A 60 Year Record of Atmospheric Aerosol Depositions Preserved in a High-Accumulation Dome Ice Core, Southeast Greenland

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Abstract The Southeastern Greenland Dome (SE-Dome) has both a high elevation and a high accumulation rate (1.01 m we yr⁻¹), which are suitable properties for reconstructing past environmental changes with a high time resolution. For this study, we measured the major ion fluxes in a 90 m ice core drilled from the SE-Dome region in 2015 and present the records of annual ion fluxes from 1957 to 2014. From 1970 to 2010, the trend of nonsea-salt (nss) SO4²⁻ flux decreases, whereas that for NH4⁺ increases, tracking well with the anthropogenic SO₂ and NH₃ emissions mainly from North America. The result suggests that these fluxes reflect histories of the anthropogenic SO₄ and NH₃ emissions. In contrast, the decadal trend of NO₃⁻ flux differs from the decreasing trend of anthropogenic NOₓ emissions. Although the cause of this discrepancy remains unclear, it may be related to changes in particle formation processes and chemical scavenging rates caused by an increase in sea salt and dust and/or a decrease in nssSO₄²⁻. We also find a high average NO₃⁻ flux (1.13 mmol m⁻² yr⁻¹) in the ice core, which suggests a negligible effect from postdepositional NO₃⁻ loss. Thus, the SE-Dome region is an excellent location for reconstructing nitrate fluxes. Over a decadal time scale, our NO₃⁻ flux record is similar to those from other ice cores in Greenland high-elevation sites, suggesting that NO₃⁻ concentration records from these ice cores are reliable.

1. Introduction

The years after 1950 include a high-pollution period involving significant emissions of anthropogenic aerosols and greenhouse gases, and then from the 1970s a subsequent conservation period of global environment regulations (e.g., IPCC, 2013). Examples of such anthropogenic aerosols that were regulated include precursors of SO₂ and NOₓ (NOₓ) (Crippa et al., 2016). SO₂ and NOₓ are converted to strong acids (H₂SO₄ and HNO₃) in the atmosphere and cause environmental destruction as acid rain (Likens et al., 1996; Stoddard et al., 1999). Sulfate and nitrate in the atmosphere also become microparticles in the atmosphere (secondary aerosols) and decrease the surface air temperature by both direct and indirect effects of radiative forcing (Andreae & Rosenfeld, 2008; Pöschl, 2005).

Recent changes in SO₂ and NOₓ emissions are mainly attributed to anthropogenic activity (Emission Database for Global Atmospheric Research (EDGAR) project; see e.g., Crippa et al., 2016). As a result, time series of the emissions differ by country both quantitively and trend-wise. Emissions from Asia are still growing very fast, with both China and India surpassing that from the United States and Western Europe for SO₂. The rate of increase in emissions from China dramatically slows after 2006, but not so for India. Thus, it is important to better understand historical changes in both source and emission of SO₂ and NOₓ to evaluate the impact of anthropogenic activity on Earth’s climate and environment.

Past SO₂ and NOₓ (NOₓ) history can be reconstructed from ice cores drilled from ice sheets and glaciers (Legrand & Mayewski, 1997; Petit et al., 1999; Plummer et al., 2012; Röthlisberger et al., 2002; Wolff et al., 2006). These compounds are preserved as SO₄²⁻ and NO₃⁻ in ice sheets and glaciers after wet or dry
deposition to surface snow in the polar and high-mountain regions (Legrand et al., 1988; Legrand & Mayewski, 1997). In the Arctic, wet deposition produces about 90% of the black carbon, sulfate, and dust depositions (Breider et al., 2014), which suggests that wet deposition probably also produces the nitrate deposition due to nitrate being a more hygroscopic material (e.g., IPCC, 2013).

An advantage of using ice cores to reconstruct SO$_4$ and NO$_x$ history is the long-term nature of their record. Previous ice core studies (e.g., Fischer et al., 1998; Patris et al., 2002) have reported changes in the concentration of SO$_4^{2-}$ from Greenland ice cores over the past 300 years. The SO$_4^{2-}$ records in Greenland ice cores agree with historical changes in anthropogenic SO$_x$ emissions from North America, indicating that Greenland ice cores are a useful archive to evaluate past emissions of anthropogenic SO$_4^{2-}$ from North America. However, for the period after 1970–1980, when SO$_x$ emissions were a maximum, few studies (e.g., Maselli et al., 2017; Plummer et al., 2012) have reconstructed the SO$_4^{2-}$ records.

In contrast to SO$_4^{2-}$, preservation of NO$_3^-$ in snow is reduced by photolysis, volatilization during snow sublimation, and stress desorption due to snow grain growth particularly at low accumulation rates (Dibb & Jaffrezo, 1997; Geng et al., 2015; Röthlisberger et al., 2002; Wagnon et al., 1999; Zatko et al., 2016). For instance, ice from the top few centimeters in inland Antarctica loses about 90% of its NO$_3^-$ (Iizuka et al., 2004; Wagnon et al., 1999). Inland Greenland may have a comparable loss to photolysis (Zatko et al., 2016), making it difficult to determine past trends in NO$_x$ from ice cores. So reconstructing historical variations of NO$_x$ concentrations in the atmosphere from ice core records is still highly uncertain.

In areas where the top few centimeters are quickly buried by new snowfall, the NO$_3^-$ recorded is better preserved. Hence, it is vital to use ice core data from a high-accumulation area to obtain a reliable record of NO$_3^-$ flux. This vital feature tends to compete against a more general requirement for precise reconstruction, specifically the use of ice from a region with minimal ice advection, such as a dome region. Due to this latter requirement, many ice cores have been drilled in ice sheet domes such as Dome Fuji (Watanabe et al., 2003), EPICA DML (EPICA community members, 2006), EPICA Dome C (EPICA community members, 2004), GRIP (Greenland Ice-core Project Members, 1993), GISP2 (Grootes et al., 1993), and NGRIP (North Greenland Ice Core Project Members, 2004). However, most domes are in a highland polar region, which tend to be dry and thus have a low accumulation rate—a disadvantage for NO$_3^-$ reconstruction.

