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The record of anthropogenic pollution in snow and ice in Svalbard, Norway

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Abstract

From the examination of the spatial distribution of pollutants and of the record from ice cores, it is demonstrated that Svalbard is strongly affected by anthropogenic pollution. This pollution has caused an increase of approximately 90% in the acidity of the snow deposited in the Archipelago since the beginning of the Industrial Revolution. High concentrations of H^+ , frequently greater than $10 \mu\text{eq l}^{-1}$ (i.e. with pHs lower than 5.0), associated with high concentrations of sulphates, indicate that Svalbard is experiencing the phenomenon of acid deposition. The first part of this work reviews the existing knowledge of atmospheric, snow, and ice pollution in Svalbard. This is followed by an examination of the acidity time series, supported by excess-sulphate measurements, performed on an ice core from central-eastern Spitsbergen that provide a historical record of acid deposition over a 54 year period. An ice core recovered from Austfonna, Nordaustlandet provided baseline values and also a record of acidity in precipitation before and during the entire industrial period, thereby allowing the evolution of acid deposition in the Archipelago to be traced. The records of these two Svalbard cores also reflect the overall regional trends. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Acid deposition; Arctic pollution; Ice cores; Trends in anthropogenic pollution

1. Introduction

For the last 25 years an extensive study of atmospheric chemistry, carried out with a view to explaining the Arctic haze, has shown that the Arctic environment is far from pristine. Of all the sites in the Arctic, Svalbard (74° – 80° N, 10° – 35° E; Fig. 1) is perhaps one of the areas most affected by anthropogenic pollution transported from industrialised areas. These high pollutant concentrations result from specific conditions of atmospheric circulation, reviewed by Barrie (1986).

Due to the seasonal expansion of Arctic high pressure into Eurasia, the mean position of the Arctic front is

pushed southward during the winter, so that the main cyclone track is deflected into the industrialised areas of central Europe, Scandinavia, and north western Russia. Areas of intense oil and coal combustion, non-ferrous metal production and other sources of man-made pollutants (Barrie, 1986) all lie in the path of these cyclones. Following their route eastward, the cyclones encounter the semi-permanent Siberian high pressure and are deflected first towards the Kara and Barents seas and then towards the Polar Basin (Fig. 2). Svalbard and the islands of Franz Josef Land are the first land masses in the pathway of these pollutant-laden air masses.

A different picture emerges during the summer. The cold dry Arctic air mass is restricted to the Polar Basin, and the Arctic front retreats to a more northerly position over Svalbard, or even farther north. The circulation pattern in the Arctic then becomes more circumpolar, and moisture-laden cyclones generally come from North America via Iceland. These systems become loaded with

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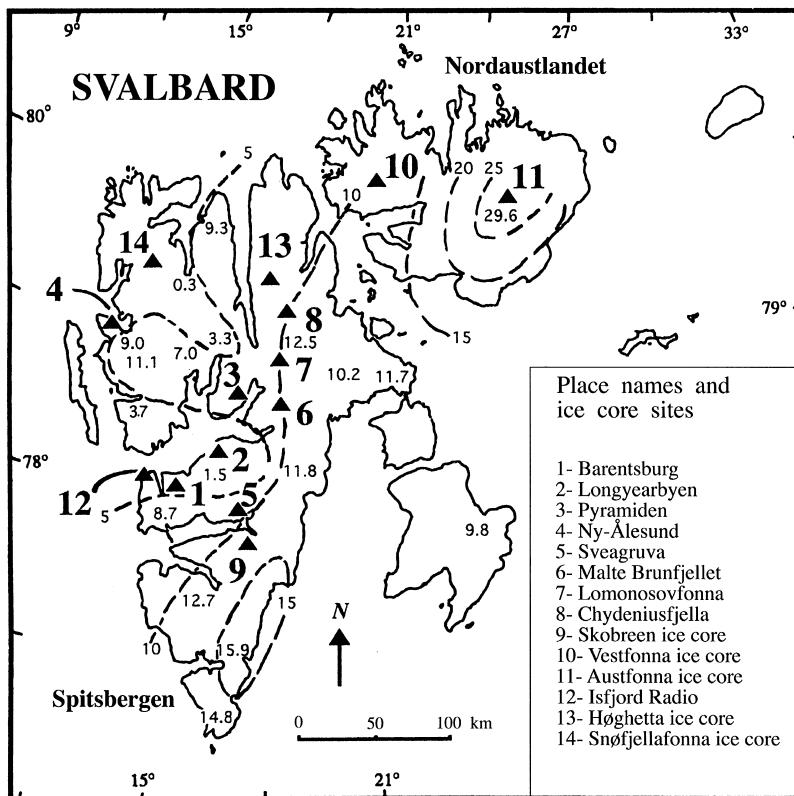


Fig. 1. Map of Svalbard showing the major place-names and ice-core sites (bold numbers). Light numbers and curves show values for spring snow acidity in 1983 (after Semb et al., 1984).

pollutants mainly from the industrial areas of north eastern North America but arrive in Svalbard greatly depleted, as most of the precipitation occurs previously over the ocean. Consequently, the Barents-Kara sea region is subject to a high influx of man-made pollutants with a maximum in late winter – early spring.

Limited sulphur emissions originate from four mining towns in Svalbard (e.g. coal dust from mining production at Barentsburg, Longyearbyen, Pyramiden, and Sveagruva). However, these emissions are not expected to influence the records from Austfonna and Skobreen ice cores examined in this work, as their sites are about 230 and 70 km leeward of Longyearbyen, respectively, and according to Steffensen (1982) southeast winds predominate in this area along all year.

