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 (NO_3^-) and ammonium (NH_4^+) analysed in a new ice core from Lomonosovfonna, Svalbard, in the Eurasian Arctic covering the period 1222-2009. We investigate the emission sources ~~and the influence of melt on the records.~~ and find that ~~During~~ during the 20th century both records are influenced by anthropogenic pollution from Eurasia. In pre-industrial times NO_3^- is highly correlated with methane-sulfonate (MSA) on decadal time-scales, which we explain by a fertilising effect. Enhanced atmospheric 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 for pre-industrial NO_3^-, but a more exact source apportionment could not be performed based on our data. This is different for NH_4^+, where biogenic ammonia (NH_3) emissions from Siberian boreal forests were identified as the dominant source of pre-industrial NH_4^+. Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on ~~excluded as major driving force for~~ the decadal variations of the investigated compounds.

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 for bio-available nitrogen in the Arctic is the deposition of reactive atmospheric nitrogen that is present primarily as ~~peroxyacetyl nitrate (PAN), but also as~~ nitrate (NO_3^-) and ammonium (NH_4^+) (Björkman et al., 2013; Kühnel et al., 2011~~2~~). Those species are predominantly removed from the atmosphere by wet deposition (Bergin et al., 1995). NO_3^- is the oxidation product of emitted NO_x (NO and NO_2). At a global scale~~In general~~, major 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). NH_4^+ derives from biogenic emissions of ammonia (NH_3) from terrestrial and marine sources, biomass burning, agriculture, and livestock breeding (Fuhrer et al., 1996; Galloway et al., 2004; Wolff, 2013). Both NO_3^- and 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 beginning of the industrialisation and intensification of agricultural activities (Galloway et al., 2004). The deposition of NO_3^- and 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 major pollutant source for south Greenland, both North America and Eurasia for central and north 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 major source of NO_3^- in a Siberian Altai ice core from the mid-latitudes. In studies on

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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 location see Figure 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 20th century, but the pre-industrial sources remain largely unidentified due to potential runoff that biased the ion records before the mid-16th century (Kekonen et al., 2002, 2005). Nevertheless, the fairly stable concentrations in the NO_3^- record from the mid-16th to the mid-19th century are interpreted as input from natural NO_3^- sources (Kekonen et al., 2002). An anthropogenic influence in the 20th century is also visible in the NO_3^- and NH_4^+ records of other Eurasian Arctic ice cores (see Figure 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 paleo-environmental proxies may be hampered by the fact that both undergo post-depositional processes leading to loss from or relocation within the snow pack 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 melt water (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 (Brimblecombe 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 NO_3^- and 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 NO_3^- and 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 asl; 78°49`24``N, 17°25`59``E), 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 (Isaksson 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°C 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 melt water 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 20th 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. Further, 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; Forsström et al., 2009; Goto-Azuma and Koerner, 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 to enter. 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 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, aerosols have very long lifetimes once within the Arctic dome (Stohl, 2006).

2.2 Sampling and analyses

The Lomonosovfonna 2009 ice core (Lomo09) was processed in the cold room (-20°C) at 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 $\delta^{18}O$ and δD. Outer core sections were analysed for ^{3}H and ^{210}Pb used for dating purposes (Eichler et al., 2000).

Concentrations of water soluble major ions, including NO_3^- and 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 are given in Table 1. ~~Values were not blank corrected.~~

2.3 Ice core dating

The Lomo09 ice core covers the time period of 1222 to 2009 (Figure 2). It was dated with a combination of reference horizons, annual layer counting (ALC), ^{210}Pb 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 sulphate concentrations and high values for the sulphate-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 $\delta^{18}O$ and Na^+ (Figure S1). 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 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 melt water percolates into deeper layers where it fills the pores and refreezes under the formation of a layer of ice poor or free of air bubbles. The percentage of annual melt in the Lomo09 core was calculated from the thickness of melt features observed during processing of the core (similar to Henderson et al., 2006). 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 four centimetre 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)~~(Figure 3)~~, 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. ~~ure 4~~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 NOx emissions as discussed in detail in Eichler et al. (2009) where the Eastern European NOx emissions are shown. In contrast, NO_3^- concentrations in records from Summit, Greenland, and Colle Gnifetti, Swiss Alps (see Fig.~~ure~~ 1 for locations), affected by Northern American and Western European air masses, respectively, kept rising into the 21st century (Fig.~~ure 4~~5). This suggests that the major sources for 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 source region for Svalbard (Hirdman et al., 2010a and b). Eurasian pollution dominates especially during the autumn and winter period characterised by Artic Haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013). We thus attribute the observed trend in NO_3^- to higher NO_x emissions from traffic, energy production, and industrial activities, and in NH_4^+ to enhanced NH_3 emissions from agriculture and livestock mainly in Eurasia (Eichler et al., 2009; Weiler et al., 2005). The anthropogenic impact is also seen in the NO_3^- and- less pronounced- in the NH_4^+ record of the Lomo97 core (Divine et al., 2011; Kekonen et al., 2005) (Figure 3), which underlines the spatial representativeness of the Lomo09 ice core data. The NO_3^- records of the Lomo09 and Lomo97 cores agree well. This is not the case for the NH_4^+ records, where the Lomo97 shows higher concentrations, especially before 1900 (Fig.~~ure 3~~4). We cannot explain this difference, but 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 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 zero (Figure S2), and 3) t~~T~~he 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Fig.~~ure 3~~4).

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In order to investigate sources of NH_4^+ and 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 melt-water 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 Lomo09 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 ~~Additionally,~~ we ~~included~~ used the 10-year-average record of melt percent in the PCA to examine the influence of melt on the NH_4^+ and NO_3^- records. The PCA was performed only for pre-industrial times (1222-1859) to exclude anthropogenic influences on the ion concentrations. Sulphate (SO_4^{2-}) from anthropogenic sources has been shown to increase already during the second half of the 19th century (Moore et al., 2006).

We obtained six principal components (PCs) from the PCA (Table 2). PC1 has high loadings of sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and chloride (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 (MSA = $CH_3SO_3^-$) and NO_3^-. MSA has a strictly marine biogenic source. It results from the oxidation of gaseous dimethyl-sulphide (DMS) which is produced by phytoplankton and emitted from the ocean to the atmosphere. This gas release across the sea-air interface differs distinctly from the way sea salt species are emitted to the atmosphere via sea spray because no droplets are involved (Stefels et al., 2007; Vogt and Liss, 2009). PC3 has a high loading of NH_4^+, representing biogenic emissions. Calcium (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. This ~~shows~~ suggests that on the considered decadal time scale the influence of melt on the ion concentration averages ~~are not influenced by melt~~is negligible, which is in agreement with Pohjola et al. (2002) and Moore et al. (2005). PC6 has a high loading of SO_4^{2-}, indicating a volcanic source because the marine part of SO_4^{2-} is covered by the sea spray component PC1.

The results of the PCA are in good correspondence with those of a correlation 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 Artic 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).

~~In the Lomo09 ice core NO_3^- is highly correlated with MSA before around 1900. The records (Figures 3 and 5) 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_x emissions (see above) and strongly decreased MSA concentrations. Whereas marine biogenic sources for MSA in the Arctic are well known (Legrand, 1997), 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 Lomo97 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 (Isaksson et al., 2005). During the period 1600-1920 Isaksson et al. (2005) detected a positive correlation of the Lomo97 MSA and winter (April) sea ice extent in the Barents Sea (Divine and Dick, 2006; Vinje, 2001). The Lomo97 MSA record reveals a pattern with twice as high values prior to about 1920 compared to those of the later 20th century (Isaksson et al., 2005). They suggest that it results from a change of 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 20th century and a decreasing trend since around 1900 (Figs.~~ure~~ ~~3~~ 4 and ~~5~~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 winter (April) Western Nordic Seas ice extent (Macias Fauria et al., 2010) (Fig.~~ure 5~~6; r=0.56, p<0.001). The most striking feature in both records is the pronounced decrease starting around 1890 which is not seen in any of the summer (August) ice records before around 1910 (Figure 5). 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 Isaksson et al. (2005) that the MSA sources prior and after 1920 were the same, i.e. the BS. We explain the positive correlation of Lomo09 MSA and Western Nordic Sea 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 MSA record with the Western Nordic Sea ice extent but not with that of the BS is well supported by the findings of Beaudon et al. (2013) pointing to the Greenland Sea as the main source for biogenic related MSA in Svalbard.

In the Lomo09 ice core ~~NO_3^-~~MSA is highly correlated with ~~MSA~~NO_3^- before around 1900. The records (Figs.~~ures~~ ~~3~~4 and ~~5~~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_x emissions (see above) and strongly decreased MSA concentrations. ~~Whereas marine biogenic sources for MSA in the Arctic are well known (Legrand, 1997), major pre-industrial NO_3^- sources in this region are still not fully understood (e.g., Wolff et al., 2008).~~

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The sources of pre-industrial NO_3^- in the Artic are not well understood. 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_3^- 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_4NO_3) has been common at Lomonosovfonna. They explain this in recent years to be due to Arctic Haze and significant natural sources of NH_4NO_3 during the earlier period. At Holtedahlfonna, Svalbard, NH_4^+ was also associated with NO_3^- before 1880 which Beaudon et al. (2013) interpreted as evidence for NH_4NO_3 to be 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.

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(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.~~ure 3~~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 time scales 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 sea water with concentrations in the micro-molar range (Chester and Jickells, 2012; Codispoti et al., 2013). The ice core NO_3^-/Na^+ ratio of ~0.066 in the Lomo09 core is up to a factor of ten higher than the sea water ratio of 0.006 to 0.038 (Keene et al., 1986). Additionally, we can exclude NO_3^- to be 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.

