

## Research Article

# 20-Year Climatology of $\text{NO}_3^-$ and $\text{NH}_4^+$ Wet Deposition at Ny-Ålesund, Svalbard

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A 20-year dataset of weekly precipitation observations in Ny-Ålesund, Svalbard, was analysed to assess atmospheric wet deposition of nitrogen. Mean annual total nitrogen deposition was  $74 \text{ mg N}/(\text{m}^2 \text{ yr})$  but exhibited large interannual variability and was dominated by highly episodic “strong” events, probably caused by rapid transport from European sources. The majority (90%) of precipitation samples were defined as “weak” ( $<2 \text{ mg N}/\text{m}^2$ ) and contributed an annual baseline of  $\sim 17 \text{ mg N}/(\text{m}^2 \text{ yr})$ , whereas 10% of precipitation samples were defined as “strong” ( $>2 \text{ mg N}/\text{m}^2$ ) and additionally contributed up to  $225 \text{ mg N}/(\text{m}^2 \text{ yr})$ . Nitrate deposition largely occurred in samples within the solid-precipitation season (16 September–2 June), and ammonium deposition occurred equally in both solid and liquid seasons. Trends of reactive nitrogen emissions from Europe are uncertain, and increasing cyclonic activity over the North Atlantic caused by a changing climate might lead to more strong deposition events in Svalbard.

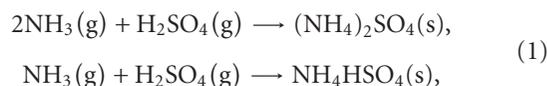
## 1. Introduction

Human activities release reactive nitrogen such as  $\text{NH}_3$  and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) to the atmosphere through energy production, fertilizer production, and cultivation of crops [1–4]. The resulting nitrogen-enriched air masses can be transported into remote, nutrient-limited regions such as the Arctic [5], primarily in the form of PAN (peroxyacetyl nitrate), but also as nitrate and ammonium aerosol. Furthermore, deposition of reactive nitrogen through precipitation is considered to be the main pathway for transfer of atmospheric nitrogen to the high Arctic surface [6]. The deposition of reactive nitrogen in the Arctic therefore results from the complex interplay of emissions, atmospheric transport, chemistry, precipitation, and snowpack processes as described below.

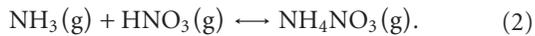
Ice core analyses from Svalbard [7] and Greenland [8] showed an increase in nitrate concentrations in the 1950's, followed by a drop in the 1980's in the Svalbard ice cores. A trend analysis of recent precipitation observations in Europe could not find any significant trends for nitrate in

Ny-Ålesund [9, 10]. In Europe and North America, the nitrogen emissions are expected to further decrease due to current and future legislations though there are regional differences which may affect the Arctic in particular. The expected intensification of shipping activity might lead to an increase of nitrogen emissions in the Arctic [4]. Reduction protocols and improvements in technology counteract the increase of nitrogen emissions, and some progress has been made in reducing emissions in the last decade [11, 12]. For general background information on the role of nitrogen in the environment, the reader is referred to the recently published “European Nitrogen Assessment” [13] as well as Monks et al. [14].

The atmospheric fate of nitrate and ammonia is linked to sulphur through atmospheric chemistry. Ammonia will neutralize sulphuric acid to ammonium sulphate particles by the reactions



where *g* and *s* indicate the gaseous and particulate phase. Remaining ammonia might neutralize nitric acid to form ammonium nitrate particles



The concentrations of sulphuric acid will thereby determine to a certain extent how much ammonia is left for the neutralization of nitric acid. Details on those processes can be found in Seinfeld and Pandis [15]. Sulphur emissions have been largely reduced over the past 20 years caused by actions undertaken in western and northern European countries to reduce air pollution through sulphate and changes in the economical situation in eastern European countries [16]. The reduction might have led to a shift towards the formation of more ammonium nitrate particles. Nitric acid is a volatile gas that undergoes dry deposition readily while ammonium nitrate particles dry deposit only slowly. The shift towards more ammonium nitrate has therefore an effect on the lifetime of  $x\text{NO}_3$  in the air [17]. It has been estimated that the reduction in Sulphur emissions has led to an increase of  $x\text{NO}_3$  in air of 15–30% [17]. These changes in the atmospheric chemistry may cause nonlinearity in trends, compared to the emission trends, due to shift in equilibrium and changes in oxidation capacity of the atmosphere [14, 17, 18]. How this influences the deposition of nitrate in the Arctic is, however, unclear.

The planetary layer of the Arctic troposphere is characterized by subzero temperatures throughout most of the year. During winter, the lack of solar radiation leads to stable stratified surface layer. Therefore, turbulent exchanges between atmospheric layers are reduced, and chemical reactions, especially photochemical processes, between different species (e.g.,  $\text{SO}_2$  to sulphate,  $\text{NO}_x$  to nitrate) are slowed down. This leads to longer species lifetimes in the Arctic troposphere [19, 20] during winter. Nitrogen-enriched air masses from middle latitudes can be transported over longer distances due to inhibited dilution and scavenging once they reached the Arctic.

