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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. 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 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., 2012). 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). 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 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).

ACPD
14, 24667–24700, 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.

ACPD
14, 24667–24700, 2014

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 a.s.l.; 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). 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

ACPD
14, 24667–24700, 2014

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). 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 (Fig. 2). It was dated with a combination of reference horizons, annual layer counting (ALC), ^{210}Pb decay, and

ACPD
14, 24667–24700, 2014

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

ACPD
14, 24667–24700, 2014

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.

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 (Fig. 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. 4) and Severnaya Zemlya (Opel et al., 2013; Weiler et al., 2005) influenced mainly by Eurasian pollution. 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. 4). 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. 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) (Fig. 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. 3). 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,

ACPD
14, 24667–24700, 2014

1999; Udisti et al., 1994). The 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Fig. 3).

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). Additionally, we included 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 that decadal ion concentration averages are not influenced by melt, 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.

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

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 Lomo09 ice core NO_3^- is highly correlated with MSA before around 1900. The records (Figs. 3 and 5) are similar with shared peaks around 1395, 1475, 1560, 1645, 1695, and 1795. 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). 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. 3 and 5). 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. 5; $r = 0.56$, $p < 0.001$). 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 (Fig. 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.

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

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.

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

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD

14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

either NO_3^- or MSA) (Table 3, Fig. 3). 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). 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 suggest 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

ACPD
14, 24667–24700, 2014

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. 4). 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. 4), 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. 6). 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 similarly a strong increasing trend in the NH_4^+ record from the 18th century on (Beaudon et al., 2013) (Fig. 3). The authors interpret the rising concentrations from

ACPD
14, 24667–24700, 2014

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 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. 6). 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

ACPD
14, 24667–24700, 2014

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. 6), 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 result in enhanced concentrations of MSA in the atmosphere. Based on our data it was not possible to resolve major pre-industrial NO_3^- sources for Svalbard.

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ACPD
14, 24667–24700, 2014

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ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

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Table 1. Detection limits and median values [$\mu eq\,L^{-1}$] 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	Detection limit	Median Pre-ind.	Ind.	Cations	Detection limit	Median 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

ACPD
14, 24667–24700, 2014

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

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

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

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

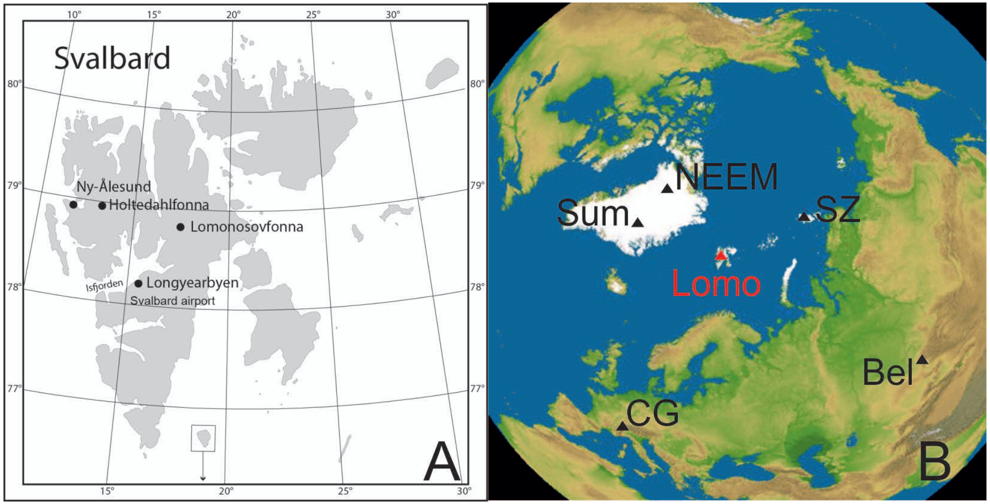

Figure 1. (a) Map of Svalbard with the locations of Lomonosovfonna and Holtedahlfonna. **(b)** Map with all ice core locations discussed in the text: Lomo = Lomonosovfonna (red triangle); NEEM, Sum = Summit, SZ = Severnaya Zemlya, Bel = Belukha, and CG = Colle Gnifetti (black triangles). Satellite image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

