



Chemical composition of arctic snow: concentration levels and regional distribution of major elements

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Abstract

At the end of the northern winter 1996/1997, 21 snow samples were collected from 17 arctic localities in Norway, Sweden, Finland, Svalbard, Russia, Alaska, Canada, Greenland and Iceland. Major element concentrations of the filtered (0.45 µm) melted snow indicate that most samples are consistent with a diluted seawater composition. Deviations from this behaviour indicate additional SO_4^{2-} and Cl^- relative to seawater, suggesting a minor contribution from (probably local) coal combustion emissions (Alaska, Finland, Sweden, Svalbard). The samples with the highest Na and Cl^- content (Canada, Russia) also have higher $\text{Na}/\text{SO}_4^{2-}$ and $\text{Cl}^-/\text{SO}_4^{2-}$ ratios than seawater, suggesting a slight contamination from (probably local) deicing activities. Local soil or rock dust inputs in the snow are indicated by 'excess' Ca contents (Alaska, Svalbard, Greenland, Sweden). No overall relationship was found between pH (range: 4.6–6.1) and total or non-seasalt SO_4^{2-} (NSS), suggesting that acidification due to long-range transport of SO_2 pollution is not operating on an arctic-wide scale. In a few samples (Alaska, Finland, Sweden, Svalbard), a significant proportion (>50%) of SO_4^{2-} is non-marine in origin. Sources for this non-marine SO_4^{2-} need not all be found in long-range atmospheric transport and more likely sources are local industry (Finland, Sweden), road traffic (Alaska) or minor snow-scooting traffic (one Svalbard locality). A few samples from northern Europe show a relatively weak trend of decreasing pH with increasing NO_3^- .

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1. Introduction

The major element composition of snow has been investigated for many years, and increasingly trace ele-

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ment and isotopic data are also being reported (e.g., Busenberg and Langway, 1979; Delmas, 1986; Gorzelska, 1989; Baisden et al., 1995; Suzuki et al., 1995; Krachler and Kosmus, 1996; Caritat et al., 1998; Douglas and Sturm, 2004). However, systematic, detailed chemical composition of snow is poorly documented, even in the Northern Hemisphere, especially with regards to its regional variability. Some studies in the Northern Hemisphere have compared snow composition over areas of up to 200,000 km² (e.g., Caritat et al., 1998), but an arctic-wide perspective is still lacking.

Single-site studies of the composition of ice, the product of the accumulation and compaction of snow over many years, have been documented in detail from various cores, such as in Greenland (Hammer et al., 1985; Herron and Langway, 1985; Dansgaard and Oeschger, 1989). The downcore chemical and isotopic compositional changes observed in ice have been related to climate change or anthropogenic pollution (Delmas, 1994, and references therein). However, there is little documentation or understanding of the changes in snow (or ice) composition laterally over *regional scales*, or of the *dominant controls* on its chemical composition. Now that analytical instrumentation enabling analysis at ultratrace levels of chemical elements has become available, regional surveys of snow chemistry can be carried out to answer such questions.

The present study was designed to address these issues, in a preliminary way, by attempting to obtain and analyse snow samples from as wide an area as possible over the Arctic. This region, being the most sparsely populated one in the Northern Hemisphere, provides a unique opportunity to study precipitation chemistry away from major human activity centres.

In 1997, the Geological Survey of Norway (NGU) supported a pilot project, dubbed 'ARCTIS' (a permutation of the acronym for Regional Composition of Snow In The Arctic), to test the feasibility of low-cost, pragmatic, arctic-wide, background (remote from point-sources) snow sampling, and, together with the Geological Survey of Canada (GSC), to assess the related analytical challenges. Scientists from universities and Government, or schoolteachers, who either lived in remote arctic areas or intended to conduct field trips there, were contacted and invited to participate in this arctic snow survey. Thus, all samples were collected with the same equipment, according to identical detailed field instructions, and analysed in a

single laboratory. Initially, more field parties were contacted (e.g., Siberia), but for a number of reasons, they were not able to participate in the end.

2. Objectives

The objectives of the ARCTIS project were:

- (1) to establish the concentration levels of a wide range of soluble chemical elements in arctic snow; and
- (2) to document the spatial variability (geochemical patterns) of these elements in arctic snow.

The results presented here are the first, to our knowledge, of an arctic-wide, internally consistent, and fully quality assurance (QA) monitored study of snow composition over such a vast area. In total, 21 samples of snow fallen during the 1996/1997 winter were obtained from 17 locations in Norway, Sweden, Finland, Svalbard, Russia, Alaska, Canada, Greenland and Iceland. All locations are from latitudes between 62 and 79°N. It is anticipated that these results will complement other initiatives to document the extent of arctic pollution (e.g., AMAP, 1998).

3. Potential sources of elements

Elements measured in arctic precipitation often originate from a mixture of natural and anthropogenic sources; both sources can contribute to the wet (soluble) and dry (aerosols, dust) components of precipitation. For example, the major sources of dissolved solids in Icelandic precipitation are seaspray, global pollution, and transient and sometimes enormous inputs from volcanic eruptions (Gíslason et al., 1992, 1996; Frogner et al., 2001).

3.1. Natural sources

The arctic region is characterised by a vast expanse of sea and sea ice, the Arctic Ocean (14 million km²). Therefore, seaspray is expected to be an important contributor in the region to the composition of the atmosphere, and thus of precipitation. The influence of *seaspray* on precipitation chemistry generally decreases with distance from the ocean and with altitude.

Volcanic activity (e.g., in Iceland) will be a sporadic, but significant, contributor to snow composition, mainly via the deposition of particulate matter from *volcanic ash* after eruptions. Quiescent volcanic emissions (*exhalations*) are now recognised as an important contributor to background atmospheric concentrations of trace metals (Matsumoto and Hinkley, 2001). Natural mechanical and chemical *weathering* of outcropping rocks, and winnowing of soil *dust* from snow-free areas are further natural sources of chemical elements to the atmosphere, and thus to snow and ice (Hansson et al., 1993; Hinkley, 1994). Migration of chemical elements from soil into the overlying snowpack (*mineralization*) is also a process that may be operating, particularly where temperatures are quite variable and occasionally high (Fedoseeva et al., 1986, 1990). Finally, *biogenic emissions* from the Arctic Ocean and surrounding seas can contribute not only S, but also trace elements such as metals through biologically mediated methylation (Buat-Ménard, 1984). This may be significant in arctic coastal areas near discontinuous ice cover or polynyas.

3.2. Anthropogenic sources

Man-induced sources of elements are an important consideration in the Arctic because the area, despite being remote and sparsely populated, is nevertheless developed and inhabited in places, especially at its periphery (3.78 million inhabitants in the Arctic, as defined by AMAP, 1998). Economic activities in the Arctic include the manufacture of chemicals, construction materials, electric power plants (powered by atomic, hydro or thermal energy), fishing and shipping, food processing, machine building, metallurgy, mineral and fuel extraction, wood processing and pulping and light industry (CIA, 1978). Of particular interest here are the mining-related activities because they have the potential to release into the environment large quantities of particulate and dissolved elements, often in typical assemblages. The most important commodities mined in the Arctic (e.g., CIA, 1978) are coal, copper, diamond, gold, iron, lead and zinc, nickel, oil and gas, tin and others (tungsten, mercury, platinum, cobalt, graphite, fluorite, manganese, aluminium, apatite, mica, silver and asbestos).

Geogenic dust is likely to be important in these regions of (often) sparse vegetation cover and harsh climate, compared to more temperate regions. Human

activity may locally result in vegetation damage or destruction, enhancing dust generation (e.g., Kola Peninsula). Thus, even if small parts of a region are not covered with snow, they may generate quite important fluxes of mineral dust (together with its chemical elements content) to the atmosphere.