2. Anthropogenic pollution in Svalbard

2.1. Atmosphere

Several investigations have shown that the Svalbard atmosphere in winter is heavily loaded with a variety of

anthropogenic impurities (e.g. Heintzenberg et al., 1981) which include: sulphates and sulphur dioxide, and soot (Rahn, 1981); heavy metals (e.g. Pb, Cu, Zn, and Ni; Pacyna et al., 1984); pesticides (Oehme and Ottar, 1984); and organic gases (e.g. alkanes; Hov et al., 1984). The presence of the organic compounds supports a mid-latitude origin for these impurities. Another main characteristic of Svalbard pollution is the strong seasonality in the concentration of these impurities in the atmosphere. Although Pacyna and Ottar (1985) have proved that even in the summer some pollutants may arrive in the Archipelago (from North America via Iceland and also from Eurasia), these concentrations are still one order of magnitude smaller than in winter. In summer, sea-salt particles predominate, as well as crustal elements.

Sulphur dioxide and nitrogen oxides, in the final form of H_2SO_4 and HNO_3 , are two of the main pollutants of the Arctic. Fig. 2 (inset) shows the mean winter concentration of excess sulphate ($\mu\text{g m}^{-3}$) at ground-level in the Arctic and environs (after Rahn, 1982). An important feature emerges from this picture – exists a broad tongue of relatively high concentration that follows the main pathway of pollutants towards the Arctic through the

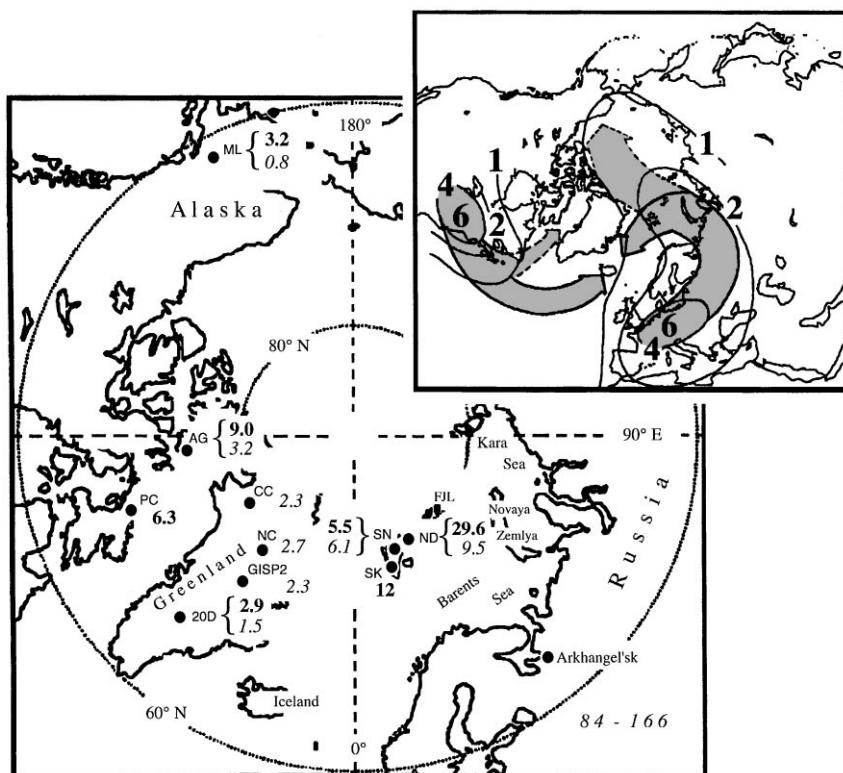


Fig. 2. Superficial H^+ (bold) and excess-sulphate (italic) concentrations in Arctic snow deposited since 1970 (in $\mu Eq l^{-1}$). The periods covered by the surface values and the sources of the data are the following: AG (H^+ , Agassiz ice cap 1970–80; Barrie et al., 1985; excess-sulphate 1988–1993, Goto-Azuma et al., 1997); CC (Camp Century 1976–77; Herron, 1982); GISP2 (Greenland Ice Sheet Project 2 1970–1989; Mayewski et al., 1993); ML (Mt. Logan 1979–81; Holdsworth and Peake, 1985); NC (North Central 1973–77; Langway and Goto-Azuma, 1988); ND (Nordautlandet 1983; Semb et al., 1984); PC (Penny ice cap 1977–79; Holdsworth, 1984; data in graph form); SK (Spitsbergen, Skobreen area 1983; Semb et al., 1984); 20D (Mayewski et al., 1990; data in graph form); SN (Snøfjellaonna, 1970–1980; Goto-Azuma et al., 1995; data in graph form). Inset shows the main pathways (grey) of pollutants to Svalbard (adapted from Barrie, 1986); the light curves show the mean winter concentration of excess sulphate at ground level in the atmosphere of the Arctic and surroundings (after Rahn, 1982); the atmospheric concentrations are given in $\mu g m^{-3}$ (bold numbers).

