

## **Soil and Stream Water Chemistry During Spring Snowmelt**

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In order to determine how water flowpath controls stream chemistry, we studied both soil and stream water during spring snowmelt, 1985. Soil solution concentrations of base cations were relatively constant over time indicating that cation exchange was controlling cation concentrations. Similarly  $\text{SO}_4$  adsorption-desorption or precipitation-dissolution reactions with the matrix were controlling its concentrations. On the other hand,  $\text{NO}_3$  appeared to be controlled by uptake by plants or microorganisms or by denitrification since their concentrations in the soil fell abruptly as snowmelt proceeded. Dissolved Al and pH varied vertically in the soil profile and their pattern in the stream indicated clearly the importance of water flowpath on stream chemistry. Although Al increased as pH decreased, the relationship does not appear to be controlled by gibbsite. The best fit of calculated dissolved inorganic Al was obtained using  $\text{AlOHSO}_4$  with a solubility less than that of pure crystalline jurbanite.

### **Introduction**

Spring snowmelt is responsible for the movement of a large quantity of water and dissolved material from watersheds into streams. During the fall, in basins covered by deciduous forests, there is an accumulation of a large mass of relatively easily mineralizable plant nutrients due to litter fall. The accumulation of snow containing wet and dry deposited atmospheric pollutants also represents a store of both plant nutrients and other soluble ions. During the melt period, before the soils have become warm enough for plant and microorganism demand to reach its peak, these nutrients may be lost from the rooting zone.

Not only are plant nutrients lost, but there is also a transport of toxic substances such as Al (Cronan and Schofield 1979). Due to the high water-table during the melt period, water moves horizontally through the upper metre of soil. This flow path through the more acidic horizons can lead to an acid shock in nearby streams and lakes that may have serious consequences for aquatic organisms (Hendershot *et al.* 1984, 1986, Cozzarelli *et al.* 1987). In areas covered by acid soils in southern Quebec, trout and salmon eggs hatch during the melt period. At this early life stage sudden drops in pH or increases in toxic forms of Al can decrease survival significantly (Driscoll *et al.* 1980, Schofield and Trojnar 1980, Campbell *et al.* 1983).

The objective of this study was to determine the relationship between the chemistry of soil solutions and stream water in a small forested catchment in the Lower Laurentians of Quebec during snowmelt.

## Materials and Methods

### Study Site

The Hermine watershed is located in the Station de Biologie de l'Université de Montréal near St-Hippolyte, Québec, Canada (45° 59'N, 74° 01'W), about 80 km north of Montréal. The catchment has a surface area of 0.06 km<sup>2</sup> with a drainage system consisting of an intermittent first-order stream (Fig. 1). The area receives about 1,100 mm of precipitation annually of which 30% falls as snow (Wilson 1971). The bedrock is Precambrian anorthosite of the Morin series (McGerrigle 1958). Except for outcrops in the downstream area and along some of the divides between watersheds, the bedrock is covered by a glacial till with a mineral composition similar to that of anorthosite. The soils are Humic Cryorthods (Soil Survey Staff 1975). The canopy vegetation is dominated by sugar maple (*Acer saccharum* – 80%), with lesser amounts of American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*).

### Field Study

During the 1985 melt season, temperature, precipitation and snow-pack depth were recorded at the meteorological station located about 1 km from the Hermine watershed. Stream discharge was calculated from the water level above a v-notch weir which was measured continuously with a Belfort water level recorder. The weir was calibrated using direct discharge measurements by the dye dilution method of Adams (1966). The water-table height was measured using shallow groundwater wells constructed of 5 cm diameter ABS plastic pipe, open at the bottom and pierced every 7.5 cm with two 10 mm holes on opposite sides. The water-table level was measured once or twice per week. At each site 4 zero-tension lysimeters were installed: 1) at the upper surface of the organic horizons of the soil (10 cm) to collect overland flow, 2) at the organic and mineral horizon interface (0

