Response to the referees

Again, we thank Prof. Joel Savarino (the handling editor) and the anonymous reviewer for their time in reviewing our revised manuscript. Below, we give a point-by-point response to the comments and suggestions of the 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).
The Reviewer #1

**We thank the reviewer very much for his/her thoughtful review of our revised manuscript. All of the comments and suggestions have been taken into account, and are included in the revised version. 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

The authors are to be commended for taking all reviewer comments seriously and implementing significant revisions to the manuscript. From my point of view I’d be happy to recommend publication after addressing the points below and carefully rechecking grammar/spelling:

(1) author's response

Again, we greatly appreciate the reviewer for his/her time in reviewing the revised version of the manuscript. We have carefully read the whole manuscript and improved grammar and spelling.

(1) author's changes in manuscript

Following the reviewer's comments, we carefully read the manuscript. Please see the revised version.

(2) comments from Referees

- please add to the introduction & discussion (4.2) the Halley study, something like:

Significant concentrations of organic nitrates (PAN and alkyl nitrates) were observed in the lower atmosphere at Halley in coastal Antarctica consistent with an oceanic source (Jones et al., 2011). They dominated the NOy budget during the winter, and were on a par with inorganic nitrate compounds during the summer. Although not a direct source of snowpack nitrate, organic nitrates would act as a source of NOx to coastal Antarctica that would ultimately contribute to nitrate within the snowpack (Jones et al., 2011). However, multi-seasonal measurements of surface snow nitrate correlate strongly with inorganic NOy species (especially HNO3) rather than organic (Jones et al., 2011).

(2) author's response
We thank the reviewer for the suggestion. The inorganic NO$_3^-$ plays an important role in the atmospheric NO$_y$ budget.

(2) author's changes in manuscript

Following the reviewer’s suggestion, in the section of introduction, the statement was added, as follows,

At Halley station in coastal Antarctica, significant concentrations of organic nitrates (peroxyacetyl nitrate (PAN) and alkyl NO$_3^-$) were observed in the lower atmosphere (Jones et al., 2011). Organic nitrates dominated the NO$_y$ (sum of reactive nitrogen oxide compounds) budget during the winter, and were on a par with inorganic nitrate compounds during the summer. Although not a direct source of snowpack NO$_3^-$, organic nitrates could act as source of NO$_x$ to coastal Antarctica that would ultimately contribute to NO$_3^-$ within the snowpack (Jones et al., 2011).

As the reviewer suggested, this point was also included in Discussion (4.2), as follows,

Although the organic nitrates can play an important role in the atmospheric NO$_y$ budget, multi-seasonal measurements of surface snow NO$_3^-$ correlate strongly with inorganic NO$_3$ species (especially HNO$_3$) rather than organic (Jones et al., 2011).

For the changes, please see the revision-tracked version of manuscript, sections 1. Introduction, and 4.2 Effects of coexisting ions on NO$_3^-$

(3) comments from Referees

- It is great that you include now the atmospheric observations. However, in my view they need to go into the main manuscript not just the supplementary material; e.g. add a panel to Fig.1 showing the variation with distance from the coast and make corresponding amendments to methods, results and discussion. Table S1 (move to main manuscript) must also include columns with site ID and sampling day.

As I pointed out before atmospheric NO$_3^-$ is key to discuss and interpret an air-snow study of nitrate in snow. In fact, this is probably the only Antarctic traverse, which produced HiVol filter samples of atmospheric NO$_3^-$, very relevant to the entire discussion in this manuscript.

(3) author's response

We agree with the reviewer. The sampling and analysis methods of atmospheric NO$_3^-$ were included in the section of methodology. The section of result and Figure 1 were revised accordingly. The full information about sampling location, sampling data, sample ID and chemical ion concentrations (NO$_3^-$ and SO$_4^{2-}$) is present in Table S1 in supporting information.
(3) author's changes in manuscript

Following the reviewer’s suggestion, the sampling method for atmospheric NO$_3^-$ was included in section 2.2 Sample collection, as follows,

To support understanding of the air-snow transfer of NO$_3^-$ on the traverse, atmospheric NO$_3^-$ was collected on glass fiber filters (Whatman G653) using a high volume air sampler (HVAS), with a flow rate of $\sim$1.0 m$^3$ min$^{-1}$ for 12-15 hr, during the inland traverse campaign in 2015/2016. The NO$_3^-$ collected on glass fiber filters are expected to equal the sum of particulate NO$_3^-$ and gaseous HNO$_3$, based upon previous investigations in East Antarctica (Savarino et al., 2007; Frey et al., 2009; Erbland et al., 2013). In total, 34 atmospheric samples were collected on the traverse. In addition, two field blanks were collected from filters installed in the HVAS without pumping and treated as samples thereafter. Detailed information about the atmospheric sampling is presented in Table S1 in supporting information.

After sample collection, all filters and snow samples were sealed in clean PE bags and preserved in clean thermal insulated boxes. All of the samples were transported to the laboratory under freezing conditions (< -20 °C).