Barents–Kara sea region. Concentrations in Svalbard during the winter can reach values as high as those for rural areas in Scotland; for example, levels of $2 \mu g m^{-3}$ were found in Ny-Ålesund, which is four times greater than concentrations in the lower atmosphere in Ellesmere Island, Canada, and up to four times greater than concentrations in southern Greenland. Furthermore, daily pulses of up to $6 \mu g m^{-3}$ of SO_2 have been observed in Bjørnøya (Rahn et al., 1980), site located at $75^\circ N$ and $19^\circ E$. The maximum concentrations of sulphur species are observed in late winter – early spring (Heintzenberg and Larssen, 1983). For example, the mean concentration of SO_4^{2-} in Ny-Ålesund ($0.57 \mu g m^{-3}$) at this time of the year can be as high as concentrations in Scotland (0.5 – $1.0 \mu g m^{-3}$) (Joranger and Ottar, 1984).

2.2. Ice and snow

Chemistry studies of surface snow in Svalbard seem to confirm an environment charged with relatively high concentrations of pollutants. Ionic measurements in pits by Gorham (1958) found $[SO_4^{2-}]^*$ concentrations of up to $14.6 \mu Eq l^{-1}$, well above baseline excess sulphate values estimated at $\sim 2 \mu Eq l^{-1}$ (Simões, 1990). Gjessing (1977)

¹ Excess-sulphate, calculated from the known sea-salt ratio of sulphates to chlorides, where $[SO_4^{2-}]^* = [SO_4^{2-}] - 0.103 [Cl^-]$ (Mulvaney and Peel, 1988). All calculations are carried out in $\mu Eq l^{-1}$.

found that the anthropogenic pollutants in the snow pack display marked seasonality and concluded that the three main man-made pollutants measured (i.e. NO_3^- , NH_4^+ , and $[\text{SO}_4^{2-}]^*$) are all highly correlated, suggesting that each is derived from the same source region. Mean concentrations in winter layers in 1974/75 were $4.5 \mu\text{Eq l}^{-1}$ for $[\text{SO}_4^{2-}]^*$, $0.5 \mu\text{Eq l}^{-1}$ for NO_3^- , associated with a mean pH of 5.2 (minimum of 4.8).

In the spring of 1983, Semb et al. (1984) carried out a detailed examination of the spatial distribution of various ions in the Archipelago, including H^+ and SO_4^{2-} . Surface snow was sampled to the previous summer layer. The measured values average the period Autumn 1982 – Spring 1983 (Fig. 1). Concentrations increase with altitude on the east side of Svalbard, denoting an orographic effect on the air masses reaching the Archipelago. Acid concentrations here are some of the highest recorded throughout the Arctic. Absolute maxima were recorded on Austfonna, where maximum acidities of $29.6 \mu\text{Eq l}^{-1}$ (i.e. pH of 4.53) – Fig. 2, $9.5 \mu\text{Eq l}^{-1}$ for sulphate, $0.97 \mu\text{Eq l}^{-1}$ for nitrate were measured. A survey by Mulvaney (1987) at Malte Brunfjellet, Sabine Land, Spitsbergen, confirmed high values for both sulphates and nitrates (3.9 and $0.9 \mu\text{Eq l}^{-1}$ respectively). Values as high as $8.14 \mu\text{Eq l}^{-1}$ for excess sulphate and $3.84 \mu\text{Eq l}^{-1}$ for nitrate were measured following precipitation events. Yevseyev and Korzun (1985) attributed high concentrations of metals (e.g. Pb, Ci, and Fe, associated with high concentrations of sulphate), found in a Vestfonna ice core to man-made pollutants.

A 1987 Høghetta ice dome core (Fig. 1, drilled at 1200 m a.s.l.) shows a clear trend towards lower pH values in the upper 30 m – approximately the last 150 years (Fujii et al., 1990), reaching a minimum of 5.2 (i.e. $6.3 \mu\text{Eq l}^{-1}$) by the end of the 1970s. A core from Snøfjellaafonna (drilled in 1992 at 1190 m a.s.l.) also records a decrease in pH from 1930 to late 1960s, accompanied by a 3–4 fold increase in sulphates (Goto-Azuma et al., 1995). A new (1997) Lomonosovfonna core shows frequent high concentration peaks (i.e. $> 10 \mu\text{Eq l}^{-1}$) of excess-sulphate in the period 1960–1990 (Elisabeth Isaksson, written communication). These results confirm the acidic character of the snow deposition² on Austfonna.

2.3. General perspective

Pollutant concentrations in snow and ice may mirror the atmospheric observations and if so, they may outline a well-defined tongue of high values from Eurasia via

²In the case of snow precipitation the terms “acid-rain” or “acid-snow” precipitation are not adequate, as the acidity of the deposited snow may be enhanced by dry deposition. It is instead more appropriate to discuss records of “acid deposition” in snow and ice.

Svalbard to the North American Arctic. Fig. 2 shows the known H^+ and SO_4^{2-} concentrations in modern snow (i.e. post-1970). Insufficient studies have been carried out to permit reconstruction of the spatial distribution of snow surface impurities in similar detail as for the atmosphere in winter, but the general trends appear to be the same. Acidity and sulphates reach their highest values in Nordaustlandet ($\text{H}^+ = 29.6 \mu\text{Eq l}^{-1}$, and $\text{SO}_4^{2-} = 9.5 \mu\text{Eq l}^{-1}$) and decrease towards the west. Acidity concentrations in Nordaustlandet can be three times greater than concentrations at the Agassiz ice cap site, Ellesmere Island ($9 \mu\text{Eq l}^{-1}$; Barrie et al., 1985). Sulphate also attain highest concentration in Nordaustlandet, existing to five times greater than concentrations at the Greenland sites ($1.8 \mu\text{Eq l}^{-1}$ at Dye 3, $2.3 \mu\text{Eq l}^{-1}$ at Camp Century, Herron, 1982; Langway and Goto-Azuma, 1988; $2.3 \mu\text{Eq l}^{-1}$ at the Greenland Ice Sheet Project 2 site – GISP2, Mayewski et al., 1993). Although these differences reflect several geographical factors (such as altitude and the continentality of the site), they are great enough to confirm the importance of the Eurasian pathway.

