800-year ice-core record of nitrogen deposition in Svalbard linked to ocean productivity and biogenic emissions

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Abstract. We present the records of the two nitrogen species nitrate ($\text{NO}_3^-$) and ammonium ($\text{NH}_4^+$) analysed in a new ice core from Lomonosovfonna, Svalbard, in the Eurasian Arctic covering the period 1222–2009. Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on the decadal variations of the investigated compounds. Accordingly, we use decadal records to investigate the major emission sources of $\text{NO}_3^-$ and $\text{NH}_4^+$ precursors and find that during the twentieth century both records are influenced by anthropogenic pollution from Eurasia. In pre-industrial times $\text{NO}_3^-$ is highly correlated with methane sulfonate (MSA), which we explain by a fertilising effect. We propose that enhanced atmospheric $\text{NO}_3^-$ concentrations and the corresponding nitrogen input to the ocean trigger the growth of dimethyl-sulfide-(DMS)-producing phytoplankton. Increased DMS production results in elevated fluxes to the atmosphere where it is oxidised to MSA. Eurasia was presumably the main source area also of pre-industrial $\text{NO}_3^-$, but a more exact source apportionment could not be performed based on our data. This is different for $\text{NH}_4^+$, where biogenic ammonia ($\text{NH}_3$) emissions from Siberian boreal forests were identified as the dominant source of pre-industrial $\text{NH}_4^+$.

1 Introduction

The Arctic is generally a nutrient limited region (Dickerson, 1985). Nutrients originate from lower latitudes and reach the remote polar areas via long-range transport; local sources are sparse. The major source of bio-available nitrogen in the Arctic is the deposition of reactive atmospheric nitrogen that is present primarily as nitrate ($\text{NO}_3^-$) and ammonium ($\text{NH}_4^+$) (Björkman et al., 2013; Kühnel et al., 2011). Those species are predominantly removed from the atmosphere by wet deposition (Bergin et al., 1995). $\text{NO}_3^-$ is the oxidation product of emitted NOx concentrations and the corresponding nitrogen input to the ocean trigger the growth of dimethyl-sulfide-(DMS)-producing phytoplankton. At a global scale, major $\text{NO}_3^-$ sources include biomass burning, emissions from microbial processes in soils, ammonia oxidation, stratospheric injection, lightning, as well as fossil fuel and biofuel combustion, and aircraft emissions (Fibiger et al., 2013; Galloway et al., 2004; Hastings et al., 2004; Wolff, 2013). $\text{NH}_4^+$ sources include biomass burning, agriculture, and livestock breeding (Fuhrer et al., 1996; Galloway et al., 2004; Wolff, 2013). Both $\text{NO}_3^-$ and $\text{NH}_4^+$ concentrations in the atmosphere have varied greatly with time and space due to changing emissions and the short atmospheric lifetimes of a few days (Adams et al., 1999; Feng and Penner, 2007). Generally, concentrations were low in pre-industrial times and increased due to stronger emissions with the beginning of the industrialisation and intensification of agricultural activities (Galloway et al., 2004). The deposition of $\text{NO}_3^-$ and $\text{NH}_4^+$ in
the Arctic is an important nutrient source. Varying concentrations thus greatly affect the nitrogen budget in the Arctic, where nutrient supply is limited.

Ice cores represent an invaluable archive of past atmospheric composition. Ice-core studies from the Arctic clearly reveal an anthropogenic influence on the concentrations of NO$_3^-$ and NH$_4^+$ approximately during the last 150 years (Fischer et al., 1998; Fuhrer et al., 1996; Goto-Azuma and Koerner, 2001; Kekonen et al., 2002, 2005; Legrand and Mayewski, 1997; Matoba et al., 2002; Simões and Zagorodnov, 2001). North America was identified as a major pollutant source for southern Greenland, both North America and Eurasia for central and northern Greenland, and Eurasia for Svalbard (Goto-Azuma and Koerner, 2001; Hicks and Isaksson, 2006). However, the pre-industrial sources of NO$_3^-$ and NH$_4^+$ are still fairly unknown (Legrand and Mayewski, 1997; Wolff, 2013). Eichler et al. (2011) identified forest fires as a major source of NO$_3^-$ in a Siberian Altai ice core from the mid-latitudes. In studies on Greenland ice, NO$_3^-$ was also associated with forest fires (Whitlow et al., 1994; Wolff et al., 2008). Pre-industrial NH$_4^+$ in ice cores from the mid-latitudes was attributed to biogenic emissions (Eichler et al., 2009; Kellerhals et al., 2010). Similarly, long-term trends in Greenland ice cores have been attributed to changing biogenic emission from North America, whereas short-term NH$_4^+$ changes were found to correlate with forest fires (Fuhrer et al., 1996; Whitlow et al., 1994; Zennaro et al., 2014).