Details on the analytical processing of atmospheric NO$_3^-$ samples were added in 2.3 Sample analysis, as follows,

In the laboratory, three quarters of individual filters were cut into pieces using pre-cleaned scissors that were rinsed between samples, placed in $\sim$100 ml of Milli-Q water, ultrasonicated for 40 min and leached for 24 hr under shaking. The sample solutions were then filtered through 0.22 μm ANPEL PTFE filters for NO$_3^-$ concentration.

Accordingly, Figure 1 in the manuscript was revised, as follows, and the main results of the atmospheric NO$_3^-$ investigation was included in section 3.1.
**Figure 1.** Concentrations of NO$_3^-$ in snow (surface snow, crystal ice and snowpits; on the primary y-axis) and atmosphere (on the secondary y-axis), with error bars representing one standard deviation of NO$_3^-$ ($\sigma$) 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), is higher than the maximum value of the primary y-axis (NO$_3^-$ concentration = 16.7 μeq L$^{-1}$ in the parentheses).

(4) comments from Referees

I77-80 weird phrasing. Better: The late winter/early secondary maximum of nitrate observed in surface snow at coastal and inland locations has been attributed to the stratospheric source based on the nitrate stable isotopic composition (Legrand, 1989; Savarino, 2007; Frey, 2009).

(4) author’s response

We thank the reviewer very much.

(4) author’s changes in manuscript

Following the suggestion of the reviewer, the sentence was rephrased, as follows,

The late winter/early spring secondary maximum of NO$_3^-$ observed in the atmosphere at coastal and inland locations has been attributed to the stratospheric source based on the NO$_3^-$ stable isotopic composition (Legrand et al., 1989; Savarino et al., 2007; Frey et al., 2009).

(5) comments from Referees

I84-90 I think you really need to distinguish between no3- spikes and no3- variability on decadal
to centennial or millennial time scales. A statistically significant link between the former and SPEs (solar proton events) has now been refuted. However, a link between the long-term variability of NO3- and solar cycles as suggested in Traversi et al. (2012) is very different in terms of time scales and likelihood of physical processes to be aligned, and may be present at some locations.

(5) author’s response

We agree with the reviewer and thanks for the comment.

(5) author’s changes in manuscript

Following the reviewer’s comment, this paragraph was rephrased, as follows,

In addition, while some studies suggested that snow/ice NO3- is possibly linked with extraterrestrial fluxes of energetic particles and solar irradiation, with solar flares corresponding to NO3- spikes (Zeller et al., 1986; Smart et al., 2014), other observations and recent modeling studies have established that there is not a clear connection between solar variability and NO3- 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). However, the potential link between the long-term (e.g., centennial to millennial time scales) variability of NO3- and solar cycles may be present at some locations (Traversi et al., 2012).

References


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. 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, and atmospheric sampling 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 ~3 cm), 20 snowpits with depths of 150 to 300 cm, and 6 crystal ice samples (the topmost needle like layer on Dome A plateau). 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 coexisting ions (nssSO$_4^{2-}$, Na$^+$ and Cl$^-$) was also investigated, and the results show a correlation between nssSO$_4^{2-}$ (fine aerosol particles) and NO$_3^-$ 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 (NOx = NO and NO2), nitrate (NO3-) is one of the major chemical species measured in polar snow and ice. The measurements of NO3- 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 NO3- in Antarctic snowpack are still not well understood in Antarctic snowpack, hampering the interpretation of ice core NO3- records.

The accumulation of NO3- in snow is associated with various environmental factors and continental, tropospheric and stratospheric sources could influence NO3- concentrations (Legrand and Kirchner, 1990; McCabe et al., 2007; Wolff et al., 2008; Lee et al., 2014). In surface snow, NO3- 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 (SO42-)), NO3- 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 NO3-, particularly methyl and ethyl NO3-, produced in surface oceans by microbiological and/or photochemical processes, are thought to be a possible contribution to Antarctic NO3- (Jones et al., 1999; Liss et al., 2004). At Halley station in coastal Antarctica, significant concentrations of organic nitrates (peroxacyetyl nitrate (PAN) and alkyl NO3-) were observed in the lower atmosphere (Jones et al., 2011). Organic nitrates dominated the NO3- (sum of reactive nitrogen oxide compounds) budget during the winter, and were on par with inorganic nitrate compounds during the summer. Although not a direct source of snowpack nitrate, organic nitrates could act as source of NO3- to coastal Antarctica that would ultimately contribute to NO3- within the snowpack (Jones et al., 2011).

While industrial and/or agricultural emissions have contributed to increasing NO3- levels in Greenland snow and ice over recent decades to hundreds of years, the anthropogenic contribution to Antarctic NO3- is less clear (Mayewski and Legrand, 1990; Hastings et al., 2009; Felix and Elliott, 2013; Geng et al., 2014). Lightning and NO3- 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 NO3- from mid-low latitude NO3 sources is an important source to the Antarctica year round, though less so in austral spring/summer (Lee et al., 2014). A recent treatment of alkyl NO3- in snow in the same global chemical transport model suggests that the recycling of NO3- and/or transport of NO3- due to photolysis of NO3- in the surface snow layer is important in determining summertime concentrations (Zatko et al., 2016). The stratospheric inputs of NO3- are thought to be the result of N2O oxidation to NO3- and formation of NO3- that is deposited via polar stratospheric cloud (PSC) sedimentation (Legrand et al., 1989; Legrand and Kirchner, 1990). The late winter/early spring secondary maximum of NO3- observed in the atmosphere at coastal and inland locations has been attributed to the stratospheric source based on the NO3- stable isotopic composition. This source has been used to explain sporadic NO3- concentration 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 NO3- 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 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; Smart et al., 2014), 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). However, the potential link between the long-term (e.g., centennial to millennial time scales) variability of NO$_3^-$ and solar cycles may be present at some locations (Traversi et al., 2012).

