).

Following the reviewer's suggestion, we re-examined the linear regression between NO_3^- concentration and inverse snow accumulation rate. It is found that the regression is significantly influenced by two sites, SP10 and Core2 (~800 km from the coast), featured by high snow accumulation rate (> 100 kg m^{-2} a^{-1}; Table 1 and Fig. 1). Consequently, the dry deposition rates (i.e., slope of the linear regression) were changed when the two sites were excluded for the linear fit. In this case, the dry deposition of NO_3^- can be re-calculated for the inland snowpack.

Also, following the reviewer's comment, we calculated the emission flux with the aid of NO_3^- profiles at the inland sites, i.e., the difference between the most recent year mean (Fig. 4) and NO_3^- concentration in the snow layer accumulated during the year before the most recent year can represent the loss rate of NO_3^-. Then, a comparison was made between the observations and the linear model prediction.

(2) author's changes in manuscript

The linear models were simplified and the parameters and the limitations were included, following the notation of Alley et al. (1995).

The negative slope of the linear regression between NO_3^- concentration and inverse snow accumulation rate was explained. In addition, the values in this study were compared with previous reports in the regions.

The linear fit was carried out to test that the slope values depend on which and how many locations are included in the regression analysis. Two sites with snow accumulation rate larger than 100 kg m^{-2} a^{-1} were excluded for the linear fit. Accordingly, the discussion on inland snowpack (Section 4.1.2) was expanded. In addition, the emission rates of NO_3^- were calculated from the snowpits NO_3^- profiles, and a comparison was made between the observations and linear model prediction.

For the changes, please see the revision-tracked version of manuscript, sections **4.1.1 NO_3^- in coastal snowpack, and 4.1.2 NO_3^- in inland snowpack**

(3) comments from Referees

- the authors make surprisingly little mentioning of new isotopic tools in their brief literature review and discussion (including their own study Shi et al;, 2014), which in my view achieved significant reduction of the uncertainties related to post-depositional no3 processes and the origin of no3 maxima in Antarctic snow. I'd recommend to highlight better the progress in no3 air-snow exchange research and integrate it into the discussion. You could set out from the beginning that you don't expect your chosen model to work on the Plateau because of strong losses.

(3) author's response

We thank the reviewer for pointing this out. We agree with the reviewer that the isotope ratios of NO_3^- provide further constraints for NO_x sources and post-depositional processing of NO_3^- in the snow. A brief overview of the contributions from isotope ratios of NO_3^- in Antarctic snow seems to be necessary in the introduction section, although no isotopic data were presented in this study.

In the discussion of NO_3^- losses in the inland snowpack, the previous works on isotopic compositions of NO_3^- in snow from Dome A plateau (Shi et al., 2015) was included. In this case, the uncertainties related to post-depositional processing of NO_3^- would be reduced. The recent works on the air-snow changes of NO_3^- were also included in the discussion (Erbland et al., 2015; Zatko et al., 2016).

In the section of the model introduction, it is clarified that the model could not well depict the complex recycling of NO_3^- in inland Antarctic snow.

(3) author's changes in manuscript

Discussion of advanced understanding based upon NO_3^- isotopes was included in the introduction section.

In the discussion section, 4.1.2 NO_3^- in inland snowpack, previous works on the Dome A plateau were referenced. Also, the previous modeling works on the air-snow transfer of NO_3^- were integrated into the discussion.

For the changes, please see the revision-tracked version of manuscript, sections **4.1.1** and **4.1.2**

(4) comments from Referees

- the authors mention their unpublished measurements of atmosperic no3 on the coast (l337-38) and on the traverse (426-428). Is there any particular reason why they are not part of a manuscript on air-snow exchange of no3? I'd like to see these included in the paper, as they could add significantly to the discussion of deposition and association to nss-so4 and sea salt (the novel part of this paper).

(4) author's response

We agree with the reviewer that the atmospheric NO_3^- could be helpful to the understanding of snow-air exchange of NO_3^-. In fact, the atmospheric NO_3^- data is a part of another manuscript in preparation, which is focused on the production pathways of atmospheric NO_3^- (i.e., the oxidation channels of NO_x) on the traverse from coast to Antarctic ice sheet summit and in the marine boundary layer. Atmospheric NO_3^- (both particulate and gaseous NO_3^-) were collected on

Whatman G653 glass-fiber filters using a high volume air sampler (HVAS), the concentration and the isotope ratios of NO_3^- ($\delta^{18}O$ and $\Delta^{17}O$) were analyzed. It is noted that the sampling time of the atmospheric NO_3^- is different from that of the snow sample collection in this study. Thus, the atmospheric concentration data was taken as a general reference to calculate the dry deposition velocity of NO_3^- (K_1 in the main manuscript).

(4) author's changes in manuscript

Following the comments of the reviewer, atmospheric concentrations of NO_3^- and SO_4^{2-} are presented in the supporting information of the paper, and the information on atmospheric NO_3^- sampling and analysis, concentration table was included.

Atmospheric NO_3^- sampling and analysis

For investigating NO_3^- levels in the atmosphere, atmospheric NO_3^-, i.e., both particulate NO_3^- and gaseous HNO_3, was collected along the traverse (coastal Zhongshan Station to Dome A) following similar protocols for previous work in East Antarctica (Savarino et al., 2007; Frey et al., 2009; Erbland et al., 2013). The atmospheric samples were collected on Whatman G653 glass-fiber filters (8 × 10 in; prebaked at 550 °C for ~24 hr) using a high volume air sampler (HVAS), with a flow rate of ~1.0 m^3 min^{-1} for 12-15 hr. In total, 34 atmospheric samples were collected on the traverse.

In the laboratory, each filter was cut into pieces using pre-cleaned scissors that were rinsed between samples, placed in ~100 ml of Milli-Q water, ultrasonicated for 40 min and leached for 24 hr under shaking. The sample solutions were then filtered through 0.22 μm ANPEL PTFE filters for NO_3^- concentration analysis.

Ion concentrations (NO_3^- and SO_4^{2-}) in extracted solutions were determined using a Dionex ion chromatograph (ICS 3000) following Shi et al. (2012). Final atmospheric NO_3^- concentrations were normalized to standard temperature and pressure (273 K; 1013 hPa), listed in Table S1.

Table S1 Atmospheric concentrations of NO_3^- and SO_4^{2-} on the traverse from coastal Zhongshan Station to Dome A in East Antarctica.

Sampling location		Atmospheric NO_3^-/ng m^{-3}	Atmospheric SO_4^{2-}/ng m^{-3}
Longitude/° E	Latitude/° S		
76.49	69.79	29	183
76.92	70.64	24	154
77.62	71.5	22	204
77.69	72.37	14	163
77.17	73.15	24	165
76.97	73.86	30	117
76.98	74.9	43	163
76.82	75.87	16	176

77.02	76.86	41	289
77.71	77.15	85	268
76.99	78.36	139	162
77.00	79.01	35	130
77.26	79.82	99	177
77.12	80.42	183	496
77.12	80.42	67	371
77.12	80.42	88	341
77.12	80.42	100	310
77.12	80.42	124	415
77.12	80.42	124	317
77.12	80.42	81	240
77.12	80.42	87	178
77.17	79.63	82	228
77.03	78.77	21	246
77.19	77.83	38	261
77.02	76.74	33	257
77.03	76.42	40	331
76.83	75.87	40	249
76.96	75.03	44	256
77.00	74.09	32	216
76.97	73.86	21	202
77.38	72.84	17	225
77.97	71.93	8	223
77.19	70.97	24	209
76.52	69.97	14	188

For the changes, please see the supporting information of the manuscript.

(5) comments from Referees

TECHNICAL CORRECTIONS l35 ... dry deposition velocity and scavenging ratio for NO3- was relatively constant near the coast ... is this not a model assumption? which then allows you to state that atmospheric nitrate is homogeneous on the coast, please clarify how you interpret the linear model.

(5) author's response

Yes, the linear model assumes spatially homogeneous values for the dry deposition velocity. A linear fit in the manuscript (Fig. 5a) supports the assumption of the spatial homogeneity.

(5) author's changes in manuscript

The assumptions of the interpretation of the linear fit was clarified in the revised manuscript. Then the interpretation of the linear regression parameters (fresh snow concentration and the dry deposition velocity of NO_3^-) was clarified based upon these assumptions, please see section **4.1.1** in the revision-tracked version of the manuscript.

(6) comments from Referees

l36 ... association ... throughout the text you use association but mean probably correlation. Please change and state R and p value

(6) author's response

Thanks for pointing this out. In most cases, the "association" means "correlation".

(6) author's changes in manuscript

Following the reviewer's suggestion, the "association" was replaced with "correlation". The values of R^2 and p were also included in the revised manuscript.

(7) comments from Referees

l55 tropospheric and stratospheric sources

(7) author's response

We agree with the reviewer.

(7) author's changes in manuscript

The "atmospheric" was replaced with "tropospheric" in the revised manuscript.

(8) comments from Referees

l75 isotopes show stratospheric origin of nitrate peak in late winter/ early spring (Savarino, 2007; Frey 2009)

(8) author's response

Agree with the reviewer.

(8) author's changes in manuscript

Changed following the reviewer’s suggestion in the revised manuscript.

(9) comments from Referees

l80-84 it seems to me that the SPE hypothesis has recently been basically refuted; please update your summary & citations including e.g. Wolff et al. (2012 & 2016), Duderstadt et al. (2014)

(9) author's response

We agree with the reviewer that the solar proton event (SPE) is generally believed to have negligible effect on the variability of NO_3^- in polar ice core at present. The citations have been updated (Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2016; Wolff et al., 2016).

(9) author's changes in manuscript

Following the reviewer’s comment, the summary has been re-stated, and the citations have been updated. Please see the revision-tracked version of manuscript.

(10) comments from Referees

l86 ... the relationship ... varies temporally and spatially

(10) author's response

Agree with the reviewer.

(10) author's changes in manuscript

Changed following the reviewer’s suggestion. Please see the revision-tracked version of manuscript.

(11) comments from Referees

l87-89 more correctly: ... Isotope studies suggest that under cold conditions photolytic loss dominates, whereas HNO3 volatilization becomes important at warmer temperatures > -20 ◦C (Frey 2009, Erbland 2013, Berhanu 2015)

(11) author's response

Thanks for the suggestion.

(11) author's changes in manuscript

Restated following the reviewer's suggestion. Please see the revision-tracked version of manuscript.

(12) comments from Referees

l93 and field measurements on the East Antarctic Plateau at Dome C suggest e-folding depths of 10 to 20 cm (France et al., 2011)

(12) author's response

Yes, the field measurements on the East Antarctic Plateau at Dome C suggest z_e of 10 to 20 cm (France et al., 2011), and the depth is dependent upon the concentration of impurities contained in the snow (Zatko et al., 2013).

(12) author's changes in manuscript

Following the reviewer's comments, the statement was rephrased. Please see the revision-tracked version of manuscript.

(13) comments from Referees

l94-95 Clarify that photolysis dominates loss. This is also in support of your own assumption that no3 is archived below the photic zone of ~1m depth, where temperature still varies on diurnal to annual time scales. It implies that physical losses are assumed to be not important throughout the study region.

(13) author's response

We appreciate the reviewer for this point. In the inland regions with low snow accumulation rate, especially on the East Antarctic plateaus, photolysis is thought to dominate the post-depositional losses of NO_3^- (Frey et al., 2009; Shi et al., 2015). This point is crucial to our assumption that NO_3^- is archived below 100 cm.

(13) author's changes in manuscript

This point was clarified following the reviewer’s suggestion. Please see the revision-tracked version of manuscript.

(14) comments from Referees

l105 please add also Bertler et al. 2005, Pasteris et al., 2014

(14) author's response

Agree.

(14) author's changes in manuscript

The two references were included in the revised version (Bertler et al., 2005; Pasteris et al., 2014).

(15) comments from Referees

l122 does SP20 correspond to the location of the station at Dome A?

(15) author's response

Yes, SP20 corresponds to the location of the Chinese inland station, Kunlun Station at Dome A.

(15) author's changes in manuscript

The sampling snowpits were clarified in section **2.2 Sample collection**. In particular, the SP20 located at the Kunlun Station at Dome A was noted. Please see the revision-tracked version of manuscript.

(16) comments from Referees

l129 add lat/lon and elevation of station

(16) author's response

Agree. The Kunlun Station, $80^{o}25'01.7''$S and $77^{o}6'58.0''$E, with altitude of 4087 m a.s.l.

(16) author's changes in manuscript

Added in the revised manuscript.

(17) comments from Referees

l134 took OR lasted 4 summer seasons

(17) author's response

Agree. Thanks.

(17) author's changes in manuscript

Corrected in the revised manuscript.

(18) comments from Referees

l194 add a note that so4 fractionation may introduce a bias in nss-so4 (Wagenbach et al., 1998)

(18) author's response

Agree. The SO_4^{2-} fractionation (the precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$)) may introduce a bias in $nssSO_4^{2-}$, especially during the winter half year (Wagenbach et al., 1998a).

(18) author's changes in manuscript

The above sentence was added in the revised manuscript.

(19) comments from Referees

l250-52 Please be precise and expand: were the pits dated? do you see 1, 2 or more annual no3 peaks?

(19) author's response

Agree with the reviewer, the section should be expanded. Among the coastal snowpits, water isotope ratios ($\delta^{18}O$ of H_2O) of samples at SP02 were also determined, thus allowing for investigating NO_3^- seasonality (Fig. S2 in supporting information). In general, the $\delta^{18}O(H_2O)$ peaks correspond to high NO_3^- concentrations (i.e., NO_3^- peaks present in summer), indicating a seasonal variability. This seasonal signature is consistent with previous observations of NO_3^- in snow and atmosphere at the coastal Antarctic sites (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007).

(19) author's changes in manuscript

Following the reviewer's suggestion, the coastal SP02 snowpit was taken as an example to examine the seasonal signature of NO_3^-.

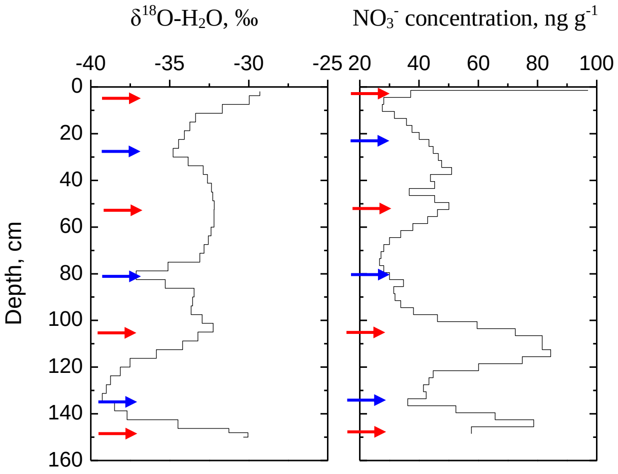

Figure S3 Profiles of $\delta^{18}O$ of H_2O (left panel) and NO_3^- concentration (right panel) in the coastal snowpit SP02. Red and blue arrows represent the middle of the identified warm and cold seasons, respectively. Red solid arrows and blue dashed arrows represent the middle of the identified warm and cold seasons, respectively. One seasonal cycle represents one $\delta^{18}O(H_2O)$ local maxima peak to the next.

For the changes, please see the revision-tracked version of manuscript (section **3.2 Snowpit NO_3^- concentrations**) and the supporting information Figure S3.

(20) comments from Referees

l256 careful with language: not maybe, but yes previous studies inland (on the Antarctic Plateau) have shown that the decrease is due to significant loss/redistribution of NO3-

(20) author's response

Agree with the reviewer. The significant losses are resulted from the post-depositional processing of NO_3^- (e.g., at Dome C; Frey et al., 2009; Erbland et al., 2013)

(20) author's changes in manuscript

Corrected in the revised manuscript.

(21) comments from Referees

l279-80 due to photolysis

(21) author's response

Agree. Thanks.

(21) author's changes in manuscript

Corrected.

(22) comments from Referees

l290-94 note you assume that photolysis is main loss process which is sensible, but explain better in intro (see comment on l94-95)

(22) author's response

We agree with the reviewer. Thanks.

(22) author's changes in manuscript

Following the reviewer's suggestion, this point was explained in the introduction.

(23) comments from Referees

l302 do you mean deposition velocity or flux? explain model assumptions (see above)

(23) author's response

We mean the dry deposition flux of NO_3^-. The assumptions of the interpretation of the linear model are spatial homogeneity of fresh snow NO_3^- levels and dry deposition flux in the regions, which were explained in the revised manuscript.

(23) author's changes in manuscript

Following the reviewer's suggestion, this section was re-organized. Please see the revision-tracked version of manuscript (section **4.1.1 NO_3^- in coastal snowpack**).

(24) comments from Referees

l306, 329-30 consolidate your model (see above)

(24) author's response

Agree with the reviewer.

(24) author's changes in manuscript

This section was re-organized. Please see the revised manuscript (section **4.1.1 NO_3^- in coastal snowpack**).

(25) comments from Referees

l311 use consistently r or r2 throughout the paper, and include p value

(25) author's response

Agree.

(25) author's changes in manuscript

Corrected throughout the manuscript, following the reviewer's suggestion.

(26) comments from Referees

l337-38 are these annual mean and std of atmospheric nitrate? Coastal observations (Neumayer, Halley, DDU) show a distinct annual cycle. how would that affect your estimate of deposition velocity?

(26) author's response

The data is the average atmospheric NO_3^- concentration (19.4 ng m^{-3}) on the coast during the austral summer time. According to previous coastal observations (e.g., Dumont d'Urville, Neumayer and Halley), atmospheric NO_3^- concentration exhibits a seasonal variation with maximum usually observed in late spring-summer (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007). In those studies, the atmospheric NO_3^- concentration mainly varied from 10 to 70 ng m^{-3}. For the calculation of the dry deposition velocity (K_1) in this study, a lower atmospheric NO_3^- concentration will yield a higher value of K_1. This point is clarified in the revised manuscript.

(26) author's changes in manuscript

A notation was added in the revised version, as follows,

It is noted that the true K_1 value could be higher than the calculation here due to the high atmospheric NO_3^- concentrations in summertime on the coast (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007).

For the changes, please see the revision-tracked version of manuscript (section **4.1.1 NO_3^- in coastal snowpack**).

(27) comments from Referees

l340 "... compares well to ..." I disagree, this is a large uncertainty, a range of 0.5 to 0.8 cm/s can make a big difference when modeling no3 in surface snow (see for example Erbland et al. 2013, Fig.7)

(27) author's response

We thank the reviewer for pointing this out. Yes, a difference of 0.3 cm s^{-1} will result in a large difference when modeling NO_3^- in the surface snowpack (Erbland et al., 2013).

(27) author's changes in manuscript

This sentence was re-written. Please see the revised manuscript.

(28) comments from Referees

l352 is negatively correlated with

(28) author's response

Agree.

(28) author's changes in manuscript

The “tied to” is replaced with “correlated with”.

(29) comments from Referees

l354 based on what exactly? the R value? please explain

(29) author's response

Yes, based on R^2 values of the regression analysis (Figs. 5b and c). A strong positive correlation between NO_3^- flux and snow accumulation rate (R^2=0.97), while a negative relationship between flux and the archived concentration of NO_3^- was found. In this case, it is proposed that NO_3^- flux is more accumulation dependent compared to the concentration.

(29) author's changes in manuscript

Clarified in the revised manuscript.

(30) comments from Referees

l365 correlation

(30) author's response

Agree.

(30) author's changes in manuscript

Replaced with “correlation”.

(31) comments from Referees

l370 the correlation ... is reatively weak and of opposite sign

(31) author's response

Agree.

(31) author's changes in manuscript

Replaced with “correlation”.

(32) comments from Referees

l375 why act surprised? we know based on previous work that this is of course due to losses, the model application is limited inland

(32) author's response

Agree.

(32) author's changes in manuscript

Following the reviewer’s suggestion, this part is re-phrased.

(33) comments from Referees

l404-05 but uncertainties have been reduced over the last decade (see comment above)

(33) author's response

Agree with the reviewer.

(33) author's changes in manuscript

This sentence was rephrased.

(34) comments from Referees

l406 and snow optical properties (e-folding depth)

(34) author's response

Agree.

(34) author's changes in manuscript

Changed.

(35) comments from Referees

l426-428 I’d be very interested to see the atmospheric data; why are they not included in this manuscript?

(35) author's response

Agree with the reviewer. See response above.

(35) author's changes in manuscript

The atmospheric data was included in the supporting information.

(36) comments from Referees

l463-464 I don’t understand, please expand (mirabilite is Na2SO4-10H2O)

(36) author's response

The fractionation of Na^+ can occur due to mirabilite precipitation in sea-ice formation at <-8 °C (Marion et al., 1999), possibly leading to the positive $nssCl^-$. Even if all of SO_4^{2-} in sea water is removed via mirabilite precipitation, only 12% of sea salt Na^+ is lost (Rankin et al., 2002). Considering the smallest sea ice extent in summertime in East Antarctica (Holland et al., 2014), the very high Cl^-/Na^+ ratio (mean = 2.1 versus 1.17 of sea water, in μeq L^{-1}) in surface snow is unlikely from sea-salt fractionation associated with mirabilite precipitation in sea-ice formation.

(36) author's changes in manuscript

Following the reviewer’s suggestion, this point was expanded. Please see section **4.2 Effects of coexisting ions on NO_3^-** in the revised manuscript.

(37) comments from Referees

FIGURES

Fig3 possibly add accumulation rate into ea figure to understand better at which threshold no3 spikes disappear

(37) author's response

Agree.

(37) author's changes in manuscript

Snow accumulation was added in each panel in Fig. 3, as below.

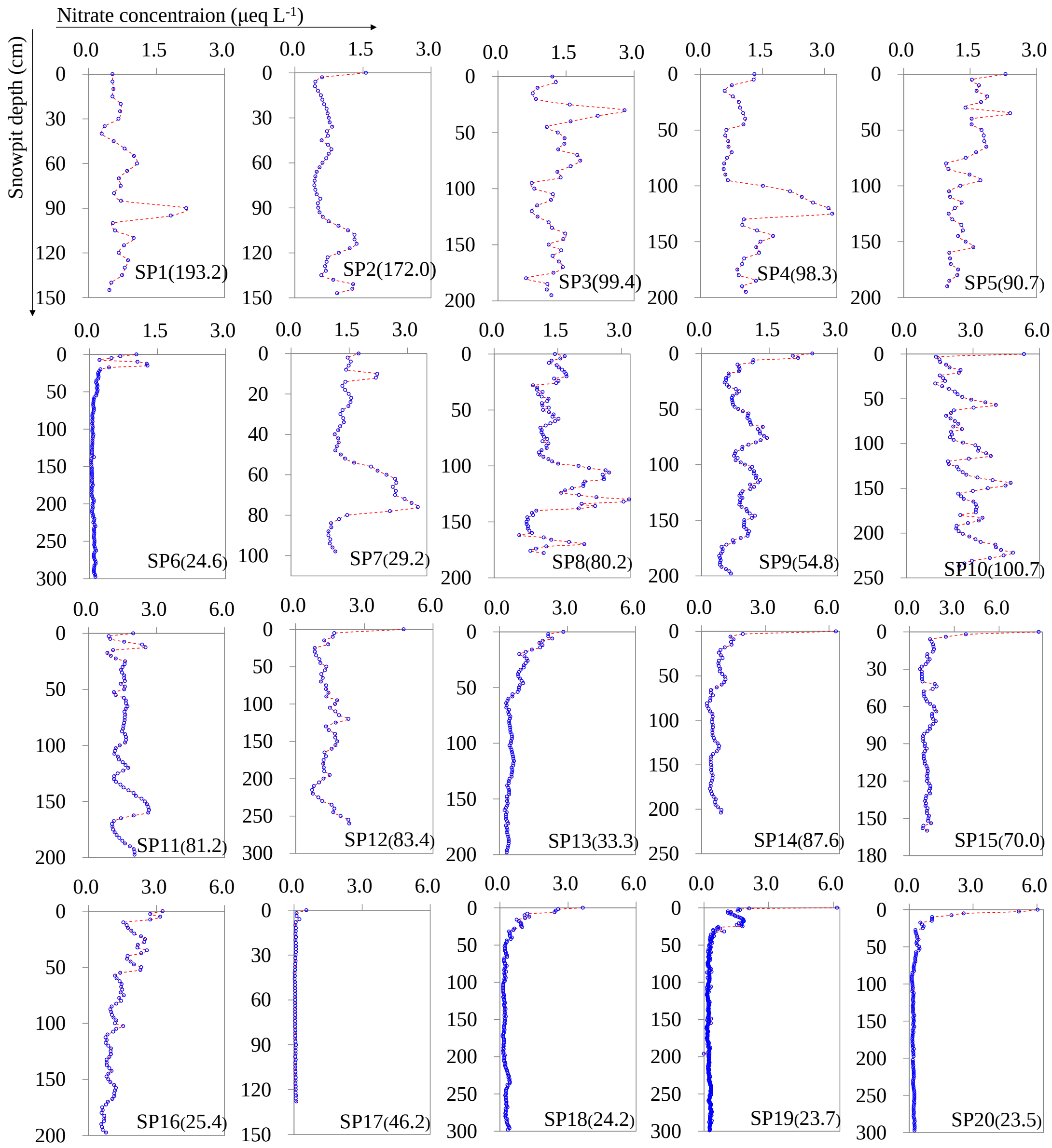

Figure 3. The full profiles of NO_3^- concentrations for snowpits collected on the traverse from the coast to Dome A, East Antarctica (SP1 is closest the coast; SP20 the furthest inland; see Figure 2). The details on sampling of the snowpits refer to Table 1. The numbers in parentheses in each panel denote the annual snow accumulation rates (kg m^{-2} a^{-1}). Note that the scales of x-axes for the snowpits SP1 – SP9 and SP10 – SP 20 are different.

