RESEARCH/REVIEW ARTICLE

Reactive nitrogen and sulphate wet deposition at Zeppelin Station, Ny-Ålesund, Svalbard

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Abstract

As a potent fertilizer, reactive nitrogen plays an important role in Arctic ecosystems. Since the Arctic is a nutrient-limited environment, changes in nitrogen deposition can have severe impacts on local ecosystems. To quantify the amount of nitrogen deposited through snow and rain events, precipitation sampling was performed at Zeppelin Station, Svalbard, from November 2009 until May 2011. The samples were analysed for NO_3^-, nss-SO_4^{2-} and NH_4^+ concentrations, and the deposition of single precipitation events was calculated using precipitation measurements taken at nearby Ny-Ålesund. The majority of observed events showed concentrations ranging from 0.01 to 0.1 mg L^{-1} N for NO_3^- and NH_4^+ and from 0.02 to 0.3 mg L^{-1} S for nss-SO_4^{2-}. The majority of calculated depositions ranged from 0.01 to 0.1 mg m^{-2} N for NO_3^- and NH_4^+ and from 0.02 to 0.3 mg m^{-2} S for nss-SO_4^{2-}. The budget was controlled by strong deposition events, caused by long-lasting precipitation episodes that lasted for several days and which had raised concentrations of nitrogen and sulphur. Three future scenarios of increasing precipitation in the Arctic were considered. The results showed that deposition is mainly controlled by the amount of precipitation, which leads to the conclusion that increased precipitation might cause increases in deposition of the same magnitude.

Research on Arctic air pollution during the second half of the last century, motivated by the observation of the Arctic Haze phenomenon in the Canadian Arctic, revealed that the Arctic is not as pristine as formerly assumed, but rather is influenced by mid-latitude atmospheric pollution through long-range transport (Rahn 1981, 1985; Raatz 1984; Barrie 1986; Ottar et al. 1986; Cheng et al. 1993; Shaw 1995). This pollution generally consists of a mixture of SO_4^{2-}, NH_4^+, NO_3^- and black carbon (Dickerson 1985; Beine et al. 1996; Quinn et al. 2002; Quinn et al. 2007). NO_3^- and NH_4^+ play a special role since they act as effective nutrients for Arctic ecosystems (Shaver & Chapin 1980).

Reactive forms of nitrogen, such as NO_x ($NO+NO_2$) and NH_3, are released by natural and anthropogenic

sources. In today's industrialized world, anthropogenic sources—primarily food, fertilizer and energy production—are the most important sources of reactive nitrogen (Galloway et al. 1995; Galloway et al. 2004; Grice et al. 2009). The reactive nitrogen is transported to the Arctic in the form of peroxyacetyl nitrate (PAN), NO_3^- and NH_4^+ aerosol (Dickerson 1985). It is finally removed from the atmosphere and transferred to the Arctic surface through wet or dry deposition; wet deposition is believed to be the main pathway (Bergin et al. 1995).

Ice core analyses from Greenland and Svalbard show increasing NO_3^- concentrations in the 1950s followed by a decrease in the 1980s (Isaksson et al. 2003; Hastings et al. 2009; Samyn et al. 2012). Concentrations in Arctic

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precipitation for the period from 1980 to the present show no significant trends for NO_3^-, but a decreasing trend for SO_4^{2-} (Hole et al. 2009; Aas et al. 2011). Mitigation programmes and improvements in technology have led to reduced emissions in Europe in the last decade (Erisman et al. 2003) and European and North American nitrogen emissions are expected to decrease further as a result of future legislations. It is, however, possible that the decrease in sea-ice cover could lead to an intensification of shipping activity that would increase emissions within the Arctic (Peters et al. 2011). The mean annual nitrogen deposition in Ny-Ålesund, Svalbard, by NO_3^- and NH_4^+ during the last two decades was about 74 mg m^{-2} N and showed a strong interannual variability caused by a few sporadic but strong deposition events (Kühnel et al. 2011). For a comparison, the average deposition at 95 European sites was 550 mg m^{-2} N in 2009 (Hjellbrekke & Fjæraa 2011). See Monks et al. (2009) and Sutton et al. (2011) for background information on nitrogen in the environment.

The transport of nitrogen is linked to the transport of sulphur through the following chemical reactions:

$$2NH_3(g) + H_2SO_4(g) \rightarrow (NH_4)_2SO_4(s), \quad (R1)$$

$$NH_3(g) + H_2SO_4(g) \rightarrow NH_4HSO_4(s). \quad (R2)$$
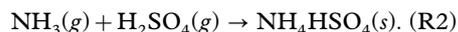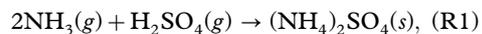
Here, g and s indicate the gaseous and particulate phase. The reactions show the neutralization of ammonia by sulphuric acid to ammonium sulphate particles. Remaining ammonia molecules might then be neutralized by nitric acid to form ammonium nitrate by this reaction:

$$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s). \quad (R3)$$
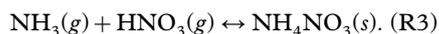
For further details on these processes, the reader is referred to Seinfeld and Pandis (2006). As a result of reduced sulphur emissions in recent decades, the chemical transformation of nitrogen may have shifted towards the formation of ammonium nitrate (Fagerli & Aas 2008). Since the typical lifetimes of nitric acid and ammonium nitrate are different, the reduction in sulphur emissions might have an impact on the lifetime of NO_3 in the air by shifting the balance to reaction R3. It has been estimated from model runs that NO_3-X in air over the European continent increased by 15–30% in the period from 1990 to 2003 (Fagerli & Aas 2008). How these nonlinearities in the atmospheric chemistry impact nitrogen deposition is unclear.

The Arctic winter atmosphere is characterized by high stability, which inhibits vertical exchanges between air-mass layers and reduces chemical reactions. Photochemical processes are also inhibited in wintertime due to the lack of sunlight. Both effects lead to longer lifetimes of chemical species in polluted air masses in the Arctic

during winter, so pollution can be transported over longer distances once they reach the Arctic (Barrie 1986; Shaw 1995). It has been suggested that the transport of contaminants into the Arctic is isentropic, i.e., the air parcels follow surfaces of constant potential temperature (Iversen 1984; Klonecki et al. 2003). Isentropic surfaces build a dome over the Arctic with minimum temperatures in the Arctic boundary layer. The regions where the isentropic surfaces intercept the ground and where there are strong horizontal gradients of potential temperature are referred to as the Polar Front, which forms an effective transport barrier (Klonecki et al. 2003). The position of the Polar Front varies seasonally. During the winter, it is located further south so that parts of the northern Eurasian continent are situated north of it (Barrie 1986). In addition, diabatic cooling of air masses over the snow-covered landmasses of northern Eurasia make the Arctic more susceptible to mid-latitude pollution during the winter months (Stohl 2006). During summer, the Polar Front is situated further north, separating mid-latitudes from the Arctic. Air is mixed vertically due to heating over mid-latitude landmasses and air masses that are transported northwards are forced to ascend along isentropic surfaces. It is assumed that these air masses are scavenged of pollutants during their ascent before they might enter the Arctic by subsidence (Stohl 2006). Surges of Eurasian air masses can occur during situations with strong east–west pressure gradients. An example of this is a strong blocking high pressure system over the Eurasian continent and an Icelandic low, which results in poleward transport between these two pressure centres (Raatz & Shaw 1984; Iversen & Joranger 1985). It seems that strong nitrogen wet deposition in Svalbard is caused by such surges of Eurasian air masses (Kühnel et al. unpubl. ms.).