In summary, factors influencing NO$_3^-$ levels in snow/ice are complicated, and the significance of the relationship between NO$_3^-$ and controlling factors varies temporally and spatially. 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 cold, sunlit conditions ultraviolet photolysis dominates NO$_3^-$ post-depositional processing, whereas HNO$_3^-$ volatilization may become more important at warmer temperatures > -20 °C (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 a $z_e$ 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). 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$_3^-$ 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 uncertain, 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 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. Based on $e_0$, 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 formation of 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— and leave 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), the data on snow chemistry are still rare, particularly detailed information on NO$_3^-$ From 2009 to 2013, we therefore conducted surface snow and snowpit sampling campaigns along the traverse route, and with the main objectives were to (1) 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 (80°25’1.77”S and 77°6’58.0”E, 4087 m above mean sea level), was established at Dome A, mainly aimed 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) took 4 summer seasons. The deep ice core drilling began in January 2013, and in total 801 m ice core was recovered by the 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 °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 a volume of 1000 cm$^3$. As the field blanks, pre-cleaned bottles filled with Milli-Q water were 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, 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 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) as 1741 snow samples, were collected.

To support understanding of the air-snow transfer of NO$_3^-$ on the traverse, atmospheric NO$_3^-$ was collected on glass fiber filters (Whatman G653) using a high volume air sampler (HVAS), with a flow rate of ~1.0 m$^3$ min$^{-1}$ for 12-15 hr, during the inland traverse campaign in 2015/2016. The NO$_3^-$ collected on glass fiber filters are expected to equal the sum of particulate NO$_3^-$ and gaseous HNO$_3$ based upon previous investigations in East Antarctica (Savarino et al., 2007; Frey et al., 2009; Erbland
et al., 2013). In total, 34 atmospheric samples were collected on the traverse. In addition, two field blanks were collected from filters installed in the HVAS without pumping and treated as samples thereafter. Detailed information about the atmospheric sampling is presented in Table S1 in supporting information.

After sample collection, all filters and snow samples were rinsed with clean PE bags again and preserved in clean thermal insulated boxes. All of the samples were transported to the laboratory under freezing conditions (<-20 °C).

2.3 Sample analysis

In the laboratory, three quarters of individual filters were 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 then filtered through 0.22 μm ANPEL PTFE filters for concentration analysis. Snow samples were melted in the closed sampling bottles on a super clean bench (class 100) before chemical measurements. Analyses of Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-} were performed using a Dionex ICS-3000 ion chromatography system. The column used for cation analysis (Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) was a Dionex column CS12 (2 × 250 mm), while the anions (Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{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\textsubscript{p}) is

\[\sigma_p = \sqrt{\frac{\sum_{i=1}^{k} (n_i - 1) s_i^2}{\sum_{i=1}^{k} n_i - 1}},\]

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\textsuperscript{-}), 0.023 (NO\textsubscript{3}\textsuperscript{-}), 0.037 (SO\textsubscript{4}\textsuperscript{2-}), 0.022 (Na\textsuperscript{+}), 0.039 (NH\textsubscript{4}\textsuperscript{+}), 0.006 (K\textsuperscript{+}), 0.006 (Mg\textsuperscript{2+}) and 0.006 (Ca\textsuperscript{2+}) μeq L\textsuperscript{-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\textsuperscript{+} are usually not measured directly, but deduced from the ion-balance disequilibrium in the snow. Here, H\textsuperscript{+} concentration is calculated through ion balance.

\[\text{[H}^+] = \text{[Cl}^{-}] + \text{[NO}_3^{-}] + \text{[SO}_4^{2-}] - \text{[Na}^+] - \text{[NH}_4^{+}] - \text{[Mg}^{2+}] - \text{[Ca}^{2+}]\ (\text{Eq. 1}),\]

where ion concentrations are in μeq L\textsuperscript{-1}. In addition, the non-sea salt fractions of SO\textsubscript{4}\textsuperscript{2-} (nssSO\textsubscript{4}\textsuperscript{2-}) and Cl (nssCl) can be calculated from the following expressions, by assuming Na\textsuperscript{+} exclusively from sea salt (in μeq L\textsuperscript{-1}).

\[\text{nssSO}_4^{2-} = \text{[SO}_4^{2-}] - 0.12 \times \text{[Na}^+]\ (\text{Eq. 2}),\]

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

It is noted that SO\textsubscript{4}\textsuperscript{2-} fractionation (the precipitation of mirabilite (Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O)) may introduce a bias in nssSO\textsubscript{4}\textsuperscript{2-}, particularly during the winter half year (Wagenbach et al., 1998a).