Whereas a few records exist from Greenland, there is less information available from the Eurasian Arctic. The NO$_3^-$ and NH$_4^+$ records of a previous ice core from Lomonosovfonna, Svalbard, retrieved in 1997 (Lomo97; for the location, see Fig. 1), cover the last 1000 years (Divine et al., 2011; Kekonen et al., 2002, 2005). For both species a clear anthropogenic impact is observed in the second half of the twentieth century, but the pre-industrial sources remain largely unidentified due to potential runoff that biased the ion records before the mid-sixteenth century (Kekonen et al., 2002, 2005). Nevertheless, the fairly stable concentrations in the NO$_3^-$ record from the mid-sixteenth to the mid-nineteenth century are interpreted as input from natural NO$_3^-$ sources (Kekonen et al., 2002). An anthropogenic influence in the twentieth century is also visible in the NO$_3^-$ and NH$_4^+$ records of other Eurasian Arctic ice cores (see Fig. 1 for locations) from Holtedahlfonna (Holte05), Svalbard (Beaudon et al., 2013), Snøfjellafonna, Svalbard (Goto-Azuma and Koerner, 2001), and Severnaya Zemlya (Weiler et al., 2005). The industrial records from these cores are discussed in detail, but pre-industrial sources and concentration changes of the inorganic nitrogen species remain unexplained.

The interpretation of NO$_3^-$ and NH$_4^+$ as paleoenvironmental proxies may be hampered by the fact that both undergo post-depositional processes leading to loss from or relocation within the snowpack even at temperatures well below the melting point (Pohjola et al., 2002). NO$_3^-$ can be relocated or lost by photolysis and/or evaporation of nitric acid (HNO$_3$) (Honrath et al., 1999; Röthlisberger et al., 2002). This loss can be severe at low accumulation sites such as Dome C, Antarctica (Röthlisberger et al., 2000, 2002). At sites with higher accumulation rates such as Summit in Greenland or Weissfluhjoch in the European Alps, the majority of NO$_3^-$ is preserved (Baltensperger et al., 1993; Fibiger et al., 2013). Many studies reveal that NH$_4^+$ and NO$_3^-$ are preserved in snow and firn cores with respect to percolating meltwater (Eichler et al., 2001; Ginot et al., 2010; Moore and Grinsted, 2009; Pohjola et al., 2002), but others report a preferential elution of these species compared to other major ions (Brim
blecombe et al., 1985; Moore and Grinsted, 2009; Pohjola et al., 2002). The underlying mechanism is not well understood, except from the fact that it depends on the overall ion composition.

In this paper we discuss the records of the two nitrogen species \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) analysed in a new ice core drilled on Lomonosovfonna, Svalbard, in 2009. The study focuses on the investigation of the major sources of \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) deposited in the Eurasian Arctic which highly affects the nutrient budget in the region, along with the effect of melt on the geochemical records of these nitrogen species which will gain importance due to the ongoing global warming.

2 Methods

2.1 Drilling site and meteorological setting

In 2009, a 149.5 m long ice core was drilled on Lomonosovfonna, Svalbard (1202 m a.s.l.; 78°49’24”N, 17°25’59”E, Lomo09), using the Fast Electromechanical Lightweight Ice Coring System (FELICS) (Ginot et al., 2002). The 2009 drilling site is 4.6 km south of that in 1997 (Lomo97) (Isaksen et al., 2001). Bedrock was not reached, but a radar survey suggested it to be at around 200 m (Pettersson, unpublished data). Measured borehole temperatures in the upper 42 m (between −1.7 and −4.3 °C) at the Lomo09 drill site are in good agreement with the average borehole temperature at the Lomo97 site of −2.8 °C with a nearly isothermal profile (Van de Wal et al., 2002). Previous studies indicate that summer meltwater in the study area is refrozen mostly within the previous winter’s snow, and the remainder within the next two to three lower annual layers (Samuelson, 2001). Percolation length was found to be up to 8 years only in the warmest years during the twentieth century (Kekonen et al., 2005; Moore et al., 2005).

Svalbard is located at a climatically sensitive area, being surrounded by the Arctic Ocean, the Barents Sea and the Atlantic Ocean, and situated at the southerly edge of the permanent Arctic sea ice and close to the over-turning point of the North Atlantic thermohaline circulation. Furthermore, it is relatively close to the industrialised areas of Eurasia which were found to highly affect the chemical composition of air reaching the archipelago, especially in spring during the Arctic haze (Eleftheriadis et al., 2009; Eneroth et al., 2003; Forström et al., 2009; Goto-Azuma and Körner, 2001; Law and Stohl, 2007; Stohl et al., 2007). The Arctic haze describes a phenomenon of increased aerosol concentration in the end of winter to early spring (Greenaway, 1950; Quinn et al., 2007; Shaw, 1995). At that time of the year, temperatures in the Arctic become very low, which leads to a thermally very stable stratification with strong surface inversions (Shaw, 1995; Stohl, 2006). This cold stratified air forms a dome over the Arctic that hinders warm air masses from lower latitudes from entering. The boundary of this dome that acts as a transport barrier is called Arctic or Polar front whose position shifts between summer and winter due to temperature. In summer, only the more northern parts of the Northern Hemisphere are cold enough to cause a stable stratification of the atmosphere, whereas in winter temperatures in more southern parts are cold enough so that the Arctic or Polar front is located as far south as 40° N. Then large areas of Eurasia and, partly, North America are included in the Arctic dome, facilitating transport of pollution from those regions. In addition, since both dry and wet deposition is reduced within the Arctic dome in winter, aerosol-related species have very long lifetimes once within the Arctic dome (Stohl, 2006).

