

THE CHEMICAL CHARACTERISTICS OF SNOW COVER IN A NORTHERN BOREAL FOREST DURING THE SPRING RUN-OFF PERIOD

by

H.G. Jones and W. Sochanska

(INRS-Eau, Université du Québec, C.P. 7500, Sainte-Foy, P.Q. G1V 4C7, Canada)

ABSTRACT

An intensive snow-cover survey at Lake Laflamme, Quebec, during the spring of 1983 showed that wet deposition in the form of rain, which was a dominant phenomenon during the 1983 melt season, gave rise, according to the intensity and chemical quality of the precipitation, to both losses and gains of ion loads (meq m^{-2}) in the snowpack. Mean values for the daily wet deposition loadings ($\text{meq m}^{-2} \text{ d}^{-1}$) of ionic species associated with atmospheric aerosols (H^+ , SO_4^{2-} , NO_3^-) were of approximately the same magnitude as the daily changes in gains recorded in the snow cover during the melt period. In contrast, the mean value for the contribution by wet deposition to the total loads of K^+ and PO_4^{3-} in the snow cover was far outweighed by the gains which were observed at the same time. The expected losses for the snowpack, calculated from the sum of the total loads stocked in the pack at the beginning of the melt period and the total loads in precipitation during the melt period, were lower than the sum of the actual losses observed for all ionic species except H^+ . The increases (%) in the loads for the major anions Cl^- , NO_3^- and SO_4^{2-} were comparable (25 to 32%). The results suggested that dry deposition either directly by aerosol interaction with the snow cover or indirectly by adsorption on organic material followed by leaching during the melt period, or by a combination of both, was a major factor in the increases observed. The values for the increases in loads for Ca^{2+} , NH_4^+ , Mg^{2+} and Na^+ (50 to 287%) probably represented, in addition to leaching of local debris, the exudates of cellular material from the cell plasmolysis of detrital organic debris. High rates of in-pack production, however, were characteristic of Al^{3+} , Mn^{2+} , K^+ and PO_4^{3-} which showed substantial increases in pack loads (480 to 750%). These increases cannot be accounted for by any local phenomena other than the dissolution or microbiological degradation of organic debris. It is suggested that ion exchange capacity of both particulate and soluble organic material led to a decrease in pack acidity; this phenomenon should thus be considered as a major factor in all attempts to model acid rain fluxes through boreal forest systems.

INTRODUCTION

The acidity of atmospheric precipitation in north-eastern North America (Likens and Butler 1981) has been identified as the prevailing factor in the acidification of poorly buffered surface waters in both the north-eastern United States and eastern Canada (Wright 1983). In the latter region, snow, which covers the ground for 5 to 9 months of the year, accumulates acidic aerosols by both wet and dry deposition during the winter period. The subsequent spring season is characterized by the rapid release of pollutant loads by the snowpack (Johannessen and Henriksen 1978) leading to high acidity values in surface waters and concomitant stress conditions for the aquatic biota (Driscoll and others 1980).

Although the major source of the acidic input to the snow cover is the deposition of SO_4^{2-} and NO_3^- aerosols transported over long distances from the industrial areas of both eastern Canada and eastern and

mid-western United States (Altshuler and McBean unpublished) local characteristics of watersheds also influence the acidity of the snow cover in winter (Jeffries and Snyder 1981, Jones and others 1984). In the Laflamme watershed of Quebec, where conifer stands are predominant, Jones and others (1984) found that, although the concentrations of ionic species (K^+ excepted) in incident snowfall was, in general, little affected by the canopy, the concentration of some ionic species (H^+ , K^+ , PO_4^{3-} , NH_4^+) in the snow on the ground showed unexpected temporal and spatial variations. It was suggested that organic debris deposited from the canopy during and between individual precipitation events could be the source of some of the changes observed.

Dry deposition of micron and submicron acidic aerosols (Ibrahim and others 1983) and larger dust particulates of a local nature (Popp and others 1982) are already known to play a role in the evolution of the chemical composition of snow cover. The local deposition of debris from the canopy, however, can be appreciable in the boreal forest; its presence may dominate other deposition to such an extent that problems are encountered both in sampling procedures and in the subsequent interpretation of the data relating the quality of incident precipitation with that of the snowpack (Jeffries and Snyder 1981, Jones and others 1984).

In the study of the role that snow cover at Lake Laflamme plays in both the retention and the release of acidic pollutants into the stream tributaries at springtime, the influence of the local deposition of organic matter on the snow surface cannot be ignored. Thus, during the spring of 1983 we carried out a snow-cover survey at Lake Laflamme, Quebec, with the purpose of determining the impact of the coniferous stands on the chemistry of the snowpack during both premelt and melt periods. The main objective of this study was to establish the relative importance of wet and dry deposition (atmospheric aerosols, dust and organic debris) to the total loads of ionic species in the snow cover of boreal forest sites receiving acid precipitation.

METHODOLOGY

Study area and sampling sites

The watershed of Lake Laflamme (0.68 km^2) lies between 777 (mean lakewater level) and 884 m a.s.l. altitude at lat $47^\circ 19'$, long $71^\circ 07'$ in the Montmorency Forest (mixed spruce, fir and birch) 80 km to the north of the city of Quebec, Canada (Fig.1). The mean annual precipitation is 1400 mm of which 34% is snow. The sampling sites for the study of the snow cover (21 baseline stations and one main station) were located within an area of 2880 m^2 (45 x 64 m). Detailed biophysical characteristics of each site are described in Jones and others (1984).