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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 ~~suggest~~ therefore propose the fertilising effect to be the dominant cause for 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 20th 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.~~ure 4~~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.~~ure 4~~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 16th and 17th century is not observed in the Lomo09

NO_3^- record and also the general pre-industrial records do not correspond well. We cannot exclude 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 13th and 18th century and an increasing trend from around 1750 onwards (Fig.~~ure 6~~7). The values are on the same order of magnitude as those from other Arctic sites and 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; Zennaro et al., 2014). Another Svalbard core from Holtedahlfonna that spans the last 300 years shows The NH_4^+ record of another Svalbard core from Holtedahlfonna, spanning the last 300 years, shows a differing pattern prior to 1800, but a similar strong increasing trend as the Lomo09 record ~~similarly a strong increasing trend in the NH_4^+ record~~ from the 18th century on (Beaudon et al., 2013) (Figure 3). The authors interpret the rising concentrations from 1880 as result of anthropogenic mid-latitude pollution reaching the Arctic. However, the earlier increase in NH_4^+ concentrations in the Lomo09 and Holte05 ice core from the 18th century on cannot be related to anthropogenic emissions. As discussed above, anthropogenic NH_3 emissions from Eurasia influence precipitation chemistry in Svalbard only after around 1940.

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Pre-industrial NH_4^+ was not studied in details in the Lomo97 core but Kekonen et al. (2002) suggested NH_4NO_3 to have been common at Lomonosovfonna before 1920. Similarly, Beaudon et al. (2013) postulated that at Holtedahlfonna natural NH_4NO_3 was a common aerosol. Our data do not support this hypothesis since NH_4^+ and NO_3^- are not significantly correlated in pre-industrial times (Tables 2 and 3). In other studies pre-industrial NH_4^+ was attributed mainly to biomass burning (e.g., Fuhrer et al., 1996; Kehrwald et al., 2010; Legrand et al., 1992; Whitlow et al., 1994). North America and Canada were identified as major sources for NH_4^+ in Greenland ice (Fuhrer et al., 1996), whereas Legrand and De Angelis (1996) and Zennaro et al. (2014) suggest an additional Eurasian source. A period of exceptional high fire activity around 1600-1680 in Siberian boreal forests of Eurasia was detected in the ice core fire tracer records from the Siberian Altai and Greenland (Eichler et al., 2011; Zennaro et al., 2014). This unique period did not lead to a maximum in the Lomo09

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NH_4^+ record. Therefore, we conclude that biomass burning is not a major source for NH_4^+ arriving at Svalbard.

The trend in the Lomo09 NH_4^+ record is very similar to that in the ice core from Belukha glacier in the Siberian Altai with increasing concentrations already from around 1750 (Eichler et al., 2009) (Fig.~~ure 6~~7). Furthermore, both records show very low concentrations around 1680 to 1750. At the Belukha site long-term NH_4^+ variations were related to temperature-induced changes of biogenic NH_3 emissions from extended Siberian boreal forests (Eichler et al., 2009). The strong increase after the 18th century was caused by a rise of 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 for NH_4^+ at Lomonosovfonna. Due to the larger distance to the emission sources the NH_4^+ concentrations in the Lomo09 core are about one order of magnitude lower than in the core from Belukha glacier. The NH_4^+ concentrations in a Greenland ice core (NEEM, for location see Figure 1) do not show the increase after the 18th century (Zennaro et al., 2014) (Fig.~~ure 6~~7), implying that biogenic emission trends in Northern 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^- and NH_4^+ records of the 2009 ice core reasonably agree with published data from two previous Svalbard ice cores, Lomonosovfonna 1997 (~~[~~Kekonen et al., 2005)~~]~~ and Holtedahlfonna 2005 (~~[~~Beaudon et al., 2013)~~]~~. On the decadal time scale 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 20th century, with peak concentrations in the 1970s/1980s. This temporal trend points to source regions in Eurasia and the Siberian Arctic, since emissions in Northern America and Western Europe kept rising into the 21st century. In pre-industrial times, i.e. prior to the 20th 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 to MSA on a decadal time scale. 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

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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.

Supplementary material

Here, an example for the annual layer counting (ALC) for the core section between 0 and 20 m weq (Fig.~~ure~~ S1) is displayed, followed by the raw data for the ionic species (Fig.~~ure~~ S2) and the ion balance along depth in m weq (Fig. S2) and the melt percent (Fig.~~ure~~ S3) of the Lomo09 ice core along depth in m weq.

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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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Table 1 Detection limits and median values [μeq/L] for the ions analysed with the Metrohm 850 Professional IC. Pre-ind. = pre-industrial time from 1222-1859; Ind. = industrial time from 1860-2009; MSA = $CH_3SO_3^-$.

Anions				**Cations**			
	Detection limit	Median			Detection limit	Median	
		Pre-ind.	Ind.			Pre-ind.	Ind.
MSA	0.005	0.09	0.05	**Na^+**	0.02	8.77	7.18
Cl^-	0.02	10.48	8.92	**NH_4^+**	0.02	0.50	0.74
NO_3^-	0.01	0.54	0.65	**K^+**	0.02	0.25	0.19
SO_4^{2-}	0.02	2.08	2.63	**Mg^{2+}**	0.03	2.10	1.32
				Ca^{2+}	0.04	1.43	1.02

Table 2 Results of the principal component analysis (PCA) after VARIMAX rotation. Time period: 1222-1859; data: 10-year averages; MSA = $CH_3SO_3^-$; melt% = melt percent. Values >0.8 marked in bold.

	PC1	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**
Na^+	**0.97**	0.06	0.05	0.11	-0.03	0.08
K^+	**0.88**	0.18	0.00	-0.04	-0.07	0.16
Mg^{2+}	**0.82**	0.37	0.02	0.27	0.07	0.19
Cl^-	**0.97**	0.08	0.06	0.12	0.01	0.08
MSA	0.33	**0.80**	0.13	0.22	0.23	0.11
NO_3^-	0.11	**0.89**	0.22	0.16	0.09	0.22
NH_4^+	0.06	0.23	**0.96**	-0.02	0.17	0.02
Ca^{2+}	0.18	0.27	-0.02	**0.92**	0.07	0.19
Melt%	-0.05	0.19	0.16	0.07	**0.96**	0.07
SO_4^{2-}	0.29	0.28	0.02	0.21	0.08	**0.88**
Variance explained [%]	38	19	11	11	11	10

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 = $CH_3SO_3^-$; $0.5<r^2<1$ marked in bold.

r^2	**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	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

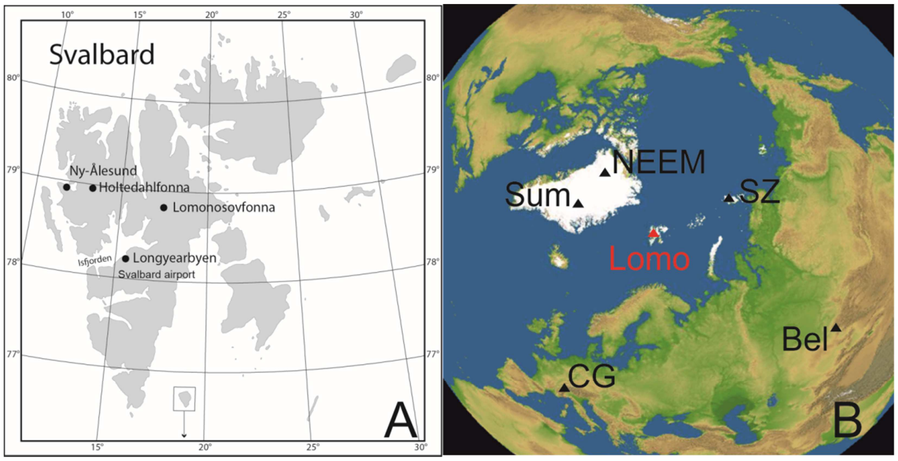


Figure 1 (A) Map of Svalbard with the locations of Lomonosovfonna and Holtedahlfonna. (B) Map with all ice core locations discussed in the text: Lomo = Lomonosovfonna (red triangle); NEEM, Sum = Summit, SZ = Severnaya Zemlya, Bel = Belukha, and CG = Colle Gnifetti (black triangles). Satellite image in (B) © PlanetObserver, extracted from DVD-ROM "Der Große 3D-Globus 4.0 Premium,"#2008 United Soft Media Verlag GmbH, Munich.

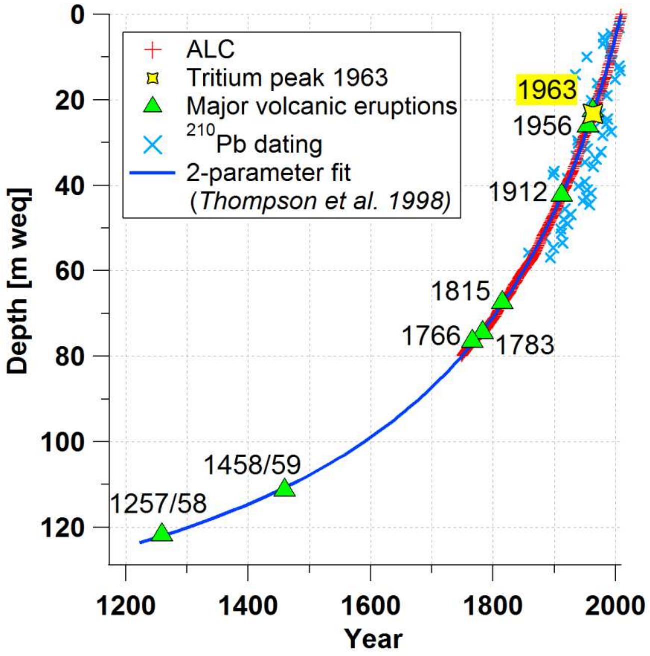


Figure 2 Depth-age relationship of the Lomo09 ice core showing all dating methods applied. Depth is given in m weq to account for density variation.