Cities, with their associated *industry, traffic* and *electricity generating plants*, can be significant centres of emissions. The most populated cities in the survey area include Murmansk, Archangelsk, Magadan, Anchorage, Fairbanks, Reykjavik and several townships in northern Norway, Sweden and Finland. Smaller centres have an impact not so much due to their population size, but to their industrial activities.

Of course, *areas outside the Arctic* can contribute to the atmospheric and precipitation chemistry recorded in the Arctic. Data from Barrie and Hoff (1984) and Raatz (1991), for example, identify zones of airflow into and out of the arctic region. According to these authors, it appears that northwestern Europe (UK, Scandinavia) and eastern Europe (via northern central Russia), together with the northern west coast of the USA and Alaska, are areas that can be on the path of arctic-bound air masses (Pfirman et al., 1994). The phenomenon of '*arctic haze*' leads to the migration of polluted air masses from the industrialized temperate zones into the Arctic, especially during late winter (Shaw, 1995; AMAP, 1998).

Snow is an efficient scavenger of aerosols in the atmosphere, and thus even moderate falls deposit a substantial proportion of elements from the atmosphere (regardless of their origin). Heavy snowfalls will therefore record a progressive drop of concentrations in snow from start to end of a snow event. To gain some appreciation of this dilution effect, average snow depth at each site is reported. It should also be noted that analysis of snow does not directly allow the differentiation between the wet and dry contributions to precipitation, and thus 'bulk' precipitation chemistry is obtained.

4. Materials and methods

4.1. Sampling

Late in the northern winter of 1997 (March–May), 21 fresh snow samples (Table 1) were collected at 17

Table 1
Overview of sampling locations and samples details

Sample ^a	Country	Subset	Latitude N (°)	Longitude E (°)	Snow depth (cm)	Date collected	Locality	Remarks
C1	Canada	C	62.83	268.02	44	April 15, 1997	Rankin Inlet	Upwind from airstrip
C2	Canada	C	62.83	268.02	71	April 15, 1997	Rankin Inlet	Close proximity to C1
F21	Finland	N	69.09	27.53	89	April 17, 1997	Inari	
F22 (D)	Finland	N	69.09	27.53	88	April 17, 1997	Inari	<i>Duplicate of F21</i>
G34	Greenland	G	76.53	291.30	26	April 5, 1997	Pittufik	
G35(D)	Greenland	G	76.53	291.30	40	April 5, 1997	Pittufik	<i>Duplicate of G34</i>
I34	Iceland	I	64.60	339.66	330	March 13, 1997	Langjökull	
I35	Iceland	I	64.58	342.67	340	March 20, 1997	Dyngjujökull	0–275 cm (above ash layer)
I36(D)	Iceland	I	64.58	342.67	340	March 20, 1997	Dyngjujökull	<i>Duplicate of I35</i>
N39	Norway	N	68.44	18.08	96	April 16, 1997	Bjørnefjell	
R57	Russia	R	69.34	54.52	53	May 3, 1997	Pechora Bay	Snow on floating icepack
R58	Russia	R	69.12	36.04	296	April 4, 1997	Jarnysknaya Inlet	Onshore
R60	Russia	R	73.03	80.38	27	April 21, 1997	Enisej Gulf	Snow on floating icepack
S68	Sweden	N	67.28	23.63	93	April 17, 1997	Pajala	
U70	USA (Alaska)	U	66.69	210.64	45	March 17, 1997	Bonanza Fork	Dalton Hwy 127.2 miles
U72	USA (Alaska)	U	69.42	212.70	32	March 19, 1997	Sagwon	Dalton Hwy 354 miles
U73	USA (Alaska)	U	67.24	210.17	51	March 20, 1997	Coldfoot	Dalton Hwy 172.5 miles
Z62	Svalbard	Z	78.18	16.83	78	April 11, 1997	Adventdalen	
Z63	Svalbard	Z	76.51	13.02	60	April 14, 1997	Hopen Island	On small offshore island
Z64	Svalbard	Z	78.93	11.81	75	May 20, 1997	Kongsfjorden	
Z65 (D)	Svalbard	Z	78.93	11.81	71	May 20, 1997	Kongsfjorden	<i>Duplicate of Z64</i>
<i>QA samples from Meech Lake</i>								
M1	Canada		45.54	284.10		March 1997	Meech Lake	15–30 cm at “Loc 2”
M2	Canada		45.54	284.10		March 1997	Meech Lake	0–60 cm at “Loc 1”
M3	Canada		45.54	284.10		March 1997	Meech Lake	0–60 cm at “Loc 1”
M4	Canada		45.54	284.10		March 1997	Meech Lake	0–70 cm at “Loc 1”
M5	Canada		45.54	284.10		March 1997	Meech Lake	15–30 cm at “Loc 1”
M6	Canada		45.54	284.10		March 1997	Meech Lake	0–60 cm at “Loc 1”
M7	Canada		45.54	284.10		March 1997	Meech Lake	0–15 cm at “Loc 2”
M8	Canada		45.54	284.10		March 1997	Meech Lake	0–15 cm at “Loc 1”
M9	Canada		45.54	284.10		March 1997	Meech Lake	0–60 cm at “Loc 1”
M10	Canada		45.54	284.10		March 1997	Meech Lake	0–60 cm at “Loc 1”

^a (D) indicates that sample is a field duplicate of previous sample (see text).

onshore (or close to shore) localities around the Arctic, north of latitude 62°N, as shown in Fig. 1. Samples originate from Norway (sample identification starts with ‘N’), Sweden (‘S’), Finland (‘F’) (these three countries are later collectively grouped as the Nordic region, ‘N’), Svalbard (Spitzbergen, ‘Z’), Russia (‘R’), Alaska (USA, ‘U’), Canada (‘C’), Greenland (‘G’) and Iceland (‘I’). The area covered by this survey is ca. 22 million km² (smallest rectangle encompassing all sampling points).

In addition to these, 10 snow samples were collected at two adjacent localities near Meech Lake (M1–M10; 45.54°N, 284.10°E), close to Ottawa in Québec (Canada). This was done to test sampling

methods, determine small-scale horizontal and vertical variations, test laboratory preparation methods and optimize QA protocols. One other sample (I38) was collected from a volcanic ash layer in the Dyngjujökull Glacier of Iceland (64.58°N, 342.67°E). Samples M1–10 and I38 are not included in the following discussion, which focuses on background, remote snow composition. Data for M1–10, however, are given in Table 3 for QA purposes.