Precipitation (snow and rain) was collected on an event basis by means of two Sangamo Type A wet-only collectors placed outside the drip zone of conifers. Samples for the chemical analysis of the snow cover were obtained by coring with a clear plastic tube (Plexiglas 2 m long and 7.5 cm internal diameter) (Jeffries and Snyder 1981). No special precautions to remove surface debris from cores were taken except where twigs, lichen

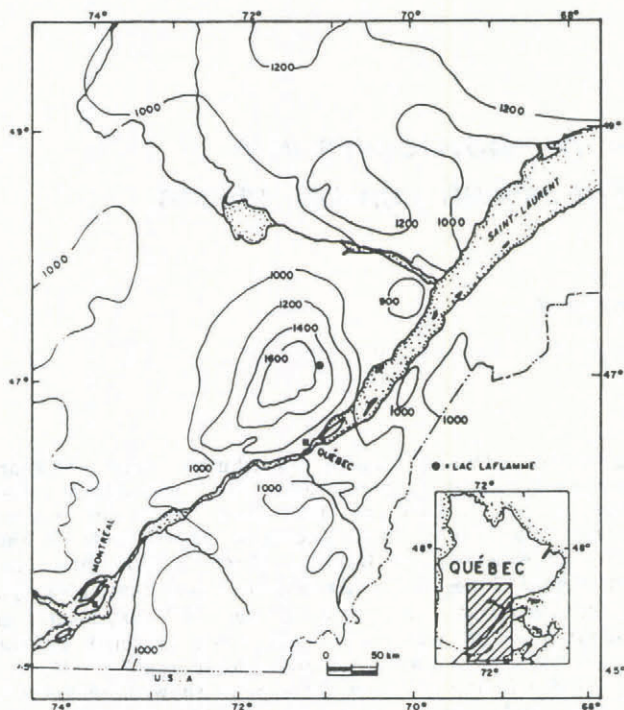


Fig.1. Study site and annual precipitation, Lake Laflamme, Québec.

clumps and animal excrement interfered with the sampling operations. All samples were placed in plastic bags (polyethylene) and kept at -20°C until melted for analysis. Sampling of the snow cover was started on 15 March 1983 and terminated on 12 May when approximately 40% of the ground cover was bare and from 9 to 10 cm of very dense snow cover remained. The snow cover had completely disappeared by 15 May.

The melt period commenced on 8 April when a large lysimeter (20 m^2) collected small discharges, although small lysimeters ($0.1, 0.125\text{ m}^2$) showed only appreciable discharges beginning on 25 April (Jones 1985). Data from the large lysimeter could not be used to verify directly the discharge of total ionic loads from the snow cover as the lysimeter was subjected to heavy infiltration by surface water during the 1983 melt season.

Analytical procedures

Snow samples were melted under an atmosphere of N_2 in large capped plastic bottles. The volumes of the melted samples were recorded and the values used to determine the water equivalent [WE] of each original snow-cover sample. Conductivity and pH were determined on the unfiltered liquid samples by means of a conductivity meter (Radiometer CDM) and a pH meter (Radiometer PHM26), respectively. The samples were subsequently filtered through polycarbonate ($47\text{ mm}, 0.4\text{ }\mu\text{m}$) and analyzed for anions ($\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{PO}_4^{3-}$) by ion chromatography (Dionex 12S) within 48 h. Cations were conserved in the filtered samples by the addition of nitric acid (0.5 ml l^{-1}) and NH_4^+ by the addition of concentrated sulfuric acid (0.2 ml l^{-1}). $\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{Al}$ and Mn were analyzed by means of atomic absorption spectrophotometers ($\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+$ by Varian 575 and Al and Mn by Varian G7A95 graphite furnace and Varian 1275) and NH_4^+ by colorimetry (Technicon AutoAnalyzer II, procedure 154-71W, indophenol-sodium nitroprusside).

Detection limits are $\text{Cl}^-: 1\text{ }\mu\text{eq l}^{-1}, \text{SO}_4^{2-}: 1\text{ }\mu\text{eq l}^{-1}, \text{NO}_3^-: 1\text{ }\mu\text{eq l}^{-1}, \text{PO}_4^{3-}: 5\text{ }\mu\text{eq l}^{-1}, \text{Ca}^{2+}: 0.5\text{ }\mu\text{eq l}^{-1}, \text{Mg}^{2+}: 0.8\text{ }\mu\text{eq l}^{-1}, \text{Na}^+: 0.5\text{ }\mu\text{eq l}^{-1}, \text{K}^+: 0.3\text{ }\mu\text{eq l}^{-1}, \text{NH}_4^+: 1\text{ }\mu\text{eq l}^{-1}, \text{Al}\text{ }\mu\text{g l}^{-1}$ and $\text{Mn}: 1\text{ }\mu\text{g l}^{-1}$.

Data analysis

Anionic deficiencies for all samples were calculated from the expression $\Sigma(\text{Cl}^- + \text{PO}_4^{3-} + \text{NO}_3^- + \text{SO}_4^{2-} + \text{HCO}_3^-)$

$-\Sigma(\text{H}^+ + \text{NH}_4^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{Al}^{3+} + \text{Mn}^{2+})\text{ }\mu\text{eq l}^{-1}$. At the pH of the samples collected, HCO_3^- concentrations are negligible. Al^{3+} and Mn^{2+} were calculated from total soluble Al, total soluble Mn and H^+ concentrations according to the method used by PGC Campbell (personal communication).

Total ionic loads from wet deposition were calculated as an average value for the two Sangamo collectors on an event and/or daily basis. In the case where a precipitation event was continuous over a period of more than 24 h, the daily loading was calculated by a repartition of the total load deposited according to the percentage volume of the total precipitation that fell in every 24 h period of the event.

The mean value for the total ionic loads (\bar{I}_x , meq m^{-2}) of the snow cover was calculated from the expression

$$\bar{I}_x = \frac{1}{n} \sum_{i=1}^n [\text{WE}]_i [\text{C}_x]_i$$

where [WE] represents the water equivalent (m), $[\text{C}_x]$ the concentration of the ionic species X ($\mu\text{eq l}^{-1}$), and n the total number of cores for baseline stations. For the premelt period, the number of cores taken at any one sampling date varied from 14 to 18. At the beginning of the melt period, seven cores were taken on every sampling date at intervals of two to four days while at the end of the melt period, five cores were taken at any one time every two days. Gains or losses in the total load of the snowpack during any particular period of time were averaged out over the period as daily rate changes ($\text{meq m}^{-2}\text{ d}^{-1}$).

Regrouping of chemical parameters by factor analysis was carried out after axes rotation with Kaiser normalization (Nie and others 1975).