In general, the Arctic is characterized by low precipitation on account of its stable atmospheric stratification and low water vapour content (due to low temperatures). The long-term mean annual precipitation for the period 1957–1990 over the Arctic Ocean, as observed at drift stations, was 260 mm, with a distinct seasonal cycle that has maximum values in autumn and winter (Yang 1999). The annual precipitation in Svalbard in the period from 1960 to 1990 ranged from 190 to 525 mm, with the highest precipitation in March and August to October (Førland et al. 1997). Precipitation in the Arctic can occur as snow or rain throughout the year. Precipitation observations are in general difficult in the Arctic due to high wind speeds and drift snow (Krupa 2002). For Ny-Ålesund, Svalbard, it has been estimated that true precipitation might be 50% higher than the uncorrected

observations using standard collection methods (Hansen-Bauer et al. 1996).

Atmospheric nitrogen, like NO_3^- and NH_4^+, is to a large extent scavenged by snow during winter and thereby accumulates in the snowpack, where it can undergo photochemical reactions (Beine et al. 2003; Grannas et al. 2007) that might alter the chemical composition of the snowpack. The nitrogen is released in spring during snowmelt and can then act as a fertilizer to local ecosystems (Shaver & Chapin 1980; Arens et al. 2008). Atmospheric nitrogen that is scavenged by rain during summer is immediately available to ecosystems. The Arctic is a nutrient-limited region, especially for nitrogen and phosphorus (Shaver & Chapin 1980). It is therefore sensitive to changes in nitrogen deposition (Gordon et al. 2001; Arens et al. 2008; Roberts et al. 2010). Phosphorus availability limits the effects of additional nitrogen deposition, as has been shown by studies in the High Arctic that found that ecosystems were able to take up more nitrogen where phosphorus availability was greater (Gordon et al. 2001; Arens et al. 2008).

Glaciers cover a significant proportion of the landscape in Svalbard so nitrogen deposition and transfer through glacier ice is an important process prior to its liberation to nutrient-limited ecosystems at the ice margin. However, microbial assimilation on the surface of glaciers is now known to be a key feature in the annual mass balance of nitrogen in the study area (Hodson et al. 2005; Hodson et al. 2008). Until this biological demand is properly understood, the impact of glacier mass balance change upon the timing, magnitude and composition of reactive nitrogen liberation to downstream ecosystems cannot be estimated from ice core and emission inventories.

Most of the precipitation on Svalbard is connected to cyclonic activity (Eneroth et al. 2003). Model studies predict an increase in the frequency of intense cyclones in the North Atlantic storm tracks. Annual net precipitation is predicted to increase by 20% over the Arctic cap, where the majority of the increase is caused by changes in atmospheric thermodynamic and precipitation physics. Changes in the moisture content of the atmosphere were suggested as a primary factor affecting the thermodynamic properties of the atmosphere (Cassano et al. 2006; Cassano et al. 2007). Another model study suggested that the absolute increase in winter precipitation will be highest over the Atlantic storm tracks and that the regions of high precipitation will extend further to the north (Saha et al. 2006). Observations by Førland et al. (1997) indicate an increase of annual precipitation in Svalbard of 25–30% during the past 85 years. However, the cause of this trend is unclear.

Since precipitation is a major driver of nitrogen deposition, the increase in cyclonic activity and precipitation might lead to stronger deposition events in Svalbard (Kühnel et al. 2011). It is therefore necessary to gain further insight into the nature of nitrogen deposition at such a sensitive site. On behalf of the Norwegian Climate and Pollution Agency, the chemical composition of precipitation in Ny-Ålesund, Svalbard, has been analysed by the Norwegian Institute for Air Research in collaboration with the Norwegian Polar Institute since 1980 (Fagerli & Aas 2008; Aas et al. 2011). A detailed study of this data set with respect to nitrogen and sulphur compounds can be found in Kühnel et al. (2011). Precipitation samples taken at Alert, Canada, for the period from 1990 to 1994 were analysed by Toom-Sauntry and Barrie (2002). However, both programmes have sampling periods of about a week, which is longer than the timescale of typical precipitation events. This makes it difficult to characterize the chemical signature of single precipitation events. In addition, synoptic weather patterns might change substantially within one sampling period. This further complicates the study of pollution transport in connection with the deposition observations. Studies with event based precipitation sampling have been conducted in Svalbard but covered short time periods of several weeks to a few months (Kang et al. 2001; Krawczyk et al. 2008).

This study presents concentration observations of NO_3^-, NH_4^+ and SO_4^{2-} with near to daily sampling that permits the analysis of single deposition events. Precipitation was sampled at Zeppelin Station near Ny-Ålesund, Svalbard, from 4 November 2009 to 19 May 2011. The sampling campaign was part of the collaborative, interdisciplinary project Sources, Sinks and Impacts of Atmospheric Nitrogen Deposition in the Arctic. Atmospheric sciences, snow physics, hydrology, biogeochemistry and aquatic/terrestrial ecology were integrated in this project that intended to give a detailed picture of nitrogen dynamics and to track the fate of reactive nitrogen in the Arctic.