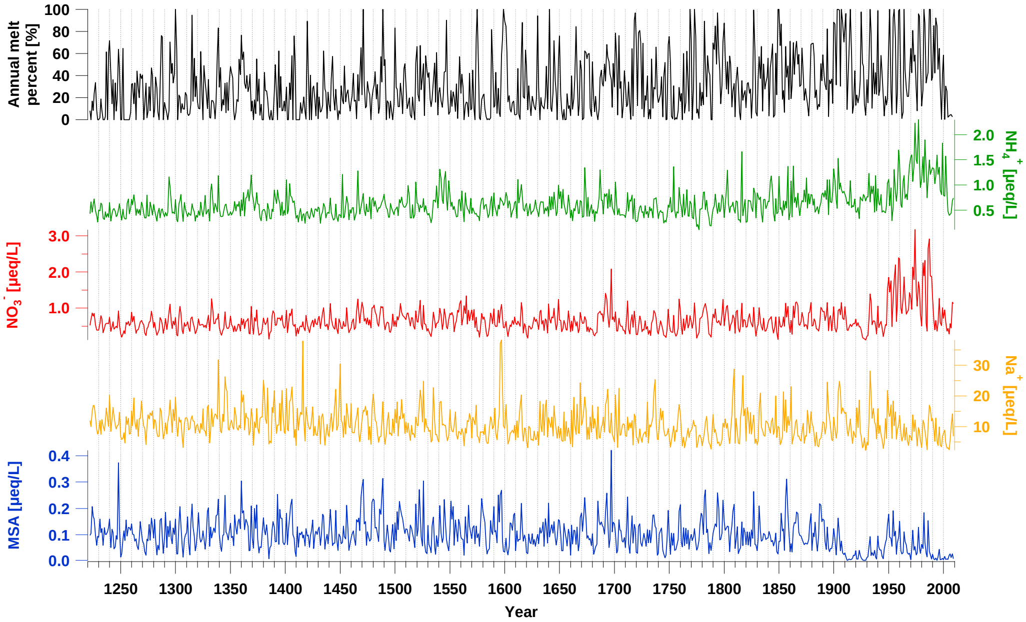


Figure 3 Temporal records of annual average concentrations of MSA, Na$^+$, NO$_3^-$ and NH$_4^+$ and annual melt percent of the Lomo09 ice core.

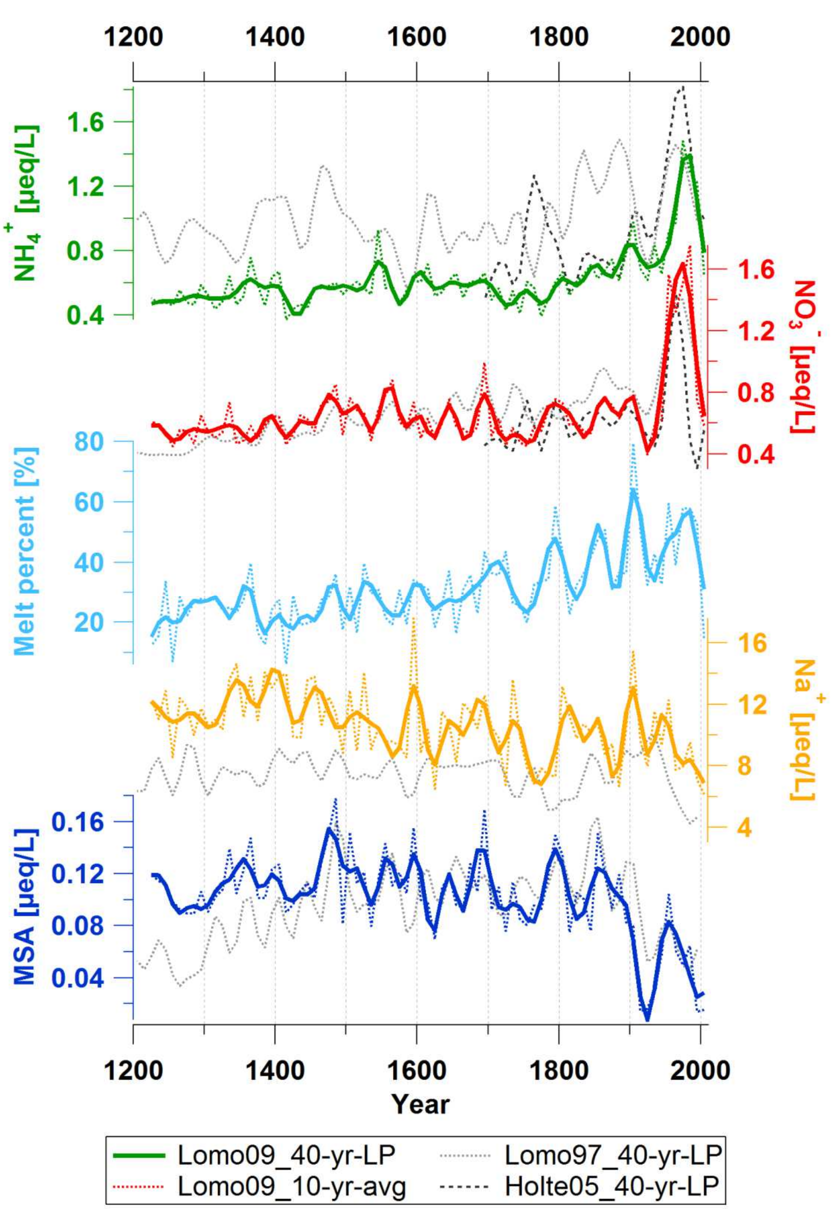
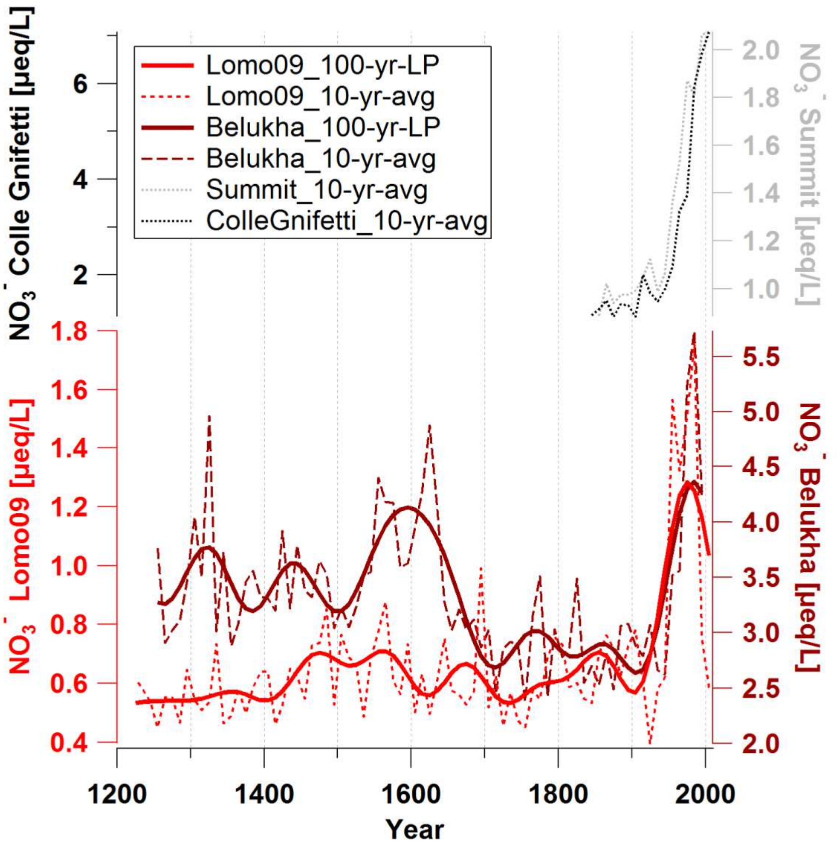


Figure ~~3~~ 4 Records of NH_4^+ (green), NO_3^- (red), melt percent (light blue), Na^+ (yellow), and MSA (dark blue) of the Lomo09 ice core. Bold lines are 40-year-lowpass-filtered (40-yr-LP); dashed lines are 10-year averages (10-yr-avg). Raw data are available in the supplementary material (Figures S2 and S3). Grey dashed lines are 40-year-lowpass-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-lowpass-filtered records of NH_4^+ and NO_3^- of the Holte05 ice core (Beaudon et al., 2013).

1 

Lomo09_100-yr-LP
Lomo09_10-yr-avg
Belukha_100-yr-LP
Belukha_10-yr-avg
Summit_10-yr-avg
ColleGnifetti_10-yr-avg
NO3- Colle Gnifetti [µeq/L]
2
4
6
NO3- Summit [µeq/L]
1.0
1.2
1.4
1.6
1.8
2.0
NO3- Lomo09 [µeq/L]
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
NO3- Belukha [µeq/L]
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
1200
1400
1600
1800
2000
Year

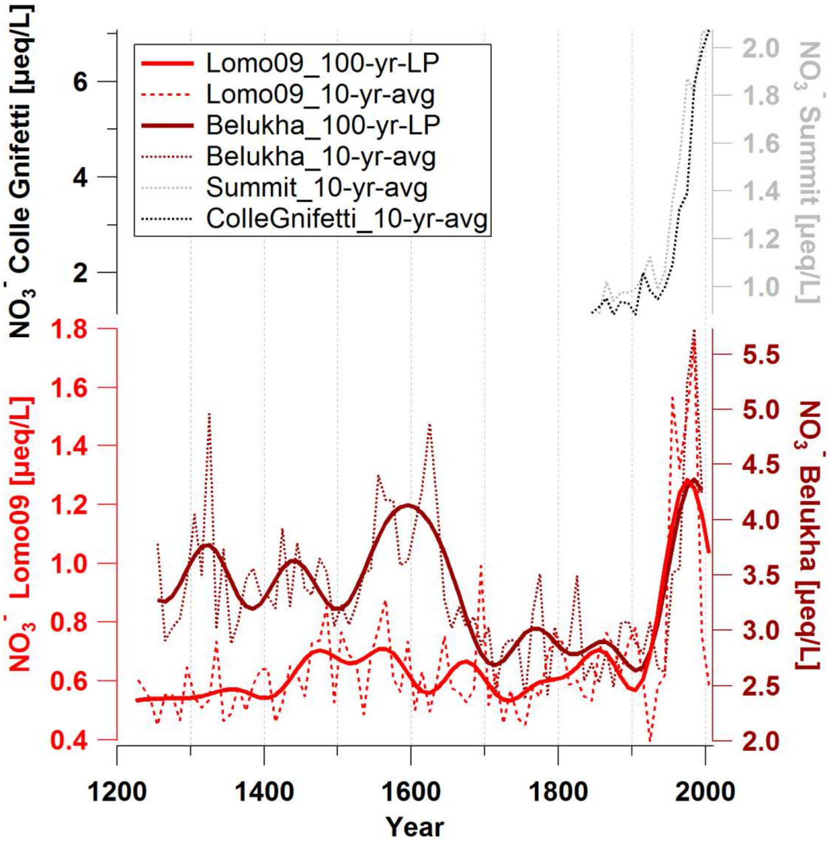


Figure ~~4~~ 5 NO_3^- records from Lomo09 (red), Belukha (dark red; Eichler et al., 2009), Summit, Greenland (grey; Geng et al., 2014), and Colle Gnifetti, Swiss Alps (black; Sigl, 2009). Bold lines are 100-year-lowpass-filtered (100-yr-LP); dashed lines are 10-year averages (10-yr-avg).