The distribution of pollutants agrees closely with the best estimate by Rahn (1982) for aerosols in the Eurasian pathway (Fig. 2). Concentrations at Mt. Logan (Yukon, Canada) are low and reflect the isolation of the site from the main sources of pollutants. Furthermore, such results are to be expected, as the atmospheric circulation is controlled by the Aleutian low rather than by the Arctic circulation (Holdsworth and Peake, 1985). A survey by Belikova et al. (1984) of the total sulphate content of winter snow cover confirms that the path of aerosol transport lies in the direction of the Barents–Kara sea region. The highest values are in the Ukraine ($> 166 \mu\text{Eq l}^{-1}$) and are followed by a band of high concentrations (84 – $166 \mu\text{Eq l}^{-1}$) which extend through central European Russia towards Arkhangel’sk. From these observations it can be suggested that the highest concentrations of anthropogenic pollutants in the Arctic are generally to be expected in the Barents–Kara sea region, maximum concentrations expected in Novaya Zemlya.

3. The record of anthropogenic pollution in two Svalbard ice cores

3.1. The Skobreen ice-core record

In Spring 1986, a 23.10 m ice core was retrieved from central Spitsbergen using an electro-mechanical drill. The site is located 600 m a.s.l. within the relatively flat accumulation area of Skobreen (Fig. 1), a 7000 m long stable and slow valley glacier (Simões, 1990), ice thickness at the drilling site is ~ 114 m (Simões, 1990).

This glacier is subject to surface melting in summer, and thus the core stratigraphy shows an intercalation of

snow, firn and ice layers and a rapid change of the snow pack to glacial ice. It is accepted that percolation and refreezing have impaired the original record of seasonal variations in acidity, stable-isotopes ratios and ionic concentrations. Nevertheless, the variations have not been totally obliterated and a quasi-seasonality was observed in the acidity profile. On the other hand, the site does not seem to suffer great flush-out, as demonstrated by similar $\delta^{18}\text{O}$ trends from another shallow core retrieved 2 km apart and at 480 m a.s.l. Furthermore, the summer (δ_s) - winter (δ_w) difference in the stable isotopes ratios are similar to the difference found in the precipitation at the Isfjord meteorological station – Spitsbergen (Simões, 1990). It is supposed, therefore, that percolation was generally contained in the previous winter's accumulation.

In dating the Skobreen core, four sequential steps were adopted: (1) the determination of the mean accumulation rate since 1963 by identifying tritium peaks resulting from nuclear testing; (2) checking the resulting net mean accumulation rate by spectral analysis of the parameters with continuous time series (i.e. acidity, $\delta^{18}\text{O}$, and electrolytic conductivity – EC); (3) identifying the maximum number of annual layers in the entire record from the stable-isotope, excess deuterium – d , acidity, and EC profiles; (4) comparing the results with a simple Nye flow model (Nye, 1963), employing the mean net accumulation rate determined from the upper layer. The mean net accumulation rate for the core is between 300 and 330 $\text{kg m}^{-2} \text{a}^{-1}$ water equivalent. According to our interpretation, the core represents a period of 54 ± 5 years of precipitation.

3.1.1. Sampling and methods

Metre-long sections of the Skobreen core were packed in plastic and placed into cardboard tubes and kept in a snow trench for a week at temperatures below -5°C . The tubes were then packed in insulated boxes and flown to the British Petroleum (BP) cold rooms in Sunbury, England in less than 24 hours. Two months later, subsampling were carried out at BP. To reduce contamination, only an inner 3.5 cm cylinder was sampled for analysis. The outer part of the core was cut and scraped with a Teflon-coated tenon saw. The sections were then placed in plastic bottles (previously washed with water distilled three times) and left to melt. Two bottles were filled with the same distilled water to serve as blanks for the chemical analysis process.

Acidity was measured in all 210 ice-core samples (each sample representing a 0.1 m section in length) with a pH meter (a gel-filled electrode, Gallenkamp PHK-120-B, precision of 0.01 at pH 7); the instrument was calibrated with buffers of pH 4 and 7. The pH was measured after the sample bottles had been open for 10 min (to achieve equilibrium with the atmospheric CO_2) in a well-ventilated clean room at ambient temperature (i.e. 21°C).

This procedure results in a constant H_2CO_3 background for all the samples, so the variations in acidity do not result from varying CO_2 uptake. For every fourth sample the pH was also measured after another 4 and 8 min. No substantial difference was observed in the later measurements, confirming that the uptake of CO_2 had achieved equilibrium. A sample of triply distilled, deionized water (pH ~ 5.7) was used as reference and was repeatedly measured over time. The 210 samples have a mean acidity of $3.09 \pm 1.49 \mu\text{Eq l}^{-1}$.

Only 38 spot samples, equally distributed down the core, for SO_4^{2-} . Sulphate concentration was measured by ion chromatograph Dionex 2010i, with an accuracy of 10%. Two blanks showed concentrations of less than $0.60 \mu\text{Eq l}^{-1}$ of SO_4^{2-} . Similarly prepared water was used to clean the plastic storage bottles. The mean SO_4^{2-} concentration in the 38 samples is $7.13 \pm 6.04 \mu\text{Eq l}^{-1}$.

