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THE CHEMISTRY OF ATMOSPHERIC DEPOSITION,
THE SNOWPACK AND SNOWMELT
IN THE TURKEY LAKES WATERSHED
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MANAGEMENT PERSPECTIVE

Chemical changes in atmospheric deposition and the snowpack are recorded during a springmelt episode at the Turkey Lakes Watershed. The results of this study should be considered in context of an overall NWRI objective at the site, i.e. to define the process of basin acidification. Because snowmelt is a major component of the hydrological budget in this north-temperate zone and certain biological species are at a sensitive stage in their development, the impact of acid-laden snowmelt on lake and stream waters can be significant. The research has shown that initial meltwaters are ten times more concentrated in H^+ and SO_4 and seven times more concentrated in NO_3 and NH_4 than the pre-melt snowpack. The predicted (and observed) effect on surface waters in the TLW is a depletion in acid neutralizing capacity, elevated H^+ , NO_3 and NH_4 levels but only an initial short-term increase in SO_4 concentrations.

Snowpack and snowmelt studies have also provided an estimate of the dry deposition of SO_4 and NO_3 to the basin. Results suggest that AES measurements of dry NO_3 at the CAPMoN station are somewhat elevated compared to the snowpack and snowmelt content. The bulk collector used for quantifying chemical inputs to the TLW and elsewhere appears to over-estimate the total atmospheric deposition, at least during the winter months. These observations have implications for Environment Canada in the design and utilization of monitoring equipment as well as in the interpretation of atmospheric chemistry data.

PERSPECTIVE-GESTION

Les changements chimiques qui s'opèrent dans les dépôts atmosphériques et le manteau nival sont enregistrés au cours de la fonte des neiges, au printemps, dans le bassin hydrographique des lacs Turkey. Les résultats de cette étude doivent être considérés dans le contexte d'un objectif global de l'INRE sur ce site, c.-à-d. la définition du processus d'acidification du bassin. L'impact des eaux de fonte acidifiées sur les eaux des lacs et des rivières peut être considérable étant donné que les eaux de fonte sont l'élément majeur du bilan hydrologique dans cette zone tempérée du nord et que certaines espèces biologiques sont à un stade vulnérable de leur développement. La recherche a démontré que les eaux de fonte initiales ont des concentrations de H^+ et SO_4 dix fois supérieures et des concentrations de NO_3 et NH_4 sept fois supérieures à celles du manteau nival. L'effet prévu (et observé) sur les eaux de surface dans le BHLT est un épuisement de la capacité de neutralisation, des teneurs élevées en H^+ , NO_3 et NH_4 , mais seulement une augmentation initiale à court terme des concentrations de SO_4 .

Les études du manteau nival et des eaux de fonte ont également fourni une évaluation du dépôt à sec de SO_4 et de NO_3 dans le bassin. Les résultats indiquent que les mesures des dépôts à sec de NO_3 par le SEA, à la station CAPMoN, sont quelque peu élevées par rapport à la teneur du manteau nival et des eaux de fonte. L'échantillonneur utilisé pour doser les apports en produits chimiques dans le BHLT, et ailleurs, semble surévaluer les dépôts atmosphériques totaux, tout au moins durant les mois d'hiver. Ces observations ont des répercussions pour Environnement Canada en ce qui a trait à la conception et à l'utilisation de l'équipement de surveillance ainsi qu'à l'interprétation des données sur la chimie atmosphérique.

ABSTRACT

Bulk and wet-only deposition and the snowpack were monitored at the Turkey Lakes Watershed in northern Ontario over the winter and spring of 1986. Based on a comparison with snowpack and cumulative snowmelt, the bulk sampler over-collected major ions by factors ranging from 6 to 22%. Nitrate appeared to be preferentially collected by the bulk sampler relative to SO_4 during snow events. Dry deposition was estimated to be 12% and 5% of total deposition for SO_4 and NO_3 , respectively. Ion budgets for cumulative bulk deposition and snowmelt supported the hypothesis that ion losses from the snowpack are insignificant during a winter having no melt episodes. Snowmelt was characterized by chemical fractionation of major ions; SO_4 and H^+ in initial meltwaters were ten times more concentrated than the premelt snowpack. Preferential elution of ions in the snowmelt followed the sequence: $\text{SO}_4 > \text{NO}_3 > \text{H}^+ > \text{Cl}$. Snowmelt chemistry was used to predict changes in lake chemistry: H^+ , NO_3 and NH_4 levels should increase in lake waters; Ca decreases through dilution by snowmelt; SO_4 concentrations remain fairly constant.

RÉSUMÉ

Les échantillons en vrac et les dépôts humides seulement ainsi que le manteau nival ont été surveillés dans le bassin hydrographique des lacs Turkey, dans le nord de l'Ontario, durant l'hiver et le printemps de 1986. D'après une comparaison avec les données sur le manteau nival et les eaux de fonte, l'échantillonneur a "prélevé" en excès les principaux ions d'un facteur allant de 6 à 22 %. Il semble que l'échantillonneur a montré une préférence pour le nitrate par rapport au SO_4 durant les chutes de neige. Le dépôt à sec a été évalué à 12 et 5 % respectivement de la totalité des dépôts de SO_4 et NO_3 . Les bilans ioniques des dépôts cumulatifs et des eaux de fonte confirmaient l'hypothèse selon laquelle les pertes d'ions du manteau nival sont négligeables au cours d'un hiver sans épisode de fonte. Les eaux de fonte étaient caractérisées par un fractionnement chimique des principaux ions; les concentrations de SO_4 et H^+ étaient dix fois plus importantes dans les eaux de fonte initiales que dans le manteau nival avant la fonte. L'élution préférentielle des ions dans les eaux de fonte suivait la séquence suivante : $\text{SO}_4 > \text{NO}_3 > \text{H}^+ > \text{Cl}$. La chimie des eaux de fonte a été appliquée pour prévoir les changements dans la chimie des lacs : les teneurs en H^+ , NO_3 et NH_4 devraient augmenter dans les eaux lacustres; les teneurs en Ca devraient diminuer à cause de la dilution par les eaux de fonte; les concentrations de SO_4 devraient demeurer à peu près constantes.