(38) comments from Referees

Fig4 possibly add site ID on the x-Axis to follow better the discussion

(38) author's response

Agree with the reviewer.

(38) author's changes in manuscript

Site ID was added on the x-axis. Please see the revised manuscript Fig. 4, as below.

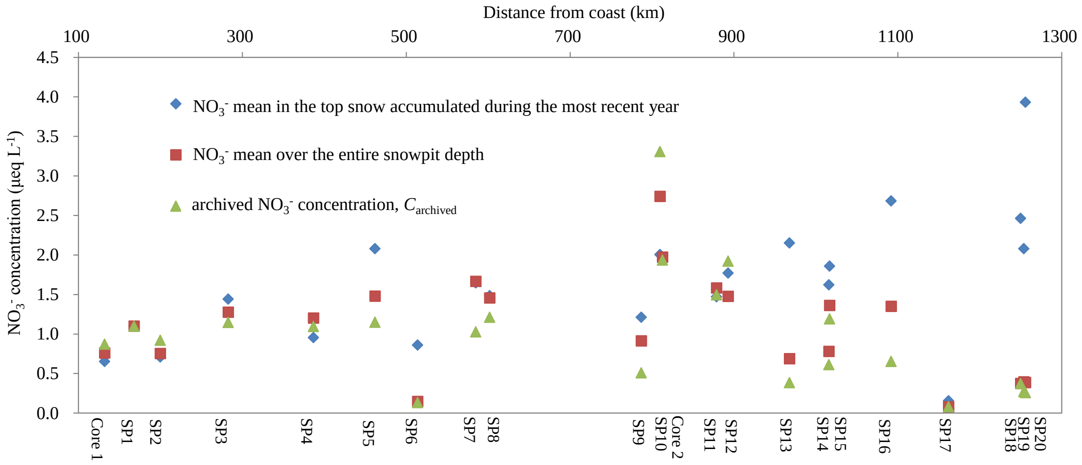

Figure 4. Mean concentrations of NO_3^- for the entire snowpit depth (in square), the uppermost layer covering one-year snow accumulation (in diamond) and the bottom layer covering a full annual cycle of deposition (archived NO_3^- concentration, $C_{archived}$, in triangle).

(39) comments from Referees

Fig5 improve figure readability (size, label font)

(39) author's response

Agree.

(39) author's changes in manuscript

Changed.

End of responses to Referee #1.

Reviewer #2

We are very grateful to reviewer#2 for his/her detailed comments and very useful suggestions. The manuscript has been substantially modified and reformatted based on these comments/suggestions. Below, we give a point-by-point response to the comments and suggestions of the reviewer, in the order of (1) comments from Referees, (2) author's response, and (3) author's changes in manuscript.
Reviewer comments are in black, and the responses are in blue.

(1) comments from Referees

This manuscript reports on nitrate in samples collected in the frame of an intensive program of snow sampling made along a traverse from the coast to Dome A (East Antarctica). The samplings include 120 surface snow samples (upper 3 cm), 20 snowpits (down to 1.5-3.0 m depth), and a few crystal ice samples. From the coast to the inner plateau, an increasing trend of nitrate present in surface snow is observed whereas the content of deeper snow pit layers are lower at inland sites than at the coast. Extremely high concentrations are found in crystal ice (reaching almost 1 ppmw). Data are discussed with respect to occurrence of post-depositional remobilization of nitrate, wet and dry deposition, and possible role of other ions (sodium and sulfate).

Overall evaluation:

First, the authors have to be congratulated for having successfully conducted such a very large snow-sampling program, likely sometimes done under harsh weather conditions. The data certainly contain valuable information in view to better understand incorporation, remobilisation and partial preservation of nitrate atmospheric signal in cold archives. This topic is clearly relevant for the Cryosphere journal.

(1) author's response

We thank the reviewer very much for reviewing our manuscript and the positive comments. As the reviewer mentioned, the snowpit sampling is usually made under the very harsh weather conditions, e.g., extremely low temperature and heavy blowing snow. We appreciate the Chinese inland Antarctic expedition team members for providing help during sampling.

(1) author's changes in manuscript

We will revise the manuscript following the reviewer’s comments and suggestions, see below.

(2) comments from Referees

As it stands the manuscript however requires major revisions and a reevaluation prior to publication. Indeed, at several places in the manuscript data discussions are incorrect, and generally do not enough consider atmospheric information available for the Antarctic atmosphere. Given the scarcity of data presented in this work, I strongly encourage the authors to reformulate the manuscript and in the following I try to identify what would be addressed in an in depth reformulated version of this manuscript.

(2) author's response

We thank the reviewer for pointing out the shortcomings of the manuscript. We agree that the atmospheric information was not considered enough. We will improve the work following the reviewer’s suggestions/comments.

(2) author's changes in manuscript

The manuscript was modified according to the comments from the reviewer, see below and section 4 in the revised manuscript.

(3) comments from Referees

Introduction.

This paragraph has to be reworded on several aspects:

Lines 54-86: You missed here several important papers that have discussed in details the origins of nitrate in Antarctica. For instance, Legrand and Kirchner (1990) extensively discussed (1) the absence of link between solar activity and nitrate in snow, (2) what are the main possible sources of nitrate for Antarctica (stratospheric reservoir and long-range transport in the upper troposphere of lightning production, etc). Also model simulations from Legrand et al. (1989) discussed the source of nitrate for Antarctic regions.

Legrand, M., and Kirchner, S.: Origins and variations of nitrate in South Polar precipitation, J. Geophys. Res., 95, 3493-3507 1990.

Legrand, M. R., F. Stordal, I. S. A. Isaksen, and B. Rognerud (1989), A model study of the stratospheric budget of odd nitrogen, including effects of solar cycle variations, Tellus B, 41(B4), 413–426, doi:10.1111/j.1600- 0889.1989.tb00318.x.

(3) author's response

We agree with the reviewer and are sorry for missing the two important references concerning Antarctic NO_3^- budget. In terms of the Antarctic NO_3^- budget, lightning and NO_x produced in the lower stratosphere were thought to play a major role (Legrand et al., 1989; Legrand and Kirchner, 1990). Also, it is suggested that there is not necessarily a connection between solar variability and NO_3^- concentrations (Legrand and Kirchner, 1990).

(3) author's changes in manuscript

The two references were included. The major contribution by lightning and by NO_x produced in the lower stratosphere to Antarctic NO_3^- budget was clarified. In addition, the investigation made by Legrand and Kirchner (1990) suggesting no correlation between solar activity (11-year solar cycle, low solar activity time periods, and solar proton events) and the NO_3^- content of south polar snow was added to the manuscript. Please see the revision-tracked version of manuscript.

(4) comments from Referees

Lines 80-83: You missed here to report two recent papers from Wolf et al. that strongly question the assumption that solar flares and SPE are recorded in ice. Also model simulations do not support at all such an assumption (Legrand et al., 1989; Duderstadt et al., 2014).

Wolff, E. W., M. Bigler, M. A. J. Curran, J. E. Dibb, M. M. Frey, M. Legrand, and J. R. McConnell (2012), The Carrington Event not observed in most ice core nitrate records, Geophys. Res. Lett., 39, L08503, doi:10.1029/2012GL051603.

Wolff, E. W., M. Bigler, M. A. J. Curran, J. E. Dibb, M. M. Frey, M. Legrand, and J. R. McConnell (2016), Comment on “Low time resolution analysis of polar ice cores cannot detect impulsive nitrate events” by D.F. Smart et al., J. Geophys. Res. Space Physics, 121, doi:10.1002/2015JA021570.

Legrand, M. R., F. Stordal, I. S. A. Isaksen, and B. Rognerud (1989), A model study of the stratospheric budget of odd nitrogen, including effects of solar cycle variations, Tellus B, 41(B4), 413–426, doi:10.1111/j.1600- 0889.1989.tb00318.x.

Duderstadt, K. A., J. E. Dibb, C. H. Jackman, C. E. Randall, S. C. Solomon, M. J. Mills, N. A. Schwadron, and H. E. Spence (2014), Nitrate deposition to surface snow at Summit, Greenland, following the 9 November 2000 solar proton event, J. Geophys. Res. Atmos., 119, 6938–6957, doi:10.1002/2013JD021389.

(4) author's response

Thanks for pointing this out. The observations and modeling works by (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014;

Duderstadt et al., 2016; Wolff et al., 2016) were included. Indeed, most of observations and recent modeling studies have established that there is not a clear connection between solar variability and NO_3^- concentrations (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014; Duderstadt et al., 2016; Wolff et al., 2016).

(4) author's changes in manuscript

The works made by Wolff et al., Legrand et al., and Duderstadt et al., are included in the revised manuscript. Please see the revised version of the manuscript.

(5) comments from Referees

A few sentences on the physical form of nitrate (partitioning between the gas phase, and particulate phase) would be welcome (see my next comment) to better introduce the data discussion with respect to deposition, remobilization, etc.

(5) author's response

A good point, thanks. A summary of the observations on partitioning of NO_3^- between the gaseous phase and particulate phase will be helpful to a better understanding of the deposition and re-emission of NO_3^-. At Dome C on the East Antarctic plateau, observations on the atmospheric NO_3^- have been carried out during the years from 2006 to 2016 (Traversi et al., 2014; Legrand et al., 2016; Legrand et al., 2017b; Traversi et al., 2017), which are important works towards a quantitative understanding of NO_3^- partitioning in the atmosphere.

(5) author's changes in manuscript

Following the reviewer's suggestion, a paragraph summarizing the partitioning between the gas phase, and particulate phase on NO_3^- was included in the revised manuscript, as follows,

In the atmosphere in Antarctica, particularly during spring and summer, NO_3^- is found to be mainly in the form of gas phase HNO_3, with NO_3^- concentration several times higher in gas phase than in the particulate phase (Piel et al., 2006; Legrand et al., 2017b; Traversi et al., 2017). During the post-depositional processes, the uptake of gaseous HNO_3 is thought to be important in NO_3^- concentrations in surface snow layers (Udisti et al., 2004; Traversi et al., 2014; Traversi et al., 2017). Due to the high concentration in summer, HNO_3 appears to play an important role in acidifying sea-salt particles, possibly accounting for the presence of NO_3^- in the particulate phase in summer (Jourdain and Legrand, 2002; Legrand et al., 2017b; Traversi et al., 2017). It is noted that the significant increase of NO_3^- during the cold periods (e.g., Last Glacial Maximum) could be associated with its attachment to dust aerosol, instead of the gas phase HNO_3 (Legrand et al., 1999; Wolff et al., 2010).

Please see the revised version of the manuscript, section 1 Introduction.

(6) comments from Referees

Data discussion (Section 3): Please reconsider your data in the light of recent papers dealing with nitric acid gas phase and nitrate in the aerosol phase and their changes over the year in Antarctica.

For instance, check the following recent paper and references therein:

Legrand, M., Preunkert, S., Wolff, E., Weller, R., Jourdain, B., and Wagenbach, D. : Year-round records of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) - Part 1 : Fractionation of sea-salt particles, Atmos. Chem. Phys., 17, 14039-14054, https://doi.org/10.5194/acp-17-14039- 2017, 2017.

(6) author's response

We thank the reviewer for the very constructive suggestion. The partitioning of NO_3^- between gas-phase and particulate phase will be of importance to NO_3^- levels in the snowpack, especially the topmost crystal ice layers. The observed high levels of gas phase HNO_3 in central Antarctica during summer support the importance of the re-emission from snow through the photolysis of NO_3^- in affecting atmospheric NO_x/NO_3^- budget (e.g., Erbland et al., 2013). The atmospheric gaseous HNO_3 likely co-condenses with water vapor (Bock et al., 2016), especially on the extensively developed crystal ice layers on Antarctic plateaus (discussed in the main text), leading to an enrichment of NO_3^- in surface snow. In addition, a large concentration of HNO_3 would enhance its reaction with sea-salt, leading to elevated particulate NO_3^- concentrations (Legrand et al., 2017b). The significant correlation between NO_3^- and H^+ (R^2 =0.65, p<0.01) and lack of correlation between NO_3^- and sea salt Na^+ in inland Antarctic surface snow seems to suggest the importance of atmospheric gas phase HNO_3 in affecting surface snow NO_3^- concentrations, in particular NO_3^- levels in the crystal ice samples (correlation between NO_3^- and H^+, R^2 =0.99, p<0.01).

(6) author's changes in manuscript

The physical form of NO_3^- affecting NO_3^- concentrations in snow was discussed and included in the revised manuscript, as follows,

In inland Antarctica, the dominant NO_3^- species in the atmosphere is gaseous HNO_3 during summertime, while particulate NO_3^- is more important in winter (Legrand et al., 2017b; Traversi et al., 2017). The high levels of gas phase HNO_3 in summer support the importance of the re-emission from snow through the photolysis of NO_3^- in affecting the atmospheric NO_x/NO_3^- budget (Erbland et al., 2013). On the one hand, the gaseous HNO_3 can be efficiently co-condensed with water vapour onto the extensively developed crystal ice layers on Antarctic plateaus (discussed above), leading to an enrichment of NO_3^- in surface snow (Bock et al., 2016). On the other hand, a large concentration of HNO_3 would enhance its reaction with sea-salt, leading to elevated particulate NO_3^- concentrations (Legrand et al., 2017b). The significant correlation between NO_3^- and H^+ in inland Antarctic surface snow (R^2 =0.65, p<0.01) seems to support the importance of atmospheric gas phase HNO_3 in affecting surface snow NO_3^- concentrations, in particular NO_3^- levels in the crystal ice samples (Fig. 1).

Please see the revised version of the manuscript, section 4.1.2 NO_3^- in inland snowpack.

(7) comments from Referees

Two overall comments:

The idea that nitrate is trapped on coarse sea-salt particles is incorrect (or not enough precise): Atmospheric data show that nitrate stays on the intermediate size particles (1-2 micron range) and not on the coarse ones like sea-salt (even at the coast): Jourdain and Legrand (2002); Teilina et al. (2000), Rankin et al. (2003), and Legrand et al. (2017).

Teinila, K., Kerminen, V.-M., and Hillamo, R. (2000), A study of sizesegregated aerosol chemistry in the Antarctic atmosphere, J. G. R.? 105, 3893- 3904.

Rankin, A. M. and Wolff, E. W.: A year-long record of size- segregated aerosol composition at Halley, Antarctica, J. Geophys. Res., 108, 4775, https://doi.org/10.1029/2003JD003993, 2003.

Jourdain, B. and Legrand, M.: Year-round records of bulk and size-segregated aerosol composition and HCl and HNO3 levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer, J. Geophys. Res., 107, 4645, https://doi.org/10.1029/2002JD002471, 2002.

(7) author's response

Atmospheric NO_3^- in Antarctica is mainly in the gas phase (HNO_3), while the particulate phase represents less, particularly in inland Antarctica. As for the particulate phase (also called "aerosol" in previous observations), most of the NO_3^- is found on the intermediate size particles (1 – 2 μm) (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017b). As the reviewer mentioned, the NO_3^- is not trapped on the coarse sea-salt particles. But the presence of sea salt aerosol can influence atmospheric NO_3^- in two ways. Firstly, higher atmospheric sea salt aerosol concentrations are expected to promote the conversion of gaseous HNO_3 to particulate phase, allowing for the efficient deposition of NO_3^- via the aerosol mechanisms. On the other hand, the saline ice in the atmosphere favors the direct uptake of gaseous HNO_3 on ice surface. Thus, sea salt aerosols play an important role in the scavenging of gaseous HNO_3 from the atmosphere (Hara et al., 2005), and elevated NO_3^- concentrations are usually accompanied by Na^+ spikes in snowpack (e.g., at Halley station, a coastal location; Wolff et al., 2008).

(7) author's changes in manuscript

Following the reviewer's comments, the relationship between NO_3^- and sea salt in the snowpack was re-discussed, as follows,

In comparison with $nssSO_4^{2-}$ aerosols, the sea-salt aerosols (Na^+) are coarser and can be removed preferentially from the atmosphere due to a larger dry deposition velocity. High atmospheric sea salt aerosol concentrations are expected to promote the conversion of gaseous HNO_3 to particulate phase, considering that most of the NO_3^- in the atmosphere is in the gas phase (HNO_3). In this case, particulate NO_3^- can be efficiently lost via aerosol mechanisms. In addition, the saline ice also favors the direct uptake of gaseous HNO_3 to the ice surface. Changes in partitioning between gas phase (HNO_3) and particulate phase will affect NO_3^- levels due to the different wet and dry deposition rates of the two species (Aw and Kleeman, 2003). Thus, sea salt aerosols play an important role in the scavenging of gaseous HNO_3 from the atmosphere (Hara et al., 2005), and elevated NO_3^- concentrations are usually accompanied by Na^+ spikes in snowpack (e.g., at Halley station, a coastal site; Wolff et al., 2008). Here, no significant correlation was found between Na^+ and NO_3^- in coastal snow (Fig. 7b). The concentration profiles of NO_3^- and Na^+ in coastal surface snow are shown in Fig. 8, and NO_3^- roughly corresponds to Na^+ in some areas, e.g., 50-150 km and 300-450 km distance inland, although in general they are not very coherent. It is noted that amongst the 4 snow samples with $Na^+ > 1.5$ μeq L^{-1} (open circles in Fig. 8), only one sample co-exhibits a NO_3^- spike. This is different from observations at Halley station, where Na^+ peaks usually led to elevated NO_3^- levels in surface snow in summer (Wolff et al., 2008). Of the 4 largest Na^+ spikes, one is a fresh snowfall sample (dashed ellipse in Fig. 8), and this sample shows the highest Na^+ concentration (2.8 μeq L^{-1}) and low NO_3^- (0.75 μeq L^{-1}). It is noted that NO_3^- concentration in this fresh snowfall is close to the model predictions (0.7 ± 0.07 μeq L^{-1}; section 4.1.1), validating that the simple linear deposition model (i.e., the Eq. 6) can well depict the deposition and preservation of NO_3^- in coastal snowpack. At inland sites, no correlation was found between NO_3^- and Na^+ (Fig. 7e), likely explained by the alteration of NO_3^- concentration by post-depositional processing (discussed above).

Please see the revised version of the manuscript, section 4.2 Effects of coexisting ions on NO_3^-.

(8) comments from Referees

The relationship between NssSO4 and nitrate: The interpretation of the correlation between nitrate and sulphuric acid referring to Brown et al. (2006) is misleading. Indeed this study discussed of the reaction of N2O5 on acidic sulphate promoting the formation of HNO3 in a polluted atmosphere at night. Whatever the Antarctic site, the acidic sulphate is maximum in summer whereas, if present, N2O5 can only exit in the Antarctic atmosphere in winter (due to photolysis of the NO3 radical in summer, N2O5 does not exist in summer). So the correlation seen in snow cannot be explained like that.

(8) author's response

We agree with the referee that the conversion of N_2O_5 to HNO_3 during austral summer could be rather negligible due to the photolysis of NO_3 radical in summertime ($NO_3 + NO_2 + M \rightarrow N_2O_5 + M$). This point was clarified in the revised manuscript. Following previous investigations, the high concentrations of $nssSO_4^{2-}$ aerosols could provide nucleation centers forming the multi-ion complexes with HNO_3 in the atmosphere, possibly leading to elevated NO_3^- concentrations in the snow (Laluraj et al., 2010). On the other hand, the presence of fine $nssSO_4^{2-}$ aerosol may also enhance the direct uptake of gas phase HNO_3 onto the surface, resulting in NO_3^- deposition via aerosol mechanisms. It is acknowledged that these are the plausible explanation of the association between the two anions, and it cannot be ruled out that other processes and/or chemistry would influence the relationship of the parameters. Further works are needed to characterize the formation of SO_4^{2-} and NO_3^- and their potential association in Antarctic atmosphere.

(8) author's changes in manuscript

Following the comments from reviewer#2 and Prof. Savarino, the correlation between SO_4^{2-} and NO_3^- was re-discussed in the revised manuscript, as follows,

In surface snow, the non-sea salt fraction of SO_4^{2-} accounts for 75 - 99 % of its total budget, with a mean of 95 %. The percentages are relatively higher in inland regions than at coastal sites. On the coast, a positive relationship was found between $nssSO_4^{2-}$ and NO_3^- ($R^2 = 0.32$, $p < 0.01$; Fig. 7a). Previous observations suggest that NO_3^- and $nssSO_4^{2-}$ peaks in the atmosphere and snow are usually present in summer (Jourdain and Legrand, 2002; Wolff et al., 2008; Sigl et al., 2016; Legrand et al., 2017a; Legrand et al., 2017b). However, the similar seasonal pattern of the two species is associated with distinct sources, i.e., SO_4^{2-} is mainly derived from marine biogenic emissions while NO_3^- is influenced by photolysis and tropospheric transport (Savarino et al., 2007; Lee et al., 2014; Zatko et al., 2016). In the atmosphere, most of SO_4^{2-} is on the submicron particles, while most of NO_3^- is gaseous HNO_3 and the particulate NO_3^- is mainly on the intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a; Legrand et al., 2017b). Thus, the correlation between NO_3^- and SO_4^{2-} is unlikely explained by the sources or their occurrence state in the atmosphere (i.e., gaseous and particulate phases). Laluraj et al. (2010) proposed that the correlation between $nssSO_4^{2-}$ vs. NO_3^- in ice ($R^2 = 0.31$, $p<0.01$) could be associated with the fine $nssSO_4^{2-}$ aerosols, which could provide nucleation centers forming the multi-ion complexes with HNO_3 in the atmosphere. This assertion, however, should be examined further, considering that the complex chemistry of SO_4^{2-} and NO_3^- in the atmosphere is far from understood (e.g.,(Wolff, 1995; Brown et al., 2006). Thus far, the mechanism of $nssSO_4^{2-}$ influencing NO_3^- in the snowpack, however, is still debated, and it cannot be ruled out that $nssSO_4^{2-}$ further affects mobilization of NO_3^- during and/or after crystallization (Legrand and Kirchner, 1990; Wolff, 1995; Röthlisberger et al., 2000). It is noted that no relationship was found between $nssSO_4^{2-}$ and NO_3^- in inland snow (Fig. 7d), possibly due to the strong alteration of NO_3^-

during post-depositional processes, as discussed in section 4.1.2.

Please see the revised version of the manuscript, section 4.2 Effects of coexisting ions on NO_3^-.