RESULTS AND DISCUSSION

During the study period, the evolution of the snow cover was divided into five main phases (Fig.2). The first two phases were separated by the first meltwaters issuing from the pack on 8 April 1983. Each of the successive phases was separated from the preceding phase by the rains that occurred on 17 April, 24-25 April and 1-4 May respectively.

The first phase (20 March to 8 April) was characterized by wet deposition in the form of snowfall (76.8 cm), a very small amount of rain (0.6 mm) in mixed precipitation, low temperatures and a stable pack (accretion stage with no water loss). From a maximum value of 21.2 cm for the water equivalent on 8 April, the

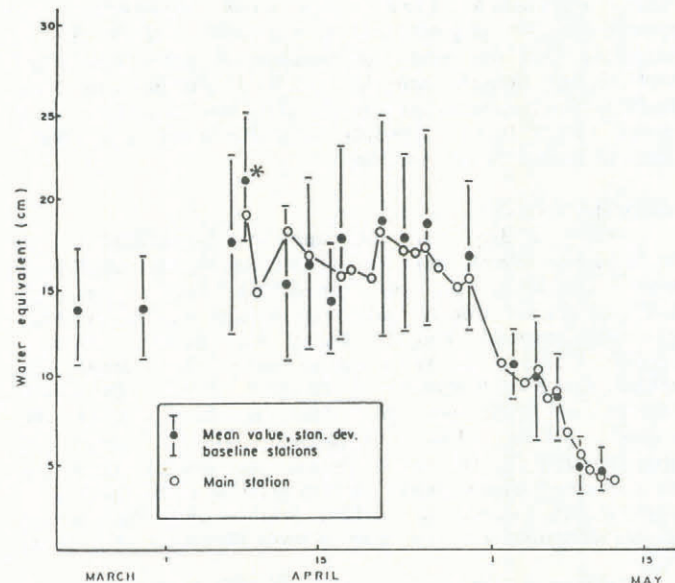


Fig.2. Mean water equivalent of the snow cover at Lake Laflamme, spring 1983. *This value (12.2 cm) is overestimated by 12%.

net loss of water from the pack due to meltwater discharge up to the rain event of 17 April (second phase) was calculated from the measured water equivalent of the snow cover to be 0.7 cm d⁻¹.

Subsequent to the rain of 17 April, the snowpack entered into the third melt phase in which losses in the total water equivalent were compensated by an input of mixed precipitation (snow and rain) which slightly increased the overall water equivalent of the pack. During the fourth phase (25-30 April), pack decline was 0.5 cm d⁻¹. The fifth phase of pack evolution was characterized by exceptionally heavy rain events (1-4 May and 7-11 May) and net pack discharges increased to 1 cm d⁻¹.

Over the whole period represented by the pre-melt and melt phases, the mean (arithmetic, non-volume-weighted) ionic concentrations of SO₄²⁻, NO₃⁻ and H⁺ in the snow cover were comparable (i.e. snow cores, n = 168; NO₃⁻: 21.6 μeq l⁻¹ (range 12.7 to 34.5 μeq

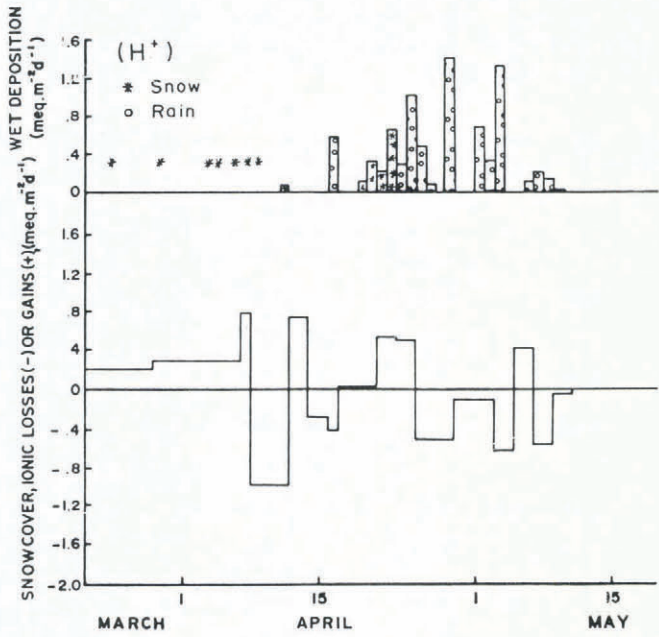


Fig.3(a). Wet deposition loading of H⁺ (meq m⁻² d⁻¹) and gains or losses in the H⁺ loading of the snow cover at Lake Laflamme, spring 1983.

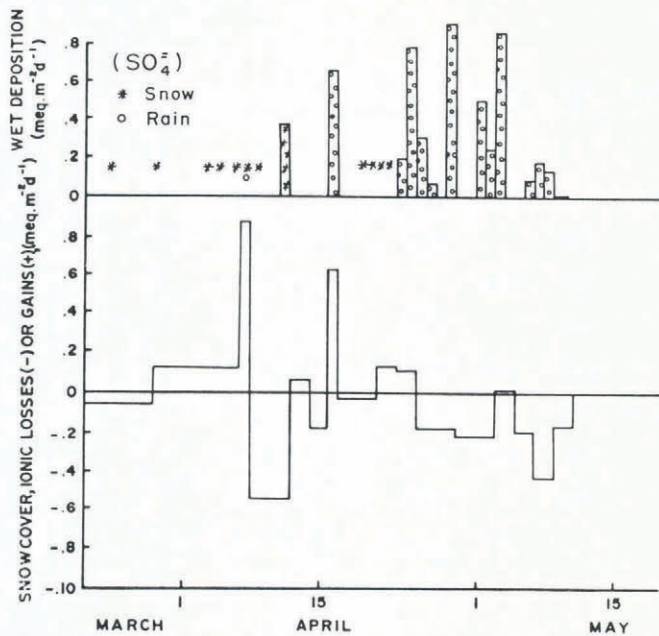


Fig.3(b). Wet deposition loading of SO₄²⁻ (meq m⁻² d⁻¹) and gains or losses in the SO₄²⁻ loading of the snow cover at Lake Laflamme, spring 1983.