The arctic snow samples, taken to represent the cumulative bulk (wet+dry) snowfall of the 1996/1997 winter, were collected prior to the onset of the spring thaw. All samples were collected using equipment centrally provided by NGU, which consisted of

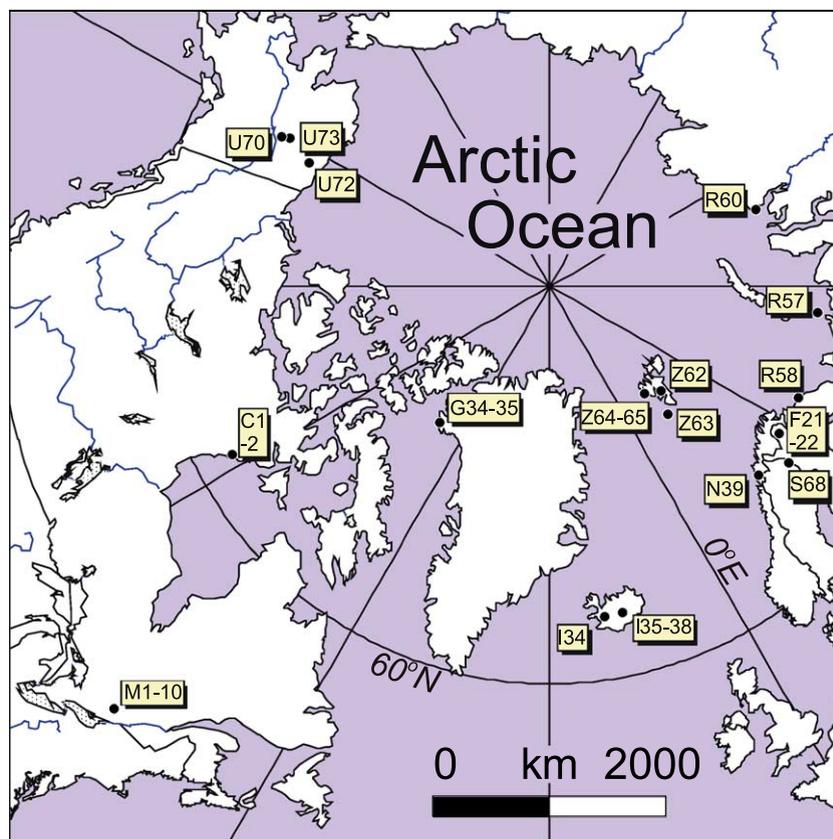


Fig. 1. Location of the arctic snow sampling sites.

polycarbonate (PC) coring tubes, pre-numbered polyethylene (PE) bags and PE gloves, and according to a clear set of instructions made available in both English and Russian (for Russia).

The clear PC coring tubes were 1 m long, with an internal diameter of 74 mm and 3-mm-thick walls. The cutting end was cut obliquely at an angle of ca. 60° and its walls were sharpened to facilitate penetration of the snow cover. The other end had two diametrically opposed holes to allow a PC rod to be inserted to assist with rotating the corer while taking samples. The corers were cleaned by immersion in a 10% Ultrapur® Merck® nitric acid bath (48 h), then rinsed with double distilled water, immersed in a double distilled water bath (24 h), air-dried and sealed off in PE sleeves at NGU before dispatching to the various field parties.

The exact locations chosen for sampling were flat, open (free of vegetation) and undisturbed (free of

tracks, etc.) spaces with a homogeneous snow cover, as shown by several depths measurements. The sampling sites were approached from the downwind side to avoid contamination. Prior to collecting a new snow sample, the corer was plunged three times into the snowpack to remove any inherited contamination from cleaning (NO_3^- from the nitric acid cleaning step), transportation or previous sampling. We believe this pre-conditioning is by far the most efficient quality control procedure one can follow for snow sampling. Each sample consists of 1 to 12 composited subsamples (depending on snow thickness) taken from an area of ca 20 × 20 m (to a total snow volume of 5–8 l). The snow cores were collected from the side (wall) of a small trench dug through the snowpack. A clean PC plate was inserted horizontally into the snow wall about 5 cm above the ground surface to stop the penetration of the corer (to avoid contamination by ground vegetation and soil/rock) and help

retrieve the snow samples. The corer was then pushed down vertically about 5–10 cm away from the trench's wall into the untouched snowpack until it contacted the horizontal PC plate. The corer was then pulled sideways out of the trench wall and the snow was emptied into bags without touching it. Where duplicate samples were taken, the same procedure was carried out about 100 m away (upwind) from the original location. Sampling was done wearing PE disposable gloves and smoking was forbidden.

4.2. Chemical analysis

Once taken, the samples were sealed in PE bags, stored in styrofoam boxes (all centrally provided) and transported frozen all the way to the laboratory of the GSC, where they were kept frozen until analysis. The total volume of meltwater was calculated by weighing each sample as received and correcting for the weight of the empty sample bag. Prior to analysis, the samples were allowed to thaw slowly and were filtered at 0.45 μm (pre-weighed Durapore[®], hydrophilic polyvinylidene fluoride membrane filters from Millipore[®], see Hall, 1998).

While the sample still contained a small portion of ice slush, the filtration was begun. The all-glass acid-washed Millipore[®] apparatus was first assembled without the Durapore[®] filter membrane and 1 l of MilliQ[®] water (18 M Ω , from MilliQ[®] Plus water system) was flushed through the frit and associated apparatus. The system was reassembled with the filter in place and 10–15 ml of the sample was filtered and this initial amount discarded. Filtering was then continued and the filtered sample was transferred into an acid-cleaned 6-l high density PE container to homogenize it. It was then immediately divided into three aliquots: a 10- to 15-ml aliquot for Hg determination; a second aliquot of 500–1000 ml for anions, pH, conductivity, dissolved organic carbon (DOC) and alkalinity; and a the third aliquot (about 4 l) was left in the 6-l container and acidified to 0.4% with Seastar[®] high-purity double-distilled HNO₃. The entire process of filtering the meltwater, splitting and acidifying was carried out in a clean room with Class-10 benches and a Class-10 hood. The chemist wore clean lab apparel throughout the entire process including powder-free vinyl gloves, Tyvec[®] lab coat, shoe covers and a bouffant cap. The sample was then

immediately refrigerated. The entire process was carried out while the sample was ice-cold to decrease any loss of elements prior to preservation.

The filtered meltwater samples only are discussed here; the composition of the filter residues will be reported separately. A series of analytical methods was applied to the filtrate aliquots, including, among others:

- Ion Chromatography (IC, Dionex[®] 2100 Ion Chromatograph) for Br⁻, Cl⁻, F⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻;
- Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Perkin-Elmer Optima[®] 3000 DV) for Ca, K, Mg, Na, S; and
- Measurements for pH, electrical conductivity (EC), alkalinity and DOC were done using various standard instruments.

Results for elements/compounds with 50% or more of the analysed samples above detection limit (DL) are of greatest interest. Thus, we shall limit the discussion in this paper to the following results: pH, EC, Cl⁻, NO₃⁻, SO₄²⁻, Ca, K, Mg, Na and S. Concentrations of particulate matter, as determined by the weighed filter residues (particles >0.45 μm) recalculated to the volume of filtered meltwater, are also included here. Discussion of trace element concentrations will be reported separately.

4.3. Quality assurance

All efforts were made throughout the project to ensure internal consistency and avoid contamination from sampling to analysis. This was achieved by issuing each field party with identical, clean sampling equipment from the same source and with clear sampling instructions. Avoidance of contamination was best achieved by cleaning the corer in the snow at each sampling locality, and by sampling only down to a PC plate inserted horizontally 5 cm above soil/vegetation to avoid physical contamination. All sample preparation and analysis were performed in the same laboratory.

Additional QA procedures included: (1) analysis of blank samples of various types (see below); (2) analysis of a number of control reference materials (CRMs); (3) analysis of each sample in duplicate; (4) analysis of field duplicate samples; and (5) verification of charge balances.

