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

**I. A. Wendl[1,2,3], A. Eichler[1,2], E. Isaksson[4], T. Martma[5], M. Schwikowski[1,2,3]**

[1]{Laboratory of Radiochemistry and Environmental Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland}

[2]{Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland}

[3]{Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland}

[4]{Norwegian Polar Institute, Framsenteret, 9296 Tromsø, Norway}

[5]{Institute of Geology, Tallinn University of Technology, Estonia}

Correspondence to: M. Schwikowski (margit.schwikowski@psi.ch)

## 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. 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 ~~$NO_3^-$ and $NH_4^+$~~decadal records to investigate ~~their~~the major emission sources of $NO_3^-$ and $NH_4^+$ precursors ~~We investigate the emission sources~~ and find that 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. We propose that e~~E~~nhanced 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 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 nitrate ($NO_3^-$) and ammonium ($NH_4^+$) (Björkman et al., 2013; Kühnel et al., 2011). Those species are predominantly removed from the atmosphere by wet deposition (Bergin et al., 1995). $NO_3^-$ is the oxidation product of emitted $NO_x$ (NO and $NO_2$). At a global scale, 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 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 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 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 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 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, 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) (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, 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 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 $\delta D$. 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.

## 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), $^{210}Pb$ 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 $Na^+$ (Supplement Fig. 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), 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 Northern American and Western European air masses, respectively, kept rising into the 21st century (Fig. 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 after 1940 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). This is in contrast to studies from Northern America and Western Europe, where anthropogenic pollution started already rising in the second half of the 19th century due to an earlier industrialization and intensification of agriculture (see e.g. Döscher et al., 1996). 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) (Fig. 4), 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. 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 (Fig. S2), and 3) the 300 year record~~s~~ of ~~$NO_3^-$ and~~ $NH_4^+$ from Holtedahlfonna (Beaudon et al., 2013) ~~are~~ is in reasonable agreement with the Lomo09 data, except the period around 1750 (Fig. 4).

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  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 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. 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 ~~a~~of major influence on the ion concentrations ~~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)~~. PC6 has a high loading of $SO_4^{2-}$, indicating a volcanic source. We can exclude a dominant sea spray and marine biogenic influence on $SO_4^{2-}$, due to the low loadings within PC1 and PC2, respectively. ~~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 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 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. 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 with 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 Sea ice extent (period 1860-2000; Vinje et al., 2001), used to calibrate the proxy records (Macias Fauria et al., 2010). The strong decrease ~~which~~ 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 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 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 $NO_x$ 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 $NO_3^-$ 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.

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 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.

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 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. 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 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. 7). The values are on the same order of magnitude as those from other Arctic sites and factor 2-3 lower compared to the ~~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). 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. 4). 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.

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 $NH_4^+$ 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 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 ~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 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 Fig. 1) do not show the increase after the 18th century (Zennaro et al., 2014) (Fig. 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 $NH_4^+$~~ record~~s~~ of the 2009 ice core agrees reasonably ~~agree~~ 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 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 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. S1) is displayed, followed by the raw data of the ionic species and the ion balance along depth in m weq (Fig. S2) and the annual melt percent (Fig. S3) of the Lomo09 ice core versus age.

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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 | $\mathbf{Na^+}$ | 0.02 | 8.77 | 7.18 |
| $\mathbf{Cl^-}$ | 0.02 | 10.48 | 8.92 | $\mathbf{NH_4^+}$ | 0.02 | 0.50 | 0.74 |
| $\mathbf{NO_3^-}$ | 0.01 | 0.54 | 0.65 | $\mathbf{K^+}$ | 0.02 | 0.25 | 0.19 |
| $\mathbf{SO_4^{2-}}$ | 0.02 | 2.08 | 2.63 | $\mathbf{Mg^{2+}}$ | 0.03 | 2.10 | 1.32 |
| | | | | $\mathbf{Ca^{2+}}$ | 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 |