3 Results

3.1 NO\textsubscript{3}\textsuperscript{-} concentration in surface snow

Concentrations of NO\textsubscript{3}\textsuperscript{-} in surface snow are shown in Fig. 1, ranging from 0.6 to 5.1 μeq L\textsuperscript{-1}, with a
267 mean of 2.4 μeq L\(^{-1}\). One standard deviation (1σ) of NO\(_3\)\(^-\) concentration in surface snow is 1.1 μeq L\(^{-1}\),
268 with coefficient of variation (CV; 1σ over mean) of 0.5, indicating a moderate spatial variability. On the
269 coastal ~450 km, NO\(_3\) shows a slightly increasing trend towards the interior, with a low variability,
270 while NO\(_3\) concentrations are higher in the inland region, with a large fluctuation. It is notable that in
271 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
272 from coast), there is a tendency for higher NO\(_3\) concentrations (> 5.0 μeq L\(^{-1}\)). Similarly, atmospheric
273 NO\(_3\) concentrations increase from the coast towards the plateau, ranging from 8 to 183 ng m\(^{-3}\) (mean =
274 55 ng m\(^{-3}\)) (Fig. 1).
275
276 The percentage that surface snow NO\(_3\) contributes to total ions (i.e., total ionic strength, sum of Na\(^+\),
277 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 %;
278 Fig. S2 in supporting information), with low values near the coast and high percentages on the plateau.
279 A strong relationship was found between NO\(_3\) and the total ionic strength in surface snow (\(R^2 = 0.55, p
280 < 0.01\)).
281
282 In the crystal ice, the means (ranges) of Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), Na\(^+\), NH\(_4\)\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) and H\(^+\)
283 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
284 (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\(^{-1}\),
285 respectively. H\(^+\) and NO\(_3\) are the most abundant species, accounting for 46.4 and 41.0 % of the total
286 ions, followed by SO\(_4\)\(^{2-}\) (5.1 %) and Cl\(^-\) (3.9 %). The other 5 cations, Na\(^+\), NH\(_4\)\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\),
287 only represent 3.6 % of the total ion budget. A significant linear relationship was found between NO\(_3\)
288 and the total ionic strength (\(R^2 = 0.99, p < 0.01\)), possibly suggesting that NO\(_3\) is the species
289 controlling ion abundance by influencing acidity of the crystal ice (i.e., H\(^+\) levels). In comparison with
290 surface snow, concentrations of H\(^+\) and NO\(_3\) are significantly higher in crystal ice (Independent
291 Samples T Test, \(p<0.01\)), while concentrations of Cl\(^-\), SO\(_4\)\(^{2-}\), Na\(^+\), NH\(_4\)\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) are
292 comparable in the two types of snow samples (Fig. S2 in supporting information). To date, the
293 information on the chemistry of ice crystal is rather limited but data from the so-called skin layer at
294 Dome C (top ~4 mm snow), where NO\(_3\) concentrations are in the range of 9 – 22 μeq L\(^{-1}\) in
295 summertime (Erbland et al., 2013), are generally comparable to our observations.
296
297 NO\(_3\) concentrations in surface snow have been widely measured across Antarctica (Fig. 2), and the
298 values vary from 0.2 to 12.9 μeq L\(^{-1}\), with a mean of 2.1 μeq L\(^{-1}\) (\(n = 594, 1\sigma = 1.7 \mu\text{eq L}^{-1}\)) and a
299 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
300 values are above 5.0 μeq L\(^{-1}\), mainly distributed on the East Antarctic plateaus. Spatially, NO\(_3\)
301 concentrations show an increasing trend with distance inland, and the values are higher in East than in
302 West Antarctica. Overall, this spatial pattern is opposite to that of the annual snow accumulation rate
303 (Arthn et al., 2006), i.e., low (high) snow accumulation corresponds to high (low) NO\(_3\)
304 concentrations. It is difficult to compare with NO\(_3\) concentrations derived from the “upper snow layer”
305 in different studies because each study sampled a different depth (Fig. 2), e.g., 2 - 10 cm for
306 DDU-Dome C traverse (Frey et al., 2009; Erbland et al., 2013), 25 cm for the 1989-1990 International
307 Trans-Antarctica Expedition (Qin et al., 1992) and 3 cm for this study. The different sampling depths
308 can result in large differences in NO\(_3\) concentration, especially on the East Antarctic plateaus (e.g., the
309 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
310 this case Because of this, any comparison of NO\(_3\) concentrations in surface snow collected in different
311 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 end, 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$_2$O) 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$_2$O) 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., 1998b; 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 year snow layer (Fig. 4).

