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

Guitao Shi1,2, Meredith G. Hastings3, Jinhai Yu2,4, Tianming Ma2,5, Zhengyi Hu2, Chunlei An2, Chuanjin Li6, Hongmei Ma2, Su Jiang2, and Yuansheng Li2

1Key Laboratory of Geographic Information Science (Ministry of Education), School of Geographic Sciences and Institute of Eco-Chongming, East China Normal University, Shanghai 200241, China
2Key Laboratory for Polar Science of State Oceanic Administration, Polar Research Institute of China, Shanghai 200062, China
3Department of Earth, Environmental and Planetary Sciences and Institute at Brown for Environment and Society, Brown University, Providence, Rhode Island 02912, USA
4School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210023, China
5School of Ocean and Earth Science, Tongji University, Shanghai 200092, China
6The State Key Laboratory of the Cryospheric Sciences, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

Correspondence: Guitao Shi (gt_shi@163.com) and Meredith G. Hastings (meredith_hastings@brown.edu)

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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 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 snow pits 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 topmost crystal ice (with a maximum of 16.1 µeq L$^{-1}$). NO$_3^-$ concentration profiles for snow pits 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 depicted well 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$_3^-$ were 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 dependent on concentration. 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 (NO, 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 under-
standing 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, transport pathways and preservation of NO$_3^-$ in Antarctic snowpack are still not well understood, hampering the interpretation of ice core NO$_3^-$ records.

The accumulation of NO$_3^-$ in snow is associated with various environmental factors and continental, 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). 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$_3^-$ (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 NO$_3^-$ to coastal Antarctica that would ultimately contribute to NO$_3^-$ within the snowpack (Jones et al., 2011).

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$_4$ produced in the lower stratosphere have long been thought to play a major role (Legrand et al., 1989; Legrand and Kirchner, 1990). Recently, model simulation suggests that tropospheric transport of NO$_3^-$ from mid-to-low-latitude NO$_4$ sources is an important source to the Antarctic year round, though less in the austral spring and summer (Lee et al., 2014). 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$_4$ due to photolysis of NO$_3^-$ in the surface snow layer is important in determining summertime concentrations (Zatko et al., 2016). The stratospheric inputs of NO$_3^-$ are thought to result from N$_2$O oxidation to NO and then formation of NO$_3^-$ that is deposited via polar stratospheric cloud sedimentation (Legrand et al., 1989; Legrand and Kirchner, 1990). 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). At some sites, the snow and 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 to affect snow NO$_3^-$ concentrations indirectly through an influence on the air mass transport and/or snow accumulation rate (Russell et al., 2004, 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, 2012, 2016; Duderstadt et al., 2014, 2016). However, the potential link between the long-term (e.g., centennial to millennial timescales) 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 and 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, 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 $z_e$ (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, 2015; Berhanu 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$_2^-$ in the summer time 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 vapor, 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 were 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 2 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, 2015). Further investigations are needed to quantify the effects of volatilization for a better understanding of NO$_3^-$ preservation in snow and ice. 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 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 snow pits (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 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, 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 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; Pastoris et al., 2014), but these provide an uneven distribution of snow NO$_3^-$ concentrations and leave large regions unsampled (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, 2011; Ma et al., 2010; Li et al., 2013; Shi et al., 2015), the data on snow chemistry are still rare, particularly detailed information on NO$_3^-$.

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‘1.7” 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 four 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 of 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 horizontally into the snow wall. When the uppermost snow layer was excavated, in particular on the sastrugi (Fig. S1 in the Supplement), the depth of the needle-like crystal ice layer (referred to as "crystal ice" in the following context) was generally < 1.0 cm. In order to investigate air–snow transfer of NO₃⁻ in this uppermost ∼ 1 cm layer, the crystal ice was collected using a clean HDPE scoop and then poured into clean, wide-mouth HDPE bottles. Approximately 30 g of crystal ice was collected for each sample. In total, six crystal ice samples were collected on the traverse near Dome A plateau.

In addition to surface snow, snow pit samples were collected during CHINARE inland traverse campaigns in 2009/2010, 2010/2011 and 2012/2013. The snow pits 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. Snow pit samples were collected from the base towards the top layer along a vertical line. During the sampling process, all personnel wore PE gloves and face masks to minimize potential contamination. Note that the snow pits are generally > 1 km from the traverse route to avoid possible contamination from the expedition activities. All information about individual snow pits, including location, distance from the coast, elevation, snow pit depth, sampling resolution, collection date and annual snow accumulation rate, is summarized.