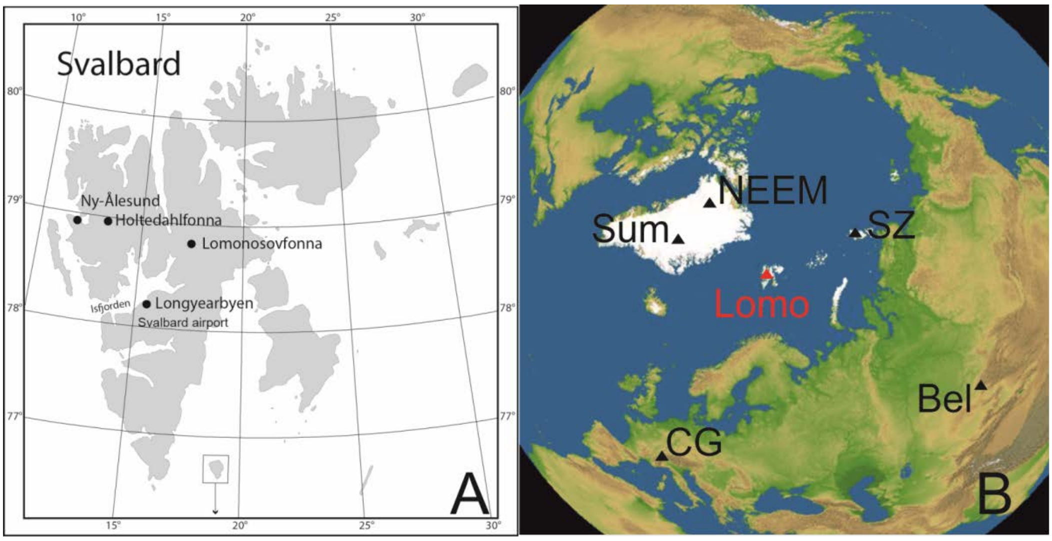

Figure 1 (A) Map of Svalbard with the locations of Lomonosovfonna and Holtedahlfonna. (B) Map with all ice core locations discussed in the text: Lomo = Lomonosovfonna (red triangle); NEEM, Sum = Summit, SZ = Severnaya Zemlya, Bel = Belukha, and CG = Colle Gnifetti (black triangles). Satellite image in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

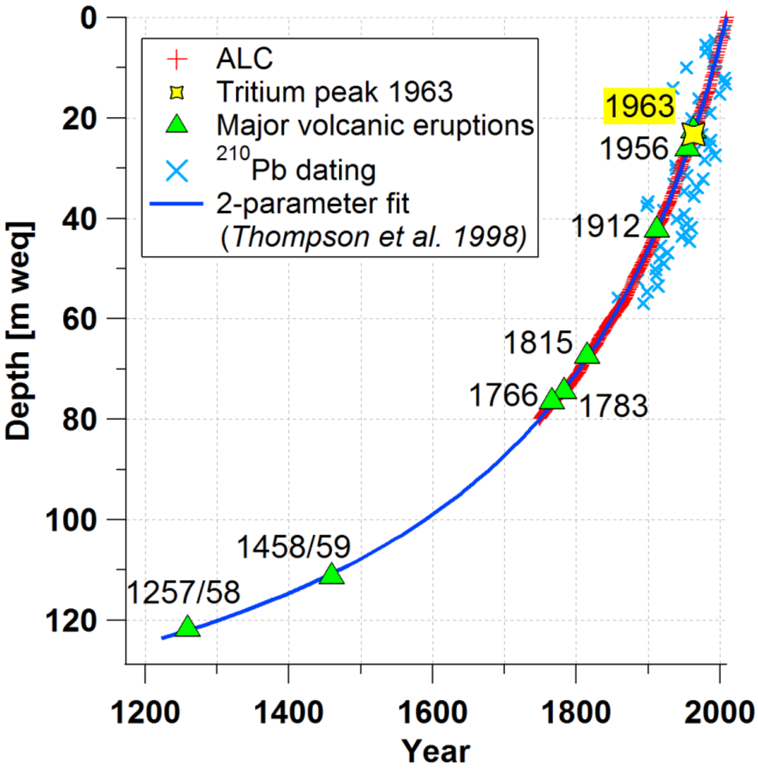

Figure 2 Depth-age relationship of the Lomo09 ice core showing all dating methods applied. Depth is given in m weq to account for density variation.