Similar NO$_3^-$ profiles for snowpits have been reported elsewhere in Antarctica, 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. 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 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, as also suggested by 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 archived NO$_3^-$ (i.e., beyond photochemical processing; denoted as “C$_{\text{archived}}$” in the following context; Fig. 4), thus allowing for calculating the archived annual NO$_3^-$ flux (i.e., the product of C$_{\text{archived}}$ and annual snow accumulation rate). Although there is uncertainty when in 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$_{\text{archived}}$ 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

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

\[ F_{\text{total}} = C_{\text{lim}} \times A \] (Eq. 5),

where $F_{\text{total}}$ is snow NO$_3^-$ flux ($\mu$eq m$^{-2}$ a$^{-1}$); $C_{\text{atm}}$ is atmospheric concentration of NO$_3^-$ (\mu eq m$^{-3}$); $A$ is annual snow accumulation rate (kg m$^{-2}$ a$^{-1}$); $C_{\text{lim}}$ is measured firm NO$_3^-$ concentration (\mu eq L$^{-1}$, here \( C_{\text{lim}} = C_{\text{archived}} \)); $K_1$ 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 conversion of atmospheric concentration to snow concentration of NO$_3^-$ in this study. From Eqs. 4 and 5, firm NO$_3^-$ concentration can be expressed as

\[ C_{\text{lim}} = K_1 C_{\text{atm}} \times 1/A + K_2 C_{\text{atm}} \] (Eq. 6).

If $K_1$ and $K_2$ are constants, a linear relationship between measured NO$_3^-$ concentration ($C_{\text{lim}}$) and snow accumulation ($A$) can be interpreted using Eq. 6, which assumes regional spatial homogeneity of fresh snow NO$_3^-$ levels and dry deposition flux in the region. The slope ($K_1 C_{\text{atm}}$) of the linear model represents an approximation of dry deposition flux of NO$_3^-$ (i.e., an apparent dry deposition flux), while the intercept ($K_2 C_{\text{atm}}$) stands for NO$_3^-$ concentration in fresh snowfall. If dry deposition ($K_1 C_{\text{atm}}$) is
much larger than wet deposition \((K_2C_{\text{air}}A)\), the concentration of \(\text{NO}_3^-\) 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 \(\text{NO}_3^-\) but decrease its concentration in snow. While this linear model is a gross over-simplification of the complex nature of air-snow exchange of \(\text{NO}_3^-\), it provides a simple approach to compare the processes occurring on the coast versus those inland. In addition, this model can provide useful parameter values in modeling \(\text{NO}_3^-\) deposition/preservation at large scales, considering that observations remain sparse across Antarctica (e.g., Zatko et al., 2016).

The relationship between \(C_{\text{archived}}\) of \(\text{NO}_3^-\) and snow accumulation rate is shown in Fig. 5. The linear fit of \(C_{\text{archived}}\) vs. inverse snow accumulation \((R^2=0.88, p<0.01; \text{Fig. } 5a)\) supports the assumptions of spatial homogeneity. The intercept and slope of the linear fit suggest a \(\text{NO}_3^-\) concentration in fresh snow and an apparent \(\text{NO}_3^-\) dry deposition flux of \(0.7\pm0.07 \frac{\text{eq}}{\text{L} \cdot \text{a}^1}\) and \(45.7\pm7.8 \frac{\text{eq}}{\text{m}^2 \cdot \text{a}^1}\), 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 \(\text{NO}_3^-\) (Pasteris et al., 2014).

Figure 5b shows the archived fluxes of \(\text{NO}_3^-\) on the coast, with values from 104 (at the lowest accumulation site) to \(169 \frac{\text{eq}}{\text{m}^2 \cdot \text{a}^1}\) (at the highest accumulation site). Taking the calculated \(\text{NO}_3^-\) dry deposition flux of \(45.7 \frac{\text{eq}}{\text{m}^2 \cdot \text{a}^1}\), dry deposition accounts for \(27-44\%\) (mean = 36 %) of total \(\text{NO}_3^-\) inputs, with higher (lower) percentages at lower (higher) snow accumulation sites. This result is in line with the observations in Taylor Valley (coastal West Antarctica), where the snowfall was found to be the primary driver for \(\text{NO}_3^-\) inputs (Witherow et al., 2006). This observation also generally 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 \(\text{NO}_3^-\) in Antarctica as < 20 % close to the coast, increasing towards the plateaus.

In Figs. 5a and b, the strong linear relationships between \(\text{NO}_3^-\) and snow accumulation support that \(K_1\) and \(K_2\) are relatively constant on the coast (Eqs. 4 and 6). The average atmospheric concentration of \(\text{NO}_3^-\) in the coastal ~450 km region is \(19.4 \frac{\text{ng}}{\text{m}^3}\) in summer (Table S1 in supporting information). Taking \(C_{\text{air}}=19.4 \frac{\text{ng}}{\text{m}^3}\), \(K_1\) is estimated to be \(0.5 \frac{\text{cm}}{\text{s}^1}\), identical to a typical estimate for \(\text{HNO}_3\) deposition velocity to a snow/ice surface \((0.5 \frac{\text{cm}}{\text{s}^1}; \text{Seinfeld and Pandis, 1997})\). This predicted \(K_1\) value is lower than that calculated for the dry deposition of \(\text{HNO}_3\) at South Pole \((0.8 \frac{\text{cm}}{\text{s}^1}; \text{Huey et al., 2004})\). It is noted that the true \(K_1\) value could be larger than the prediction \((0.5 \frac{\text{cm}}{\text{s}^1})\) due to the higher values of \(C_{\text{air}}\) atmospheric \(\text{NO}_3^-\) concentrations during in summer (i.e., \(19.4 \frac{\text{ng}}{\text{m}^3}\) for the calculation of \(K_2\) in the other seasons (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007). The scavenging ratio for precipitation \((K_2)\) is calculated to be \(0.2x10^4 \frac{\text{m}^3}{\text{kg}^1}\), i.e., \(2 \frac{\text{m}^3}{\text{g}^1}\).