Table 1. Snow pit information on the traverse from coastal Zhongshan Station to Dome A, East Antarctica.

<table>
<thead>
<tr>
<th>Snow pit 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>
</tr>
</thead>
<tbody>
<tr>
<td>SP1</td>
<td>−70.52</td>
<td>76.83</td>
<td>1613</td>
<td>132</td>
<td>193.2</td>
<td>150</td>
<td>5.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP2</td>
<td>−71.13</td>
<td>77.31</td>
<td>2037</td>
<td>200</td>
<td>172.0</td>
<td>150</td>
<td>3.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP3</td>
<td>−71.81</td>
<td>77.89</td>
<td>2295</td>
<td>283</td>
<td>99.4</td>
<td>200</td>
<td>5.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP4</td>
<td>−72.73</td>
<td>77.45</td>
<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>
<td>−73.40</td>
<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>
<tr>
<td>SP6</td>
<td>−73.86</td>
<td>76.98</td>
<td>2627</td>
<td>514</td>
<td>24.6</td>
<td>300</td>
<td>2.5</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP7</td>
<td>−74.50</td>
<td>77.03</td>
<td>2696</td>
<td>585</td>
<td>29.2</td>
<td>100</td>
<td>2.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP8</td>
<td>−74.65</td>
<td>77.01</td>
<td>2734</td>
<td>602</td>
<td>80.2</td>
<td>180</td>
<td>2.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP9</td>
<td>−76.29</td>
<td>77.03</td>
<td>2843</td>
<td>787</td>
<td>54.8</td>
<td>200</td>
<td>2.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP10</td>
<td>−76.54</td>
<td>77.02</td>
<td>2815</td>
<td>810</td>
<td>100.7</td>
<td>240</td>
<td>3.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP11</td>
<td>−77.13</td>
<td>76.98</td>
<td>2928</td>
<td>879</td>
<td>81.2</td>
<td>200</td>
<td>2.5</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP12</td>
<td>−77.26</td>
<td>76.96</td>
<td>2962</td>
<td>893</td>
<td>83.4</td>
<td>265</td>
<td>5.0</td>
<td>2009/2010</td>
</tr>
<tr>
<td>SP13</td>
<td>−77.91</td>
<td>77.13</td>
<td>3154</td>
<td>968</td>
<td>33.3</td>
<td>200</td>
<td>2.0</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP14</td>
<td>−78.34</td>
<td>77.00</td>
<td>3368</td>
<td>1015</td>
<td>87.6</td>
<td>216</td>
<td>3.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP15</td>
<td>−78.35</td>
<td>77.00</td>
<td>3366</td>
<td>1017</td>
<td>70.0</td>
<td>162</td>
<td>2.0</td>
<td>2009/2010</td>
</tr>
<tr>
<td>SP16</td>
<td>−79.02</td>
<td>76.98</td>
<td>3738</td>
<td>1092</td>
<td>25.4</td>
<td>200</td>
<td>2.5</td>
<td>2012/2013</td>
</tr>
<tr>
<td>SP17</td>
<td>−79.65</td>
<td>77.21</td>
<td>3969</td>
<td>1162</td>
<td>46.2</td>
<td>130</td>
<td>2.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP18</td>
<td>−80.40</td>
<td>77.15</td>
<td>4093</td>
<td>1250</td>
<td>24.2</td>
<td>300</td>
<td>2.0</td>
<td>2010/2011</td>
</tr>
<tr>
<td>SP19</td>
<td>−80.41</td>
<td>77.11</td>
<td>4092</td>
<td>1254</td>
<td>23.7</td>
<td>300</td>
<td>1.0</td>
<td>2009/2010</td>
</tr>
<tr>
<td>SP20</td>
<td>−80.42</td>
<td>77.12</td>
<td>4093</td>
<td>1256</td>
<td>23.5</td>
<td>300</td>
<td>2.5</td>
<td>2012/2013</td>
</tr>
<tr>
<td>Core 1²</td>
<td>−70.83</td>
<td>77.08</td>
<td>1850</td>
<td>168</td>
<td>127.0</td>
<td>–</td>
<td>–</td>
<td>1996/1997</td>
</tr>
<tr>
<td>Core 2³</td>
<td>−76.53</td>
<td>77.03</td>
<td>2814</td>
<td>813</td>
<td>101.0</td>
<td>–</td>
<td>–</td>
<td>1998/1999</td>
</tr>
</tbody>
</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).
in Table 1. All together, 20 snow pits (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 h, during the inland traverse campaign in 2015/2016. The NO$_3^-$ collected on glass fiber filters is 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 the Supplement.