1. INTRODUCTION

The chemistry of the snowpack at the Turkey Lakes Watershed (TLW) was studied over the 1986 winter and spring months. Previous work at this site has shown that the snow cover is an important reservoir of H^+ , SO_4 , NO_3 , and NH_4 (Semkin and Jeffries 1986b) and that the release of these ions during snowmelt produced significant changes in surface water chemistry, including the loss of buffering capacity and an increase in NO_3 and NH_4 concentrations (Jeffries and Semkin 1983).

The snowpack not only determines the chemistry of the snowmelt and its impact on lake and stream waters but serves as a composite collector of atmospheric deposition for approximately four months of the year. At the TLW, bulk, wet-only and dry atmospheric deposition are sampled on a routine basis. Bulk deposition has been used to measure the atmospheric input of major ions in the study basin (Jeffries et al. 1986) and in other calibrated watersheds in North America (Likens et al. 1977, Dillon et al. 1982) and elsewhere (Christophersen and Wright, 1980). By comparing the snowpack chemistry with that of cumulative bulk deposition, information can be obtained on the effectiveness of the bulk sampler in measuring total atmospheric deposition. Furthermore, this comparison can shed some insight into the controversy surrounding the ionic stability of a snowpack prior to spring thaw. Jones and Bisson (1984) and Jeffries and Snyder (1981) have both recorded changes in the snowpack composition during the sub-zero temperatures of northern winters.

Snowmelt studies at the TLW in 1985 revealed that the concentration of major ions in the early melt were two to ten times greater than levels in the snowpack; approximately 50% of H^+ , SO_4 , and NO_3 were exported from the snowpack with the first 30% of the melt; the highest concentrations of H^+ , SO_4 , and NO_3 in snowmelt were coincident with heavy rain events (Semkin and Jeffries 1986b). Cadle et al. (1984) observed similar results during the melting of the snowpack in northern Michigan. They reported that the first 20% of the snowmelt contained 50% of the acids exported and that rainfall occurring during the melt period deposited an additional amount of H^+ and NO_3 equivalent to that exported from the snowpack. Sulphate deposited by spring rains were double that generated by the ablating snowpack.

Based upon the significant effect of meltwater on basin hydrology and geochemistry, intensive snowmelt studies were undertaken in 1986 at the TLW. Climatological conditions in the study year differed from previous years in that the melt period was relatively brief and characterized by warm air temperatures and infrequent rainfall. The importance of meteorological factors in melt production was addressed as was the chemical fractionation of major ions in snowmelt and the role of preferential elution in regulating melt chemistry. The temporal variation in snowmelt chemistry was used to predict changes in lakewater composition at the TLW.

2. STUDY AREA

The Turkey Lakes Watershed is an undisturbed, forested basin located on the Precambrian Shield approximately 50 km north of Sault Ste. Marie, Ontario. The catchment area is 10.5 km². Details on the physical and biological characteristics of the watershed are provided by Jeffries et al. (this volume).

Intensive snowpack and snowmelt studies were carried out at the TLW camp several kilometers south of the basin. This is also the site of the main meteorological facility and the Algoma Canadian Air and Precipitation Monitoring Network (CAPMoN) station which is part of a Canada-wide system for evaluating air and precipitation chemistry (Barrie et al. 1980). Most of the snowpack work took place in an open, hill-top setting approximately 200 m² in area and adjacent to the CAPMoN site.

3. METHODS

To assess changes in snowpack chemistry through the winter, a plexiglas tube (diameter = 14.5 cm) was used to sample the snowpack on a weekly schedule at the main monitoring station. Additional snowpack cores were collected monthly at other sites in the TLW to assess the spatial variability in snowpack chemistry. In both sampling programs, more frequent measurements were taken as the spring progressed. The snow cores were transferred to clean, polyethylene bags, weighed and transported to the lab where the samples were melted at room temperature.

Bulk deposition was collected weekly in a teflon-lined, stainless-steel funnel (0.25 m^2) housed in a box approximately 1 m above ground level. The bulk collector was continuously open and consequently sampled both wet and dry atmospheric deposition. The funnel directed the bulk deposition sample into a bucket lined with a polyethylene bag identical to that used for the wet-only sample. A second bulk sampler was deployed to collect rainfall during the melt period.

Wet-only deposition was sampled daily in a Sangamo-type collector which was only operational during precipitation events (Sirois and Vet, this volume). Precipitation was measured with a standard rain gauge and Nipher-shielded snow gauge. A continuous measurement of precipitation was also obtained with a Belfort gauge.

Dry atmospheric deposition was estimated from the difference between bulk and wet-only deposition and also from the difference between the chemical content of the snowpack and cumulative wet-only deposition.

Snowmelt was collected from an automatic water sampler located in an insulated cave beneath the snowpack. For the melt studies, snow falling above the cave was confined to a 1 m^2 plexiglas chamber with side panels that were added or removed to coincide with the height of the surrounding snow cover. Further information on the melt sampling equipment and methodology is given by Semkin and Jeffries (1986b).

Bulk deposition, snowpack and snowmelt samples were analysed for pH and specific conductivity immediately after collection. Cations and nutrients were measured in accordance with procedures outlined by

the Department of the Environment (1979); anions were determined on a Dionex model 20101 ion chromatograph. Wet-only deposition was sampled and analysed following the standardized methods defined in the CAPMON program (Sirois and Vet, this volume).

4. RESULTS

4.1 Climate

In the period from November 1985 to April 1986, approximately 390 mm water equivalent of snow fell on the TLW. This quantity is close to the six-year average (1981-1986) of 375 mm snowfall at the main meteorological station and about 30% greater than the normal snowfall (years 1951-1980) recorded at the Sault Ste. Marie airport.

The period December through February experienced almost continuous sub-zero temperatures (Figure 1) so that most atmospheric deposition, both water and chemicals, falling on the TLW was preserved in the snowpack. The air temperature increased in early March but this only served to ripen the snowpack. Snow did not melt until mid-March when the daily average temperature was approximately 0°C and daily maximum temperature was about +3.5°C. Melting was well underway by March 25, 1986, under the combined influence of rain and daily maximum temperatures near 10°C.