(9) comments from Referees

Other comments:

Information on the chemistry of ice crystal are rather rare, so may important to develop this aspect in the revised manuscript (showing the full chemical composition and its comparison with snow).

Did you have measured MSA ?

I think you can say that nssCl is HCl and it can be interesting to compare with gas phase HNO3.

End of the review.

(9) author's response

Thanks to the reviewer for this suggestion. As the reviewer mentioned, the information on the crystal ice samples on Antarctic plateaus remain limited. So, showing the full chemical composition of the crystal ice can provide important information on snow chemistry in Antarctica. In addition, a comparison of chemical ion concentrations between surface snow and crystal ice was made in the revised manuscript.

Unfortunately, we did not measure the concentrations of MSA now. But we will measure the MSA concentrations in the samples of surface snow/snowpits. Possibly it will be another paper focusing on the biogenic sulfur ($nssSO_4^{2-}$ and MSA).

Yes, the $nssCl^-$ can be taken as HCl. This point was re-discussed in the manuscript.

(9) author's changes in manuscript

Following the reviewer's comment, a figure was included in the supporting information, as follows,

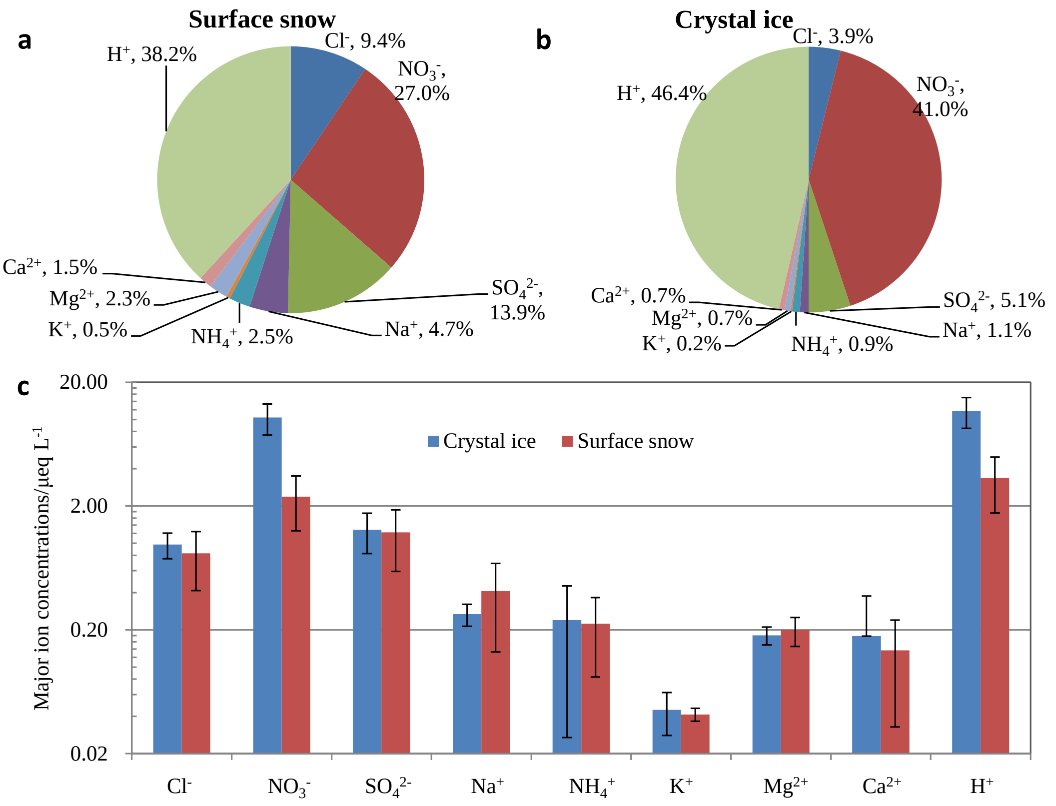

Figure S2 Major chemical ions in surface snow and crystal ice samples on the traverse from coast to the ice sheet summit (Dome A) in East Antarctica. Contribution percentages of each ion to total ion concentrations are shown in (a) and (b), respectively. Concentrations of ions in surface snow and crystal ice are shown in (c), with error bars of one standard deviation (1σ). The concentration of H^+ is calculated from the difference between sum anions and sum cations. Note that a base-10 log scale is used for ion concentrations in (c).

In addition, the major chemical ion concentrations and a comparison between surface snow and crystal ice was included in the updated version of the manuscript (**3.1 NO_3^- concentration in surface snow**), as follows,

In the crystal ice, the means (ranges) of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} and H^+ concentrations are 0.98 (0.62 – 1.27), 10.40 (8.35 – 16.06), 1.29 (0.87 – 2.13), 0.27 (0.21 – 0.33), 0.24 (0.03 – 0.56), 0.05 (0.03 – 0.08), 0.18 (0.15 – 0.22), 0.18 (0.05 – 0.57) and 11.75 (9.56 – 18.12) μeq L^{-1}, respectively. H^+ and NO_3^- are the most abundant species, accounting for 46.4 and 41.0 % of the total ions, followed by SO_4^{2-} (5.1 %) and Cl^- (3.9 %). The other 5 cations, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, only represent 3.6 % of the total ion budget. A significant linear relationship was found between NO_3^- and the total ionic strength ($R^2 = 0.99$, $p < 0.01$), possibly suggesting that NO_3^- is the species controlling ion abundance by influencing acidity of the crystal ice (i.e., H^+ levels). In comparison with surface snow, concentrations of H^+ and NO_3^- are significantly higher in crystal ice (Independent Samples T Test, p<0.01), while concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} are comparable in the two types of snow samples (Fig. S2 in supporting information). To date, the information on the chemistry of ice crystal is rather limited but data from the so-called skin layer at Dome C, where NO_3^- concentrations in the top 0.4 cm snow layer are in the range of 9 – 22 μeq L^{-1} in summertime (Erbland et al., 2013), generally comparable to our observations.

In addition, the association between NO_3^- and the major chemical ions in crystal ice was re-discussed (**4.2 Effects of coexisting ions on NO_3^-**), as follows,

With regard to the crystal ice, no significant correlation was found between NO_3^- and the coexisting ions (e.g., Cl^-, Na^+ and SO_4^{2-}), possibly suggesting that these ions are generally less influential on NO_3^- in this uppermost thin layer, compared to the strong air-snow transfer process of NO_3^- (Erbland et al., 2013). It is noted that NO_3^- accounts for most of the calculated H^+ concentrations (81 - 97 %, mean = 89 %), and a strong linear relationship was found between them (R^2 = 0.96), suggesting that NO_3^- is mainly deposited as acid, HNO_3, rather than in particulate form as salts (e.g., $NaNO_3$ and $Ca(NO_3)_2$). This deduction is in line with the observations at Dome C, where atmospheric NO_3^- was found to be mainly in gaseous phase (HNO_3) in summer (Legrand et al., 2017b). On average, the deposition of HNO_3 contribute >91% of NO_3^- in the crystal ice (the lower limit, 91 %, calculated simply by assuming all of the alkaline species (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) neutralized by HNO_3 in the atmosphere), suggesting a dominant role of HNO_3 deposition in snow NO_3^- levels. The elevated high atmospheric NO_3^- concentrations observed at Dome A (>100 ng m^{-3}; 77.12°E, 80.42°S; Table S1 in supporting information) possibly indicate oxidation of gaseous NO_x to HNO_3, suggesting that NO_3^- recycling driven by photolysis plays an important role in its abundance in snowpack on East Antarctic plateaus.

The relationship between $nssCl^-$ (i.e., the HCl) and NO_3^- in snow was re-discussed in the revised manuscript, please see the revised manuscript, **4.2 Effects of coexisting ions on NO_3^-**

End of responses to Referee #2.

Prof. Joel Savarino

We thank Prof. Savarino very much for his careful and thoughtful review of our work. Please see below for point-by-point responses in blue following Prof. Savarino's comments, in the order of (1) comments from Referees, (2) author's response, and (3) author's changes in manuscript.
Reviewer comments are in black, and the responses are in blue.

(1) comments from Referees

The paper needs major revisions before being accepted. The authors should better present their data in light of recent and past publications. Many important works are not referenced and it seems difficult to follow the conclusions (mainly part 4) of the authors based on only snow concentrations when other publications measuring all aspects of atmospheric parameters struggle to conclude on the fate of nitrate, its origin, formation, transport deposition and post deposition.

(1) author's response

We agree with Prof. Savarino. Some recent/past publications were not referenced in previous version. Following the comments from Prof. Savarino and two anonymous referees, the references were updated.

The discussion section (part 4) was substantially revised following the comments/suggestions, with the aid of publications on the atmospheric parameters. In addition, our recent measurements of atmospheric NO_3^- were included in the discussion (see responses to Referee 1).

(1) author's changes in manuscript

The references were updated.

The discussion part was revised

Please see the revision-tracked version of manuscript.

(2) comments from Referees

Reference to work suggesting an extraterrestrial source of nitrate in ice has been repeatedly dismissed (1-3 just for the most recent publications). Clearly state this fact or remove any reference to those works. 1-Wolff, E. W., Jones, A. E., Bauguitte, S. J.-B., and Salmon, R. A.:

Reassessment of the factors controlling temporal profiles of nitrate in polar ice cores using evidence from snow and atmospheric measurements, Atmospheric Chemistry and Physics Discussion, 8, 11039-11062, 2008. 2-Wolff, E. W., Bigler, M., Curran, M. A. J., Dibb, J. E., Frey, M. M., Legrand, M., and McConnell, J. R.: The Carrington event not observed in most ice core nitrate records, Geophys. Res. Lett., 39, L08503, 10.1029/2012gl051603, 2012. 3-Duderstadt, K. A., Dibb, J. E., Schwadron, N. A., Spence, H. E., Solomon, S. C., Yudin, V. A., Jackman, C. H., and Randall, C. E.: Nitrate ion spikes in ice cores not suitable as proxies for solar proton events, Journal of Geophysical Research: Atmospheres, n/a-n/a, 10.1002/2015JD023805, 2016.

(2) author's response

Thanks for this point. The references were now included in the revised manuscript.

(2) author's changes in manuscript

The recent works, both observations and model simulations (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014; Duderstadt et al., 2016; Wolff et al., 2016), were included in the manuscript, as follows,

In addition, while some studies suggested that snow/ice NO_3^- is possibly linked with extraterrestrial fluxes of energetic particles and solar irradiation, with solar flares corresponding to NO_3^- spikes (Zeller et al., 1986; Traversi et al., 2012), other observations and recent modeling studies have established that there is not a clear connection between solar variability and NO_3^- concentrations (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014; Duderstadt et al., 2016; Wolff et al., 2016).

Please see the revision-tracked version of manuscript, section **1 Introduction**

(3) comments from Referees

Volatilization of nitrate. In Erbland et al. 2013 and Berhanu et al., 2014, 2015 (4-5) isotope fractionations demonstrate that vitalization is not an important loss process in contradiction with the authors statement (line 96). This should be clearly mentioned. What do you call post depositional effects beside photo-dissociation and volatilization? For me they are the post depositional effects. If you think there is more effects to take into accounts please, indicate which ones? 4- Berhanu, T. A., Meusinger, C., Erbland, J., Jost, R., Bhattacharya, S. K., Johnson, M. S., and Savarino, J.: Laboratory study of nitrate photolysis in Antarctic snow. II. Isotopic effects and wavelength dependence, The Journal of Chemical Physics, 140, 244305, 10.1063/1.4882899, 2014. 5- Berhanu, T. A., Savarino, J., Erbland, J., Vicars, W. C., Preunkert, S., Martins, J. F., and Johnson, M. S.: Isotopic effects of nitrate photochemistry in snow: a field study at Dome C, Antarctica, Atmos. Chem. Phys., 15, 11243-11256, 10.5194/acp-15-11243-2015, 2015.

(3) author's response

We agree with Prof. Savarino. The post-depositional effects refer to the two processes, photolysis and volatilization.

In comparison with photolysis, the extent and isotopic effects of NO_3^- volatilization remains poorly understood. Although several laboratory and field experiments have been conducted to examine the volatilization effects, the outcomes seem to vary remarkably among different experiments. Freshly-falling snow in Hanover, New Hampshire was used for examining NO_3^- loss with sublimation at -5 ^oC under controlled laboratory conditions, and NO_3^- loss was found to be negligible after a few days (Cragin and McGilvary, 1995). Similarly, a field experiment conducted on a subtropical glacier also showed that no significant loss of NO_3^- occurs over the course of one month sublimation (with temperature near zero; Ginot et al., 2001). The negligible NO_3^- loss during these experiments could be associated with that deposition of NO_3^- is mainly in particulate form rather than in the form of HNO_3 in the experimental snow. In a laboratory experiment, no detectable NO_3^- loss from the surface of frozen $NaNO_3$ solution acidified to pH=4 at -6^oC, and the high dissociation constant of HNO_3 was possibly a main reason (Sato et al., 2008; Riikonen et al., 2014). The wind-blown snow collected from Dome C was exposed to a flow of N_2 for one week in the dark at about -30 ^oC, no NO_3^- loss was detected, consequently the isotopic composition of NO_3^- is relatively constant during the sublimation process (Berhanu et al., 2014). However, the field experiment conducted at Dome C showed 17% (-30 ^oC) to 67% (-10 ^oC) of NO_3^- lost after 14-day sublimation (Erbland et al., 2013). Further investigations are needed to quantify the effects of volatilization for a better understanding of NO_3^- preservation in the snow/ice.

(3) author's changes in manuscript

Following the comments, we re-phrased these sentences, as follows, and also noted that volatilization might be important at warmer temperatures,

The effects of volatilization of NO_3^- are uncertain, given that one field experiment suggests that this process is an active player in NO_3^- loss (17 % (-30 ^oC) to 67 % (-10 ^oC) of NO_3^- lost after two weeks′ physical release experiments; Erbland et al., 2013), while other laboratory and field studies show that volatilization plays a negligible role in NO_3^- loss (Berhanu et al., 2014; Berhanu et al., 2015). Further investigations are needed to quantify the effects of volatilization for a better understanding of NO_3^- preservation in the snow/ice.

Please see the revision-tracked version of manuscript, section **1 Introduction**

(4) comments from Referees

Please also consider this publication for your introduction Bock, J., Savarino, J., and Picard, G.: Air–snow exchange of nitrate: a modelling approach to investigate physicochemical processes in surface snow at Dome C, Antarctica, Atmos. Chem. Phys., 16, 12531-12550, 10.5194/acp-16-12531-2016, 2016

(4) author's response

The very recent modeling work performed by Bock et al. (2016) suggest that co-condensation is the most important process to explain NO_3^- incorporation in snow undergoing temperature gradient metamorphism. The observed summer NO_3^- peaks in surface snow can be explained by this process.

(4) author's changes in manuscript

This reference was included in the revised manuscript, as follows,

However, snow physical characteristics play a crucial role in NO_3^- deposition and preservation. For instance, summertime concentrations in the surface skin layer of snow (the uppermost ~4 mm) can be explained as the result of co-condensation of HNO_3 and water vapour, with little to no photolytic loss in this microlayer (Bock et al., 2016). The combination of concentration and isotopic studies, along with physical aspects of the snow, could lead to the reconstruction and interpretation of atmospheric NO_3^- over time (e.g., Erbland et al., 2015; Bock et al., 2016), if there is detailed understanding of the NO_3^- deposition and preservation in different environments in Antarctica.

Please see the revision-tracked version of manuscript, section 1 Introduction

(5) comments from Referees

Acidity calculation is wrong. H+ = Σanions - Σcations, the equation used is a simplifi- cation and do not for instance takes into account ammonium ions.

(5) author's response

As Prof. Savarino suggested, the formula in the previous version ($[H^+] = [SO_4^{2-}] - 0.12 \times [Na^+] + [NO_3^-] + [Cl^-] - 1.17 \times [Na^+]$, Eq. 1; Legrand and Delmas, 1988) do not consider the effects of ammonium ions. In this case, the calculated H^+ concentrations were potentially over-estimated. In the updated version H^+ concentration is calculated through ion balance, i.e., $[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] - [Na^+] - [NH_4^+] - [Mg^{2+}] - [Ca^{2+}]$ (Eq. 2), where ion concentrations are in μeq L^{-1}. Concentrations of H^+ calculated from the two methods are as follows,

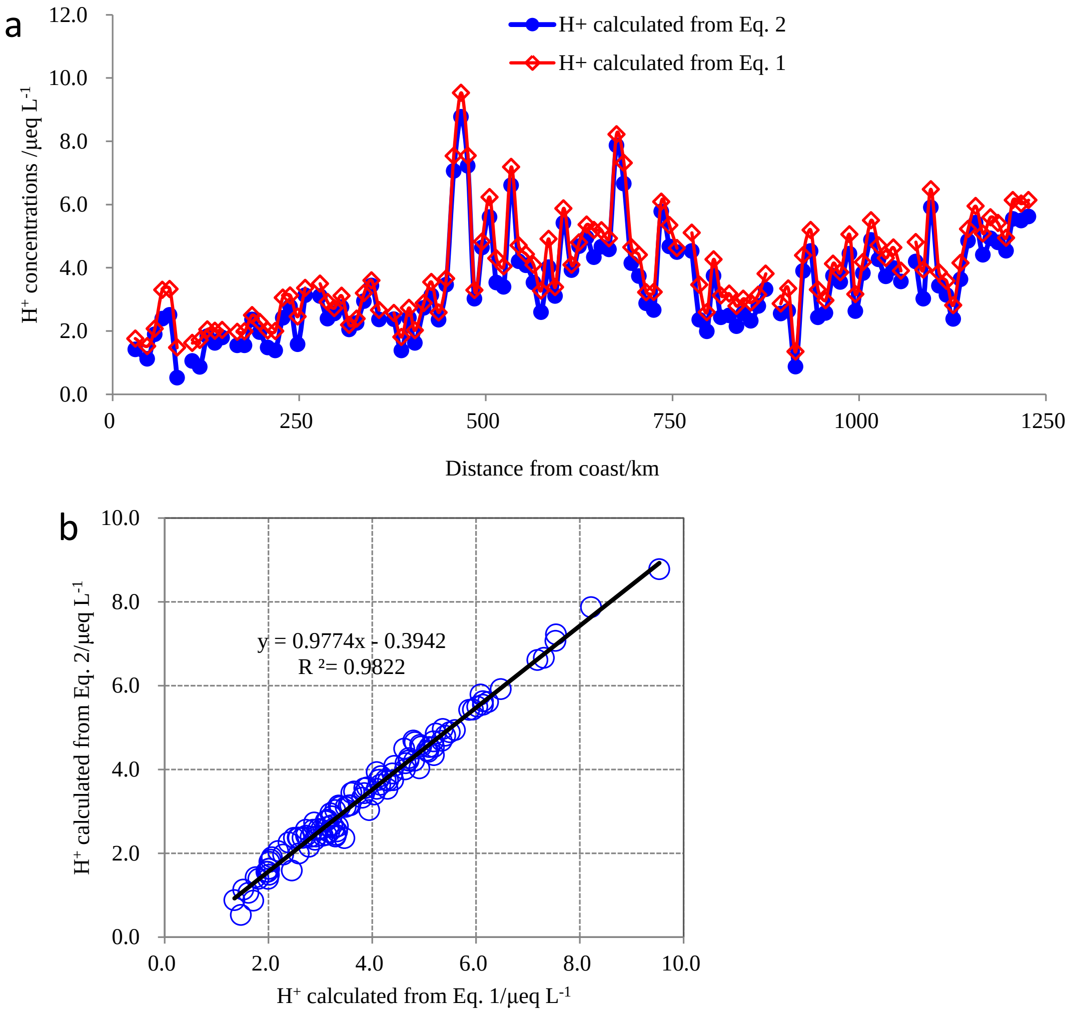

Figure Concentrations of H^+ in surface snow calculated from the two methods (a, upper panel) and the relationship between H^+ levels from the two calculations (b, bottom panel).

In general, H^+ concentrations from the two calculations are generally very close due to the relatively low concentrations of NH_4^+ in Antarctic snow. On average, the difference between the two calculations is <10%. In the revised manuscript, all of the H^+ data was calculated through Eq. 2, following Prof. Savarino' s suggestion.

(5) author's changes in manuscript

Revised, as follows,

For Antarctic snow samples, the concentrations of H^+ are usually not measured directly, but deduced from the ion-balance disequilibrium in the snow. Here, H^+ concentration is calculated through ion balance.

$[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] - [Na^+] - [NH_4^+] - [Mg^{2+}] - [Ca^{2+}]$ (Eq. 1),

where ion concentrations are in μeq L^{-1}.

Please see the revised manuscript, section **2.3 Sample analysis.**

(6) comments from Referees

Cv is not defined (line 206)

(6) author's response

Cv, the Coefficient of Variation.

(6) author's changes in manuscript

Defined in the manuscript.

(7) comments from Referees

Erbland 2013 sampled many snow pits at a higher resolution than Frey 2009 (line 231). It is this reference that should be used and cited here.

(7) author's response

Yes, Erbland et al. (2013) sampled 17 snowpits at a higher resolution on the traverse from DDU to Dome C than Frey et al. (2009). In the work of Frey et al. (2009), only the top ~10 cm of snow (called 'surface snow') was sampled on that traverse (in total, 15 samples). In the section of 3.1 NO_3^- concentrations in surface snow, we only compare NO_3^- concentrations in the surface snow. Thus, we cited the work of Frey et al. (2009) in the previous version. We also cited the work of Erbland et al. (2013) in the revised version.

(7) author's changes in manuscript

The work of Erbland et al. (2013) was included in the revised manuscript.

(8) comments from Referees

Line 257 replace "may be" by "as a result of post depositional processing" This is no doubt about that.

(8) author's response

Agree, thanks.

(8) author's changes in manuscript

Replaced.

(9) comments from Referees

Line 288 change proposed by demonstrated - Again isotopes of nitrate have demonstrated the correctness of this assertion.

(9) author's response

Agree. Thanks.

(9) author's changes in manuscript

Changed.

(10) comments from Referees

line 291: Please add France 2011 reference, the first publication to have measured the optical depth of the snow pack in the UV range, years before Zatko 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, Atmos. Chem. Phys., 11, 9787-9801, 10.5194/acp-11-9787-2011, 2011.

(10) author's response

Yes, France et al. (2011) reported the *e*-folding depth (z_e), where the actinic flux is reduced to 37 % (i.e. 1/*e*) of the surface value, of 10 to 20 cm at Dome C on the East Antarctic plateau, while Zatko et al. (2013) calculated the *e*-folding depth at different sites in Antarctica.

(10) author's changes in manuscript

The reference France et al. (2011) was added.

(11) comments from Referees

line 293 The idea that below the photic zone, nitrate is archived without further modification is an idea developed in Frey 2009, Erbland 2013 and 2015. This should be recognized.

(11) author's response

Agree.

(11) author's changes in manuscript

The statement was re-phrased, and the references were included in the manuscript, as follows,

In this case, NO_3^- in the bottom snowpit, i.e., below the photic zone, can be taken as the archived fraction without further modification on the basis of previous observations (Frey et al., 2009; Erbland et al., 2013; Erbland et al., 2015).

(12) comments from Referees

line 306: Change dry deposition by apparent dry deposition. See Bock et al. but also the second reviewer's comments.

(12) author's response

Agree. Please also see the responses to the Referee#2.

(12) author's changes in manuscript

Changed in the revised version. This section was substantially revised following the comments from Prof. Savarino and the two anonymous referees, please see the revised manuscript, sections **4.1.1 NO_3^- in coastal snowpack** and **4.1.2 NO_3^- in inland snowpack**

(13) comments from Referees

line 320: it is not the strong correlation between deposition flux and accumulation that makes wet deposition to dominate but the comparison between "dry" and wet fluxes (see your eq 5). The fact that a correlation exists only means that the scavenging ratio of atmospheric nitrate by snowfall is constant or in other words the concentration in snow fall is independent of the snow accumulation (see your equation 5).

(13) author's response

Agree. Thanks for pointing this out.

(13) author's changes in manuscript

This statement was re-phrased in the revised manuscript.