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).

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 leached for 24 h under shaking. The sample solutions were 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$^+$, 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, and the gradient elution method was employed for anion analysis, with eluent of potassium hydroxide. 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 ($\sigma_p$; $\sigma_p = \sqrt{\frac{\sum_{i=1}^{k} (n_i - 1) s_i^2}{\sum_{i=1}^{k} (n_i - 1)}}$), 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$^-$), 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 (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.

\[
[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] - [Na^+] - [NH_4^+] - [K^+] - [Mg^{2+}] - [Ca^{2+}].
\]

(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$^{-1}$).

\[
[nssSO_4^{2-}] = [SO_4^{2-}] - 0.12 \times [Na^+]
\]

(2)

\[
[nssCl^-] = [Cl^-] - 1.17 \times [Na^+]
\]

(3)

It is noted that SO$_4^{2-}$ fractionation (the precipitation of mirabilite, Na$_2$SO$_4$·10H$_2$O) 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, 1σ over mean) of 0.5, indicating a moderate spatial variability. About 450 km from the coast, NO$_3^-$ shows a slightly increasing trend towards the interior, with 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$^{-1}$). Similarly, atmospheric NO$_3^-$ concentrations increase from the coast towards the plateau, ranging from 6 to 118 ng m$^{-3}$ (mean of 38 ng m$^{-3}$) (Fig. 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 of 27.0 %; Fig. S2 in the Supplement), 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 five 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 the Supplement). 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 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 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). Because of this, any comparison of NO\(_3\) concentrations in surface snow collected in different campaigns should be made with caution.

### 3.2 Snow pit NO\(_3\) concentrations

Mean NO\(_3\) concentrations for snow pits are shown in Fig. 1. From the coast to ∼ 450 km inland, snow pit NO\(_3\) means are comparable to those of surface snow, whereas NO\(_3\) means are lower in inland snow pits than in surface snow with the exception of sites ∼ 800 km from the coast. In general, the differences between snow pit 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 snow pits 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 snow pits 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 snow pits is likely suggestive of a seasonal signature (Wagenbach et al., 1998b; Grannas et al., 2007; Shi et al., 2015). Among the coastal snow pits, water isotope ratios (δ\(^{18}\)O of H\(_2\)O) of samples at SP2 were also determined, thus allowing for investigating NO\(_3\) seasonal variability (Fig. S3 in the Supplement).

In general, the δ\(^{18}\)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., 1998; Wagenbach et al., 1998b; Savarino et al., 2007).

In contrast, most of the inland snow pits 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 snow pits are typically lower than those of the most recent year snow layer (Fig. 4). Similar NO\(_3\) profiles for snow pits 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
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 are from Frey et al. (2009). The other surface snow NO$_3^-$ concentrations are from compiled data (Bertler et al., 2005) and references therein. Also illustrated are the locations of snow pits on the traverse route from Zhongshan to Dome A in this study (SP1 to SP20, solid short blue line; Table 1).

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 on 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 had 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 snow pit 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, 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 snow pits (Sect. 3.1 and 3.2) as well as the spatial pattern of snow accumulation rate (Fig. 1).

As for snow pits, 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). Photochemical processing is responsible for NO$_3^-$ distribution in inland snow pits (Erbland et al., 2013; Berhanu et al., 2015). Considering that the actinic flux is al-
ways negligible below the depth of 1 m, the bottom layers of the snow pits (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 snow pit, i.e., below the photic zone, can be taken as the archived fraction without further modification, as also suggested by previous observations (Frey et al., 2009; Erbland et al., 2013, 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 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 are unavailable in most of Antarctica. It is noted that $C_{\text{archived}}$ is generally close to (lower than) the NO$_3^-$ means for entire snow pits 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

\[
F_{\text{total}} = K_1 C_{\text{atm}} + K_2 C_{\text{atm}} A,
\]

(4)

\[
F_{\text{total}} = C_{\text{firm}} \times A,
\]