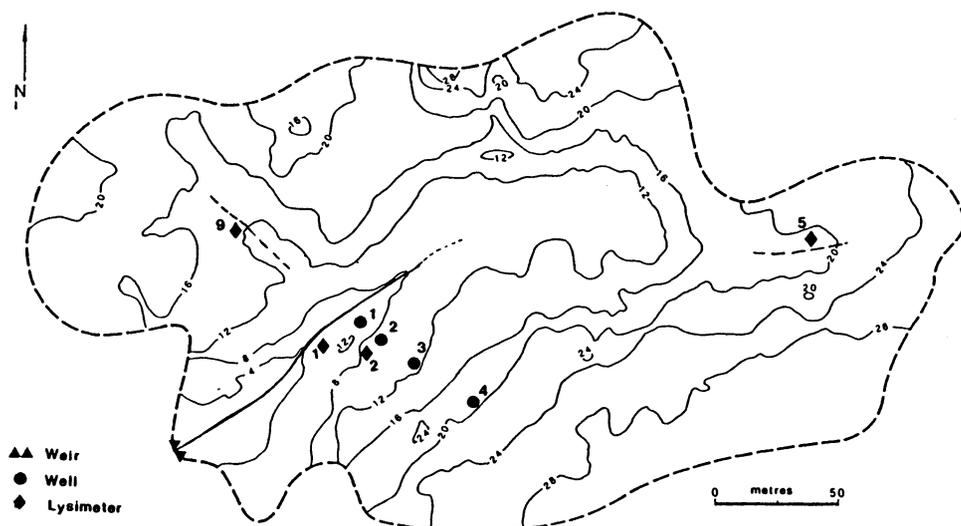


Fig. 1. Map of the Hermine watershed showing location of weir, shallow ground water wells and lysimeters; contour lines are metres above weir.

cm), 3) in the spodic horizon (-25 cm), and 4) at the approximate boundary between B and C horizons (-75 cm). The soil solution collectors at 10, 0 and -25 cm depths were constructed of 10 cm ABS plastic pipe. The lower end was capped and 6 holes (8 mm dia.) drilled around the circumference at 40 cm from the base. These samplers only collect water when the water-table rises above the level of the holes but they hold the water collected when the water-table drops. The collectors at -75 cm were made from 5 cm ABS plastic pipe capped at the bottom and pierced just above the cap. The solutions from each lysimeter were analysed separately. Stream water was sampled 4 to 12 times per day with an automatic water sampler located just upstream from the v-notch weir while soil solutions were sampled once or twice per week.

### Laboratory Analyses

Electrical conductivity (EC) and pH were measured in a field laboratory within 4 hours of sample collection on unfiltered samples. Solutions were filtered through 0.4  $\mu\text{m}$  polycarbonate membranes and stored at 4°C in the dark in polyethylene bottles. Total F in solution was measured with an Orion ion selective electrode and total ionic strength adjustment buffer (TISAB II) solution (Anonymous 1983). Total  $\text{SO}_4$  was measured by the method of Wagner and Steele (1982) and  $\text{NO}_3$  was measured colorimetrically (Lavkulich 1981). Calcium, Mg, and K were measured by atomic absorption spectrophotometry. Aluminum speciation was performed

using the pyrocatechol violet (PCV) method (Henriksen and Bergmann-Paulsen 1975; Røgeberg and Henriksen 1985) modified to give three forms of Al: Acid extractable Al (Al<sub>t</sub>) was measured after acidifying the sample to 2% HNO<sub>3</sub>. Total monomeric Al (Al<sub>m</sub>) was measured on an unacidified sample. For a limited number of samples monomeric organic Al (Al<sub>o</sub>) was separated from Al<sub>t</sub> by suspending a 1,000 molecular weight cut off dialysis tube containing 30 mL of solution in 500 mL of deionized water for 24 h (LaZerte 1984). At the end of this period the labile Al inside the dialysis tubing was reanalysed for monomeric Al. Inorganic Al was able to migrate through the dialysis tubing while the larger organic complexes were retained. Al<sub>t</sub>, the difference between Al<sub>m</sub> and Al<sub>o</sub>, was further speciated into Al<sup>3+</sup> and its different complexes with OH, F and SO<sub>4</sub> using the ALSPEC program; solubility constants and activity coefficients were adjusted to 2°C (Hendershot and Courchesne 1988; Courchesne and Hendershot 1990).

Data for stream flow and stream chemistry were smoothed by median-3 smoothing to eliminate outliers and reduce noise (Wilkinson 1989).