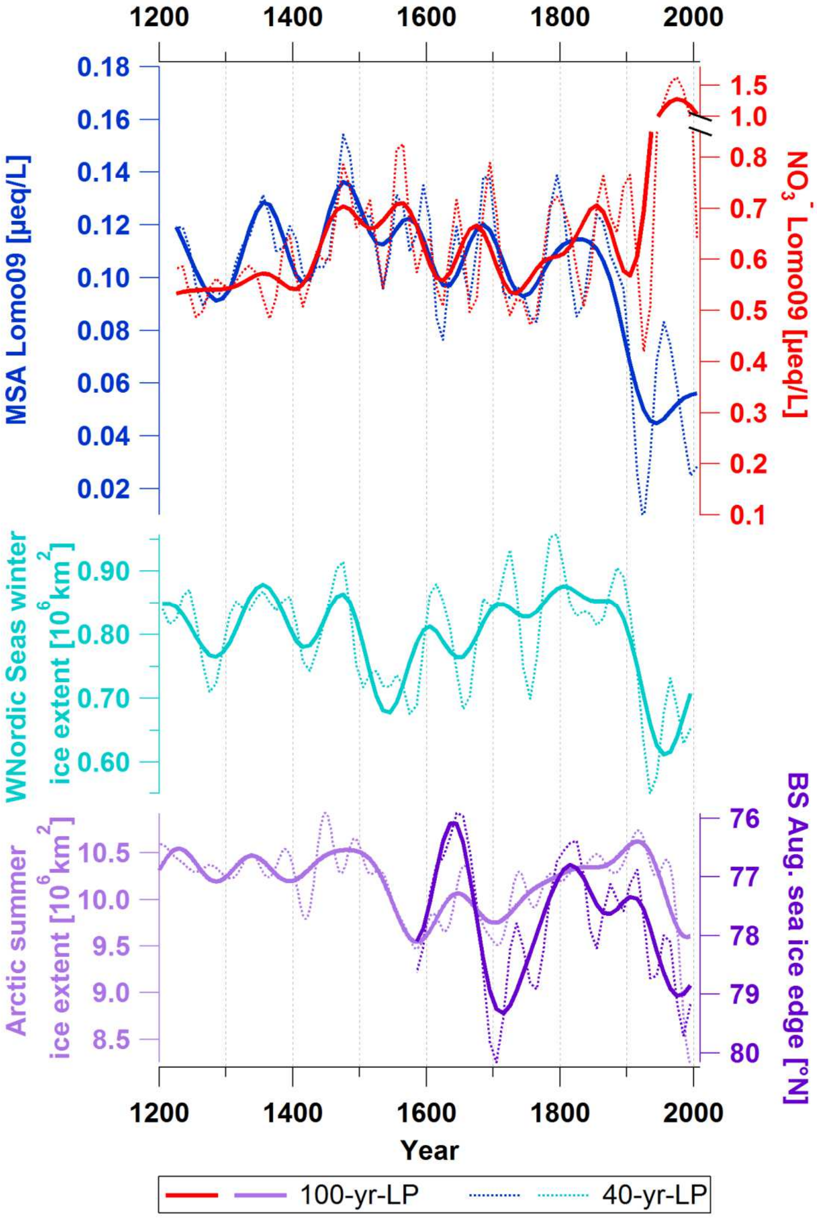


Figure ~~5~~ 6 Records of Lomo09 MSA (dark blue), pre-industrial NO_3^- (red), Western Nordic Seas winter (April) ice extent (turquoise; Macias Fauria et al., 2010), Arctic summer (August) sea ice extent (light purple; Kinnard et al., 2011), and August sea ice edge position in the Barents Sea (BS; dark 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).

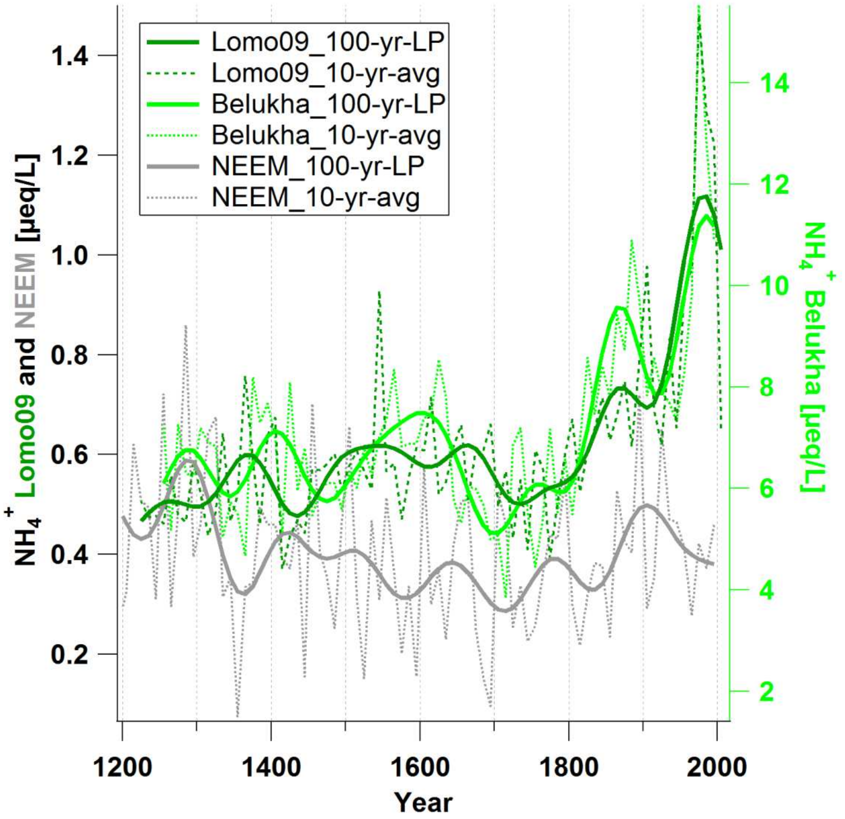


Figure ~~6~~ 7 NH_4^+ records of the Lomo09 (green), Belukha (light green; Eichler et al., 2009), and the NEEM (grey; Zennaro et al., 2014) ice cores. Bold lines are 100-year-lowpass-filtered (100-yr-LP); dashed lines are the 10-year-averages (10-yr-avg).

Response to comments by E. Wolff

We thank Eric Wolff for the valuable and helpful comments. We believe that addressing the issues is considerably improving our manuscript.

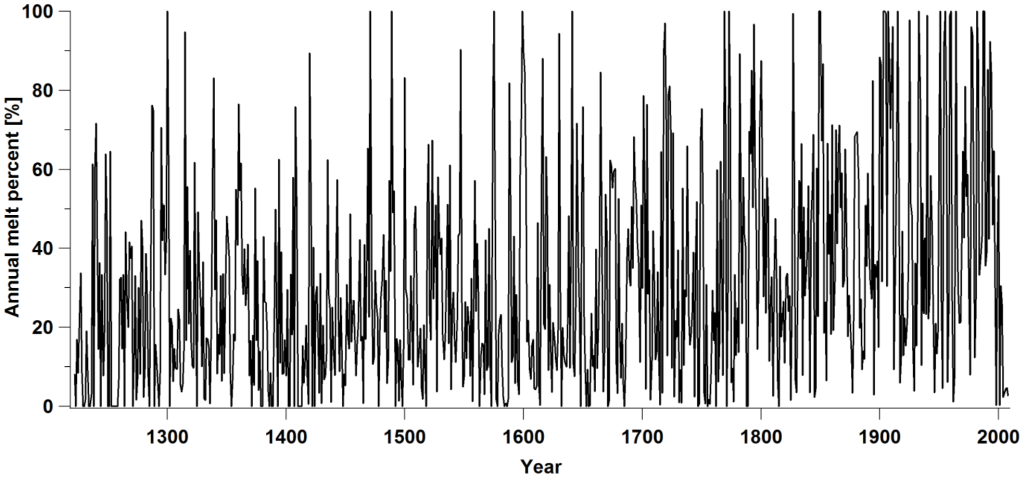
Please see our reply to each comment below.

Note: All reviewer comments are in bold. All author responses are in normal format (blue) and changes in the manuscript in italics (red).

This paper presents ionic chemistry data covering 800 years from an ice core in Svalbard. This is a good time period to study as it allows recent anthropogenic changes to be assessed in the light of a long period that was at least not influenced by industrial emissions. Svalbard has an interesting location, within the Arctic but influenced by different air masses compared to the more-studied Greenland records. The paper shows some intriguing trends and correlations, and will certainly become publishable. It does require some further work, mainly in two areas: firstly there are some general points that need drawing out a bit more, and secondly the authors should be a little more precise in some of their statements about what their data show (which will lead to greater caution in the conclusions).