Methods

Sampling

The sampling campaign started on 4 November 2009 and continued until 19 May 2011. Precipitation was sampled at Zeppelin Station (78.90°N, 11.88°E), at an altitude of 474 m a.s.l. (Fig. 1). The samplers used in this study were an open bucket-system from 4 November 2009 to 6 May 2010 and 31 August 2010 to 19 May 2011, and a
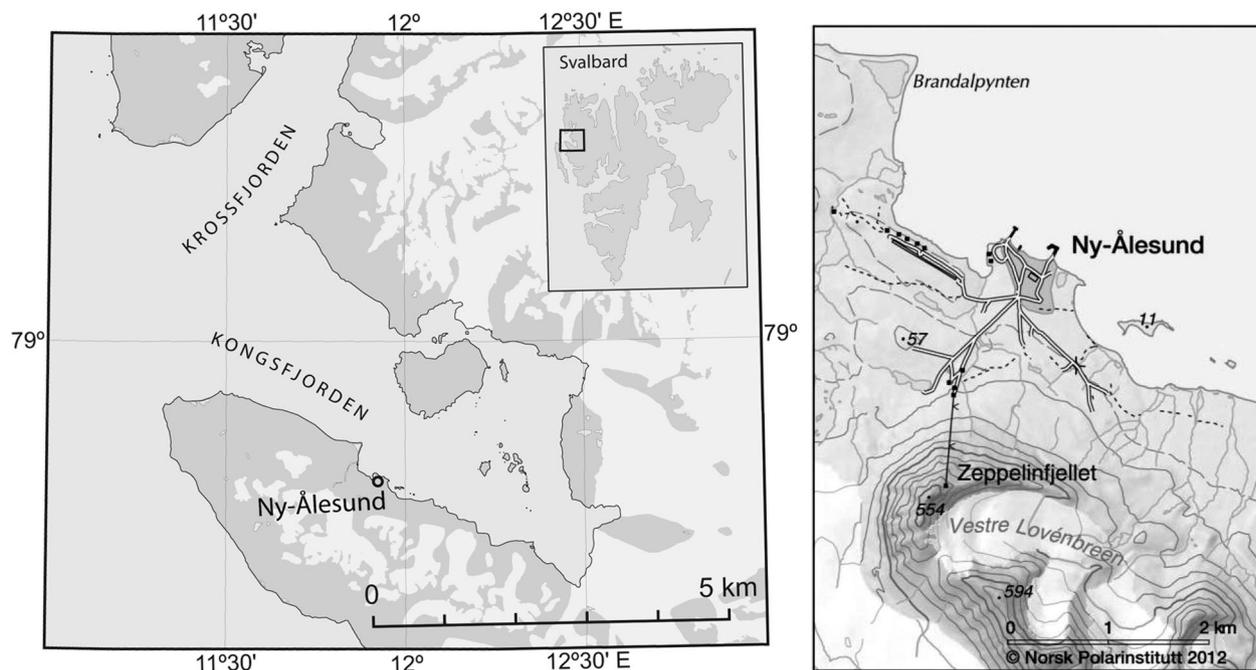
Fig. 1 Maps of Kongsfjorden and Ny-Ålesund.

funnel-bottle system from 6 May 2010 to 1 September 2010 (Fig. 2).

The bucket system utilized a container with an opening diameter of 30 cm mounted on a wooden rail outside Zeppelin Station. Polyethylene plastic bags were fitted inside the bucket for sampling and secured with a strong rubber strap around the outside of the bucket. The bucket was fitted with a valve and a vacuum pump was used to evacuate the space between bucket and plastic bag to keep the bag in place. The funnel-bottle system consisted of a polyethylene plastic funnel with an opening of 20 cm. High-density polyethylene bottles (250 ml) were fitted under the funnel for sampling. The funnel was rinsed with ultrapure water between each sampling. Two different samplers were used for optimal performance during different precipitation conditions.
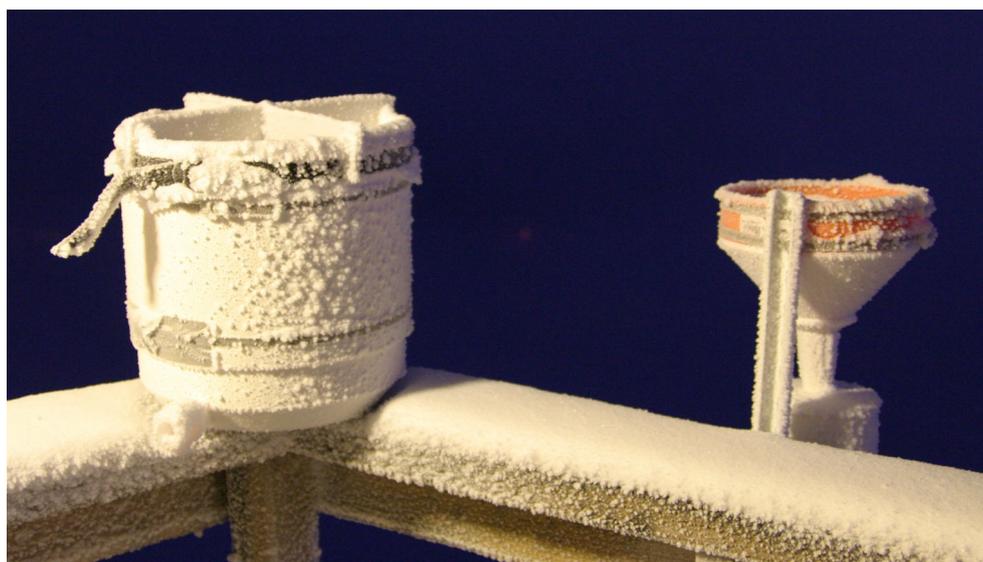
Fig. 2 Bucket sampler for solid precipitation (left) and funnel sampler for liquid precipitation (right).

The bucket sampler had a wider opening for efficient snow sampling. Designed for sampling liquid precipitation, the funnel-bottle system used a bottle with a narrow opening that limited loss through evaporation and possible contamination by blown dust.

The samplers were maintained by staff from the Norwegian Polar Institute during their routine maintenance at Zeppelin Station on weekdays. During weekends and bad weather conditions the station was not attended and samples were retrieved during the next visit to the station.

Precipitation samples taken in both plastic bags and bottles were stored frozen and in the dark until further preparations for analysis were performed. The preparations included melting of the samples at room temperature and vacuum filtering on cellulose nitrate filters with 0.45 μm pore sizes. After filtration the samples were bottled and kept frozen until ion chromatographic analysis took place in Sheffield, UK, or Uppsala, Sweden. The equipment was triple rinsed with ultrapure water and blanks were analysed along with the samples to identify possible baseline noise values.

Ion chromatography analysis

The samples were analysed for major ions (Na^+, Ca^{+2}, Mg^{+2}, NH_4^+, F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} and Ox^{2-}) at the Department of Geography, University of Sheffield, UK, and at the University of Uppsala, Sweden.

Analysis at the University of Sheffield was performed on 5 ml samples using two Dionex DX 90 ion chromatographs (Thermo Fisher Scientific, Waltham, MA, USA) with 4400 integrators and AS40 auto-samplers (Thermo Fisher Scientific) with a 0.2 μm Nuclepore™ prefilter (Whatman, Maidstone, Kent, UK) and a six standard calibration range between 0 to 2000 μg/L that was run at least once every 20 samples. Precision errors of less than 5% were also estimated from 10 replicate analyses of a single snow sample. A detection limit of 1 μg/L was imposed for all analyses using Chromeleon software. This was never exceeded by results for laboratory blanks, which were prepared using the 18 O ohm water supply and analysed once every 10 samples.