## Results and Discussion

### Melt Periods

Although there had been three small peaks in the hydrograph before March 15 the maximum discharge did not exceed 0.9 L s<sup>-1</sup>. Between March 15 and 27 temperatures rose above 0°C during the day and although the water-table height increased slightly, stream discharge was not significantly affected. Maximum daily temperatures rose above 0°C on March 28 and there was a total of 16 mm of rain (Fig. 2). This led to a rise of the water-table and an increase in stream discharge to about 3 L s<sup>-1</sup> (Figs. 2 and 3). A similar pattern was observed on April 5 to 8 when 16 mm of rain fell over a two-day period. The majority of the melt occurred during the period from April 15 to 28; temperatures remained warm except for April 16 to 17 and rain fell on April 15, 16 and 18. During the period from April 15 to 28 the water-table remained near the soil surface and stream discharge remained between 10 and 25 L s<sup>-1</sup>. By the end of April there was virtually no snow remaining; water-table levels fell and the stream discharge returned to near base flow values (<2 L s<sup>-1</sup>) by May 10.

### Stream and Soil Solution Chemistry

Concentrations of the sum of the non-hydrolyzable base cations Ca, Mg, K (BC) fell in the stream during the early melt period from initial values of about 240 μmol<sub>c</sub> L<sup>-1</sup> to about 150 μmol<sub>c</sub> L<sup>-1</sup> (Fig. 3). There was a small additional depression during the latter part of the main snowmelt (April 21-25). Data are not available for BC in soil solutions before April 3 so it is impossible to say if the same pattern was

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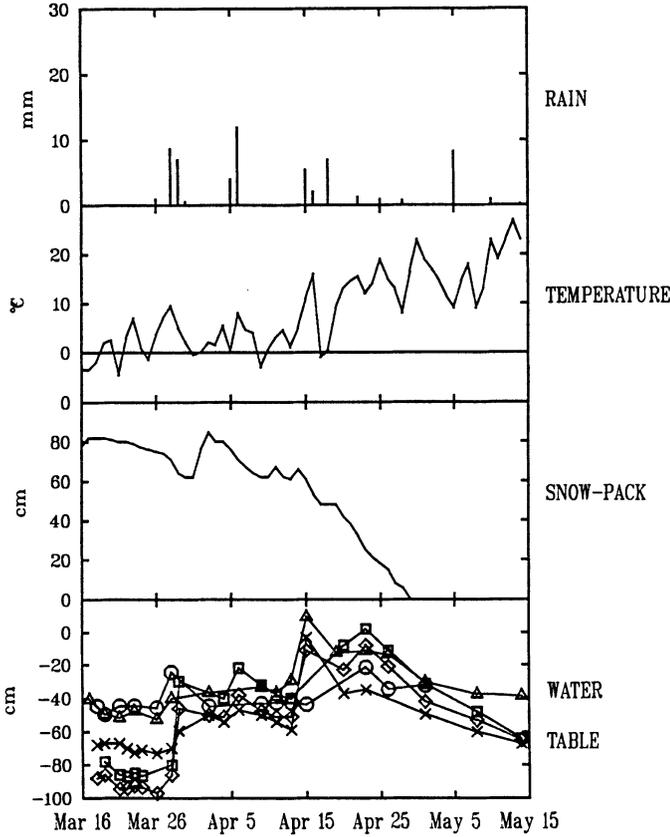


Fig. 2. Rainfall, maximum daily temperature, snow-pack depth and water-table position. Note that the zero level in the latter is the boundary between organic and mineral horizons. The symbols refer to different well locations:  $\circ$  = P1,  $\triangle$  = P2,  $\square$  = P3,  $\diamond$  = P4,  $\times$  = P5.

followed. Throughout the period from April 3 to the end of the melt BC concentrations in the soil solutions at all depths remained fairly constant with median values falling near  $150 \mu\text{mol}_c \text{L}^{-1}$ . Cation exchange reactions between cations in solution and adsorbed on exchange sites would be expected to buffer changes in ion concentrations very strongly. In this study the collectors at 10 cm only collect water flowing across the surface of the soil. It is noteworthy that the chemistry of this overland flow is very similar to that of the water flowing deeper in the soil profile. In contrast, the rain or snow contains much lower concentrations of BC (data not presented). We conclude that the water flowing overland is either upwelling return flow or, at least, has had enough contact with the soil to adopt its chemical signature.