A 90.45 m depth ice core was obtained at a high-elevation (above 3,000 m above sea level (asl)) dome site in southeast Greenland called SE-Dome (Iizuka et al., 2016). The SE-Dome region has the distinct characteristic of having the highest accumulation rate of any known dome of the Antarctic and Greenland ice sheets, a value in water equivalent (we) of 1.01 ± 0.22 m yr$^{-1}$ (1960–2014), which is about 4 times that of a typical inland Greenland ice core and about 30 times that of a typical inland Antarctic ice core (Iizuka et al., 2017). Moreover, the precise age scale for the SE-Dome ice core allows us to investigate seasonal variations of the climatic records from 1960 to 2014 (Furukawa et al., 2017). In this paper, we argue that the SE-Dome ice core preserves the NO$_3^-$ flux better than previous polar ice records, and we evaluate the SO$_4^{2-}$ and NO$_3^-$ record against known emissions of SO$_x$ and NO$_x$ over the past 60 years.

### 2. Sample and Analytical Methods

#### 2.1. SE-Dome Ice Core and Age Scale

We used a 90.45 m depth ice core obtained at a dome site on the SE-Dome (67.18°N, 36.37°W, 3,170 m asl). The annual mean temperature at the SE-Dome is −20.9°C, based on 20 m deep firn-temperature measurements (Iizuka et al., 2017). For a time scale, we use the SEIS2016 age scale for 1960–2014, which is determined by the oxygen-isotope matching method (Furukawa et al., 2017). The SEIS2016 scale has been carefully evaluated with independent age markers, and its precision is within a few months. From 1957 to 1959, we regard Na$^+$ maxima as marking depths of February precipitation. Then, linear interpolation is adapted to convert the depths to the beginning of the year. The measured number of samples is 1637 from 1957 to 2014, corresponding to 29 samples per year on average.

#### 2.2. Ion Concentration Measurements

In a cold room (Institute of Low Temperature Science, Hokkaido University, Japan), we divided the ice core into 50 mm depth sections. Above 12.5 m, the low firn density gave a low sampling volume, so we instead
divided this shallow part of core into 100 mm sections. The samples were divided using a clean ceramic knife in a cold clean room (class 10,000), put into a cleaned polyethylene bottle, and then melted in the bottle at room temperature in a clean room. The ion concentrations of CH$_3$SO$_3^-$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, Na$^+$, Ca$^{2+}$, NH$_4^+$, Mg$^{2+}$, and K$^+$ were measured by ion chromatography (Thermo Scientific IC-2100; column is Dionex CS-12A, and eluent is 20 mM MSA for cation; column is Dionex AS-14A, and eluent is 23 mM NaOH for anion). The injection volumes are 1,000 μL for anion and 500 μL for cation. Most CH$_3$SO$_3^-$ and K$^+$ concentrations were below the detection limit and thus not discussed in this paper. Analytical precision of the ion concentration is 10%. To confirm that any large peak in ion concentration is not caused by analytical errors, signifi-
cantly different values from two adjacent samples (based on a 3-point running standard deviation (>3σ)) were checked by remeasuring the ice sample from the same depth. To detect NH$_4^+$ accurately, the surface decontamination and sample melting were done within 1 week and 1 day, respectively, of the ion-chromatography measurement. For SO$_4^{2-}$ and Ca$^{2+}$, their nonsea-salt (nss) fractions were calculated as follows. If all Na$^+$ is assumed to come from sea salt (ss), then the sea-salt fraction is [ssSO$_4^{2-}$] = 0.060 [Na$^+$] and [ssCa$^{2+}$] = 0.022 [Na$^+$]. Thus, [nssSO$_4^{2-}$] = [SO$_4^{2-}$] − [ssSO$_4^{2-}$]; [nssCa$^{2+}$] = [Ca$^{2+}$] − [ssCa$^{2+}$].

2.3. Flux Estimation

The seasonal ion fluxes are based on the seasonal average value of each ion concentration multiplied by the seasonal accumulation rate. The seasonal boundaries are 1 March, 1 June, 1 September, and 1 December for spring (MAM), summer (JJA), autumn (SON), and winter (DJF). The annual ion fluxes are based on the sum of four seasons with the boundary of 1 March. These annual and seasonal accumulation rates are precisely estimated based on the SEIS2016 age scale (Furukawa et al., 2017). This method is similar to that used previously for the NO$_3^-$ concentration of the SIGMA-D ice core in northwestern Greenland. In that study, the annual NO$_3^-$ flux from 1950 to 2013 is obtained using the annual accumulation rate (from Matoba et al., 2015) multiplied by the annual average value of NO$_3^-$ concentration.

2.4. Isotope Measurement

The nitrogen isotopic composition of NO$_3^-$ is δ$^{15}$N, where δ$^X$ = $R_{\text{Sample}}/R_{\text{Standard}}$ − 1 and $R$ is $^{15}$N/$^{14}$N in the sample or in the standard (atmospheric N$_2$ for the nitrogen isotope). Nitrogen isotopic composition of nitrate in surface snow at the SE-Dome region was measured according to method described in Hattori et al. (2016). NO$_3^-$ in the surface snow samples collected in Iizuka et al. (2016) were concentrated and separated from other ions using the ion-chromatographic method described in Ishino et al. (2017). NO$_3^-$ was converted to N$_2$O using a strain of denitrifying bacteria that has no N$_2$O reductase. The produced N$_2$O was then separated from other species by chemical traps and gas chromatography and decomposed to O$_2$ and N$_2$ with a microwave-induced plasma. The isotopic ratios of each gas were measured by a MAT253 isotope-ratio mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The analytical uncertainty of the measurements here is 0.3‰ for δ$^{15}$N values.