(14) comments from Referees

line 331: K2 is not dimensionless as it allows to convert atmospheric concentration (mass/volume) to snow concentration (mass/mass), it has a unit of m3/g. How K2 is calculated? According to Eq5, K2 x Catm = Cf-snow, so K2 = 43/20 = 2.1 meaning that 1 g of snow scavenged 2 m3 of air. Also note that eq 5 & 6 is nothing else than your eq4. These models are not different models but the same, expressed in different way. It is thus not surprising to find the same dry deposition flux. Comment your dry deposition with respect to previous publication (eg Pasteris 2014)

(14) author's response

Agree, and thanks for this comment. Because the unit of NO_3^- flux, F_{total}, is μeq m^{-2} a^{-1}, the unit of $K_2C_{atm}A$ should be μeq m^{-2} a^{-1}. Considering that the units of C_{atm} and A are μeq m^{-3} and kg m^{-2} a^{-1}, respectively, the unit of K_2 should be m^3 kg^{-1}. Following the linear relationship between NO_3^- flux and snow accumulation rate (A), i.e., $F_{total} = K_1C_{atm} + K_2C_{atm}A$, the slope of the linear fit, K_2C_{atm}, is 0.6 (y = 0.6x + 50.3). The atmospheric NO_3^- concentration on the coast was observed to be 19.4 ng m^{-3} (i.e., 0.3×10^{-3} μeq m^{-3}), then K_2 is estimated to be ~0.2×10^4 m^3 kg^{-1}, i.e., about 2 m^3 g^{-1}.

Yes, the equations 5 and 6 are the same with equation 4 in previous version, i.e., not different models. This section was substantially revised in the manuscript.

The apparent dry deposition flux is compared to previous observations in Dronning Maud Land (DML) region and at Kohnen Station, where the negative dry deposition flux suggests a net loss of NO_3^- (Weller et al., 2004; Weller and Wagenbach, 2007; Pasteris et al., 2014).

(14) author's changes in manuscript

Following the comments from Prof. Savarino and Referee#1, the models were consolidated. Accordingly, this discussion was revised. Please see the revision-tracked version of the manuscript, sections **4.1.1 NO_3^- in coastal snowpack** and **4.1.2 NO_3^- in inland snowpack**.

(15) comments from Referees

line 342: give the reference for the deposition velocity at South Pole.

(15) author's response

Thanks for this point.

(15) author's changes in manuscript

The following reference was added,
Huey, L.G., Tanner, D.J., Slusher, D.L., Dibb, J.E., Arimoto, R., Chen, G., Davis, D., Buhr, M.P., Nowak, J.B., Mauldin Iii, R.L., Eisele, F.L., and Kosciuch, E.: CIMS measurements of HNO_3 and SO_2 at the South Pole during ISCAT 2000, Atmos. Environ., 38, 5411-5421, doi:10.1016/j.atmosenv.2004.04.037, 2004.

(16) comments from Referees

Line 347: K2 in eq7 cannot be equal to K2 in eq5. K2 in eq5 takes implicitly into account , the density of air, as K2/ = K in eq7, unless I have missed something

(16) author's response

We thank Prof. Savarino very much for pointing this out, and we are sorry for the confusion about the scavenging ratio for NO_3^- in the previous version. K_2 is the scavenging ratio for precipitation (m^3 kg^{-1}), which allows to convert atmospheric concentration to snow concentration of NO_3^- in this study.

If it is assumed that NO_3^- concentration in snow is related to its concentration in the atmosphere, the scavenging ratio for NO_3^- (W) can be calculated on a mass basis from the following expression (Kasper-Giebl et al., 1999),

$$W = \rho_{atm} \times (C_{f\text{-}snow} / C_{atm}) \text{ (Eq. 7),}$$

where ρ_{atm} is air density (g m^{-3}), and $C_{f\text{-}snow}$ and C_{atm} are NO_3^- concentrations in fresh snow (ng g^{-1}) and atmosphere (ng m^{-3}) respectively. If taking $\rho_{atm} \approx 1000$ g m^{-3} (on average, ground surface temperature $t \approx 255$ k, ground pressure $P \approx 0.08$ MPa, in the coastal region), $C_{f\text{-}snow} = 43$ ng g^{-1} (see the main context), and $C_{atm} = 19.4$ ng m^{-3}, W is calculated to be ~2200, generally comparable to previous reports (Barrie, 1985; Kasper-Giebl et al., 1999; Shrestha et al., 2002). It is noted that the calculation here may be subject to uncertainty, due to the complex transfer of atmospheric NO_3^- into the snow. However, the scavenging ratio provides useful insights into the relation between NO_3^- concentrations in the atmosphere and snow and reference values for modeling NO_3^- deposition at large scale in Antarctica.

(16) author's changes in manuscript

K_2, the scavenging ratio for precipitation, and the scavenging ratio for NO_3^- (W) were clarified in the updated version. Please see the revision-tracked version of the manuscript, sections 4.1.1 NO_3^- in coastal snowpack

(17) comments from Referees

line 352: not sure these inferred parameters are better than concentration observations to provide useful reference values for modeling. These are macroscopic, apparent parameters that are unable to describe processes at microscopic scale. See Bock 2016.

(17) author's response

We agree that the calculations here are macroscopic and apparent parameters, which possibly cannot characterize the microscopic processes (e.g., co-condensation; Bock et al., 2016). However, they possibly can provides useful parameter values for modeling NO_3^- deposition at large scale in Antarctica. It is noted that previous modeling work of Zatko et al. (2016) do not include the microscopic processes (i.e., models at the regional to global scale).

(17) author's changes in manuscript

The statement was rephrased in the revised manuscript, as follows,

It is noted that the calculation here may be subject to uncertainty, due to the complex transfer of atmospheric NO_3^- into the snow. However, the scavenging ratio provides useful insights into the relation between NO_3^- concentrations in the atmosphere and snow, which might be useful in modeling NO_3^- deposition at large-scale.

Please see the revision-tracked version of the manuscript, sections **4.1.1 NO_3^- in coastal snowpack**

(18) comments from Referees

Fig5a and fig5b are in contradiction. The same parameter (p-concentration) cannot be linear with respect to a variable A and its reverse 1/A (same for fig5e & fig5f). I also found p-concentration not very expressive. Archived, deep concentration seems more appropriate.

(18) author's response

Thanks for pointing this out. For a direct comparison with previous investigations, only the relationship between archived concentration of NO_3^- and inverse snow accumulation rate was presented, for the observations both at inland and coastal sites.

Agree, and p-concentration was replaced with archived concentration (C_{archived}) in the revised version.

(18) author's changes in manuscript

Figures 5 was re-drawn, and only the correlation between archived concentration of NO_3^- and inverse snow accumulation rate was included, as follows,

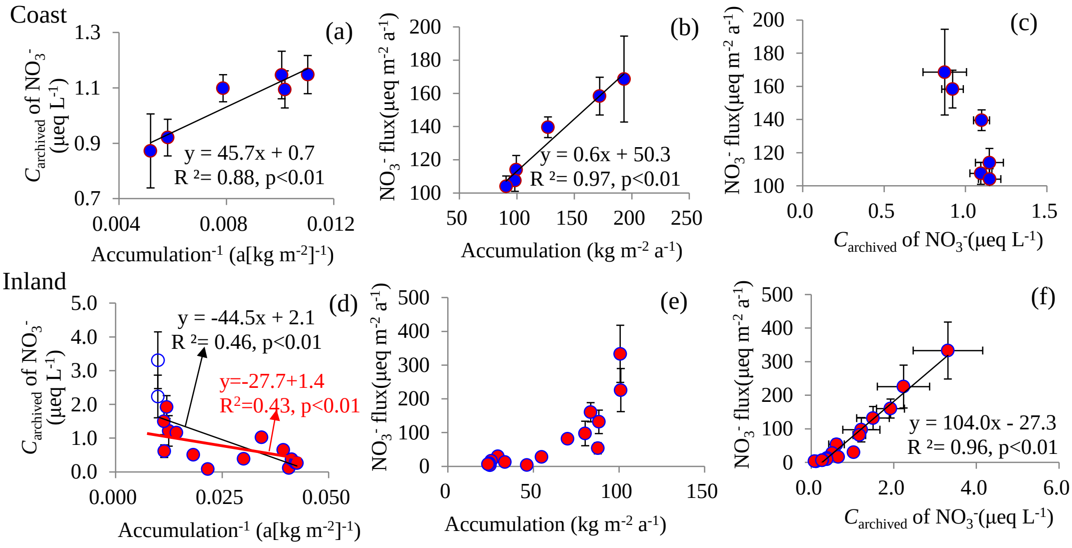

Figure 5. The relationship among snow accumulation rate, the archived concentration ($C_{archived}$), and flux of NO_3^- in coastal (top row, (a), (b) and (c)) and inland (bottom row, (d), (e) and (f)) Antarctica. In panel (d), the linear fit in back line (y = -44.5 + 2.1) include the full date set, while the linear equation in red (y = -7.7 + 1.5) was obtained by excluding two cases (open circles) with snow accumulation rate larger than 100 kg m^{-2} a^{-1} (see the main text). The flux values are the product of $C_{archived}$ of NO_3^- and snow accumulation rate, namely the archived flux. Least squares regressions are noted with solid lines and are significant at $p < 0.01$. Error bars represent one standard deviation (1σ).

The p-concentration was not used throughout the context, please see the revised version of the manuscript.

(19) comments from Referees

Why slope of fig5a & fig6b are so different if no nitrate is lost in coastal region ? In general, Cfirn, Cp-concentration, Cf-snow are poorly labeled on figures (why not using the same as Pasteris 2014), why in fig6 f-snow label is not used, same for fig4? This makes the reading of the figures very confusing.

(19) author's response

Now, we can make a comparison between the two figures (Figures 5a versus 6a), as follows,

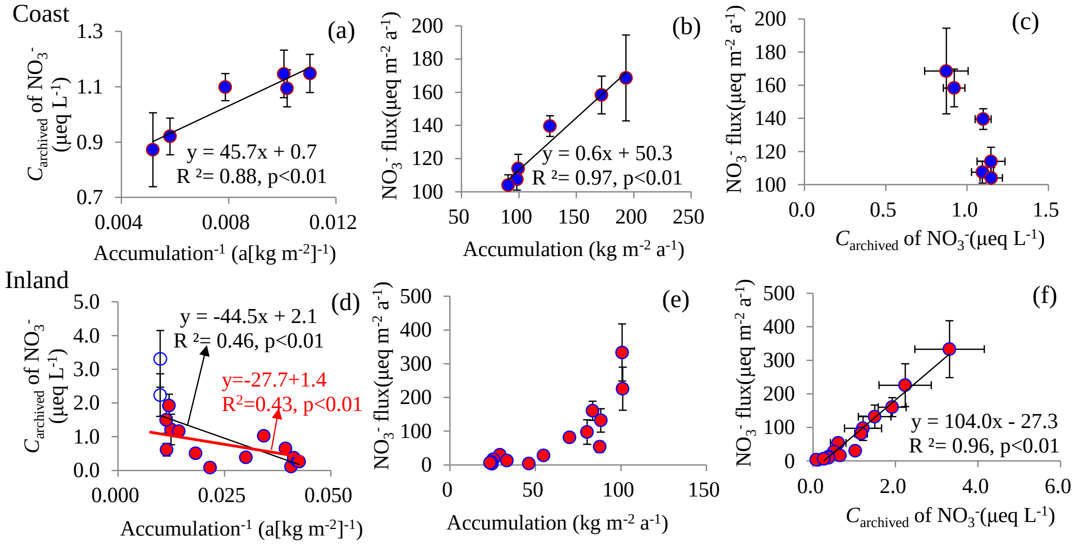

Figure 5. The relationship among snow accumulation rate, the archived concentration ($C_{archived}$), and flux of NO_3^- in coastal (top row, (a), (b) and (c)) and inland (bottom row, (d), (e) and (f)) Antarctica. In panel (d), the linear fit in back line (y = -44.5 + 2.1) include the full date set, while the linear equation in red (y = -7.7 + 1.5) was obtained by excluding two cases (open circles) with snow accumulation rate larger than 100 kg m^{-2} a^{-1} (see the main text). The flux values are the product of $C_{archived}$ of NO_3^- and snow accumulation rate, namely the archived flux. Least squares regressions are noted with solid lines and are significant at $p < 0.01$. Error bars represent one standard deviation (1σ).

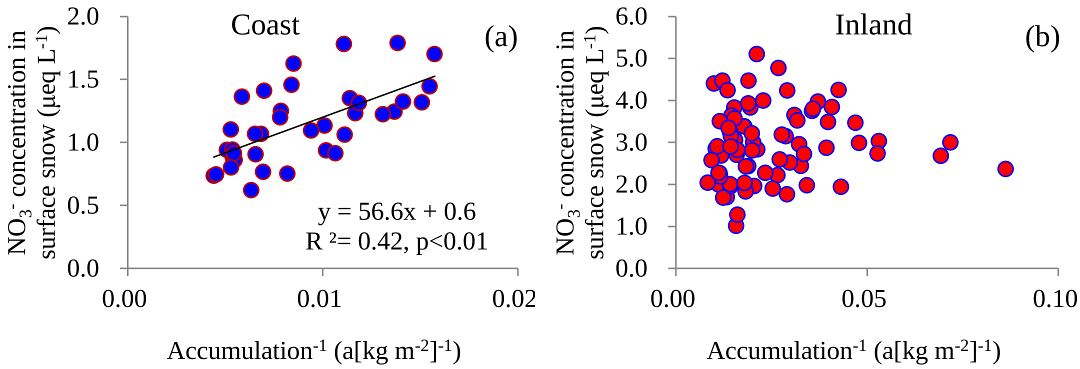

Figure 6. The relationship between NO_3^- concentration and inverse snow accumulation rate in surface snow in coast (panel (a)) and inland (panel (b)) Antarctica. Least squares regressions are noted with solid line and are significant at $p < 0.01$.

In terms of surface snow on the coast, NO_3^- may be disturbed by the katabatic winds and wind convergence located near the Amery Ice Shelf (that is, the snow-sourced NO_x and NO_3^- from Antarctic plateau possibly contribute to coastal snow NO_3^-) (Parish and Bromwich, 2007; Ma et al., 2010). In addition, the sampled ~3 cm surface layer roughly corresponds to the net accumulation in the past 0.5-1.5 months assuming an even distribution of snow accumulation in the course of a single year. This difference in exposure time of the surface snow at different sampling sites, could possibly affect the concentration of NO_3^-, although the post-depositional alteration of NO_3^- was thought to be minor on the coast (Wolff et al., 2008; Erbland et al., 2013; Shi et al., 2015). Taken together, NO_3^- in coastal surface snow might represent some post-depositional alteration. Even so, a negative correlation between NO_3^- concentration and snow accumulation rate was found at the coast ($R^2=0.42$, $p<0.01$; Fig. 6a). It is noted that the parameters obtained from Figure 6a ($y = 56.6x + 0.6$) are generally comparable to those of the coastal snowpits ($y = 45.7x + 0.7$; Figure 5a), and the small difference could be associated with the influences discussed above. Both the snowpit and surface snow observations suggest that overall the majority of the NO_3^- appears to be preserved and is driven by snow accumulation on the coast.

(19) author's changes in manuscript

All of the figures (Figures 4, 5 and 6) were labeled clearly following the comments, please see the revised manuscript.

(20) comments from Referees

line 381: replace snow accumulation by inverse snow accumulation. Also please comment the difference of nitrate flux loss between you (-73.9 ueq m-2 a-1) and Pasteris 2014 (-22 ueq m-2 a-1), as well as for the slope, 2.7 vs 1.1 when accumulation rates cover the same range.

(20) author's response

Thanks for this comment. A comparison between our observations and previous reports of Pasteris et al. (2014) and Weller and Wagenbach (2007) was made.

(20) author's changes in manuscript

Following Prof. Savarino’s comments and suggestion, this paragraph was re-written, as follows,

In comparison with the coast, the correlation between C_{archived} and inverse snow accumulation is relatively weak in inland regions (Fig. 5d), suggesting more variable conditions in ambient concentrations and dry deposition flux of NO_3^-. In addition, the relationship of C_{archived} vs. inverse accumulation in inland is opposite to that of coast. Based on current understanding of the post-depositional processing of NO_3^-, the negative correlation between C_{archived} and inverse snow accumulation (Fig. 5d) suggests losses of NO_3^-.The slope of the linear relationship indicates apparent NO_3^- dry deposition flux of -44.5 ± 13.0 μeq m^{-2} a^{-1}, much larger than that of DML (-22.0 ± 2.8 μeq m^{-2} a^{-1}), where the snow accumulation is generally lower than 100 kg m^{-2} a^{-1} (Pasteris et al., 2014). At Kohnen Station (an inland site in East Antarctica), with snow accumulation of 71 kg m^{-2} a^{-1}, the emission flux of NO_3^- is estimated to be -22.9 ± 13.7 μeq m^{-2} a^{-1} (Weller and Wagenbach, 2007), which is also smaller in comparison with this observation. Weller et al. (2004) proposed that loss rate of NO_3^- does not depend on snow accumulation rate and the losses become insignificant at accumulation rates above 100 kg m^{-2} a^{-1}. Among the inland sites, SP10 and Core2 (~800 km from the coast), featured by high snow accumulation rate (> 100 kg m^{-2} a^{-1}; Table 1 and Fig. 1), exhibit even higher values of C_{archived} and archived fluxes of NO_3^- than those of the coastal sites. It is noted that the two cases influence the linear regression significantly (Fig. 5d). If the two sites are excluded, we can get a linear regression with the slope of -27.7±9.2 μeq m^{-2} a^{-1}, which is comparable to previous reports in DML (Pasteris et al., 2014).

Please see the revision-tracked version of the manuscript, first paragraph in section **4.1.2 NO_3^- in inland snowpack.**

(21) comments from Referees

Figure 6h: There is something difficult to understand and seems to be a circular reasoning in fig6. Since Flux = snow concentration x snow accumulation, and only concentration and accumulation are measured, how fig6g and 6h can produce both a linear trend. In fig6g, slope gives snow concentration, the linear trend then suggests a constant homogeneous snow concentration in fresh snow. Slope of fig6h gives a constant homogeneous accumulation (in clear contradiction with measurements), well if accumulation is constant and snow concentration is constant, how the flux can vary? (same observation for fig5) Your conclusion that accumulation is not the main driver of the preserved nitrate (line 387) contradicts fig6g and the linear trend plotted. I will suggest to remove the linear trend of fig6g, which obviously looks like more exponential than linear.

(21) author's response

Agree, thanks for the comment. In the previous version of the manuscript, data in Figure 6g (snow accumulation rate versus archived NO_3^- flux) can be better depicted by an exponential regression, instead of a linear model, while the strong linear relationship between the archived NO_3^- concentration and flux suggest that accumulation rate is not the main driver of the preserved NO_3^- concentration. In this case, the linear fit was removed and Figure 6 was therefore re-drawn.

(21) author's changes in manuscript

Following the comments, Figure 6 was redrawn, and accordingly the discussion was re-made. Please see the revised manuscript, section **4.1.2 NO_3^- in inland snowpack.**

(22) comments from Referees

line 403: in reference add Erbland 2013, France, 2011

(22) author's response

Agree, added.

(22) author's changes in manuscript

The references were added in the revised manuscript.

(23) comments from Referees

line 405: add Davis et al., 2004 reference
Davis, D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F., Mauldin, L., and Hogan, A.: South Pole NOx Chemistry: an assessment of factors controlling variability and absolute levels, Atmos. Environ., 38, 5375-5388, 10.1016/j.atmosenv.2004.04.039, 2004.

(23) author's response

Added.

(23) author's changes in manuscript

Added. Please see the revised manuscript.

(24) comments from Referees

line 413: do you mean fig6e, f instead of 6c & d ?

(24) author's response

In previous version, no significant correlation was found in Figures 6 c and d. Also, the relationship was not so strong (Figure 5f) compared to the correlation for coast (Figure 5b). Figure 6 was redrawn in the revised manuscript.

(24) author's changes in manuscript

Please see the revised manuscript Figure 6 and the main text.

(25) comments from Referees

The part4 needs to be revisited in light of the references given by reviewer 2. There are many misconceptions. The first is that a correlation does not imply a causal effect. nitrate and sulfate summer peaks may have completely unconnected reasons (max photo-denitrification and max marine emission respectively followed by dry and wet depositions). Nitrate aerosols are not on the same aerosols size bin than sulfuric acid (Jourdain and Legrand, 2002). Even in heavily sea salt impacted coastal sites, half of the nitrate is in acid form and rapidly goes to almost 100% inland. There are no reasonable observations to support the conversion of NOx to nitrate by sulfate aerosols (in addition than N2O5 does not exist in summer), neither than nitrate is internally mixed with sulfate aerosols. Jourdain, B., and Legrand, M.: Year-round records of bulk and size-segregated aerosol composition and HCl and HNO3 levels in the Dumont d'Urville (coastal Antarctica) atmosphere: Implications for sea-salt aerosol fractionation in the winter and summer, J. Geophys. Res., 107, 4645, 10.1029/2002jd002471, 2002.

(25) author's response

We agree that a correlation between NO_3^- and the co-existing impurities does not necessarily suggest a causal link. In the surface snow on the traverse from coast to the ice sheet summit, Dome A, non sea salt fraction account for 75 - 99 % of total SO_4^{2-}, with a mean of 95 %, suggesting a dominant source from ocean bioactivities. The percentages are relatively higher in inland regions than at coastal sites. Field observations show that NO_3^- and $nssSO_4^{2-}$ peaks in the atmosphere and snow are usually present in summer (Jourdain and Legrand, 2002; Wolff et al., 2008; Sigl et al., 2016; Legrand et al., 2017a; Legrand et al., 2017b). But this similar seasonal pattern of the two species is unlikely associated with the sources, i.e., SO_4^{2-} is mainly derived from marine biogenic emissions while NO_3^- is influenced by photolysis and tropospheric transport (Savarino et al., 2007; Lee et al., 2014; Zatko et al., 2016). In addition, most of SO_4^{2-} is on the submicron particles, while most of NO_3^- is gaseous HNO_3 and the particulate NO_3^- is mainly on the intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a; Legrand et al., 2017b). Laluraj et al. (2010) found a close correlation between $nssSO_4^{2-}$ vs. NO_3^- in ice ($R^2 = 0.31$, $p<0.01$), and they attributed the relationship to the fine $nssSO_4^{2-}$ aerosols, which have long residence time in the atmosphere (Hara et al., 2014) and could provide nucleation centers forming the multi-ion complexes with HNO_3 in the atmosphere. It is acknowledged that this proposal should be examined further, considering that the complex chemistry of SO_4^{2-} and NO_3^- in the atmospheric is far from understood (e.g., Wolff, 1995; Brown et al., 2006).

In addition, the mechanism of $nssSO_4^{2-}$ influencing NO_3^- in the snowpack, however, is still debated, and it cannot be ruled out that $nssSO_4^{2-}$ further affects mobilization of NO_3^- during and/or after crystallization (Legrand and Kirchner, 1990; Wolff, 1995; Röthlisberger et al., 2000).