If it is assumed that \(\text{NO}_3^-\) concentration in snow is related to its concentration in the atmosphere, the scavenging ratio for \(\text{NO}_3^-\) \((W)\) can be calculated on a mass basis from the following expression (Kasper-Giebl et al., 1999),

\[
W = \rho_{\text{air}} \times \frac{(C_{\text{snow}} / C_{\text{air}})}{\text{(Eq. 7)}},
\]

where \(\rho_{\text{air}}\) is air density \((\text{g} / \text{m}^3)\), and \(C_{\text{snow}}\) and \(C_{\text{air}}\) are \(\text{NO}_3^-\) concentrations in fresh snow \((\text{ng} / \text{g}^1)\) and atmosphere \((\text{ng} / \text{m}^3)\) respectively. If taking \(\rho_{\text{air}} \approx 1000 \frac{\text{g}}{\text{m}^3}\) (on average, ground surface temperature \(\approx 255 \text{k}, \text{ground pressure } P \approx 0.08 \text{MPa} \text{in the coastal region}), C_{\text{snow}} = 43 \frac{\text{ng}}{\text{g}^1}\) (see discussion above and section 4.2 below), and \(C_{\text{air}} = 19.4 \frac{\text{ng}}{\text{m}^3}\), \(W\) 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 \(\text{NO}_3^-\) into the snow. However, the scavenging ratio provides useful valuable insights into the relation between \(\text{NO}_3^-\)
concentrations in the atmosphere and snow, which might be useful in modeling NO\textsubscript{3}\textsuperscript{-} deposition at a large-scale.

Figure 5c shows the distribution of flux is negatively correlated with C\textsubscript{archived} of NO\textsubscript{3}\textsuperscript{-}, which is not surprising since C\textsubscript{archived} is positively related to inverse accumulation (Fig. 5a). Based on the observed strong linear relationship between NO\textsubscript{3}\textsuperscript{-} flux and snow accumulation (Fig. 5b), the archived NO\textsubscript{3}\textsuperscript{-} flux is more accumulation dependent compared to C\textsubscript{archived}. This is compatible with the observations in Greenland (Burkhart et al., 2009), where accumulation is generally above 100 kg m\textsuperscript{-2} a\textsuperscript{-1}, similar to the coastal values in this study.

In terms of surface snow on the coast, NO\textsubscript{3}\textsuperscript{-} may be disturbed by the katabatic winds and wind convergence located near the Amery Ice Shelf (that is, the snow-sourced NO\textsubscript{3} and NO\textsubscript{2} from the Antarctic plateau possibly contributes to coastal snow NO\textsubscript{3}\textsuperscript{-}) (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\textsubscript{3}\textsuperscript{-}, although the post-depositional alteration of NO\textsubscript{3}\textsuperscript{-} was thought to be minor on the coast (Wolff et al., 2008; Erbland et al., 2013; Shi et al., 2015). Taken together, NO\textsubscript{3}\textsuperscript{-} in coastal surface snow might represent some post-depositional alteration. Even so, a negative correlation between NO\textsubscript{3}\textsuperscript{-} concentration and snow accumulation rate was found at the coast ($R^2=0.42$, p<0.01; Fig. 6a), suggesting that overall the majority of the NO\textsubscript{3}\textsuperscript{-} appears to be preserved and is determined by snow accumulation.