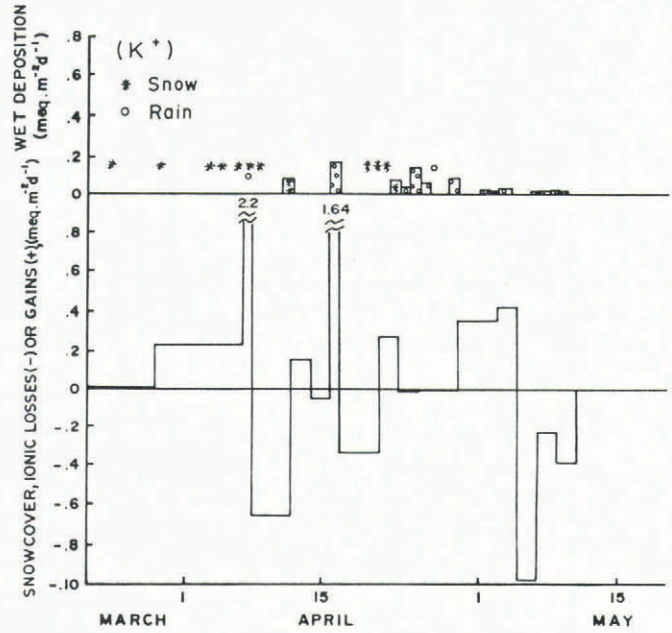


Fig.4(a). Wet deposition loading of K⁺ (meq m⁻² d⁻¹) and gains or losses in the K⁺ loading of the snow cover at Lake Laflamme, spring 1983.

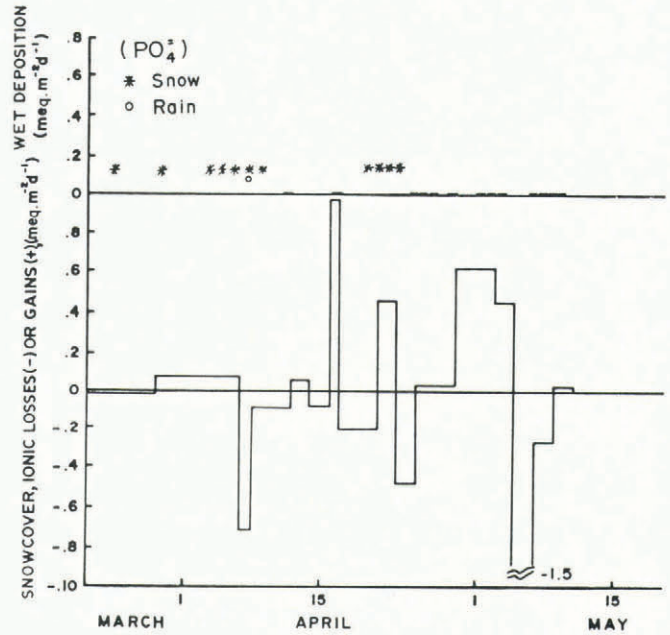


Fig.4(b). Wet deposition loading of PO₄³⁻ (meq m⁻² d⁻¹) and gains or losses in the PO₄³⁻ loading of the snow cover at Lake Laflamme, spring 1983.

l⁻¹); SO₄²⁻: 21.4 μeq l⁻¹ (range 5.7 to 46.2 μeq l⁻¹) and H⁺: 29.5 μeq l⁻¹ (range 10.0 to 53.1 μeq l⁻¹) while the mean concentrations of K⁺ and PO₄³⁻ were lower but fluctuated greatly around the mean values (K⁺: 10.8 μeq l⁻¹ (range below the detection limit (BDL) to 82 μeq l⁻¹) and PO₄³⁻: 5 μeq l⁻¹ (range BDL to 42.1 μeq l⁻¹)). Large fluctuations in the concentration of these latter ions were particularly evident during rain episodes when K⁺ and PO₄³⁻ distribution in the pack was heterogeneous.

The concomitant evolution of gains and losses in total ionic loads of the snow cover and the wet deposition loadings to the snow cover during the main phases of the spring melt are shown in Figures 3 (H⁺, SO₄²⁻) and 4 (K⁺, PO₄³⁻).

Wet deposition, in the form of rain, was dominant during the 1983 melt season; from the onset of melt on 8 April to the disappearance of the pack on 15 May as much water fell from the atmosphere (rain: 19.2 cm,

snowfall: water equivalent 2 cm) as was stocked originally (21 cm) in the pack on 8 April. These large amounts of wet deposition gave rise, according to the intensity and chemical content of the precipitation (eg: mean concentrations H^+ : $48.2 \mu\text{eq l}^{-1}$, SO_4^{2-} : $29.4 \mu\text{eq l}^{-1}$, NO_3^- : $18.26 \mu\text{eq l}^{-1}$, K^+ : $4 \mu\text{eq l}^{-1}$, PO_4^{3-} : BDL), to both losses and gains in the ionic loads of the snowpack. Although there was no consistent pattern of load losses and gains common to all the ionic species, gains were generally recorded during periods when snow fell or when rain filled up a drained pack close to the calculated saturation values for water retention (Anderson 1976). Losses were noted during the pack by snow-melt or after rain events. In certain periods, losses were also recorded when continual rain and warm temperatures led to very high rates of meltwater discharge from the snow cover.

Mean values for the daily wet deposition loadings of ionic species associated with atmospheric aerosols (NO_3^- :

0.32 ± 0.17 , SO_4^{2-} : $0.51 \pm 0.34 \text{ meq m}^{-2} \text{ d}^{-1}$) were of approximately the same magnitude as the daily changes in gains (NO_3^- : 0.66 ± 0.47 , SO_4^{2-} : $0.62 \pm 0.39 \text{ meq m}^{-2} \text{ d}^{-1}$) recorded in the snow cover during the melt period. In contrast, the mean value for the loading contribution by wet deposition to the total load of K^+ ($0.08 \pm 0.04 \text{ meq m}^{-2} \text{ d}^{-1}$) (Fig.4(a)) in the snow cover was far outweighed by the gains ($0.94 \pm 0.82 \text{ meq m}^{-2} \text{ d}^{-1}$) which were recorded at this time. This observation was even more pronounced in the case of PO_4^{3-} (Fig.4(b)). The very low concentrations of this ionic species in wet deposition were not reflected in the snow cover, where large gains in PO_4^{3-} loads ($0.74 \pm 1.05 \text{ meq m}^{-2} \text{ d}^{-1}$) comparable to those shown by SO_4^{2-} , NO_3^- , K^+ and H^+ took place. K^+ and PO_4^{3-} production thus originated mainly from local phenomena within and/or on the snow cover while SO_4^{2-} and NO_3^- gains were due mainly to atmospheric inputs.