(5)

where $F_{\text{total}}$ is snow NO$_3^-$ flux (µeq m$^{-2}$ a$^{-1}$); $C_{\text{atm}}$ is atmospheric concentration of NO$_3^-$ (µeq m$^{-3}$); $A$ is annual snow accumulation rate (kg m$^{-2}$ a$^{-1}$); $C_{\text{firm}}$ is measured firn NO$_3^-$
concentration (µeq L⁻¹, here \(C_{\text{firm}} = C_{\text{archived}}\)): \(K_1\) is the dry deposition velocity (cm s⁻¹); and \(K_2\) is the scavenging ratio for precipitation (m³ kg⁻¹), which allows conversion of atmospheric concentration to snow concentration of NO₃⁻ in this study. From Eqs. (4) and (5), firm NO₃⁻ concentration can be expressed as

\[
C_{\text{firm}} = K_1 C_{\text{atm}} \times \frac{1}{A} + K_2 C_{\text{atm}}.
\]  

If \(K_1\) and \(K_2\) are constants, a linear relationship between measured NO₃⁻ concentration \((C_{\text{firm}})\) and snow accumulation \((A)\) can be interpreted using Eq. (6), which assumes regional spatial homogeneity of fresh snow NO₃⁻ levels and dry deposition flux. The slope \((K_1 C_{\text{atm}})\) of the linear model represents an approximation of dry deposition flux of NO₃⁻ (i.e., an apparent dry deposition flux), while the intercept \((K_2 C_{\text{atm}} A)\) stands for NO₃⁻ concentration in fresh snowfall. If dry deposition \((K_1 C_{\text{atm}})\) is much larger than wet deposition \((K_2 C_{\text{atm}} A)\), the concentration of NO₃⁻ 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 NO₃⁻ but decrease its concentration in snow. While this linear model is a gross oversimplification of the complex nature of air–snow exchange of NO₃⁻, 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 NO₃⁻ deposition and preservation on large scales, considering that observations remain sparse across Antarctica (e.g., Zatko et al., 2016).

The relationship between \(C_{\text{archived}}\) of NO₃⁻ 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 NO₃⁻ concentration in fresh snow and an apparent NO₃⁻ 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 a negative dry deposition flux suggested net losses of NO₃⁻ (Pasteris et al., 2014).

Figure 5b shows the archived fluxes of NO₃⁻ on the coast, with values from 104 (at the lowest accumulation site) to 169 µeq m⁻² a⁻¹ (at the highest accumulation site). Taking the calculated NO₃⁻ dry deposition flux of 45.7 µeq m⁻² a⁻¹, dry deposition accounts for 27–44 % (mean of 36 %) of total NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ in Antarctica as <20 % close to the coast, increasing towards the plateaus.

In Fig. 5a and b, the strong linear relationships between NO₃⁻ 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 NO₃⁻ in the coastal ∼450 km region is 15.6 ng m⁻³ in summer (Table S1 in the Supplement). Taking \(C_{\text{atm}} = 15.6 \text{ ng m}^{-3}\), \(K_1\) is estimated to be 0.6 cm s⁻¹, close to a typical estimate for HNO₃ deposition velocity to a snow/ice surface (0.5 cm s⁻¹; Seinfeld and Pandis, 1997). This predicted \(K_1\) value is lower than that calculated for the dry deposition of HNO₃ 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 (0.6 cm s⁻¹) due to the higher values of \(C_{\text{atm}}\) in summer (i.e., 15.6 ng m⁻³ for the calculation of \(K_1\)) than in other seasons (Mulvaney et al., 1998; Wagenbach et al., 1998b; Savarino et al., 2007).
The scavenging ratio for precipitation \((K_2)\) is estimated to be about 0.2 \(\times 10^4\) 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 be calculated on a mass basis from the following expression (Kasper-Giebl et al., 1999):

\[
W = \rho_{atm} \times (C_{\text{f-snow}} / C_{\text{atm}}),
\]

where \(\rho_{atm}\) is air density \((\text{g m}^{-3})\), and \(C_{\text{f-snow}}\) and \(C_{\text{atm}}\) are NO\(_3\) concentrations in fresh snow \((\text{ng g}^{-1})\) and atmosphere \((\text{ng m}^{-3})\), 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), \(C_{\text{f-snow}} = 43\) ng g\(^{-1}\) (see discussion above and Sect. 4.2 below) and \(C_{\text{atm}} = 15.6\) ng m\(^{-3}\), \(W\) is calculated to be \(\approx 2700\), 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 valuable insights into the relation between NO\(_3\) concentrations in the atmosphere and snow, which might be useful in modeling NO\(_3\) deposition on a large scale.