The transport of air parcels is assumed to follow surfaces of constant potential temperature in the absence of diabatic heating. Above the Arctic, surfaces of constant potential temperature form a dome with minimum temperatures in the Arctic boundary layer. Regions with strong horizontal gradients of potential temperature near the surface are referred to as the polar front that builds a transport barrier [21]. Direct transport is less restricted by the polar dome in the cold months, when the polar front is situated south of important source regions, and cyclonic activity in the middle latitudes is enhanced [19, 22]. In addition, air masses are able to penetrate the polar front after diabatic cooling through the snow-covered surface in the northern parts of Eurasia. In the summer months, the polar front is situated further north and builds a more effective barrier in the lower atmosphere, isolating the Arctic from the midlatitudes [23]. Diabatic heating over midlatitude landmasses mixes air vertically. Air that is transported towards the Arctic without diabatic heating is forced to ascent along the isentropic surfaces. Such air masses might enter the Arctic Dome at higher

altitudes by subsidence. It is, however, assumed that these air masses would be scavenged during ascent and are thereby cleaned from nitrogen constituents before entering the Arctic dome [23]. The differences in the transport patterns between summer and winter can be seen in how long time that air has spent in the Arctic. The mean time that air has spent north of  $70^\circ\text{N}$  is about 6 days in January and about 10 days in July in the Svalbard region [23].

Model studies predict that the occurrence of synoptic patterns dominated by strong Icelandic low-pressure systems will increase while the frequency of strong Arctic high-pressure patterns decreases during the winter months (December–February) [24]. The same study predicts an increase in the frequency of synoptic patterns with low pressure over the Arctic Ocean and around Greenland during the summer months (June–August). This results in a prediction for increased frequency of intense cyclones in the Atlantic storm tracks, hence increased probability of strong air-mass transport into the Arctic from midlatitudes. In addition, increase of net precipitation over the Arctic cap of 20% during the next century is predicted [25].

Precipitation is in general low in the Arctic due to the stable stratification of air masses, low temperatures, and hence low water vapour content [19, 20]. Annual precipitation in the period from 1960 to 1990 in the Svalbard region ranged between 190 and 525 mm [26]. Precipitation on Svalbard can occur as snow and rain throughout the year due to large temperature variations. However, accurate precipitation observations are difficult [27] in the Arctic due to high wind speeds and drift snow that can lead to biases. Thus, true precipitation has been estimated to be approximately 50% higher than the uncorrected observations for Ny-Ålesund, Svalbard [28]. Monthly precipitation in Svalbard shows the highest precipitation in March and during August to October, whereas the months with the lowest precipitation are April to June [26]. This seasonality corresponds to the fact that most of the precipitation in Svalbard is connected to cyclonic activity, which is low in spring and high in autumn and winter [22]. Førland et al. [26] did find that annual precipitation has increased by 25% to 30% during the past 85 years, mostly due to increased spring and summer precipitation. It is possible that the observed trend in precipitation amount is a result of an ongoing shift in cyclonic activity.

During winter, precipitation occurs largely as snow and accumulates in the snowpack. Pollution scavenged by snow, such as  $\text{NO}_3^-$  (an oxidation product of  $\text{NO}_x$ ), and ammonium ( $\text{NH}_4^+$ ) is also accumulated within the snowpack. Photolytic reactions in the surface snow may alter the snowpack composition, releasing  $\text{NO}_x$  back to the atmosphere [29] although observations to date have found such  $\text{NO}_x$  reemission to be limited in the Ny-Ålesund area [30]. The remaining accumulated nitrogen is released in spring during snowmelt, providing a periodic input of reactive nitrogen in the melt water, which can act as a fertilizer to local ecosystems. The winter snowpack, thereby, acts as a temporal buffer to this process. However, nitrogen that is scavenged by rain during summer will be available to those ecosystems instantaneously. The Arctic is a nutrient

limited region, especially for nitrogen and phosphorus [31] and therefore susceptible to changes in nitrogen deposition [32, 33]. The amount and timing of deposition events play a key role. Strong nitrogen deposition events in spring or early summer could alter the growth season substantially, while the impact of strong nitrogen deposition in autumn might be negligible. Detailed studies on a strong episodic nitrogen deposition event in summer 1999 showed the importance of such events on glacial ecosystems during the melt-season [34, 35].

In order to assess the present and future importance of deposited nitrogen as a nutrient to Arctic ecosystems, or as a potential source of  $\text{NO}_x$  to the atmosphere, it is necessary to quantify the deposition of reactive nitrogen through precipitation and the driving mechanisms behind it. This is particularly important given the ongoing anthropogenic emissions of reactive nitrogen to the atmosphere that can be transported and deposited in the nutrient-limited Arctic, as revealed by Svalbard ice-core records over the 20th century. Here, we present a detailed analysis of weekly precipitation samples over more than two decades (1982–2007), a climatology of nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) wet deposition in Ny-Ålesund, Svalbard.

## 2. Methods

**2.1. Data Origin and Quality.** Sampling of the chemical composition of precipitation has been performed by the Norwegian Institute for Air Research (NILU), facilitated logistically by the Norwegian Polar Institute (NPI), since 1980 in Ny-Ålesund on behalf of the Norwegian Climate and Pollution Agency [10, 17], and is publicly available [36]. Precipitation was collected on a weekly basis using a bulk collector from NILU products, a bucket funnel system in summer and a snow sampler, so called particulate fallout collector, in winter. The collectors are made of high density polyethylene with a opening diameter of 200 mm and a height of 400 mm [37]. The collector has a bird ring to prevent bird droppings; however, the birds are sometimes able to contaminate the sample. These samples are deleted from the official dataset. Furthermore, the precipitation is frequently influenced by substantial sea salt episodes due to the proximity to open ocean. This is especially a problem for the sulphate measurements which need to be corrected for sea salt in order to quantify the contribution of anthropogenic sulphur. This leads to some uncertainty in the non-sea-salt sulphate estimates, since the sea-salt correction ratios are not always ideal. A bulk collector will to some extent also collect dry deposition as deposition of gaseous and particulate may occur. The magnitude of this is difficult to quantify, and it may vary by season. It is worth noticing that the collector, and funnel is washed every week, also between periods with no rain, preventing to a large extent collection of dry deposition in dry periods. The precipitation amount is measured by measuring the volume of liquid water precipitate or its equivalent of melted snow. An aliquot of the sample is sent to the laboratory at NILU for analysis using ion chromatograph.