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

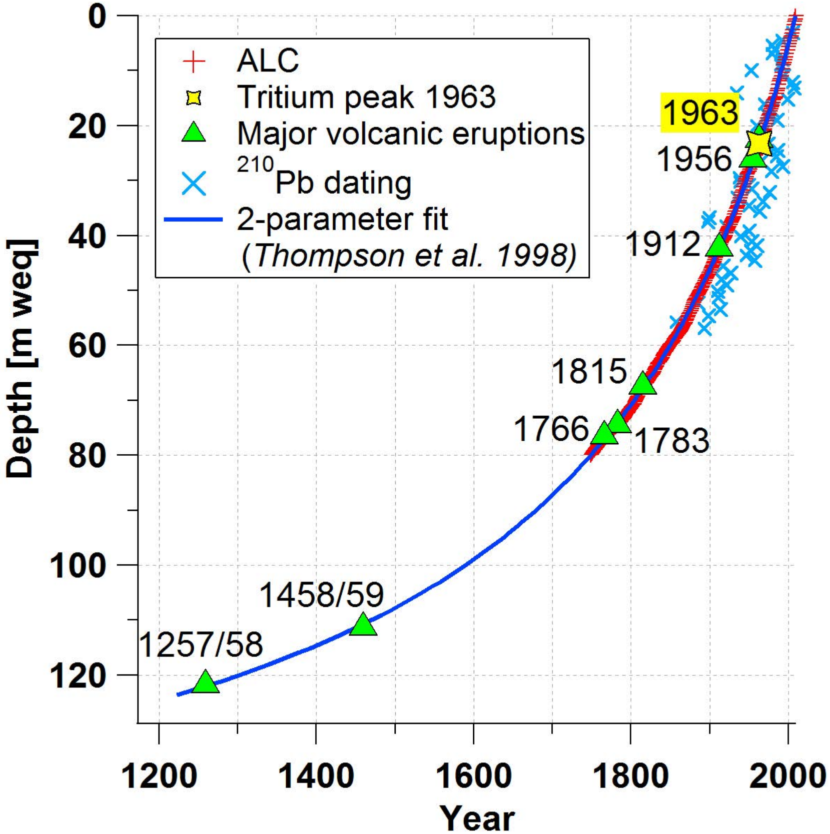

Figure 2. Depth–age relationship of the Lomo09 ice core showing all dating methods applied. Depth is given in m weq to account for density variation.

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

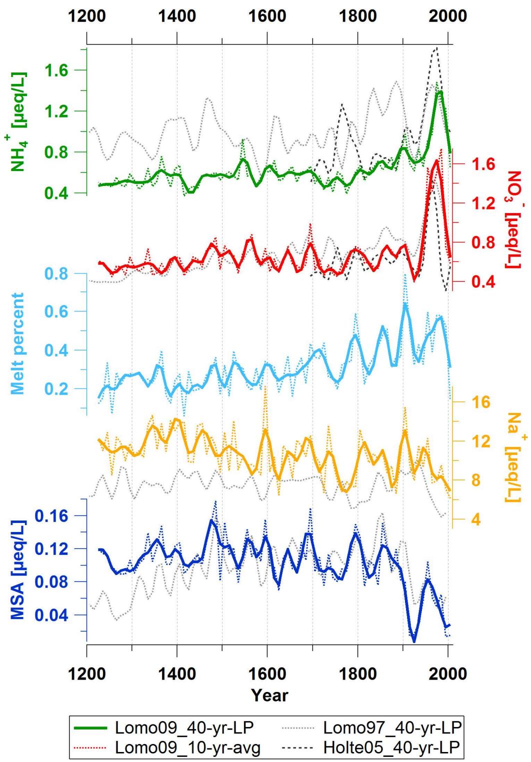

Figure 3. Records of NH_4^+ (green), NO_3^- (red), melt percent (light blue), Na^+ (yellow), and MSA (dark blue) of the Lomo09 ice core. Bold lines are 40 year-lowpass-filtered (40 year-LP); dashed lines are 10 year averages (10 year-avg). Raw data are available in the Supplement (Figs. S2 and S3). Grey 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).

