

## SPATIAL AND TEMPORAL VARIABILITY OF SURFACE SNOWFALL AND SNOWPACK CHEMISTRY IN CENTRAL ONTARIO

by

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### ABSTRACT

The physical and chemical structure of the snowpack near North Bay, Ontario was examined during the winter of 1984. Precipitation chemistry measurements were also made. A marked areal uniformity was noted in the layered structure of the snowpack and in the vertical variation of the chemical composition. In late January, pH values of the snowpack varied from ~4.1 at the surface to ~4.8 near the ground. After rain and a major thaw in February the pH was near 4.8 throughout. Nitrate concentrations exceeded those of sulfate in the snowpack. The molar concentration ratio of  $\text{SO}_4^{2-}/\text{NO}_3^-$  was typically 0.5.

Samples of precipitation from six sites had pH values ranging from 3.4 to 5.2.  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  equivalent ratios were <1 in snow and near 1 or >1 in rain. The chemical composition of the precipitation was closely related to the airmass trajectory. Southerly trajectories yielded the lowest pH values and highest pollutant concentrations. The one-month period from 20 January to 21 February had a  $\text{SO}_4^{2-}$  deposition of  $0.2 \text{ g m}^{-2}$  and a  $\text{NO}_3^-$  deposition of  $0.35 \text{ g m}^{-2}$ . For  $\text{SO}_4^{2-}$ , this deposition would be about one-twelfth the expected annual deposition and for  $\text{NO}_3^-$  about one-fifth.

### 1. INTRODUCTION

The results presented in this paper form part of the data set obtained during the Acid Snow Project (ASP). Operations were conducted from the air base at North Bay, Ontario from 15 January to 25 February 1984. The general objective of the ASP was to obtain chemical and micro-physical databases characterizing winter clouds and precipitation.

The primary instrumentation platforms for the experiment were two instrumented research aircraft, a Twin

Otter and a DC-3. In addition, there was a ground research station at Powassan about 30 km south of North Bay. On two days during ASP, a helicopter was used to make snow-core measurements across the project area.

This paper will present results concerning the variations in space and time and the chemical composition of precipitation and the snowpack.

### 2. EQUIPMENT AND PROCEDURES

Samples from specific snow events were obtained at the six sites shown in Figure 1. The sites form an east-west line of three stations and a north-south line of four stations. Each site was separated from its nearest neighbour by ~45 km. Two containers for the collection of precipitation, separated by ~5 m, were set up at each site; they were made of commercial plastic with an opening 48 cm wide. A strong, sterile plastic bag was placed in the container at the start of each sample period. The bag, which was handled with sterile laboratory gloves, was folded over the edge of the container and held in place with an elasticized cord. The collected samples were returned to North Bay, melted, and the chemical analysis was begun within 24 h.

At each site snow-pits were dug several times during the period of the project. The structure of the snowpack was noted, then the outer surface was removed with a sterile glove and samples taken from each layer of interest.

The seven snow-core sites visited by helicopter are shown in Figure 1. The snow cores were separated into segments of interest, bagged and stored in the helicopter. The cores were collected by means of a Plexiglas snow-corer made from a semi-cylindrical tube 1 m long and 16 cm in diameter.