(25) author's changes in manuscript

Following the comments and suggestions from Prof. Savarino and Reviewer#2, this section was re-organized, as follows,

In surface snow, the non-sea salt fraction of SO_4^{2-} accounts for 75 - 99 % of its total budget, with a mean of 95 %. The percentages are relatively higher in inland regions than at coastal sites. On the coast, a positive relationship was found between nssSO_4^{2-} and NO_3^- ($R^2 = 0.32$, $p < 0.01$; Fig. 7a). Previous observations suggest that NO_3^- and nssSO_4^{2-} peaks in the atmosphere and snow are usually present in summer (Jourdain and Legrand, 2002; Wolff et al., 2008; Sigl et al., 2016; Legrand et al., 2017a; Legrand et al., 2017b). However, the similar seasonal pattern of the two species is associated with distinct sources, i.e., SO_4^{2-} is mainly derived from marine biogenic emissions while NO_3^- is influenced by photolysis and tropospheric transport (Savarino et al., 2007; Lee et al., 2014; Zatko et al., 2016). In the atmosphere, most of SO_4^{2-} is on the submicron particles, while most of NO_3^- is gaseous HNO_3 and the particulate NO_3^- is mainly on the intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a; Legrand et al., 2017b). Thus, the correlation between NO_3^- and SO_4^{2-} is unlikely explained by the sources or their occurrence state in the atmosphere (i.e., gaseous and particulate phases). Laluraj et al. (2010) proposed that the correlation between nssSO_4^{2-} vs. NO_3^- in ice ($R^2 = 0.31$, $p<0.01$) could be associated with the fine nssSO_4^{2-} aerosols, which could provide nucleation centers forming the multi-ion complexes with HNO_3 in the atmosphere. This assertion, however, should be examined further, considering that the complex chemistry of SO_4^{2-} and NO_3^- in the atmosphere is far from understood (e.g.,(Wolff, 1995; Brown et al., 2006). Thus far, the mechanism of nssSO_4^{2-} influencing NO_3^- in the snowpack, however, is still debated, and it cannot be ruled out that nssSO_4^{2-} further affects mobilization of NO_3^- during and/or after crystallization (Legrand and Kirchner, 1990; Wolff, 1995; Röthlisberger et al., 2000). It is noted that no relationship was found between nssSO_4^{2-} and NO_3^- in inland snow (Fig. 7d), possibly due to the strong alteration of NO_3^- during post-depositional processes, as discussed in section 4.1.2.

End of responses to Prof. Savarino.

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End of the responses.

Nitrate deposition and preservation in the snowpack along a traverse from coast to the ice sheet summit (Dome A) in East Antarctica

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Abstract. ~~The~~ Antarctic ice core nitrate (NO_3^-) can provide a unique record of the atmospheric reactive nitrogen cycle. However, the factors influencing the deposition and preservation of NO_3^- at the ice sheet surface must first be understood. Therefore, an intensive program of snow sample collections was made on a traverse from the coast to the ice sheet summit, Dome A, East Antarctica. Snow samples in this observation include 120 surface snow samples (top ~3cm), 20 snowpits with depths of 150 to 300cm, and 6 crystal ice samples (the topmost needle like layer on Dome A plateau)~~, and NO_3^- concentrations in these samples were determined~~. The main purpose of this investigation is to characterize the distribution pattern and preservation of NO_3^- concentrations in the snow in different environments. Results show that an increasing trend of NO_3^- concentrations with distance inland is present in surface snow, and NO_3^- is extremely enriched in the crystal ice (with a maximum of 16.1 μeq L^{-1}). NO_3^- concentration profiles for snowpits vary between coastal and inland sites. On the coast, the deposited NO_3^- was largely preserved, and the archived NO_3^- fluxes are dominated by snow accumulation. The relationship between the archived NO_3^- and snow accumulation rate can be well depicted by a linear model, suggesting a homogeneity of atmospheric NO_3^- levels. It is estimated that dry deposition contributes 27-44 % of the archived NO_3^- fluxes, and the dry deposition velocity and scavenging ratio for NO_3^- was relatively constant near the coast. Compared to the coast, the inland snow shows a relatively weak correlation between archived NO_3^- and snow accumulation, and the archived NO_3^- fluxes were more concentration dependent. The relationship between NO_3^- and ~~the~~ coexisting ions ($nssSO_4^{2-}$, Na^+ and Cl^-) was ~~assessed~~also investigated, and the results show a correlation between $nssSO_4^{2-}$ (~~the~~ fine aerosol particles) ~~could potentially influence~~and NO_3^- ~~concentrations~~in surface snow, while the correlation between NO_3^- and Na^+ (mainly associated with coarse aerosol particles) is not significant. In inland snow, there were no significant relationships found between NO_3^- and the coexisting ions, suggesting a dominant role of NO_3^- recycling in determining the concentrations.

1 Introduction

As the major sink of atmospheric nitrogen oxides (NO_x= NO and NO_2), nitrate (NO_3^-) is one of the major chemical species measured in polar snow and ice. The measurements of NO_3^- in ice cores may offer potential for understanding the complex atmospheric nitrogen cycle as well as oxidative capacity of the atmosphere through time (Legrand and Mayewski, 1997; Alexander et al., 2004; Hastings et al., 2009; Geng et al., 2017). However, the sources, transported pathways, and preservation of NO_3^- are still not well understood in Antarctic snowpack, hampering the interpretation of ice core NO_3^- records.

The accumulation of NO_3^- in snow is associated with various environmental factors and continental, ~~atmospheric~~ tropospheric and stratospheric sources could influence NO_3^- concentrations (Legrand and Kirchner, 1990; McCabe et al., 2007; Wolff et al., 2008; Lee et al., 2014). In surface snow, NO_3^- levels are thought to be linked with snow accumulation rate, and higher values are usually present in areas with low accumulation, e.g., East Antarctic plateaus (Qin et al., 1992; Erbland et al., 2013; Traversi et al., 2017). Unlike sea salt related ions (e.g., chloride (Cl^-), sodium (Na^+), and occasionally sulfate (SO_4^{2-})), NO_3^- does not usually show an elevated level in coastal Antarctic snow (Mulvaney and Wolff, 1994; Bertler et al., 2005; Frey et al., 2009), suggesting a negligible contribution from sea salt aerosols. However, the marine emissions of alkyl NO_3^-, particularly methyl and ethyl NO_3^-, produced in surface oceans by microbiological and/or photochemical processes, are thought to be a possible contribution to Antarctic NO_3^- (Jones et al., 1999; Liss et al., 2004).

~~The anthropogenic contribution, so far, is negligible in Antarctica w~~While industrial and/or agricultural emissions have contributed to increasing NO_3^- levels in Greenland snow and ice over recent decades to hundreds of years, the anthropogenic contribution to Antarctic NO_3^- is less clear (Mayewski and Legrand, 1990; Hastings et al., 2009; Felix and Elliott, 2013; Geng et al., 2014). Lightning and NO_x produced in the lower stratosphere have long been thought to play a major role (Legrand et al., 1989; Legrand and Kirchner, 1990). Recently, adjoint model simulations proposed that tropospheric transport of NO_3^- from ~~the~~ mid-low latitudes NO_x sources is an important source ~~of~~ to the Antarctica ~~NO_3^-~~ year round, though less so in austral spring/summer (Lee et al., 2014). A recent treatment of NO_3^- in snow in the same global chemical transport model suggests that the recycling of NO_3^- and/or transport of NO_x due to photolysis of NO_3^- in the surface snow layer is ~~likely~~ important in determining summertime concentrations (Zatko et al., 2016). The stratospheric inputs of NO_3^- are thought to be the result of N_2O oxidation to NO and formation of NO_3^- that is deposited via polar stratospheric cloud (PSC) sedimentation (Legrand et al., 1989; Legrand and Kirchner, 1990). ~~is also thought to be an important origin of Antarctic NO_3^-, and t~~This source has been used to explain ~~the~~ sporadic NO_3^- concentration ~~spikes~~ peaks and its associated isotopic composition in later winter and/or early spring at both coastal and inland locations (Legrand et al., 1989; Savarino et al., 2007; Frey et al., 2009). At some sites, the snow/ice core NO_3^- concentrations were found to be linked with regional atmospheric circulation (e.g., sea level pressure gradient; Goodwin et al., 2003; Russell et al., 2006). In general, atmospheric circulation appears not to affect snow NO_3^- concentrations directly, but indirectly through an influence on the air mass transport and/or snow accumulation rate (Russell et al., 2004; Russell et al., 2006). In addition, while some studies suggested that ~~Antarctic~~ snow/ice NO_3^- is ~~also thought to be~~ possibly linked with extraterrestrial fluxes of energetic particles and solar irradiation~~, and it has been reported that~~, with solar flares ~~can lead~~corresponding to ~~significant~~ NO_3^- spikes ~~in polar ice~~ (Zeller et al., 1986; Traversi et al., 2012), other observations and recent modeling studies have established that there is not a clear~~. However, there are also investigations suggesting that there is not~~

~~necessarily a~~ connection between solar variability and ~~snow~~ NO_3^- concentrations (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014; Duderstadt et al., 2016; Wolff et al., 2016). In summary, factors influencing NO_3^- levels in snow/ice are complicated, and the significance of the relationship between NO_3^- and controlling factors ~~may be~~ varies temporally and spatially ~~dependent~~.

Gas phase and snow concentration studies, and recent isotopic investigations and modeling have shown that NO_3^-, particularly in snow on the Antarctic plateau, is a combination of deposition of HNO_3 and post-depositional loss or recycling of NO_3^- (e.g., Röthlisberger et al., 2002; Davis et al., 2004; Dibb et al., 2004; Erbland et al., 2013; Erbland et al., 2015; Shi et al., 2015; Bock et al., 2016; Zatko et al., 2016). Based upon a suite of isotopic studies in the field and laboratory, it has been demonstrated that under ~~and~~ cold, sunlit conditions ultraviolet photolysis dominates NO_3^- post-depositional processing, whereas HNO_3 volatilization may become more important at warmer temperatures > -20 °C ~~and possibly volatilization are thought to be the main processes of NO_3^- loss~~ (Röthlisberger et al., 2002; Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2015). In snowpack, the solar radiation decreases exponentially, with attenuation described in terms of an *e*-folding depth (z_e) where the actinic flux is reduced to 37 % (i.e. 1/*e*) of the surface value. Thus, about 95 % of snowpack photochemistry is expected to occur above the depth of three times z_e (Warren et al., 2006). Field measurements at Dome C on the East Antarctic plateau suggest~~At remote Antarctic sites, the~~ a z_e ~~is calculated to be~~of 10 to 20 cm (France et al., 2011)~~ about 20 cm~~, and ~~this~~ the depth is dependent upon the concentration of impurities contained in the snow (Zatko et al., 2013). In the inland regions with low snow accumulation rates, particularly on the East Antarctic plateaus, photolysis has been shown to lead to significant post-depositional loss of NO_3^-, demonstrated by significant enrichment in ^{15}N of snow NO_3^- (i.e., high $\delta^{15}N$) (Frey et al., 2009; Erbland et al., 2013; Berhanu et al., 2015; Erbland et al., 2015; Shi et al., 2015), as well as a decrease in $\delta^{18}O$ and $\Delta^{17}O$ due to reformation of NO_3^- in the condensed phase (Erbland et al., 2013; Shi et al., 2015 and references therein). The transport and recycling of NO_x sourced from photolysis of snow NO_3^- in the summertime has been invoked to model the distribution of snowpack NO_3^- across the Antarctic plateau (Zatko et al., 2016). However, snow physical characteristics play a crucial role in NO_3^- deposition and preservation. For instance, summertime concentrations in the surface skin layer of snow (the uppermost ~4 mm) can be explained as the result of co-condensation of HNO_3 and water vapour, with little to no photolytic loss in this microlayer (Bock et al., 2016). The combination of concentration and isotopic studies, along with physical aspects of the snow, could lead to the reconstruction and interpretation of atmospheric NO_3^- over time (e.g., Erbland et al., 2015; Bock et al., 2016), if there is detailed understanding of the NO_3^- deposition and preservation in different environments in Antarctica.

The effects of volatilization of NO_3^- are ~~currently in debate~~uncertain, ~~and a~~ given that one field experiment suggests that this process is an active player in NO_3^- loss (17 % (-30 °C) to 67 % (-10 °C) of NO_3^- lost after two weeks' physical release experiments; Erbland et al., 2013), while other laboratory and field studies show that volatilization plays a negligible role in ~~of~~ NO_3^- ~~is negligible~~loss (Berhanu et al., 2014; Berhanu et al., 2015). Further investigations are needed to quantify the effects of volatilization for a better understanding of NO_3^- preservation in the snow/ice.~~examine the potential effects of this process, for a better understanding of post-depositional processing of NO_3^- in the snow.~~ Based on z_e, NO_3^- at deeper depths in Antarctic snow (e.g., > 100 cm), well beyond the snow photic zone, may be taken as the archived fraction. Thus, NO_3^- in deeper snow possibly provides an opportunity to investigate the archived fraction and potential influencing factors (e.g., snow accumulation rate). Given that an extensive array of ice core measurements is unavailable in most of Antarctica, the deeper snowpits (with depth > 100 cm) may offer a useful way to investigate the archived NO_3^-.

In the atmosphere in Antarctica, particularly during spring and summer, NO_3^- is found to be mainly in the form of gas phase HNO_3, with NO_3^- concentration several times higher in gas phase than in the particulate phase (Piel et al., 2006; Legrand et al., 2017b; Traversi et al., 2017). During the post-depositional processes, the uptake of gaseous HNO_3 is thought to be important in NO_3^- concentrations in surface snow layers (Udisti et al., 2004; Traversi et al., 2014; Traversi et al., 2017). Due to the high concentration in summer, HNO_3 appears to play an important role in acidifying sea-salt particles, possibly accounting for the presence of NO_3^- in the particulate phase in summer (Jourdain and Legrand, 2002; Legrand et al., 2017b; Traversi et al., 2017). It is noted that the significant increase of NO_3^- during the cold periods (e.g., Last Glacial Maximum) could be associated with its attachment to dust aerosol, instead of the gas phase HNO_3 (Legrand et al., 1999; Wolff et al., 2010).

To date, investigations on spatial and temporal patterns of snow NO_3^- have been performed on several traverses in Antarctica (e.g., 1990 International Trans-Antarctica Expedition, and DDU to Dome C; Qin et al., 1992; Bertler et al., 2005; Frey et al., 2009; Erbland et al., 2013; Pasteris et al., 2014), but these provide an uneven distribution of snow NO_3^- concentrations, leaving large regions un-sampled (e.g., Lambert Glacier basin and Dome A plateau). Over the past few decades, while several glaciological observations have been carried out on the Chinese inland Antarctic traverse route from Zhongshan to Dome A, East Antarctica (Hou et al., 2007; Ding et al., 2010; Ma et al., 2010; Ding et al., 2011; Li et al., 2013; Shi et al., 2015), ~~detailed~~ the data on snow chemistry are still rare, ~~especially~~ particularly detailed information on NO_3^-. From 2009 to 2013, we therefore conducted surface snow and snowpit sampling campaigns along the traverse route, and the main objectives were (1) to describe NO_3^- distribution in surface snow and snowpits, (2) to characterize the relationship between archived NO_3^- and snow accumulation rate, and (3) to examine the potential effects of coexisting ions on NO_3^- preservation. The results of this study may help to better understand NO_3^- deposition and preservation in the snowpack, which is critical to the interpretation of ice core NO_3^- records.

2 Methodology

2.1 Study area (Zhongshan to Dome A traverse)

The Zhongshan to Dome A CHINARE (Chinese National Antarctic Research Expedition) inland traverse is an important leg of the ITASE (International Trans-Antarctic Scientific Expedition). The traverse is in the Indian Ocean sector of East Antarctica, passing through the Lambert Glacier, the largest glacier in Antarctica. In January 1997 the first Chinese Antarctic inland expedition reached an area ~300 km from the coast; in January 1998 the traverse was extended to 464 km, and in December 1998, to the Dome A area ~1100 km from the coast. In the austral 2004/2005 summer for the first time, the traverse extended to the ice sheet summit, Dome A, a total distance of ~1260 km. In January 2009, the Chinese inland research base, Kunlun ~~Station~~station (80°25′01.7″S and 77°6′58.0″E, 4087 m above mean sea level), was established at Dome A, mainly aiming at deep ice core drilling and astronomical observations. Now, Kunlun base is a summer station, and the CHINARE team typically conducts an annual inland traverse from the coastal Zhongshan station to Dome A.

In January 2010, the Dome A deep ice core project was started, and the construction of basic infrastructure (including drill trench and scientific workroom) ~~cost~~ took 4 summer seasons. The deep ice core drilling began in January 2013, and in total 801 m ice core was recovered by 2016/2017 season. The investigation of NO_3^- deposition and preservation in the snowpack will be of help to the interpretation of Dome A deep ice core NO_3^- records.

2.2 Sample collection

During the 2010/2011 CHINARE, surface snow samples (the topmost ~3 cm) were collected at an interval of ~10 km along the traverse route from Zhongshan to Dome A, using 3.0 cm diameter high-density polyethylene (HDPE) bottles (volume = 100 ml). The bottles were pre-cleaned with Milli-Q ultrapure water (18.2 MΩ), until electrical conductivity of the water stored in bottles (> 24 h) decreased to <0.5 µS cm^{-1}. Then, the bottles were dried under a class 100 super clean hood at 20 ^{o}C. Immediately after the drying procedure, the bottles were sealed in clean PE bags that were not opened until the field sampling started. At each sampling site (typically > 500 m away from the traverse route), the bottles were pushed into surface snow layers in the windward direction. In total, 120 surface snow samples were collected. In addition, at each sampling site, the upper snow density (~10 cm) was measured using a density scoop with the volume of 1000 cm^3. Pre-cleaned bottles filled with Milli-Q water taken to the field and treated to the same conditions as field samples to represent field blanks (*n* = 3).

On the Dome A plateau, the snow is soft and non-cohesive, and morphology of the surface snow is different from other areas on the traverse, with a needle ice crystal layer extensively developed, ~~especially~~ in particular on the sastrugi (Fig. S1 in supporting information). The depth of the needle-like crystal ice layer (referred to as the “crystal ice” in the following context) is generally < 1.0 cm. In order to investigate air-snow transfer of NO_3^- in this uppermost ~1 cm layer, the crystal ice was collected using a clean HDPE scoop, and then was poured into the clean wide mouth HDPE bottles. Approximately 30 g of crystal ice was collected for each sample. In total, 6 crystal ice samples were collected on the traverse near Dome A plateau.

In addition to surface snow, snowpit samples were collected during CHINARE inland traverse campaigns in 2009/2010, 2010/2011, and 2012/2013. The snowpits were excavated manually, and the snow wall in the windward direction was scraped clean and flat with a clean HDPE scraper. Then the bottles were pushed horizontally into the snow wall. Snowpit samples were collected from the base towards the top layer along a vertical line. During the sampling process, all personnel wore PE gloves and facemasks to minimize potential contamination. Note that the snowpits are generally > 1 km from the traverse route to ~~also~~ avoid possible contamination from the expedition activities. The full information about individual snowpits, including location, distance from the coast, elevation, snowpit depth, sampling resolution, collection date, and annual snow accumulation rate, is summarized in Table 1. All together, 20 snowpits (SP1 to SP20 in Fig. 2, with SP20 corresponding to the location of Kunlun station at Dome A), 1741 snow samples, were collected.

After snow collection, the bottles were sealed in clean PE bags again and preserved in clean thermal insulated boxes. All of the samples were transported to the laboratory under freezing conditions (< -20 ^{o}C).

2.3 Sample analysis

Snow samples were melted in the closed sampling bottles on a super clean bench (class 100) before chemical measurements. Analyses of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} were performed using a Dionex ICS-3000 ion chromatography system. The column used for cation analysis (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was a Dionex column CS12 (2×250 mm), with a guard column CG12 (2×50 mm); while the anions (Cl^-, NO_3^- and SO_4^{2-}) were analyzed using a Dionex column AS11 (2×250 mm) with a guard column AG11 (2×50 mm). The eluent for cations was 18.0 mM methanesulfonic acid (MSA), and the gradient elution method was employed for anion analysis, with eluent of potassium hydroxide (KOH). More details on this method are described in a previous report (Shi et al., 2012). During sample analysis, duplicated samples and field blanks were synchronously analyzed. The pooled standard deviation (σ_p, $\sigma_p = \sqrt{\sum_{i=1}^{k}(n_i-1)s_i^2/\sum_{i=1}^{k}(n_i-1)}$, where n_i and s_i^2 are the size and variance of the *i*th samples respectively, and k is the total number of sample sets) of all replicate samples run at least twice in two different sample sets is 0.019 (Cl^-), 0.023 (NO_3^-), 0.037 (SO_4^{2-}), 0.022 (Na^+), 0.039 (NH_4^+), 0.006 (K^+), 0.006 (Mg^{2+}) and 0.006 (Ca^{2+}) μeq L^{-1} respectively (n = 65 pairs of samples). Ion concentrations in field blanks (n = 3) are generally lower than the detection limit (DL, 3 standard deviations of water blank in the laboratory).

For Antarctic snow samples, the concentrations of H^+ are usually not measured directly, but deduced from the ion-balance disequilibrium in the snow. Here, H^+ concentration is calculated through ion balance~~ as follows (Legrand and Delmas, 1988)~~.

$[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] - [Na^+] - [NH_4^+] - [Mg^{2+}] - [Ca^{2+}]$ (Eq. 1),

where ion concentrations are in μeq L^{-1}. In addition, the non-sea~~-~~ salt fractions of SO_4^{2-} (nssSO_4^{2-}) and Cl^- (nssCl^-) can be calculated from the following expressions, by assuming Na^+ exclusively from sea salt (in μeq L^{-1}).

$[nssSO_4^{2-}] = [SO_4^{2-}] - 0.12 \times [Na^+]$ (Eq. 2),

$[nssCl^-] = [Cl^-] - 1.17 \times [Na^+]$ (Eq. 3).

It is noted that SO_4^{2-} fractionation (the precipitation of mirabilite ($Na_2SO_4 \cdot 10H_2O$)) may introduce a bias in nssSO_4^{2-}, particularly during the winter half year (Wagenbach et al., 1998a).

3 Results

3.1 NO_3^- concentration in surface snow

Concentrations of NO_3^- in surface snow are shown in Fig. 1, ranging from 0.6 to 5.1 μeq L^{-1}, with a mean of 2.4 μeq L^{-1}. One standard deviation (1σ) of NO_3^- concentration in surface snow is 1.1 μeq L^{-1}, with coefficient of variation ~~*Cv*~~ (*Cv*, 1σ over mean) of 0.5, indicating a moderate spatial variability. On the coastal ~450 km, NO_3^- shows a slightly increasing trend towards the interior, with a low variability, while NO_3^- concentrations are higher in the inland region, with a large fluctuation. It is notable that in the area ~800 km from the coast, where snow accumulation is relatively high, NO_3^- concentrations decrease to < 2.0 μeq L^{-1}, comparable to the values on the coast. Near the Dome A plateau (> 1000 km from coast), there is a tendency for higher NO_3^- concentrations (> 5.0 μeq L^{-1}).

The percentage that surface snow NO_3^- contributes to total ions (i.e., total ionic strength, sum of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} and H^+, in μeq L^{-1}) varies from 6.7 to 37.6 % (mean = 27.0 %; Fig. S2 in supporting information), with low values near the coast and high percentages on the plateau. A strong relationship was found between NO_3^- and the total ionic strength in surface snow (R^2 = 0.55, p < 0.01).

In the crystal ice, the means (ranges) of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} and H^+ concentrations are 0.98 (0.62 – 1.27), 10.40 (8.35 – 16.06), 1.29 (0.87 – 2.13), 0.27 (0.21 – 0.33), 0.24

(0.03 – 0.56), 0.05 (0.03 – 0.08), 0.18 (0.15 – 0.22), 0.18 (0.05 – 0.57) and 11.75 (9.56 – 18.12) μeq L^{-1}, respectively. H^+ and NO_3^- are the most abundant species, accounting for 46.4 and 41.0 % of the total ions, followed by SO_4^{2-} (5.1 %) and Cl^- (3.9 %). The other 5 cations, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, only represent 3.6 % of the total ion budget. A significant linear relationship was found between NO_3^- and the total ionic strength ($R^2 = 0.99$, $p < 0.01$), possibly suggesting that NO_3^- is the species controlling ion abundance by influencing acidity of the crystal ice (i.e., H^+ levels). In comparison with surface snow, concentrations of H^+ and NO_3^- are significantly higher in crystal ice (Independent Samples T Test, $p<0.01$), while concentrations of Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} are comparable in the two types of snow samples (Fig. S2 in supporting information). To date, the information on the chemistry of ice crystal is rather limited but data from the so-called skin layer at Dome C (top ~4 mm snow), where NO_3^- concentrations are in the range of 9 – 22 μeq L^{-1} in summertime (Erbland et al., 2013), are generally comparable to our observations.