3.1.2. Results

Profiles of both acidity³ and $[\text{SO}_4^{2-}]^*$ are shown in Fig. 3A. Concentrations of H^+ have increased at a rate of $0.03 \mu\text{Eq l}^{-1} \text{a}^{-1}$ since the 1930s, with $r = 0.44$ and $\alpha < 0.001$. This mean rate of change represents an increase of about 67% in acidity over a period of 50 years (1930–80) when compared with mean values for the 1930s. Maximum values of both acidity and excess-sulphate were reached in middle 1970s.

Fluctuations of $[\text{SO}_4^{2-}]^*$ may be explained by the discontinuous sampling frequency. As demonstrated above, the concentration of pollutants in the Arctic shows a strong seasonality. Therefore, it is possible that in some years only snow deposited in summer had been sampled, which would give a false impression of low impurity content. Furthermore, the limited number of samples does not allow for any trend estimation. This sampling problem, however, can not explain the great fluctuations observed in the acidity record, as these measurements were continuous. Most likely melting and percolation have been great enough to elute part of the H^+ and SO_4^{2-} , and so ionic redistribution would be causing false peaks. Nevertheless, a significant correlation of Cl^- with total sulphates is a strong evidence that the core has not been homogenised by melting beyond recognition of major trends. In an elution sequence, SO_4^{2-} is the first anion to be flushed out with Cl^- being the last. Furthermore, the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio would decrease rapidly with melt migration as the elution is also differential

³pH has been converted to H^+ concentrations to facilitate cross-comparison with other acidity time series, and the calculation of the mean and trends. The main contribution to the acidity in polar precipitation is made by the strong acids, and weak acids (such as organic acids) are in general insignificant in the background precipitation of the polar regions (Legrand and Saigne, 1988).

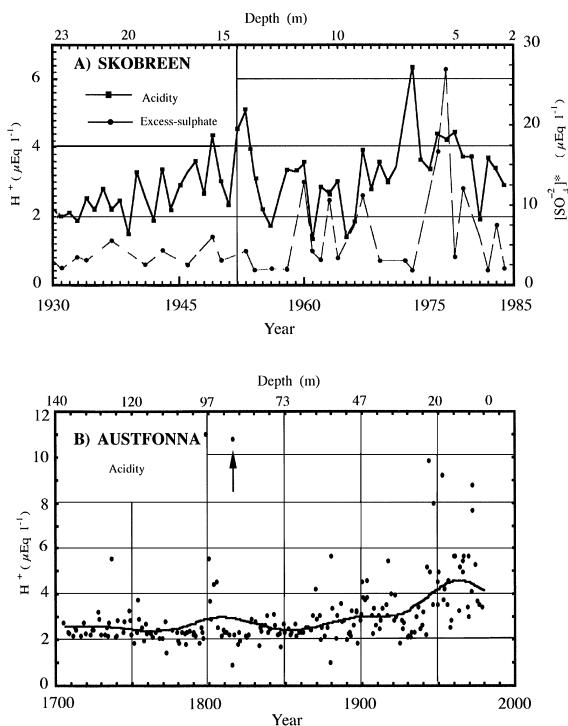


Fig. 3. Svalbard cores: (A) Mean annual acidity (solid line) and excess-sulphate (dashed line) values in the Skobreen core. Note the different resolution of the two time series. (B) Acidity concentration in the Austfonna ice core since 1700. A distance-weighted least squares model was used to fit a curve to the data. The arrow indicates the acid peak attributed to the Tambora (1816) volcanic event.

(i.e. sulphates are removed faster), an effect not observed in Skobreen.

3.2. The Austfonna ice-core record

In 1987 an ice core was recovered from the ice divide (750 m a.s.l.) of Austfonna, an ice cap on the island of Nordaustlandet (Zagorodnov and Arkhipov, 1990). The core reached bedrock at 566.7 m and is estimated to represent about 4000 years of accumulation. One of the ice parameters measured was pH, thereby providing a long-term record of acidity for Svalbard and leading to the derivation of a pre-Industrial Revolution baseline.

Because this island is situated in a colder environment farther north and east of Skobreen, it was thought to guarantee better preservation of the original signal, but melting and percolation was observed to be intense in some years. The proportion of firn layers tends to increase below a depth of 45 m, confirming reduced melting before this century.

3.2.1. Sampling and methods

Only a central column (0.02–0.04 m diameter) of the ice core was sampled to reduce contamination. A thermal sampler allowed the operator to place each of 0.1–0.8 m subcore long sections into a polyethylene bag without contact with any tools except the inner surface of the sampler (a titanium coring head). Sampling bags, filtering apparatus, filters, and plastic bottles were washed with a solution of 10–20% of HNO_3 and three to four times with distilled water. The pH of flushing water was measured after these rinses and no substantial change was detected. A Russian-made EV-74 voltmeter and a Ag–Cl balance electrode was used to measure pH. Further details on sampling and methods are given in Zagorodnov and Arkhipov (1990).

3.2.2. Dating of the Austfonna ice core

The methodology adopted for the dating of the 1987 Austfonna core was to generate different runs with a simple Nye model (Nye, 1963), varying mean accumulation rates between 300 and 900 $\text{kg m}^{-2} \text{a}^{-1}$. For the upper part of the ice core, Nye's model provides reliable dating (Paterson, 1994). The dated acidity profiles were then cross-checked with the acidity record at Skobreen and also against the sum of sulphates and nitrates in the 20D Greenland core (Mayewski et al., 1986, 1990). The best results were obtained with mean net accumulation rates between 511 and 526 $\text{kg m}^{-2} \text{a}^{-1}$, although some uncertainties may exist, given that similar variations and trends could occur with some time lag at different ice-core sites (Zagorodnov and Arkhipov, 1990).