2.5. Backward Trajectory Analysis

To investigate source regions of the chemical species preserved in the ice core, transport pathways of air masses are analyzed using the HYPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory), which is distributed by NOAA (National Oceanographic and Atmospheric Administration) (Stein et al., 2015). Points at 0, 500, 1,000, and 1,500 m above ground level (agl), which correspond to 1,550, 2,050, 2,550 and 3,050 m asl in the model, are set as starting points of the 30 day backward trajectories. The probability distribution of the air mass at altitudes between 0 and 1,500 m agl is calculated at a 1° resolution. We assume wet deposition for the preserved aerosols. And thus, the probability is weighted by the daily amount of precipitation when the air mass arrived at the core site. We used the daily precipitation in the reanalysis data sets of ERA-40 and ERA-Interim, both produced by European Centre for Medium-Range Weather Forecasts (Dee et al., 2011; Uppala et al., 2005). To maintain consistency among the two precipitation products for the whole period (1958–2014), the daily precipitation of ERA-40 (p40) is calibrated with that of ERA-Interim (pi) by a linear regression obtained for the period 1979–2001 (pi = 1.36 p40, $R^2$ = 0.862, $p < 0.001$). From the probability distribution, we also calculate the regional contribution for each day and for all land regions in the Northern Hemisphere, which is divided into 13 regions in the national boundary data (http://www.naturalearthingdata.com/, last access: 5 June 2017).
3. Results and Discussion

3.1. General Characteristics of Ion Concentrations in SE-Dome Ice Core

The major cation is NH$_4^+$, with a core average of 0.70 $\mu$mol L$^{-1}$, and the major anion is NO$_3^-$, at 0.94 $\mu$mol L$^{-1}$ (Table 1). These values correspond well to those in surface snow (Iizuka et al., 2016). Moreover, in their time series (Figure 1), these two ions correlate strongly with $r^2 = 0.62$ (Table 2). The table also shows that NH$_4^+$ correlates with SO$_4^{2-}$ ions ($r^2 = 0.75$), whereas Cl$^-$, Na$^+$, and Mg$^{2+}$ ions strongly correlate with each other ($r^2 > 0.70$). Summing values in Table 1, the total anion concentration (2.87 $\mu$eq L$^{-1}$) is higher than that of the total cation concentration (2.07 $\mu$eq L$^{-1}$), indicating that acid compounds (HCl, H$_2$SO$_4$, and HNO$_3$) are also contained in this ice.

These ion species can be separated into three groups using principal component analysis. Table 3 shows their principal component loadings. In the first component, Cl$^-$, Na$^+$, and Mg$^{2+}$ have high absolute loading values. Other than their strong correlations, they have ratios nearly equal to the sea-salt ratios (Table 1), suggesting that Cl$^-$, Na$^+$, and Mg$^{2+}$ mainly originate from sea salt. Previous studies suggest

<table>
<thead>
<tr>
<th></th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value (standard deviation)</td>
<td>0.59 (0.42–0.85)</td>
<td>0.67 (0.48–0.94)</td>
<td>0.94 (0.70–1.26)</td>
<td>0.47 (0.31–0.72)</td>
<td>0.70 (0.46–1.08)</td>
<td>0.16 (0.10–0.26)</td>
<td>0.29 (0.19–0.45)</td>
</tr>
</tbody>
</table>

Note. The statistical values are calculated assuming a lognormal distribution.

Figure 1. Time series of NO$_3^-$ (green), nssSO$_4^{2-}$ (red), and NH$_4^+$ (purple) concentrations ($\mu$mol L$^{-1}$). (a) 1957–1975, (b) 1975–1995, and (c) 1995–2015. The asterisks in 1992, 2010, and 2014 are volcanic contribution of Pinatubo (Philippines), Eyjafjallajökull (Iceland), and Bardarbunga (Iceland), respectively (Iizuka et al., 2017). The Pinatubo signature has peak NO$_3^-$, nssSO$_4^{2-}$, and NH$_4^+$ values of 11.38, 13.74, and 17.35 $\mu$mol L$^{-1}$, respectively.
that they have seasonal peaks during winter (e.g., Legrand & Mayewski, 1997; Whitlow et al., 1992). In the second component, \( \text{SO}_4^{2-} (-0.79) \), \( \text{NO}_3^- (-0.79) \), and \( \text{NH}_4^+ (-0.85) \) all have high absolute loading values. They also strongly correlate with each other and are the primary ion species in the SE-Dome ice core. In the third component, only \( \text{Ca}^{2+} (-0.85) \) has a high absolute loading value. This component can be explained as a soluble terrestrial contribution (e.g., Legrand & Mayewski, 1997; Whitlow et al., 1992).

The cumulative contribution ratio (Table 3), summed from the first to third components, is 89.0% of the total contribution, indicating that these three components well explain the general characteristics of ion concentrations in the SE-Dome ice core. In the following sections, we discuss the flux fluctuations of the sea-salt and terrestrial components (first and third components), and then the flux fluctuations of the N and S species in detail (second component).