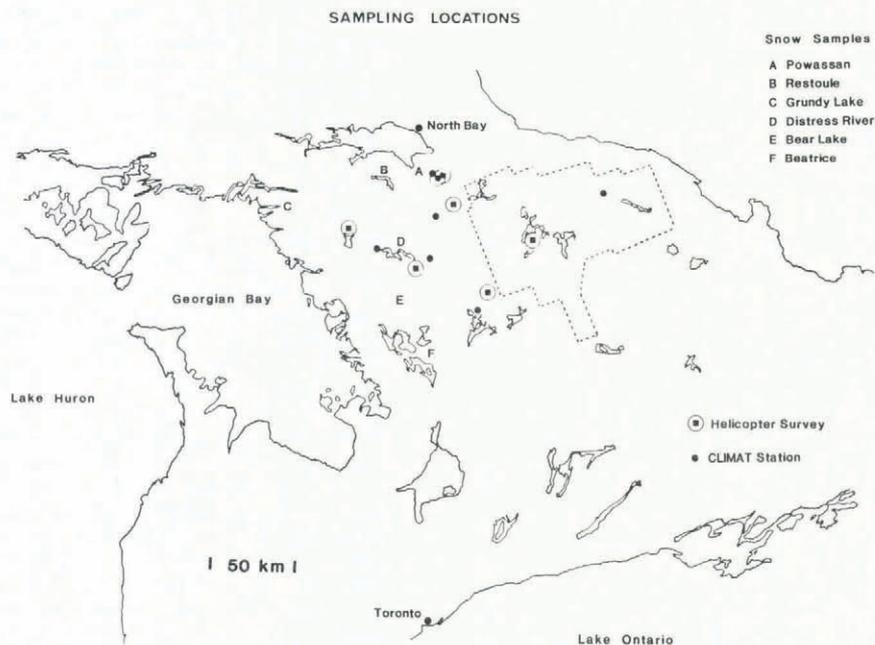


Fig.1. Map of the project area.

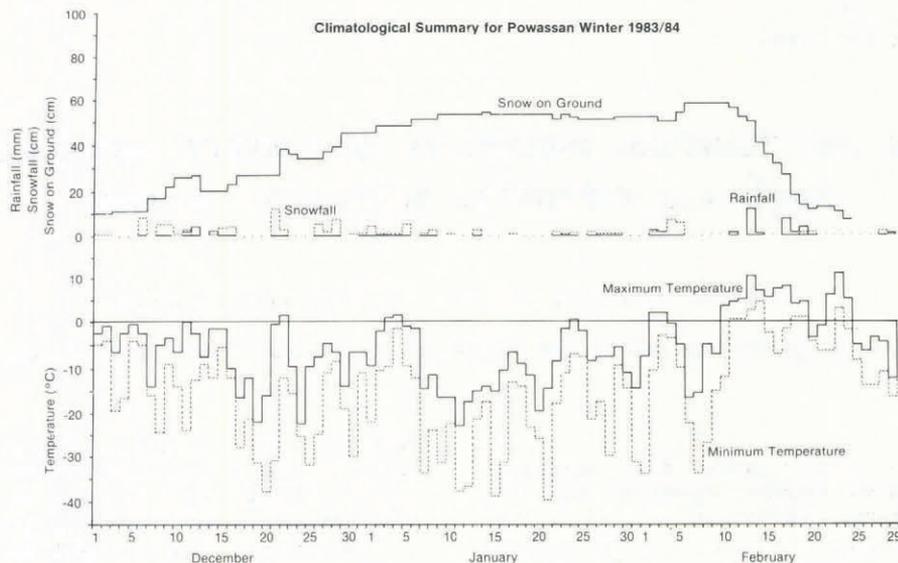


Fig.2. Weather summary for Powassan.

### 3. ANALYTICAL TECHNIQUES

Ion-exchange chromatography was used for the routine analysis of cations and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by atomic absorption flame photometry or by a DCD emission spectrograph. Hydrogen ion concentrations (pH) were measured using moderate flow glass electrodes.

As a result of inter-laboratory comparisons, the expected uncertainty in the pH measurements is  $\pm 0.05$  pH units; for the measured ion concentrations, it is  $\pm 0.03$  ppm or 2%, whichever is greater. Hence, the probable error in the  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  equivalent ratios is expected to be less than  $\pm 0.02$  for high concentrations and less than  $\pm 0.07$  for low concentrations. The detection limits were 0.05 ppm for the ion chromatograph measurements and 0.02 ppm for the atomic absorption measurements. Rinse samples of the bags and bottles were below these limits.

The anion-to-cation comparison for the precipitation and snow-pit data set indicate a reasonable balance (within 10%) for samples not contaminated by road salt. Contaminated samples ( $\text{Ca}^{2+} > 2$  ppm and  $\text{Cl}^- > 5$  ppm) showed a consistent difference between the anion and cation sums, with an anion-to-cation ratio between 0.4 and 0.6, and probably is explained by uncertainty in the pH measurement. If the ion imbalance is due solely to bias in the  $\text{H}^+$  concentration, measured pH values corrected for this ion difference would be typically 0.25 and as much as 0.5 pH units larger.