Despite the large spatial variability of  $\text{NO}_3$  concentrations in the soil solution,

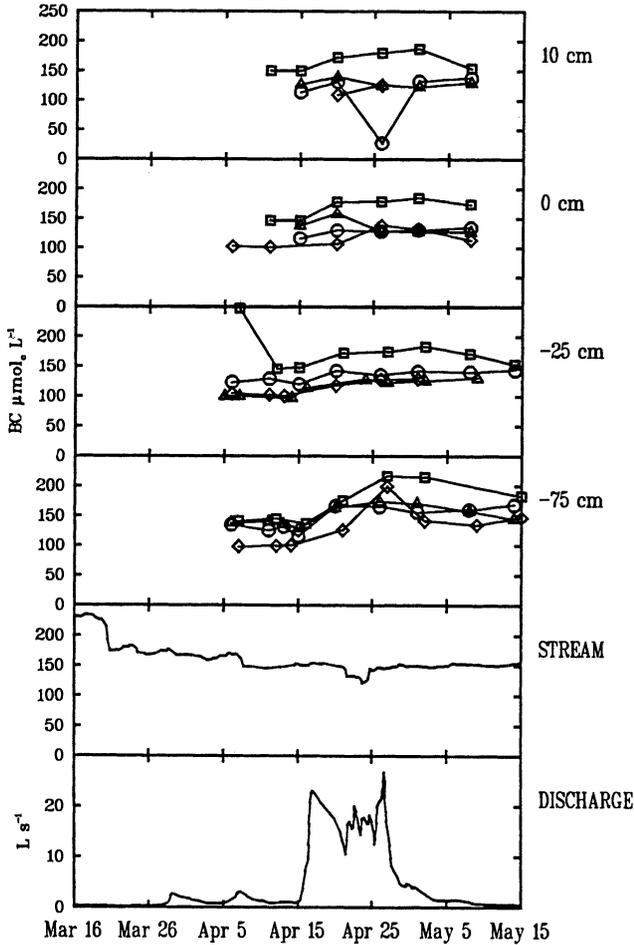


Fig. 3. Base cation content in soil solution and stream water. The symbols represent different sites in the basin:  $\circ$  = L1,  $\triangle$  = L2,  $\square$  = L5,  $\diamond$  = L9.

the pattern is clear (Fig. 4). Early in the melt period  $\text{NO}_3$  concentrations in the mineral horizons reached a maximum of over  $40 \mu\text{mol}_c \text{L}^{-1}$  and, at all sites except L5, decreased below  $5 \mu\text{mol}_c \text{L}^{-1}$  as the end of the melt period was reached. The  $\text{NO}_3$  concentration in the stream at base flow at the beginning of the melt stayed near  $6 \mu\text{mol}_c \text{L}^{-1}$  and reached peaks of 8 to  $9 \mu\text{mol}_c \text{L}^{-1}$  during the first three melt events on March 28, April 8 and 15. These peaks may be related to periods of flow through the upper soil that washed  $\text{NO}_3$  into the stream and helped to decrease the concentration in the soil. The peaks could also be a function of rain-on-snow events capable of mobilizing the brine that forms between relatively pure ice crystals as the snow ages. After April 20 both soil and stream concentrations dropped off simultaneously with stream  $\text{NO}_3$  concentrations falling to below  $5 \mu\text{mol}_c \text{L}^{-1}$ . The