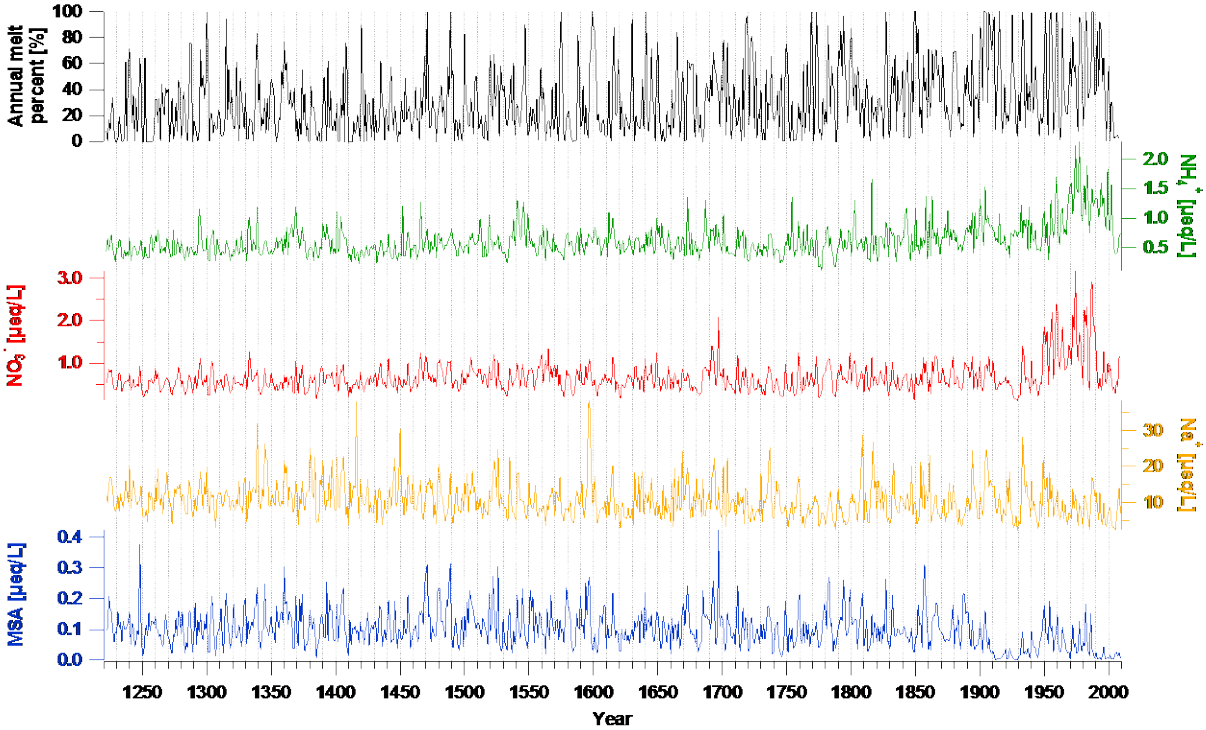

Figure 3 Temporal records of annual average concentrations of MSA, $Na^+$, $NO_3^-$ and $NH_4^+$ and annual melt percent of the Lomo09 ice core.