### 4. GENERAL WEATHER CONDITIONS

The six-week project experienced a period of very cold temperatures in mid-January, normal conditions in late January and early February, then temperatures from 10 to 15°C above the normal maximum from mid-February to the end of the project. Figure 2 presents a summary of the winter weather conditions at the Powassan climate station. Of particular interest are the melt events associated with above-freezing temperatures from 23 to 24 January, 1 to 4 February and 9 to 24 February. Figure 2 also shows the duration and amounts of precipitation. A change in precipitation type from snow to rain occurred on 9 February. The rain persisted through to 19 February.

Local surface winds are important in so far as they reflect low-level air mass trajectories. The trajectories are a major control factor for pollution levels in precipitation. The wind roses for January and February at North Bay show an above-normal frequency of south-westerly and southerly winds, near normal northerly winds and below normal frequencies of westerly and easterly winds.

The total depth of the snowpack in late January varied across the project area. The depth decreased from west (Georgian Bay) to east by ~35% and decreased from south to north by ~40%. The decrease in snowpack depth (e.g. Fig.2) in mid February was similar at all sites. The data as

a whole show a notable uniformity in gross snowpack changes over the entire project area. This implies a uniformity in the controlling meteorological factors during the project period over the ~150 km<sup>2</sup> area.

### 5. SNOWPACK STRUCTURE AND CHEMISTRY

#### 5(a). Snow-pit data in late January

Figure 3 shows an example of the snowpack structure from late January at Bear Lake. The total snowpack depth was 84 cm. The very solid ice layer, from 22 to 26 cm, was evident everywhere in the area under study. It is probably associated with the thaw-freeze cycle and the rain that occurred in the area in mid-December. Above and below this layer are regions of rounded grains consistent with the small ( $< 0.1^\circ\text{C cm}^{-1}$ ) temperature gradient in the snowpack. The thin ice layer at 59 cm was probably created by the thaw of 3 to 4 January. The upper part of the snowpack contained crystals whose angularity was still evident. This region consisted of snow that had fallen in the week before the digging of the snow-pit. The dendrites on the surface were falling as the pit was being examined.

Six representative samples (Fig. 3) were removed from the pit for chemical analysis. The pH values were found to increase from snow to ground surface; that is, the most acidic snow was near the snowpack surface. The most likely reason for this is that meltwater moving through the snowpack removes ionic species that contribute to the acidity of the snowpack (Johannessen and Henriksen 1978). The lowest part of the snowpack is older and thus has experienced more meltwater movement. Frequently, but not always, an ice layer such as the lower one in Figure 3 exhibited a higher pH than layers on either side of it. Presumably, the ions removed from the snowpack are deposited in the soil since these mid-winter melts are not associated with significant run-off.

These late-January, early-February snowpacks exhibited  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  equivalent concentration ratios that increased from values of ~0.3 near the snowpack surface to ~0.8 near the ground. The six samples in Figure 3 had ratios (top to bottom) of 0.38, 0.32, 1.04, 0.64, 0.97 and 0.85. Nitrate clearly dominates sulfate in the snowpack in agreement with the snowfall data as we will see below. The two layers where  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations are almost equivalent (ratios of 1.04 and 0.97) are the ice layers.

A comparison of the surface snowpack chemistry to that of recent snowfalls shows good agreement. The top snowpack (Fig.3) sample had pH: 4.0,  $\text{SO}_4^{2-}$ : 1.82 ppm and  $\text{NO}_3^-$ : 6.15 ppm. The snow that fell during the previous two days at the site had pH: 4.2,  $\text{SO}_4^{2-}$ : 1.06 ppm,  $\text{NO}_3^-$ : 4.34 ppm. The snow falling at the time that the surface sample was taken had  $\text{SO}_4^{2-}$ : 3.82 ppm and  $\text{NO}_3^-$ : 8.13 ppm (pH is not available). Clearly a mix of the event snow samples could produce the snow at the top of the pack.