Analysis at the University of Uppsala was performed on 5 ml samples using a ProfIC850 ion chromatographer (Metrohm, Herisau, Switzerland). A calibration range from 1 ppb (μg/L) to 1000 ppb (μg/L) was employed using 12 calibration points. The regression coefficients for each calibration curve were in the range of 0.9998–0.9999. Three sample blanks made of ultrapure water were measured at the beginning and end of every analysis batch and sample checks made of melted bulk

snow were analysed every 10 samples to ensure the continuity of the analysed samples. The detection limits (DLs) for each ion were calculated as the average value of six ultrapure blanks plus 1.65 times the standard deviation of the six measurements (DL = $blank_{average}$ + 1.65 × $blank_{standar\ deviation}$), which results in concentrations in the samples having to be higher than the concentrations in the ultrapure water at the 0.05 significance level to be valid. The DLs were below 5 ppb for all ions. A minimum of 5 ml per sample was required, and so lower volumes were diluted using ultrapure water (18 Ω) to a final volume of 5 ml. The result of these lower volumes was corrected for dilution afterwards.

Correction of SO_4^{2-} for sea-salt component

The observed total SO_4^{2-} was corrected for its sea-salt component using:

$$[nss - SO_4^{2-}] = [SO_4^2] - \left(\frac{[SO_4^{2-}]}{[Na^+]} \right)_{sea-salt} \times [Na^+] \quad (1)$$

where nss-SO_4^{2-} is the concentration of non-sea-salt sulphate, SO_4^{2-} is the total sulphate observed and Na^+ is the observed concentration of sodium (Kärkäs et al. 2005). The mass concentration ratio of SO_4^{2-} to Na^+ in sea-salt was set to 0.252 (Millero et al. 2008).

Calculation of deposition

The precipitation samplers were placed at Zeppelin Station to limit the influence of local contamination from the settlement of Ny-Ålesund. The samplers had the sole purpose of collecting precipitation for chemical analysis and have not been tested or calibrated for measurements of precipitation quantity. Since no official precipitation observations are performed at Zeppelin Station, the Norwegian Meteorological Institute's measurements of precipitation amount at Ny-Ålesund were used, along with the concentration observations from Zeppelin Station, for the calculation of nitrogen and sulphur deposition. The precipitation observations at Ny-Ålesund are conducted twice daily, at 07:00 and 19:00, by Norwegian Polar Institute staff on behalf of the Norwegian Meteorological Institute's routine weather observations. Deposition of NO_3^-, NH_4^+ and nss-SO_4^{2-} was calculated by multiplying the observed precipitation amount with the observed concentrations of the same time. Due to dissimilar starting and ending times of the concentration and precipitation sampling, it was possible that precipitation observations were covered by more than one concentration observation. Precipitation observations that were covered by several concentration

observations were therefore fractionated into observations with shorter timescales that fit the time periods of the concentration observations. It was assumed that the precipitation rate was constant during each precipitation observation.

Deposition events

Consecutive, non-interrupted precipitation/deposition observations were merged to single observations, which are hereafter referred to as events. For our purposes, an event is defined as a precipitation period starting from the start time of the first nonzero precipitation observation until the start time of next first zero precipitation observation. Due to the precipitation sampling interval, the shortest precipitation/deposition events recognizable in this study had durations of 12 h. Furthermore, one or several precipitation periods of timescales less than 12 h falling within one observation period would be registered as a single precipitation event. An event was considered *isolated* if it shared no concentration observations with other events. An event was considered *complete* if all of its precipitation observations were covered by concentrations observations. For each event the average concentration of NO_3^-, NH_4^+ and nss-SO_4^{2-} was calculated, that is, the deposited mass of NO_3^-, NH_4^+ or nss-SO_4^{2-} divided by the total mass of precipitation. Cumulative distribution functions were calculated for the number densities and mass densities, for the event average concentrations and the event deposition magnitude. A linear regression analysis of event average concentrations versus precipitation amount, as well as event deposition magnitude versus precipitation amount was then performed.

Future scenarios

Facing projections of increasing precipitation over the Arctic (Cassano et al. 2007), three scenarios of future nitrogen and sulphur deposition were considered. The events were divided into two subgroups by arbitrarily choosing the 75th percentile of the precipitation across all the events—4.4 mm—as the dividing line. Group A consisted of events with 4.4 mm of precipitation or less while Group B comprised events with precipitation exceeding 4.4 mm. Sensitivity tests were also carried out when dividing the events at the 50th and 90th percentiles. The data from these tests are not presented in this manuscript, but will be touched upon briefly in the discussion below.

The mean of the event average concentrations was calculated for both groups. In Scenario I, the precipitation amounts of all events increased by 20%;

in Scenario II, only the precipitation amounts of Group A increased by 20%; in Scenario III, only the precipitation amounts of Group B increased by 20%. In the control scenario the quantity of the precipitation was not increased in any of the groups. The average concentrations of the groups were then multiplied by the precipitation amount of the events to give the event deposition. The total deposition was calculated by summing over all events. Finally, the total deposition amounts of all three scenarios were compared to the total deposition of the control scenario.

Results

A total of 313 precipitation observations were made during the sampling campaign by the Norwegian Meteorological Institute. The number of precipitation observations covered with concentration observations from Zeppelin Mountain is 260 (83%) for NO_3^-, 257 (82%) for nss-SO_4^{2-} and 263 (84%) for NH_4^+. The total number of precipitation/deposition events, as defined in the previous section, is 125. The events had a median duration of 1.25 days. The longest precipitation event during the sampling campaign lasted for 7 days. The median amount of precipitation of all events was 1.5 mm; the largest precipitation event was 89.6 mm. The number of *isolated* precipitation events was 62 (49.6%). The number of *complete* deposition events was 96 (76.8%) for NO_3^-, 94 (75.2%) for nss-SO_4^{2-} and 99 (79.2%) for NH_4^+. A monthly overview of precipitation events and the number of reconstructed deposition events are presented in Table 1.

Figure 3 shows the cumulative distribution function of the event average concentrations of only *isolated* and *complete* events. The majority of event average concentrations of NO_3^- and NH_4^+ were in the range between 0.01 and 0.1 mg L^{-1} N, with a median of 0.02 mg L^{-1} N (Fig. 3). The majority of the event average concentrations of nss-SO_4^{2-} were somewhat higher, lying in the range of 0.02–0.3 mg L^{-1} S, with a median of 0.08 mg L^{-1} S (Fig. 3). The mass distributions show that approximately half of the deposited mass of nitrogen through NO_3^- was associated with events that had average concentrations greater than 0.1 mg L^{-1} N. Half of the deposited mass of nitrogen through NH_4^+ was associated with event average concentrations greater than 0.05 mg L^{-1} N. Half of the deposited nss-sulphur was associated with event average concentrations of greater than approximately 0.3 mg L^{-1} S. The average concentration during 2010, calculated as the ratio of total deposition amount to total precipitation amount, for NO_3^-, NH_4^+ and nss-SO_4^{2-} was

Table 1 Number of precipitation events during sampling campaign, number of reconstructed deposition events (percentage of precipitation events reconstructed) and number of complete and isolated deposition events (percentage of isolated and complete deposition events). A single asterisk marks NO_3^- events and double asterisks mark nss-SO_4^{2-} and NH_4^+ events.