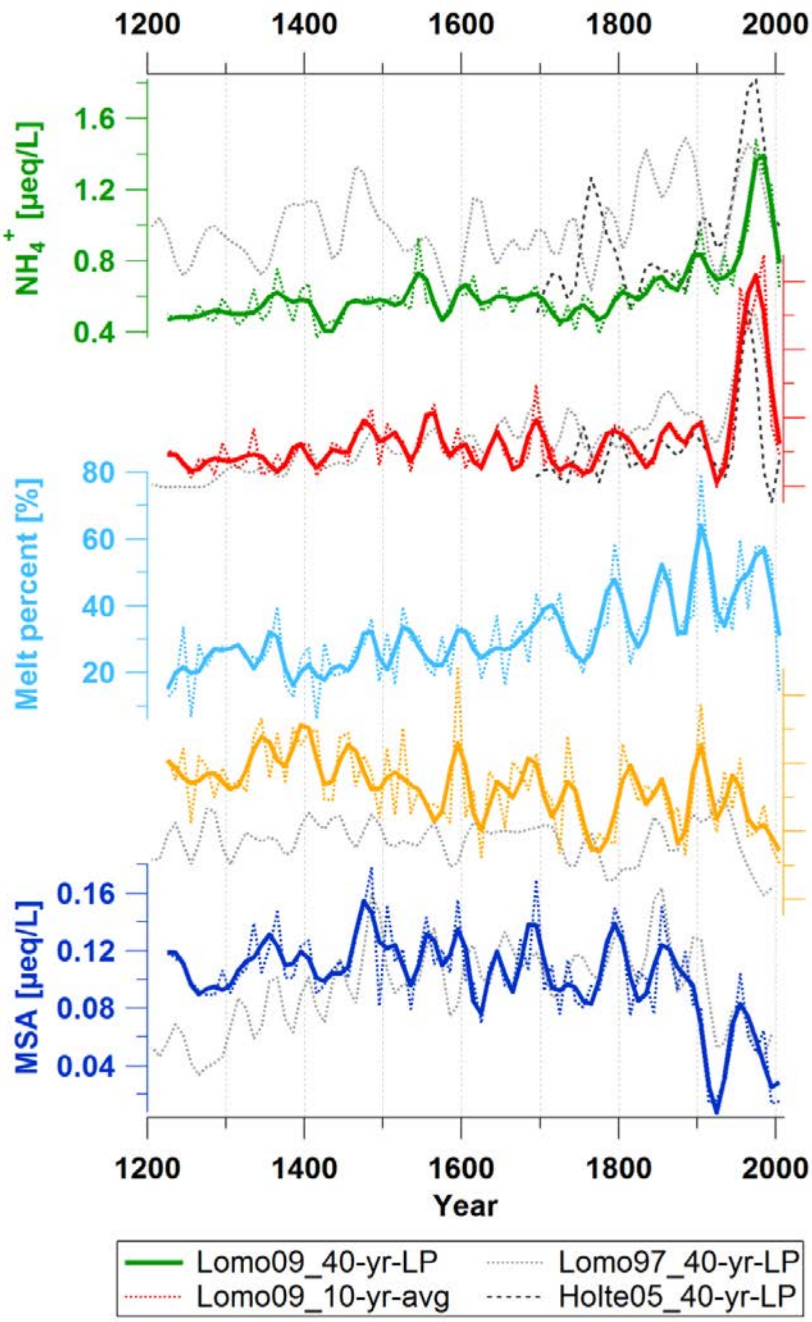

Figure 4 Records of $NH_4^+$ (green), $NO_3^-$ (red), melt percent (light blue), $Na^+$ (yellow), and MSA (dark blue) of the Lomo09 ice core. Bold lines are 40-year-lowpass-filtered (40-yr-LP); dashed lines are 10-year averages (10-yr-avg). Raw data are available in the supplementary material (Figs. 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).