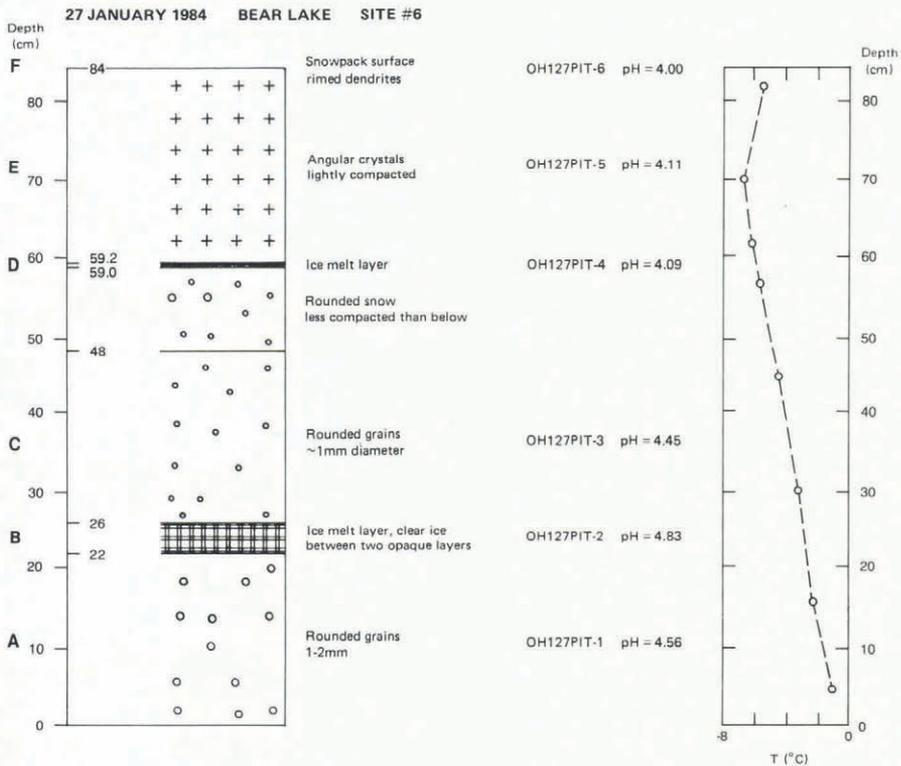


Fig.3. Bear Lake snow-pit showing structure, pH and temperature, 27 January 1984. The sample numbers are given beside the layers from which they were taken.

5(b). Snow-pit data in mid-February

Figure 4 shows the structure of the snow-pit near Bear Lake on 17 February 1984. This was during the latter part of the major February melt/rain event. The differences from Figure 3 are pronounced.

The snowpack is now isothermal and close to zero throughout. The depth has been reduced by almost one-half, from 84 to 46 cm. The ice-melt layer at 21 cm is still visible and relatively solid. The rest of the snowpack is formed of wet coarse snow.

The pH values have risen throughout the snowpack and are more uniform with depth. The  $SO_4^{2-}$  to  $NO_3^-$  equivalent ratios from top to bottom are 0.52, 0.79, 1.02 and 0.99. These values are somewhat higher than on 27 January. The lowest layer has lost both  $SO_4^{2-}$  and  $NO_3^-$ , from 1.03 and 1.56 ppm, respectively, on 27 January down to 0.79 and 1.03 ppm on 17 February. Layer 2, the ice layer, is almost exactly the same: 0.53 and 0.71 ppm compared to 0.53 and 0.67 ppm. Direct comparisons are not possible for the upper layers.