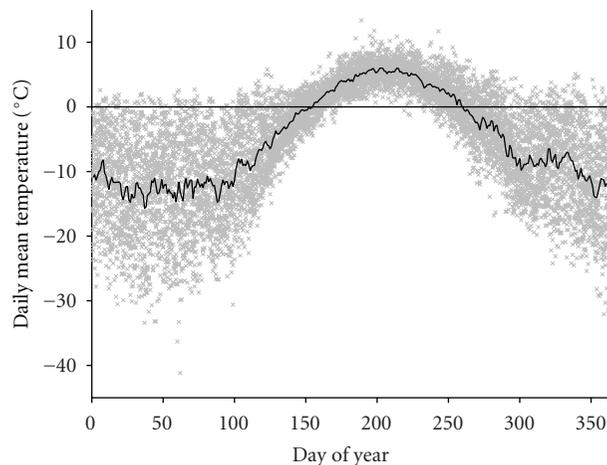


FIGURE 1: Daily mean temperature at Ny-Ålesund. Solid line indicates the average for each day over the period 13.9.1982 till 17.9.2007.

The data used in this study covers the time from 13 September 1982 for nitrate ( $\text{NO}_3^-$ ) and non-sea-salt sulphate ( $\text{nss-SO}_4^{2-}$ ) and from 12 September 1987 for ammonium ( $\text{NH}_4^+$ ) to 17 September 2007. About 15% of the samples, both for nitrate and ammonium, are missing or considered invalid due to suspected contamination or because there was too little sample to be analysed.

The precipitation amount from the bulk collector has been used to calculate the deposition in this work. However, there are sometimes relatively large differences between the precipitation amount measured by the bulk collector and the official amount measured by a rain gauge. The precipitation amount of the official rain gauge has been used in these cases. Though it implies that on occasion, there is relatively large uncertainty in the deposition measurements. This is due to the measuring conditions at Ny-Ålesund that are sometimes very challenging.

The weekly deposited mass of nitrogen ( $\text{mg N/m}^2$ ) and non-sea-salt sulphur ( $\text{mg S/m}^2$ ) was calculated as the product of nitrogen respectively sulphur concentration ( $\text{mg N/L}$ ,  $\text{mg S/L}$ ) and precipitation amount (mm).

**2.2. Definition of Solid and Liquid Precipitation Season.** Figure 1 shows the daily mean temperatures at Ny-Ålesund for the period of interest, observed by the Norwegian Meteorological Office, and freely available [38]. The relative number of the different precipitation types: “Snow,” “Mixed,” and “Rain” for the same period of time can be seen in Figure 2. As expected, there is a close relationship between temperature and precipitation type. From DOY 150 on, a rapid shift in temperature and precipitation type from subzero to plus degrees, respectively, snow to rain can be observed. From about DOY 250, temperatures are predominately subzero. This is accompanied by an increase in the relative occurrence of snow precipitation in favour of liquid precipitation.

Since the type of precipitation is important for the efficiency by which nitrogen is deposited, deposition was divided into solid and liquid precipitation seasons. The solid

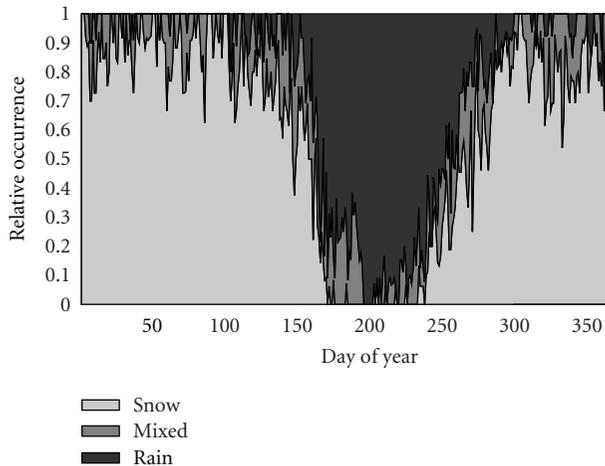


FIGURE 2: Relative occurrence of precipitation types in the period 13.9.1982 till 17.9.2007 at Ny-Ålesund.

season (16 September–2 June) was defined as the period of the year, in which the daily mean 2 m-temperature was on average below  $0^{\circ}\text{C}$ . The liquid season (3 June–15 September) was defined accordingly as the period with averaged daily mean temperatures above  $0^{\circ}\text{C}$ . For annual budgets, the precipitation year was defined to be the time covered by a solid season and the following liquid season (16 September–15 September).

**2.3. Data Classification.** The precipitation samples were divided into two categories: “weak deposition” and “strong deposition.” The following method was used to define these categories.

The accumulated mass of deposited nitrogen was calculated for each precipitation year. Hereby, only samples below a given magnitude were included in the calculation. The relative standard deviation (RSD: standard deviation of the sample divided by the sample mean) in these annual budgets was then calculated. The procedure was repeated, whereby the limiting magnitude was varied to cover the whole spectrum of observed nitrogen deposition magnitudes. So each limiting magnitude can be attributed to a specific value of relative interannual variation. The limiting magnitude of the minimum RSD was used to divide all samples into the categories “weak” and “strong.” Budgets consisting only of “weak” samples can be interpreted as a relative constant baseline deposition that can be augmented by “strong” samples. The relative standard deviation was used since variations of different magnitudes were compared.

The relative interannual variation was found to be the smallest for a limiting magnitude of  $1\text{--}3\text{ mg N/m}^2$ , both for ammonium and nitrate. The absolute minimum was at a size limit of  $2.3\text{ mg N/m}^2$  for nitrate and  $2.7\text{ mg N/m}^2$  for ammonium. Varying the threshold showed that the actual position of the threshold in the range between  $1$  and  $3\text{ mg N/m}^2$  had little effect on the results presented. Thus,  $2\text{ mg N/m}^2$  was chosen as the threshold between “weak-” and “strong” deposition.