It was also possible to attribute some of the strongest peaks to well known volcanic eruptions in the Northern Hemisphere. For example, a H^+ peak of 10.7 $\mu\text{Eq l}^{-1}$ occurs at a depth of 89 m (Fig. 3B), which is estimated to have been deposited in about 1812 and is attributed to the eruption of Tambora in 1816, an event marked elsewhere in the Arctic (e.g. Clausen and Hammer, 1988). The acidity profile for Austfonna is plotted in Fig. 3B assuming a mean net accumulation rate of 526 $\text{kg m}^{-2} \text{a}^{-1}$ for the period 1700–1987.

3.3. Results

Fig. 3B shows the record of acidity concentration since 1700: present values are more than twice the values at the beginning of the 19th century. A linear-regression analysis for the period 1800–1980 yields a trend of $0.012 \pm 0.002 \mu\text{Eq l}^{-1} \text{a}^{-1}$, with $r = 0.39$ at a highly significant level ($\alpha < 0.001$). This slope represents a total increase of about 2.2 $\mu\text{Eq l}^{-1}$ over 180 years, or about 85% above an estimated baseline value of $2.6 \pm 1.0 \mu\text{Eq l}^{-1}$ (i.e. the mean acidity for the period before 1800). A mean acidity of $2.7 \pm 1.2 \mu\text{Eq l}^{-1}$ is found in the Austfonna core samples for the period

1800–1900, $3.4 \pm 1.6 \mu\text{Eq l}^{-1}$ for the period 1900–1950, and 4.9 ± 1.8 for the period 1950–1980.

4. Discussion

4.1. Comparison with the record of other ice cores

4.1.1. Acidity

Acidity profiles from Svalbard are compared with other cores in Fig. 4. The main graph depicts the records from the Austfonna and Høghetta cores. The data for the upper 40 m of the latter were digitised and converted to acidity from a smoothed pH profile obtained by Fujii et al. (1990). The two sites are approximately 150 km apart. The Høghetta record was “fixed” to the Austfonna time scale taking as reference the major trends observed in both profiles and an acid peak identified at about 1816 AD in the two cores. Natural variance in the net accumulation rate at the two sites during the 19th century may have resulted in small dating errors. Neither record shows statistically significant trends during the first part of the 19th century. On the other hand, H^+ increased in the period 1830–1920 at a rate of $0.012 \mu\text{Eq l}^{-1} \text{a}^{-1}$ in both cores. The 1920–1929 decade is marked by a slight decrease in acidity.

An inset in Fig. 4 showing the Snøfjellafonna (A) and Skobreen (B) acidity records provides further evidence for increasing acidity in the regional precipitation. The former profile is digitised from Goto-Azuma et al. (1995). The four profiles all show relatively high H^+ for the period 1930–1980. On the other hand, only three cores

produce statistically significant trends (i.e. $\alpha < 0.001$) and at different rates ($0.051 \pm 0.009 \mu\text{Eq l}^{-1} \text{a}^{-1}$ at Austfonna, $0.040 \pm 0.011 \mu\text{Eq l}^{-1} \text{a}^{-1}$ at Høghetta, $0.034 \pm 0.004 \mu\text{Eq l}^{-1} \text{a}^{-1}$ at Skobreen). This disparity may reflect local post-depositional modification in the records such as partial melting and percolation of H^+ to lower layers, and homogenisation of signal (as seems to be the case for Snøfjellafonna).

H^+ concentration decreased within the four cores in the late 1950s. Three main factors could cause changes in concentration at the deposition site (i.e. the original precipitation at the core sites): (1) modifications in the path followed by air masses transporting impurities from source to receptor; (2) the scavenging process; and (3) changes in the strength of the source (Neftel et al., 1985). The production of precursors of strong acids (e.g. SO_2) were actually increasing rapidly by the 1950s, and the third hypothesis is therefore disregarded. The other two controls remain to explain the decrease in the late 1950s – early 1960s. Two hypotheses are now put forward: (1) Changes in the precipitation or post-depositional alteration – the decrease would be explained either by partial elution of the H^+ or by a higher precipitation rate for the given period. Both options are supported by meteorological data for Svalbard for this period (i.e. an exceptionally warm period with high precipitation; Simões, 1990). For the other sites, it would be necessary to examine the variations in both the annual accumulation rate and the summer melt conditions before reaching any conclusion. (2) Strengthening of the zonal air circulation, forcing a position of retreat for the Arctic front, and less frequent passage of cyclones