The evolution of H^+ and SO_4^{2-} loads in the pack

TABLE I. CORRELATION COEFFICIENTS BETWEEN DATA RELATING THE CONCENTRATIONS OF CHEMICAL SPECIES IN SNOW CORES TAKEN FROM THE SNOW COVER WITHIN THE BOREAL FOREST SITE AT LAKE LAFLAMME IN 1983 BETWEEN 15 MARCH AND 8 APRIL (n = 59) AND BETWEEN 15 MARCH AND 16 APRIL (n = 81) INCLUSIVE

H^+	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Γ^+	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Γ^-	Al	Mn	
						0.66								H^+
	0.36*													NH_4^+
				0.37	0.30*	0.37*	0.50		0.36*		0.35*			Na^+
				0.81	0.87	0.76							0.88	K^+
					0.93	0.73			0.35*				0.83	Ca^{2+}
						0.77			0.33*				0.88	Mg^{2+}
													0.67	Γ^+
									0.47	0.43	0.68			Cl^-
											0.57			NO_3^-
										0.41	0.71			SO_4^{2-}
											0.74			PO_4^{3-}
														Γ^-
														Al
														Mn
n = 59, P < 0.001, P < 0.01*														
H^+	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Γ^+	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Γ^-	Al	Mn	
						0.69								H^+
		0.35				0.37	0.28*	0.31*			0.28*			NH_4^+
				0.34		0.32*	0.38		0.28*		0.28*			Na^+
				0.61	0.84	0.72			0.31*	0.26*			0.76	K^+
					0.84	0.64			0.38		0.27*	0.79		Ca^{2+}
						0.69			0.42	0.26*	0.30*	0.79		Mg^{2+}
							0.38	0.33*	0.42		0.45	0.35	0.67	Γ^+
									0.57	0.47	0.80			Cl^-
									0.29*		0.66			NO_3^-
										0.49	0.78	0.26*		SO_4^{2-}
											0.73			PO_4^{3-}
														Γ^-
														Al
														Mn
n = 81, P < 0.001, P < 0.01*														

TABLE II. CORRELATION COEFFICIENTS BETWEEN DATA RELATING THE CONCENTRATIONS OF CHEMICAL SPECIES IN SNOW CORES TAKEN FROM THE SNOW COVER WITHIN THE BOREAL FOREST SITE AT LAKE LAFLAMME IN 1983 BETWEEN 17 APRIL AND 25 APRIL (n = 35) AND BETWEEN 26 APRIL AND 11 MAY (n = 44) INCLUSIVE

H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Γ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ²⁻	Γ ⁻	Al	Mn		
													0.40*	H ⁺	
		0.61	0.72	0.53	0.49	0.78	0.62	0.42*	0.83	0.63	0.74	0.47*	0.43*	NH ₄ ⁺	
			0.76	0.65	0.65	0.77	0.92		0.69	0.71	0.79	0.57	0.49	Na ⁺	
				0.68	0.71	0.86				0.97	0.98	0.76	0.57	K ⁺	
					0.95	0.86	0.68		0.62	0.69	0.71	0.66	0.86	Ca ²⁺	
						0.84	0.68		0.61	0.71	0.71	0.63	0.91	Mg ²⁺	
							0.80		0.86	0.82	0.89	0.76	0.78	Γ ⁺	
									0.76	0.87	0.90	0.63	0.47*	Cl ⁻	
									0.45*					NO ₃ ⁻	
										0.81	0.92	0.69	0.51	SO ₄ ²⁻	
											0.97	0.71	0.55	PO ₄ ³⁻	
												0.74		Γ ⁻	
													0.57	Al	
														Mn	
n = 35, P < 0.001, P < 0.01*															
H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Γ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Γ ⁻	Al	Mn		
		-0.43*	-0.28*											0.40*	H ⁺
									0.33		0.27*				NH ₄ ⁺
			0.71	0.79	0.66	0.60	0.56		0.59	0.63	0.50	0.47			Na ⁺
				0.87	0.89	0.96	0.62		0.73	0.49	0.75	0.51	0.64		K ⁺
					0.91	0.73	0.39*		0.76	0.33	0.61	0.35	0.54		Ca ²⁺
						0.76	0.49		0.62	0.55	0.75	0.31	0.72		Mg ²⁺
							0.50		0.80	0.54	0.81	0.76	0.56		Γ ⁺
									0.45	0.71	0.68		0.42*		Cl ⁻
									0.39*		0.40*		0.59		NO ₃ ⁻
										0.40	0.67	0.91	0.36		SO ₄ ²⁻
											0.79		0.73		PO ₄ ³⁻
												0.49	0.61		Γ ⁻
															Al
															Mn
n = 44, P < 0.001, P < 0.01*															

showed similar behaviour during the end of the stable first phase (29 March-8 April) and during the second melt phase (8-16 April) (Figs. 3(a) and 3(b)). However, the subsequent overall relative increases and the concomitant patterns for losses and gains in the loads for the two ionic species in the pack differed considerably. As an example, a comparison of Figures 3(a) and 3(b) shows that on 17 April, when the SO₄²⁻ load in the pack increased in response to the wet deposition input for that day, the H⁺ load diminished in spite of a similar amount of wet deposition loading. An appreciable increase in K⁺ loading for this day largely compensated for the H⁺ loss in the ionic balance of the pack. Subsequently, the patterns for losses and gains in the snowpack for H⁺ and SO₄²⁻ were in opposition for periods in the fourth (25-30 April) and fifth (1-12 May) rain phases of the melt.