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

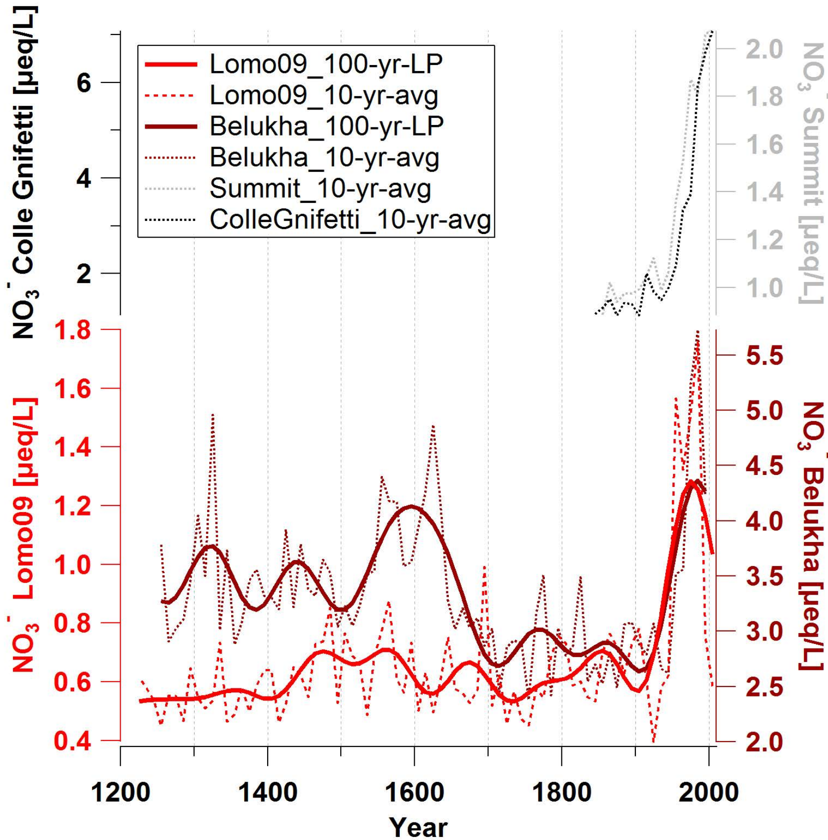

Figure 4. NO_3^- records from Lomo09 (red), Belukha (dark red; Eichler et al., 2009), Summit, Greenland (grey; Geng et al., 2014), and Colle Gnifetti, Swiss Alps (black; Sigl, 2009). Bold lines are 100 year-lowpass-filtered (100 year-LP); dashed lines are 10 year averages (10 year-avg).