~~NO_3^- concentrations range from 8.4 to 16.1 μeq L^{-1} (mean = 10.4 μeq L^{-1}), significantly higher than those of surface snow (Independent Samples t Test, $p<0.01$; Fig. 1). In the crystal ice, the percentage of NO_3^- accounting for the total ions is 38-42 %, higher than the values of surface snow. In general, NO_3^- concentrations in crystal ice are comparable to the values of the top 0.4 cm snow layer at Dome C (9 – 22 μeq L^{-1} in summertime;(Erbland et al., 2013). If H^+ is excluded for the calculation of total ionic strength in crystal ice, the percent increases to 72-80 %. In addition, a significant correlation was found between NO_3^- and the total ionic strength in crystal ice ($r = 0.99$, $p < 0.01$).~~

NO_3^- concentrations in surface snow have been widely measured across Antarctica (Fig. 2), and the values vary from 0.2 to 12.9 μeq L^{-1}, with a mean of 2.1 μeq L^{-1} (n = 594, 1σ = 1.7 μeq L^{-1}) and a median of 1.4 μeq L^{-1}. Most of the data (87 %) fall in the range of 0.5 - 4.0 μeq L^{-1}, and only 7 % of the values are above 5.0 μeq L^{-1}, mainly distributed on the East Antarctic plateaus. Spatially, NO_3^- concentrations show an increasing trend with distance inland, and the values are higher in East than in West Antarctica. Overall, this spatial pattern is opposite to that of the annual snow accumulation rate (Arthern et al., 2006), i.e., low (high) snow accumulation corresponds to high (low) NO_3^- concentrations. It is difficult to compare with NO_3^- concentrations derived from the "upper snow layer" in different studies because each study sampled a different depth (Fig. 2), e.g., 2 - 10 cm for DDU-Dome C traverse (Frey et al., 2009; Erbland et al., 2013), 25 cm for the 1989-1990 International Trans-Antarctica Expedition (Qin et al., 1992) and 3 cm for this study. The different sampling depths ~~appears to~~can result in large differences in NO_3^- concentration, especially on the East Antarctic plateaus (e.g., the values of the topmost 1 cm of snow, the crystal ice in this study, can be up to >15 μeq L^{-1}; Fig. 1). In this case, any comparison of NO_3^- concentrations in surface snow collected in different campaigns should be made with caution.

3.2 Snowpit NO_3^- concentrations

Mean NO_3^- concentrations for snowpits are shown in Fig. 1. On the coastal ~450 km, snowpit NO_3^- means are comparable to those of surface snow; whereas, NO_3^- means are lower in inland snowpits than in surface snow with the exception of sites ~800 km from the coast. In general, the differences between snowpit NO_3^- means and the corresponding surface snow values are small at sites with high snow accumulation (e.g., close to coast), while the differences are large in low snow accumulation areas (e.g., near Dome A).

The profiles of NO_3^- for all snowpits are shown in Fig. 3. NO_3^- concentrations vary remarkably with depth in pits SP1 - SP5, which are located near the coast. Although SP2 and SP5 show high NO_3^-

concentrations in the topmost sample, the data from deeper depths can be compared with the surface values. In addition, NO_3^- means for the entire snowpits are close to the means of the topmost layer covering a full annual cycle of accumulation (i.e., the most recent year of snow accumulation) at SP1-SP5 (Fig. 4). Given the high snow accumulation (Fig. 1), NO_3^- variability in coastal snowpits is likely suggestive of a seasonal signature (Wagenbach et al., 1998b; Grannas et al., 2007; Shi et al., 2015). Among the coastal snowpits, water isotope ratios ($\delta^{18}O$ of H_2O) of samples at SP02 were also determined, thus allowing for investigating NO_3^- seasonal variability (Fig. S3 in supporting information). In general, the $\delta^{18}O(H_2O)$ peaks correspond to high NO_3^- concentrations (i.e., NO_3^- peaks present in summer). This seasonal pattern is in agreement with previous observations of NO_3^- in snow/ice and atmosphere in coastal Antarctica (Mulvaney and Wolff, 1993; Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007).

In contrast, most of the inland snowpits show high NO_3^- concentrations in the top layer, and then fall sharply from > 2.0 μeq L^{-1} in top snow to < 0.2 μeq L^{-1} in the first meter of depth (Fig. 3). NO_3^- means for the entire snowpits are typically lower than those of the most recent ~~one-~~year snow layer (Fig. 4). Similar NO_3^- profiles for snowpits have been reported elsewhere in Antarctica, ~~maybe resulted from~~as a result of post-depositional processing of NO_3^- (Röthlisberger et al., 2000; McCabe et al., 2007; Erbland et al., 2013; Shi et al., 2015).

Comparison of the NO_3^- profile patterns reveals significant spatial heterogeneity, even for neighboring sites. For instance, sites SP11 and SP12, 14 km apart, feature similar snow accumulation rate (Table 1). If it is assumed that snow accumulation is relatively constant during the past several years at SP11 (sampled in 2012/2013), snow in the depth of ~54 cm corresponds to the deposition in 2009/2010 (snow density = 0.45 g cm^{-3}, from field measurements). NO_3^- concentrations are much higher in the top snow of SP12 (sampled in 2009/2010) than in the depth of ~54 cm in SP11 (Fig. 3). This variation in NO_3^- profiles at a local scale has been reported, possibly related to local morphologies associated with sastrugi formation and wind drift (Frey et al., 2009; Traversi et al., 2009). It is interesting that higher NO_3^- concentrations were not found in the uppermost layer at sites SP7 and SP8 (~600 km from coast; Fig. 3), where large sastrugi with hard smooth surfaces was extensively developed (from field observations; Fig. ~~S2~~S4 in supporting information). Snow accumulation rate in this area fluctuates remarkably, and the values of some sites are rather small or close to zero due to the strong wind scouring (Fig. 1) (Ding et al., 2011; Das et al., 2013). In this case, the snowpit NO_3^- profiles appear to be largely influenced by wind scour on snow, possibly resulting in missing years and/or intra-annual mixing.

4 Discussion

4.1 Accumulation influence on NO_3^-

The preservation of NO_3^- is thought to be closely associated with snow accumulation, where most of the deposited NO_3^- is preserved at sites with higher snow accumulation (Wagenbach et al., 1994; Hastings et al., 2004; Fibiger et al., 2013). Whereas, NO_3^- may be altered significantly at sites with low snow accumulation, largely due to photolysis (Blunier et al., 2005; Grannas et al., 2007; Frey et al., 2009; Erbland et al., 2013; Erbland et al., 2015). In the following discussion, we divide the traverse into two zones, i.e., the coastal zone (~< 450 km from the coast, including SP1-SP5 and Core 1; Table 1) and the inland region (~450 km to Dome A, including pits SP6-SP20 and Core 2; Table 1), following NO_3^- distribution patterns in surface snow and snowpits (sections 3.1 and 3.2) as well as the spatial pattern of snow accumulation rate (Fig. 1).

As for snowpits, NO$_3^-$ levels in top and deeper layers are comparable near the coast, while NO$_3^-$ differs considerably between the upper and deeper snow at inland sites (Figs. 3 and 4). It is ~~proposed~~ demonstrated that photochemical processing is responsible for NO$_3^-$ distribution in inland snowpits (Erbland et al., 2013; Berhanu et al., 2015). Considering that the actinic flux is always negligible below the depth of 1 m, the bottom layers of the snowpits (i.e., > 100 cm; Table 1) are well below the photochemically active zone (France et al., 2011; Zatko et al., 2013). In this case, NO$_3^-$ in the bottom snowpit, i.e., below the photic zone, can be taken as the archived fraction without further modification on the basis of previous observations (Frey et al., 2009; Erbland et al., 2013; Erbland et al., 2015). Here, we define NO$_3^-$ in the bottom layer covering a full annual cycle of deposition as an approximation of the annual mean of ~~preserved~~ archived NO$_3^-$ (i.e., beyond photochemical processing; denoted as "~~p-concentration~~$C_{archived}$" in the following context; Fig. 4), thus allowing for calculating the archived annual NO$_3^-$ flux (i.e., the product of $C_{archived}$~~p-concentration~~ and annual snow accumulation rate). Although there is uncertainty over the calculation of archived NO$_3^-$ flux due to interannual variability in NO$_3^-$ inputs and snow accumulation, this assumption provides a useful way to investigate the relationship between preservation of NO$_3^-$ and physical factors considering that an extensive array of ice core measurements is unavailable in most of Antarctica. It is noted that $C_{archived}$~~p-concentration~~ is generally close to (lower than) the NO$_3^-$ means for entire snowpits in coastal (inland) Antarctica (Fig. 4).

4.1.1 NO$_3^-$ in coastal snowpack

The simplest plausible model to relate flux and concentration of NO$_3^-$ in snow to its atmospheric concentration (Legrand, 1987; Alley et al., 1995) can be expressed as

$$F_{total} = K_1 C_{atm} + K_2 C_{atm} A \text{ (Eq. 4)},$$

$$F_{total} = C_{firn} \times A \text{ (Eq. 5)},$$

where F_{total} is snow NO$_3^-$ flux (μeq m^{-2} a^{-1}); C_{atm} is atmospheric concentration of NO$_3^-$ (μeq m^{-3}); A is annual snow accumulation rate (kg m^{-2} a^{-1}); C_{firn} is measured firn NO$_3^-$ concentration (μeq L^{-1}, here $C_{firn} = C_{archived}$); K_1 is the dry deposition velocity (cm s^{-1}); and K_2 is the scavenging ratio for precipitation (m^3 kg^{-1}), which allows to convert atmospheric concentration to snow concentration of NO$_3^-$ in this study. From Eqs. 4 and 5, firn NO$_3^-$ concentration can be expressed as,

$$C_{firn} = K_1 C_{atm} \times 1/A + K_2 C_{atm} \text{ (Eq. 6)}$$

If K_1 and K_2 are constants, a linear relationship between measured NO$_3^-$ concentration (C_{firn}) and snow accumulation (A) can be interpreted using Eq. 6, which assumes spatial homogeneity of fresh snow NO$_3^-$ levels and dry deposition flux in the regions. The slope ($K_1 C_{atm}$) of the linear model represents an approximation of dry deposition flux of NO$_3^-$ (i.e., an apparent dry deposition flux), while the intercept ($K_2 C_{atm}$) stands for NO$_3^-$ concentration in fresh snowfall. If dry deposition ($K_1 C_{atm}$) is much larger than wet deposition ($K_2 C_{atm} A$), the concentration of NO$_3^-$ in snow will be proportional to its concentration in the atmosphere. In the condition of a constant atmospheric concentration, larger snow accumulation will increase the flux of NO$_3^-$ but decrease its concentration in snow. While this linear model is a gross over-simplification of the complex nature of air-snow exchange of NO$_3^-$, it provides a simple approach to compare the processes occurring on the coast versus those inland. In addition, this model can provides useful parameter values in modeling NO$_3^-$ deposition/preservation at large scale, considering that observations remain sparse across Antarctica (e.g., Zatko, et al., 2016). ~~(Erbland et al., 2015; Zatko et al., 2016)If it is assumed that atmospheric NO$_3^-$ aerosol levels and dry deposition are similar at~~

~~various sites, the linear relation between concentration and inverse accumulation can present information about fresh snowfall NO_3^- levels and dry deposition fluxes, interpreted as the following model (Fischer and Wagenbach, 1996).~~

~~$C_{\text{firn}} = F(NO_3^-) \times 1/A + C_{\text{f snow}}$ (Eq. 4),~~

~~where C_{firn} is measured firn NO_3^- concentration, here taking $C_{\text{firn}} \approx$ p-concentration of NO_3^-; $F(NO_3^-)$ is annual dry deposition flux of NO_3^-; A is annual snow accumulation rate; and $C_{\text{f snow}}$ is NO_3^- concentration in fresh snowfall. A strong relationship of C_{firn} vs. $1/A$ suggests spatial homogeneity of fresh snow NO_3^- levels and dry deposition flux, and a weak correlation implies a variable condition.~~

The relationship between ~~Figure 5a shows that~~ C_{archived}~~p-concentration~~ of NO_3^- and snow accumulation rate is shown in Fig. 5. ~~is closely related to snow accumulation on the coast ($r^2 = 0.95$), and~~ The~~a very strong linear~~ linear fit of C_{archived} vs. inverse snow accumulation (R^2=0.88, p<0.01; Fig. 5a) supports the assumptions of spatial homogeneity.~~ was found between p-concentration of NO_3^- and $1/A$ for coastal snowpits (Fig. 5b), suggesting that fresh snow concentration and dry deposition flux of NO_3^- are spatially homogeneous on the coast.~~ The intercept and slope of the linear fit suggest a NO_3^- concentration in fresh snow and an apparent NO_3^- dry deposition flux of 0.7 ±0.07 μeq L^{-1} and 45.7 ±7.8 μeq m^{-2} a^{-1} respectively. The apparent dry deposition flux is opposite to the observation in Dronning Maud Land (DML) region, where the negative dry deposition flux suggested net losses of NO_3^- (Pasteris et al., 2014).

Figure ~~5c~~ 5b shows the archived fluxes of NO_3^- on the coast, with values from 104 (at the lowest accumulation site) to 169 μeq m^{-2} a^{-1} (at the highest accumulation site). ~~The strong relationship between NO_3^- flux and snow accumulation suggests that wet deposition dominates the archived NO_3^- flux.~~ Taking the calculated NO_3^- dry deposition flux of 45.7 μeq m^{-2} a^{-1}, dry deposition accounts for 27-44 % (mean = 36 %) of total NO_3^- inputs, with higher (lower) percentages at lower (higher) snow accumulation sites. This result is ~~consistent~~ in line with the observations in Taylor Valley (coastal West Antarctica), where the snowfall was found to be the primary driver for NO_3^- inputs (Witherow et al., 2006). This ~~result~~ observation ~~is~~ also generally ~~consistent~~ agrees with, but is greater than that in the modeling study of Zatko et al. (2016), which predicts a ratio of dry deposition to total deposition of NO_3^- in Antarctica as < 20 % close to the coast, increasing towards the plateaus.

In Figs. 5a and b, the strong linear relationships between NO_3^- and snow accumulation ~~Alley et al. (1995) proposed a model describing the relationship among snow NO_3^- flux (F_{total}) and atmospheric concentration of NO_3^- (C_{atm}) and snow accumulation rate (A), where::~~

~~$F_{\text{total}} = K_1 C_{\text{atm}} + K_2 C_{\text{atm}} A$ (Eq. 5),~~

~~$F_{\text{total}} = C_{\text{firn}} \times A$ (Eq. 6),~~

~~where K_1 is the dry deposition velocity (cm s^{-1}); dimensionless K_2 is the scavenging ratio for precipitation; and C_{firn} is the same as that in Eq 4. If K_1 and K_2 are constants, a straight line would be expected between total flux and snow accumulation, with the intercept $K_1 C_{\text{atm}}$ being an approximation of dry deposition rate. So, NO_3^- flux vs. accumulation fitting a simple straight line (Fig. 5c) suggests~~ support that K_1 and K_2 are relatively constant on the coast (Eqs. 4 and 6).~~, and the dry deposition flux value (50.3 ±8.1 μeq m^{-2} a^{-1}) is comparable to that yielded from Eq. 4 (45.7 ±7.8 μeq m^{-2} a^{-1}). Both model results support that NO_3^- dry deposition is homogeneous on the coast. If taking~~The average atmospheric concentration of NO_3^- in the coastal ~450 km region is ~~C_{atm} =~~19.4 ng m^{-3} in summer ~~near the coast~~ (Table S1 in supporting information)~~(unpublished data),~~. Taking C_{atm}=19.4 ng m^{-3}, K_1 is estimated to be 0.5 cm s^{-1}, identical to a typical estimate for HNO_3 deposition velocity to a snow/ice surface (0.5 cm s^{-1}; Seinfeld and Pandis, 1997). This predicted K_1 value ~~also compares well to~~is lower than that ~~estimated~~ calculated for the dry deposition of HNO_3 at South Pole (0.8 cm s^{-1}~~)~~; Huey et al., 2004). It is noted that the true K_1 value could be larger than the prediction (0.5 cm s^{-1}) due to the higher atmospheric NO_3^- concentrations during summertime (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007). The scavenging ratio for ~~NO_3^-~~ precipitation (K_2) is ~~estimated~~ calculated to be 0.2×10^4~~,~~, $m^3\ kg^{-1}$, i.e., 2 $m^3\ g^{-1}$.~~–~~

If it is assumed that NO_3^- concentration in snow is related to its concentration in the atmosphere, the scavenging ratio for NO_3^- (*W*) can ~~The scavenging ratio for NO_3^- (K_2) can also~~ be calculated on a mass basis from the following expression (Kasper-Giebl et al., 1999),

$$W = \rho_{atm} \times (C_{f\text{-}snow} / C_{atm})\ \text{(Eq. 7)},$$

where ρ_{atm} is air density (g m^{-3}), and $C_{f\text{-}snow}$ and C_{atm} are NO_3^- concentrations in fresh snow (ng g^{-1}) and atmosphere (ng m^{-3}) respectively. If taking $\rho_{atm} \approx 1000$ g m^{-3} (on average, ground surface temperature $t \approx 255$ k, ground pressure $P \approx 0.08$ MPa, in the coastal region~~the average ground surface temperature $t \approx 255$ k, and ground pressure $P \approx 0.08$ MPa near the coast~~), $C_{f\text{-}snow}$ = 43 ng g^{-1} (see discussion above and section 4.2 below), and C_{atm} = 19.4 ng m^{-3}, *W*~~K_2~~ is calculated to be ~2200, generally comparable to previous reports (Barrie, 1985; Kasper-Giebl et al., 1999; Shrestha et al., 2002). It is noted that the calculation here may be subject to uncertainty, due to the complex transfer of atmospheric NO_3^- into the snow. However, the scavenging ratio provides useful insights into the relation between NO_3^- concentrations in the atmosphere and snow, which might be useful in modeling NO_3^- deposition at large-scale.

Figure ~~5d~~ 5c shows the distribution of flux is negatively ~~tied~~ correlated with ~~to~~ $C_{archived}$~~p-concentration~~ of NO_3^-, which is not surprising since $C_{archived}$~~p-concentration~~ is ~~negatively~~ positively related to inverse accumulation (Fig. 5a). Based on the observed strong linear relationship between NO_3^- flux and snow accumulation~~the regression analysis~~ (Figs. ~~5c~~ 5b~~and d~~), the archived NO_3^- flux is more accumulation dependent compared to $C_{archived}$~~the concentration~~.~~–~~ This is compatible with the observations in Greenland (Burkhart et al., 2009), where accumulation is generally above 100 kg $m^{-2}\ a^{-1}$~~.~~, similar to the coastal values in this study.

In terms of surface snow on the coast, NO_3^- may be disturbed by the katabatic winds and wind convergence located near the Amery Ice Shelf (that is, the snow-sourced NO_x and NO_3^- from Antarctic plateau possibly contribute to coastal snow NO_3^-) (Parish and Bromwich, 2007; Ma et al., 2010; Zatko et al., 2016). In addition, the sampled ~3 cm surface layer roughly corresponds to the net accumulation in the past 0.5-1.5 months assuming an even distribution of snow accumulation in the course of a single year. This difference in exposure time of the surface snow at different sampling sites, could possibly affect the concentration of NO_3^-, although the post-depositional alteration of NO_3^- was thought to be minor on the coast (Wolff et al., 2008; Erbland et al., 2013; Shi et al., 2015). Taken together, NO_3^- in coastal surface snow might represent some post-depositional alteration. Even so, a negative ~~correlation~~ correlation between NO_3^- concentration and snow accumulation rate was found at the coast (~~R^2~~R^2=0.42, p<0.01; Fig. 6a), suggesting that overall the majority of the NO_3^- appears to be preserved and is driven by snow accumulation.

4.1.2 NO_3^- in inland snowpack

In comparison with the coast, the ~~association~~ correlation between $C_{archived}$~~p-concentration~~ and inverse snow accumulation is relatively weak in inland ~~Antarctica~~ regions (Fig~~s~~. 5~~e and f~~d), suggesting more variable conditions in ambient concentrations and dry deposition flux of NO_3^-. In addition, the relationship of $C_{archived}$~~p-concentration~~ vs. ~~(~~inverse~~)~~ accumulation in inland is opposite to that of coast.

Based on current understanding of the post-depositional processing of NO_3^-, the negative correlation between $C_{archived}$~~p concentration~~ and inverse snow accumulation (Fig. ~~5f~~5d) ~~possibly~~ suggests losses of NO_3^-. The slope of the linear relationship indicates apparent NO_3^- dry deposition flux of -44.5 ±13.0 μeq m^{-2} a^{-1}, much larger than that of DML (-22.0 ±2.8 μeq m^{-2} a^{-1}), where the snow accumulation is generally lower than 100 kg m^{-2} a^{-1} (Pasteris et al., 2014). At Kohnen Station (an inland site in East Antarctica), with snow accumulation of 71 kg m^{-2} a^{-1}, the emission flux of NO_3^- is estimated to be -22.9 ±13.7 μeq m^{-2} a^{-1} (Weller and Wagenbach, 2007), which is also smaller in comparison with this observation. Weller et al. (2004) proposed that loss rate of NO_3^- does not depend on snow accumulation rate and the losses become insignificant at accumulation rates above 100 kg m^{-2} a^{-1}. Among the inland sites, SP10 and Core2 (~800 km from the coast), featured by high snow accumulation rate (> 100 kg m^{-2} a^{-1}; Table 1 and Fig. 1), exhibit even higher values of $C_{archived}$ and archived fluxes of NO_3^- than those of the coastal sites. It is noted that the two cases influence the linear regression significantly (Fig. 5d). If the two sites are excluded, we can get a linear regression with the slope of -27.7 ±9.2 μeq m^{-2} a^{-1}, which is comparable to previous reports in DML (Pasteris et al., 2014).

The depths of inland snowpits cover past several to tens of years′ snow accumulation, thus allowing for direct investigating NO_3^- emission rate. The difference between NO_3^- concentrations in the snow layer accumulated during the most recent year (Fig. 4) and in the snow accumulated during the year before the most recent year can represent the loss rate of NO_3^-. If it is assumed that snow accumulation rate is relatively constant during past decades at specific-sites, on average, 36.7 ±21.3 % of NO_3^- (in μeq L^{-1}) was lost during one year (two sites (SP10 and Core2) with snow accumulation >100 kg m^{-2} a^{-1} excluded). The percentages are generally higher at the sites with lower snow accumulation rate. Together with snow accumulation rate, the emission flux of NO_3^- is calculated to be -28.1 ±23.0 μeq m^{-2} a^{-1}, close to the linear model prediction (-27.7 ±9.2 μeq m^{-2} a^{-1}).

The significant losses can account for NO_3^- profiles at inland sites, i.e., NO_3^- concentration decrease with increasing depths. Previous observations and modeling works suggested that photolysis dominates the losses (Frey et al., 2009; Erbland et al., 2013; Shi et al., 2015). During photolysis of NO_3^-, some of the photoproducts (NO_x) are emitted into the gas phase (Davis et al., 2004; France et al., 2011), and these products should undergo reoxidation by the local oxidants (e.g., hydroxyl radical, $NO_2 + OH + M \rightarrow HNO_3 + M$), forming gas phase HNO_3. In inland Antarctica, the dominant NO_3^- species in the atmosphere is gaseous HNO_3 during summertime, while particulate NO_3^- is more important in winter (Legrand et al., 2017b; Traversi et al., 2017). The high levels of gas phase HNO_3 in summer support the importance of the re-emission from snow through the photolysis of NO_3^- in affecting the atmospheric NO_x/NO_3^- budget (Erbland et al., 2013). On the one hand, the gaseous HNO_3 can be efficiently co-condensed with water vapour onto the extensively developed crystal ice layers on Antarctic plateaus (discussed above), leading to an enrichment of NO_3^- in surface snow (Bock et al., 2016). On the other hand, a large concentration of HNO_3 would enhance its reaction with sea-salt, leading to elevated particulate NO_3^- concentrations (Legrand et al., 2017b). The significant correlation between NO_3^- and H^+ in inland Antarctic surface snow (R^2 =0.65, p<0.01) seems to support the importance of atmospheric gas phase HNO_3 in affecting surface snow NO_3^- concentrations, in particular NO_3^- levels in the crystal ice samples (Fig. 1).