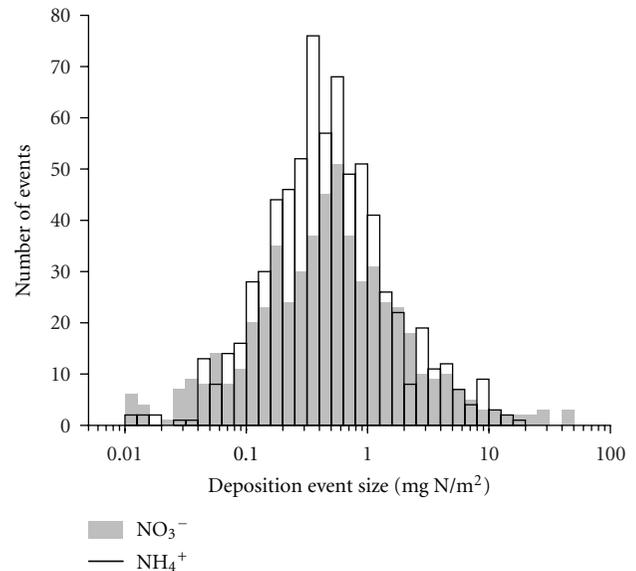


FIGURE 3: Histogram of nitrogen deposition samples. Grey bars show nitrate histogram; black lines show ammonium histogram.

The nitrogen deposition samples have been split into four categories to study if concentration or precipitation amount is the important factor leading to high nitrogen deposition. Those categories were “high concentration-high precipitation amount” (CP), “high concentration-low precipitation amount” (Cp), “low concentration-high precipitation amount” (cP) and “low concentration-low precipitation amount” (cp). Samples with concentrations above the 75th-percentile of all concentrations were categorized as high concentration samples, and the ones below this threshold were denoted as low. The same was true for the precipitation amounts. The categorisation has been done separately for a dataset consisting of only strong, respectively weak deposition samples. Ratios of the number of samples in each category to all samples have been calculated.

**2.4. Correlations of Nitrate, Ammonium, and Non-Sea-Salt Sulphate.** Pearson correlation coefficients were calculated between nitrate, ammonium, and non-sea-salt sulphate, where nss-sulphate was determined by correcting the measured total sulphate concentration with the concentrations of sea-salt constituents (Na, Cl, Mg) using the reference method defined by EMEP and WMO/GAW [39, 40]. Correlations were determined for both ion concentrations and deposited mass. Only samples where all three components were available have been used for the calculations. Correlations were calculated for three different compositions of data, the complete set of samples, a set that consisted of samples only within the solid-season and a set that consisted of samples only within the liquid season.

### 3. Results

**3.1. Event Distribution and Annual Budgets.** The number of nitrogen deposition samples shows a log-normal distribution (Figure 3) with a median distribution at approximately

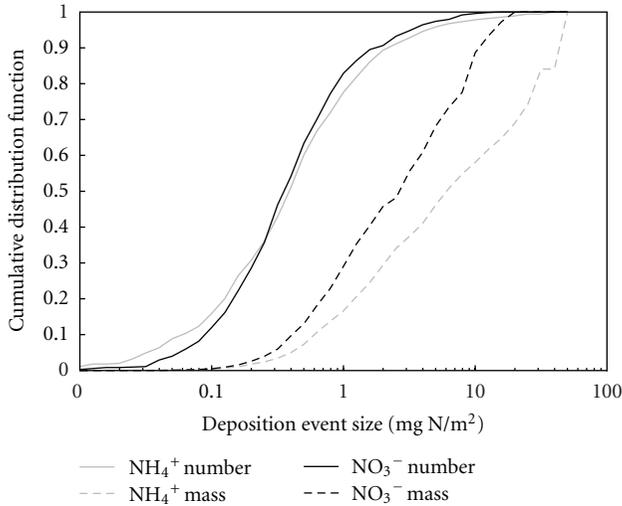


FIGURE 4: Cumulative distribution function of number and mass distributions for nitrate and ammonium.

TABLE 1: Mean annual number fraction of samples that deliver less or equal mass to the threshold level, and mass fraction of deposited nitrogen through these samples. The precipitation year as defined in the Section 2 was used for the calculations of the annual mean.

Sample threshold	Number fraction		Mass fraction	
	Nitrate	Ammonium	Nitrate	Ammonium
0.5 mg N/m <sup>2</sup>	0.54	0.50	0.17	0.11
1 mg N/m <sup>2</sup>	0.78	0.72	0.39	0.26
2 mg N/m <sup>2</sup>	0.90	0.86	0.58	0.45
3 mg N/m <sup>2</sup>	0.93	0.90	0.61	0.53

0.5 mg N/m<sup>2</sup> both for nitrate and ammonium. Cumulative distribution functions of the number and mass distributions for nitrate and ammonium are shown in Figure 4. The higher fraction of mass is deposited by “strong” samples (>2 mg N/m<sup>2</sup>), which are few, approximately 10%, while approximately 90% of all samples are “weak” (<2 mg N/m<sup>2</sup>). “Weak” samples contribute on average only to 50% of the annual nitrogen mass (Table 1).

The budgets for the solid- and liquid precipitation seasons show that most of the nitrate is deposited in the solid precipitation season (Figure 5), where also a large interannual variability can be found caused by strong deposition samples. The deposited mass of nitrogen through nitrate ranges from 6 to 60 mg N/m<sup>2</sup> in the solid precipitation season with an average of 22 mg N/(m<sup>2</sup> yr). In the liquid precipitation season, the mass of nitrogen deposited through nitrate shows values between 1 and 28 mg N/m<sup>2</sup> and an average of 7 mg N/(m<sup>2</sup> yr). The relative standard deviation gives an indication for the difference of variances between weak and strong samples. Nitrate shows a RSD of 0.23 for weak samples and 0.93 for strong samples.