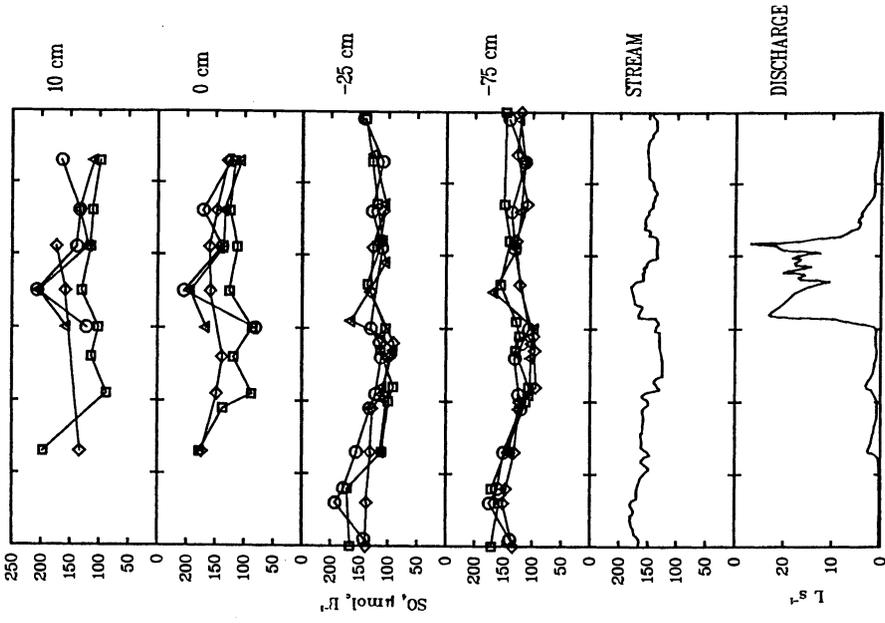
concentration pattern in the soil solutions is similar to that observed for melt waters leaving the snow-pack (Seip 1978). Given the large decrease in  $\text{NO}_3$  concentration in the soil solution and the modest peaks in the stream during high flow periods we concluded that some mechanism other than leaching must be responsible for the decline in concentration. Two possibilities can be suggested: 1) uptake by plants or microorganisms or 2) denitrification caused by reduction below the water-table. To date the data needed to correctly interpret these results are not available.

The pattern of  $\text{SO}_4$  during the melt period is very different from that of  $\text{NO}_3$  (Fig. 5). The concentration of  $\text{SO}_4$  in the soil profile was relatively constant over both depth and time. There was a slight decrease from about 160 to 140  $\mu\text{mol}_c \text{L}^{-1}$  during the period from March 15 to April 5 with the values in the soil remaining at this level until the end of the melt. Concentrations of  $\text{SO}_4$  in the stream followed a complex pattern with a slight drop from values of 180 to less than 150  $\mu\text{mol}_c \text{L}^{-1}$  during the period March 15 to April 14; and increased to over 175  $\mu\text{mol}_c \text{L}^{-1}$  during the first really large melt on April 15 to 25 and then decreased to values of about 140-150  $\mu\text{mol}_c \text{L}^{-1}$  for the remainder of the melt period.

The pH of the soil solutions at each depth did not display any clear trends during the melt period (Fig. 6). The water in contact with the surface organic layers (collectors at 10 and 0 cm) had pH ranging from 4.7 to 5.9 with most of the values falling around 5.1. Soil solution pH increased somewhat with depth with a median near 5.25 at -25 cm and 5.5 at -75 cm depths. Spatial variability was greater at -75 than at -25 cm, although the reason for this is unclear. Stream water pH was higher than soil solution pH throughout the melt period. During base flow conditions most of the water entered the stream from deep groundwater where long residence times favoured the neutralization of  $\text{H}^+$  by mineral weathering reactions. At this time stream pH was near 6.0. However during the maximum melt period (April 15 to 30) pH dropped to about 5.5 as a much greater proportion of stream flow was generated by water moving through the upper metre of soil. Stream pH rose again as flow decreased after May 1.