- (1) Blanks: Three types of blanks were analysed: a reagent blank as part of the calibration, an acid blank created four times at equal intervals during the processing of the samples, using identical equipment; and an acidified filter blank, again created four times during the sample processing. All of these samples were found to contain the analytes under discussion at levels below the method detection limits. Thus, contamination from cleaning, transportation or previous samples was satisfactorily minimized.
- (2) CRMs: The National Research Council of Canada (NRCC) river water standard SLRS-3 was interspersed five times among the samples and the GSC in-house CRM, OTT-96, an Ottawa River sample collected about 100 km upstream from SLRS-3, was analysed eight times. Results for major cations and S are presented in Table 2. Both precision and accuracy are excellent: the relative standard deviations (RSDs) for the two CRMs are in the range 1–3% and results for SLRS-3 are well within the limits of the certified values. CRMs were not available for the anions determined by IC but the results for the Dionex reference solution analysed with the samples were accurate to within 5%.
- (3) Analytical duplicates: All analyses were performed in duplicate on different aliquots of each sample. The analytical reproducibility (relative standard errors about the averages) for the major elements ranges from 0 to 19% and average 2.2%. The three cases where the reproducibility is worse than 10% are for S determination in samples Z62, Z64 and Z65. We regard the analytical reproducibility of results in this study to be excellent.
- (4) Field duplicates: Field duplicates were taken at four locations, yielding a sampling reproducibility (relative standard errors about the averages) ranging from 0 to 48% and averaging 17% for the major elements. The 10 separate field duplicates collected at Meech Lake yield sampling reproducibility values of 9% to 47% (Table 2). Given the inherent difficulty in obtaining perfect sampling reproducibility for typically heterogeneous precipitation samples (rain, snow), we consider the sampling reproducibility obtained here to be good overall.
- (5) Charge balance: Charge balance based on Na^+ , Ca^{2+} , Mg^{2+} , K^+ , H^+ , Cl^- , NO_3^- and SO_4^{2-} ranges from –6.8% to +19.6% and averages +1.5%. The four samples with charge balances >10% (S68, U70, U73, Z62) are either the most acid (S68) or very dilute (others), suggesting that the imbalances are probably caused by analytical errors in very dilute systems ($\text{EC} < 7 \mu\text{S}/\text{cm}$) and perhaps an anion, or anions, not determined (organic anions, see Toom-Saunty and Barrie, 2002). The slightly positive average charge balance obtained suggests that concentrations of NH_4^+ (not determined here) are overall relatively minor; alternatively, they are balanced by anions not analysed for here.

4.4. Data analysis

Prior to statistical analysis and plotting, all values <DL were set to 1/2 DL. Geochemical maps based on Exploratory Data Analysis (EDA) principles (Tukey, 1977; Velleman and Hoaglin, 1981) were prepared using the DAS[®] software (Dutter et al., 1995). Kürzl (1988), Reimann et al. (1988), Rock (1988) and

Table 2

Results for major ions by ICP-OES (in mg/l) in control reference materials (CRMs) SLRS-3 (NRCC international standard) and OTT-96 (GSC in-house control) and in QA samples M1–10

Sample CRMs	Ca	K	Mg	Na	S
SLRS-3 ($n=5$)	5.94 ± 0.07 (1%)	0.68 ± 0.02 (2%)	1.66 ± 0.02 (1%)	2.30 ± 0.03 (1%)	3.06 ± 0.06 (2%)
SLRS-3 Certified	6.0 ± 0.4	0.7 ± 0.1	1.6 ± 0.2	2.3 ± 0.2	
OTT-96 ($n=8$)	9.70 ± 0.07 (1%)	0.79 ± 0.03 (3%)	2.35 ± 0.02 (1%)	2.61 ± 0.03 (1%)	2.99 ± 0.08 (3%)
<i>QA samples</i>					
MEECH ($n=10$)	0.18 ± 0.08 (47%)	0.06 ± 0.01 (9%)	0.02 ± 0.01 (45%)	0.04 ± 0.01 (33%)	0.23 ± 0.04 (19%)

Numbers in parentheses indicate the RSD.

O'Connor and Reimann (1993) provide an introduction to the advantages of using exploratory data analysis methods when dealing with geochemical data. Correlation coefficients (r) presented in this study are based on raw data (not log-transformed).

5. Results and discussion

Results of the melted snow analyses are presented in Table 3. The snow is moderately acidic with pH values between 4.6 and 6.1 (Table 3). The most acid

Table 3
Chemical composition of <0.45- μ m-filtered meltwater from arctic snow survey, winter 1996/1997

Analyte	pH	EC	Particles	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca	K	Mg	Na	S
Method ^a	pH meter	Conductivity meter		IC	IC	IC	ICP	ICP	ICP	ICP	ICP
DL		5.0		0.10	0.050	0.05	0.01	0.05	0.005	0.01	0.05
Unit		μ S/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
C1	5.85	436	42.31	134.50	0.427	9.56	2.77	2.50	8.125	65.31	3.09
C2	5.18	282	8.90	81.50	0.285	3.61	1.63	1.63	5.245	37.74	1.25
F21	4.77	7.6	5.37	0.77	0.608	0.40	0.02	<0.050	0.051	0.39	0.12
F22(D)	4.73	7.3	2.60	0.71	0.579	0.40	0.02	<0.050	0.049	0.37	0.18
G34	5.99	25.5	55.17	8.93	0.356	1.22	0.40	0.21	0.623	4.08	0.47
G35(D)	6.13	17.8	65.68	5.68	0.549	0.95	0.60	0.17	0.449	2.55	0.30
I34	5.35	17.9	1.20	6.22	0.108	0.88	0.12	0.18	0.377	2.86	0.32
I35	5.45	<5.0	1.41	1.11	<0.050	0.22	0.02	<0.050	0.071	0.57	0.07
I36(D)	5.42	<5.0	1.65	1.17	<0.050	0.23	0.02	<0.050	0.071	0.57	0.08
N39	5.37	34.2	1.27	11.50	0.137	1.71	0.25	0.22	0.746	5.66	0.54
R57	4.73	56.5	0.53	19.35	0.380	2.34	0.45	0.49	1.381	8.87	0.79
R58	4.85	33.8	40.32	11.05	0.158	1.75	0.26	0.25	0.608	5.46	0.57
R60	5.68	1317	2.54	415.50	0.894	22.25	7.82	7.33	23.642	232.3	7.64
S68	4.61	6.5	13.25	0.23	0.673	0.35	0.03	<0.050	0.026	0.15	0.13
U70	5.11	<5.0	7.71	<0.10	0.146	0.19	0.03	<0.050	0.008	0.02	0.06
U72	5.77	<5.0	90.27	0.15	0.328	0.28	0.23	<0.050	0.023	0.05	0.11
U73	5.64	<5.0	12.75	0.18	0.217	0.24	0.20	<0.050	0.020	0.08	0.10
Z62	5.66	6.1	7.20	0.82	0.114	0.47	0.35	<0.050	0.086	0.46	0.17
Z63	5.23	80.4	5.07	20.70	0.162	2.82	0.48	0.47	1.378	9.76	0.88
Z64	6.04	46.5	9.91	11.80	0.145	1.83	0.59	0.30	0.827	5.50	0.58
Z65(D)	5.63	32.8	7.36	8.36	0.071	1.29	0.36	0.20	0.540	3.91	0.38
Min	4.61	<5.0	0.53	<0.10	<0.050	0.19	0.02	<0.050	0.008	0.02	0.06
Med	5.42	17.9	7.36	6.22	0.217	0.95	0.26	0.18	0.449	2.86	0.32
Max	6.13	1317	90.27	415.50	0.894	22.25	7.82	7.33	23.642	232.3	7.64
<i>QA samples from Meech Lake</i>											
M1	4.43	10.25	14.41	0.13	1.619	0.73	0.13	0.059	0.017	0.06	0.26
M2	4.47	10.70	35.47	0.16	1.913	0.69	0.18	<0.050	0.026	0.09	0.24
M3	4.52	8.04	29.41	0.12	1.427	0.47	0.11	<0.050	0.014	0.05	0.15
M4	4.66	9.79	30.20	0.14	1.797	0.66	0.17	<0.050	0.024	0.07	0.23
M5	4.54	11.85	11.86	0.13	1.926	0.83	0.12	0.067	0.018	0.06	0.29
M6	4.59	7.70	14.89	<0.10	1.356	0.46	0.10	<0.050	0.013	0.05	0.16
M7	4.46	11.22	19.68	0.12	2.191	0.79	0.32	<0.050	0.042	0.08	0.24
M8	4.46	11.31	13.60	0.12	2.201	0.79	0.32	<0.050	0.043	0.08	0.26
M9	4.49	9.45	17.37	0.13	1.639	0.62	0.13	<0.050	0.017	0.06	0.23
M10	4.36	10.49	15.91	0.15	1.882	0.70	0.17	<0.050	0.024	0.08	0.25

(D): duplicate; DL: (lower) detection limit; EC: electrical conductivity.