Month	Precipitation events	Reconstructed deposition events	
		Total number	Complete and isolated
Nov 2009	6	4 (67%)	2 (33%)
Dec 2009	9	5 (56%)	0 (0%)
Jan 2010	9	5 (56%)	1 (11%)
Feb 2010	2	1 (50%)	1 (50%)
Mar 2010	6	4 (67%)	3 (50%)
Apr 2010	6	5 (83%)	5 (83%)
May 2010	5	5 (100%)	3 (60%)
Jun 2010	5	3 (60%)	3 (60%)
Jul 2010	6	5 (83%)	1 (17%)
Aug 2010	7	*5 (71%), **3 (43%)	*1 (14%), **0 (0%)
Sep 2010	10	5 (50%)	4 (40%)
Oct 2010	8	8 (100%)	4 (50%)
Nov 2010	8	8 (100%)	4 (50%)
Dec 2010	9	8 (89%)	4 (44%)
Jan 2011	7	5 (71%)	5 (71%)
Feb 2011	4	4 (100%)	2 (50%)
Mar 2011	6	4 (67%)	2 (33%)
Apr 2011	8	8 (100%)	7 (88%)
May 2011	4	4 (100%)	1 (25%)

0.05 mg L^{-1} N, 0.02 mg L^{-1} N and 0.1 mg L^{-1} S, respectively.

The cumulative distribution functions of the deposition event sizes of only the isolated and complete events are shown in Fig. 4. The bulk of events show deposition of NO_3^- and NH_4^+ between 0.01 and 0.1 mg m^{-2} N, with a median of 0.02 mg m^{-2} N. For nss-SO_4^{2-}, the bulk of

events was in the range of 0.02– 0.3 mg m^{-2} S, with a median of 0.09 mg m^{-2} S. Similar to the event average concentrations, the majority of deposited mass was associated with large deposition event sizes. For NO_3^-, NH_4^+ and nss-SO_4^{2-}, half of the deposited mass was associated with events greater than 2 mg m^{-2} N, 0.6 mg m^{-2} N and 2 mg m^{-2} S, respectively.
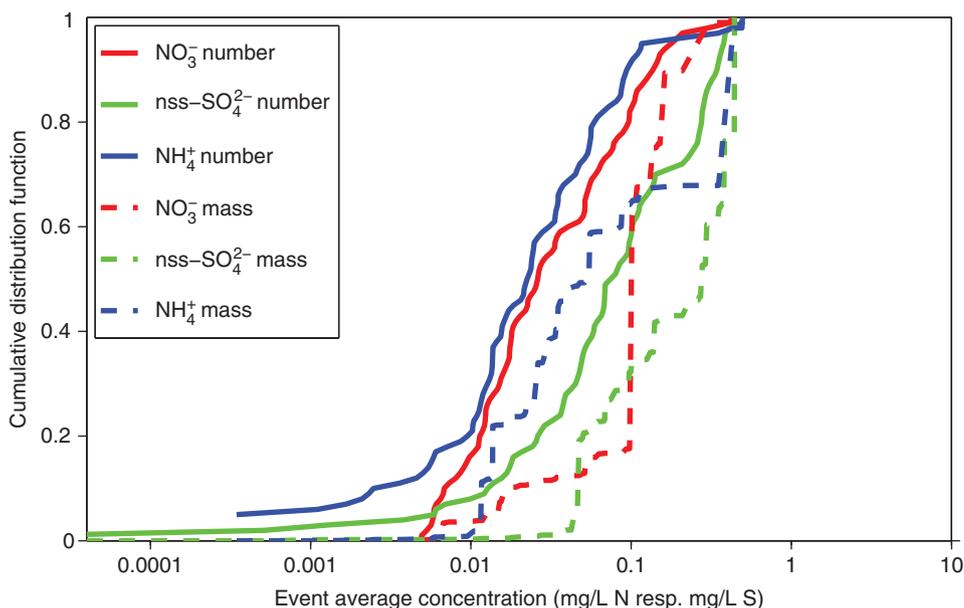
Fig. 3 Cumulative distribution function of number and mass distributions of NO_3^--, nss-SO_4^{2-}- and NH_4^+-concentration.
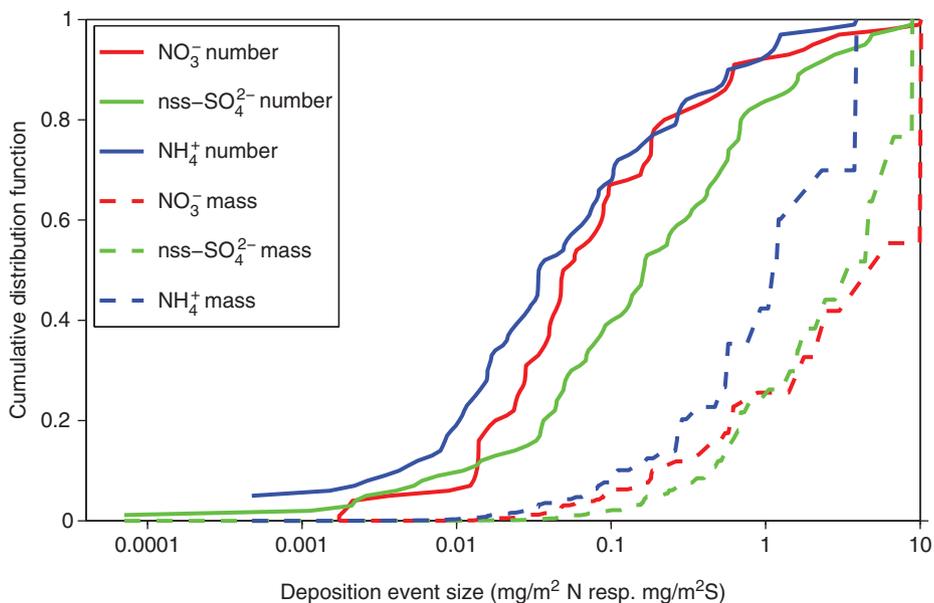
Fig. 4 Cumulative distribution function of number and mass distributions of NO_3^--, nss-SO_4^{2-}- and NH_4^+-deposition.