### 4.1.2 NO\textsubscript{3}\textsuperscript{-} in inland snowpack

In comparison with the coast, the correlation between C\textsubscript{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\textsubscript{3}\textsuperscript{-}. In addition, the relationship of C\textsubscript{archived} vs. inverse accumulation—in inland is opposite to that of coast. Based on current understanding of the post-depositional processing of NO\textsubscript{3}\textsuperscript{-}, the negative correlation between C\textsubscript{archived} and inverse snow accumulation (Fig. 5d) suggests losses of NO\textsubscript{3}\textsuperscript{-}. The slope of the linear relationship indicates apparent NO\textsubscript{3}\textsuperscript{-} dry deposition flux of -44.5±13.0 μeq m\textsuperscript{-2} a\textsuperscript{-1}, much larger than that of DML (-22.0±2.8 μeq m\textsuperscript{-2} a\textsuperscript{-1}), where the snow accumulation is generally lower than 100 kg m\textsuperscript{-2} a\textsuperscript{-1} (Pasteris et al., 2014). At Kohlen Station (an inland site in East Antarctica), with snow accumulation of 71 kg m\textsuperscript{-2} a\textsuperscript{-1}, the emission flux of NO\textsubscript{3} is estimated to be -22.9±13.7 μeq m\textsuperscript{-2} a\textsuperscript{-1} (Weller and Wagenbach, 2007), which is also smaller in comparison with this observation. Weller et al. (2004) proposed that loss rate of NO\textsubscript{3} does not depend on snow accumulation rate and the losses become insignificant at accumulation rates above 100 kg m\textsuperscript{-2} a\textsuperscript{-1}. Among the inland sites, SP10 and Core2 (~800 km from the coast), featured by high snow accumulation rate (> 100 kg m\textsuperscript{-2} a\textsuperscript{-1}; Table 1 and Fig. 1), exhibit even higher values of C\textsubscript{archived} and archived fluxes of NO\textsubscript{3} than those of the coastal sites. It is noted that these two cases influence the linear regression significantly (Fig. 5d). If the two sites are excluded, we can get a linear regression with the a slope of -27.7±9.2 μeq m\textsuperscript{-2} a\textsuperscript{-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 directly investigating NO\textsubscript{3} emission rate. The difference between NO\textsubscript{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\textsubscript{3}. If it is assumed that snow accumulation
rate is relatively constant during past recent decades at specific-sites, on average, 36.7±21.3 % of NO$_3^-$ (in μeq L$^{-1}$) was lost during one year, with the two sites (SP10 and Core2) with snow accumulation >100 kg m$^{-2}$ a$^{-1}$ excluded from the calculations. 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$^{-1}$). Significant losses can account for NO$_3^-$ profiles at inland sites, i.e., NO$_3^-$ concentration decreases decreasing with increasing depths. Previous observations and modeling works suggested that photoysis 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$_3^-$) 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 (OH), NO$_2$ + OH + M → 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/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 (e.g., Fig. S1 in supporting information 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, each employs different assumptions and large uncertainty remains about in quantifying NO$_3^-$ recycling and preservation. It is thought that emission and transport strength are the main 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).

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 (Fig. 5e). However, the nearly 1:1 relationship between $C_{archived}$ and NO$_3^-$ flux (Fig. 5f), suggests that accumulation rate is not the main driver of the 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 be explained by snow accumulation rate.

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\textsubscript{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). **Although organic nitrates can play an important role in the atmospheric NO\textsubscript{3} budget, multi-seasonal measurements of surface snow, NO\textsubscript{3} correlate strongly with inorganic NO\textsubscript{3} species (especially HNO\textsubscript{3}) rather than organic (Jones et al., 2011).** We investigate whether NO\textsubscript{3} in snow is closely associated with coexisting ions (e.g., Cl, SO\textsubscript{4}\textsuperscript{2-}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) since these ions have different main sources, e.g., Cl and Na\textsuperscript{+} are predominantly influenced by sea salt, and SO\textsubscript{4}\textsuperscript{2-} is likely dominated by marine inputs (e.g., sea salt and bio-activity source) (Bertler et al., 2005). In the snow, Cl, Na\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} are the most abundant ions in addition to NO\textsubscript{3}, and the potential association between NO\textsubscript{3} and the three ions in the surface snow is discussed here.

In surface snow, the non-sea salt fraction of SO\textsubscript{4}\textsuperscript{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\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} (R\textsuperscript{2} = 0.32, p < 0.01; Fig. 7a). Previous observations suggest that NO\textsubscript{3} and nssSO\textsubscript{4}\textsuperscript{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\textsubscript{4}\textsuperscript{2-} is mainly derived from marine biogenic emissions while NO\textsubscript{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\textsubscript{4}\textsuperscript{2-} is typically found on the submicron particles, while most of the NO\textsubscript{3} is gaseous HNO\textsubscript{3} and the particulate NO\textsubscript{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\textsubscript{3} and SO\textsubscript{4}\textsuperscript{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\textsubscript{4}\textsuperscript{2-} vs. NO\textsubscript{3} in ice (R\textsuperscript{2} = 0.31, p<0.01) could be associated with the fine nssSO\textsubscript{4}\textsuperscript{2-} aerosols, which could provide nucleation centers forming the multi-ion complexes with HNO\textsubscript{3} in the atmosphere. This assertion, however, should be examined further, considering that the complex chemistry of SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} in the atmosphere is far from understood (e.g., Wolff, 1995; Brown et al., 2006). Thus far, the mechanism of nssSO\textsubscript{4}\textsuperscript{2-} influencing NO\textsubscript{3} in the snowpack, however, is still debated, and it cannot be ruled out that nssSO\textsubscript{4}\textsuperscript{2-} further affects mobilization of NO\textsubscript{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\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} in inland snow (Fig. 7d), possibly due to the strong alteration of NO\textsubscript{3} during post-depositional processes, as discussed in section 4.1.2.

In comparison with nssSO\textsubscript{4}\textsuperscript{2-} aerosols, the sea-salt aerosols (Na\textsuperscript{+}) 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\textsubscript{3} to the particulate phase, considering that most of the NO\textsubscript{3} in the atmosphere is in the gas phase (HNO\textsubscript{3}). In this case, particulate NO\textsubscript{3} can be efficiently lost via aerosol mechanisms. In addition, the saline ice also favors the direct uptake of gaseous HNO\textsubscript{3} to the ice surface. Changes in partitioning between gas phase (HNO\textsubscript{3}) and particulate phase will affect NO\textsubscript{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\textsubscript{3} from the atmosphere (Hara et al., 2005), and elevated NO\textsubscript{3} concentrations are usually accompanied by Na\textsuperscript{+} spikes in the snowpack (e.g., at Halley station; Wolff et al., 2008). **Surprisingly**, no significant correlation was found between Na\textsuperscript{+} and NO\textsubscript{3} in coastal snow (Fig. 7b). The concentration profiles of NO\textsubscript{3} and Na\textsuperscript{+} 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 lead 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).