2.2 Sampling and analyses

The Lomonosovfonna 2009 ice core was processed in the cold room (−20 °C) at the Paul Scherrer Institut, Switzerland, resulting in 3997 samples with a depth resolution of 3–4 cm (details on the method in Eichler et al., 2000). The resolution was adapted to layer thinning with depth, so that even in the deepest and oldest part of the core, each year is at least represented by one sample. The inner part of the core was sampled for the analysis of water soluble major ions and the water stable isotopes \( \delta^{18} \text{O} \) and \( \delta \text{D} \). Outer core sections were analysed for \( ^3 \text{H} \) and \( ^{210} \text{Pb} \) used for dating purposes (Eichler et al., 2000).

Concentrations of water soluble major ions, including \( \text{NO}_3^- \) and \( \text{NH}_4^+ \), were determined using ion chromatography (Metrohm 850 Professional IC combined with a 872 Extension Module and a 858 Professional Sample Processor autosampler). Prior to analyses, ice samples were melted in a N\(_2\) atmosphere to reduce contamination from laboratory air. A list of the measured ionic species, their detection limits and median concentrations is given in Table 1.
Table 1. Detection limits and median values (µeq L⁻¹) for the ions analysed with the Metrohm 850 Professional IC. Pre-ind.: pre-industrial time from 1222 to 1859; Ind.: industrial time from 1860 to 2009; MSA: CH₃SO₃⁻.

| Anions       | Detection Limit | Median Pre-ind. | Median Ind. | | Cations       | Detection Limit | Median Pre-ind. | Median Ind. |
|--------------|----------------|----------------|-------------| | Na⁺          | 0.02            | 8.77          | 7.18         | | NH₄⁺         | 0.02            | 0.50          | 0.74         | | K⁺           | 0.02            | 0.25          | 0.19         | | Mg²⁺         | 0.03            | 2.10          | 1.32         | | Ca²⁺         | 0.04            | 1.43          | 1.02         | | Cl⁻          | 0.02            | 10.48         | 8.92         | | NO₃⁻         | 0.01            | 0.54          | 0.65         | | SO₄²⁻        | 0.02            | 2.08          | 2.63         | | MSA          | 0.005           | 0.09          | 0.05         | |

Figure 3. Temporal records of annual average concentrations of MSA, Na⁺, NO₃⁻ and NH₄⁺ and annual melt percent of the Lomo09 ice core.

2.3 Ice-core dating

The Lomo09 ice core covers the time period of 1222 to 2009 (Fig. 2). It was dated with a combination of reference horizons, annual layer counting (ALC), ²¹⁰Pb decay, and a simple glacier flow model. The reference horizons include the tritium peak indicating the year 1963, and the major volcanic eruptions of Bezymianny (1956), Katmai (1912), Tambora (1815), Laki (1783), Hekla (1766), Kuwae (1458/59; Sigl et al., 2013), and Samalas (1257/58; Lavigne et al., 2013) marked by high non-sea-salt sulfate concentrations and high values for the sulfate residual of the multiple linear regression of all measured ions, a method previously described in Moore et al. (2012). Annual layer counting was performed down to a depth of ~79.7 m weq (~1750) using the pronounced seasonality of δ¹⁸O and Na⁺ (Fig. S1 in the Supplement). A simple glacier flow model (Thompson et al., 1998) was fitted through the volcanic reference horizons. This was used to date the core below ~79.7 m weq where ALC was limited due to strong layer thinning. The dating uncertainty for the core down to a depth of ~68 m weq is estimated to be ±1 year within ±10 years of the reference horizons and increases to ±3 years in between. Down to a depth of ~80 m weq the dating uncertainty enlarges to ±3 years also in the proximity of the reference horizons, and below ~80 m weq it increases to ±10 years. This was calculated using the difference of the year of the volcanic eruptions and the modelled date. The average annual accumulation rate is 0.58 ± 0.13 m weq.

2.4 Calculation of annual melt percent

Melt features are formed when surface snow melts and the meltwater percolates into deeper layers where it fills the pores and refreezes under the formation of a layer of ice poor in or free of air bubbles. The percentage of annual melt in the Lomo09 core was calculated from the thickness of melt fea-
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Figure 4. Records of NH$_4^+$ (green), NO$_3^-$ (red), melt percent (light blue), Na$^+$ (yellow), and MSA (dark blue) of the Lomo09 ice core. Bold lines are 40-year low-pass-filtered (40-yr-LP); dashed lines are 10-year averages (10-yr-avg). Raw data are available in the Supplement (Figs. S2 and S3). Grey dashed lines are 40-year low-pass-filtered records of NH$_4^+$, NO$_3^-$, Na$^+$, and MSA of the Lomo97 ice core (Kekonen et al., 2005) calculated with the updated chronology of Divine et al. (2011). Black dashed lines are 40-year low-pass-filtered records of NH$_4^+$ and NO$_3^-$ of the Holte05 ice core (Beaudon et al., 2013).