There are two worrying general aspects of this study. The first concerns the issue of melt in the core. The high amount of melt in Svalbard cores has long been a concern, with the potential to disrupt and confuse records. I would like first to consider the issue of how much melt does occur in the ice. According to Fig S3 in the supplement and the middle panel of Fig 3, the annual melt percent is up to 1%, and when I saw this I thought the authors had been lucky and might not have a problem. However I then looked at data from Kekonen et al for the previous core near this location and found typical melt percents of more than 50%. This leads me to suspect that Fig S3 actually plots melt proportion (ie values not of 1% but of up to 100%). This should be corrected, and is such an important melt proportion that it needs much more discussion.

The melt percent in Figures 3 and S3 was corrected and is now given in %.



Given this very high amount of melt, I don't feel the authors can be entirely confident in dismissing the role melt could have played in the profiles they observe. They need to discuss it more. Firstly, the paper needs to present the temperature context of the core: what is the mean annual temperature and the seasonal range? What is the profile of temperature in the ice itself (i.e. is this a temperate glacier, important for knowing whether melt is purely a surface phenomenon, or whether water is also present and moving at depth)? Really the only evidence given here is the reference to previous papers suggesting movement by only 2-8 annual layers, which would justify trusting decadal values – but the authors really need to expand on this, and indicate whether their data can be used to support that previous inference. The observation of low correlations between melt percent and concentration does not seem to me to be evidence that melt is not important: it is by no means obvious why you would expect a correlation. As an example, if melt occurs in a layer you may expect some (but not all) ions to move downwards out of the layer, but that doesn't allow you to predict a low concentration in the layer because you don't know what is being transported into the layer from above. It would be surprising if the eventual balance of ions in and out should depend on the amount of melt in just the single layer.

On the issue of melt therefore I suspect there will be no proof that it has not affected the profiles significantly, but it does need to be discussed more and left on the table as a concern.

We agree with this comment. As indicated by Figures 3 and S3, melt does occur regularly at Lomonosovfonna in summer and we will include a corresponding discussion in the manuscript. There are only few direct air-temperature measurements from Lomonosovfonna. Mean near-surface temperature estimated by Soviet expeditions was -12.5°C at 1020 m a.s.l. (Pohjola et al. 2002:" Effect of periodic melting on geochemical and isotopic signals in an ice core from Lomonosovfonna, Svalbard"). The seasonal temperature range at Lomonosovfonna is unknown, but the long-term 1961-1990 instrumental record at the lower-altitude Svalbard airport (27 m a.s.l.) shows an average DJF temperature of -15°C and JJA temperature of 4.2°C with an annual average of -6.7°C (Nordli et al., 2014: "Long-term temperature trends and variability on Spitsbergen: the extended Svalbard Airport temperature series, 1898-2012"). Measured borehole temperatures in the upper 42 m (between -1.7°C and -4.3°C) at the Lomo09 drill site are in good agreement with the average borehole temperature at the Lomo97 drill site of -2.8°C with a nearly isothermal profile (Van de Wal et al. 2002:" Reconstruction of the historical temperature trend from measurements in a medium-length borehole on the Lomonosovfonna plateau, Svalbard"). No liquid water was seen during drilling. Lomonosovfonna is therefore not a temperate glacier. We attribute the discrepancy between the annual air temperature at the low elevation Svalbard airport (-6.7°C) and the mean borehole temperature to the input of energy by the release of latent heat during refreezing of melt water. Because of the strong seasonal T cycles we assume that meltwater formed in summer refreezes within deeper layers. Since ice lenses are formed, the percolation to deeper layers is hindered as supported by the well-preserved tritium and ^{210}Pb signals. Though runoff of melt water for the strongest melt events in the 20th century cannot totally be excluded (see Moore et al., 2005), it is assumed to be much reduced in the period of interest before 1859, for which the melt percentage was generally lower.

Abstract: Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on the decadal variations of the investigated compounds.

Drilling site and meteorological settings: Measured borehole temperatures in the upper 42 m (between -1.7°C 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 melt water 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 20th century (Kekonen et al., 2005; Moore et al., 2005).

Page 24675: The average annual melt percent of the Lomo97 core was 41% (Pohjola et al., 2002) compared to 31% of the Lomo09 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 NH_4^+ *and* NO_3^- *records.*

The melt percent is the only parameter that has a high loading in PC5. This suggests that on the considered decadal time scale the influence of melt on the ion concentration averages is negligible, which is in agreement with Pohjola et al. (2002) and Moore et al. (2005).

A second issue concerns the existence of a second set of data from a core of the same length from nearby (Lomo97). In Fig 3, the Lomo97 (grey) lines look very different from the new data, even after a long averaging, and especially for NH4+ and Na. Especially for NH4+ (compare grey and green in top panel), one's conclusion about anthropogenic versus natural variability would be quite different from Lomo97 than from Lomo09. The authors cannot therefore avoid commenting on the comparison. Is the difference due to analytical issues or is there really enough spatial variability to explain such different concentrations and variability (rendering conclusions less robust)?

The preindustrial (before 1859) concentrations of NH_4^+ at both sites are close to the detection limits of the analytical methods. In addition, NH_4^+ is prone to contamination during samples preparation and analysis. We therefore assume that the discrepancy is due to contamination and analytical issues. During our sample preparation steps we minimize NH_4^+ contamination from lab air by melting ice samples in a N_2 atmosphere.

Three observations indicate that the Lomo09 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 zero, and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

The concentrations of all sea salt constituents (Na^+, Cl^-, K^+, Mg^{2+}) are higher by a factor of 1.5 in Lomo09 than in Lomo97, whereas NO_3^-, SO_4^{2-}, and MSA show similar levels (period 1222-1997). Since also the annual accumulation rate is a factor of 1.6 higher at Lomo09 this suggests slightly different humidity source regions or air mass trajectories.

The ion balance is now included in Figure S2.

Sampling: Prior to analyses ice samples were melted in a N_2 *atmosphere to reduce contamination from the laboratory air.*

Three observations indicate that the Lomo09 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 zero*

(Figure S2), and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

I now discuss a range of more detailed issues that occur in the text:

Page 24674, line 14: I am not sure that the shape of the trends alone is sufficient to define the source region for Svalbard. There surely must be data about where air masses to Svalbard originate that would more usefully define the source region?

Several publications deal with source identification for pollutants in Svalbard based on transport modelling and trajectory analysis. Hirdman et al. (2010a and b) identified Eurasia as source region, whereas Tunved et al. (2013) showed that there is a strong seasonality of dominating source areas, with Eurasia dominating during the autumn and winter period and dominance of North Atlantic air during the summer months.

Hirdman, D., Sodemann, H., Eckhardt, S., Burkhart, J. F., Jefferson, A., Mefford, T., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Source identification of short-lived air pollutants in the Arctic using statistical analysis of measurement data and particle dispersion model output, Atmospheric Chemistry and Physics, 10, 669–693, 2010a.

Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic: changes in atmospheric transport and source region emissions, Atmospheric Chemistry and Physics, 10, 9351–9368, 2010b. doi:10.5194/acp-10-9351-2010

Tunved, P., Ström, J. and Krejci, R.: Arctic aerosol life cycle: linking aerosol size distributions observed between 2000 and 2010 with air mass transport and precipitation at Zeppelin station, Ny-Ålesund, Svalbard, Atmospheric Chemistry and Physics, 13(7), 3643–3660, doi:10.5194/acp-13-3643-2013, 2013.

Our finding is in agreement with results from transport modelling and trajectory analysis, identifying Eurasia as source region for Svalbard (Hirdman et al., 2010a and b). Eurasian pollution dominates especially during the autumn and winter period characterized by Artic Haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013).

Page 24676, line 15-18. For MSA-sea ice correlations in the Antarctic, I am surprised you don't cite papers by Curran et al or Abram et al.

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).

Abram, N. J., Wolff, E. W. and Curran, M. A. J.: A review of sea ice proxy information from polar ice cores, Quaternary Science Reviews, 79, 168-183, 2013. doi:10.1016/j.quascirev.2013.01.011.

Section 3.1. The order in which this is written is a little strange. You start with the nitrate-MSA correlation, the jump over to MSA-sea ice correlations, and then jump back (page 24678) to nitrate. I think this could be re-ordered in a way that makes it easier to follow.

We changed the order as suggested.

Section 3.1. The idea you are presenting is that MSA is controlled partly by winter sea ice and partly by nitrate fertilisation. This is intriguing, but I struggled to see how you thought the two influences interact, and I think you overstate your case on both counts:

***The correlation between MSA and nitrate looks interesting, but breaks down completely between 1300 and 1400. This should be acknowledged. *The relationship between MSA and sea ice is then tricky to assess in isolation: if you are suggesting that the main features of MSA are explained by nitrate until 1900, then it is only the residual (after accounting for that) which you would expect to correlate with sea ice. I'd have to say that, apart from the period from 1900, I don't really see much correlation.**

***The idea seems to then be that low ice extent after 1900 draws MSA away from its link to nitrate. In fact you need a really strong effect as the extra (industrial nitrate) should be fertilising the ocean strongly, increasing MSA by your hypothesis, but instead MSA drops way below its long term mean. In contradiction to that idea, ice extent is quite low from 1500-1600, with no apparent effect on MSA.**

Taken together I think your story is not quite straight, and needs to be presented in a less definite way.

We agree that the nitrate/MSA break correlation breaks down between 1300 and 1400, and we acknowledge that fertilization effect is a hypothesis. However, we do not totally agree that the low sea ice extent from 1500-1600 is a strong argument against our hypothesis. The skill of reconstruction of sea ice extent decreases before AD 1600 and the data are much more uncertain.

The only exception is the period at about 1350 when the correlation breaks down.

We therefore propose the fertilising effect to be the dominant cause for the high correlation of NO_3^- *and MSA in pre-industrial times.*

Page 24679, line 12. Although I don't think nitrate is of marine origin, your correlations show only that nitrate does not derive mainly from sea spray. After all, we all agree MSA is of marine origin, but that also has a very weak correlation with sodium. Therefore your statement in line 14 "not the ocean" is a bit too broad.

Yes, the correlation does only show that NO_3^- is not derived from sea spray. Because of the high solubility of nitrate in water, outgassing of HNO_3 from the ocean is unlikely.