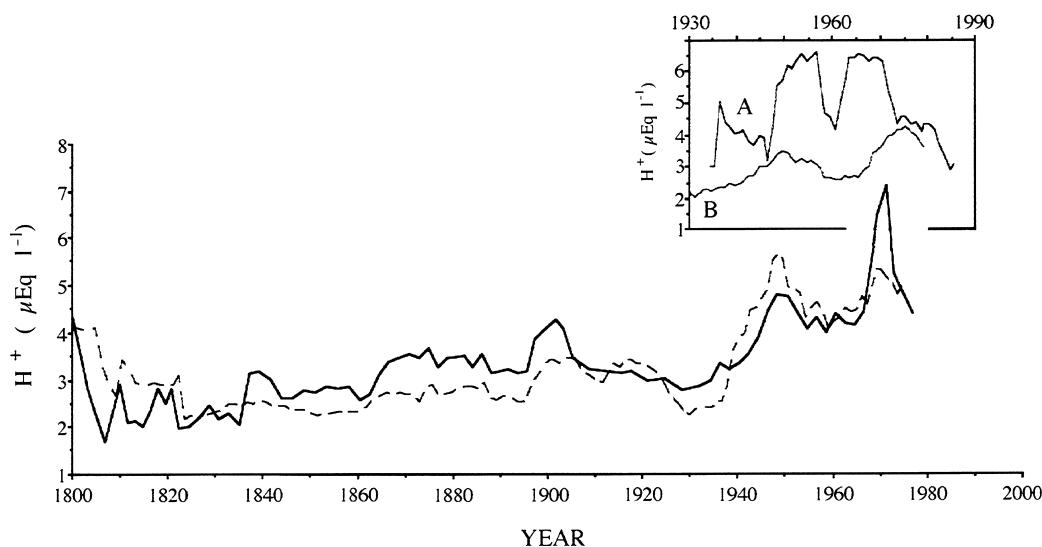


Fig. 4. Acidity concentration in the Svalbard cores: Austfonna (solid line) and the Høghetta (dashed line), the former is derived from data shown in Fig. 3B and is smoothed by a 10 sample moving average model. The latter is digitised from a 20-point running mean profile published by Fujii et al. (1990). The inset shows the Snøfjellafonna (A) the Skobreen (B) records from 1930s; the former is digitised from Goto-Azuma et al. (1995). Both series have been smoothed by a 5-point moving average model.

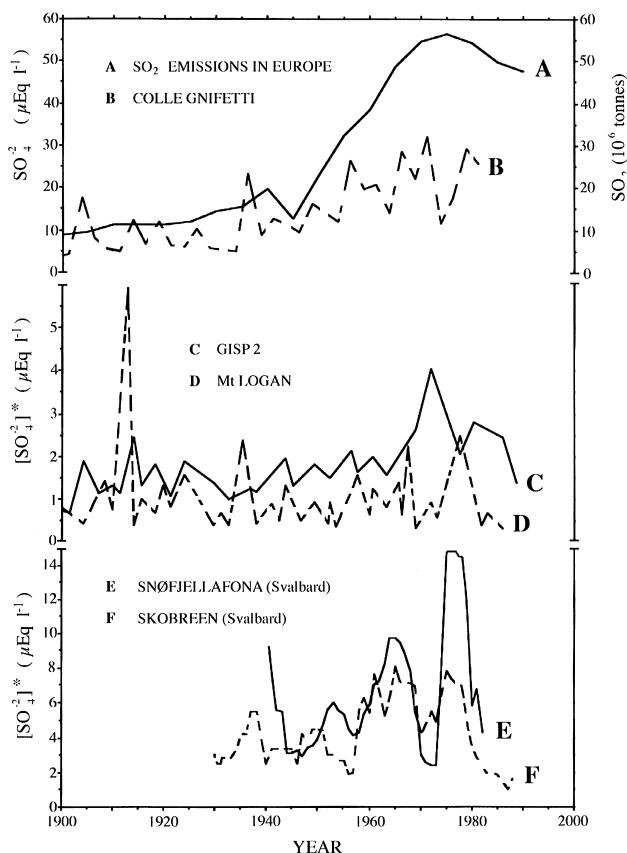


Fig. 5. Twenty century excess-sulphate ($[\text{SO}_4^{2-}]^*$) series: Skobreen, this work; Snøfjellafonna, digitised from Goto-Azuma et al. (1995); GISP2 and Mt Logan, both profiles digitised from Mayewski et al. (1993). The graph also includes data for Europe: the total sulphate profile of the Colle Gnifetti core from Döscher et al. (1995) and the SO_2 anthropogenic emissions estimated by Mylona (1996).

through the source areas in Eurasia, during the warm 1950s. This scenario would naturally result in a reduced load of anthropogenic impurities in the troposphere. Air chemistry observations under zonal and azonal vortex flow conditions on longer time scales (i.e. decadal) would be necessary to confirm this hypothesis.

Maximum acidity was reached in all cores by the early 1970s when the mean annual concentration frequently surpassed $6 \mu\text{Eq l}^{-1}$. The ratio between H^+ concentrations in the 1970s and the estimated regional baseline value (Section 3.3) is about 1.9 for Austfonna and 2.1 for Høghetta. These values are assumed to indicate greater emission of anthropogenic sulphur dioxide and nitrogen oxides due to industrialisation, as there is no evidence for an increase in natural production (such as a period of great volcanic activity). This hypothesis is also supported by the relatively high mean excess sulphate from the two shallow cores representing the period 1930–1980 (Fig. 5).

4.1.2. Excess sulphate

The excess sulphate profiles from Skobreen and Snøfjellafonna are compared in Fig. 5 with similar records from two Arctic cores, GISP2 and Mt. Logan (both profiles digitised from Mayewski et al., 1993). These two sites were chosen because they represent different climatic settings in the Arctic. GISP2 is Greenland site at 3207 m a.s.l.; Mt. Logan, in the Yukon Territory, is at 5300 m a.s.l. and its climate is controlled by the Pacific–North American atmospheric circulation. Fig. 5 also includes the total sulphate data from Colle Gnifetti (obtained from Döscher et al., 1995), a site at 4450 m a.s.l. in the Monte Rosa massif that it is suggested to represent the pollution history of central Europe. All of these cores are also compared to the historical sulphur dioxide emissions inventoried by Mylona (1996), supposed to reflect mainly coal combustion before World War II and fossil fuel combustion thereafter (Mylona, 1996).