The picture is somewhat different for ammonium (Figure 6). There is still a large interannual variability caused by strong-deposition samples. However, this is caused by both samples in the solid- and liquid precipitation season.

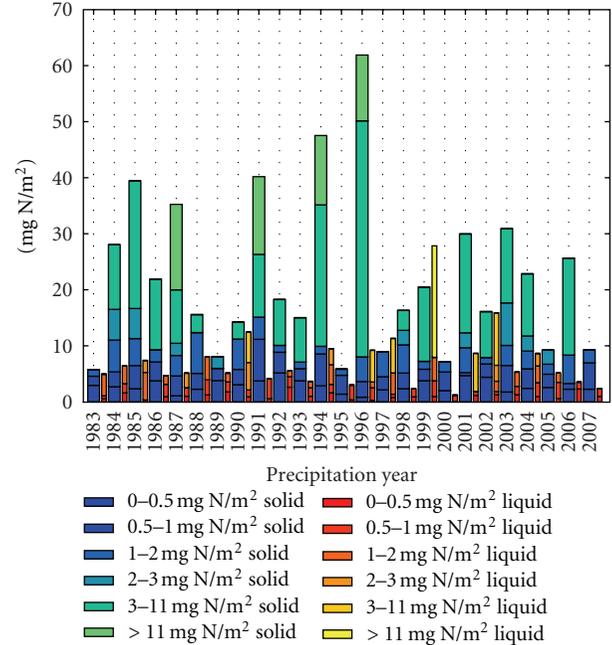


FIGURE 5: Annual budgets for nitrogen wet deposition through nitrate. Wide bars: solid precipitation season; narrow bars: liquid precipitation season.

The deposited mass of nitrogen through ammonium ranges from 5 to 66 mg N/m<sup>2</sup> in the solid precipitation season with an average of 22 mg N/(m<sup>2</sup> yr). The mass of nitrogen deposited through ammonium shows values between 4 and 98 mg N/m<sup>2</sup> with an average of 24 mg N/(m<sup>2</sup> yr) in the liquid precipitation season. The RSD is 0.28 for weak samples and 1.22 for strong samples.

The budgets for nss-sulphate (Figure 7) show similar behaviour as that of nitrate. The interannual variability is strong, and most of the deposition takes place in the solid season. Between 12 to 212 mg S/m<sup>2</sup> are deposited in each solid season with an average of 77 mg S/(m<sup>2</sup> yr). Deposition ranges from 5 to 58 mg S/m<sup>2</sup> in the liquid season with an average of 26 mg S/(m<sup>2</sup> yr). Less nss-sulphate is deposited in the solid seasons after 1996. The RSD for the weak and strong samples is 0.34 and 0.64, respectively.

The mass of total nitrogen contributed through nitrate plus ammonium varies between 24 and 236 mg N/m<sup>2</sup>. The annual average is 74 mg N/(m<sup>2</sup> yr). Between 11 and 128 mg N/m<sup>2</sup> are deposited in the solid season with an average of 44 mg N/(m<sup>2</sup> yr). In the liquid season, total nitrogen deposition varies between 7 and 108 mg N/m<sup>2</sup> and shows an average of 31 mg N/(m<sup>2</sup> yr). On average 17 mg N/(m<sup>2</sup> yr) of total nitrogen are delivered by small samples. The RSD is 0.33 for weak samples and 0.93 for strong samples.

The monthly distributions for the deposited mass of nitrogen through nitrate and ammonium (Figure 8) show a distinct seasonal cycle. The median varies around 0.5 mg N/m<sup>2</sup> both for nitrate and ammonium. The bulk of nitrate deposition is highest during spring (Apr–July) while there is a minimum in autumn (September–November). The same minimum can be seen in the case of ammonium. In

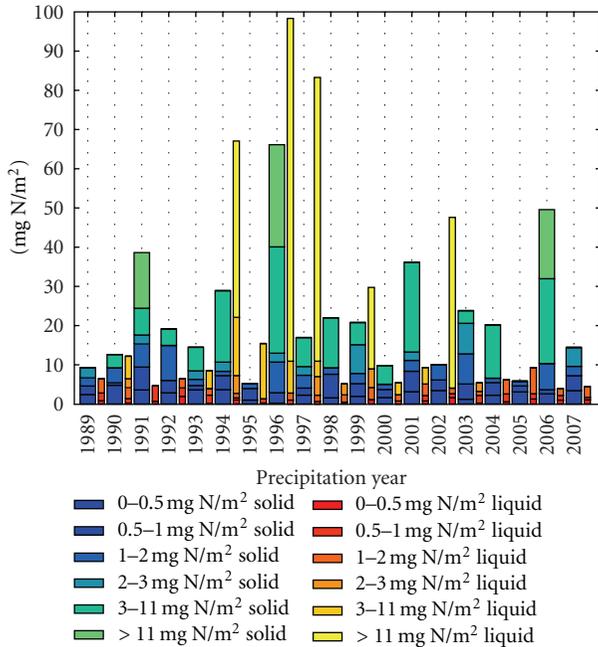


FIGURE 6: Annual budgets for nitrogen wet deposition through ammonium. Wide bars: solid precipitation season; narrow bars: liquid precipitation season.