Figure 5c shows the distribution of flux is negatively correlated with \(C_{\text{archived}}\) of NO\(_3\), which is not surprising since \(C_{\text{archived}}\) is positively related to inverse accumulation (Fig. 5a). Based on the observed strong linear relationship between NO\(_3\) flux and snow accumulation (Fig. 5b), the archived NO\(_3\) flux is more accumulation-dependent compared to \(C_{\text{archived}}\). 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\(_3\) and NO\(_3\) from the Antarctic plateau possibly contributes 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; Ernland 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), suggesting that overall the majority of the NO\(_3\) appears to be preserved and is determined by snow accumulation.

### 4.1.2 NO\(_3\) in inland snowpack

In comparison with the coast, the correlation between \(C_{\text{archived}}\) 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 \(C_{\text{archived}}\) vs. inverse accumulation inland is opposite to that on the coast. Based on current understanding of the post-depositional processing of NO\(_3\), the negative correlation between \(C_{\text{archived}}\) and inverse snow accumulation (Fig. 5d) suggests losses of NO\(_3\). The slope of the linear relationship indicates an apparent NO\(_3\) dry deposi-
tion flux of $-44.5 \pm 13.0 \mu\text{eq m}^{-2}\text{a}^{-1}$, much larger than that of DML ($-22.0 \pm 2.8 \mu\text{eq m}^{-2}\text{a}^{-1}$), 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 $-22.9 \pm 13.7 \mu\text{eq m}^{-2}\text{a}^{-1}$ (Weller and Wagenbach, 2007), which is also smaller in comparison with this observation. Weller et al. (2004) proposed that the 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 ($\sim 800$ km from the coast), characterized by high snow accumulation rate ($> 100$ kg m$^{-2}$ a$^{-1}$; Table 1 and Fig. 1), exhibit even higher values of $C_{\text{archived}}$ and archived fluxes of NO$_3^-$ 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 a slope of $-27.7 \pm 9.2 \mu\text{eq m}^{-2}\text{a}^{-1}$, which is comparable to previous reports in DML (Pasteris et al., 2014).

The depths of inland snow pits cover several to tens of years snow accumulation, thus allowing for directly 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 recent decades at specific sites, on average, $36.7 \pm 21.3$ % of NO$_3^-$ (in $\mu\text{eq L}^{-1}$) was lost during 1 year, with the two sites (SP10 and Core2) with snow accumulation $> 100$ kg m$^{-2}$ a$^{-1}$ excluded from the calculation. 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 $-28.1 \pm 23.0 \mu\text{eq m}^{-2}\text{a}^{-1}$, close to the linear model prediction ($-27.7 \pm 9.2 \mu\text{eq m}^{-2}\text{a}^{-1}$). Significant losses can account for NO$_3^-$ profiles at inland sites, i.e., NO$_3^-$ concentration decreasing 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 photoproduts (NO$_x$) are emitted into the gas phase (Davis et al., 2004; France et al., 2011), and these products could undergo reoxidation by the local oxidants (e.g., hydroxyl radical (OH), 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 vapor onto the extensively developed crystal ice layers on Antarctic plateaus (e.g., Fig. S1 in the Supplement), 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).

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), but each employs different assumptions and large uncertainty remains 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 (Wolf 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 $\sim 3$ to $333 \mu\text{eq m}^{-2}\text{a}^{-1}$, with high values generally corresponding to high snow accumulation (Fig. 5e).
However, the nearly 1 : 1 relationship between \( C_{\text{archived}} \) 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\(_3^-\) 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\(_3^-\) 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). Here, 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 bioactivity source) (Bertler et al., 2005). In the snow, Cl\(^-\), Na\(^+\) and SO\(_4^{2-}\) are the most abundant ions in addition to NO\(_3^-\).

In surface snow, the non-sea-salt fraction of SO\(_4^{2-}\) accounted for 75–99% of its total budget, with a mean of 95%. The percentages were 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, b). 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, SO\(_4^{2-}\) is typically found on the submicron particles, while most of the NO\(_3^-\) is gaseous HNO\(_3\) and the particulate NO\(_3^-\) is mainly on intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a, b). 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\(_4^{2-}\) and NO\(_3^-\) in ice \((R^2 = 0.31, p<0.01)\) could be associated with fine nssSO\(_4^{2-}\) aerosols, which provide nucleation centers forming 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 atmo-
sphere 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 Sect. 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. High atmospheric sea-salt aerosol concentrations are expected to promote the conversion of gaseous HNO$_3$ to the 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 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 the snowpack (e.g., at Halley station; Wolff et al., 2008). Surprisingly, 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 and 300–450 km distance inland, although they are not very coherent. It is noted that amongst the four 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 four 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$^{-1}$; Sect. 4.1.1), validating that the simple linear deposition model (i.e., the Eq. 6) can depict well 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.