4.2 Snowpack

By November 26, 1985, a permanent snow cover was established at the TLW, which was several weeks earlier than normal for this northern location. An analysis of the snow chemistry at 11 sampling sites in the basin (Table 1) revealed that H^+ , NO_3^- , SO_4^{2-} and NH_4^+ were the predominant ions in winter deposition, respectively accounting for 34%, 24%, 21% and 9% of the total ionic loading. The relative abundance of major ions in the 1986 snowpack paralleled that in winter bulk deposition at the TLW for the period 1981 to 1984 (Semkin and Jeffries 1986a).

The concentration of major ions is fairly constant throughout the basin (coefficient of variation <10% for H^+ , NO_3^- and SO_4^{2-} , Table 1). The higher variability in Mg, Na and K was attributable to analysis of these ions near or at the limits of analytical detection. This constancy was noteworthy because the snow sampling sites were exposed to varying degrees of cover by the forest canopy and, as shown in Figure 2, the water equivalent of the snowpack increased by 45% from the TLW campsite to the upland sections of the watershed - traversing a relief of about 100 m.

4.3 Bulk and Wet-Only Deposition

The collection efficiency of the bulk sampler in 1986 was calculated by comparing the bulk sample volume to the precipitation quantity in the standard gauge (Table 2). The relatively low values

recorded for snow events undoubtedly reflected the impaired collection capability of the bulk unit during the often severe and turbulent storms accompanying winter.

Cumulative precipitation at the main monitoring site agreed reasonably well (usually within 5%) with the water equivalent of the late February snowpack (Figure 3). The conservation of water in the winter snowpack permitted a comparison of the major ion concentrations in cumulative bulk and wet-only deposition with the chemical content of the snowpack. Volume-weighted concentrations in bulk deposition generally exceeded levels in the snowpack and in wet-only deposition (Table 3). The elevated Ca content of the February 25, 1986 snowpack was likely an analytical error and/or a result of sample contamination.

A material balance was calculated to compare the ion loading in cumulative bulk and wet-only deposition with the snowpack for the period of snow accumulation and ablation (i.e. November 26, 1985 to April 19, 1986). The cumulative input of major ions in bulk deposition was greater than the snowpack loading prior to the melt period (Figure 4). Furthermore, the ionic content of the snowpack exceeded that of cumulative wet-only deposition for H^+ , NO_3 , SO_4 , and NH_4 , suggesting that the role of dry deposition at the TLW may be significant. Wet-only deposition of Cl and Ca was observed to exceed the bulk loading and, in the case of chloride, was greater than the snowpack content (Figure 4). This discrepancy could be attributed to analytical errors.

4.4 Snowmelt

Samples were first collected from the melt chamber on March 16, 1986. Compared to the chemical composition of the pre-melt snowpack, which had remained fairly constant over the winter, the initial meltwater was enriched in all major ions (Figure 5). Chemical fractionation of ions in snowmelt occurred to the extent that an average 55% of the total H^+ , SO_4 , and NO_3 was exported from the snowpack with the first 20% of the melt (Figure 6). Preferential release of major ions in snowmelt was evident (Figure 6) with a removal rate in the order $SO_4 > NO_3 > H^+ > Cl$. This elution sequence is also defined by decreasing SO_4/NO_3 equivalent ratios (Figure 7) and by diminishing SO_4/H^+ , NO_3/H^+ and SO_4/Cl equivalent ratio values for the ablating snowpack in early-mid April (Figure 8).

Rainfall events during the melt period were primarily characterized by increasing SO_4 levels relative to NO_3 (Table 4). The high permeability of the snowpack to rain was indicated by peaks in the melt concentration profile (Figure 5); as an example, elevated NH_4 and Ca concentrations in the meltwater were coincident with the March 25 rainfall which was enriched in these ions (Table 4).

The material output via snowmelt was compared to the input of major ions in both bulk and wet-only deposition (Table 5). Cumulative bulk but not wet-only deposition generally exceeded the cumulative output in snowmelt - a situation analogous to the enrichment in bulk chemistry relative to the snowpack content (Table 3). The exceptions were the elevated output of H^+ and higher Ca and Cl loadings in

snowmelt. These disparities were attributable to the analytical errors in pH measurements with very dilute melt solutions and measurement of Ca and Cl at or below detection levels, particularly during the late stages of snowmelt.

4.5 Dry Deposition

Assuming that the mass loading in the pre-melt snowpack and in cumulative snowmelt represented the total atmospheric deposition to the TLW, dry deposition as a percentage of the total was estimated by the difference between cumulative wet-only deposition and either the snowpack content (Table 3) or cumulative snowmelt (Table 5). The average of the two methods (Table 6) revealed that dry deposition accounted for 5 to 28% of the total atmospheric loading of major ions in the basin. In terms of the predominant anions in dry atmospheric deposition, the levels of SO_4 and NO_3 were comparable or lower than those recorded at other studies in this region (Table 6).

5. DISCUSSION

5.1 Bulk Collector

The major ion loading in cumulative bulk deposition is greater than both the measured snowpack content and the ion export in snowmelt. By averaging bulk/snowpack ratios (Table 3) and bulk/snowmelt ratios (Table 5), it is apparent that the bulk sampler overestimates atmospheric deposition by factors of 1.05 for H^+ , 1.22 for

NH₄, 1.08 for SO₄ and 1.15 for NO₃. These enrichment factors are similar to values reported at a research site in northern Michigan. Here Cadle et al. (1986) compared the cumulative wet plus dry deposition to the snowpack loading and recorded over-collection factors of 1.06, 1.29, 1.11 and 0.98 for H⁺, NH₄, SO₄ and NO₃ ions, respectively. The low nitrate ratio in the Michigan study was attributed to an error in the analysis of a single wet-only deposition sample (Cadle et al. 1986)

Although Ibrahim et al. (1983) reported that bulk collectors (including the version used here) should under-collect submicrometer-size particles such as SO₄ and NH₄, the sampling dynamics of the bulk unit produce an over-estimation of atmospheric deposition at the TLW. With the relatively low efficiency of the bulk collector for snowfall, i.e. 74% (Table 2), it appears that the sampler preferentially collects the early fraction of precipitation when the chemical content may be most concentrated. The data on collector efficiency do suggest that bulk deposition would best approximate the total atmospheric loading during the non-winter months when rain is the dominant form of precipitation.