An overview of the precipitation amount and event average concentrations of all events during the sampling campaign can be seen in Fig. 5. Most of the events show a precipitation amount of less than 5 mm. These events can be found throughout the sampling campaign. Larger events seem to be missing in the summer (June–September) 2010. The four largest events had precipitation amounts exceeding 50 mm and occur during
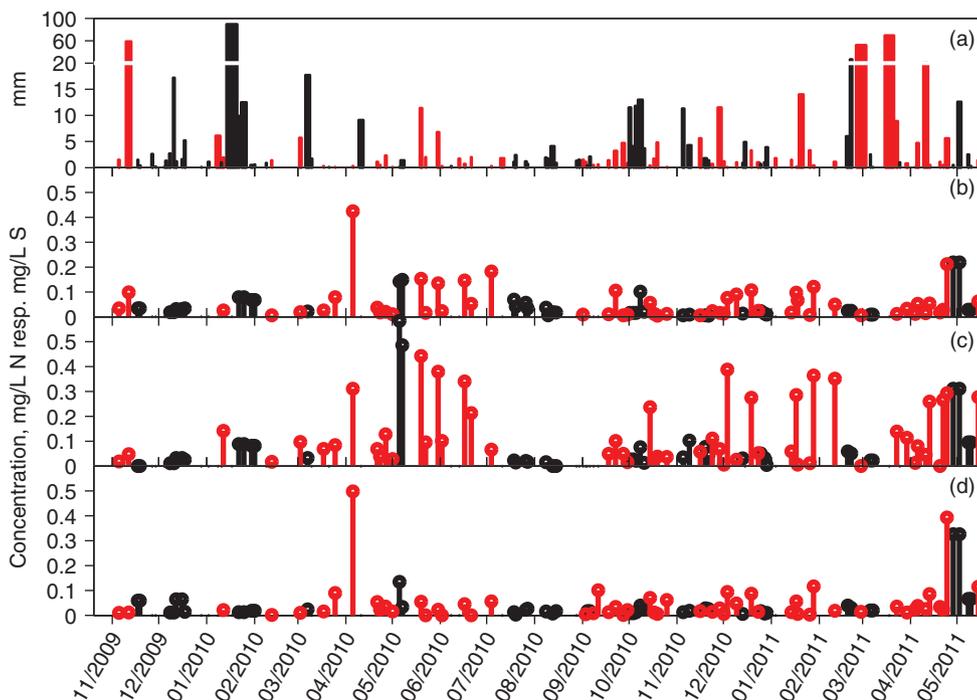
Fig. 5 (a) Precipitation amount. Black bars indicate precipitation events with non-isolated concentration observations. Red bars indicate precipitation events with isolated concentration samples. Event average concentrations of (b) NO_3^-, (c) nss-SO_4^{2-} and (d) NH_4^+ during the sampling campaign. Red markers indicate isolated and complete events.

autumn, winter and early spring and lasted over several days.

The event average concentrations of NO_3^- and NH_4^+ show values mainly under 0.1 mg L^{-1} N (Fig. 5). Some high concentrations in the range of 0.1–0.2 mg L^{-1} N occurred during April–June 2010, October–November 2010 and April 2012. Two events with extremely high concentrations occurred during April 2010 and April 2011 with values in the range of 0.2–0.5 mg L^{-1} N. Concentrations of NH_4^+ were lower than the NO_3^- concentrations in general, and the nss-SO_4^{2-} concentrations are mostly to be found below 0.2 mg L^{-1} S (Fig. 5). The events with higher nss-SO_4^{2-} concentrations seem to be the same as the ones with high NO_3^- and NH_4^+ concentrations, and mostly occurred during spring. In general, the nss-SO_4^{2-} concentrations show higher absolute values but considering that the ratio of molecular weight of sulphur to nitrogen is 3:1, the molar concentrations seem to be similar.

The majority of NO_3^- and NH_4^+ deposition events were below 0.1 mg m^{-2} N, as apparent from the cumulative distribution function (Fig. 3), although strong events in the range of 0.1– 1 mg m^{-2} N were observed throughout the whole sampling campaign (Fig. 6). Five NO_3^- deposition events with even higher values were observed in November 2009, May 2010, October 2010, the end of

April and the beginning of May 2011. The highest event in November 2009 reached values close to 6 mg m^{-2} N. Even though the strongest deposition events of NH_4^+ seem to be the same as for NO_3^-, the values were in general lower; except for the two strong events at the end of April 2011 and beginning of May 2011. The majority of nss-SO_4^{2-} deposition events were below 0.4 mg m^{-2} S (Fig. 5). As for NH_4^+ and NO_3^-, strong events in the range between 0.4 and 1 mg m^{-2} S were observed throughout the sampling campaign. The strongest events coincided with those of NH_4^+ and NO_3^- and show values between 2 and 5 mg m^{-2}.

Using the same definitions of the solid (16 September– 2 June) and liquid (3 June–15 September) precipitation season as in Kühnel et al. (2011), the total depositions during the 2009 solid season were 12 mg m^{-2} N for NO_3^-, 16 mg m^{-2} S for nss-SO_4^{2-} and 3 mg m^{-2} N through NH_4^+. Total depositions during the solid season of 2010 were 10 mg m^{-2} N for NO_3^-, 18 mg m^{-2} S for nss-SO_4^{2-} and 12 mg m^{-2} N for NH_4^+. During the liquid precipitation season of 2010, the deposition was 0.7 mg m^{-2} for NO_3^-, 0.8 mg m^{-2} S for nss-SO_4^{2-} and 0.3 mg m^{-2} N for NH_4^+.