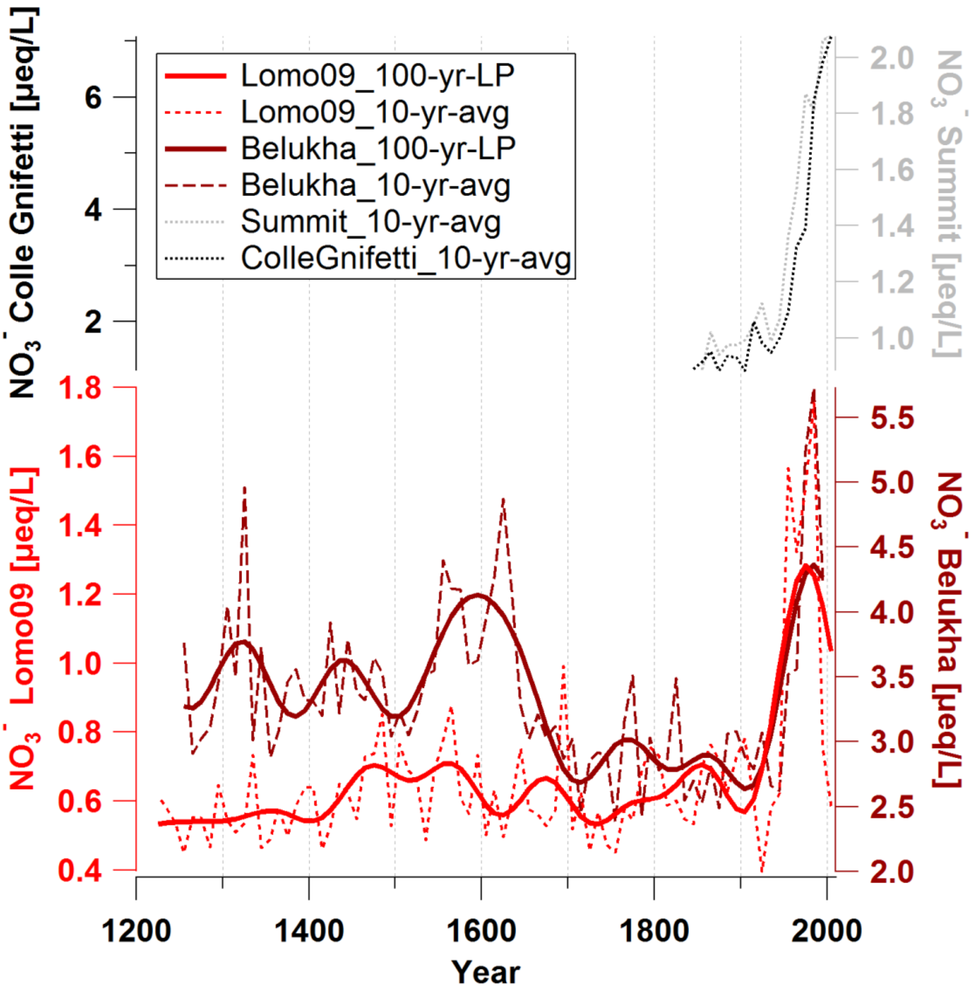

Figure 5 $NO_3^-$ records from Lomo09 (red), Belukha (dark red; Eichler et al., 2009), Summit, Greenland (grey; Geng et al., 2014), and Colle Gnifetti, Swiss Alps (black; Sigl, 2009). Bold lines are 100-year-lowpass-filtered (100-yr-LP); dashed lines are 10-year averages (10-yr-avg).