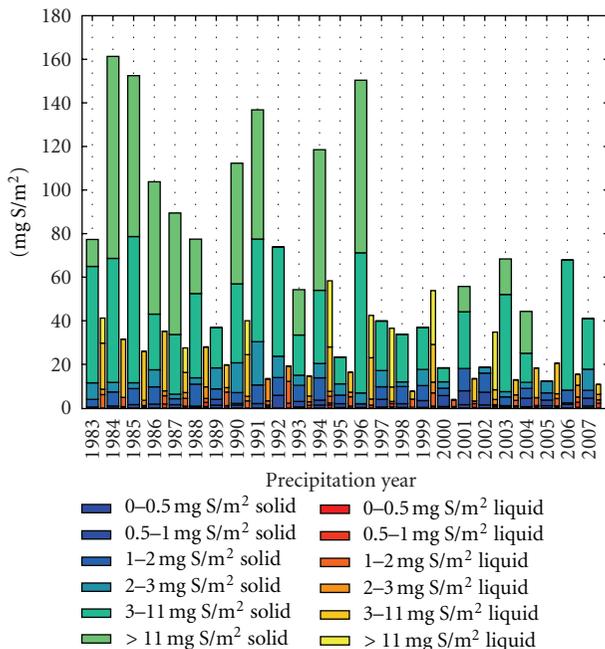


FIGURE 7: Annual budgets for wet deposition of sulphur through non-sea-salt sulphate. Wide bars: solid precipitation season; narrow bars: liquid precipitation season.

addition to the spring maximum in April to May, ammonium shows a second maximum during summer (July–September) with the highest values for the bulk of deposition samples (2nd–3rd Quartile) and increased variability. The highest number of strong samples of nitrate deposition occurs during the winter months November till March while

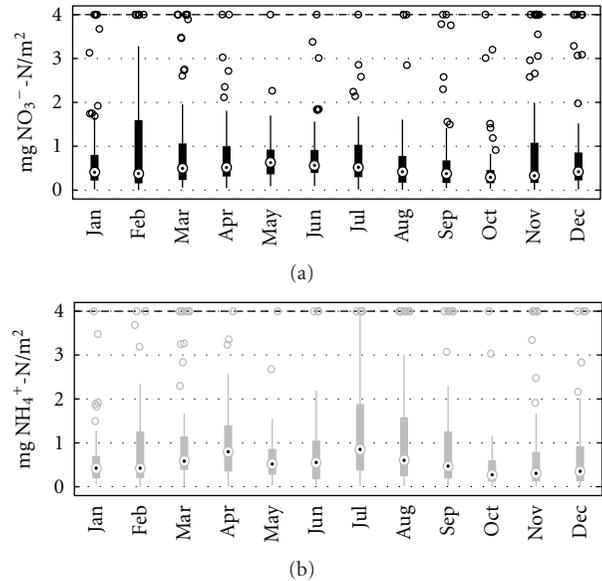


FIGURE 8: Monthly distribution of nitrogen wet deposition through nitrate (a) and ammonium (b). Black dots show the median; boxes show 25th–75th percentile; lines extend to most extreme data points that are not outliers; empty circles show outliers; outliers are defined as data points, that are  $1.5 \times (P_{75} - P_{25})$  above  $P_{75}$  or below  $P_{25}$ , where  $P_{25}$  and  $P_{75}$  are the 25th and 75th percentile. Outliers  $> 4 \text{ mg N/m}^2$  were set to  $4 \text{ mg N/m}^2$ .

there is a minimum from May till August. For ammonium, there is a second maximum in the strong samples number from July to September.

**3.2. Nitrate-Ammonium-nss-Sulphate Correlations.** For all three sets of correlations (Table 2): nitrate-ammonium, nitrate-nss-sulphate, and ammonium-nss-sulphate, the deposition load correlations show higher values than those for the precipitation concentrations.

The nitrate-ammonium deposited mass- and concentration correlation coefficients show an increase from the total precipitation year to the solid season. The deposited mass correlation coefficient increased from 0.46 to 0.69, and the concentration correlation coefficient increased from 0.30 to 0.66. The comparison of the total precipitation year to the liquid season shows almost equal correlation coefficients for the deposited mass but a drop for the concentration correlation coefficients from 0.30 to 0.12.

The deposited mass correlation coefficient of nitrate-nss-sulphate shows a small increase from the total precipitation year to the solid season, from 0.79 to 0.82, and a small drop from the total precipitation year to the liquid season, from 0.79 to 0.71. The opposite trend can be observed for the concentration correlation coefficients. It drops from 0.63 for the total precipitation year to 0.57 for the solid season and rises to 0.69 for the liquid season.

The deposited mass correlation coefficients of ammonium-nss-sulphate are 0.62 for the total precipitation year, but distinct higher for the solid season with 0.70 and the liquid season with 0.80. The correlations for the concentrations

TABLE 2: Pearson correlation coefficients of nitrate, ammonium, and nss-sulphate for the complete precipitation year, solid- and liquid season. The values in brackets show the 0.95 confidence interval.

		Total	Solid season	Liquid season
$\text{NO}_3^- - \text{NH}_4^+$	Mass	0.46 (0.39–0.52)	0.69 (0.63–0.74)	0.45 (0.31–0.57)
	Concentration	0.30 (0.22–0.38)	0.66 (0.60–0.72)	0.12 (–0.04–0.28)
$\text{NO}_3^- - \text{SO}_4^{2-}$	Mass	0.79 (0.72–0.82)	0.82 (0.78–0.85)	0.71 (0.63–0.79)
	Concentration	0.63 (0.58–0.68)	0.57 (0.50–0.64)	0.69 (0.60–0.78)
$\text{NH}_4^+ - \text{SO}_4^{2-}$	Mass	0.62 (0.56–0.67)	0.70 (0.65–0.75)	0.80 (0.73–0.85)
	Concentration	0.43 (0.35–0.49)	0.60 (0.53–0.67)	0.37 (0.22–0.51)

TABLE 3: Ratio of the number of samples in the categories low/high concentration (c/C) and low/high precipitation amount (p/P) to the number of all samples, calculated for both nitrate and ammonium. Values for weak and strong samples are shown separately. Values in brackets show the number of samples in each category.