^a Method-ICP: ICP-OES.

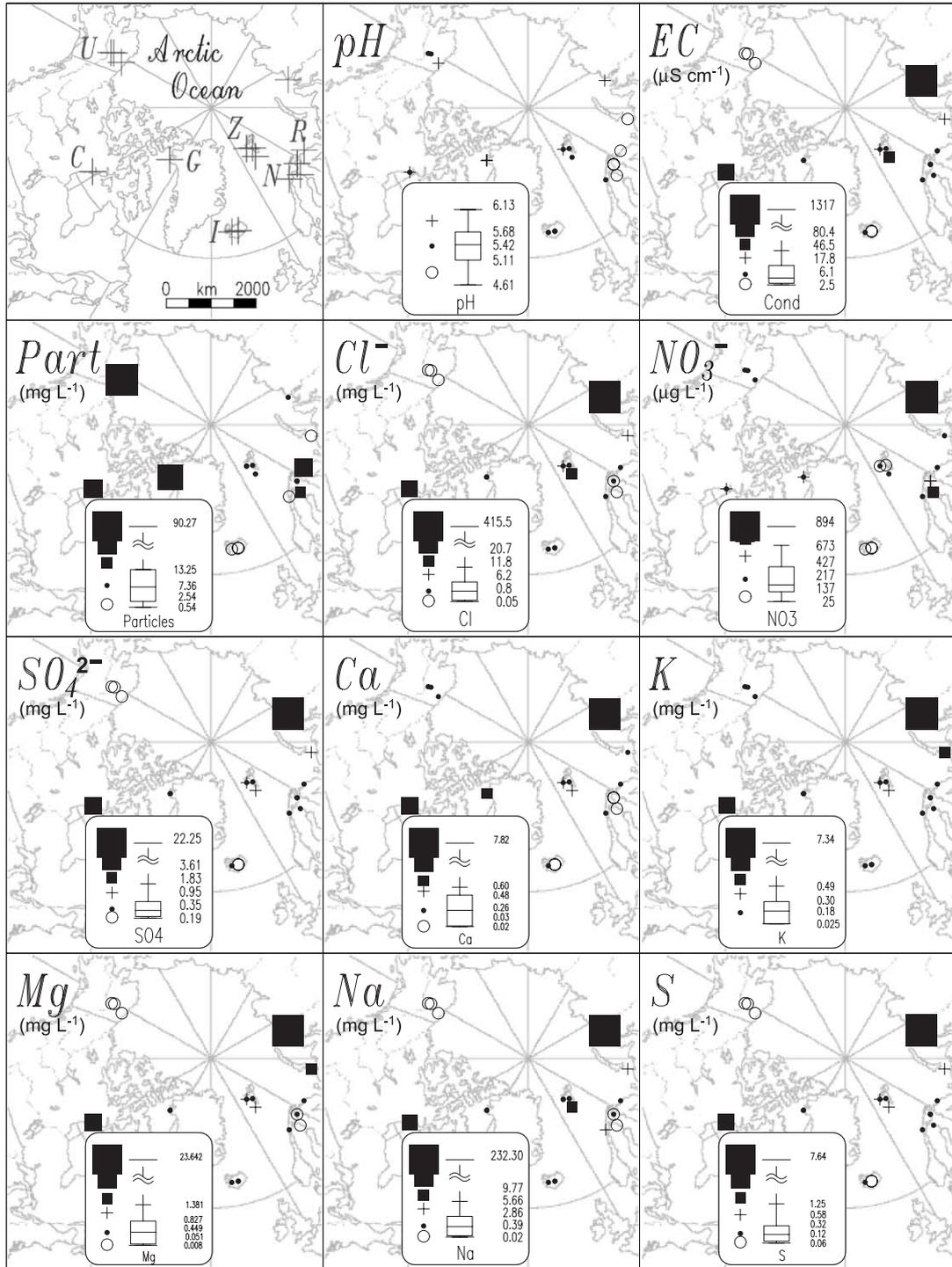


Fig. 2. Regional geochemical maps of arctic snow samples. 'Part' is the particles retained on a 0.45-µm filter; all other parameters are from filtered (<0.45 µm) meltwaters.

samples ($\text{pH} < 5.11$, the 25th percentile) are from the sector of northern Europe between Sweden and Nova Zembya (Fig. 2). Samples from more remote areas or higher latitudes tend to have a higher pH.

The samples are all (very) dilute, with EC values between 2 and 1320 $\mu\text{S}/\text{cm}$ (all but one sample are $< 500 \mu\text{S}/\text{cm}$). The most saline sample (R60) is from the vicinity of Dickson, not far from Norilsk, and may have contained more soluble rock/soil dust than the others, as shown by its high pH and high concentration of all major elements; it may also shown sign of slight contamination with deicing salts (see below).

Particle concentrations range from 0.5 to 90 mg/l. The highest concentrations of insoluble particles ($> 13 \text{ mg}/\text{l}$, the 75th percentile) are found in snow samples U72, G35, G34, C1, R58 and S68.

Major elements (Cl^- , NO_3^- , SO_4^{2-} , Na, Ca, Mg, K, S) range in concentrations from about 0.008 to 416

mg/l (Table 3). Histograms (not shown) and geographic distributions (Fig. 2) for the major elements are very similar, with generally highest concentrations (> 75 th percentile) at R60 and C1 (for all major elements), Z63 (Na, Cl^-), G34 (Ca), S68 (NO_3^-) and R57 (K, Mg). The range of concentrations observed was great, especially for Mg, Na and Cl^- , reaching four orders of magnitude. This indicates a large range of natural variation in the composition of snow in the Arctic.

The order of decreasing median concentrations of cations (in meq/l) was found to be Na (0.1244) \gg Mg (0.0369) $>$ Ca (0.0129) $>$ K (0.0047) $>$ H^+ (0.0038). The order of decreasing median concentrations of anions (in meq/l) was found to be Cl^- (0.1755) \gg SO_4^{2-} (0.0197) \gg NO_3^- (0.0035). These sequences are quite different from, if not opposite to, those found closer to more densely populated and industrialized places