Clear and bubbly ice appears as transparent area when the core is backlit. If the melt did not affect the whole core diameter, this was accounted for by multiplying the length of the melt feature with the percentage of the core diameter it covered. If for example a melt feature was 20 cm long but only affected one-fifth of the core diameter, this melt feature would count the same as a 4 cm long melt feature affecting the whole core diameter. The observed melt features were then summed up per year to calculate the annual melt percent (Fig. 3).

3 Results and discussion

The records of NO$_3^-$ and NH$_4^+$ of the Lomo09 core both show the highest concentrations during the period of approximately 1940 to 1980 (Figs. 3 and 4), similar to findings from other Arctic sites (Goto-Azuma and Koerner, 2001). This clearly indicates a strong influence of anthropogenic emissions in recent decades on the chemical composition of aerosols reaching Lomonosovfonna. Both records show a significant decrease after 1980, a trend similarly observed in the NO$_3^-$ and NH$_4^+$ records of ice cores from the Siberian Altai (Eichler et al., 2009, 2011) (Fig. 5) and Severnaya Zemlya (Opel et al., 2013; Weiler et al., 2005) influenced mainly by Eurasian pollution. The Siberian Altai core ends in 2001, explaining why the continuation of the decrease seen at Lomonosovfonna is not recorded there. The nitrate trend in the Siberian Altai fits well with NO$_x$ emissions as discussed in detail in Eichler et al. (2009), where the eastern European NO$_x$ emissions are shown. In contrast, NO$_3^-$ concentrations in records from Summit, Greenland, and Colle Gnifetti, Swiss Alps (see Fig. 1 for locations), affected by North American and western European air masses, respectively, kept rising into the twenty-first century (Fig. 5). This suggests that the major sources of the increased concentrations of NO$_3^-$ and NH$_4^+$ in the Lomo09 core are similar to those for the Siberian Altai and Severnaya Zemlya, whereas the influence of emissions in North America and Europe is of minor importance. Our finding is in agreement with results from transport modelling and trajectory analysis, identifying Eurasia as a source region for Svalbard (Hirdman et al., 2010a, b). Eurasian pollution dominates especially during the autumn and winter periods characterised by Arctic haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013). We thus attribute the observed trend after 1940 in NO$_3^-$ to higher NO$_x$ emissions from traffic, energy production, and industrial activities, and...
in $\text{NH}_4^+$ to enhanced $\text{NH}_3$ emissions from agriculture and livestock mainly in Eurasia (Eichler et al., 2009; Weiler et al., 2005). This is in contrast to studies from North America and western Europe, where anthropogenic pollution already started rising in the second half of the nineteenth century due to an earlier industrialisation and intensification of agriculture (see e.g. Döscher et al., 1996). The anthropogenic impact is also seen in the $\text{NO}_3^−$ and – less pronounced – in the $\text{NH}_4^+$ record of the Lomo97 core (Divine et al., 2011; Kekonen et al., 2005) (Fig. 4), which underlines the spatial representativeness of the Lomo09 ice-core data. The $\text{NO}_3^−$ records of the Lomo97 and Lomo97 cores agree well. This is not the case for the $\text{NH}_4^+$ records, where the Lomo97 shows higher concentrations, especially before 1900 (Fig. 4). We cannot explain this difference, but $\text{NH}_4^+$ is known to be prone to contamination during analysis (Jauhiainen et al., 1999; Kaufmann et al., 2010; Legrand et al., 1984, 1993, 1999; Udisti et al., 1994). Three observations indicate that the Lomo09 $\text{NH}_4^+$ concentrations are robust: (1) the preindustrial Lomo09 values are generally lower than those of Lomo97 and therefore contamination seems unlikely; (2) the Lomo09 preindustrial ion balance is close to 0 (Fig. S2), and (3) the 300-year record of $\text{NH}_4^+$ from Holtedahlfonna (Beaudon et al., 2013) is in reasonable agreement with the Lomo09 data, except for the period around 1750 (Fig. 4).