Thus far, several modeling works have been performed to understand NO_3^- recycling processes across Antarctica (e.g., Erbland et al., 2015; Zatko et al., 2016; Bock et al., 2016), however, uncertainty remains about NO_3^- recycling and preservation. It is thought that emission and transport strength are the factors controlling the recycling of NO_3^-, while the former is associated with initial NO_3^-

concentrations, UV and snow optical properties, and the latter is linked with air mass movement (Wolff et al., 2008; Frey et al., 2009). As a result, snow accumulation alone is likely insufficient to account for NO_3^- variability in surface snow (i.e., no significant correlation between NO_3^- concentration and snow accumulation; Fig. 6b).~~A similar relationship has also been documented in Dronning Maud Land (DML, with snow accumulation of 27-70 kg m^{-2} a^{-1}), where NO_3^- concentrations are strongly correlated with snow accumulation (r^2 > 0.9) (Pasteris et al., 2014). The difference in the relationship strength (NO_3^- vs. accumulation) between DML and this study is possibly related with the relatively small variability of accumulation in DML (vs. inland region under very varied conditions; Fig. 1).~~

The archived NO_3^- fluxes vary considerably among inland sites, from ~3 to 333 μeq m^{-2} a^{-1}, with high values generally corresponding to high snow accumulation~~, similar to coastal results~~ (~~compare~~ Fig~~s~~. 5~~c and g~~e). However, the nearly 1:1 relationship between $C_{archived}$~~p-concentration~~ and NO_3^- flux (Fig. ~~5h~~5f), suggests that accumulation rate is not the main driver of the ~~preserved~~ archived NO_3^- concentration. In inland Antarctica, the archived NO_3^- fraction is largely influenced by the length of time that NO_3^- was exposed to UV radiation (Berhanu et al., 2015), which decreases exponentially in the snowpack. The *e*-folding depth, z_e value, is thought to be influenced by a variety of factors, such as co-existent impurities (e.g., black carbon), bulk density and grain size (Zatko et al., 2013). In addition, the snow albedo is also dependent on snow physical properties (Carmagnola et al., 2013). Taken together, this suggests that the inland plateau is below a "threshold" of accumulation rate such that the archived NO_3^- flux ~~cannot~~cannot be explained by snow accumulation rate.

~~Among the inland sites, it is noted that SP10 and Core2 (~800 km from the coast), featured by high snow accumulation rate (> 100 kg m^{-2} a^{-1}; Table 1 and Fig. 1), exhibit higher values of p-concentration and archived fluxes of NO_3^- than those of the coastal sites. The high concentration and flux values near the two sites may be associated with NO_3^- recycling driven by photolysis (Frey et al., 2009; Zatko et al., 2016), but this speculation should be tested further (e.g., studying the isotopes of NO_3^-).~~

~~The inland region is generally characterized with low accumulation (<55 kg m^{-2} a^{-1}; Fig. 1). At these sites, snow NO_3^- is more likely to undergo post-depositional alteration, e.g., a severe loss of NO_3^- (Frey et al., 2009; Zatko et al., 2016). During photolysis, the lost NO_3^- can be recycled in the local environment, i.e., re-formed NO_3^- from photoproducts can be re-deposited, resulting in concentrated NO_3^- in surface snow (Erbland et al., 2013). It appears that the high NO_3^- concentrations in inland surface snow and crystal ice near Dome A (Fig. 1) can be explained by this mechanism. Thus far, several modeling works have been performed to understand NO_3^- recycling processes across Antarctica (e.g.,, however, much uncertainty remains about NO_3^- recycling and preservation. It is thought that emission and transport strength are the factors controlling the recycling of NO_3^-, while the former is associated with initial NO_3^- concentrations, UV and snow accumulation, and the latter is linked with air mass movement (Wolff et al., 2008; Frey et al., 2009). As a result, snow accumulation alone is insufficient to explain NO_3^- variability in the surface snow (i.e., no significant correlation between NO_3^- concentration and snow accumulation; Figs. 6c and d).~~

4.2 Effects of coexisting ions on NO_3^-

Atmospheric NO_3^- in Antarctica is thought to be mainly associated with mid-latitude sources, re-formed NO_3^- driven by snow-sourced photolysis products, and/or stratospheric inputs (Savarino et al., 2007; Lee et al., 2014; Traversi et al., 2017 and references therein). We investigate whether NO_3^- in snow is closely associated with coexisting ions (e.g., Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}) since these ions have different main sources, e.g., Cl^- and Na^+ are predominantly influenced by sea salt, and SO_4^{2-}

is likely dominated by marine inputs (e.g., sea salt and bio-activity source) (Bertler et al., 2005). In the snow, Cl^-, Na^+ and SO_4^{2-} are the most abundant ions in addition to NO_3^-, and the potential association between NO_3^- and the three ions in the surface snow is discussed here.

~~During austral summer~~In surface snow, the non-sea salt fraction of SO_4^{2-} accounts for 75 - 99 % of its total budget, with a mean of 95 %. The percentages are relatively higher in inland regions than at coastal sites.~~snow nssSO_4^{2-}, mainly derived from ocean bioactivities, accounts for 75 – 99 % (mean=95%) of SO_4^{2-} in surface snow.~~ On the coast, a positive relationship was found between~~high~~ nssSO_4^{2-} ~~levels correspond to elevated~~and NO_3^- ~~concentrations~~ (~~r^2~~ R^2 = 0.32, p < 0.01; Fig. 7a). Previous observations suggest that NO_3^- and nssSO_4^{2-} peaks in the atmosphere and snow are usually present in summer (Jourdain and Legrand, 2002; Wolff et al., 2008; Sigl et al., 2016; Legrand et al., 2017a; Legrand et al., 2017b). However, the similar seasonal pattern of the two species is associated with distinct sources, i.e., SO_4^{2-} is mainly derived from marine biogenic emissions while NO_3^- is influenced by photolysis and tropospheric transport (Savarino et al., 2007; Lee et al., 2014; Zatko et al., 2016). In the atmosphere, most of SO_4^{2-} is on the submicron particles, while most of NO_3^- is gaseous HNO_3 and the particulate NO_3^- is mainly on the intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a; Legrand et al., 2017b). Thus, the correlation between NO_3^- and SO_4^{2-} is unlikely explained by the sources or their occurrence state in the atmosphere (i.e., gaseous and particulate phases). Laluraj et al. (2010) proposed that the correlation between nssSO_4^{2-} vs. NO_3^- in ice (R^2 = 0.31, p<0.01) could be associated with the fine nssSO_4^{2-} aerosols, which could provide nucleation centers forming the multi-ion complexes with HNO_3 in the atmosphere. This assertion, however, should be examined further, considering that the complex chemistry of SO_4^{2-} and NO_3^- in the atmosphere is far from understood (e.g., Wolff, 1995; Brown et al., 2006). Thus far, the mechanism of nssSO_4^{2-} influencing NO_3^- in the snowpack, however, is still debated, and it cannot be ruled out that nssSO_4^{2-} further affects mobilization of NO_3^- during and/or after crystallization (Legrand and Kirchner, 1990; Wolff, 1995; Röthlisberger et al., 2000). It is noted that no relationship was found between nssSO_4^{2-} and NO_3^- in inland snow (Fig. 7d), possibly due to the strong alteration of NO_3^- during post-depositional processes, as discussed in section 4.1.2.

In comparison with nssSO_4^{2-} aerosols, the sea-salt aerosols (Na^+) are coarser and can be removed preferentially from the atmosphere due to a larger dry deposition velocity. ~~(Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017b)~~High atmospheric sea salt aerosol concentrations are expected to promote the conversion of gaseous HNO_3 to particulate phase, considering that most of the NO_3^- in the atmosphere is in the gas phase (HNO_3). In this case, particulate NO_3^- can be efficiently lost via aerosol mechanisms. In addition, the saline ice also favors the direct uptake of gaseous HNO_3 to the ice surface. Changes in partitioning between gas phase (HNO_3) and particulate phase will affect NO_3^- levels due to the different wet and dry deposition rates of the two species (Aw and Kleeman, 2003). Thus, sea salt aerosols play an important role in the scavenging of gaseous HNO_3 from the atmosphere (Hara et al., 2005), and elevated NO_3^- concentrations are usually accompanied by Na^+ spikes in snowpack (e.g., at Halley station, a coastal site; Wolff et al., 2008). Here, no significant correlation was found between Na^+ and NO_3^- in coastal snow (Fig. 7b). The concentration profiles of NO_3^- and Na^+ in coastal surface snow are shown in Fig. 8, and NO_3^- roughly corresponds to Na^+ in some areas, e.g., 50-150 km and 300-450 km distance inland, although in general they are not very coherent.~~the relation seems not so strong.~~ It is noted that amongst the 4 snow samples with Na^+ > 1.5 μeq L^{-1} (open circles in Fig. 8), only one sample co-exhibits a NO_3^- spike. This is different from observations at Halley station, where Na^+ peaks usually led to elevated NO_3^- levels in surface snow in summer (Wolff et al., 2008). Of the 4 largest Na^+ spikes, one is a fresh snowfall sample (dashed ellipse in Fig. 8), and this sample shows the highest Na^+ concentration (2.8 μeq L^{-1}) and low NO_3^- (0.75 μeq L^{-1}). It is noted that NO_3^- concentration in this fresh snowfall is close to the model predictions~~ above~~ (0.7±0.07 μeq L^{-1}; section 4.1.1), validating that the simple linear deposition model (i.e., the Eq. ~~4~~6) can well depict the deposition and preservation of NO_3^- in coastal snowpack. At inland sites, no ~~association~~ correlation was found between NO_3^- and Na^+ (Fig. 7e), likely explained by the alteration of NO_3^- concentration by post-depositional processing (discussed above).

In surface snow, $nssCl^-$ represents 0-64 % (mean = 40 %) of the total Cl^-. On the coast, it is of interest that $nssCl^-$ in the 4 samples with the highest Na^+ concentrations (open circles in Figs. 7b and 8) are close to 0, and positive $nssCl^-$ values were found for the other samples. The fractionation of Na^+ can occur due to mirabilite precipitation in sea-ice formation at <-8 °C (Marion et al., 1999), possibly leading to the positive $nssCl^-$. However, even if all of SO_4^{2-} in sea water is removed via mirabilite precipitation, only 12 % of sea salt Na^+ is lost (Rankin et al., 2002). Considering ~~the very high Cl^-/Na^+ ratio (mean = 2.1) and~~ the smallest sea ice extent in summertime in East Antarctica (Holland et al., 2014), the high Cl^-/Na^+ ratio (mean = 2.1, well above 1.17 of sea water, in μeq L^{-1}) ~~$nssCl^-$ is~~ in surface snow is unlikely from sea~~-~~ salt fractionation associated with mirabilite precipitation in sea-ice formation. In this case, $nssCl^-$ could be mainly related to the deposition of volatile HCl, which is from the reaction of H_2SO_4 and/or HNO_3 with NaCl (Röthlisberger et al., 2003). In this case, $nssCl^-$ in snowpack can roughly represent the atmospherically deposited HCl. In the summertime, most of the dechlorination (i.e., production of HCl) is likely associated with HNO_3 due to its high atmospheric concentrations (Jourdain and Legrand, 2002; Legrand et al., 2017b). Thus, the observed relationship between NO_3^- and $nssCl^-$ (Fig. 7c) appears to suggest that HCl production can be enhanced by elevated HNO_3 levels in the atmosphere.~~In other words, the presence of HNO_3 possibly favors the formation of HCl, and this then result in an excess of Cl^- in the snowpack due to emissions and re-deposition of HCl, which could explain the observed relationship between NO_3^- and $nssCl^-$ (Fig. 7c).~~

With regard to the crystal ice, no significant correlation was found between NO_3^- and the coexisting ions (e.g., Cl^-, Na^+ and SO_4^{2-}), suggesting that these ions are generally less influential on NO_3^- in this uppermost thin layer, compared to the strong air-snow transfer process of NO_3^- (Erbland et al., 2013). It is noted that NO_3^- accounts for most of the calculated H^+ concentrations (81 - 97 %, mean = 89 %), and a strong linear relationship was found between them (~~r^2~~ R^2 = 0.96, $p<0.01$), suggesting that NO_3^- is mainly deposited as acid, HNO_3, rather than in particulate form as salts (e.g., $NaNO_3$ and $Ca(NO_3)_2$). This deduction is in line with the atmospheric observations at Dome C, where NO_3^- was found to be mainly in gaseous phase (HNO_3) in summer (Legrand et al., 2017b). On average, the deposition of HNO_3 contributes > 91 % of NO_3^- in the crystal ice (the lower limit, 91 %, calculated by assuming all of the alkaline species (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) are neutralized by HNO_3 in the atmosphere), suggesting a dominant role of HNO_3 deposition in snow NO_3^- concentrations. The elevated high atmospheric NO_3^- concentrations observed at Dome A (>100 ng m^{-3}; 77.12° E and 80.42° S, Table S1 in supporting information) possibly indicate oxidation of gaseous NO_x to HNO_3, providing further evidence that NO_3^- recycling driven by photolysis plays an important role in its abundance in snowpack on East Antarctic plateaus.~~If all of the HNO_3 dissociates to produce H^+ and NO_3^- ions, then the deposition of HNO_3 contributed 76 – 84 % (mean = 80 %) to the total chemical constituents in the crystal ice.~~

5 Conclusions

Samples of surface snow, snowpits and the uppermost layer of crystal ice, collected on the traverse from the coast to Dome A, East Antarctica, were used to investigate the deposition and preservation of NO_3^- in snow. In general, a spatial trend of NO_3^- in surface snow was found on the traverse, with high (low) concentrations on the plateau (coast). Extremely high NO_3^- levels (e.g., > 10 μeq L^{-1}) were observed in the uppermost crystal ice layer, possibly associated with re-deposition of the recycled NO_3^-. As for the snowpits, NO_3^- exhibits high levels in the top layer and low concentrations at deeper depths in the inland region, while no clear trend was found on the coast.

On the coast, the archived NO_3^- flux in snow is positively correlated with snow accumulation rate, but negatively with NO_3^- concentration. A linear model can well depict the relationship between archived NO_3^- and snow accumulation, ~~suggesting~~ supporting that atmospheric levels and dry deposition fluxes of NO_3^- are spatially homogeneous on the coast, and ~~the~~ that dry deposition plays a minor role in snow NO_3^- inputs. The dry deposition velocity and scavenging ratio for NO_3^- are estimated to be 0.5 cm s^{-1} and ~~0.2×10^4~~2200 respectively. In inland Antarctica, the archived NO_3^- fluxes, varying significantly among sites, are largely dependent on NO_3^- concentration. A weak correlation between snow accumulation and archived NO_3^- suggests variable ambient concentrations and dry deposition flux of NO_3^-, and the relationship is opposite to that for the coast. This supports the idea that post-depositional processing dominates NO_3^- concentration and distribution in inland Antarctica (e.g., Erbland et al., 2013; Erbland et al., 2015; Shi et al., 2015; Zatko et al., 2016).

~~The post-depositional processing of NO_3^- seems to dominate NO_3^- distribution patterns in surface snow and snowpits in inland Antarctica.~~

The major ions, Cl^-, SO_4^{2-} and Na^+, originate from different sources from NO_3^-, but could potentially affect the scavenging and preservation of NO_3^-. In coastal surface snow, a positive correlation between $nssSO_4^{2-}$ and NO_3^- ~~possibly supports~~ suggests the potential influence of ~~the presence of~~ fine aerosols ~~favoring~~ on NO_3^- formation and/or scavenging, while the coarse sea salt aerosol (e.g., Na^+) is likely less influential. In contrast to the coast, NO_3^- in inland surface snow is ~~likely~~ dominated by post-depositional processes, and the effects of coexisting ions on NO_3^- appear to be rather minor. In inland surface snow, the strong relationship between NO_3^- and H^+ suggests a dominant role of gaseous HNO_3 deposition in determining NO_3^- concentrations.

Associated content

Please see the file of Supporting Information.

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Table 1. Snowpit information on the traverse from coastal Zhongshan ~~station~~ Station to Dome A, East Antarctica.

Snowpit No.	Latitude, °	Longitude, °	Elevation, m	Distance to coast, km	Annual snow accumulation, kg m^{-2} a^{-1} 1)	Depth, cm	Sampling resolution, cm	Sampling year
SP1	-70.52	76.83	1613	132	193.2	150	5.0	2010/2011
SP2	-71.13	77.31	2037	200	172.0	150	3.0	2012/2013
SP3	-71.81	77.89	2295	283	99.4	200	5.0	2012/2013
SP4	-72.73	77.45	2489	387	98.3	200	5.0	2012/2013
SP5	-73.40	77.00	2545	452	90.7	200	5.0	2012/2013
SP6	-73.86	76.98	2627	514	24.6	300	2.5	2012/2013
SP7	-74.50	77.03	2696	585	29.2	100	2.0	2012/2013
SP8	-74.65	77.01	2734	602	80.2	180	2.0	2010/2011
SP9	-76.29	77.03	2843	787	54.8	200	2.0	2012/2013
SP10	-76.54	77.02	2815	810	100.7	240	3.0	2010/2011
SP11	-77.13	76.98	2928	879	81.2	200	2.5	2012/2013
SP12	-77.26	76.96	2962	893	83.4	265	5.0	2009/2010
SP13	-77.91	77.13	3154	968	33.3	200	2.0	2012/2013
SP14	-78.34	77.00	3368	1015	87.6	216	3.0	2010/2011
SP15	-78.35	77.00	3366	1017	70.0	162	2.0	2009/2010
SP16	-79.02	76.98	3738	1092	25.4	200	2.5	2012/2013
SP17	-79.65	77.21	3969	1162	46.2	130	2.0	2010/2011
SP18	-80.40	77.15	4093	1250	24.2	300	2.0	2010/2011
SP19	-80.41	77.11	4092	1254	23.7	300	1.0	2009/2010
SP20	-80.42	77.12	4093	1256	23.5	300	2.5	2012/2013
Core 1 2)	-70.83	77.08	1850	168	127.0	-	-	1996/1997
Core 2 3)	-76.53	77.03	2814	813	101.0	-	-	1998/1999

1) Annual snow accumulation rate is obtained from the field bamboo stick measurements (2009 - 2013), updated from the report (Ding et al., 2011). Note that snow accumulation rate at the two ice core sites are derived from ice core measurements.

2) Core 1, ice core data of previous report (Li et al., 1999; Xiao et al., 2004).

3) Core 2, ice core data of previous report (Li et al., 2009).

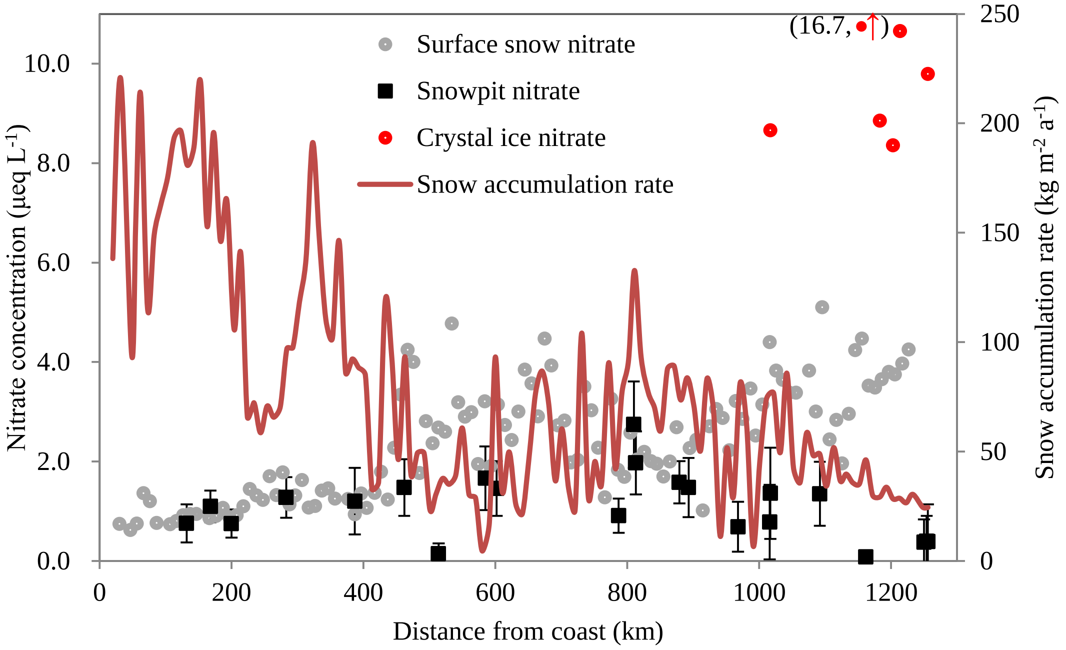


Figure 1. Concentrations of NO_3^- in surface snow, crystal ice and snowpits, with error bars representing one standard deviation of NO_3^- (1σ) for individual snowpits. Also shown is the annual snow accumulation rate on the traverse (red solid line; based on Ding et al. (2011)). Note that NO_3^- concentration in one crystal ice sample (red dot), 16.7 μeq L^{-1} in the parentheses, is higher than the maximum value of the primary *y*-axis (NO_3^- concentration).