A scatter plot of event average concentration versus precipitation amount is shown in Fig. 7. The plot shows a large variety of observed concentration–precipitation
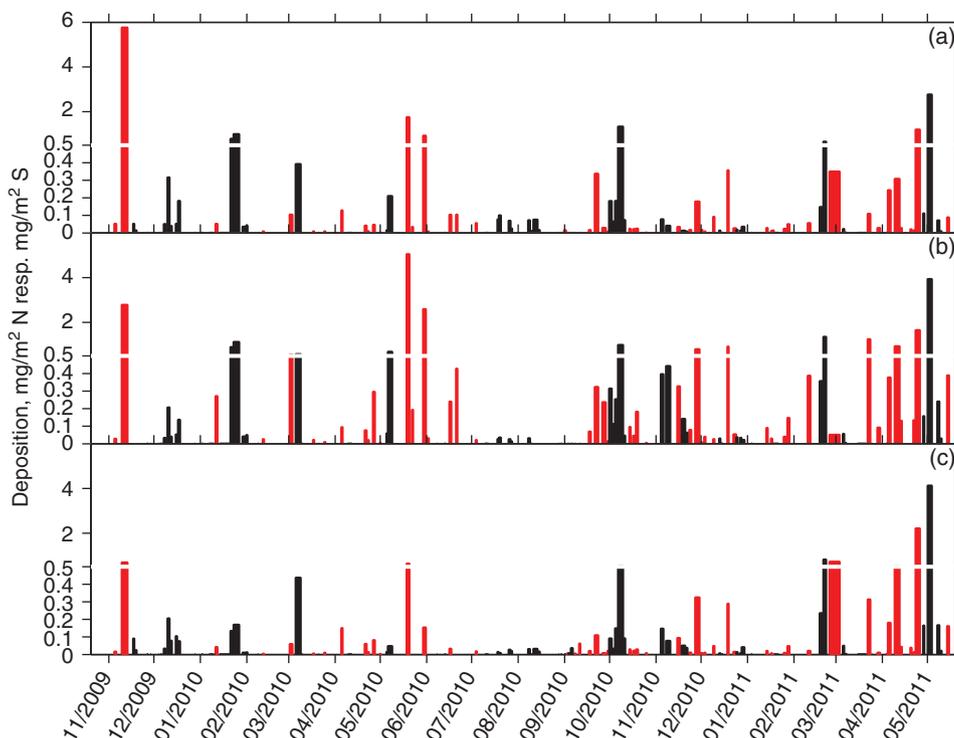
Fig. 6 Deposition events of (a) NO_3^-, (b) nss-SO_4^{2-} and (c) NH_4^+ during the sampling campaign. Red bars indicate isolated and complete events.
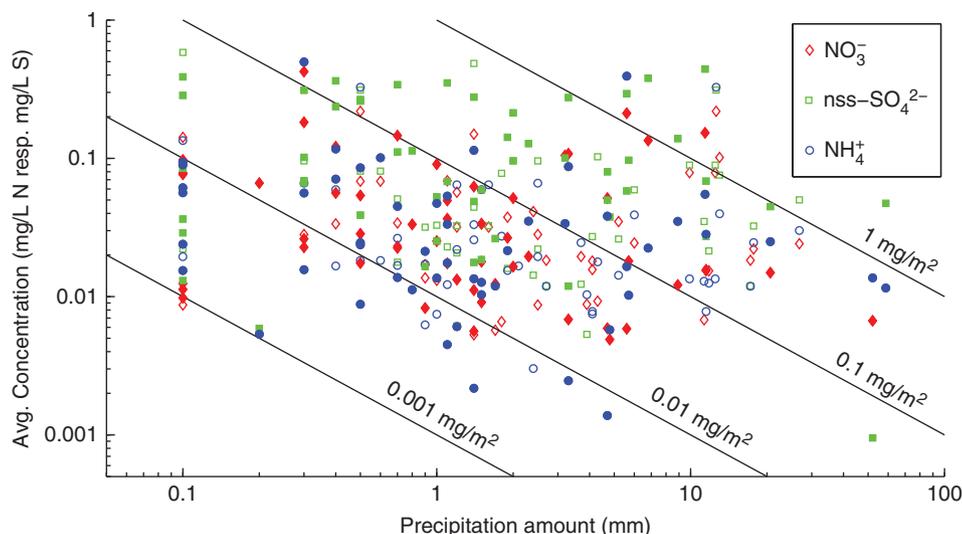
Fig. 7 Scatter plot of precipitation amount versus event average concentrations. Filled markers indicate data from isolated and complete events. Diagonal lines show event deposition of NO_3^-, NH_4^+ and nss-SO_4^{2-} in mg m^{-2} N resp. mg m^{-2} S.

combinations for all three chemical components. No significant linear relationship between event average concentration and precipitation amount could be found and R^2 values are close to zero for the analysis of both all events and the analysis of only isolated and complete events.

The mean event average concentration of the events in Group A was 0.05 mg L^{-1} N for NO_3^-, 0.11 mg m^{-2} S for nss-SO_4^{2-} and 0.04 mg m^{-2} N for NH_4^+. The mean event averages of Group B were 0.05 mg m^{-2} N for NO_3^-, 0.10 mg m^{-2} S for nss-SO_4^{2-} and 0.05 mg m^{-2} N for NH_4^+. The total deposition of the different scenarios and the control run, as well as the increase of the total deposition compared to the control run as a percentage, are given in Table 2. Scenario I gave the biggest increase with 20%, as expected. Scenario II gave an increase of only 3–4%, while Scenario II gave an increase of 16–17%.

Discussion

Precipitation sampling, especially in the harsh and windy environment of Zeppelin Station is a difficult task. A comparison of true and measured precipitation showed that the true precipitation might be 50% higher than the observed value (Hansen-Bauer et al. 1996). The

differences are normally greater for solid deposition than for liquid precipitation. Therefore, the deposition magnitudes presented in this paper might be underestimated. Another problem while sampling solid precipitation is drifting snow. Under strong wind conditions, snow from the ground might be transported into the sampler, where it mixes with freshly fallen snow affecting the chemical signature of the precipitation as well as precipitation amount. It is important to keep these effects in mind when interpreting the results presented here.

The calculation of deposition values was further complicated by the different sampling intervals of the concentration and precipitation measurements. While the precipitation samplers at Zeppelin Station have the advantage of being remote from local contamination at Ny-Ålesund, the distance between Zeppelin Station and the precipitation measurement site in Ny-Ålesund introduces uncertainties into the deposition calculations.

In addition to differing precipitation amounts caused by dissimilar catch efficiencies of the samplers as well as by influences of drift snow, the observed precipitation amount might differ through precipitation generated below Zeppelin Station, riming effects at either site, and evaporation or condensation below Zeppelin Station. Precipitation generation in the lowest 500 m is unlikely.

Table 2 Total deposition of scenarios and increase compared to control in percent.

	Control	Scenario I	Scenario II	Scenario III
NO_3^- mg/m^2 N	36	43 (+20%)	37 (+3%)	42 (+17%)
nss-SO_4^{2-} mg/m^2 S	69	83 (+20%)	72 (+4%)	80 (+16%)
NH_4^+ mg/m^2 N	32	37 (+20%)	33 (+3%)	37 (+17%)
Precipitation (mm)	667	801 (+20%)	691 (+4%)	777 (+16%)

Precipitating clouds are expected to be vertically thicker with precipitation forming in the upper parts of a cloud. Loss through evaporation in the lowest 500 m is expected to happen only during weak precipitation events whilst an increase in precipitation particles in this altitude range would need a surplus of moisture and enough time for the condensation process itself to make a significant difference. A possible addition of precipitation by riming of fog inside the samplers might occur at both sites. However, this would be limited to a few events per season. The gain from such events is not expected to be comparable to medium or strong deposition events.

The techniques employed in this study assume that the chemical signature of the precipitation at Zeppelin Station is similar to that in Ny-Ålesund. Deviations from this assumption might arise if the precipitation at the two observation locations is coming from different air masses or if additional atmospheric nitrogen is washed out below Zeppelin Station. Although the spatial separation of the sampling locations is small enough to assume that they receive precipitation from the same air masses, additional wash-out of atmospheric nitrogen pollution below Zeppelin Station cannot be ruled out. Simultaneous sampling campaigns at Zeppelin Station and Ny-Ålesund would be needed to quantify the effect of additional wash-out.