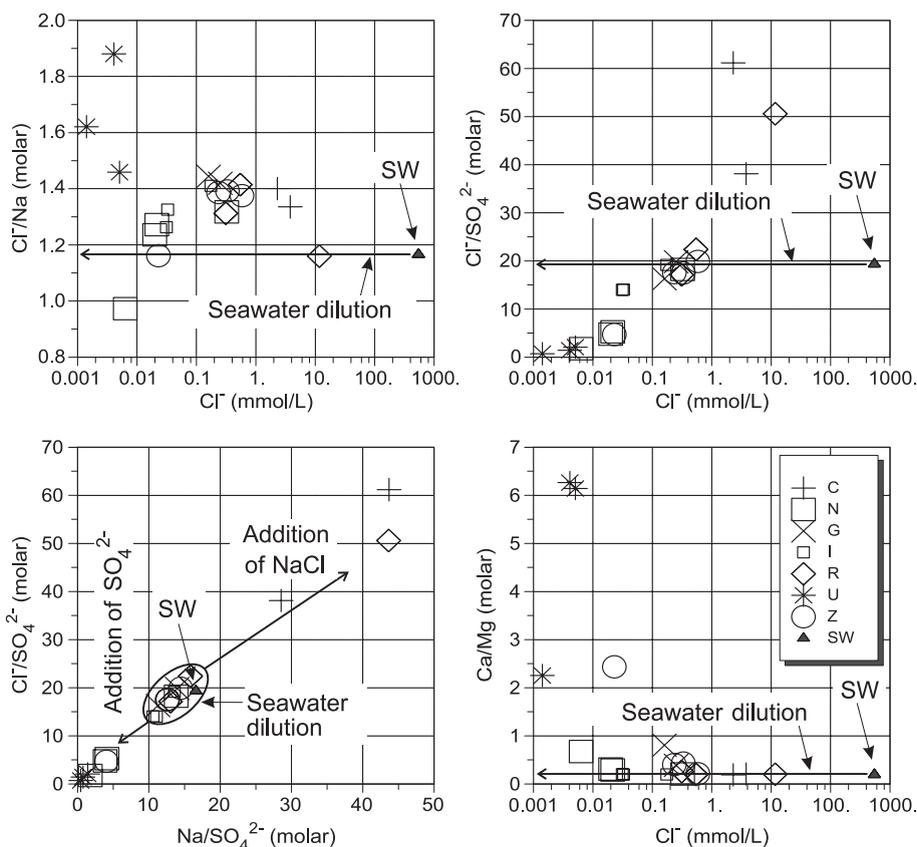


Fig. 3. Scatterplots of major elements of arctic snow samples ($< 0.45\text{-}\mu\text{m}$ meltwaters). Ratios based on mmol/l values. Intermediate log scale ticks are at $2 \times$, $4 \times$, $6 \times$ and $8 \times$ the labelled values. Location abbreviations as per Table 1. SW: seawater.

(e.g., samples M1–10 in Table 3; Turk et al., 2001), indicating that we were successful in obtaining largely uncontaminated, or background, snow samples.

Scatterplots of major elements show that snow composition is dominated by seawater dilution (as expected), but deviations from this behaviour (as brought out in Fig. 3) shed light on additional processes. Most (18 of 21) samples have Cl^-/Na (molar) ratios (slightly) higher than that of seawater (1.166). The samples with the highest Cl^-/Na ratios (>1.415 , the 75th percentile) are those from Alaska (1.881 for U72) and Greenland (1.419–1.444) (NB: The samples from Alaska are among the most dilute, see Table 3, and hence, the errors on their reported concentrations are greater, making interpretations more speculative, as explained above).

In order to explain these high Cl^-/Na ratios, one must look for sources with such characteristics or

processes that may increase the ratio from its original value close to seawater. Coal combustion contributes both Cl^- and Na to the atmosphere, usually in a ratio higher than that of seawater, up to a value of 2 (Wagner and Steele, 1989; Möller, 1990). Thus, samples with high Cl^-/Na ratios may reflect some contribution of atmospheric pollution from coal combustion plants either locally or more distant (Europe, Canada, USA). However, an estimate of the relative importance of this contribution necessitates rather detailed knowledge of the composition (ion concentrations) of this end member at the time and place of the snowfall event. Alternatively, Baisden et al. (1995) argued that aerosol with an original Cl^-/Na ratio of 1 may progressively increase its ratio by volatilization of HCl vapour and sedimentation of coarse particulate Na. This may lead to Cl^-/Na ratios >1 in the atmosphere and in snow, which has a greater affinity for

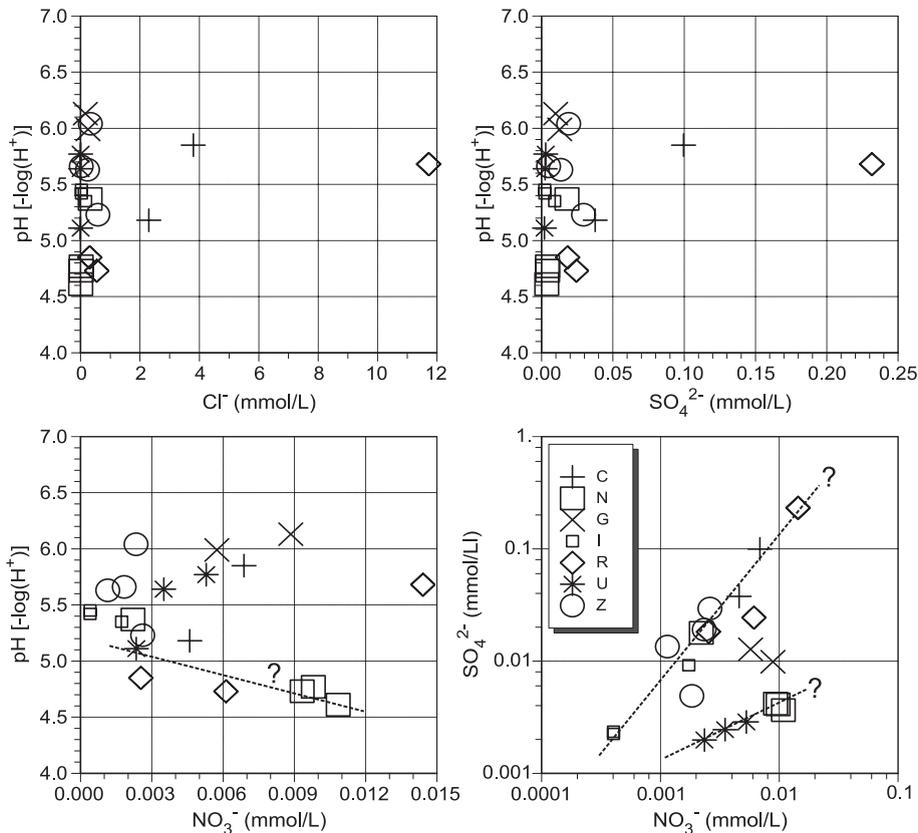


Fig. 4. Scatterplots of pH and major anions of arctic snow samples ($<0.45\text{-}\mu\text{m}$ meltwaters). Intermediate log scale ticks are at $2\times$, $4\times$, $6\times$ and $8\times$ the labelled values. Location abbreviations as per Table 1.

vapour phase pollutants. The lowest Cl^-/Na ratio (0.973) occurs in sample S68; this ratio is lower than it is in seawater and is nearly equivalent to that of halite (1.0).