In wet deposition, the concentrations and daily ionic loading of H⁺ was strongly correlated with that of SO₄²⁻

(r² = 0.85, n = 14, p < 0.001). No such correlation was found between H⁺ and SO₄²⁻ in the snow cores either before or during the snow melt period (Tables I and II). Although the sampling and analytical work-up of snow core samples (Jones 1985) can contribute to the disappearance of the relationship found between these two ions in precipitation, the hydrogen ion also reacts to other autochthonous ionic transformations in the pack not common to precipitation chemistry. We suggest that the mechanisms responsible for losses and gains of other selected species such as the high K⁺ and PO₄³⁻ loadings observed on 17 April can lead to the disappearance of atmospheric H⁺ and SO₄²⁻ correlation coefficients in the pack. These ionic transformations within the pack are associated with organic matter and we further suggest that the main autochthonous mechanism for H⁺ suppression in boreal forest snow cover is that of ion exchange processes on organic material. This material may be either

particulate or leached in soluble form from organic substrates during melt and rain periods. Organic matter may donate or accept protons depending depending on its structure, association with other ions (e.g. Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , Al^{3+}) and biophysical context (Lee and Weber 1982, Bache 1983, Krug and Frink 1983, Driscoll and Schafran 1984). The presence of relatively large amounts of particulate organic matter in the pack is evident simply by direct observation. Although the presence of soluble organic matter in the snow cover was not measured directly during the snow melt of 1983, H G Jones and others (unpublished snow-melt data 1984) have noted net increases in the concentrations of soluble organic carbon in snowpacks and meltwaters over those recorded in the incident precipitation.

Further indirect evidence for the presence or transformation of organic matter in the chemical evolution of snow cover is the correlation coefficients between data relating the concentrations of the ionic species K^+ , Ca^{2+} , Mg^{2+} and Mn in the snow cores. Tables I and II show that, for all periods, K^+ , Ca^{2+} , Mg^{2+} and Mn were strongly correlated ($P \ll 0.001$). Factor analysis of the data also showed a regrouping that is indicative of a strong relationship between K^+ , Ca^{2+} , Mg^{2+} and Mn (Fig.6). The factor relating the evolution of these chemical species together is their common source within the organic litter at the snow-cover level. These elements are strongly associated with vegetative tissue and are leached by precipitation in appreciable quantities from both detrital (e.g. Mn (Tiffin 1972)) and living matter such as forest canopies (K^+ , Mg^{2+} and Ca^{2+} (Abrahamsen and others 1977)).

The expected losses for the snowpack, as calculated from the sum of the total loads stocked in the pack at the beginning of the melt periods and the total loadings in precipitation during the melt period, were lower than the sum of the actual losses observed for all ionic species except H^+ (Table III). The increases (%) which occurred in the snowpack loads over and above that expected from the calculated losses during the melt may be regrouped into three groups (Table IV). The first grouping comprises the major anions Cl^- , NO_3^- and SO_4^{2-} , the increases of which were comparable (25 to 32%). These increases are

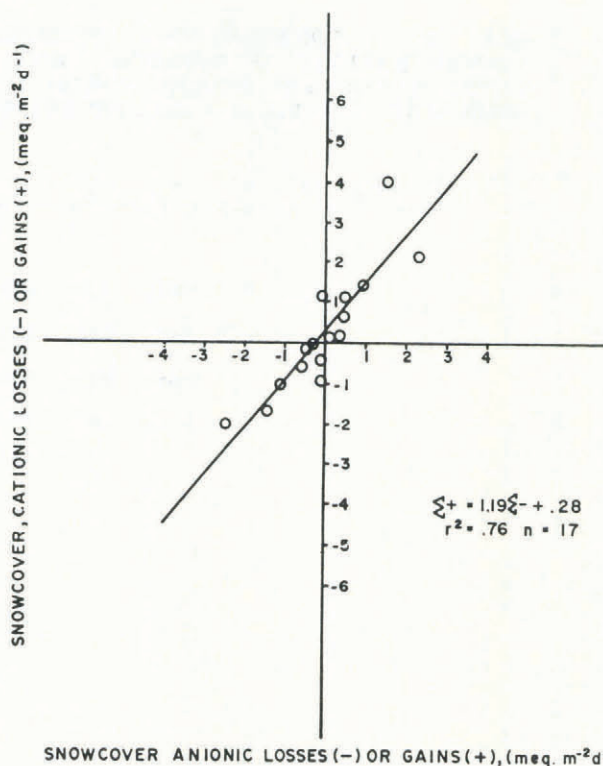


Fig.5. Relationship between changes in anionic and cationic loadings ($\text{meq m}^{-2} \text{d}^{-1}$) (losses or gains) in the snow cover at Lake Laflamme, 1983.

net increases over the whole of the snowmelt period and, as such, cannot give any information as to the relative chemical or biochemical dynamics of the ionic species in the pack. As an example, we may point out that although Cl^- and SO_4^{2-} are often thought of as conservative ions (Skartveit and Gjessing 1979), cyclic mechanisms of adsorption and desorption of these ions (particularly SO_4^{2-}) in the pack could lead to the same net changes as those

TABLE III. CHEMICAL BUDGETS FOR SNOW-COVER TOTAL LOADING LOSSES (meq m^{-2}) DURING THE MELT SEASON AT LAKE LAFLAMME, 1983

	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Al^{2+}	Mn^{2+}	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	(+) cationic (-) anionic
Total loading in pack at start of melt (7 April 1983)	6.13	0.69	0.36	0.94	0.26	0.63	0.09	0.09	1.74	4.35	4.30	1.15	(-) 2.35
Total loading in precipitation during melt period	7.97*	1.03**	1.03**	0.96**	0.31**	1.18**	0.01**	0.01**	1.99***	4.70***	4.10***	0.00***	(+) 1.71
Calculated total loading loss by pack during the melt period (ppt + pack loadings)	4.10	1.72	1.39	1.90	0.57	1.81	0.10	0.10	3.73	9.05	8.40	1.15	(-) 0.64
Observed total loading loss by pack during the melt period (E periodic losses by pack)	12.93	3.94	5.38	13.67	1.64	2.72	0.58	0.78	4.94	11.73	10.47	9.82	(-) 4.68
Net addition or removal (-) of ionic species by other phenomena, i.e. dry deposition, in-pack production and suppression	(-)1.17	2.22	3.99	11.77	1.07	0.91	0.48	0.68	1.21	2.68	2.07	8.67	(-) 4.04

* As measured for all precipitation events (21.2 cm, precipitation).