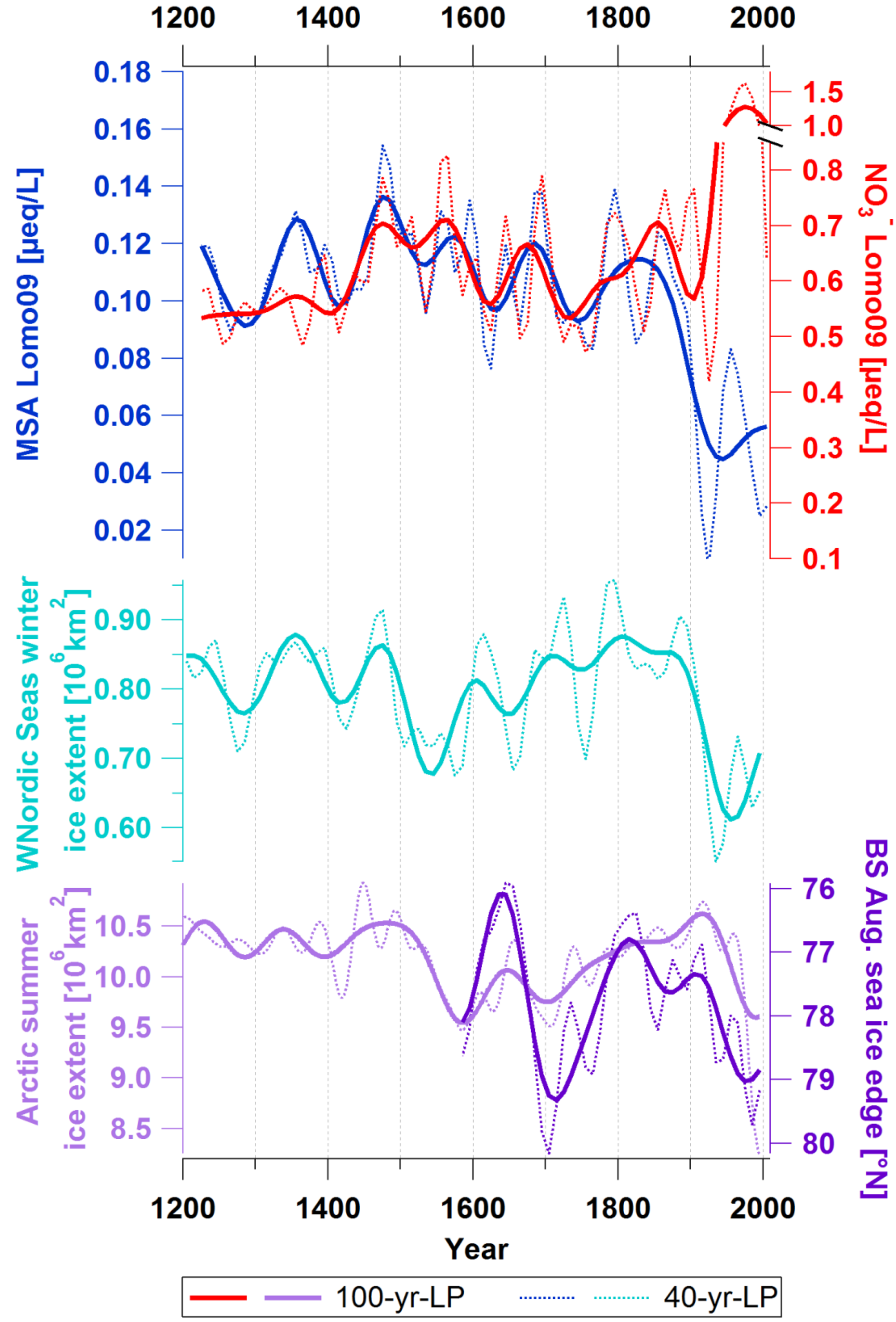

Figure 6 Records of Lomo09 MSA (dark blue), pre-industrial $NO_3^-$ (red), Western Nordic Seas winter (April) ice extent (turquoise; Macias Fauria et al., 2010), Arctic summer (August) sea ice extent (light purple; Kinnard et al., 2011), and August sea ice edge position in the Barents Sea (BS; dark purple; Kinnard et al., 2011). Bold lines are 100-year-lowpass-filtered (100-yr-LP); dashed lines are 40-year-lowpass-filtered (40-yr-LP).

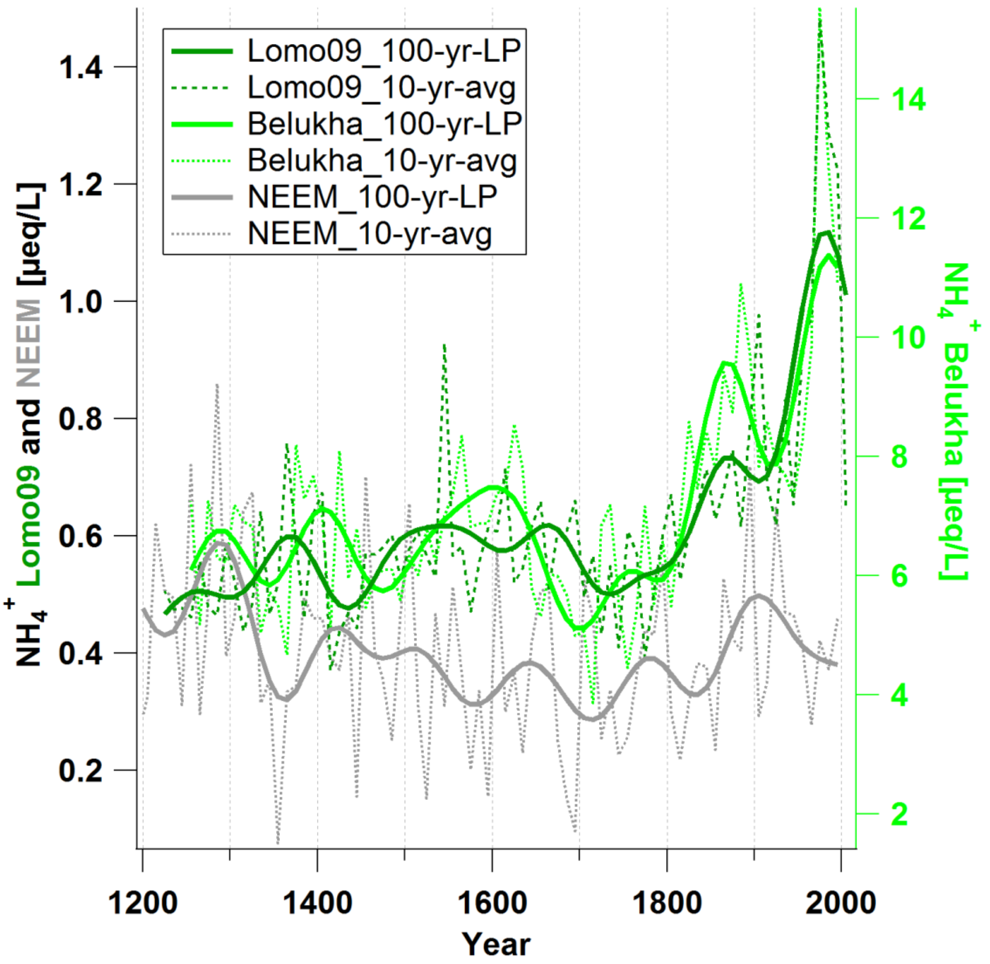

Figure 7 $NH_4^+$ records of the Lomo09 (green), Belukha (light green; Eichler et al., 2009), and the NEEM (grey; Zennaro et al., 2014) ice cores. Bold lines are 100-year-lowpass-filtered (100-yr-LP); dashed lines are the 10-year-averages (10-yr-avg).

# Responses to comments by Michel Legrand

We thank Michel Legrand for reviewing our manuscript again and for his 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).