Category	Nitrate		Ammonium	
	Weak samples	Strong samples	Weak samples	Strong samples
cp	0.56 (407)	0.00 (0)	0.56 (310)	0.01 (3)
Cp	0.17 (124)	0.02 (14)	0.15 (83)	0.04 (23)
cP	0.17 (124)	0.05 (35)	0.15 (86)	0.05 (28)
CP	0.00 (0)	0.04 (27)	0.00 (0)	0.04 (22)

show an increase in the solid season and a slight decrease in the liquid season. The correlation for the total season is 0.43, the one of the solid season 0.60 and the one of the liquid season 0.37.

**3.3. What Causes High Nitrogen Deposition, Precipitation Amount, or Concentration of Nitrate and Ammonium?** The ratios of the number of samples in the different categories to all samples described above are similar for nitrate and ammonium (Table 3). The majority of weak samples are associated with low concentrations and low precipitation amount (cp), which is about half the samples. The remaining weak samples are evenly distributed to the categories cP and Cp with a ratio of 0.17 for nitrate and 0.15 for ammonium. Approximately 10 percent of all samples are strong, that is,  $>2 \text{ mg N/m}^2$  (Figure 4). In the case of ammonium, those are almost evenly distributed between the categories Cp, cP, and CP with 0.04 to 0.05. Nitrate, however, shows a smaller ratio for category Cp with 0.02, while the ratios in the categories cP and CP are almost identical with 0.04 to 0.05.

The annual seasonality of the samples in the single categories shows distinctly different characteristics. For category cp, the samples are uniformly distributed throughout the year with values  $<1.5 \text{ mg N/m}^2$ . The events of category Cp in contrast show an increased number in the summer months, with most of the samples delivering less than  $2 \text{ mg N/m}^2$  and some in the range up till  $10 \text{ mg N/m}^2$ . The categories involving high precipitation, cP and CP, follow the precipitation seasonality closely in the case of nitrate with strong-deposition samples from September to April. Category cP seems to lack this characteristic for ammonium. The samples with the strongest ammonium deposition are to

be found in category CP in the months January to March and June to September.

## 4. Discussion

**4.1. Budget and Seasonality Difference in Mechanisms.** Weak samples are frequent but contribute on average only about half of the mass of the annual nitrogen loading, even though these events account for about 90% of the number of the samples. With small differences between years, on average about  $17 \text{ mg N/m}^2$  is delivered each year by weak samples. The remaining mass of deposited nitrogen is a result of a small number of strong samples that may contribute up to  $225 \text{ mg N/(m}^2 \text{ yr)}$ . Those samples are sporadic and lead to a strong interannual variability. There are years with no strong samples as well as years with several ones. This results in a total deposition that is highly dependent on if and how many strong samples occur. For comparison, the average nitrogen deposition for 95 sites on the European mainland was  $550 \text{ mg N/m}^2$  in the year 2009 with a standard deviation of  $370 \text{ mg N/m}^2$ . The large standard deviation shows that deposition is highly dependent on location [41].

Precipitation sampling, particularly snow sampling, is difficult in the Arctic due to high wind speeds. Therefore, the result might be biased to some extent. It was estimated that true precipitation is in general higher than measured observations and that the error is highest in the winter months. Estimated ratios between observed and true precipitation amounts are 0.59 for solid and 0.93 for liquid precipitation [28]. Snow occurs during winter, when wind speeds are typically higher than in the summer months when it rains, and catch efficiencies are therefore lower for snow. However, strong winds may blow surface snow into the sampler and falsely raise the measured precipitation amount or alter the chemical concentrations of the sampled snow. While the first effect would lead to an underestimation of precipitation in the solid season, the second one would overestimate precipitation amount and make further chemical analysis difficult. Another factor that influences the data quality is dry deposition. Since the sampler is an open bucket system, it will to some extent also sample dry deposition. This would lead to observations that are positively biased. The sampler is rinsed between each sampling period to keep this effect at a minimum. It is assumed that the impact on the collected data is small; however, a faster sampling rate or a wet only sampler would be needed to better avoid dry deposition. It is important to keep these factors in mind when interpreting the results.

Dispersion of air masses will tend to lower the concentrations of air pollutants. Soluble species, like nitrogen and sulphate compounds, are affected by scavenging processes that will remove all or a fraction of the chemical constituents. The probability of scavenging and the degree of dilution via dispersion increase with increasing transport time. The intensity and sporadic nature of strong samples suggest that those might be caused by fast and direct transport while weak samples are related to nitrogen-enriched air masses with longer travel times. A cluster study of Eneroth et al. [22] identified transport from the Eurasian continent and the North Atlantic as the main patterns for transport of mid-latitude air to Svalbard. The same study found that large positive anomalies of CO<sub>2</sub> during winter are associated with transport from Eurasian anthropogenic sources [22]. It is, therefore, likely that strong samples are caused by rapid transport from European sources.

For nitrate, the strong events occur mainly during the solid precipitation season (Figure 5), hence during the winter months. Ammonium deposition seems to be dominating in the liquid precipitation season including several years with strong samples which are not present for nitrate (Figure 6). The solid precipitation season is similar to that of nitrate, a fact which is also evident by the raised correlation coefficients of nitrate and ammonium both for the deposited mass and the concentration (Table 2). This codeposition of ammonium and nitrate might be expected if both species are cotransported following their industrial/agricultural emissions from similar source regions. However, no significant correlation can be found between ammonium and nitrate in the liquid precipitation season.