Many samples have a $\text{Cl}^-/\text{SO}_4^{2-}$ (molar) ratio similar to that of seawater (19.346) (Fig. 3), but several have much lower ratios with the lowest ones from samples in Alaska (down to 0.713 for U70), three samples from the Nordic countries and one from Svalbard. Other samples (C2, R60, C1) have a $\text{Cl}^-/\text{SO}_4^{2-}$ ratio distinctly greater than that of seawater. It is interesting to note that, in contrast with the Cl^-/Na ratio discussed previously, the $\text{Cl}^-/\text{SO}_4^{2-}$ ratio increases fairly regularly with increasing salinity (or Cl^-). In order to interpret what this may be

caused by, we need to consider how Na behaves. The diagram of $\text{Cl}^-/\text{SO}_4^{2-}$ vs. $\text{Na}/\text{SO}_4^{2-}$ (Fig. 3) shows that the bulk of the samples preserve ratios close to those of seawater, thus reflecting only dilution of seawater (which conserves ion ratios). Some samples, however, show systematic trends of concurrent decreases or increases in these ratios. The same samples as above (three from USA, three Nordic, one Svalbard) form the trend with lower $\text{Na}/\text{SO}_4^{2-}$ and $\text{Cl}^-/\text{SO}_4^{2-}$ ratios, suggesting addition of SO_4^{2-} (removal of Na and Cl^- appearing unlikely). Again, this may be a consequence of a slight contribution of SO_2 , subsequently oxidised to SO_4^{2-} , from coal (or other fuel) combustion, consistent with the above. Both samples from Canada and one from

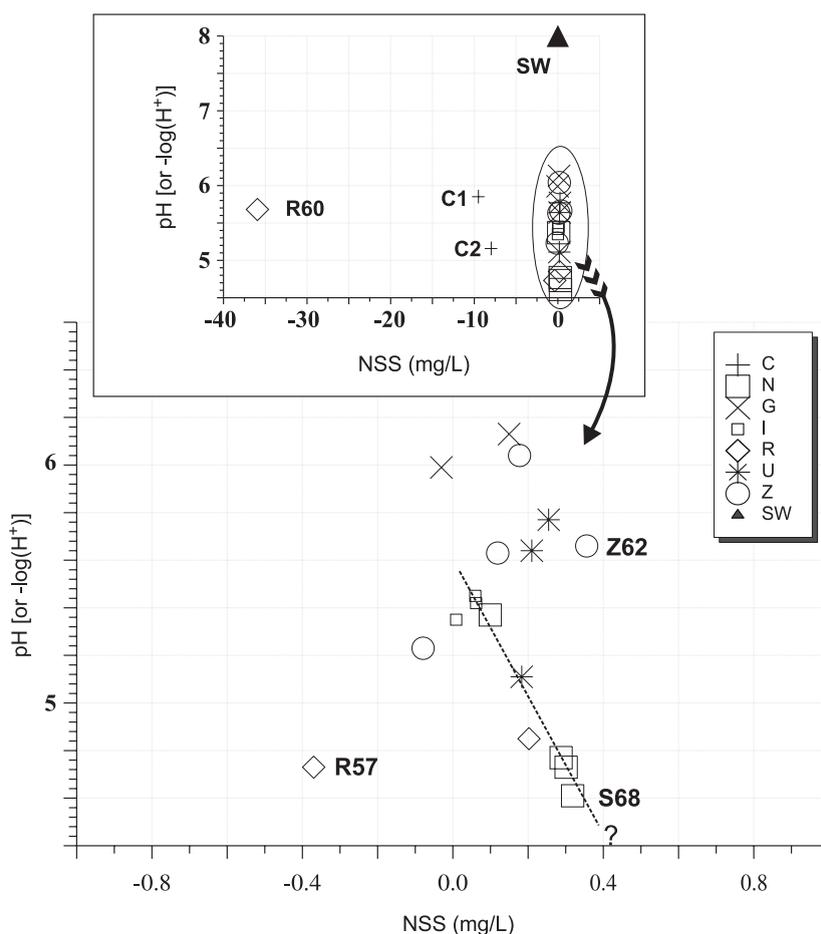


Fig. 5. Scatterplot of pH and non-seasalt SO_4^{2-} (NSS) of arctic snow samples ($<0.45\text{-}\mu\text{m}$ meltwaters). Location abbreviations as per Table 1. SW: seawater.

Russia (R60) have higher ratios, suggesting addition of Na and Cl^- (removal of SO_4^{2-} appearing unlikely). This may reflect a small contamination from NaCl (halite) aerosols from local deicing activities (Rankin Inlet has an airstrip, which was downwind of the sampling location; the Dickson sample was collected on driftice from a ship, whose deck may have been deiced).

The relationship between Ca, Mg and Cl^- (Fig. 3) shows that all but two samples have greater Ca/Mg (molar) ratios than seawater (0.194). This probably represents a contribution from mineral particles comprising calcium carbonate (calcite), which, where present, would be soluble in these dilute, acidic meltwaters. The highest Ca/Mg ratios (0.674, the 75th percentile, to 6.26, the maximum) are from samples from USA (all three), one from Svalbard (Z62), one from Greenland (G35) and one from Sweden (S68). The next highest are also from Svalbard and Greenland. Local rock (or soil) dust is likely the source of this Ca ‘excess’.

Relationships between pH and Cl^- or SO_4^{2-} (Fig. 4) show no obvious trend, suggesting the lack of a dominant ‘acidification’ process for the whole area. The six samples with the lowest pH (<5.11, the 25th percentile) are not necessarily associated with high Cl^- or SO_4^{2-} concentrations. The seven samples mentioned above with a slight SO_4^{2-} addition (three USA, three Nordic, one Svalbard) do not form a trend of decreasing pH with increasing SO_4^{2-} . This suggests that the additional amount of SO_4^{2-} that these samples contain is not sufficient to influence the acidity of the meltwaters, in contrast to interpretations based on local snow samples for example on Svalbard (Simões and Zagorodnov, 2001). In terms of NO_3^- , some samples (three Nordic, two Russia, one USA, one Canada, one Svalbard) do form a broad trend of decreasing pH with increasing NO_3^- concentration (Fig. 4), but the rest are rather scattered, or perhaps even define a rough trend of increasing pH. The strong correlation between pH (or H^+) and NO_3^- commonly observed in snow samples from areas with a higher population density at

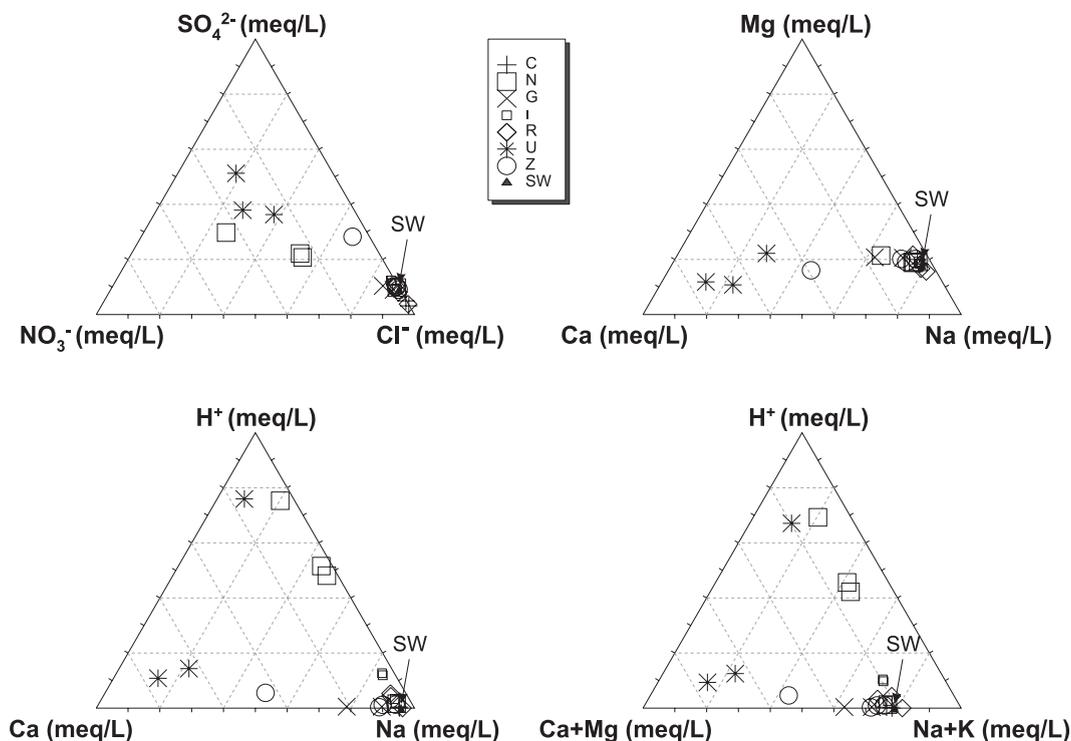


Fig. 6. Ternary diagrams of major cations and anions of arctic snow samples (<0.45- μm meltwaters). Proportions based on meq/l values. Location abbreviations as per Table 1. SW: seawater.

lower latitudes (e.g., Baisden et al., 1995; Turk et al., 2001) is not as obvious here, where the relationship appears to be more complex.