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 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$^{-1}$) 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$_2$SO$_4$ 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).

Accordingly, 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.

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 ($R^2 = 0.96, p<0.01$), 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$_3$ 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.

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\textsubscript{3} in snow. In general, a spatial trend of NO\textsubscript{3} in surface snow was found on the traverse, with high (low) concentrations on the plateau (coast). Similarly, NO\textsubscript{3} concentrations in the atmosphere are higher on the plateau than at coastal sites, with a range of 8 to 183 ng m\textsuperscript{-3}. Extremely high NO\textsubscript{3} levels (e.g., > 10 \textmu eq L\textsuperscript{-1}) were observed in the uppermost crystal ice layer, possibly associated with re-deposition of the recycled NO\textsubscript{3} from snow-sourced NO\textsubscript{3}. As for the snowpits, NO\textsubscript{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\textsubscript{3} flux in snow is positively correlated with snow accumulation rate, but negatively with NO\textsubscript{3} concentration. A linear model can well depict the relationship between archived NO\textsubscript{3} and snow accumulation, supporting that atmospheric levels and dry deposition fluxes of NO\textsubscript{3} are spatially homogeneous on the coast, and that dry deposition plays a minor role in snow NO\textsubscript{3} inputs. The dry deposition velocity and scavenging ratio for NO\textsubscript{3} are estimated to be 0.5 cm s\textsuperscript{-1} and 2200, respectively. In inland Antarctica, the archived NO\textsubscript{3} fluxes, varying significantly among sites, are largely dependent on NO\textsubscript{3} concentration. A weak correlation between snow accumulation and archived NO\textsubscript{3} suggests variable ambient concentrations and dry deposition flux of NO\textsubscript{3}, and the relationship is opposite to that for the coast. This supports the idea that post-depositional processing dominates NO\textsubscript{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 major ions, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and Na\textsuperscript{+}, originate from different sources from than NO\textsubscript{3}, but could potentially affect the scavenging and preservation of NO\textsubscript{3}. In coastal surface snow, a positive correlation between nssSO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} suggests the potential influence of fine aerosols on NO\textsubscript{3} formation and/or scavenging, while the coarse sea salt aerosol (e.g., Na\textsuperscript{+}) is likely less influential. In contrast to the coast, NO\textsubscript{3} in inland surface snow is dominated by post-depositional processes, and the effects of coexisting ions on NO\textsubscript{3} appear to be rather minor. In inland surface snow, the strong relationship between NO\textsubscript{3} and H\textsuperscript{+} suggests a dominant role of gaseous HNO\textsubscript{3} deposition in determining NO\textsubscript{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 to Dome A, East Antarctica.

<table>
<thead>
<tr>
<th>Snowpit No.</th>
<th>Latitude, °</th>
<th>Longitude, °</th>
<th>Elevation, m</th>
<th>Distance to coast, km</th>
<th>Annual snow accumulation, kg m⁻² a⁻¹</th>
<th>Depth, cm</th>
<th>Sampling resolution, cm</th>
<th>Sampling year</th>
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<td>SP1</td>
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<td>76.83</td>
<td>1613</td>
<td>132</td>
<td>193.2</td>
<td>150</td>
<td>5.0</td>
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<td>2037</td>
<td>200</td>
<td>172.0</td>
<td>150</td>
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<td>SP3</td>
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<td>283</td>
<td>99.4</td>
<td>200</td>
<td>5.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP4</td>
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<td>2489</td>
<td>387</td>
<td>98.3</td>
<td>200</td>
<td>5.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP5</td>
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<td>77.00</td>
<td>2545</td>
<td>452</td>
<td>90.7</td>
<td>200</td>
<td>5.0</td>
<td>2012/2013</td>
</tr>
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<td>SP6</td>
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<td>2627</td>
<td>514</td>
<td>24.6</td>
<td>300</td>
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<td>29.2</td>
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<td>80.2</td>
<td>180</td>
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</table>

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 snow (surface snow, crystal ice and snowpits; on the primary y-axis) and atmosphere (on the secondary y-axis), 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 $= 16.7$ μeq L$^{-1}$ in the parentheses).
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).
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 – SP20 are different.
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).
Figure 5. The relationships amongst snow accumulation rate, the archived concentration ($C_{\text{archived}}$), 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 black line ($y = -44.5x + 2.1$) includes the full data 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 $C_{\text{archived}}$ 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 relationships between NO$_3^-$ concentration and inverse snow accumulation rate in surface snow in coastal (panel (a)) and inland (panel (b)) Antarctica. Least squares regressions are noted with solid line and are significant at $p < 0.01$.

$$y = 56.6x + 0.6$$

$$R^2 = 0.42, p < 0.01$$
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.