** Extrapolated values for 21.2 cm of precipitation from the mean values of H^+ and the ionic species in 20.3 cm of the total precipitation collected.

*** Extrapolated values for 21.2 cm of precipitation from the mean values of H^+ and the ionic species in 19.8 cm of the total precipitation collected.

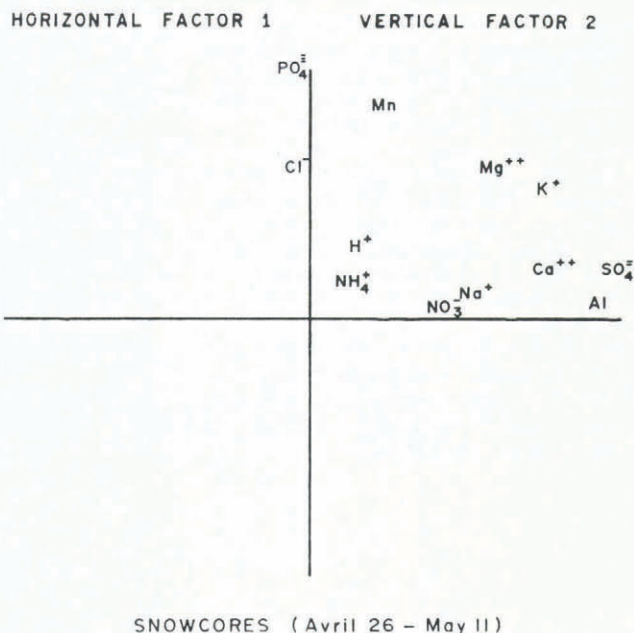


Fig.6. Factor analysis of concentration data for ionic species in snow cores ($n = 168$) at Lake Laflamme during the spring season, 1983.

of a conservative ion. Organic matter in soils can retain SO_4^{2-} by physical adsorption (Johnson and others 1981) and the detrital organic matter in the pack may also have the capacity to adsorb this ion during certain periods. Although the net increases in loads do not give any information on chemical dynamics within the pack which could lead to a better understanding of ionic transformations and ion exchange processes in the snow cover, they do suggest, however, a common source for the increases in Cl^- , NO_3^- and SO_4^{2-} . This would be dry deposition either directly by aerosol and gas interaction with the snow cover or indirectly by adsorption of the aerosols and gases on organic material followed by leaching during the melt period, or both. We believe that the latter phenomenon is probably the major source of these anions in the context of the boreal forest sites. The canopies of coniferous trees are scavengers of atmospheric aerosols (Ibrahim and others 1983) which are then removed by rain either from the canopy or from canopy material, which has been deposited on the snow.

The second group of ionic species is composed of Ca^{2+} , NH_4^+ , Mg^{2+} and Na^+ ; the values for the increases in loads for these ionic species (50 to 287%) may represent, in addition to leaching of local debris, the exudates of cellular material from the cell plasmolysis of detrital organic debris (particularly Ca^{2+} , Mg^{2+} and Na^+). In the case of NH_4^+ , microbiological activity of a heterotrophic nature within the pack (i.e. snow fungi, bacteria) is also a factor to be considered (Stein and Amundsen 1967, Visser 1973). High rates of production within the pack, however, are characteristic of the third group of ionic species (Al^{3+} , Mn^{2+} , K^+ and PO_4^{3-}) which show substantial increases in pack loads (480 to 750%). These increases cannot be accounted for by any other local phenomena other than the dissolution and/or microbiological degradation of organic debris.

The presence of PO_4^{3-} is particularly indicative of heterotrophic microbiological activity or secondary productivity of organic matter at higher levels. K^+ and PO_4^{3-} may be released into the pack by dissolution subsequent to microbiological degradation of organic material. An alternate source may be macrobiological excretion of PO_4^{3-} by the high populations of Collembola (Humbert 1980) present in the pack in spring time at Lake Laflamme. PO_4^{3-} is a strong acid anion and could, at the ionic loadings recorded, have compensated in part for the proposed mechanism of H^+ removal in the pack.

One must, however, be cautious in arriving at any conclusions that may be drawn from this type of data

analysis in snow-cover studies. Certain paradoxes exist, which may or may not be related to the difficulties inherent in the sampling of such a heterogeneous milieu, in the treatment of the samples during analytical techniques (Jones 1985) and even in the expressions used to calculate mean values for concentrations or loads of ionic species in the pack. For example, the water-equivalent budget (38.29 cm) for the snow cover calculated from the sum of periodic losses of water equivalent in the declining pack is very similar to the water equivalent budget (38.54 cm) calculated from the initial mean water equivalent of the pack before the spring melt and the water equivalent of precipitation inputs. As outlined above, the method used for the calculation of ionic loadings from periodic losses leads to a total loss in the load of SO_4^{2-} which is 25% higher than that expected from the calculated loadings from precipitation. As the

TABLE IV. INCREASES (%) OR DECREASES (-) OF MEASURED IONIC LOADING LOSSES FROM THE SNOW COVER OVER THOSE CALCULATED FROM PRECIPITATION LOADINGS AND ORIGINAL SNOW COVER LOADING BEFORE THE SPRING MELT

Ions	Increase (%)
H^+	-8
SO_4^{2+}	25
NO_3^-	30
Cl^-	32
Ca^{2+}	50
NH_4^+	129
Mg^{2+}	187
Na^+	287
Al^{3+}	480
K^+	619
Mn^{2+}	680
PO_4^{3-}	750

load in the pack has increased but the water equivalent has not, one would expect to find higher mean concentrations of SO_4^{2-} in the snow cover than in the precipitation. This was, however, not observed. The lower mean (arithmetic) values of SO_4^{2-} in the snow cores compared to mean SO_4^{2-} concentrations in the precipitation for the snowmelt period may be an artifact due to the large variability of SO_4^{2-} concentrations observed in the snow cover and the method used for the calculation of SO_4^{2-} load.