The bulk sampler also over-estimates nitrate deposition to a greater degree than sulphate. This is corroborated by the relatively higher bulk loading versus snowpack loading (Figure 4) and by the higher over-collection factors of 1.12 to 1.17 for NO₃, as opposed to 1.06 to 1.09 for SO₄. Furthermore, SO₄:NO₃ equivalent ratios show reduced values for cumulative bulk deposition compared to the snowpack and to cumulative wet-only deposition, at least during the period of snow accumulation (Figure 7). The inference is that the bulk sampler

favours the collection of NO_x relative to SO_2 during snowfall. This may reflect the collection efficiency of the sampler and an enrichment of NO_x in the initial phase of deposition events.

5.2 Snowpack

Various studies have addressed the notion of ion stability in the snowpack during the winter months. Jeffries and Snyder (1981), on the one hand, reported that NO_x and SO_2 were lost from the snowpack prior to melting with SO_2 being depleted at a relatively higher rate. Jones and Bisson also (1984) observed that NO_x and SO_2 migrated at different rates through the snowpack and were continuously exported. On the other hand, a three-year comparison of snowpack loading to cumulative wet plus dry deposition in northern Michigan led Cadle et al. (1986) to observe no significant major ion losses from the pre-melt snowpack.

At the TLW, no material was exported from the snowmelt collector during the winter months. If one assumes that the melt chamber had collection characteristics similar to the surrounding snow cover, then a comparison between cumulative bulk deposition and cumulative snowmelt will provide insight into the stability of the snowpack ionic content prior to any melting. Since the bulk sampler was shown earlier to over-collect with respect to the snowpack, such a comparison must use bulk deposition that has been corrected using the bulk/snowpack ratios in Table 3. Having done this, the close agreement between adjusted cumulative bulk deposition and cumulative

snowmelt of SO_4 , NO_3 , and NH_4 suggests that the overall content of ions in the snowpack remains relatively stable throughout a winter in the TLW with no major melting.

5.3 Dry Deposition

Dry deposition (Table 6) was estimated from the difference between cumulative wet deposition and both the winter snowpack (Table 3) and cumulative snowmelt (Table 5). There are other methods, the results of which are presented in Table 6, by which dry deposition is calculated. Cadle et al. (1986) used both a bucket technique and the measurement of concentration increases in exposed, elevated snow samples. At the TLW, Sirois and Vet (this volume) analysed the air and particulate chemistry and calculated dry deposition from deposition velocities which were based on surface type and atmospheric stability factors.

The dry loading of H^+ in this study is somewhat high and most likely reflects the cumulative analytical error in pH measurements in snowmelt. Sulphate dry deposition values are consistent with other data collected in northern Michigan and at the TLW. Nitrate dry deposition is approximately 20% of the amount estimated by Sirois and Vet (this volume) and 30% of the three-year winter average calculated by Cadle et al. (1986).

The lower percentage of dry nitrate deposition in this study arises from the use of the snowpack loading/cumulative wet deposition comparison instead of the deposition velocities utilized by Sirois and

Vet (this volume). These authors reported that gaseous HNO_3 contributed about 90% of the total dry nitrate deposition at the TLW. The relative importance of HNO_3 as a major component of dry nitrate deposition was also noted by Cadle et al. (1985) at a rural site in northern Michigan. Sirois and Vet (this volume) assumed that the surface resistance of the snowpack was constant and allowed for maximum deposition of gaseous HNO_3 . However, Johansson and Granat (1986) have determined that the surface resistance of the snowpack and hence the dry deposition of gaseous HNO_3 is temperature-dependent. They reported that the deposition velocity of HNO_3 to the snowpack decreased by a factor of at least 5 with decreasing air temperatures from -3°C to -18°C . At their study site, the contribution of HNO_3 via dry deposition was estimated to be less than 4% of the wet nitrate deposition. Consequently, the dry NO_3 deposition value expressed as a percentage of the total nitrate deposition in Table 6 (3 to 7%) is feasible in view of the sub-zero air temperatures prevalent at the TLW during the winter months. With warmer temperatures such as accompany spring melt, the surface resistance of the snowpack decreases and the deposition velocity of HNO_3 increases appreciably.

5.4 Snowmelt

The 1986 melt period at the TLW was unusually short in duration and marked by relatively warm air temperatures (Figure 1) and the absence of major freeze/thaw cycles observed in past years (Semkin and

Jeffries 1986b). Rainfall occurred less frequently in the study year and therefore had a reduced impact on melt production and snowmelt chemistry. As an example, the 1986 spring rain accounted for 14% of the melt volume and 12%, 22% and 16% of the H^+ , SO_4 , and NO_3 loading respectively, whereas in 1985, the rain contributed 18% of the total water, 51%, 49% and 37% of the H^+ , SO_4 , and NO_3 ions (Semkin and Jeffries 1986b). Rainfall during spring melt can have a deleterious effect on surface waters in a basin such as the TLW. At this time, the soil cover is already saturated with meltwater. If rainfall is intense, the high permeability of the snowpack combined with a high water table will permit a rapid influx of rainwater into streams and lakes.

The initial meltwaters are ten times more concentrated in H^+ and SO_4 , and seven times more concentrated in NO_3 and NH_4 than the pre-melt snowpack (Figure 5). The chemical fractionation is comparable to that recorded in the 1985 melt at the TLW (Semkin and Jeffries 1986b) and somewhat higher than that cited by Cadle et al. (1987) for SO_4 and NO_3 in a northern Michigan snowpack (concentration factor of 5) and by Johannessen and Henriksen (1977) for a snowpack in southern Norway (concentration factor of 6.5).

The elution sequence in snowmelt, i.e. $SO_4 > NO_3 > H^+ > Cl^-$, is not unique to the TLW. Tranter et al. (1986) reported on the preferential elution of SO_4 and NO_3 in snowmelt and subsequent evolution in melt chemistry towards a dilute, but Cl^- -rich, phase. This phenomenon is in evidence at the study site, albeit less clearly demonstrated due to the lower Cl^- concentrations of this continental

snow cover (SO_4/Cl equivalent ratios average 4.6 in the pre-melt snowpack at the TLW whereas Tranter et al. (1986) recorded average values of 0.23 for within-pack snows in the Scottish Highlands). At the TLW also there is a second pulse of Cl enrichment in the melt coincident with a 50% water equivalent loss (Figure 6), suggesting that the deposition and release of chloride from the snowpack may be regulated by factors dissimilar to those controlling the acidic components.