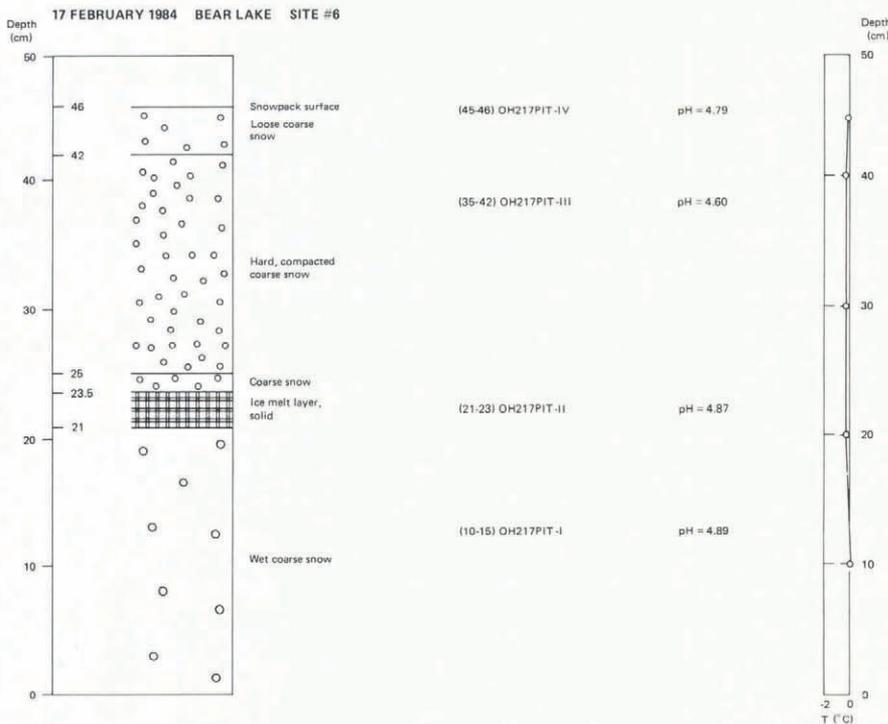


Fig.4. Bear Lake snow-pit showing structure, pH and temperature, 17 February 1984. The sample numbers are given beside the layers from which they were taken.

Even though the rain contained high ionic concentrations (see below) the net effect of the meltwater and the rain was to reduce the ionic concentrations in the snowpack.

6. SNOW CORE DATA

6(a). Introduction

Two helicopter snow surveys (28 January and 7 February 1984) examined five sites on each survey and a total of 77 snow cores was analyzed.

In all cases the ice layer shown at 22 to 26 cm in Figure 3 was taken to be the bottom level of the core. The region above this layer was divided into two or three sections for chemical analysis.

The agreement between the physical and chemical structure of the snowpack as seen by the snow-pits (see section 5) and the helicopter snow cores was generally very good. Table I serves as an indication of the level of agreement in the snowpack chemistry. The snow core and snow-pit samples were obtained on the same day. The pit data are from six levels (ground to snow surface), whereas the snow core data are from three levels above 26 cm. The corresponding pit and core levels are grouped together. The comparison is satisfactory considering that the sites were separated by 40 km, different sampling techniques were used, and different laboratories performed the chemical analyses. For example, the mean difference in pit and core NO<sub>3</sub><sup>-</sup> values for the top and bottom levels was 0.08 ppm and in SO<sub>4</sub><sup>2-</sup> values it was 0.21 ppm. The middle level cannot be compared directly but certainly some combination of the two pit samples could produce the observed core values. As was noted in section 3, the snow core pH values are low by ~0.25 pH units.

6(b). Sample uniformity

Three snow cores were analyzed from each site. The cores were taken at distances several metres apart. Typical coefficients of variation (ratio of standard deviation to mean) were 10% or less, except where concentrations were very low. The practice of taking up to five cores at each site and analyzing three of them enabled any irregularities in sampling or sample analysis to be identified.

6(c). Inter-site variability

A comparison was made of snow cores from five different sites (Fig.1) obtained on the same day. Coefficients of variation were normally 25% or less for the major ions and for pH. This confirms the uniformity of the snowpack chemistry within the project area noted above.

7. PRECIPITATION EVENTS

7(a). Project period overview

The variation of pH in precipitation with time was examined. A pH value near 4 was typical. The extremes observed at Powassan were 3.4 and 4.7. The extreme pH values observed at all six sites were 3.4 and 5.2.

Precipitation episodes characterized by three or four

samples showed a variety of time histories. The snow event of 21 to 25 February showed a marked decrease in pH with time. The snow event of 3 to 6 February exhibited relatively constant pH. The rain event from 13 to 14 February, at the start of the marked warming trend, showed a rapid increase in pH. The rain and snow event from 18 to 21 February, at the end of the project, also showed a rapid rise in pH. Examination of these pH trends shows that they can often be explained in terms of air mass trajectories. The event at the end of the project will be discussed in some detail below.