Comparing the average concentrations from Zeppelin Station in 2010 with the average concentrations in Europe during 2009, one can see that the concentrations from Zeppelin Station are one order of magnitude smaller in the case of NO_3^- and NH_4^+. The average values in Europe for NO_3^- and NH_4^+ were in the range of 0.2–0.7 mg L^{-1} N (Hjellbrekke & Fjæraa 2011). The highest concentrations were observed in central Europe while coastal regions showed comparatively low concentrations. The nss-SO_4^{2-} concentrations on the European mainland ranged from 0.1 to 1.0 mg L^{-1} (Hjellbrekke & Fjæraa 2011) with lower values in the coastal areas. The observed average from Zeppelin Station is comparable to low values found in Ireland, Scotland and Norway (Hjellbrekke & Fjæraa 2011).

The cumulative distribution functions presented in this study corroborate the findings of Kühnel et al. (2011) in their analysis of weekly precipitation observations that about half of the mass of NO_3^-, NH_4^+ and nss-SO_4^{2-} by wet deposition is deposited by the strongest 5 to 10% of deposition events. These events can be identified from the overview plots (Figs. 5 and 6) and the scatter plot (Fig. 7) as longer lasting, strong precipitation events with elevated concentrations. There are several events with either high concentrations but low precipitation or vice versa. However, it is the combination of both high

concentrations and high precipitation amount that is responsible for strong deposition events controlling the budget. The strongest events—with deposition greater 1 mg m^{-2} N or 1 mg m^{-2} S—occur during November 2009, May 2010 and April/May 2011. These are the months when precipitation events are stronger in general, the ground is covered by snow and soil productivity is limited. The deposited nitrogen is stored in the snowpack and might be re-emitted to a limited extent into the atmosphere (Beine et al. 2003). The remaining nitrogen will be flushed from the snowpack during snowmelt in spring and become available to soil ecosystems when productivity picks up. Although deposition took place throughout the whole sampling campaign, no strong events were observed in the time period when the tundra soils were snow-free and productive.

Deposition during the sampling campaign was less than the average deposition presented by Kühnel et al. (2011). This was especially marked for nss-SO_4^{2-} and NH_4^+, which had distinctly lower deposition during both the solid and liquid seasons. NO_3^- showed distinctly lower values compared to the average during the liquid season 2010. However, the observed deposition during the solid season was still in the range of observed deposition presented by Kühnel et al. (2011), which is not the case for the liquid season. Part of this difference was caused by the incomplete reconstruction of deposition events and the fact that the solid seasons were not completely covered by the sampling campaign. The rest of the difference might be caused by the difference in sampling location. While Kühnel et al. (2011) calculated averages from observations in Ny-Ålesund, close to sea level, the observations of the campaign reported here were collected at Zeppelin Mountain. This might especially influence the NH_4^+ and SO_4^{2-} budgets. For example, NH_4^+ deposition might be augmented in Ny-Ålesund due to emissions from guano produced by local bird colonies, or by NH_4^+ emission from the nearby ocean. Sea-salt sulphur causes an uncertainty of the nss-SO_4^{2-} estimates since the correction ratios are not always ideal. Hence, the difference in elevation and proximity to the ocean, and therefore different loadings of sea-salt sulphur, could introduce differences between the two sets of observations.

Precipitation over the Arctic is predicted to increase by 20% during the 21st century (Cassano et al. 2007). Synoptic patterns are expected to change such that occurrences of situations with strong Icelandic lows increase (Cassano et al. 2007). The increase in winter precipitation is expected to be highest over the North Atlantic storm tracks and regions of extreme precipitation are expected to extend further north (Saha et al. 2006).

Based on the observations presented here and an as yet unpublished trajectory study by Kühnel (unpubl. ms.), this increase is expected to augment nitrogen and sulphur deposition on Svalbard. However, the magnitude of this increase is hard to quantify. No significant association between precipitation amount and NO_3^--, nss-SO_4^{2-}- and NH_4^+ concentrations could be found. The differences between the mean event average concentrations of groups A and B were very small. Increasing the precipitation by 20% resulted in 20% more deposition, as expected (Scenario I). Increasing only low precipitation events by 20% (Scenario II) resulted in a slight deposition increase of 3–4%, while increasing the strong precipitation events by 20% resulted in an increase in deposition of 16–17%. As is apparent from Table 1, this pattern is caused by the gain in precipitation amount itself: the concentrations of the events play a minor role. The amount of deposition in each group depends, of course, on the chosen divide between groups A and B. Lowering the threshold tends to lower the deposition rise in Scenario II and augments the deposition rise in Scenario III. The opposite is true for raising the threshold. The basic finding that the deposition increase is caused mainly by the increase in precipitation, however, remains. Nevertheless, it is important to keep in mind that changes in the quantity of Arctic precipitation might lead to changes in the distribution of concentrations of sulphur and nitrogen. Assuming the pollution burden to stay the same, concentrations would decrease with increasing precipitation. In addition, if precipitation increases for air parcels en route to the Arctic, the scavenging on the way will also be greater, which removes parts of the nitrogen burden before it reaches the Arctic. A similar effect was observed in a model study of future nitrogen deposition in north-western Europe (Hole & Engardt 2008). Those scavenging effects are, however, not included in the scenarios presented in this study. Changes in transport patterns and the chemical signature of precipitation need to be included in any well-grounded estimate of future changes in nitrogen and sulphur deposition, an analysis which is beyond the scope of this paper.

Summary and conclusion

Precipitation sampling for chemical analysis was conducted from November 2009 until May 2011 at Zeppelin Station, Svalbard, with a close to daily sampling rate. During the campaign, 125 precipitation events were registered. The collected samples were analysed for NO_3^-, NH_4^+ and nss-SO_4^{2-} by ion chromatography. Deposition of the same chemical species was calculated by utilizing precipitation observations from the Norwegian Meteorological Institute in Ny-Ålesund.

The bulk of NO_3^- and NH_4^+ deposition events were in the range of 0.01–0.1 mg m^{-2} N while the bulk of nss-SO_4^{2-} deposition events were in the range of 0.02–0.3 mg m^{-3} S. The observations made during the campaign supported the findings of Kühnel et al. (2011) that half of the deposited nitrogen and sulphur mass is caused by the strongest 10% of deposition events. These have been identified as longer lasting events with raised concentrations of nitrogen and sulphur and higher quantities of precipitation. The calculated budgets in this study showed lower values compared to the ones by Kühnel et al. (2011), which may be partly explained by gaps during the sampling campaign and the difference in altitude of the sampling location.

The observations of this study did not allow for a thorough projection of future nitrogen and sulphur deposition on Svalbard, given the expected 20% increase in precipitation over the Arctic (Cassano et al. 2007). The scenarios studied in this paper indicated that deposition is closely connected to precipitation amount, and increasing precipitation can be expected to lead to increasing deposition, assuming constant emissions of reactive nitrogen and sulphur on the European continent. For further projections, future changes in the nitrogen and sulphur concentration in precipitation and the transport of pollution into the Arctic need to be undertaken. Changes in the occurrence of blocking situations over the European continent require special attention as they are responsible for surges of polluted air masses to the Arctic, leading to strong deposition (Iversen & Joranger 1985).

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