The temporal variation in snowmelt chemistry can be used to explain changes in the water chemistry of lakes and streams at the TLW and elsewhere. The short-term acidification of surface and ground waters during the spring melt period results from a combination of two phenomena: an influx of acidic anions and a dilution of base cations. In three Adirondack lakes (Galloway et al., 1984), acidification was characterized by both a decrease in base cations through dilution by snowmelt and a marked increase in NO_3 concentrations. Sulphate levels remained virtually constant throughout the melt period. At the TLW, the loss of acid neutralizing capacity in a headwater stream was associated with a five-fold increase in H^+ levels and a doubling of NO_3 concentrations during spring melt (Jeffries and Semkin, 1983). Spring sulphate concentrations also showed little variation across the basin (Semkin et al., 1984).

By comparing major ion concentrations in snowmelt to the median concentrations in surface waters at the TLW, it is possible to predict the perturbations in water chemistry that can be expected over

the melt period (Table 7). At the onset of melting, snowmelt entering the lake systems will generate pronounced increases in H^+ concentrations (and hence a depletion of acid neutralizing capacity) and in NO_3 and NH_4 levels. Calcium and other base cations will decrease with dilution by snowmelt. Sulphate levels will increase but only at the initial stages of melting. As snowmelt progresses, concentrations of H^+ , NO_3 and NH_4 will remain relatively high whereas Ca and other base cations will be reduced and SO_4 levels will reflect pre-melt concentrations.

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Table 1. Composition of the accumulating snowpack in the TLW, February 4, 1986. Data represent the mean values of 11 sampling sites and are expressed as meq.L⁻¹ unless specified otherwise.

	Mean	C.V. % ¹
Water Equivalent (mm)	251.6	10.7
Snow Depth (m)	0.99	8.7
Snow Density	0.25	4.0
H ⁺	0.0266 (pH=4.57)	7.3
NH ₄	0.0075	17.0
Ca	0.0034	19.9
Mg	0.0009	27.7
Na	0.0010	151.0
K	0.0002	37.1
SO ₄	0.0170	8.1
NO ₃	0.0190	5.0
Cl	0.0037	46.5

$$^1\text{C.V.}\% = \text{Coefficient of Variation} \equiv \frac{\text{standard deviation}}{\text{mean}} \times 100\%$$

Table 2. Collection efficiency¹ of the bulk sampler in 1986².

Sampler Type	Number of Samples	Efficiency	
		Mean	Coeff. Variation %
Snow	11	74%	20%
Snow + Mixed	21	80%	22%
Rain	25	93%	10%

$$^1\text{Collector Efficiency} = \frac{\text{Bulk sample volume (mm)}}{\text{Standard precipitation gauge (mm)}} \times 100\%$$

²Results based on unpublished data.

Table 3. Comparison of major ion concentrations in the pre-melt snowpack and in cumulative bulk and wet-only deposition. Units are in meq.L⁻¹ unless otherwise specified.

	Cumulative Deposition Nov. 26/85-Feb. 25/86		Snowpack	Bulk/ Snowpack
	Bulk	Wet-Only	Feb. 25/86	
Water Equivalent (mm)	246.8	246.8	256.5	0.96
H ⁺	0.0374	0.0276	0.0331	1.13
NH ₄	0.0134	0.0091	0.0110	1.22
Ca	0.0023	0.0028	0.0055	0.42
SO ₄	0.0239	0.0195	0.0219	1.09
NO ₃	0.0225	0.0180	0.0193	1.17
Cl	0.0025	0.0027	0.0023	1.09
SO ₄ /NO ₃	1.06	1.08	1.13	

Table 4. Chemistry of rain events during the 1986 melt period. Ion concentrations are in meq.L⁻¹.

	March 25	March 31	April 01	April 05	April 07	April 19
Precip.						
Depth (mm)	5.2	4.8	3.0	12.0	25.2	2.1
H ⁺	0.0002	0.0162	0.0021	0.0851	0.0302	0.1047
(pH)	(6.77)	(4.79)	(5.68)	(4.07)	(4.52)	(3.98)
NH ₄	0.2642	0.0381	0.0367	0.0287	0.0227	0.0324
Ca	0.3019	0.0469	0.0469	0.0065	0.0030	0.0499
SO ₄	0.1918	0.0506	0.0396	0.0589	0.0277	0.1106
NO ₃	0.1399	0.0371	0.0243	0.0250	0.0079	0.0514
SO ₄ /NO ₃	1.37	1.36	1.63	2.36	3.51	2.15

Table 5. Material balance for input from bulk and wet-only deposition and snowmelt output, November 26, 1985 - April 19, 1986.

Units are in eq.ha^{-1} unless otherwise specified.

	Input		Output	Bulk/ Snowmelt
	Bulk	Wet-Only	Snowmelt	
Water Equivalent (mm)	400.8	400.8	374.5	1.07
H ⁺	164.2	133.5	171.0	0.96
NH ₄	87.4	69.4	72.0	1.21
Ca	37.4	37.3	39.4	0.95
SO ₄	141.5	116.3	133.9	1.06
NO ₃	106.8	92.4	95.2	1.12
Cl	11.4	10.7	14.8	0.77
SO ₄ /NO ₃	1.32	1.26	1.41	

Table 6. Dry deposition as a percentage of total atmospheric deposition.

Ion	Feb. 25/86 Snowpack	Cumulative Snowmelt	Average	N. Michigan 1982-1984¹	TLW 1981-1984²
H ⁺	16.6	21.9	19.3	1-13	
NH ₄	17.3	3.6	10.5	14-25	
Ca	-	5.3	5.3	19-45	
SO ₄	11.0	13.1	12.1	11-30	14-26
NO ₃	6.7	2.9	4.8	10-28	22-34
Cl	-	27.7	27.7	15-44	

¹Cadle et al. (1986)

²Sirois and Vet (this volume)

Table 7. Comparison of major ion concentrations (meq.L⁻¹) in snowmelt and lake waters¹ from Batchawana Lake North (L1) and Turkey Lake (L5). Initial snowmelt concentration is from the first litre of meltwater collected; the 20% concentration is the volume-weighted value for the first 20% of the total melt. The ratio of the initial and 20% melt concentration to the lake concentration is also presented.