In order to investigate sources of $\text{NH}_4^+$ and $\text{NO}_3^−$ and other ionic species in the Lomo09 ice core, we performed a principal component analysis (PCA). We used 10-year averages to account for dating uncertainties and smoothing effects by meltwater relocation. Previous studies on the Lomo97 core suggested that the percolation lengths at the site can reach two to eight annual layers in the warmest years (Moore et al., 2005; Pohjola et al., 2002). The average annual melt percent of the Lomo97 core was 41 % (Pohjola et al., 2002) compared to 31 % of the Lomo97 core. We thus assume that the maximum percolation lengths in the Lomo09 core do not exceed the eight annual layers determined for the Lomo97 core. As a conservative estimate we used the 10-year-average record of melt percent in the PCA to examine the influence of melt on the $\text{NH}_4^+$ and $\text{NO}_3^−$ records. The PCA was performed only for pre-industrial times (1222–1859) to exclude anthropogenic influences on the ion concentrations. Sulfate ($\text{SO}_4^{2−}$) from anthropogenic sources has been shown to increase already during the second half of the nineteenth century (Moore et al., 2006).

We obtained six principal components (PCs) from the PCA (Table 2). PC1 has high loadings of sodium ($\text{Na}^+$), potassium ($\text{K}^+$), magnesium ($\text{Mg}^{2+}$), and chloride ($\text{Cl}^−$). This component explains 38 % of the total variance and contains species that are directly emitted by sea spray. PC2 has high loadings of methane sulfonate ($\text{MSA} = \text{CH}_3\text{SO}_3^−$) and $\text{NO}_3^−$. MSA has a strictly marine biogenic source. It results from the oxidation of gaseous dimethyl sulfide (DMS) which is produced by phytoplankton and emitted from the ocean into the atmosphere. This gas release across the sea–air interface differs distinctly from the way sea salt species are emitted into the atmosphere via sea spray because no droplets are involved (Stefels et al., 2007; Vogt and Liss, 2009). PC3 has a high loading of $\text{NH}_4^+$, representing biogenic emissions. Calcium ($\text{Ca}^{2+}$) is the only species that has a high loading in PC4. This suggests that PC4 represents a mineral dust component. The melt percent is the only parameter that has a high loading in PC5. Although we do not expect a simple correlation between melt in a particular layer and net chemical flux, this result suggests that there is at least not a net loss of the investigated major ions from layers of extreme melt, which together with the findings of Pohjola et al. (2002) and Moore et al. (2005) supports our conclusion that melt has not been of major influence on the ion concentrations on the considered decadal timescale. PC6 has a high loading of $\text{SO}_4^{2−}$, indicating a volcanic source. We can exclude a dominant sea spray and marine biogenic influence on $\text{SO}_4^{2−}$, due to the low loadings within PC1 and PC2, respectively. The results of the PCA are in good correspondence to those of a correlation analysis.
Table 3. $R^2$ values of the correlation analysis of the ionic species and the melt percent (Melt %). Time period: 1222–1859; data: 10-year averages; MSA: CH$_3$SO$_3^-$; 0.5 < $R^2$ < 1 marked in bold.

|       | Na$^+$ | K$^+$ | Mg$^{2+}$ | Cl$^-$ | MSA  | NO$_3^-$ | NH$_4^+$ | Ca$^{2+}$ | Melt % | SO$_4^{2-}$ |
|-------|--------|-------|-----------|--------|------|----------|----------|----------|--------|------------|
| Na$^+$ | 1      |       |           |        |      |          |          |          |        |            |
| K$^+$  | 0.71   | 1     |           |        |      |          |          |          |        |            |
| Mg$^{2+}$ | 0.71 | 0.59  | 1         |        |      |          |          |          |        |            |
| Cl$^-$ | 0.98   | 0.67  | 0.78      | 1      |      |          |          |          |        |            |
| MSA    | 0.17   | 0.16  | 0.41      | 0.20   | 0.20 | 1        |          |          |        |            |
| NO$_3^-$| 0.04  | 0.08  | 0.27      | 0.06   | 0.60 | 1        |          |          |        |            |
| NH$_4^+$| 0.01  | 0.01  | 0.03      | 0.02   | 0.14 | 0.19     | 1        |          |        |            |
| Ca$^{2+}$| 0.09  | 0.06  | 0.27      | 0.10   | 0.26 | 0.21     | 0.00     | 1        |        |            |
| Melt % | 0.00   | 0.00  | 0.02      | 0.00   | 0.15 | 0.11     | 0.13     | 0.04     | 1      |            |
| SO$_4^{2-}$| 0.16 | 0.18  | 0.33      | 0.17   | 0.26 | 0.26     | 0.02     | 0.24     | 0.04  | 1          |

analysis of the 10-year-averaged records of the ionic species and the melt percent for the pre-industrial period (Table 3). Strong correlation is observed for the sea-spray-related ions Na$^+$, K$^+$, Mg$^{2+}$, and Cl$^-$ ($0.59 < R^2 < 0.98$). Furthermore, MSA and NO$_3^-$ are highly correlated and share 60% of data variability. NH$_4^+$, Ca$^{2+}$, melt percent and SO$_4^{2-}$ are not significantly correlated with any other species.

3.1 Nitrate and methane sulfonate (NO$_3^-$ and MSA)

In the Arctic, MSA is well known to originate from marine biogenic sources (Legrand, 1997). However, major pre-industrial NO$_3^-$ sources in this region are still not fully understood (e.g. Wolff et al., 2008).