Because of the high solubility of nitrate in water, outgassing of HNO_3 *from the ocean is unlikely.*

Page 24680, section 3.2. I already pointed out that the two Lomo cores have very different patterns. In line 26, you state that the Holte05 core shows the same increasing trend as Lomo09: however in that case you need also to point out the strongly different patterns in the 1700-1800 period.

The NH_4^+ *record of another Svalbard core from Holtedahlfonna, spanning the last 300 years, shows a differing pattern prior to 1800 but a similar strong increasing trend as the Lomo09 record from the 18th century on (Beaudon et al., 2013) (Fig. 3).*

Page 24681, line 20. While Lomo and Belukha ammonium are similar in the 20th century they appear uncorrelated before that (what is the correlation before 1900?) I don't feel you can just ignore that and claim that the same source controls both of them.

It looks more as if they may see the same industrial source, but a different pre-industrial source (or at least a different influence on transport from the source), doesn't it (as also for nitrate)?

Indeed NH_4^+ concentration trends between Lomo and Belukha agree less before ~1500. In this part, dating uncertainty of both records increases. Furthermore, NH_4^+ levels in the Lomo are very low before ~1800. The strongest argument for a similarity of the pre-industrial sources is the pronounced common NH_4^+ increase at the Lomo and Belukha site above background values already from the 18th century on, long before the industrialization. Thus, we think it is justified to state that they do have the same pre-industrial source as described in the manuscript.

Changes in manuscript (Chapter 3.2.): "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) (Figure 6). Before ~1500 NH_4^+ concentration records agree less, which could be explained by increasing dating uncertainty.

Response to comments by Michel Legrand

We thank Michel Legrand for the valuable and helpful comments. We believe that addressing the issues raised by Michel Legrand will considerably improve our manuscript.

Please see our reply to each comment below.

Note: All reviewer comments are in bold. All author responses are in normal format (blue) and changes in the manuscript in italics (red).

1. As for any ice core extracted from Svalbard, the large presence of melted snow layers rise the question to what extend the chemical ice core signals can be here safety related to atmospheric chemistry change. This crucial point needs to be addressed furthermore in the manuscript. As it stands, it is claimed in the abstract and the conclusion that this question is discussed in the paper but in fact it is only indirectly discussed when the common feature of nitrate and MSA is discussed in section 3.1 (see my other comments below). Since the effect of melt would differ from one chemical species to another one, I strongly suggest addressing more carefully this point as follows:

Put your Figures S1 and S2 (only available in the supplementary material) in the main text, for S1 please report not only 18O and sodium but also melt, nitrate, ammonium, and MSA.

We agree with this comment. As indicated by Figures 3 and S3, melt does occur regularly at Lomonosovfonna in summer and we will include a corresponding discussion in the manuscript. Measured borehole temperatures in the upper 42 m (between -1.7°C and -4.3°C) at the Lomo09 drill site are in good agreement with the average borehole temperature at the Lomo97 drill site of -2.8°C with a nearly isothermal profile (Van de Wal et al. 2002:" Reconstruction of the historical temperature trend from measurements in a medium-length borehole on the Lomonosovfonna plateau, Svalbard"). No liquid water was seen during drilling. Lomonosovfonna is therefore not a temperate glacier. Because of the strong seasonal T cycles we assume that meltwater formed in summer refreezes within deeper layers. Since ice lenses are formed, the percolation to deeper layers is hindered as supported by the well-preserved tritium and ^{210}Pb signals. Though runoff of melt water for the strongest melt events in the 20th century cannot totally be excluded (see Moore et al., 2005), it is assumed to be much reduced in the period of interest before 1859, for which the melt percentage was generally lower.

We changed Figures S1 and S2 by including nitrate, ammonium, and MSA, but left them in the Supplement. Referee 3 suggested adding a Figure with the raw concentration data of MSA, Na^+, NO_3^- and NH_4^+ and annual averages of melt on a time scale into the main text (see responses to Referee 3). Since we do not discuss the raw data in the manuscript we preferred not to include Figures S1 and S2 into the main text. Please note that melt cannot be resolved on a depth-scale since it was calculated as annual melt percent.

Abstract: Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on the decadal variations of the investigated compounds.

Drilling site and meteorological settings: Measured borehole temperatures in the upper 42 m (between -1.7°C 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 melt water 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 20th century (Kekonen et al., 2005; Moore et al., 2005).*

Page 24675: The average annual melt percent of the Lomo97 core was 41% (Pohjola et al., 2002) compared to 31% of the Lomo09 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 NH_4^+ and NO_3^- records.

The melt percent is the only parameter that has a high loading in PC5. This suggests that on the considered decadal time scale the influence of melt on the ion concentration averages is negligible, which is in agreement with Pohjola et al. (2002) and Moore et al. (2005).

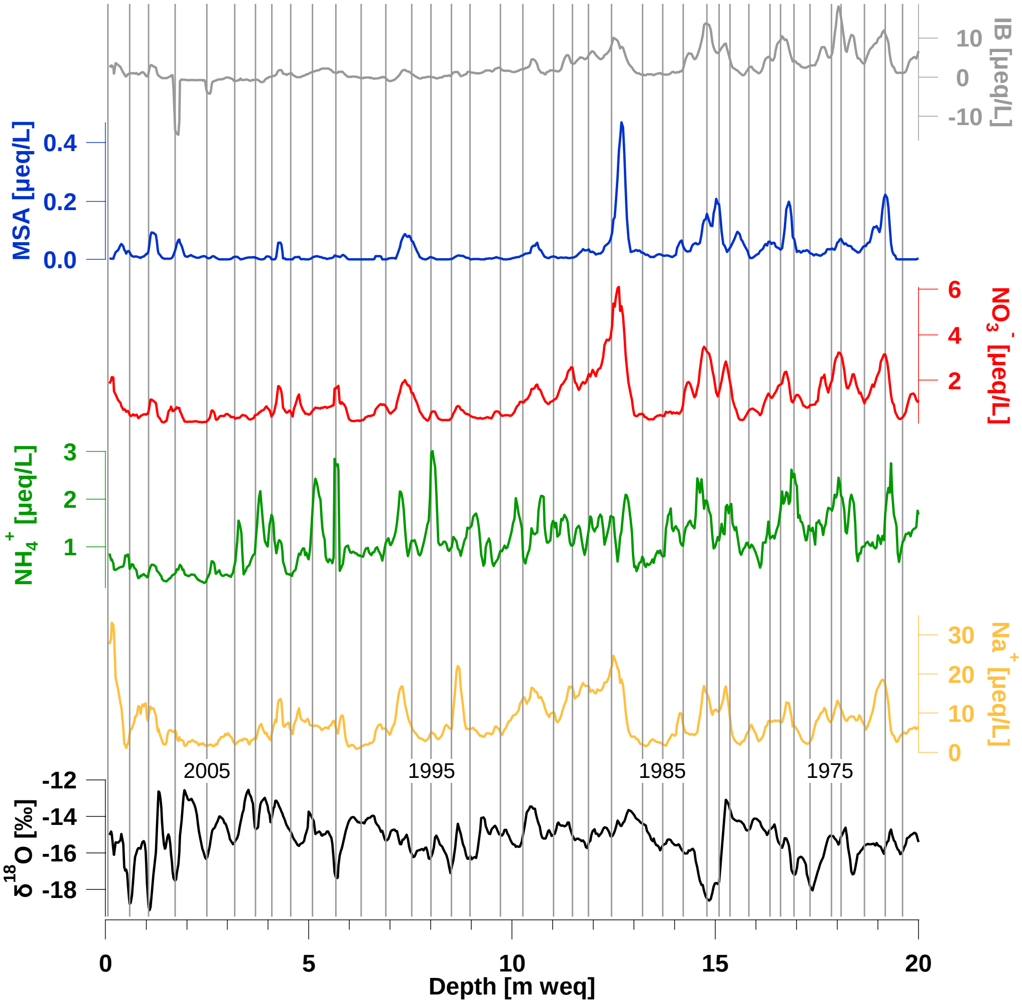


Figure S1 Example for annual layer counting (ALC) for the core section between 0 and 20 m weq using the records of $\delta^{18}O$, Na^+, NH_4^+, NO_3^-, and MSA. Data are five-point-moving averages to facility identification of the annual cycles. Grey vertical lines indicate the single counted years; numbers within the graph give the resulting year. IB is the ion balance (sum of anions-sum of cations).

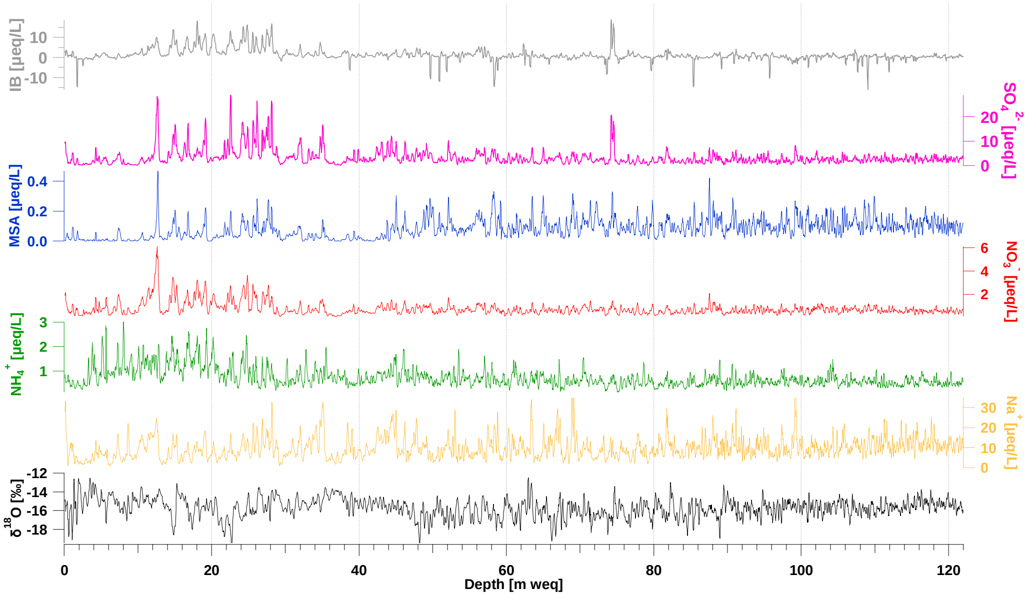


Figure S2 Raw data of $\delta^{18}O$ *and of concentrations of* Na^+*,*NH_4^+*,* NO_3^-*, MSA, and* SO_4^{2-} *of the Lomo09 ice core versus depth. IB is the ion balance (sum of anions-sum of cations). Data shown are 5-point-moving-averages for better visibility especially for the IB.*

Please explain how your vertical lines (annual layer counting) were identified (at the first glance on the basis of 18O but did the sodium profile really useful?).