ACPD
14, 24667–24700, 2014

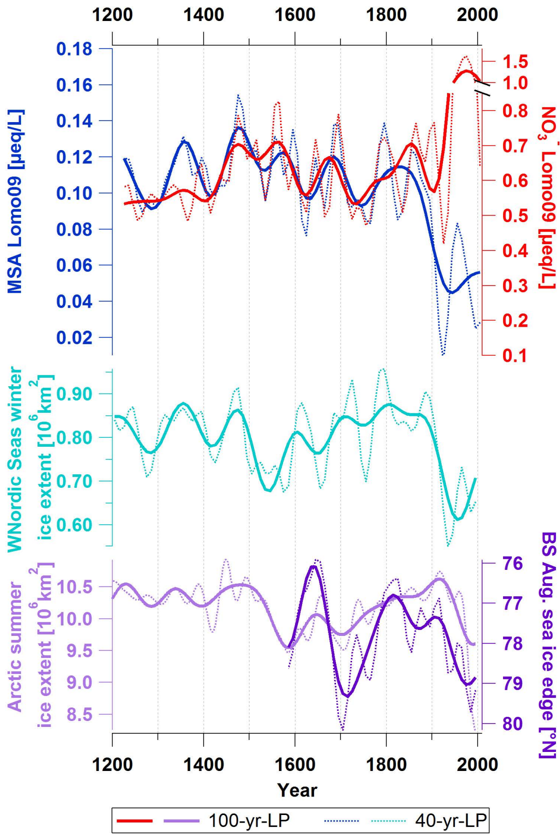

Figure 5. Records of Lomo09 MSA (dark blue), pre-industrial NO_3^- (red), Western Nordic Seas winter (April) ice extent (turquoise; Macias Fauria et al., 2010), Arctic summer (August) sea ice extent (light purple; Kinnard et al., 2011), and August sea ice edge position in the Barents Sea (BS; dark purple; Kinnard et al., 2011). Bold lines are 100 year-lowpass-filtered (100 year-LP); dashed lines are 40 year-lowpass-filtered (40 year-LP).

ACPD
14, 24667–24700, 2014

800 year ice-core record of nitrogen deposition in Svalbard

I. A. Wendl et al.

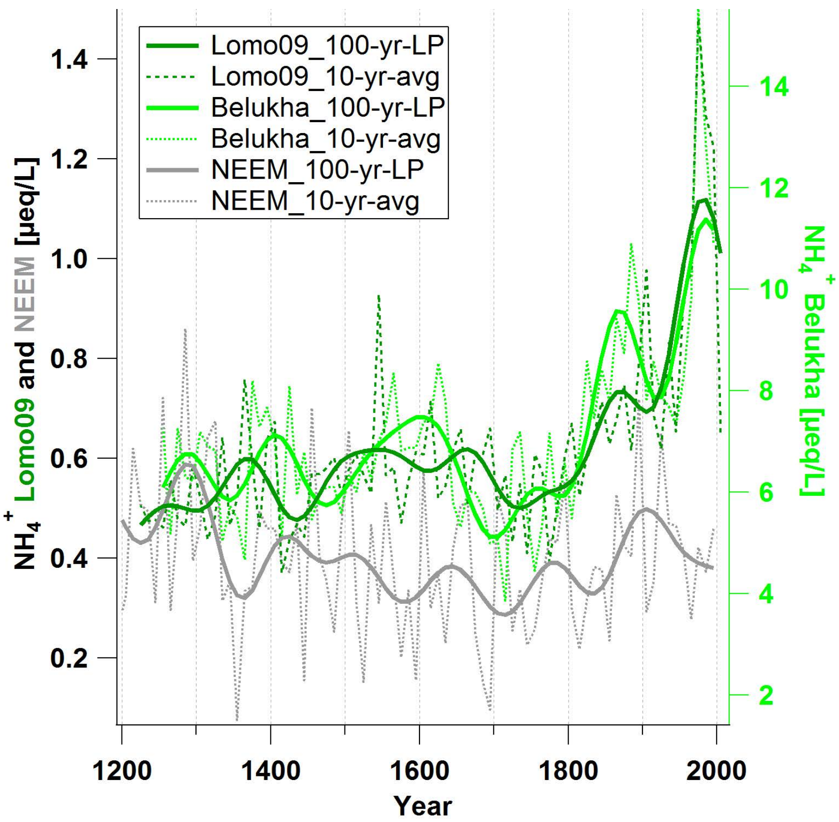

Figure 6. NH_4^+ records of the Lomo09 (green), Belukha (light green; Eichler et al., 2009), and the NEEM (grey; Zennaro et al., 2014) ice cores. Bold lines are 100 year-lowpass-filtered (100 year-LP); dashed lines are the 10 year-averages (10 year-avg).

ACPD
14, 24667–24700, 2014