### 3.2. Sea Salt and Terrestrial Components

To help determine the sources, we calculated the probability distributions of an air mass arriving at the SE-Dome site. The results in Figure 2, from back trajectory analyses, suggest three main findings. (1) The air mass at upper elevations (1,000 and 1,500 m agl) comes from a broader region than that at lower elevations (0 and 500 m agl). (2) The air mass at lower elevations (0 and 500 m agl) comes not only from the region including southern-southeastern Greenland and the North Atlantic Ocean in the 7 day analysis (Figure 2a) but also from eastern Canada in the 14 and 25 day analyses (Figures 2b and 2c) and from Russia in the 25 day analysis (Figure 2c). (3) The air mass at upper elevations (1,000 and 1,500 m agl) also comes from eastern Canada, as well as from a broad region that includes southern and southeastern Greenland, the North Atlantic Ocean, and northern and western Europe in the 7 and 14 day analyses (Figures 2d and 2e), and also from Russia and northern Alaska in the 25 day analysis (Figure 2f). There is little contribution from East Asia (Japan and China) and India, which are high anthropogenic \( \text{SO}_4^{2-}, \text{NO}_3^- \), and \( \text{NH}_3 \) emission regions (Crippa et al., 2016).

From the trajectory analyses, we estimate the interannual variability of the regional contributions. Five regions are selected as possible source regions of anthropogenic emission for the SE-Dome site (Figure 3, top). The interannual variability during 1957 to 2014 is smaller than the trajectory counting days (7, 14, and 25 days). The air mass at the lower elevations (0 and 500 m agl) comes from Greenland (7 and 14 days), North America (7 and 14 days), Europe (7, 14, and 25 days), and Russia (7, 14, and 25 days). The air mass at the upper elevations (1,000 and 1,500 m agl) comes mainly from North America and also from Greenland, Europe, and Russia (7, 14, and 25 days).

The \( \text{Cl}^- \), \( \text{Na}^+ \), and \( \text{Mg}^{2+} \) fluxes are highly correlated with each other (\( r^2 > 0.70 \) in Table 2). The ratio of \( \text{Cl}^-/\text{Na}^+ (1.25 \text{ average}) \) nearly equals the sea-salt ratios (1.18). The back trajectory analyses (Figure 2) suggest that the sea-salt particles are transported from the North Atlantic Ocean. Sporadically high flux peaks occur during (1) winter in

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**Table 2**

*Correlation Coefficients Between Ion Species*

<table>
<thead>
<tr>
<th></th>
<th>( \text{Cl}^- )</th>
<th>( \text{SO}_4^{2-} )</th>
<th>( \text{NO}_3^- )</th>
<th>( \text{Na}^+ )</th>
<th>( \text{NH}_4^+ )</th>
<th>( \text{Mg}^{2+} )</th>
<th>( \text{Ca}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}^- )</td>
<td>—</td>
<td>0.14</td>
<td>0.06</td>
<td>0.97</td>
<td>0.07</td>
<td>0.72</td>
<td>0.33</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>0.25</td>
<td>—</td>
<td>0.59</td>
<td>0.08</td>
<td>0.75</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>( \text{NO}_3^- )</td>
<td>0.38</td>
<td>0.51</td>
<td>—</td>
<td>—</td>
<td>0.62</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>( \text{Na}^+ )</td>
<td>0.95</td>
<td>0.23</td>
<td>0.23</td>
<td>—</td>
<td>0.01</td>
<td>0.70</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{NH}_4^+ )</td>
<td>0.53</td>
<td>0.46</td>
<td>0.62</td>
<td>0.49</td>
<td>—</td>
<td>0.13</td>
<td>0.19</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} )</td>
<td>0.78</td>
<td>0.18</td>
<td>0.36</td>
<td>0.72</td>
<td>0.31</td>
<td>—</td>
<td>0.64</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>0.61</td>
<td>0.01</td>
<td>0.21</td>
<td>0.60</td>
<td>0.33</td>
<td>0.71</td>
<td>—</td>
</tr>
</tbody>
</table>

**Note:** Values above the diagonal are between ion concentrations \( n = 1637 \), and values below the diagonal are between annual ion fluxes \( n = 57 \).

Figure 2. Probability distribution of an air mass arriving at the SE-Dome site from a 25 day 3-D backward-trajectory analysis for two elevations and three terms. The color scale at the bottom. (left column) "Lower" means 0 and 500 m agl, and (right column) "upper" means 1,000 and 1,500 m agl air masses. Trajectory periods are (top row) 7 days, (middle) 14 days, and (bottom) 25 days. Existence of the air mass is weighted by the daily precipitation in reanalysis data sets of ERA-40 and ERA-Interim.
The \text{nssCa}^{2+} \text{ flux is nearly constant from 1957 to 2000 (Figure 4c), but then trends upward till the present. This \text{nssCa}^{2+} \text{ (and dust) deposited in high-elevation sites of Greenland is thought to originate mainly from Asia, primarily from China deserts (Bory et al., 2003; Fischer et al., 2007; Prospero et al., 2002). However, the flux of Asian dust shows a decreasing trend in recent decades, associated with the warming of Mongolia that represents a northward shift of the westerlies (Nagashima et al., 2016; Zhu et al., 2008), which seems to contradict the increasing trend of \text{nssCa}^{2+} \text{ flux in SE-Dome. The relatively high \text{nssCa}^{2+} \text{ fluxes after 2000 may instead link to a local source, such as an increase in land-area exposure around the southeastern Greenland coast. In particular, the retreat rates of ice sheets (marine- and land-terminating) and local glaciers accelerated after 2000 (Bjerk et al., 2012). This retreat acceleration is common in Greenland; for example, van den Broeke et al. (2009) showed a cumulative mass anomaly of the Greenland Ice Sheet and a decreasing trend of ice mass from \sim 1990 to present. These ice retreats tend to expose more land from snow-covered areas in the coastal regions. Mesoscale wind around the SE-Dome region is mainly from the northeast and/or east regions (Hanna et al., 2006; Moore et al., 2015) where there are many nunataks. Thus, the wind direction and glacial trends suggest a local source of \text{nssCa}^{2+}.}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Time series of regional contributions of air mass origins. The regions are shown at the top. Greenland in gray, North America in purple (Canada and the U.S.), Europe in green, Russia in blue (includes Ukraine), and East Asia in red (China and Japan). Each panel corresponds to panels in Figure 2.}
\end{figure}
Micrographs of nonvolatile particles in the SE-Dome ice core support the evidence for a local source. Figure 5 shows that some particles have a diameter exceeding 10 μm with a silicon component (indicating silicate minerals). Such huge particles suggest a local dust origin due to their shorter lifetime in the atmosphere. The increases of nssCa\(^{2+}\) flux (Figure 4c) occur not only in spring (2001 and 2008) but also in summer (2003 and 2012) and autumn (2014). These seasonal contributions can be explained not by the increasing trend of Asian spring dust, but by seasonal land exposure in coastal regions around southeastern Greenland. Thus, the land exposure in these coastal regions likely increases the supply of local dust to the SE-Dome region and thus increases the nssCa\(^{2+}\) flux. In support of this argument, the back trajectory plots show that the southeastern and southern Greenland coastal regions are potential aerosol source regions for the air mass at lower atmosphere (0 and 500 m agl, Figures 2a–2c). Moreover, the Greenland contribution in the 7 and 14 day plots at lower atmosphere (Figure 3) increases after 2000.