The annual layer counting in the Lomo09 was performed using the seasonality of the $\delta^{18}O$ record and, where it was critical to identify single years, additionally the Na^+ record was used which shows higher values in summer due to more open water that can lead to sea spray formation. It was possible to count years down to a depth of 79.86 m weq which was attributed to the year 1749 AD. Below that depth it was difficult to identify the annual cycles. The annual layer counting was supported by reference horizons and ^{210}Pb dating as detailed in the manuscript.

Where are located other ions compared to sodium at such a seasonal scale? Did the delocalization due to melt differs from MSA to nitrate?

In this study the focus was on decadal variations, except for annual layer counting for the dating. The seasonality is different for instance for sodium and ammonium see above Figure 1, but we cannot rule out that melt influenced the observed seasonal variations. We do not see any difference in delocalisation in MSA and nitrate, and again this would not be relevant on the decadal time scales considered here.

Could you calculate the ionic balance to evaluate the acidic character of snow layers and melted snow layers that may have influenced the remobilisation? Please comment.

The ion balance shows a surplus of anions between 10 to 30 m weq, which is explained by anthropogenic input of acidic aerosols (we did not analyse H^+ which is therefore missing in the ion balance). Below 30 m weq the ion balance is balanced (close to zero), except for the acidic layer at 78 m weq which is the volcanic layer from the Laki eruption. We do not see remobilisation of MSA from acidic to less acidic layers (see Figure S1), since the diffusion process is hindered by the formation of ice lenses. And again this would also not be relevant on the decadal time scales considered here.

2. The discussion of data in terms of sources (natural and anthropogenic) is rather vague, often based on comparison with other smoothed records extracted at other places in the northern hemisphere to identify sources or source regions. What are missed in the manuscript, that may help the reader to follow the comparison with various records (Altai, Alps, Greenland), are air mass back trajectories calculated for winter and summer at your site using HYSPLIT and the NCEP reanalysis for instance.

Such analyses were already done by Eichler (GRL, 2009) for Altai in Siberia, by Kahl (JGR, 1997) for Summit in central Greenland or Fagerli (JGR, 2007) for the Alps (here with the EMEP transport-chemistry model). They need to be done for Svalbard as well. Such information would then strengthen (or not) your argument based on correlations between records that may be sometimes coincidental.

Kahl, J. D. W., Martinez, D. A., Kuhns, H., Davidson, C. I., Jaffrezo, J. L., and Harris, J. M.: Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic events, J. Geophys. Res. Oceans, 102, 26861–26875, doi:10.1029/97jc00296, 1997.

Fagerli, H., M. Legrand, S. Preunkert, V. Vestreng, D. Simpson, and M. Cerqueira, Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps, J. Geophys. Res., 112, D23S13, doi:10.1029/2006JD008044, 2007.

Several publications deal with source identification for pollutants in Svalbard based on transport modelling and trajectory analysis. Hirdman et al. (2010a and b) identified Eurasia as source region, whereas Tunved et al.(2013) showed that there is a strong seasonality of dominating source areas, with Eurasia dominating during the autumn and winter period and dominance of North Atlantic air during the summer months. Concerning the sources for Greenland and the Alps: It is mentioned on page 24669 L.17 onwards that emissions from North America and Europe reach Greenland. It is mentioned on page 24674 L.13 that Western Europe mainly influences the Alps.

Hirdman, D., Sodemann, H., Eckhardt, S., Burkhart, J. F., Jefferson, A., Mefford, T., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Source identification of short-lived air pollutants in the Arctic using statistical analysis of measurement data and particle dispersion model output, Atmospheric Chemistry and Physics, 10, 669–693, 2010a.

Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic: changes in atmospheric transport and source region emissions, Atmospheric Chemistry and Physics, 10, 9351–9368, 2010b. doi:10.5194/acp-10-9351-2010

Tunved, P., Ström, J. and Krejci, R.: Arctic aerosol life cycle: linking aerosol size distributions observed between 2000 and 2010 with air mass transport and precipitation at Zeppelin station, Ny-Ålesund, Svalbard, Atmospheric Chemistry and Physics, 13(7), 3643–3660, doi:10.5194/acp-13-3643-2013, 2013.

Our finding is in agreement with results from transport modelling and trajectory analysis, identifying Eurasia as source region for Svalbard (Hirdman et al., 2010a and b). Eurasian pollution dominates especially during the autumn and winter period characterised by Artic Haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013).

Sometimes your conclusions drawn when comparing different records are a bit subjective. I here take the example of the nitrate change and your comparison with Altai, the Alps and Greenland. My conclusion is very different from your. When discussing source regions of concern for anthropogenic NOx emissions you pointed out the similarity between your record and the one from Altai indicating that both records show a strong anthropogenic trend followed by a decrease after 1980 that contrasts with Alpine and Greenland records showing persisting high values after 1980. From that you concluded that the main source region for anthropogenic emissions at your site is Eurasia. First, it has be recognized that Greenland ice archives anthropogenic emissions from North America and Eurasia (polluted air masses from these two regions being advected in winter in the Arctic basin and transported over Greenland and lower latitudes in spring). Note that for Greenland you can also report in your Figure 4, in addition to Geng et al. (2014) the record from Savarino and Legrand (which, as your ice core, extend back to 1200 AD). For the Alps, the main source region is western Europe (see Preunkert et al., 2003 or Preunkert and Legrand, 2013, for nitrate records).

Savarino, J., and M. Legrand, High northern latitude forest fires and vegetation emissions over the last millenium inferred from the chemistry of a central Greenland ice core, J. Geophys. Res., 103, 8267-8279, 1998.

Preunkert, S., and M. Legrand, Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from Alpine ice cores, Clim. Past, 9, 1403-1416, doi:10.5194/cp-9-1403-2013, 2013.

Preunkert, S., Wagenbach, D., and M. Legrand, A seasonally resolved Alpine ice core Record of Nitrate: Comparison with Anthropogenic Inventories and estimation of Pre-Industrial Emissions of NO from Europe, J. Geophys. Res., 108, D21, 4681, doi : 10.1029/2003JD003475, 2003.

Second, comparing Altai and your record my conclusions are different from you: whereas your nitrate level drops after 1980, this change is far less pronounced in the Altai record. I think you may have difficulties to fit your recent nitrate decrease with recent change of nitrogen oxide emissions. Furthermore, the Altai record clearly shows that anthropogenic emissions do not dominate preindustrial sources, and since a large variability is obvious for these natural sources in your Figure 4 (reported below), you cannot use the small decrease seen after 1980 as a sign of decreasing anthropogenic emissions there. In fact, except after 1980 your record is more similar to the Greenland one with a rather low preindustrial level compared to the strong post 1940 increase at the opposite to the record at Altai where clearly natural sources can be as high as anthropogenic emissions.

The Greenland nitrate record published by Savarino and Legrand (1998) covers only the time prior to 1980 AD. This record does therefore not help to identify if there was a decrease after 1980. Nevertheless we will include this record in Fig. 4 since it extends further back in time than the record from Geng et al. (2014) if we can get access to the data.

In the Siberian Altai record from Belukha ice core the decrease from 1980 to 2000 is similar to the decrease at Lomonosovfonna, but the record ends in 2001. At Lomonosovfonna the decrease continues until 2009 which is the end of that record. The nitrate trend in the Siberian Altai fits well with NOx emissions as discussed in Eichler et al. (2009) where the Eastern European NOx emissions are shown. The anthropogenic nitrate peak is larger than the preindustrial peak (6 μeq/L compared to 5 μeq/L, 10-year averages). We will change the colours in Fig. 4 to make this more visible.

For Europe the record from Mt. Blanc also did not show a nitrate concentration decrease before 1995 (Preunkert and Legrand, 2013) in agreement with the record from Colle Gnifetti which we show in Fig. 4.

Overall we think that the NOx emissions trends in North America, Western Europe and Eastern Europe were significantly different to distinguish the impact of these source areas on the corresponding nitrate records.

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 NOx emissions as discussed in detail in Eichler et al. (2009) where the Eastern European NOx emissions are shown.

Section 3.1: Whereas I found the idea to explain positive correlation between nitrate and MSA innovative and interesting, I would suggest to be more careful in your conclusion drawn by examining your 3 hypothesis (line 23-25, page 24678). I am not sure that you can discard an effect of melt as you did it, based on examination of correlation since the redistribution of nitrate may be different from the one of MSA. Please also recognize that the good correlation between nitrate and MSA works for the periods around 1480, 1560, and 1680 but fails for the peak of MSA seen around 1350 (see Figure 5).

The correlation analysis is based on 10-year-averages, so we think that melt effects can really be excluded as outlined above. We agree that the nitrate/MSA correlation breaks down between 1300 and 1400, and we acknowledge that fertilization effect is a hypothesis. MSA is influenced by both factors, fertilization by nitrate input and sea ice extent (shows maximum in 1350).

The only exception is the period at about 1350 when the correlation breaks down.

We therefore propose the fertilizing effect to be the dominant cause for the high correlation of NO_3^- *and MSA in pre-industrial times.*

In discussing MSA, I always like to see the sulphate record (especially during the pre-industrial time). I am sure that the record is available since you used it for the dating purpose. It would have been also interesting as additional (back-up)

We added the raw sulphate data in Figure S2 in the Supplement, see above.