In surface snow, nssCl$^-$ represents 0–64 % (mean of 40 %) of the total Cl$^-$. On the coast, it is of interest that nssCl$^-$ in the four 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 (< −8°C (Marion et al., 1999), possibly leading to the positive nssCl$^-$. However, even if all of SO$_4^{2-}$ in seawater 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 of 2.1, well above 1.17 of seawater, 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). Thus, nssCl$^-$ in snowpack can roughly represent the atmospherically deposited HCl. In 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$_3^-$ (Bock et al., 2016). It is noted that NO$_3^-$ accounts for most of the calculated H$^+$ concentrations (81–97 %, mean of 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 HNO₃ contributes >91 % of NO₃⁻ in the crystal ice (the lower limit, 91 %, calculated by assuming all of the alkaline species (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) are neutralized by HNO₃ in the atmosphere), suggesting a dominant role of HNO₃ deposition in snow NO₃⁻ concentrations. The elevated high atmospheric NO₃⁻ concentrations observed at Dome A (>100 ng m⁻³, 77.12° E and 80.42° S; Table S1 in the Supplement) possibly indicate oxidation of gaseous NO₂ to HNO₃, providing further evidence that NO₃⁻ recycling driven by photolysis plays an important role in its abundance in snowpack on East Antarctic plateaus.

5 Conclusions

Samples of surface snow, snow pits 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 NO₃⁻ in snow. In general, a spatial trend of NO₃⁻ in surface snow was found on the traverse, with high (low) concentrations on the plateau (coast). Similarly, NO₃⁻ concentrations in the atmosphere are higher on the plateau than at coastal sites, with a range of 6 to 118 ng m⁻³. Extremely high NO₃⁻ levels (e.g., >10 μeq L⁻¹) were observed in the uppermost ice crystal layer, possibly associated with re-deposition of recycled NO₃⁻ from snow-sourced NO₂. As for the snow pits, NO₃⁻ 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 NO₃⁻ flux in snow is positively correlated with snow accumulation rate, but negatively with NO₃⁻ concentration. A linear model can well depict the relationship between archived NO₃⁻ and snow accumulation, supporting that atmospheric levels and dry deposition fluxes of NO₃⁻ are spatially homogeneous on the coast and that dry deposition plays a minor role in snow NO₃⁻ inputs. The dry deposition velocity and scavenging ratio for NO₃⁻ are estimated to be 0.6 cm s⁻¹ and 2700, respectively. In inland Antarctica, the archived NO₃⁻ fluxes, varying significantly among sites, are largely dependent on NO₃⁻ concentration. A weak correlation between snow accumulation and archived NO₃⁻ suggests variable ambient concentrations and dry deposition flux of NO₃⁻, and the relationship is opposite to that on the coast. This supports the idea that post-depositional processing dominates NO₃⁻ concentration and distribution in inland Antarctica (e.g., Erbland et al., 2013, 2015; Shi et al., 2015; Zatko et al., 2016).

The major ions, Cl⁻, SO₄²⁻ and Na⁺, originate from different sources than NO₃⁻ but could potentially affect the scavenging and preservation of NO₃⁻. In coastal snow surface, a positive correlation between nssSO₄²⁻ and NO₃⁻ suggests the potential influence of fine aerosols on NO₃⁻ formation and/or scavenging, while the coarse sea-salt aerosol (e.g., Na⁺) is likely less influential. In contrast to the coast, NO₃⁻ in inland surface snow is dominated by post-depositional processes, and the effects of coexisting ions on NO₃⁻ appear to be rather minor. In inland surface snow, the strong relationship between NO₃⁻ and H⁺ suggests a dominant role of gaseous HNO₃ deposition in determining NO₃⁻ concentrations.

Data availability. Data on nitrate concentrations in snow on the traverse from coast (Zhongshan Station) to Dome A are available from the Chinese National Arctic and Antarctic Data Center, https://doi.org/10.11856/SNS.D.2018.001.v0 (Shi, 2018).

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Competing interests. The authors declare that they have no conflict of interest.

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