Varying atmospheric MSA concentrations have been related to changing sea-ice conditions. Studies from Arctic and Antarctic ice cores found positive (Becagli et al., 2009; Legrand et al., 1997) but also negative correlations of MSA and sea-ice extent (Rhodes et al., 2009; Sharma et al., 2012); see also the review on MSA and sea ice in Antarctica by Abram et al. (2013). After 1920 the Lomo09 core MSA correlates negatively with summer (August) sea-ice extent and sea surface temperature in the Barents Sea (O’Dwyer et al., 2000) and positively with the instrumental summer temperature record from Svalbard (Isaksen et al., 2005). During the period 1600–1920 Isaksen et al. (2005) detected a positive correlation of the Lomo09 MSA and winter (April) sea-ice extent in the Barents Sea (Divine and Dick, 2006; Vinje, 2001). The Lomo09 MSA record reveals a pattern with twice as high values prior to about 1920 compared to those of the later twentieth century (Isaksen et al., 2005). They suggest that it results from a change of the source and/or more favourable growing conditions for the DMS-producing phytoplankton in a more extensive sea-ice environment before 1920.

In the MSA record of the Lomo09 core we find a similar pattern as in the Lomo97 core with higher concentrations prior to the twentieth century and a decreasing trend since around 1900 (Figs. 4 and 6). Hence, we investigate if a coupling of MSA with sea-ice conditions around Svalbard exists, using three long-term reconstructions of sea-ice extent. These reconstructions include the winter (April) ice extent in the western Nordic Seas covering the last 800 years (Macias Fauria et al., 2010), the summer (August) location of the sea-ice edge in the Barents Sea (BS) that covers the last 400 years (Kinnard et al., 2011), and the summer sea-ice extent in the Arctic seas extending back to the year 563 (Kinnard et al., 2011). The best agreement was observed between the 40-year lowpass-filtered records of Lomo09 MSA and reconstructed winter (April) western Nordic Seas ice extent (Macias Fauria et al., 2010). However, less than 50% of the variability in the MSA record is explained by changing sea-ice conditions (Fig. 6; $r = 0.56$, $p < 0.001$). The most striking feature in both records is the pronounced decrease starting around 1890. This remarkable drop was also observed in the time series of the western Nordic Seas ice extent (period 1860–2000; Vinje et al., 2001), used to calibrate the proxy records (Macias Fauria et al., 2010). The strong decrease is not seen in any of the summer (August) ice records before around 1910 (Fig. 6). Furthermore, the pronounced minimum around 1710 and the peak around 1640 in the BS ice record are not reflected in the Lomo09 MSA record. Thus, our data do not support the connection of MSA at Lomonosovfonna and the BS ice extent stated in O’Dwyer et al. (2000) for the period 1920–1997, nor the assumption of Isaksen et al. (2005) that the MSA sources prior to and after 1920 were the same, i.e. the BS. We explain the positive correlation of Lomo09 MSA and western Nordic Seas ice extent as follows. The marginal ice zone is known to be the area of highest DMS production (Perrette et al., 2011). The larger the sea-ice area, the more ice edge area is available for phytoplankton growth and thus DMS production. Furthermore, more ice leads to higher freshwater inflow by melting ice. This results in a stronger stratification of the ocean water (Perrette et al., 2011) which keeps the phytoplankton in the euphotic zone. The good correspondence of the Lomo09
et al., 2000, 2002), suggesting that nss Ca from sea-salt Ca(NO$_3^-$) species with enhanced NO$_3^-$ there is a decoupling of both species with enhanced NO$_3^-$ 1350 when the correlation breaks down. After around 1900 1695, and 1795. The only exception is the period at about 1395, 1475, 1560, 1645, similar, with shared peaks around 1395, 1475, 1560, 1645, 1695, and 1795. The only exception is the period at about 1350 when the correlation breaks down. After around 1900 there is a decoupling of both species with enhanced NO$_3^-$ concentrations from anthropogenic Eurasian NO$_3^-$ emissions (see above) and strongly decreased MSA concentrations. 

In previous studies, NO$_3^-$ was found to correlate with non-sea-salt Ca$^{2+}$ (nss Ca$^{2+}$) (Legrand et al., 1999; Röthlisberger et al., 2000, 2002), suggesting that nss Ca$^{2+}$ prevents NO$_3^-$ from being re-emitted from the snowpack. However, those studies are from Greenland; consider glacial timescales, and include e.g. the last glacial maximum (LGM) with much higher nss-Ca$^{2+}$ concentrations. Other studies observed a correlation of NO$_3^-$ and Ca$^{2+}$ in summer and with sea salt in winter, but they considered only industrial times (Beine et al., 2003; Geng et al., 2010; Teinilä et al., 2003). The empirical orthogonal function (EOF) analysis performed on the ion data of the Lomo97 core suggests in general no correlation between Ca$^{2+}$ and NO$_3^-$, but in some parts of the last 200 years the two species are clearly associated (Kekonen et al., 2002). Kekonen et al. (2002) found NO$_2^-$ and NH$_4^+$ to covariate during the last 100 years. However, the EOF of the whole core did not show a clear association of NH$_4^+$ and NO$_3^-$ . Nevertheless, they suggested that before 1920 and after 1960 ammonium nitrate (NH$_4$NO$_3$) has been common at Lomonosovfonna. They explain this in recent years to be due to Arctic haze and significant natural sources of NH$_4$NO$_3$ during the earlier period.