The diagram of SO_4^{2-} vs. NO_3^- (Fig. 4) indicates that most samples fall along one of two trends. One has a higher $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio (~ 17) and comprises two samples from Russia, two from Canada, two from Iceland, one of the Nordic and three from Svalbard. The other trend is characterised by a lower $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio (< 1) and comprises three USA and three Nordic samples. Other samples (two Greenland, one Svalbard, one Russia and one Iceland) have intermediate compositions. All these values are well below the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio of seawater (~ 40). The median $\text{SO}_4^{2-}/\text{NO}_3^-$ molar ratio of the snow samples is 5.29, but it decreases to between 0.34 (minimum) and 0.84 (25th percentile) in the samples from Sweden, Finland and Alaska, suggesting that NO_3^- might be a major source of ecosystem acidity during snowmelt (Schaefer and Driscoll, 1993) here.

Fig. 5 shows the relationship between non-seasalt SO_4^{2-} (NSS) and pH. NSS is calculated by assuming all the Cl^- to be of marine origin:

$$\text{NSS} = \text{SO}_4^{2-} - (0.14 \cdot \text{Cl}^-)$$

where 0.14 is the mass ratio $\text{SO}_4^{2-}/\text{Cl}^-$ in seawater. Three samples stand out immediately because they have very high deficits in SO_4^{2-} : R60, C1 and C2 (Fig. 5 inset). These are the samples suspected above of having experienced some contamination through deicing salts (NaCl). Thus, for these three samples, the

assumption inherent to the calculation of NSS is clearly not justified. Thus, looking more closely at the rest of the samples (Fig. 5 main), there is only a minor correlation of increasing NSS and decreasing pH, which holds for four Nordic, one USA, one Russia and two or three Iceland samples. For the bulk of the samples, however, one cannot conclusively show an overriding trend of acidification related to NSS. Thus, no evidence is found here for acidification processes to be operating at the arctic-wide scale of this survey.

Ternary diagrams for major anions and cations (Fig. 6) indicate that Cl^- and Na are commonly the dominant major ions. However, for some samples, other ions are also relatively important, even dominant: SO_4^{2-} and NO_3^- (for USA, three Nordic and one Svalbard samples), Ca (USA, one Svalbard) and, importantly, H^+ (one USA, three Nordic). The two Russian samples with low pH (R57 and R58) do not stand out on these ternary diagrams with a high relative importance of H^+ because they also contain high amounts of other major cations. It is also clear from Fig. 6 that Mg and K are of secondary importance as major cations relative to those discussed above.

The least-square regression between SO_4^{2-} and S concentrations (not shown) yields a slope of 2.94 ($r=1$) (Table 4), very similar to the $\text{SO}_4^{2-}/\text{S}$ mass ratio (2.99), indicating, as expected, that most S in the snow samples is oxidised and present as dissolved SO_4^{2-} .

Correlation coefficients between the various physical parameters and major elements (Table 4) indicate that pH is not strongly correlated with any other chemical variable under consideration. The highest

Table 4

Correlation coefficients (r) for the measured parameters in arctic snow samples ($n=21$)

	EC	Particles	Cl^-	NO_3^-	SO_4^{2-}	Ca	K	Mg	Na	S
pH	0.186	0.460	0.188	-0.160	0.206	0.249	0.188	0.190	0.184	0.202
Cond		-0.095	1**	0.564*	0.990*	0.997**	1**	1**	0.998**	0.993**
Particles			-0.093	0.165	-0.073	-0.048	-0.091	-0.091	-0.099	-0.075
Cl^-				0.565*	0.991**	0.997**	0.999**	1**	0.999**	0.994**
NO_3^-					0.550*	0.566*	0.562*	0.563*	0.569*	0.557*
SO_4^{2-}						0.990**	0.992**	0.991**	0.987**	1**
Ca							0.997**	0.997**	0.995**	0.993**
K								1**	0.997**	0.994**
Mg									0.997**	0.994**
Na										0.991**

Based on raw values in mg/l, except pH (pH units) and EC ($\mu\text{S}/\text{cm}$).

* Correlation significant at $p=0.01$ level.

** Correlation significant at $p=0.001$ level.

degree of correlation of pH values is with the particle content ($r=0.46$, which is significant at $p<0.05$), suggesting that dust acts to neutralise the acidity of the snowpack (see above), decreasing negative ecosystem impacts attending snowmelt in spring. EC does not correlate with the particle concentration of snow, suggesting that the meltwater's dissolved ions do not dominantly originate from dissolution of solid particles during melting of the samples. This shows that the wet component of precipitation is chemically quite independent of the dry precipitation component: more solute laden snow may or may not be dust-rich. The particle concentration does not correlate strongly, in fact, with any of the other variables. Finally, as expected, all major anions and cations are strongly correlated to each other ($p<0.01$ or $p<0.001$ in all cases).

6. Conclusions

Arctic snow samples were collected in 1997 from 17 localities in Norway, Sweden, Finland, Svalbard, Russia, Alaska, Canada, Greenland and Iceland. The pH of the meltwaters varies from 4.6 to 6.1 (median 5.4), the EC from <5 to $1317 \mu\text{S}/\text{cm}$ (median 17.9) and the particulate matter load from 0.5 to $90 \text{ mg}/\text{l}$ (median 7.4). The median concentration (in meq/l) of the major elements decreases in the order Cl^- (0.1755) $>$ Na (0.1244) \gg Mg (0.0369) $>$ SO_4^{2-} (0.0197) $>$ Ca (0.0129) $>$ K (0.0047) $>$ H^+ (0.0038) $>$ NO_3^- (0.0035). This sequence is quite different from that typical of snow collected closer to more densely populated and industrialized places.

Snow composition varies regionally by up to four orders of magnitude in terms of major element concentrations. Therefore, while attempting to reconstruct past changes in snow (or ice) composition, it is important to consider that at least part of the reported variability can depend on geographic location and weather pattern changes (influence of seaspray, etc.) from winter to winter or within any season's accumulated snowpack.

The overall major element composition of meltwaters is consistent with seawater diluted to various degrees, indicating the dominant influence of this natural source of atmospheric aerosols over the whole region. However, departures from seawater dilution trends indicate the subtle influence of coal combustion

emissions (addition of SO_4^{2-} and Cl^- relative to seawater, observed in Alaska, Finland, Sweden, Svalbard) or deicing activities ($\text{Na}/\text{SO}_4^{2-}$ and $\text{Cl}^-/\text{SO}_4^{2-}$ ratios higher than seawater, observed in Canada, Russia). These probably result from local (proximal) point-sources imparting only a weak contamination to the surrounding snow.

Mineral dust inputs are detected by 'excess' Ca contents relative to seawater dilution trends, as observed in Alaska, Svalbard, Greenland and Sweden. There is no overall correlation between meltwater pH and total SO_4^{2-} concentration, although some samples define a trend of decreasing pH with increasing non-seasalt SO_4^{2-} . A weak local relationship exists between pH and NO_3^- in Sweden, Finland and Russia.

No arctic-wide contamination or acidification process was detected, suggesting that long-range atmospheric transport is not operating at this scale.

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