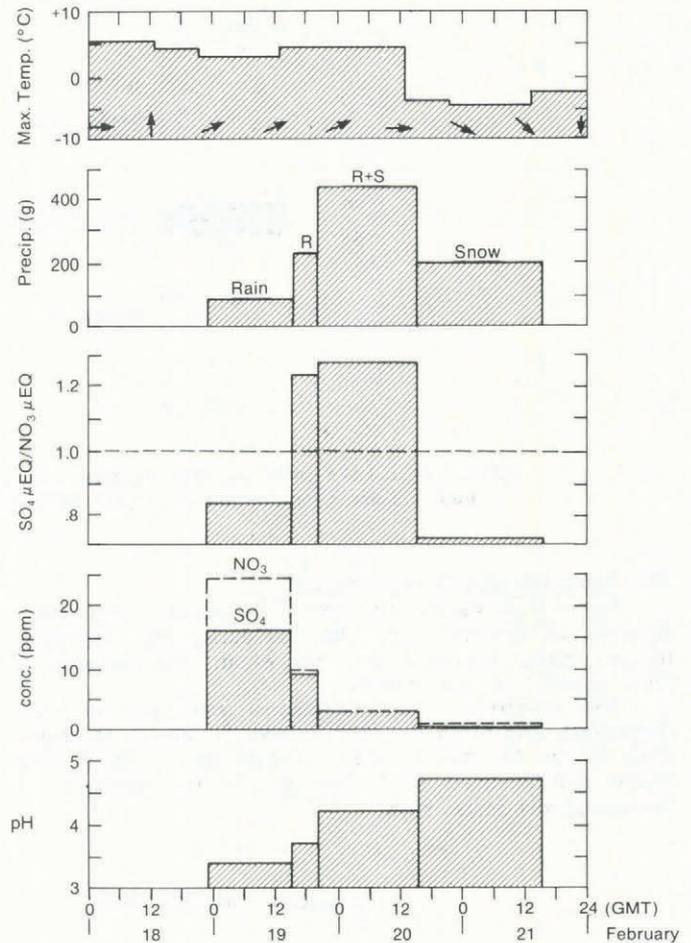


Fig.5. Summary of precipitation episode at Powassan, 18-21 February 1984 (see text for details). The small arrows give the direction from which the 925 mbar wind originated 48 h previously.

TABLE I. COMPARISON OF THE SNOW CORE AT POWASSAN TO THE SNOW-PIT AT RESTOULE, 28 JANUARY 1984 (The core was separated into three levels; the pit samples were grouped with the corresponding core levels. Pit samples 5 and 1 were taken below the core.)

	Concentration (ppm)								
	pH	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Core top	4.0	0.28	3.13	0.71	0.14	0.13	0.02	0.06	0.09
Pit sample 4	4.3	0.24	2.99	0.79	0.05	0.10	0	0.23	0.01
Core middle	4.1	0.19	2.04	0.80	0.14	0.13	0.03	0.66	0.12
Pit sample 6	4.4	0.11	3.15	1.37	0.03	0.54	0	0.14	0.01
Pit sample 3	4.5	0.16	2.65	0.70	0.07	0.09	0	0.45	0.02
Core bottom	4.2	0.10	1.85	0.77	0.09	0.09	0.02	0.68	0.17
Pit sample 2	4.6	0.09	1.87	1.11	0.15	0.09	0	0.24	0.04
Pit sample 5	4.7	0.04	1.00	0.70	0	0.08	0	0.09	0
Pit sample 1	4.7	0.07	1.35	0.48	0.02	0.09	0	0.13	0.01

The ratio of the  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  concentrations was below 1 for each of the snow samples. Values below 0.5 are typical and are in good agreement with the ratios found in the upper part of the snowpack. During the warm weather of mid- to late-February the situation was quite different. The  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  ratio for each sample was near or in excess of 1. The relative importance of sulfate to the acidity of the snowpack was much higher. These ratios are much closer to those found in the summer.

#### 7(b). Episode of 18 to 21 February

Figure 5 shows that this was a period of rapidly increasing pH. As the pH increased, both the  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations decreased rapidly. Initially, and at the end of the period,  $\text{NO}_3^-$  was the dominant species. In the middle, the  $\text{SO}_4^{2-}$  concentration was higher. The small arrows on the figure show the direction from which the air at 925 mbar (~760 m) originated 48 h previously.