At Holtedalhfonna, Svalbard, NH$_4^+$ was also associated with NO$_2^-$ before 1880, which Beaudon et al. (2013) interpreted as evidence of NH$_4$NO$_3$ being present. Teinilä et al. (2003) also discovered a correlation of NO$_3^-$ and NH$_4^+$ in recent times which they concluded to result from anthropogenic emissions. Our data neither support a correlation of NO$_3^-$ and Ca$^{2+}$, nor of NO$_3^-$ and the sea salt species Na$^+$, nor of NO$_3^-$ and NH$_4^+$ in pre-industrial times. Instead, they clearly suggest an association of NO$_3^-$ with MSA. Three hypotheses for the high correlation are discussed: (1) post-depositional processes caused by melt water percolation affecting NO$_3^-$ and MSA in the same way, (2) a common source of NO$_3^-$ and MSA, and (3) NO$_3^-$ fertilisation of the ocean which triggers phytoplankton growth and thus DMS and MSA formation.

1. The pre-industrial record of the melt percent does share some features with NO$_3^-$ and MSA, but there is no significant correlation with NO$_3^-$ or MSA ($r^2 = 0.1$ with either NO$_3^-$ or MSA) (Table 3, Fig. 4). This is also seen in the PCA where the melt percent and the two ionic species have their highest loadings in different PCs (Table 2). Thus, the correlation of NO$_3^-$ and MSA is not a result of similar relocation during melt events on the decadal timescales considered here.

2. If both species have a common source, this would have to be the ocean, because MSA results only from marine DMS production and its oxidation in the atmosphere. NO$_3^-$ is only a minor component in seawater, with concentrations in the micro-molar range (Chester and Jickells, 2012; Codispoti et al., 2013). The ice-core NO$_3^-$ / Na$^+$ ratio of $\sim 0.066$ in the Lomo09 core is up to a factor of 10 higher than the seawater ratio of 0.006 to 0.038 (Keene et al., 1986). Additionally, we can exclude NO$_3^-$ from being derived from sea spray because NO$_3^-$ and the major sea spray components Na$^+$, K$^+$, Mg$^{2+}$, and Cl$^-$ (PC1) do not correlate, as seen in the PCA and the correlation analysis (Tables 2 and 3). Because of the high solubility of nitrate in water, outgassing of HNO$_3$ from the ocean is unlikely. Thus, the major NO$_3^-$ source is not the ocean, which excludes a common source to cause the strong correlation of NO$_3^-$ and MSA.

Figure 6. Records of Lomo09 MSA (dark blue), pre-industrial NO$_3^-$ (red), western Nordic Seas winter (April) ice extent (turquoise; Macias Fauria et al., 2010), Arctic summer (August) sea-ice extent (light purple; Kinnard et al., 2011), and August sea-ice edge position in the Barents Sea (BS; dark purple; Kinnard et al., 2011). Bold lines are 100-year lowpass-filtered (100-yr-LP); dashed lines are 40-year lowpass-filtered (40-yr-LP).

MSA record to the western Nordic Seas ice extent but not to that of the BS is well supported by the findings of Beaudon et al. (2013) pointing to the Greenland Sea as the main source of biogenic-related MSA in Svalbard.

In the Lomo09 ice core, MSA is highly correlated with NO$_3^-$ before around 1900. The records (Figs. 4 and 6) are similar, with shared peaks around 1395, 1475, 1560, 1645, 1695, and 1795. The only exception is the period at about 1350 when the correlation breaks down. After around 1900 there is a decoupling of both species with enhanced NO$_3^-$ concentrations from anthropogenic Eurasian NO$_3^-$ emissions (see above) and strongly decreased MSA concentrations.

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3. Elevated atmospheric NO$_3^−$ concentrations due to high NO$_x$ emissions and/or enhanced transport to the Arctic in the end of winter lead to an increased amount of NO$_3^−$ dissolved in the ocean surface water. Nutrient supply in the Arctic is known to be limited and nitrate depletion is common during the vegetative season (Codispoti et al., 2013). Hence, an increased nitrogen input by dissolved NO$_3^−$ leads to a fertilisation of the phytoplankton (Duce et al., 2008). As soon as light becomes available this results in an enhanced production of DMS and finally higher MSA concentrations in the atmosphere. This process takes weeks to months (Codispoti et al., 2013; Sharma et al., 2012). However, such a potential short time lag cannot be resolved from our data.