The Skobreen and Snøfjellaonna cores contain mean excess sulphate levels for the period 1930–1980 (5.2 and 5.9 $\mu\text{Eq l}^{-1}$, respectively) higher than any other site excluding Colle Gnifetti. Interestingly, the two cores record an early increase in 1930s, also observed in Colle Gnifetti, Mt. Logan and in the European sulphur dioxide production. In Svalbard this peak is followed by a concentration trough in the 1940s that may reflect a reduction in SO_2 emissions during the World War II years as it is also observed in Colle Gnifetti. More recently, a clear trend to higher values has been observed in Skobreen, reaching a maximum by the late 1970s ($0.14 \pm 0.025 \mu\text{Eq l}^{-1} \text{ a}^{-1}$, $r = 0.62$, $\alpha < 0.001$). By then, the mean annual concentration was $10.6 \mu\text{Eq l}^{-1} \text{ a}^{-1}$ (140% increase in 40 years), concomitant, therefore, with the maximum European SO_2 emission (a peak of 55×10^6 tons). Since 1970, all cores show a trend towards lower excess sulphate which may also reflect the decreasing European sulphur dioxide production (a fall of 30% by 1980). No similar trend is found in the Snøfjellaonna profile.

Although the GISP2 core also records an increase in excess sulphate for the period of study, this profile differs from Skobreen. This discrepancy is to be expected as the GISP2 site is under a different atmospheric circulation regime, it being strongly affected by pollutant emissions from North America. In general, it can be said that the Skobreen core reflects the general sulphur dioxide emissions in Europe, but no linear relationship is found between the two time series.

The decrease in acidity and $[\text{SO}_4^{2-}]^*$ from the late 1980s to the present in Svalbard can be attributed to a decrease in source inputs (i.e. stringent pollution controls, as reflected in the SO_2 emissions profile for Europe). It also may have resulted from a greater wash-out of ions due to increasing melting, but there is no evidence of that change in the meteorological record (Simões, 1990).

Finally, it is clear that some of the acids are removed from the snow/firn layers even at an altitude of 600 m in central Spitsbergen, following examination of the chemistry of the Skobreen core (Simões, 1990). Davies et al. (1982) demonstrated that ions are eluted from snow differentially in a manner that accentuates the loss of strong acids (i.e. mainly H_2SO_4 and HNO_3). These great losses happen during the first weeks of the thaw and can lead to a three-to-fivefold increase in acidity concentrations (i.e. an “acid shock”). Our study does not examine melting processes at low elevations, but a more intense release of acids and meltwater flush-out will certainly occur there. It is therefore recommended that monitoring of the composition of meltwater, lakes, and fjords in Svalbard (to assess the impact of the acidic run-off) be carried in the future.

5. Summary and conclusions

Svalbard is one of the areas in the Arctic most affected by anthropogenic pollution. The expansion southwards

in the winter of the cold dry Arctic air mass forces the main cyclone tracks over the heavily polluted atmosphere of central Europe, Scandinavia, and north western Russia, and subsequently deflected towards the Arctic. Svalbard is one of the first land masses in the path of these pollutant-laden air masses and as a consequence of these atmosphere, snow, and ice have a high content of anthropogenically derived impurities. Atmospheric winter concentrations of excess sulphate are similar to those in the north of Scotland. Measurements carried out on the seasonal snow cover over the last two decades confirmed the atmospheric observations. Maximum values are reached in Nordaustlandet, where excess sulphate can surpass $8 \mu\text{Eq l}^{-1}$, and for H^+ , $15 \mu\text{Eq l}^{-1}$.

The examination of an acidity profile for an ice core from Austfonna provides baseline values and trends from the beginning of the Industrial Revolution. Pre-industrial acidity oscillated between 2.3 and $2.8 \mu\text{Eq l}^{-1}$, with a mean value of $2.6 \mu\text{Eq l}^{-1}$. Since the mid-19th century, a trend towards higher values is observed, most probably due to the increase in production of sulphur compounds in Europe. Since 1800 the H^+ concentration in Austfonna has risen to a total of $2.4 \mu\text{Eq l}^{-1}$, which represents an increase of about 90% when compared to the baseline concentration. Two shallow cores (Skobreen and Snøfjellaonna) confirm that this increase in acidity is associated with a relatively high excess sulphate ($> 5 \mu\text{Eq l}^{-1}$). In short, it can be said that the results from the two ice cores, Austfonna and Skobreen, confirm the atmospheric and surface snow observations of an environment heavily loaded with anthropogenic impurities that at least partially reflect the European sulphur dioxide emissions. The high concentrations of H^+ , frequently greater than $10 \mu\text{Eq l}^{-1}$ (i.e. $\text{pH} < 5.0$) and associated with high concentrations of sulphates, indicate that Svalbard is suffering at least sporadically from the phenomenon of acid deposition.

The stratigraphic profiles of the Skobreen and Austfonna cores, on the other hand, show strong signs of post-depositional alteration due to melting, percolation and refreezing of the surface layers. Some annual layers may have even been affected by preferential ionic elution. Therefore, concentration values and trends reported in this paper may need confirmation from ice cores taken in more favourable glaciological conditions (i.e., colder sites). It is suggested that a shallow ice core from one of the small glaciers in the Chydeniusfjella mountain range (1300 a.s.l., Fig. 1) may provide a better record for the last two centuries.

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