Section 3.2: same comments as for nitrate: when comparing Altai and Svalbard: Fig 6 first indicates me that Svalbard and Greenland pre-industrial ammonium level are similar but are both one order of magnitude lower than at Altai, clearly pointing out the importance of continental biospheric emissions in Siberia compared to Greenland and Svalbard located far away from continental emissions.

We do not totally agree with this statement. Preindustrial ammonium levels are lower in Greenland than in Svalbard and there is no increase after the 1750s visible in the Greenland record. The difference in order of magnitude between Siberia and Svalbard is already explained in the paper as different distance to source.

Minor points:

Page 24668, line 23: I don’t think that you can claim that PAN is efficiently wet deposited (PAN is not very soluble in acidic water).

We agree. PAN will be deleted.

The major source for bio-available nitrogen in the Arctic is the deposition of reactive atmospheric nitrogen that is present primarily as nitrate (NO_3^-) and ammonium (NH_4^+) (Björkman et al., 2013; Kühnel et al., 2011).

Page 24668, line 25: Replace "in general" by "at a global scale"

Will be changed.

Page 24670, line 16-18: I agree with your statement for nitrate but I don't see how possible is a migration of ammonium in a cold archives (without melting). At the opposite I am surprised that you don't mention previous studies having shown migration of MSA in snow and ice.

We do not discuss migration of ammonium, but the potential relocation by melting. The focus is here more on the loss processes or in general on the preservation of nitrate and ammonium in ice cores and the reliability of the records. We think that migration is not so relevant for our study, since we discuss decadal variations as already mentioned above.

Page 24672, line 7: Please note that nitrate is not at all totally present in the aerosol phase.

We agree that nitrate is mainly present as HNO_3 with a shorter lifetime, but also for HNO_3 wet and dry deposition should be reduced.

…aerosol related species…

Page 24668, line 24: What do you mean by "Values were not blank corrected" ? Either skips it or explains how blank are done, report if they are significant or not

We skipped this sentence since the procedure blanks are not relevant for the measured concentrations (e.g. 0.06 µeq/L for NH_4^+).

Response to comments by Referee 3

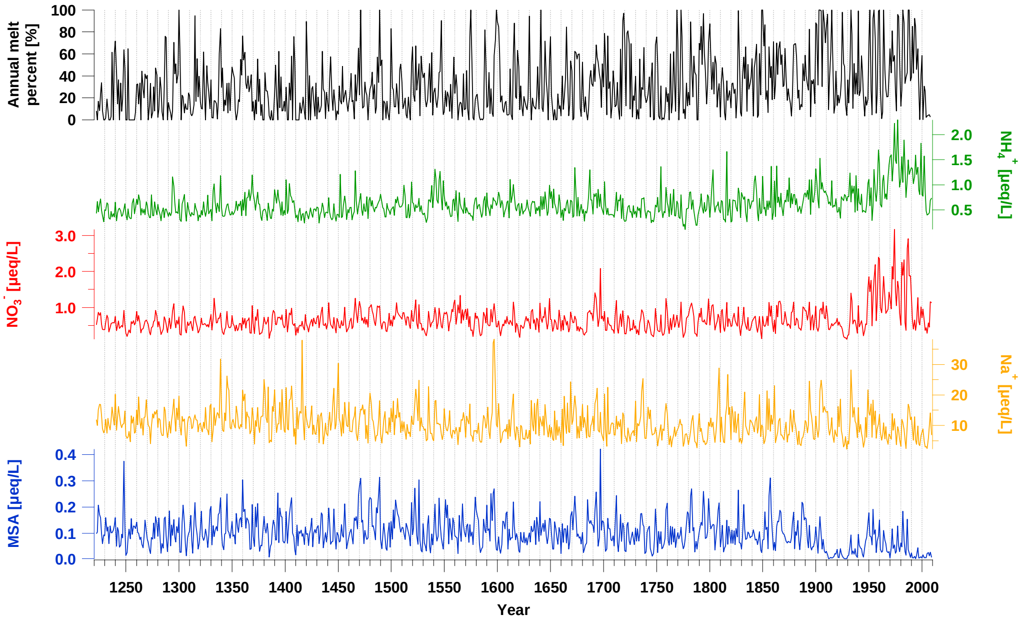
We thank the referee for the valuable and helpful comments. We believe that addressing the issues is considerably improving our manuscript.

Please see our reply to each comment below.

Note: All reviewer comments are in bold. All author responses are in normal format (blue) and changes in the manuscript in italics (red).

After the 1997 core this is the second ice core recovered from Lomonosovfonna glacier and the authors have to be commended on their sound dating of the ice core, including age uncertainties as a function of depth. However the interpretation raises questions. Most importantly the authors' claim that post-depositional effects due to percolating melt water are small and do not affect the ion records at the site is questionable. Some of the features present at the higher resolution are masked when working with decadal averages. For example, Figure S2 in the appendix shows a marked decrease in absolute concentration, concentration amplitude (smoothing) and frequency of annual spikes for nitrate, MSA and to some extent also sodium (ammonium) over two depth intervals: one between 0 and 10 m-weq (_1994-2009) and one between 30 and 42 m-weq (_1912-1955); the interval between 10 and 30 m-weq stands out with comparably larger spikes. To my eye this suggests a post-depositional artefact. Indeed, during the 20th century annual melt fractions (not percent as the y-axis suggests) frequently exceed 0.8 (Figure S3) supporting the suspicion that their may be an impact of melt on the ion record. Before making any further strong conclusions based on an ice core record potentially biased by post-depositional processes the authors need to take advantage of the available high resolution chemistry data and a) report raw data in the main paper and b) investigate in more detail the relationship between melt fraction and relative position of ion spikes. Is there any (possibly preferential) elution and displacement of the measured ions? If so, could post-depositional displacement explain some of the observed inconsistencies between the Lomo97 and Lomo09 cores (e.g. a correlation between ammonium and nitrate in Lomo97 but not in Lomo09)?

We will include a figure with annual averages of MSA, Na^+, NO_3^-, NH_4^+ and melt on a time scale into the main text. To be consistent, annual averages are presented instead of raw concentration data, since melt is available only on an annual scale.



New Figure 3: Temporal records of annual average concentrations of MSA, Na^+, NO_3^- and NH_4^+ and annual melt percent of the Lomo09 ice core.

We included a general paragraph about the amount of melt. In addition, we discuss that the observed amount of melt may have induced a maximum percolation length in the Lomo09 core not exceeding eight annual layers. The focus of this study is on decadal variability and not on short-term intra-annual variations, possibly caused by melt events. As a conservative estimate we therefore used the 10-year-average record of melt percent in the PCA to examine the influence of melt on the NH_4^+ and NO_3^- records. In the new figure with the raw data it is visible that at decadal time scales there is no relation between melt and ion concentrations. For instance the higher concentrations between 10-30 m weq (~1950-1990 AD) seen for MSA, NO_3^- and NH_4^+ are accompanied by high melt percent, whereas high melt seen at earlier times (~1900) did not result in higher ion concentrations.

Abstract: Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on the decadal variations of the investigated compounds.

Drilling site and meteorological settings: Measured borehole temperatures in the upper 42 m (between -1.7°C 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 melt water 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 20th century (Kekonen et al., 2005; Moore et al., 2005).

Page 24675: The average annual melt percent of the Lomo97 core was 41% (Pohjola et al., 2002) compared to 31% of the Lomo09 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 NH_4^+ and NO_3^- records.

The melt percent is the only parameter that has a high loading in PC5. This suggests that on the considered decadal time scale the influence of melt on the ion concentration averages is negligible, which is in agreement with Pohjola et al. (2002) and Moore et al. (2005).

Regarding the inconsistencies between Lomo97 and Lomo09, we likewise conducted a PCA with the Lomo97 data set for the pre-industrial period. Similarly to the Lomo09, NO_3^- and MSA have a high loading in the same component. The Lomo09 and Lomo97 nitrate records agree well. This is also the case for the MSA records, but only back to 1500. Before, the Lomo97 MSA shows an unexplained decreasing trend towards 1200. For an actual comparison between the two sites, further analyses have to be performed investigating records of common time periods and resolution. This will be the subject of another study.

A few more specific comments:

p24672 - l23 As acknowledged by the authors ammonium analyse can be tricky, and the lower values compared to the Lomo97 results raise confidence in the data. However, what was the ammonium blank concentration? Is it possible that the higher values in Lomo97 are due to a higher blank, which had not been corrected for?

The procedure blanks of Lomo09 are not relevant for the measured concentrations (e.g. 0.06 μeq/L for NH_4^+). We therefore deleted the sentence about blanks from the manuscript. We do not have information how the blank was treated for the Lomo97 core. In general, at both sites, concentrations of NH_4^+ (raw data) are frequently close to the detection limits of the analytical methods during the preindustrial period. We therefore assume that the discrepancy is due to contamination and analytical issues. During our sample preparation steps we minimise NH_4^+ contamination from lab air by melting ice samples in a N_2 atmosphere.

Three observations indicate that the Lomo09 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 zero, and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

Sampling: Prior to analyses ice samples were melted in a N_2 atmosphere to reduce contamination from the laboratory air.

Three observations indicate that the Lomo09 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 zero (Figure S2), and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

p24673 - l16 annual accumulation rate vs time along with the raw ion data, as well as relative change in temperature (from d18O-H2O) to further check for post-depositional artefacts

Annual accumulation rates cannot be added since they are available only for the period which could be dated by annual layer counting (2009-1749). We also did not include a temperature proxy, since the post-depositional artefacts are not relevant on decadal time scales (see above).

p24675 - l1 Not really, Fig.3 shows that Holte05 ammonium is quite different compared to Lomo09.

NH_4^+ records of Holte05 and Lomo09 agree very well after around 1800, but reveal indeed different pattern in the 1700-1800 period.

The NH_4^+ *record of another Svalbard core from Holtedahlfonna, spanning the last 300 years, shows a differing pattern prior to 1800 but a similar strong increasing trend as the Lomo09 record from the 18th century on (Beaudon et al., 2013) (Fig. 3).*