### 3.3. Time Series of Sulfate, Nitrate, and Ammonium Fluxes

The time series of nssSO\(_4^{2-}\), NO\(_3^-\), and NH\(_4^+\) fluxes have generally high contribution during summer (Figure 6), which is a common feature in Greenland ice cores (Fischer et al., 2015; Fuhrer et al., 1996; Geng et al., 2014; Hansson & Holmén, 2001; Silvente & Legrand, 1993). In some periods, such as around 1970 and after 1996, spring and autumn contributions also occur, suggesting an increasing frequency of anthropogenic pollution plumes (Whitlow et al., 1992). As identified in Iizuka et al. (2017), volcanic signals (Figure 1) also appear in spring 1992 (from Pinatubo in the Philippines), in spring 2010 (from Eyjafjallajökull in Iceland), and in autumn–winter 2014 (from Bardarbunga in Iceland).

Overall, the nssSO\(_4^{2-}\) flux from 1957 to 2014 (Figure 6a) shows a decreasing trend. But until the mid-1980s, the flux remains within 0.5 to 1.0 mmol m\(^{-2}\) yr\(^{-1}\) with peaks at 1977 (1.21 mmol m\(^{-2}\) yr\(^{-1}\)) and 1984 (1.18 mmol m\(^{-2}\) yr\(^{-1}\)). Then, the flux goes down to about 0.3 to 0.5 mmol m\(^{-2}\) yr\(^{-1}\) except for the volcanic years (1992 and 2014). The peaks at 1977, 1984, 1987, and 1990 arise from spring and/or summer.

The NO\(_3^-\) flux from 1957 to 2014 (Figure 6b) is generally constant or slightly increasing, with larger peaks during 1987–1995. The highest of these peaks are in 1987 (2.53 mmol m\(^{-2}\) yr\(^{-1}\)), 1990 (1.92 mmol m\(^{-2}\) yr\(^{-1}\)), 1992 (2.25 mmol m\(^{-2}\) yr\(^{-1}\)), and 1995 (1.78 mmol m\(^{-2}\) yr\(^{-1}\)). Outside of this period, the NO\(_3^-\) flux remains at 1.0 ± 0.5 mmol m\(^{-2}\) yr\(^{-1}\) except peaks at 1977 (1.69 mmol m\(^{-2}\) yr\(^{-1}\)) and 2002 (1.75 mmol m\(^{-2}\) yr\(^{-1}\)). The peaks at 1977, 1987, 1990, 1992, 1995, and 2002 arise during spring and/or summer.

Finally, the NH\(_4^+\) flux from 1957 to 2014 shows an increasing trend (Figure 6c). Until the mid-1980s, the NH\(_4^+\) flux sometimes dips below 0.5 mmol m\(^{-2}\) yr\(^{-1}\). But thereafter, it remains between 0.5 and 1.0 mmol m\(^{-2}\) yr\(^{-1}\) except for a few peaks, including 1984 (1.04 mmol m\(^{-2}\) yr\(^{-1}\)), 1990 (1.19 mmol m\(^{-2}\) yr\(^{-1}\)), 1992 (1.74 mmol m\(^{-2}\) yr\(^{-1}\)), 2007 (1.08 mmol m\(^{-2}\) yr\(^{-1}\)), 2008 (1.03 mmol m\(^{-2}\) yr\(^{-1}\)), and 2014 (1.73 mmol m\(^{-2}\) yr\(^{-1}\)). The peaks at 1984 and 1990 occur mainly in summer, but those in 1992, 2007, 2008, and 2014 occur from spring to autumn.