**In this revised version, the authors have made very significant efforts to improve their manuscript. That makes it an acceptable paper for publication in the ACP journal. Nevertheless I still have a few comments that the authors may consider when producing the final version of the manuscript.**

**Section 3, end of page 7 (discussion on ammonium records): The wording of the sentence "the 300 year records of nitrate and ammonium from Holtedahlfonna are in reasonable good agreement with the Lomo09 data" is diplomatically correct, but I recommend a different wording since the agreement is quite (very) good for nitrate but is far less good for ammonium: the wave around 1760 seen in the Holte05 ice**

**core (Beaudon et al., 2013) is not seen in the Lomoo9 ice core.**

We added a comment: *the 300 year record of $NH_4^+$ from Holtedahlfonna (Beaudon et al., 2013) is in reasonable agreement with the Lomo09 data, except the period around 1750.* We changed also the Summary accordingly: *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.*

**Also your argument (in response to one of the other reviewers) that the preindustrial ammonium levels are close to detection limit is not true: the preindustrial level (new Figure 4) is above 0.5 microEq. L-1 (i.e. more than 9 ppb) whereas referring to your table 1 your detection limit is 0.02 (0.4 ppb).**

The pre-industrial level given is the median for the period 1222-1859. During this period about 10% of the values are below 3 ppb. The referee is right, the major argument for the discrepancy between the Lomo09 and Lomo97 pre-industrial $NH_4^+$ records is most probably a possible contamination e.g. from lab air. This is already written in the manuscript: "but $NH_4^+$ is known to be prone to contamination during analysis". The detection limit issue was only discussed in the response to the reviewers, but is not mentioned in the manuscript.

**Notation IB (ionic balance): may be better for the reader to use the wording « acidity».**

Since only for a positive ionic balance (IB) the wording "acidity" can be used, whereas samples with a negative balance are basic, we prefer to leave the IB in the manuscript.

**Overall comment based on your figure S2:**

**I think that your figure S2 in which you now report (as recommended) sulfate data is for me the key figure of the paper. Looking at it through a magnifying glass, I realize that over the recent (1950-2010) you have an excellent co-variation of MSA with nitrate but the same is true for sulphate (????, a short comment on that would be welcome). Of course that cannot be seen in your Table 3 since there you considered only the pre-industrial period.**

**When discussing the post 1950 period and having in mind your S2 Figure I would have discuss the data in another way (I guess that it is too late at this stage of the review but may in a future paper more focused on the recent decades?). I would have used this period for which historical Eastern European emission estimates of NH3 [Van Aardenne et al., 2001]), NOx [Van Aardenne et al., 2001], and SO2 [Stern, 2005, 2006] are known, to test the assumption that, in spite of melt, such ice core are still useful to examine decadal atmospheric changes. Indeed, the decadal trends of ammonium, nitrate and sulfate extracted from the ice records may differ (as corresponding emissions did: the post 1970-80 decrease is far more pronounced for SO2 than for NOx for instance). Note that this difference was already detectable in the sulphate and nitrate ice core records reported in Figure 3 of the Eichler's GRL paper. If no difference in the trends of sulphate and nitrate appears in the Svalbard ice core, I will tend to conclude that everything is driven by melting, handicapping the use of such records to extract atmospheric information even at the decadal scale.**

We thank the referee for the valuable comments. On decadal time scales the sulphate increase started earlier (~1950) than the nitrate increase (~1960) and ended earlier (1980). Ammonium shows a different trend. We therefore conclude that these trends are not driven by melt. We will include this discussion in a further study, specifically investigating the sulphate-record. Thus, we prefer not to discuss them already in the present manuscript.

# Responses to comments by Eric Wolff

We thank Eric Wolff for reviewing our manuscript again and for his 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).

**The authors have taken on board many of the most serious comments, and they have made important improvements to the paper based on this. I still find the interpretation too strong (too definite) in places, and feel that one more round of edits is needed before publication, to ensure that tentative conclusions do not become embedded in the literature as facts. However none of the changes are major ones and it should be possible for the editor to manage the remaining changes. Once the changes are made, this will be a useful paper.**

**Abstract, line 19. I suggest "We propose that enhanced atmospheric NO3-…" to emphasise that this is a new suggestion that needs further confirmation.**

We changed the Abstract accordingly.

**Abstract lines 25-27. This statement about the melt should go up to line 16. Then the next sentence would start "Accordingly, we use records to investigate the emission sources and…".**

We changed the Abstract accordingly.