The correlation coefficients between nitrate, ammonium, and nss-sulphate of the deposited mass of nitrogen are in general higher than those for the concentrations. This is probably caused by the precipitation component in the calculation of the deposited mass. Since it is the same for all three chemical components, it has an equalizing effect on the correlations and in addition applies a weighting so that low precipitation values are less important.

Nitrate and nss-sulphate are well correlated both in the solid and liquid season and both for the deposited mass and the concentration without any significant change in the correlation coefficients. This suggests that it is the same mechanisms that drive the transport and deposition. Nitrate and ammonium show significant higher correlation coefficients for the solid season both for the deposited mass and concentration, and a distinctively lower correlation for the concentration in the liquid season. This pattern is also evident in the correlations of ammonium with nss-sulphate.

Transport and source regions might, therefore, be the same for nitrate, sulphate, and ammonium in the solid season. Low temperatures and the lack of sunlight as well as a stable stratification reduce interactions between chemical components during winter and thereby leave them as largely passive tracers. However, in the liquid season, the deposition of ammonium may have a different cause. This might suggest an additional summer source for ammonia, either local (e.g., ammonia gas emissions from bird guano with subsequent

ammonium deposition to the sampler) or long range (e.g., biomass burning or forest fires).

Concentrations of nitrogen and sulphate components in air are higher in winter than in summer [10, 42], which corresponds to the stronger deposition of nitrate and sulphate in the solid season compared to the liquid season. A direct comparison of air concentrations and wet deposition is difficult, as can be seen for example in Hodson et al. [35], since both are connected by complex scavenging and wash-out processes. However there are similarities in the long-term trends of nitrogen and sulphur compounds in air concentrations and deposition. A decreasing trend of sulphate deposition and air concentrations of sulphur compounds can be observed, whereas both deposition and air concentrations of nitrogen compounds did not show significant trends [9].

Dividing the samples in categories of high and low concentration/precipitation (cp, Cp, cP, and CP) gave no clear indication on whether precipitation amount, concentration, or both are the driving factor for nitrogen deposition. The samples are distributed rather evenly into the categories. The seasonality of the categories gave an indication that categories of low precipitation amount (cp and Cp) contribute a distinct smaller part to the nitrogen budget compared to the events including high precipitation.

It should be mentioned that this classification is highly dependent on the threshold criteria of dividing samples into high or low concentration/precipitation. The 75th percentile was used in this study. Variations of this threshold for nitrate are found to have significant effects on the results. As the threshold was moved from the 50th to the 100th percentile, the categories Cp and cP gradually lost all their samples to category cp. Their ratios showed, therefore, a linear decrease, while the ratio in cp exhibited a linearly increase. Samples from CP were either lost to Cp, cP, or cp by raising the threshold.

## 5. Conclusions

A dataset of weekly precipitation observations over the past 20 years in Ny-Ålesund, Svalbard, was analysed to assess atmospheric nitrogen wet deposition through ammonium and nitrate. The analysed data included precipitation observations from 1982 till 2007. A solid (16 September–2 June) and liquid (3 June–15 September) precipitation season was defined in accordance with the average form in which precipitation occurred during those periods. The deposition samples were divided into the categories “weak” (<2 mg N/m<sup>2</sup>) and “strong” (>2 mg N/m<sup>2</sup>).

Nitrate deposition occurred mainly during the solid season, whereas ammonium deposition occurred equally in both the solid and liquid season. Weak and strong samples showed a ratio of occurrence of 9/1. However, the contribution to the deposited mass of nitrogen through weak and strong samples had a ratio of 1/1. A strong interannual variability was observed due to the episodicity of the strong samples.

The mean annual sum of total nitrogen deposition (nitrate + ammonium) was 74 mg N/(m<sup>2</sup> yr). Weak samples contribute an annual baseline of nitrogen deposition of

approximately 17 mg N/(m<sup>2</sup> yr) that can be augmented by strong samples. Rapid and direct transport is likely the key factor for strong samples.

No significant trend has been observed for nitrate concentrations in precipitation in Ny-Ålesund over the last two decades [9]. However, future trends of nitrogen emissions are unclear, and cyclonic activity in the North Atlantic is predicted to increase [24]. With these predictions, an increase in strong deposition events in Svalbard can be expected. Even without increased emissions of nitrogen in Europe, an increased frequency of intense cyclones in the North Atlantic would increase the probability for more strong deposition events in Svalbard. As terrestrial and glacial ecosystems in the high Arctic are nitrogen and phosphorus limited, we highlight the importance of episodic nitrogen precipitation events to remote areas.

Event-based sampling campaigns are necessary to further assess the structure of nitrogen deposition in remote areas. Sampling rates of approximately one week are longer than the timescales of typical precipitation events. Precipitation events with different chemical signature might, therefore, occur during a single sampling period and in addition synoptic weather patterns hence air-mass transport might change substantially over one week. Event-based sampling would, therefore, provide the possibility to study the transport and sources of nitrogen deposition in much greater detail.

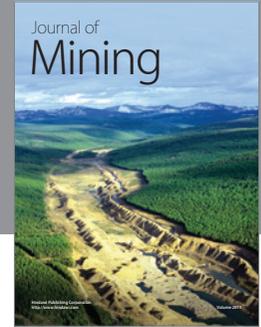
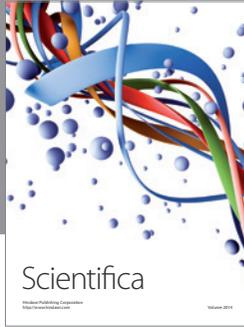
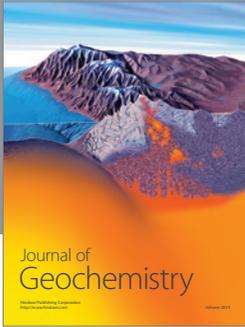
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