The maximum nssSO\(_4^{2-}\), NO\(_3^-\), and NH\(_4^+\) fluxes are in 1992 and are also notably high around 1990. Prior to about 1995, the NO\(_3^-\) flux is at a similar level as the nssSO\(_4^{2-}\) flux. Then, after about 1995, the NO\(_3^-\) (as well as the NH\(_4^+\)) flux exceeds that of nssSO\(_4^{2-}\). The following section examines the NO\(_3^-\) record by focusing on the postdepositional loss, the causes of the long-term trend, and comparison with other ice cores.
3.4. Limited Postdepositional Loss of Nitrate Ions

The postdeposition effect decreases the amount of NO$_3^-$, particularly at low accumulation rates (Dibb & Jaffrezo, 1997; Geng et al., 2015; Röthlisberger et al., 2002; Wagnon et al., 1999; Zatko et al., 2016). The dependence on accumulation rate (e.g., Röthlisberger et al., 2002; Zatko et al., 2016) occurs because a lower accumulation rate results in a longer exposure time in surface snow, allowing more photolysis and greater evaporation of the snow’s impurities (e.g., Wagnon et al., 1999). For NO$_3^-$, recent studies suggest that photolysis is the main cause of postdepositional loss in Antarctica (Erbland et al., 2013; Frey et al., 2009) and Greenland (Geng et al., 2014). For these reasons, the NO$_3^-$ fluxes in Greenland ice cores depend on the annual accumulation rate (Röthlisberger et al., 2002) (Figure 7a).

At the higher accumulation rates, the NO$_3^-$ flux increases with annual accumulation rate largely because the NO$_3^-$ flux is mainly from wet deposition (Figure 7a). But at low accumulation rates, the postdepositional loss increases the difference between higher and lower accumulation sites. This leads to an expected logarithmic relation between the NO$_3^-$ flux and annual accumulation rate. Indeed, we find that the data well fit such a relation in Figure 7a ($r^2 = 0.93$). In fact, the fits with and without the SE Dome data (not shown) are nearly exactly the same. In the case of Summit, where the accumulation rate is 0.25 m yr$^{-1}$ we (Dibb & Fahnestock, 2004), the estimated postdepositional effect ranges from negligible (Fibiger et al., 2013, 2016) to 6% (Geng et al., 2014) and up to 20% (Dibb et al., 2007). The accumulation rate for the SE-Dome ice core is 1.01 m we yr$^{-1}$, 4 times that at Summit, suggesting that the NO$_3^-$ is preserved without the postdepositional effect. In fact, the NO$_3^-$ flux at SE-Dome’s core, 1.13 mmol m$^{-2}$ yr$^{-1}$ (average of 1957–2014), lies on the asymptotic line of the logarithmic curve in Figure 7a.

SE-Dome’s high NO$_3^-$ flux is also high for its altitude (Figure 7b) and its latitude (Figure 7c). The NO$_3^-$ flux has no clear relationship with altitude but correlates significantly ($r^2 = 0.54$) with latitude (Figure 7c). The correlation with latitude may suggest that the NO$_3^-$ flux in Greenland is mainly controlled by the location’s closeness to the sources in the south and also to North America and Europe, which is consistent with the back trajectory analyses described above (Figure 2). The correlation may also reflect the trend of decreasing accumulation (and hence NO$_3^-$ flux) with latitude in Greenland. The NO$_3^-$ flux at SE-Dome (1.13 mmol m$^{-2}$ yr$^{-1}$)
is the highest of all of the cores included in Figure 7. Thus, these data suggest a uniquely high NO$_3^-$ flux regardless of regional differences in depositional settings.

The photolysis of NO$_3^-$ in the snowpack occurs at depths of up to 20 cm (Grannas et al., 2007; Zatko et al., 2013). The snow accumulation at the SE-Dome is 23 cm per month in snow equivalent, as estimated from the surface density of about 360 kg m$^{-3}$ in the ice core (Iizuka et al., 2017). Zatko et al. (2016) showed that the lifetime of photolabile NO$_3^-$ against photolysis is longer than its lifetime in the snow photic zone in southeastern Greenland, which reduces postdepositional photolysis of snow NO$_3^-$ (Figure 10b in Zatko et al., 2016). Such modeling indicates that the photolysis effect around the SE-Dome region is negligible (Figure 10d in Zatko et al., 2016).

In addition, the nitrogen isotopic composition of NO$_3^-$ is consistent with a negligible influence of postdepositional loss of NO$_3^-$ at the SE-Dome region. In a low snow-accumulation site such as East Antarctica (~10 cm yr$^{-1}$ snow accumulation), high $\delta^{15}$N values of NO$_3^-$ ranging from +50 to +300‰ are observed between the surface and 70 cm depth (Blunier et al., 2005; Frey et al., 2009). The high $\delta^{15}$N values result from a combination of a large photolytic loss of NO$_3^-$ and a large isotopic fractionation of NO$_3^-$ photolysis (~40 to ~74‰; Frey et al., 2009; Berhanu et al., 2014). In contrast, the $\delta^{15}$N value of NO$_3^-$ in surface snow (spring 2015) at the SE-Dome region is only ~4.3‰. The $\delta^{15}$N (NO$_3^-$) value of SE-Dome ice equals the lower values measured at Summit, Greenland (~8.7 to 14.3‰; Geng et al., 2014; Fibiger et al., 2016), suggesting no significant influence of postdepositional loss of NO$_3^-$.

Taken together, the comparison with other ice core data, the modeling, and the low $\delta^{15}$N value all show that the SE-Dome region has negligible postdepositional loss of NO$_3^-$- as the SE-Dome is located in a highland above 3,000 m asl, aerosols are transported from not only local regions around Greenland but also from more distant, remote regions, including nearby continents and oceans. Thus, our results suggest that the SE-Dome region is an excellent region for evaluating and reconstructing nitrate and other volatile material fluxes.

### 3.5. Comparison With nssSO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ Fluxes and the EDGAR Emissions

Here we consider how the regional emissions of SO$_x$, NO$_x$, and NH$_x$ based on the EDGAR 4.3.1 model (Crippa et al., 2016), may have influenced levels at the SE-Dome site. We multiply the regional emissions, shown in Figures 8a–8c, by the regional contributions of air mass in Figure 3, and then consider the relative changes from the 1970–1980 average values.