In conclusion, the results suggest that organic matter plays a major role in the evolution of the chemical load of many ionic species in the snow cover of boreal forest sites. The ion exchange capacity of both particulate and soluble organic material leads to a decrease in pack acidity and large increases in the loadings of essential nutrients and micronutrients such as K^{2+} , PO_4^{3-} and Mn . These in-pack transformations then destroy the relationship between concentrations of (H^+) and the concentrations of strong acid anions (SO_4^{2-} , NO_3^-) that are found in precipitation as it is deposited from the atmosphere. The influence of organic matter on snowpack chemistry should thus be taken into consideration in any attempt to model acid rain fluxes through boreal forest systems.

REFERENCES

- Abrahamsen G, Horntvedt R, Tveite B 1977 Impacts of acid precipitation on coniferous forest ecosystems. *Water, Air, and Soil Pollution* 8(1): 57-73
- Altshuller A P, McBean G A Unpublished. The LRTAP problem in North America: a preliminary overview. Report prepared by the United States - Canada Research Consultation Group on the Long Range Transport of Air Pollutants [1979]
- Anderson E A 1976 *A point energy and mass balance model of snowcover*. Silver Spring, MD, National Oceanic and Atmospheric Administration, National Weather Service (NOAA Technical Report, NWS 19)
- Bache B W 1983 The role of soil in determining surface water composition. *Water Science and Technology* 15: 33-45
- Driscoll C T, Schafran G C 1984 Short-term changes in the base neutralizing capacity of an acid Adirondack lake, New York. *Nature* 310(5975): 308-310
- Driscoll C T, Baker J P, Bisogni J J, Schofield C L 1980 Effect of aluminium speciation on fish in dilute acidified waters. *Nature* 284(5752): 161-164
- Humbert W 1980 Les collemboles. *Montagne et Sport* (Chamonix) 6: 105-108
- Ibrahim M, Barrie L A, Fanaki F 1983 An experimental and theoretical investigation of the dry deposition of particles to snow, pine trees and artificial collectors. *Atmospheric Environment* 17(4): 781-788
- Jeffries D S, Snyder W R 1981 Variations in the chemical composition of the snowpack and associated meltwaters in central Ontario. *Proceedings of the Eastern Snow Conference*, 38th annual meeting: 11-22
- Johannessen M, Henriksen A 1978 Chemistry of snow meltwater: changes in concentration during melting. *Water Resources Research* 14(4): 615-619
- Johnson D W, Hendersen G S, Todd D E 1981 Evidence of modern accumulations of adsorbed sulfate in an eastern Tennessee forested Ultisol. *Soil Science* 132: 422-426
- Jones H G 1985 The chemistry of snow and meltwaters within the mesostructure of a northern boreal forest snow cover. *Annals of Glaciology* 7: 161-166
- Jones H G, Sochanska W, Bougie R, Charette J Y 1984 *Développement d'une méthodologie d'étude sur les facteurs contrôlant la qualité des eaux de fonte et des eaux de ruissellement printanier au lac Laflamme, Québec*. Sainte-Foy, Québec, Environnement Canada. Direction Générale des Eaux Intérieures (INRS-Eau, Rapport Scientifique 165)
- Krug E C, Frink C R 1983 Acid rain on acid soil: a new perspective. *Science* 221(4610): 520-25
- Lee J J, Weber D E 1982 Effects of sulfuric acid rain on major cation and sulfate concentrations of water percolating through two model hardwood forests. *Journal of Environmental Quality* 11(1): 57-64
- Likens G E, Butler T J 1981 Recent acidification of precipitation in North America. *Atmospheric Environment* 15(7): 1103-1109
- Nie N H, Hull C H, Jenkins J G, Steinbrenner K, Bent D H 1975 *SPSS. Statistical package for the social sciences. Second edition*. New York etc, McGraw-Hill Book Company
- Popp C J, Jensen C M, Brandvold D K, Brandvold L A 1982 Precipitation analysis in central New Mexico. In Keith L H (ed) *Energy and environmental chemistry*. Ann Arbor, MI, Ann Arbor Science: 89-101
- Skartveit A, Gjessing Y T 1979 Chemical budgets and chemical quality of snow and runoff during spring snowmelt. *Nordic Hydrology* 10(2-3): 141-154
- Stein J R, Amundsen C C 1967 Studies on snow algae and fungi from the front range of Colorado. *Canadian Journal of Botany* 45(11): 2033-2045
- Tiffin L O 1972 Translocation of micronutrients in plants. In Mortvedt J J, Giordano P M, Lindsay W L (eds) *Micronutrients in agriculture. Proceedings of a symposium held at Muscle Shoals, Alabama, April 20-22, 1971, and cosponsored by the Tennessee Valley Authority and the Soil Science Society of America*. Madison, WI, Soil Science Society of America: 199-229
- Tomassini F D, Lavoie P, Puckett K J, Nieboer E, Richardson D H S 1977 The effect of time of exposure to sulphur dioxide on potassium loss from and photosynthesis in the lichen *Cladonia rangiferina* (L.) Harm. *New Phytologist* 79: 147-155
- Tucker W A, Lyman W J, Preston A L 1983 Estimation of the dry deposition velocity and scavenging ratio for organic chemicals. In *Precipitation scavenging, dry deposition and resuspension. Proceedings of the Fourth International Conference, Santa Monica, California, 19 November - 3 December. Coordinated by H R Pruppacher, R G Semonin and W G N Slinn*. New York, Elsevier: 1243-1258
- Visser S A 1973 The microflora of a snow depository in the city of Québec. *Environmental Letters* 4: 267-272
- Wright R F 1983 *Predicting acidification of North American lakes*. Oslo, Norwegian Institute for Water Research (NIVA-Report 0-81036)