Ion	Snowmelt		Batchawana Lake North			Turkey Lake	
	Initial	20%	L1	Ratio		L5	Ratio
				Initial	20%		
H ⁺	0.3236	0.1183	0.0010	324	118	0.0002	1618
Ca	0.0205	0.0181	0.1108	0.2	0.2	0.2760	0.1
NH ₄	0.0447	0.0374	0.0036	12	10	0.0010	45
SO ₄	0.2344	0.0998	0.1068	2	0.9	0.1250	2
NO ₃	0.1564	0.0676	0.0079	20	9	0.0143	11
Cl	0.0116	0.0080	0.0092	1	0.9	0.0096	1
							0.8

¹Lake concentrations represent median values for volume-weighted, whole lake samples collected from 1980 to 1985 (Jeffries et al., this volume).

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FIGURE 1

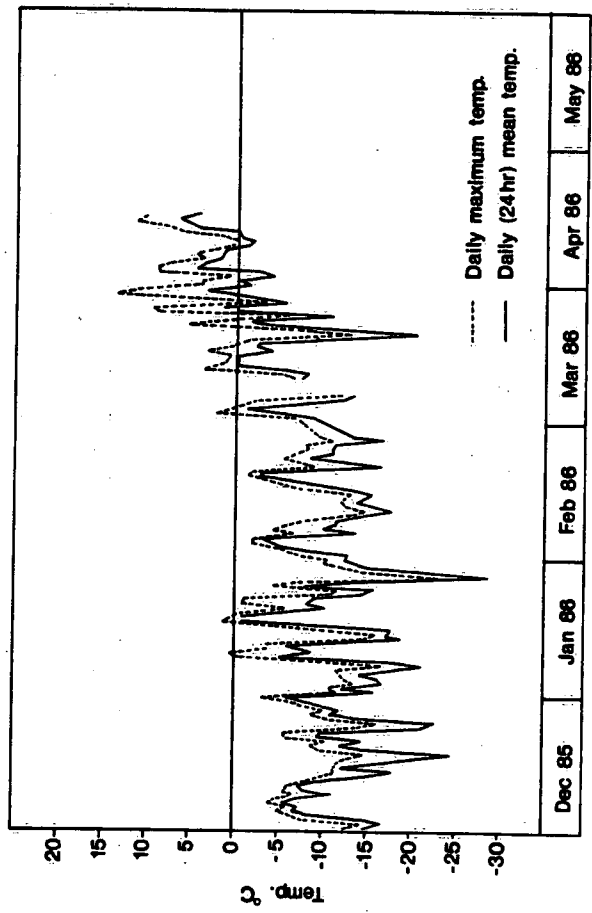


FIGURE 2