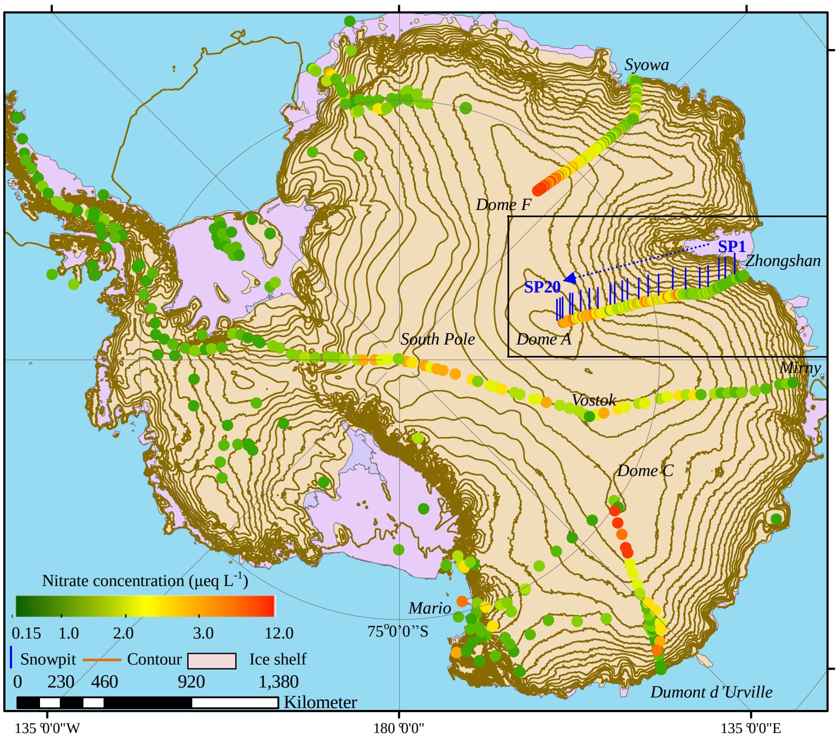
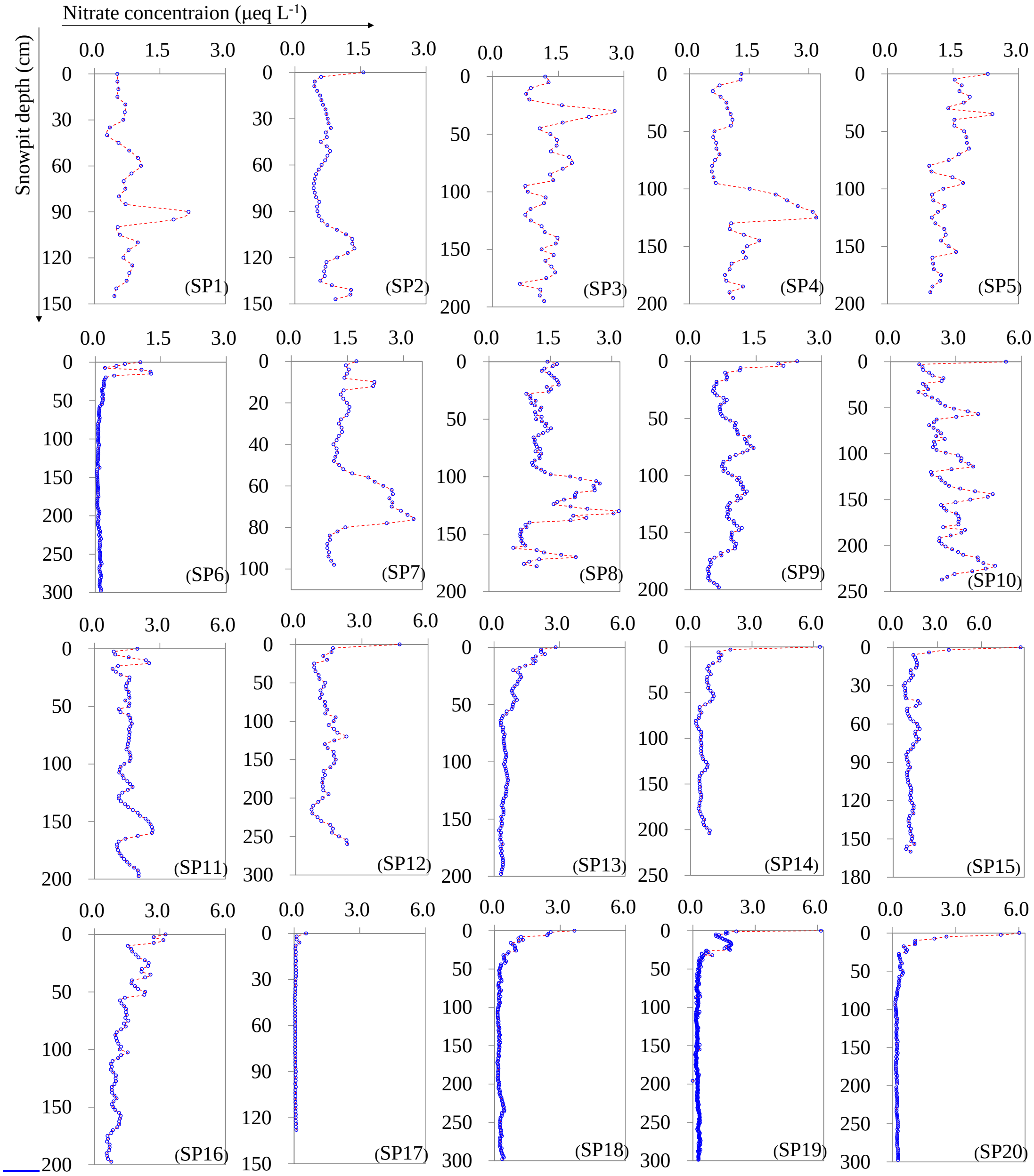


Figure 2. Concentrations of NO$_3^-$ in surface snow across Antarctica. Note that the values of crystal ice around Dome A were not included. The data of DDU to Dome C is from Frey et al. (2009). The other surface snow NO$_3^-$ concentrations are from the compiled data (Bertler et al., 2005 and references therein). Also illustrated are the locations of snowpits on the traverse route from Zhongshan to Dome A in this study (SP1 to SP20, solid short blue line; Table 1).


Nitrate concentraion (μeq L-1)
Snowpit depth (cm)
0.0 1.5 3.0
0.0 3.0 6.0
0 30 60 90 120 150
0 50 100 150 200
0 50 100 150 200 250 300
0 20 40 60 80 100
0 50 100 150 200 250
0 30 60 90 120 150 180
(SP1)
(SP2)
(SP3)
(SP4)
(SP5)
(SP6)
(SP7)
(SP8)
(SP9)
(SP10)
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(SP19)
(SP20)

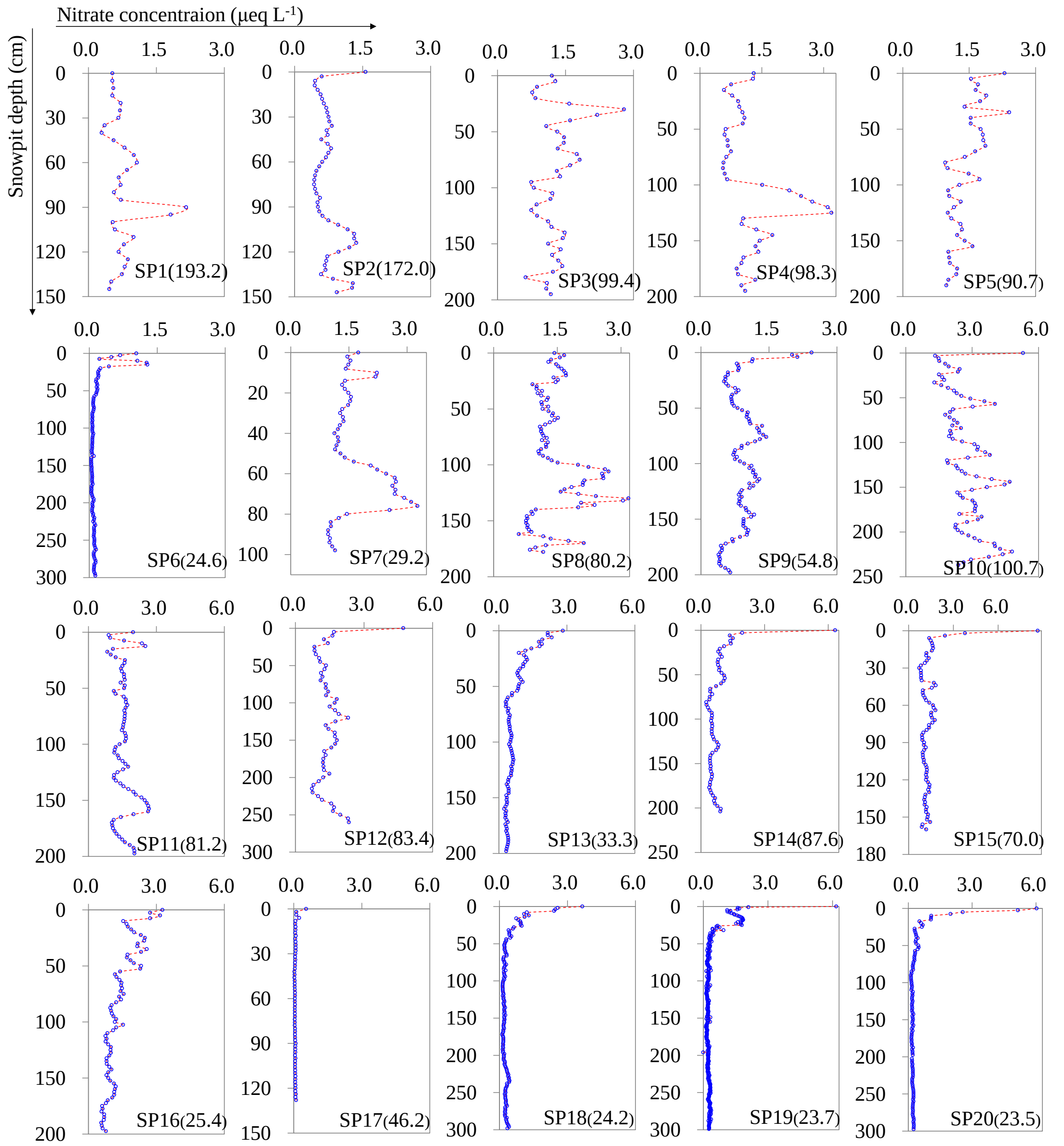
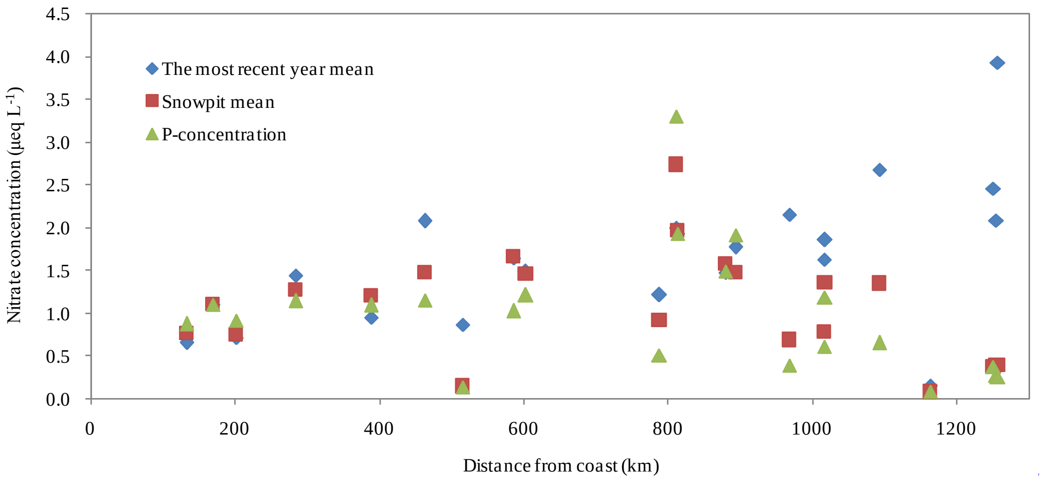


Figure 3. The full profiles of NO_3^- concentrations for snowpits collected on the traverse from the coast to Dome A, East Antarctica (SP1 is closest the coast; SP20 the furthest inland; see Figure 2). The details on sampling of the snowpits refer to Table 1. The numbers in parentheses in each panel denote the annual snow accumulation rates (kg m^{-2} a^{-1}). Note that the scales of x-axes for the snowpits SP1 – SP9 and SP10 – SP 20 are different.



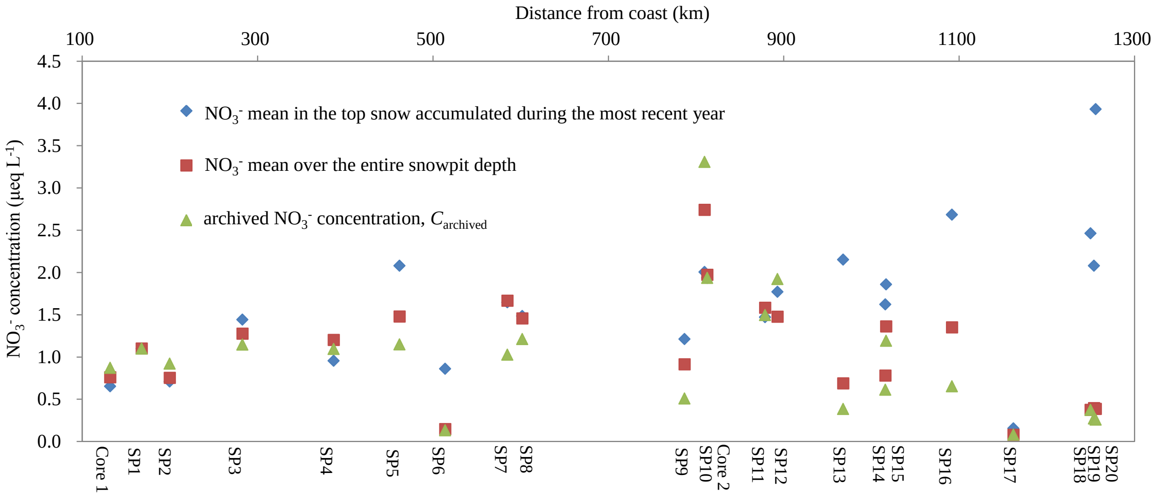
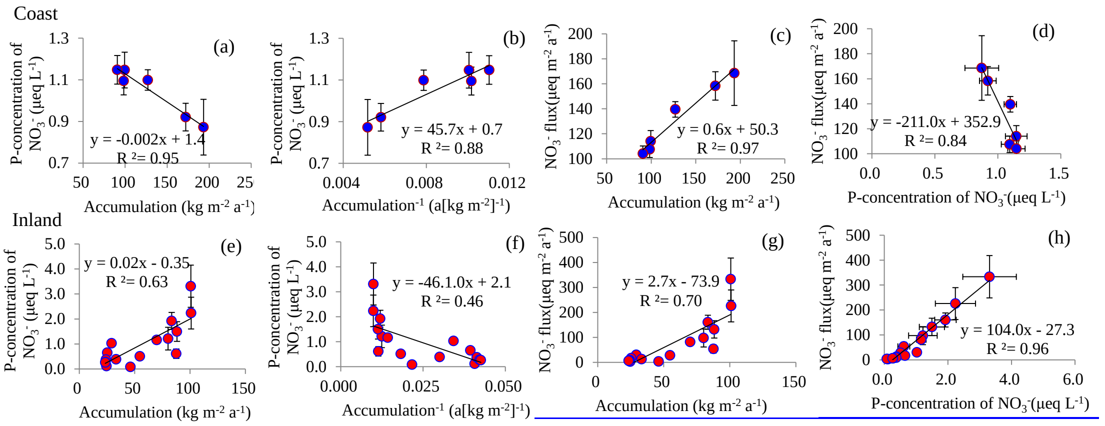


Figure 4. Mean concentrations of NO_3^- for the entire snowpit depth (~~snowpit mean,~~ in square), the uppermost layer covering one-year snow accumulation (~~the most recent year mean,~~ in diamond) and the bottom layer covering a full annual cycle of deposition (~~p-concentration~~archived NO_3^- concentration, $C_{archived}$, in triangle).



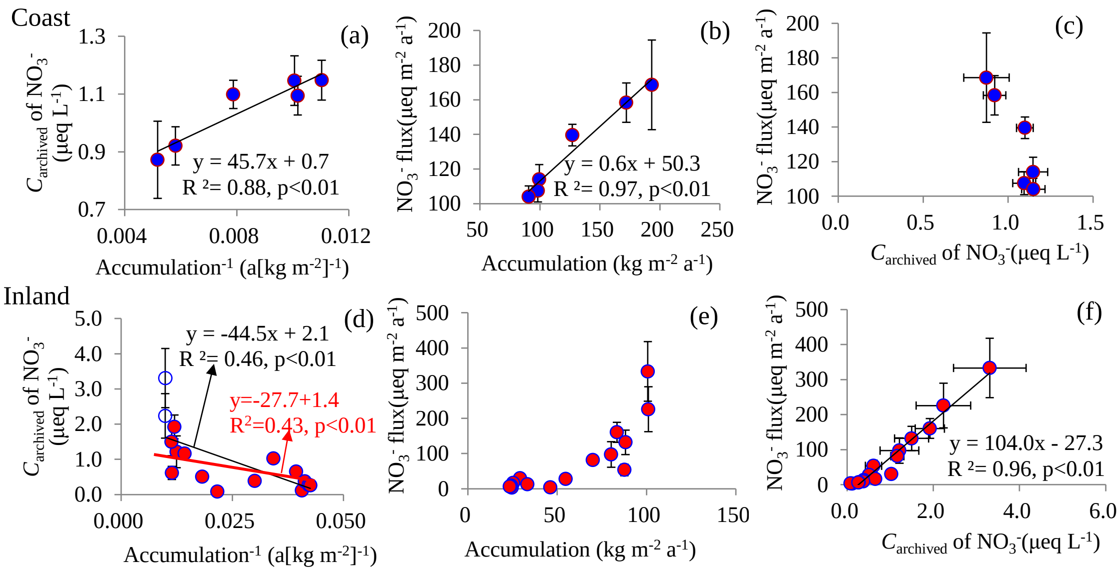
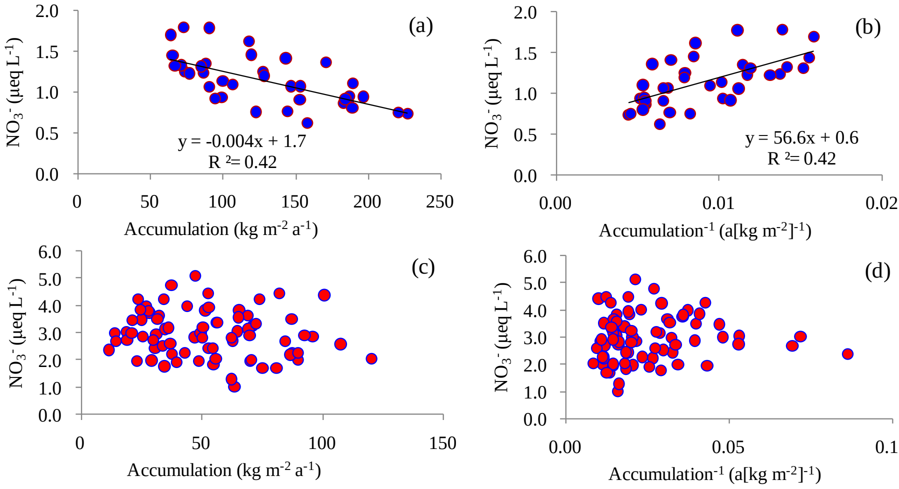


Figure 5. The relationships among snow accumulation rate, the archived concentration ($C_{archived}$), and flux of NO$_3^-$ in coastal (top row, (a), (b)~~, (c)~~ and (~~d~~c)) and inland (bottom row, (~~e~~d), (~~f~~e~~),~~) and (~~g~~f)~~ and (h)~~) Antarctica. In panel (d), the linear fit in back line (y = -44.5x + 2.1) include the full date set, while the linear equation in red (y = -27.7x + 1.5) was obtained by excluding two cases (open circles) with snow accumulation rate larger than 100 kg m^{-2} a^{-1} (see the main text). The flux values are the product of $C_{archived}$~~p-concentration~~ of NO$_3^-$ ~~(for details see main text)~~ and snow accumulation rate, namely the archived flux. Least squares regressions are noted with solid lines and are significant at $p < 0.01$. Error bars represent one standard deviation (1σ).



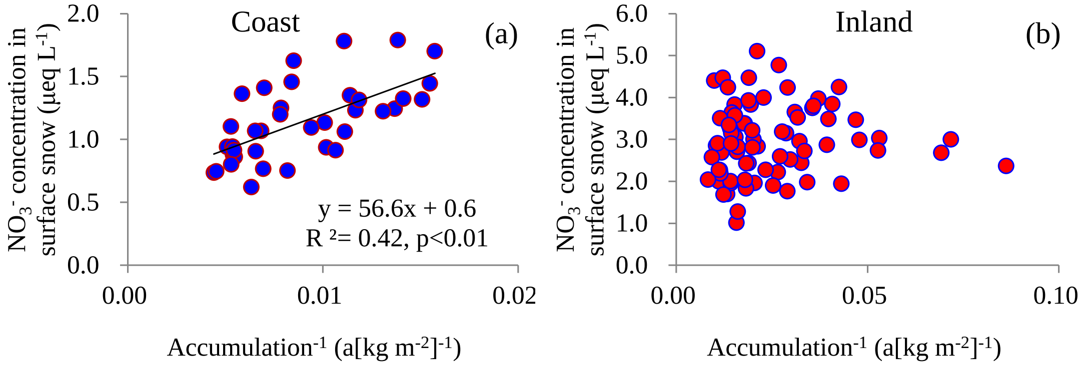


Figure 6. The relationships between NO$_3^-$ concentration and inverse snow accumulation rate in surface snow ~~at~~ in~~the~~ coastal (~~top row,~~panel (a)~~ and (b)~~) and inland (~~bottom row,~~panel (~~c~~b)~~ and (d)~~) Antarctica. Least squares regressions are noted with solid line and are significant at $p < 0.01$.

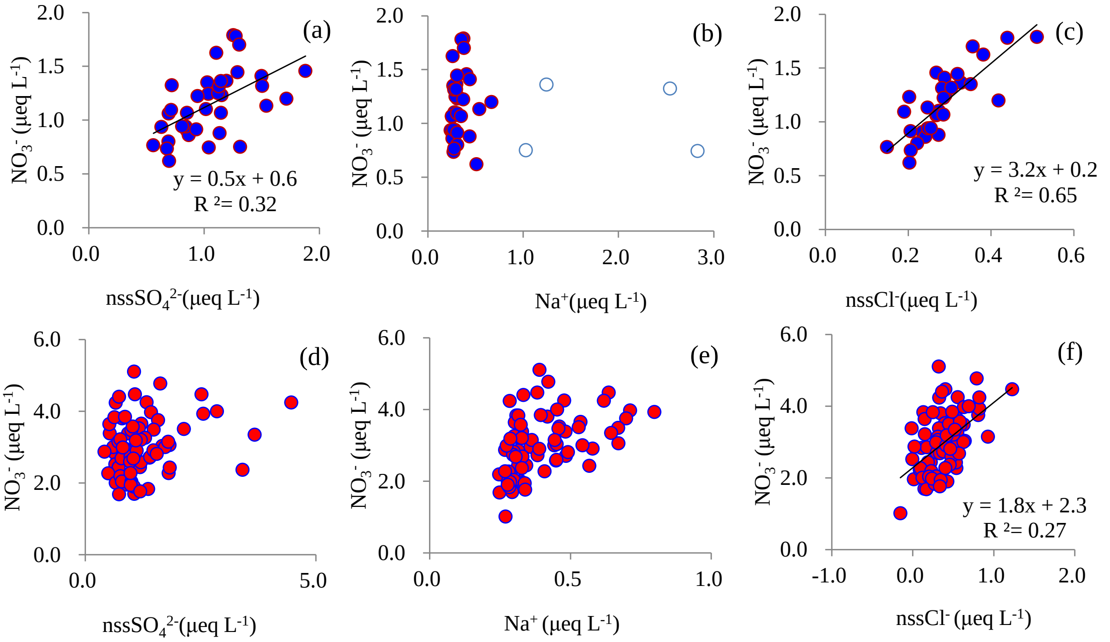


Figure 7. Relationships between NO_3^- and co-existing major ions in surface snow in coastal (top row, (a), (b) and (c)) and inland (bottom row, (d), (e) and (f)) Antarctica. Least squares regressions are noted with solid line and are significant at $p < 0.01$. The 4 samples with high Na^+ concentrations are denoted by blue open circles (b), the same as those in Figure 8 (the blue open circles). Note that the 4 samples were excluded in the plot of NO_3^- vs. nssCl$^-$ (c).

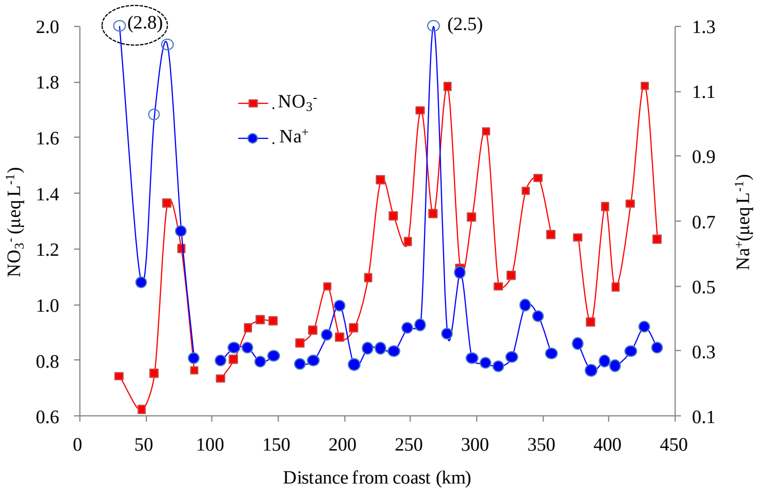


Figure 8. Concentrations of NO_3^- and Na^+ in surface snow samples on the coast. Four samples with high Na^+ concentrations are denoted by open circles, corresponding to those in Fig. 7b. Note that Na^+ concentrations in two samples, 2.5 and 2.8 µeq L^{-1} in parentheses, are above the maximum value of the secondary *y*-axis (Na^+ concentration). The sample in the dashed ellipse, with Na^+ concentration of 2.8 µeq L^{-1}, is the fresh snowfall.