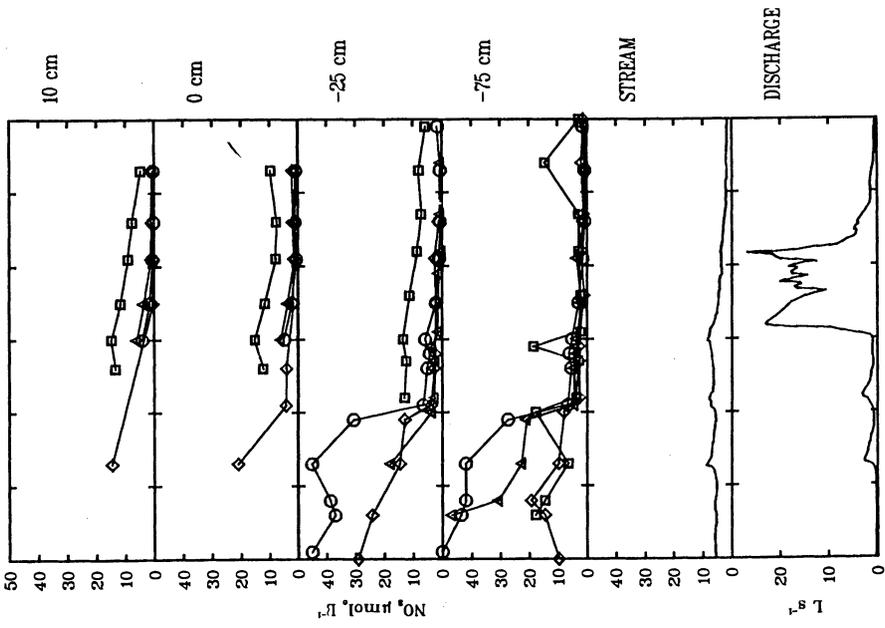
Both Alt and Alm followed a similar pattern with values of Alt being approximately 50% higher than Alm; only the data for Alm are presented (Fig. 7). Concentrations of Alm varied greatly from one site to another as was evidenced by the large scatter of points, particularly for depths of 10, 0 and -25 cm. At -75 cm reactions with the soil solid phase appear to have led to a reduction in the concentration of Alm and a damping out of both temporal and spatial variability. The median concentration in the upper three layers was about 11  $\mu\text{mol}_c \text{L}^{-1}$  while at -75 cm depth the median value was about 6  $\mu\text{mol}_c \text{L}^{-1}$ . The pattern of Alm in the stream was the opposite of that observed for pH, with low values of about 4  $\mu\text{mol}_c \text{L}^{-1}$  observed early in the melt rising to near 10  $\mu\text{mol}_c \text{L}^{-1}$  during the peak melt period and then dropping back as the discharge decreased at the end of the melt. This pattern is indicative of a greater contribution of Al-rich water flowing through near-surface horizons during high flow periods.

The symbols represent different sites in the basin:  $\circ = L1$ ,  $\triangle = L2$ ,  $\square = L5$ ,  $\diamond = L9$ .



Mar 16 Mar 26 Apr 5 Apr 15 Apr 25 May 5 May 15

Fig. 5. Sulfate content in soil solution and stream water.



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Fig. 4. Nitrate content in soil solution and stream water.

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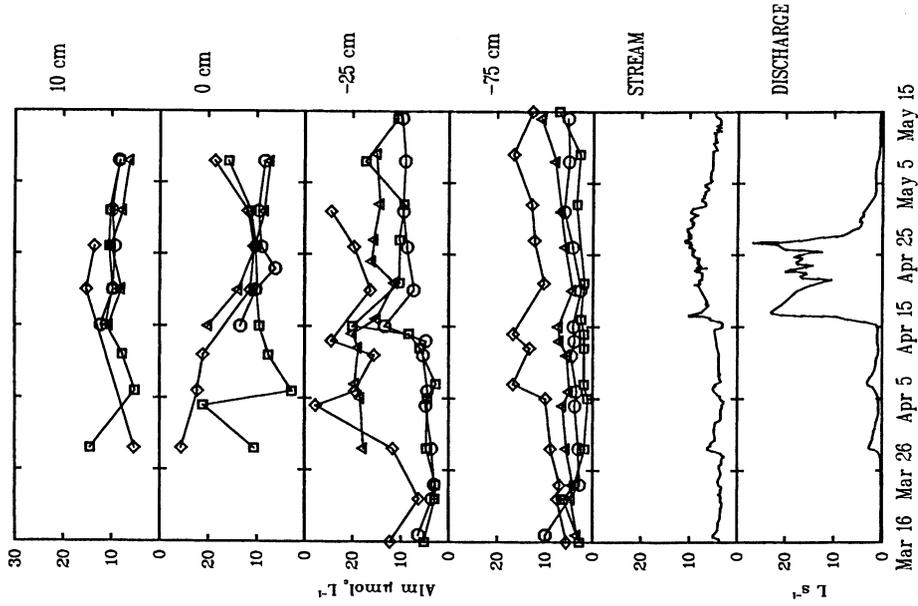


Fig. 7. Monomeric Al content in soil solution and stream water.