We therefore propose the fertilising effect as being the dominant cause of the high correlation of NO$_3^−$ and MSA in pre-industrial times. In industrial times the records of NO$_3^−$ and MSA diverge with increasing NO$_3^−$ and decreasing MSA concentrations. This reveals that during the twentieth century the effect of decreasing MSA concentrations following reduction in ice extent in the western Nordic Seas predominates compared to an expected MSA increase caused by enhanced anthropogenic NO$_3^−$ levels.

The major NO$_3^−$ source region for the industrial time is Eurasia, indicated by the similarity of the NO$_3^−$ records observed in the last 30–40 years in the ice cores from Lomo09, the Siberian Altai, and Severnaya Zemlya (Eichler et al., 2009; Weiler et al., 2005) (Fig. 5). We assume that the source region has not changed from pre-industrial to industrial times. In the period 1250–1940, NO$_3^−$ in the Siberian Altai ice core was ascribed to forest fires and mineral dust as main pre-industrial sources (Eichler et al., 2011). That NO$_3^−$ record shows a maximum between 1540 and 1680 (see Fig. 5), attributed to an increased mineral dust input from Central Asian deserts (1540–1600) and enhanced fire activity from Siberian boreal forests (1600–1680). This distinct peak in the sixteenth and seventeenth centuries is not observed in the Lomo09 NO$_3^−$ record and, also, the general pre-industrial records do not correspond well. We cannot exclude the possibility that other regional-scale NO$_3^−$ sources in Eurasia had a significant impact on the low pre-industrial concentration level. From our data we can therefore not identify major pre-industrial NO$_3^−$ sources for the Lomo09 core.

3.2 Ammonium (NH$_4^+$)

The Lomo09 NH$_4^+$ record shows very low concentrations between the thirteenth and eighteenth centuries and an increasing trend from around 1750 onwards (Fig. 7). The values are on the same order of magnitude as those from other Arctic sites and a factor 2–3 lower compared to the Lomo97 ice core (Beaudon et al., 2013; Fuhrer et al., 1996; Kehrwald et al., 2012; Kekonen et al., 2005; Legrand and De Angelis, 1996; Legrand et al., 1992; Whitlow et al., 1994; Zen-
that biomass burning is not a major source of NH$_4^+$ arriving at Svalbard. The trend in the Lomo09 NH$_4^+$ record is similar to that in the ice core from Belukha glacier in the Siberian Altai, with increasing concentrations already from around 1750 and very low concentrations between 1680 and 1750 (Eichler et al., 2009) (Fig. 7). Before $\sim 1500$, NH$_4^+$ concentration records agree less, which could be explained by increasing dating uncertainty. At the Belukha site, long-term NH$_4^+$ variations were related to temperature-induced changes in biogenic NH$_3$ emissions from extended Siberian boreal forests (Eichler et al., 2009). The strong increase after the eighteenth century was caused by a rise in Siberian temperatures since that time. Hence, from the similarity in the Lomo09 and Siberian Altai NH$_4^+$ concentration records, we conclude that biogenic NH$_3$ emissions from Siberian boreal forests are the dominant source of NH$_4^+$ at Lomonosovfonna. Due to the larger distance to the emission sources, the NH$_4^+$ concentrations in the Lomo09 core are about 1 order of magnitude lower than in the core from Belukha glacier. The NH$_4^+$ concentrations in a Greenland ice core (NEEM; for the location, see Fig. 1) do not show the increase after the eighteenth century (Zennaro et al., 2014) (Fig. 7), implying that biogenic emission trends in North America and Eurasia differ.

4 Summary

We presented the 800-year records of the two nitrogen species NO$_3^-$ and NH$_4^+$ analysed in a new ice core collected from Lomonosovfonna, Svalbard, in 2009. In general, the NO$_3^-$ record of the 2009 ice core agrees reasonably with published data from two previous Svalbard ice cores, Lomonosovfonna 1997 (Kekonen et al., 2005) and Holtedahlfonna 2005 (Beaudon et al., 2013), whereas there is less correspondence between the different NH$_4^+$ records. On the decadal timescale considered here, melt-related effects did not significantly alter the concentrations of the nitrogen compounds. Both species show a clear impact of anthropogenic pollution in the twentieth century, with peak concentrations in the 1970s/1980s. This temporal trend points to source regions in Eurasia and the Siberian Arctic, since emissions in North America and western Europe kept rising into the twenty-first century. In pre-industrial times, i.e. prior to the twentieth century, the dominant source of NH$_4^+$ was biogenic NH$_3$ emissions from Siberian boreal forests. During the same period, NO$_3^-$ was highly correlated with MSA on a decadal timescale. We explained this by a fertilising mechanism where higher atmospheric NO$_3^-$ concentrations yield higher nitrogen input to the ocean, triggering the growth of DMS-producing phytoplankton. Elevated DMS concentrations then result in enhanced concentrations of MSA in the atmosphere. Based on our data it was not possible to resolve major pre-industrial NO$_3^-$ sources for Svalbard.

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This is a contribution to cryosphere–atmosphere interactions in a changing Arctic climate (CRAICC), a top-level research initiative (TRI).

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