**Page 8, line 21. I still emphasise that, if melt was important at the decadal timescale then this would not be likely to cause a correlation between melt and chemistry at the decadal timescale, because it is very complex to estimate how a pattern of melt will result in chemistry going in and out of particular layers. I propose "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 chemistry from layers of extreme melt, which together with the findings of ….supports our conclusion that melt has not been a major influence on the ion concentrations"**

We changed it accordingly.

**Page 8, line 24. In principle sulfate could be an indicator of marine biogenic. This would not be ruled out by the PC1 influence but would perhaps be expected to be seen in PC2 with MSA. So your conclusion may be OK, but needs a few extra words.**

As suggested, we added a comment: *We can exclude a dominant sea spray and marine biogenic influence on* $SO_4^{2-}$*, due to the low loadings within PC1 and PC2, respectively.*

**Page 9-10. I think the conclusion that the MSA change around 1900 is due to a major change in ice extent in the west Nordic Seas needs to be made extremely tentative, as it rests on a lot of very uncertain conjectures.**

**1. It assumes there are good sea ice reconstructions, but these are really tentative, with many of the proxies involved being generally considered proxies for temperature rather than ice extent. However, having said that, the calibration data that Macias-Fauria et al used (Vinje et al) does also show a sharp decrease in ice extent across 1900, and this should really be included as part of the argument.**

**2. You claim a good correlation between MSA and W Nordic sea ice over 800 years. However, this is probably dominated by the step change at 1900, and anyway since you are about to explain MSA through nitrate, you should not be expecting a strong correlation before 1900 with the ice extent (otherwise the nitrate argument is redundant).**

**3. While it is clear that MSA is affected by sea ice, the exact relationship you propose is handwaving and unclear (more ice does not necessarily mean more ice edge, and may mean the ice edge is further away so this could be argued either way. Probably, as in Antarctica, it is the seasonal contrast that matters as it is the retreating ice that leaves the ocean primed for productivity). It is certainly unclear why a 25% reduction in ice extent would give a 50% reduction in MSA, especially given that the nitrate increase would have been expected to lead to a significant increase in MSA.**

**So, in my view your discussion of Fig 6 essentially leads to the observation that there is a coincidence in timing of the MSA step change and the sea ice change, and this might tentatively be causal, but should be definitely labelled as tentative.**

As suggested, we included a comment about the calibration data: *This remarkable drop was also observed in the time series of the Western Nordic Sea ice extent (period 1860-2000; Vinje et al., 2001), used to calibrate the proxy records (Macias Fauria et al., 2010).*

A relation between MSA and sea ice extent in the Arctic was already proposed by different authors (see second paragraph Chapter 3.1.). In agreement with those studies, we found a significant correlation between MSA and SIE. However, we agree with the referee that based on the correlation analysis (r=0.56) less than 50% of the variability in the MSA record is explained with changing SIE in the Western Nordic Seas and added a comment accordingly (Chapter 3, third paragraph).

**Page 12, line 23. The preindustrial ammonium values are not the same order of magnitude as at Lomo97 unless you take a very literal meaning of the phrase. They are a factor 2-3 different, which you already implied might be due to contamination of Lomo97. Please change this statement.**

We changed the statement to: *The values are on the same order of magnitude as those from other Arctic sites and factor 2-3 lower compared to the Lomo97 ice core….*

**Page 13, line 1. I don't understand on what basis you are asserting that increasing anthropogenic emissions are not important for ammonium until 1940. Fertilisers have a long history. On the last line of page 12, you say "As discussed above" but I couldn't see where you made that case. The reasoning seems circular to me, and probably to be based mainly on the fact that you already made the same assertion for Belukha. Please make it more tentative again.**

The source region for air pollution reaching the Svalbard site is Eurasia as explained in the manuscript. As shown in the Eichler et al. (2009) paper, anthropogenic $NH_4^+$ and $NO_3^-$ in Eastern Europe increased only after ~1940. This is in contrast to Western Europe and Northern America, where industrialization and intensification of agriculture, and thus anthropogenic $NO_3^-$ and $NH_4^+$ concentrations, started already in the second half of the 19th century.

We slightly modified the manuscript (page 7) accordingly: *We thus attribute the observed trend after 1940 in* $NO_3^-$ *to higher NOx 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). This is in contrast to studies from Northern America and Western Europe, where anthropogenic pollution started already rising in the second half of the 19th century due to an earlier industrialization and intensification of agriculture (see e.g. Döscher et al., 1996).*

**Page 14, line 4. As per comment on page 12, ammonium values do not "reasonably agree" with those of Lomo 1997. Please remove this statement.**

We changed it accordingly: *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.*