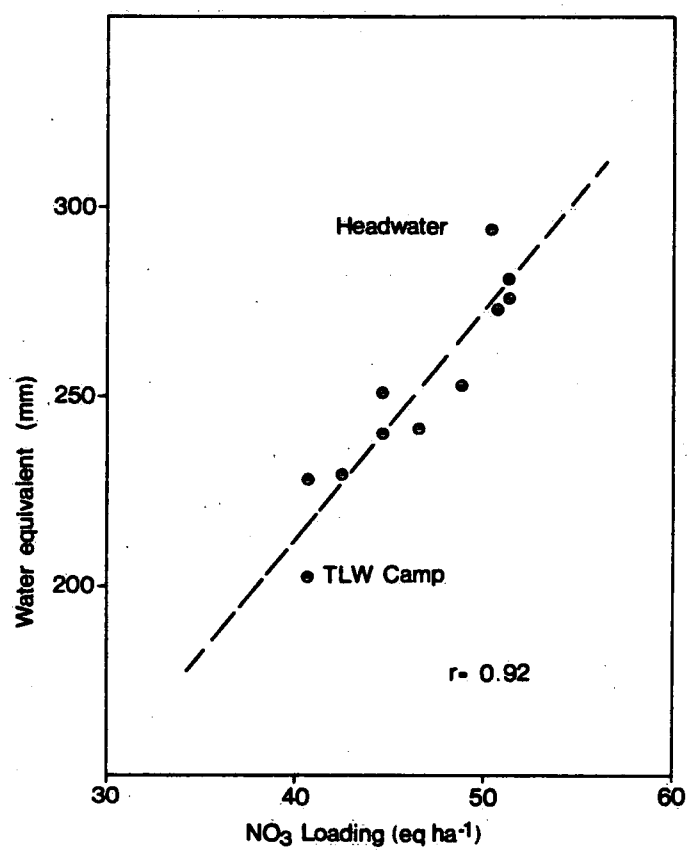


FIGURE 3

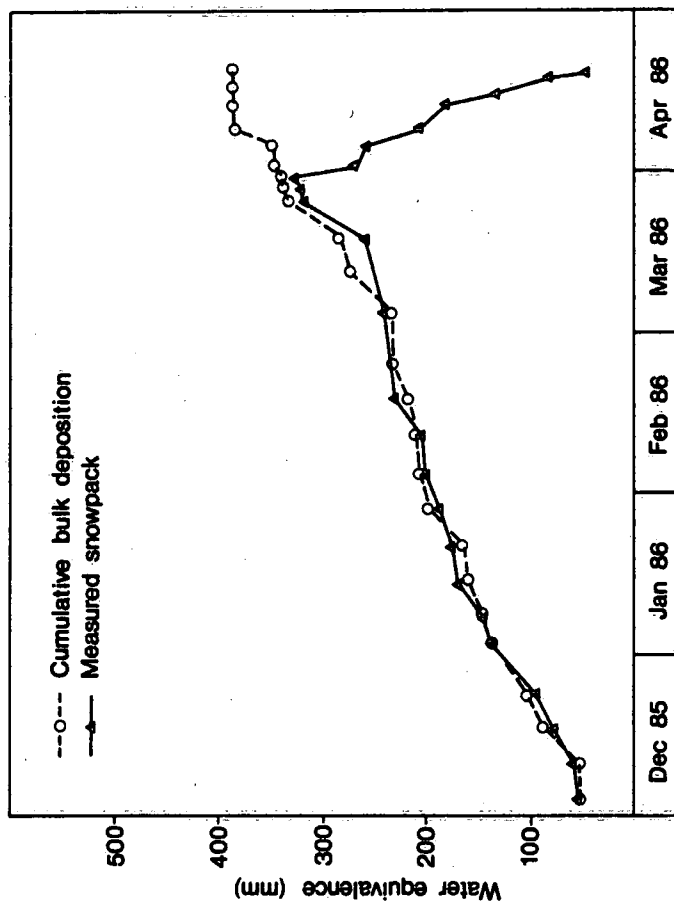


FIGURE 4

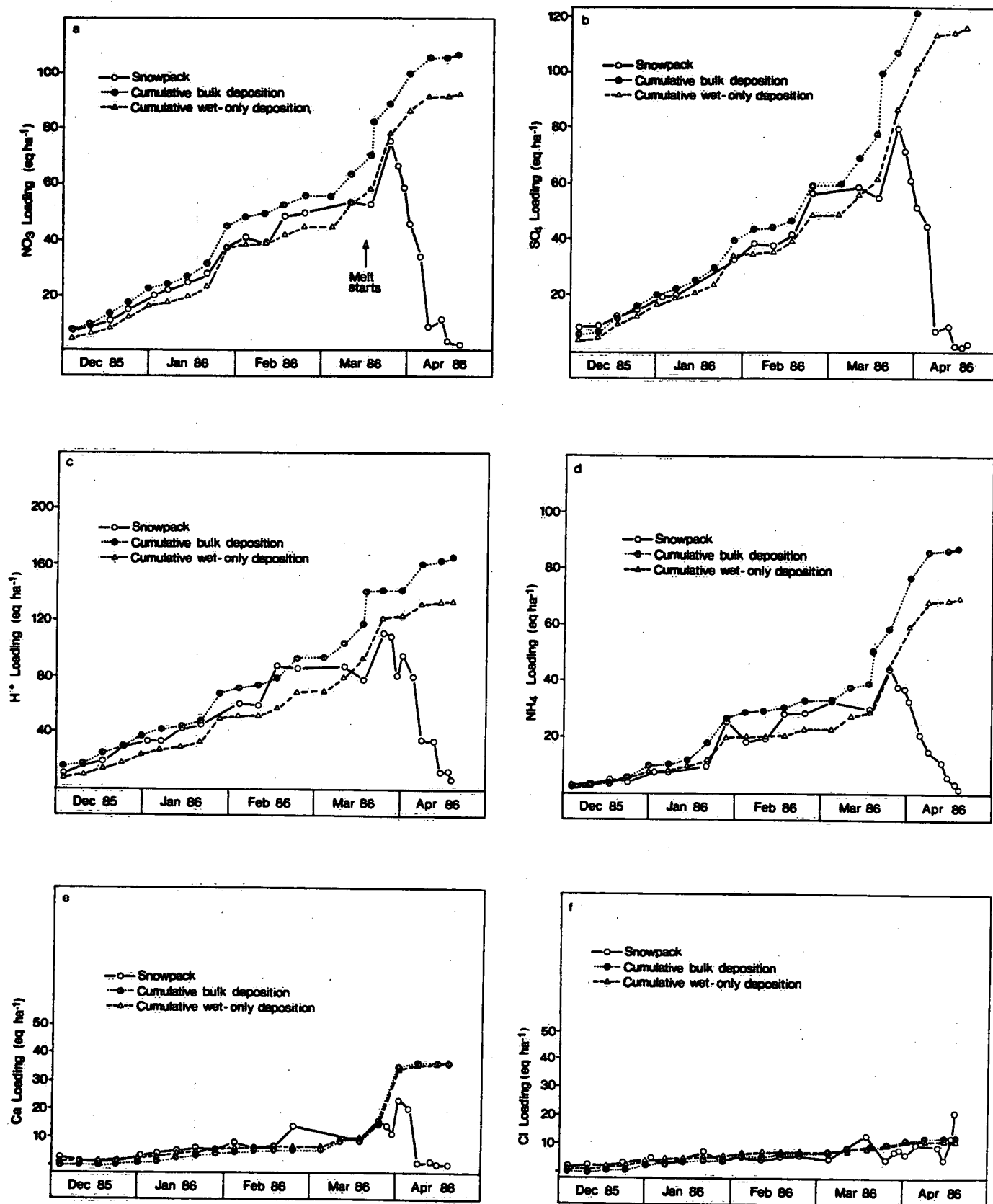


FIGURE 5

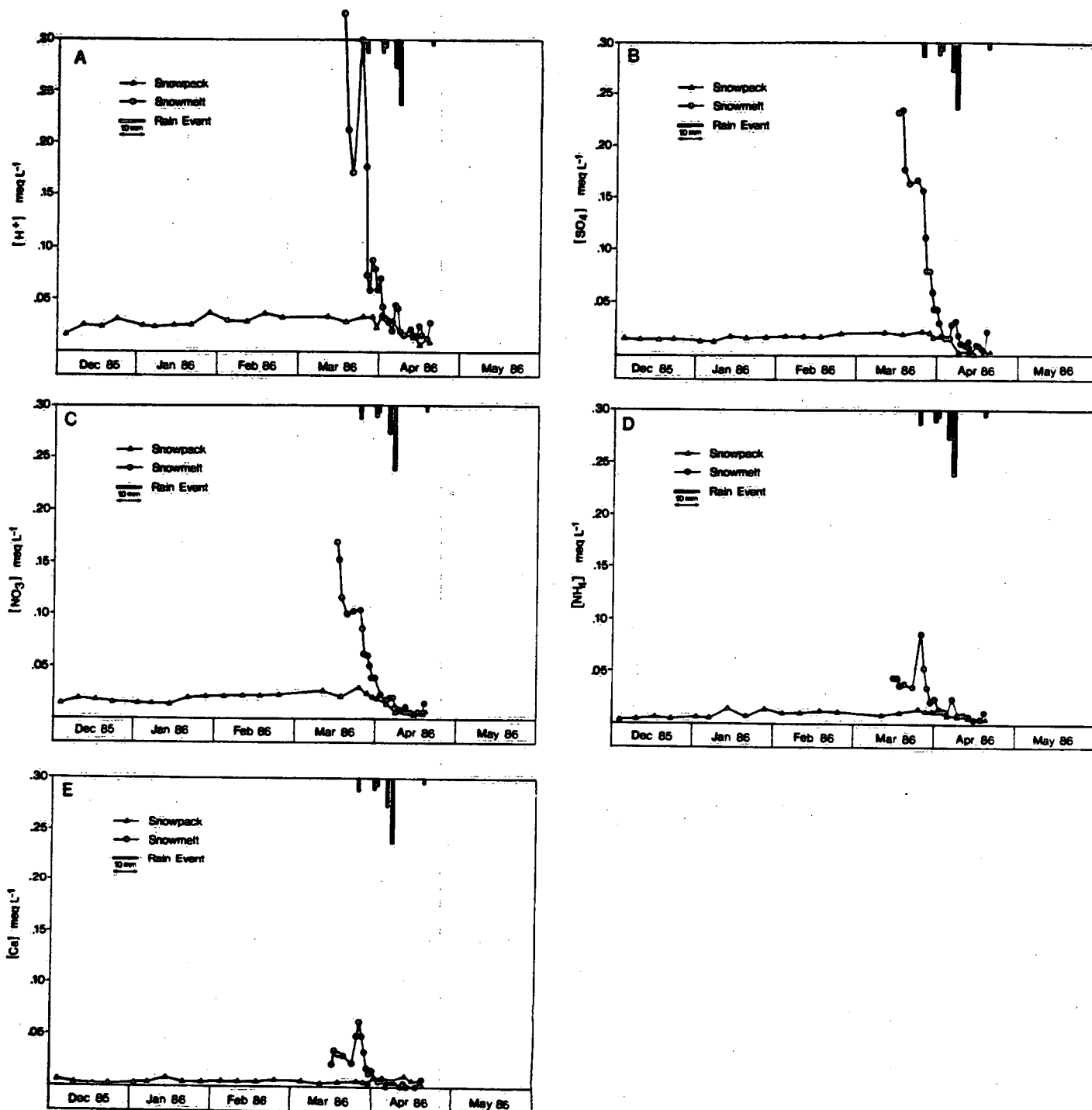


FIGURE 6

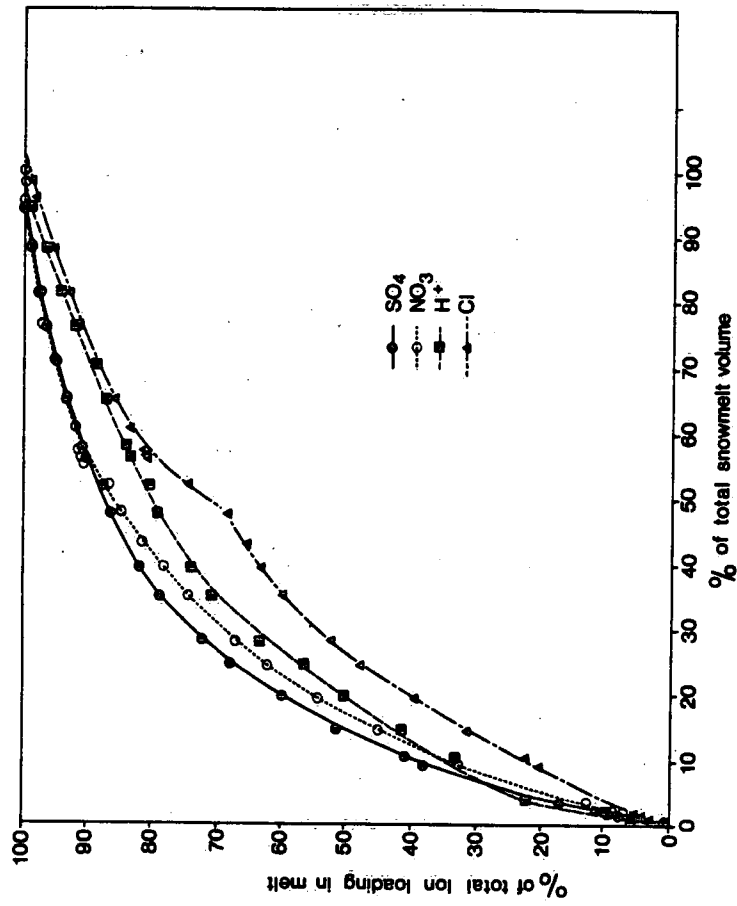


FIGURE 7

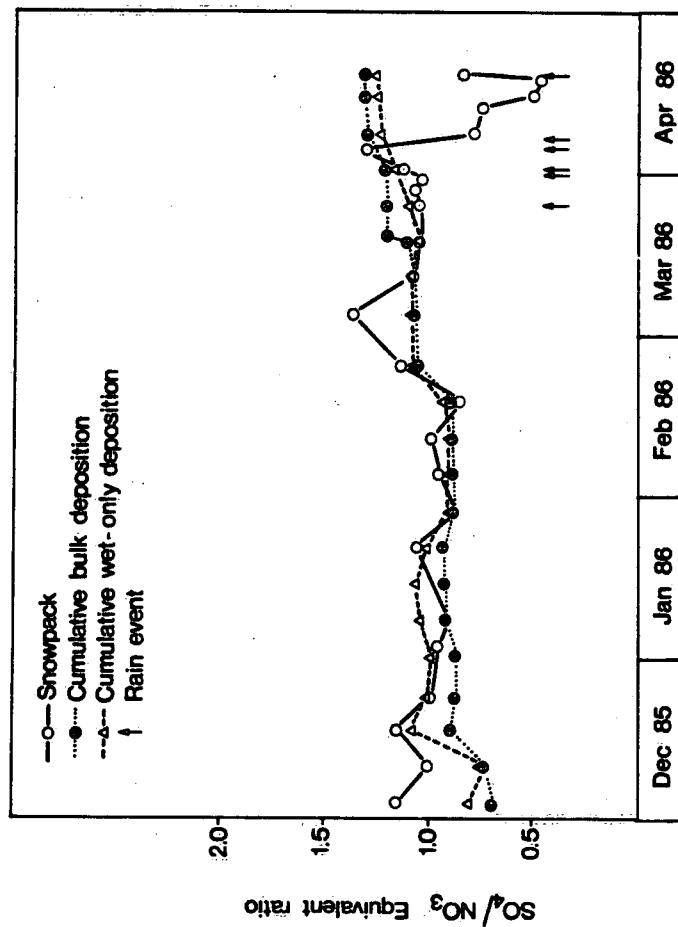


FIGURE 8