A 7 day trajectory, as used for Figure 3, is expected to be a median for the aerosol lifetimes of various species. For example, for SO$_2$, the lifetime ranges from 13 h (near ground in the U.S.; Lee et al., 2011) to 13 days (Arctic upper troposphere; Höpfner et al., 2015), whereas sulfate is estimated as 8.27 days (Breider et al., 2014), NH$_3$(g) as 0.46 days, NH$_4^+$ as 3.23 days, HNO$_3$(g) as 4.76 days, and nitrate as 3.92 days (Xu & Penner, 2012). However, Qi et al. (2017) pointed out that a 7 day trajectory is not sufficient for aerosol transport by an atmospheric model that includes geochemical processes, and they instead considered a 25 day trajectory. To include a range of aerosol behavior, we consider the 7, 14, and 25 day trajectories at the two elevations.

All resulting trajectory cases of 7, 14, and 25 days at the upper and lower elevations show similar trends in Figures 8d–8f. The similarity arises from the similar trends of NO$_x$ and SO$_x$ emissions in North America and
Europe. The 5 year running averages of nssSO$_4^{2-}$ and NH$_4^+$ fluxes in the SE-Dome ice core (black curve) agree well with the regionally weighted SO$_2$ and NH$_3$ from the EDGAR emissions (red curves). In contrast, the NO$_3^-$ flux does not follow the decreasing trend of NO$_x$ emissions very well (Figure 8e). We next consider how two features in the NO$_3^-$ flux record (Figure 6b) may explain this discrepancy.

First, note the remarkably high spring and summer contributions to the NO$_3^-$ flux peaks from 1985 to 1995 (Figure 6b). During this time, the nssSO$_4^{2-}$, and NH$_4^+$ fluxes are also higher than the emission lines (Figure 8). The large NH$_4^+$ flux during spring and summer around 1990 (Figure 6c) suggests a forest-fire source because NH$_4^+$ spikes in Greenlandic ice cores likely reflect forest fires in North America (Fischer et al., 2015; Fuhrer et al., 1996; Zennaro et al., 2014). High $\delta^{15}$N(ND$\delta$) values as well as high concentrations from 1980 to 1990 in Summit ice core also suggested an increase of natural sources like biomass burning (Hastings et al., 2009). Moreover, the forest fire activity increased in the western United States and Canada around 1990 (Fauria & Johnson, 2008; Westerling et al., 2006). Other causes for the NO$_3^-$ flux discrepancy include a source region discrepancy between emission and deposition (Lloret & Valiela, 2016) and a change in atmospheric circulation during this period. But forest fires are likely the dominant cause.

Second, despite a clear reduction in NO$_x$ emissions since 1970 in all regions except East Asia, the SE-Dome NO$_3^-$ record shows much less decrease after 1996. In fact, the NO$_3^-$ flux remains high enough to maintain an average value above the pre-1980 average (Figure 8e). The NO$_3^-$ record after 1996 may be explained by a shift in equilibrium driven by a reduction in SO$_2$ emissions toward more particulate NH$_4$NO$_3$ relative to HNO$_3$. The NH$_4$NO$_3$ particles dry deposit only slowly and thus may lead to a longer residence time than nitric acid (Fagerli & Aas, 2008). However, a recent study found a relatively constant summer-particle pH throughout the 15 years of decreasing atmospheric sulfate concentrations, indicating that nitrate is likely to form HNO$_3$ rather than NH$_4$NO$_3$ among the ammonia-sulfate-nitrate system (Weber et al., 2016). The gaseous HNO$_3$ also reacts with sea salt (Na$^+$) and dust (nssCa$^{2+}$). In fact, Na$^+$ and nssCa$^{2+}$ fluxes increased after 2000, whereas the nssSO$_4^{2-}$ flux decreased after the mid-1990s (section 3.3). In such an ion balance, the formation of NaNO$_3$ and Ca(NO$_3$)$_2$ may accelerate and may lead to a longer residence time. Thus, several chemical processes during transport may be involved. Clearly, a comprehensive understanding of the NO$_3^-$ record in the SE-Dome ice core requires a more complete atmospheric model that includes detailed atmospheric chemical processes (section 3.6).

Finally, variations in regional deposition may be important. For example, nitrate in precipitation in Europe decreased by 25% overall since 1990, but the variation from country to country is large (Tørseth et al., 2012). In North America, a recent compilation of nitrogen oxide deposition revealed that the regional-scale variations are highly affected by emission from, and transport through, neighboring source areas (Lloret & Valiela, 2016). Concerning historical changes, in Europe, despite a 31% reduction of NO$_x$ emission from 1990 to 2009, the concentrations of total airborne nitrate decreased only 8% (Tørseth et al., 2012). In North America, during 1980–2000, only minor changes and even increases were observed at some sites, then, after 2000, most sites showed significant decreasing trends (Lloret & Valiela, 2016).
Overall, the inconsistency between SE-Dome NO3⁻ flux and the NOx emission record suggests that the NO3⁻ flux reflects the combined effect of changes in NOx emissions in source areas, transport of air masses from source areas, and atmospheric chemical processes during transport. In contrast, the SOx and NH3 records based on emissions and air mass contributions (Figure 8) agree well with the nssSO4²⁻/C0 fluxes. This result suggests that unique and complex atmospheric chemical processes (i.e., preferential scavenging and/or sustaining) may have a larger influence on NO3⁻ than for nssSO4²⁻ and NH4⁺.