Figure 6 presents the trajectories for this period in more detail. The synoptic weather pattern was characterized

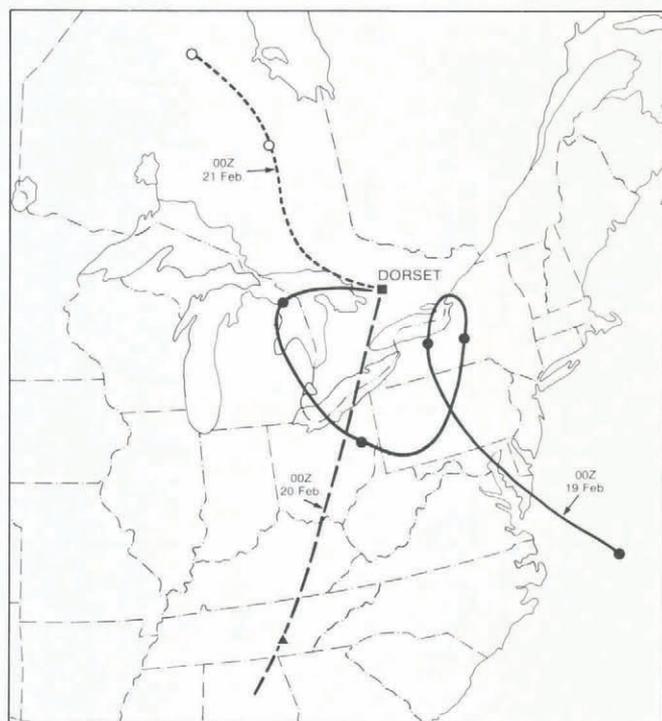


Fig. 6. Trajectories (925 mbar) showing history of air arriving on three consecutive days. Marker points are at 24 h intervals.

by a slow-moving, filling, low-pressure area. As a result, air (925 mbar) arriving in the project area on 19 February had a slow looping trajectory taking a total of 4 d to cross the regions where the source of pollution was highest, around the lower Great Lakes. By 1200 GMT on 19 February, rain ahead of a deepening low reached the region and contained high concentrations of both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  giving a very low pH of 3.4.

By midnight on 20 February the windflow had increased bringing maritime tropical air from the south-south-west. A shorter residence time over the regions

associated with the emission of pollution, coupled with depletion by rain en route, reduced the  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations in the rainfall by a factor of 7. The rain became mixed with snow by 0500 GMT on 20 February, then intermittent periods of snow continued through until late on 21 February. As the low moved north-east, winds veered first to the west and then north-west, with air arriving from north-west Ontario during the last sampling period which gave "clean" snow containing background levels of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  and having a pH of 4.7.

#### 8. DEPOSITION ESTIMATES

Estimates of the wet deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were made at two locations having the most complete data sets. A plot of the cumulative precipitation measured in the snow-collector containers at Powassan and Distress River versus the cumulative precipitation at the nearest climate station showed a fairly consistent container deficit of about 25%. The deposition estimates were, therefore, made using the precipitation record from the climate station and the concentrations measured in the snow-collector containers. The results are shown in Table II. Both the total amount of precipitation and the species concentrations were higher at the more southerly station giving deposition rates at Distress River about double those for Powassan. Extrapolating these monthly average rates ( $0.2 \text{ g m}^{-2}$  for  $\text{SO}_4^{2-}$  and  $0.35 \text{ g m}^{-2}$  for  $\text{NO}_3^-$ ) gives an annual  $\text{SO}_4^{2-}$  wet deposition close to that obtained from routine monitoring networks. But for  $\text{NO}_3^-$ , the extrapolation gives two to three times the measured annual deposition (Barrie and Hales 1984). In other words, the ratio of  $\text{NO}_3^-$  to  $\text{SO}_4^{2-}$  being wet-deposited during this mid-winter period was more than double the average annual value. It is also interesting to note that about half of the total deposition of both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  during this period occurred during the extended rain events of 11 to 14 February at Distress River and 17 to 19 February at Powassan.