3.6. Limitations of the Emission and Trajectory Analyses

A limitation of these arguments (section 3.5) is that the back trajectory analysis estimates the transport of the air parcel, not the aerosol itself. For example, the 25 day trajectory plot in Figure 2f suggests a contribution from Alaska. Such a contribution of nitrate may have come from Asian nitrate that transports to the North Pacific Ocean via peroxyacetyl nitrate formation (e.g., Brock et al., 2004; Dunlea et al., 2009). In this case, we should account for NOx being a short-lived radical that influences the oxidizing capacity of the atmosphere via interactions with ozone (O₃) and hydroxyl radical (OH). But we do not consider these reactions in detail here.
Also, one should consider the possibility of wet deposition prior to air mass arrival at the site. For example, compound removal via precipitation scavenging during transport can occur but is not included in the trajectory modeling. In future studies, our NO$_3^-$, nssSO$_4^{2-}$, and NH$_4^+$ data set may be useful for testing the more detailed chemical transportation models, such as GEOS-Chem (http://acmg.seas.harvard.edu/geos/index.html). However, current chemical transport models in the Arctic are not yet well-designed for reactive gases (e.g., Emmons et al., 2015) and aerosols (e.g., Eckhardt et al., 2015).

### 3.7. Comparison With Ice Cores From Low-Accumulation Regions

The NO$_3^-$ flux linearly correlates with the annual accumulation rate because the NO$_3^-$ falls mainly through wet deposition. The dark-blue line in Figure 7a connects the SE-Dome ice core and the summit core values. If the NO$_3^-$ flux in the summit core is unaffected by postdepositional loss (Fibiger et al., 2013, 2016), then the resulting line would represent a lower-limit line for simple accumulation versus NO$_3^-$ correlation without postdepositional effect. But if, as suggested by Dibb et al. (2007), a 20% loss in NO$_3^-$ occurs at summit via postdepositional processes, then the line connecting SE-Dome data and the point 1.2 times the NO$_3^-$ flux at summit would represent an upper limit of the post depositional effect (the light blue line in Figure 7a). The intersection of these two lines with the data-fit curve (dashed black) suggests that the postdepositional effect on NO$_3^-$ would be negligible in an ice core drilling site with accumulation rate exceeding 0.19–0.36 m yr$^{-1}$.

Finally, we compare the SE Dome’s NO$_3^-$ concentration/flux after 1950 to those of two other Greenland sites. Both the NO$_3^-$ concentration and flux trends are quite similar. The profiles in Figure 9 show that the peak levels and annual variations differ among the three sites, yet their 5 year running means show a similar trend despite the low annual accumulation in the Summit (central Greenland) and SIGMA-D (northwest Greenland) ice cores (both about 0.25 m yr$^{-1}$). These NO$_3^-$ concentration/flux records have two common features: (1) large peaks in 1985–1995 and (2) levels in 1996 to 2014 at or above those during 1960–1980. We assume that years with a lower annual accumulation would have had a greater postdepositional effect. In such years, the NO$_3^-$ may not be a good proxy of dry/wet deposition. Thus, for the summit data in Figure 9, the NO$_3^-$ concentration trend may differ between them and from the flux trend. However, the similar features among the three data sets indicate that these cores well preserve past NO$_3^-$ fluctuations over more than a decade. About 0.25 m yr$^{-1}$ of annual accumulation is typical over Greenland (Figure 7a), and the regions of some deep ice cores (e.g., GRIP, NGRIP, GISP2, and NEEM) so far obtained have about the same accumulation rate during the Holocene. However, the Dye 3 deep ice core has 0.49 m yr$^{-1}$ of annual accumulation and may have an advantage for discussing nitrate fluctuation from the last glacial period to the Holocene. Our results for the SE-Dome ice core, an excellent location for evaluating and reconstructing nitrate fluxes, guarantee the reliability of NO$_3^-$ concentrations as the proxy of dry/wet deposition of general ice cores in Greenland over decadal or longer time scales.

### 4. Summary

We have shown that the high-accumulation rate of the SE-Dome region (1.01 m yr$^{-1}$) makes it an excellent location for evaluating and reconstructing ion fluxes, especially nitrate. The Cl$^-$, Na$^+$, and Mg$^{2+}$ ions were mainly from sea salt, all having winter maxima. For nssCa$^{2+}$, an increasing trend after 2000 could be explained as coming from the local dust around southeastern Greenland. The nssSO$_4^{2-}$ flux had a maximum during the 1960s–1970s but decreased after 1970–1980, indicating a proxy of anthropogenic SO$_2$. In contrast, the NH$_4^+$...
flux increased during 1957–2014, indicating a proxy of NH₃ emissions. The NO₃⁻ flux was about 1.13 mmol m⁻² yr⁻¹ (68.9 μg L⁻¹ concentration) with negligible postdepositional influences. This flux did not follow the decreasing trend of NO₂ emissions, differing in two ways. First, large spikes in the flux were detected from 1985 to 1995. Second, the NO₃⁻ flux from 1996 to 2014 was roughly constant and slightly higher compared with that from the 1960s to the 1980s, a time period when the anthropogenic NO₃ emission was higher. The NO₃⁻ fluxes/concentrations in some Greenland ice cores have a low accumulation rate (~0.25 m we yr⁻¹) yet show similar features as those at the SE-Dome ice core, suggesting that NO₃ concentrations may be a reliable proxy of wet deposition of ice cores in Greenland over decadal time scales. In the near future, the relationships between NOₓ, NH₃, and SO₄²⁻ emissions and the handling by Scientific Editor L. Russell, to whom we are greatly indebted. This study was supported by MEXT/JSPS KAKENHI grants 26257201, 16K12573, 17H06105, and 16H05884; the Joint Research Program of the Institute of Low Temperature Science, Hokkaido University; and the Readershup Program of the Institute of Low Temperature Science, Hokkaido University. This study is partly responsible for ArCS (Arctic Challenge for Sustainability Project). The data used in this publication. We are grateful to the drilling and initial analysis teams of SE-Dome ice core.