The amounts of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  present in the snowpack in late January were  $\sim 0.2 \text{ g m}^{-2}$  ( $2 \text{ kg ha}^{-1}$ ) for  $\text{SO}_4^{2-}$  and  $\sim 0.5 \text{ g m}^{-2}$  ( $5 \text{ kg ha}^{-1}$ ) for  $\text{NO}_3^-$ .

#### 9. DISCUSSION AND SUMMARY

The surface measurements associated with an airborne study of wintertime precipitation have been described in this paper. The main observations and conclusions pertaining to the snow chemistry are summarized below.

- (i) It was shown that snow-pits and snow cores are compatible techniques for determining the chemistry of the snowpack.
- (ii) In late January the pH of the snowpack decreased from  $\sim 4.1$  at the surface to  $\sim 4.8$  at ground level. In mid-February, after a major thaw and period of rain, the pH was relatively constant throughout the snowpack at  $\sim 4.8$ .
- (iii) Nitrate concentrations exceeded those of sulfate in the snowpack. The sulfate-to-nitrate ratio, in the absence of rain or a major thaw, was lowest near the snowpack surface and increased towards ground-level. On 28 January the five snow-core sites had an average  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  equivalents ratio of  $0.32 \pm 0.05$  near the snowpack surface and  $0.55 \pm 0.06$  at the lowest measured level. The values for the unmelted upper part of the snowpack are well below the mean ratio of  $0.63 \pm 0.22$  found by Barrie and Vet (1984) for an area extending from Georgian Bay to Quebec city in 1981. But the present data agree well with the two values (0.44 and 0.35) obtained from the present project area. Thus

TABLE II. SUMMARY OF THE PRECIPITATION AMOUNT, CONCENTRATION AND WET DEPOSITION OF  $\text{SO}_4^{2-}$  AND  $\text{NO}_3^-$  FOR 20 JANUARY TO 21 FEBRUARY 1984

Site	Total precipitation (mm)	Precipitation weighted concentration ( $\mu\text{eq l}^{-1}$ )		Total deposition ( $\text{g m}^{-2}$ )	
		$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$
Powassan	60	47	65	0.14	0.24
Distress River	80	74	96	0.28	0.47

$\text{SO}_4^{2-}/\text{NO}_3^-$  ratios may show persistent geographical differences from year to year. On 7 February, after rain and a thaw, the corresponding values were  $0.73 \pm 0.11$  and  $0.57 \pm 0.09$ . At the very bottom of the snowpack the ratios from the snow-pits were  $0.64 \pm 0.19$  in January and  $0.77 \pm 0.17$  in February.

(iv) Variations in concentration of the major ions between snow cores at one site yielded standard deviations <10% of the mean.

(v) Examination of snow cores from five different sites across the  $22500 \text{ km}^{-2}$  area showed good agreement in the chemical structure, yielding standard deviations <25% of mean concentrations in agreement with Barrie and Vet (1984).

(vi) The precipitation samples collected at the six sites had values ranging from 3.4 to 5.2. A value near 4 was typical. The chemistry of the precipitation was closely related to the airmass origin and the nature of the trajectory. The highest  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations and the lowest pH values were associated with southerly trajectories.

(vii) The chemistry of the upper part of the snowpack was consistent with the chemistry of recent snowfalls.

(viii)  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  ratios were <1 in snow and near 1 or >1 in rain.

(ix) The deposition of  $\text{SO}_4^{2-}$  on the surface by precipitation during the six week project was estimated to be  $\sim 0.2 \text{ g m}^{-2}$ . The deposition of  $\text{NO}_3^-$  was  $\sim 0.35 \text{ g m}^{-2}$ .

(x) The  $\text{SO}_4^{2-}$  available in the snowpack before the mid-February melt was estimated to be  $0.2 \text{ g m}^{-2}$ , while the  $\text{NO}_3^-$  available was  $0.5 \text{ g m}^{-2}$ .

#### 10. ACKNOWLEDGEMENTS

The authors would like to thank all of the participants in the Acid Snow Project for their cooperation in the collection of the data contained in this paper. In particular, the work of Craig Donovan, Jim Grabenstetter and Brian Handy of Ontario Hydro was greatly appreciated as was that of the Concord Scientific Corporation, who conducted the helicopter surveys.

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