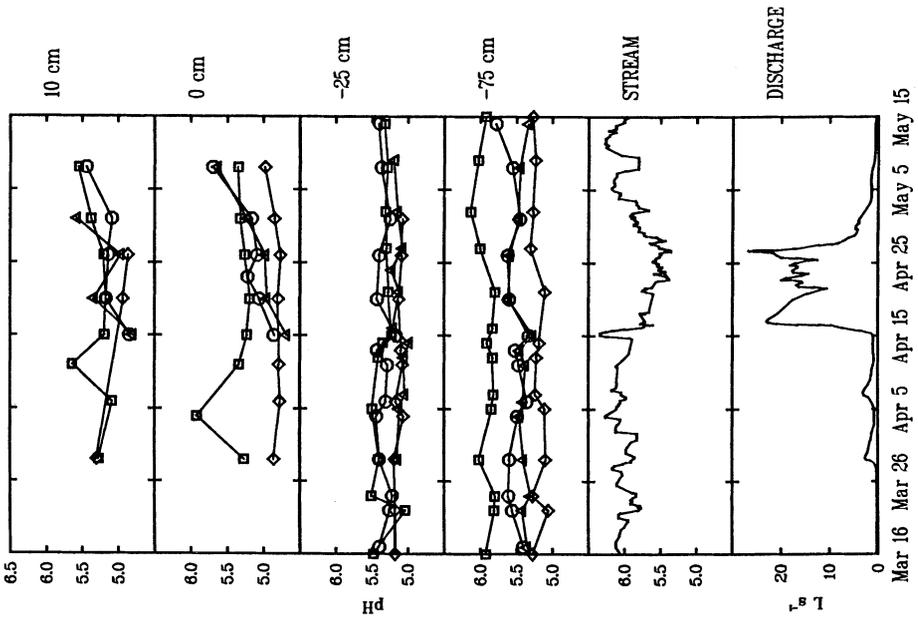


Fig. 6. pH of soil solution and stream water.

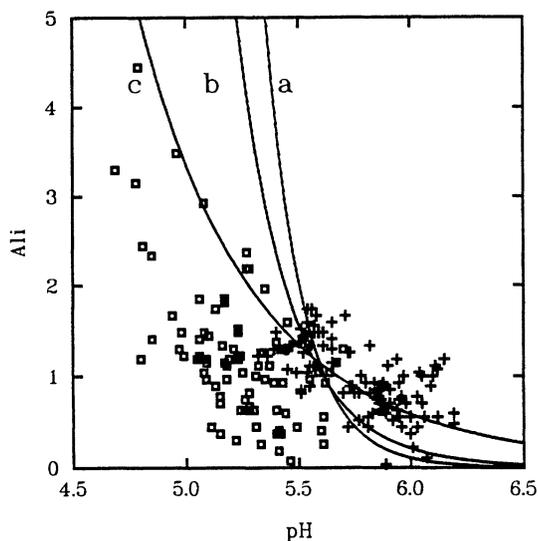


Fig. 8. Inorganic Al *versus* pH in stream water and soil solution, + = stream, □ = soil solution and the curves indicate calculated curves based on gibbsite (a), alunite (b) and jurbanite (c).

### Speciation of Inorganic Aluminium

In Fig. 8 calculated values of Ali in soil and stream water are compared to measured values. As pointed out by Neal (1988) the calculation of  $\text{Al}^{3+}$  from measured solution Al concentration requires the use of pH. Thus there is an autocorrelation in the conventional approach of plotting  $\log \text{Al}^{3+}$  versus pH; this tends to give the impression that Al solubility is controlled by an  $\text{Al}(\text{OH})_3$  mineral even if this is not the case. In contrast the use of linear plots of measured Ali *versus* pH avoids this problem.

Based on the activities of the ions in solution at 2°C, the median ion activity products (IAP) were calculated for gibbsite ( $\text{Al}(\text{OH})_3$ ), alunite ( $\text{KAl}_3\text{OH}_6(\text{SO}_4)_2$ ) and jurbanite ( $\text{AlOHSO}_4$ ). The calculated values of Ali plotted in Fig. 8 were obtained by determining the amount of  $\text{Al}^{3+}$  that would be in solution if gibbsite, alunite or jurbanite with solubilities determined by the median measured IAP values were, in fact, controlling  $\text{Al}^{3+}$  solubility. The resulting  $\text{Al}^{3+}$  values were then used in conjunction with measured values of pH, F and  $\text{SO}_4$  to obtain the calculated values of Ali for each sample solution (F concentration was about 1  $\mu\text{M}$  while  $\text{SO}_4$  was about 150  $\mu\text{M}$ ). In order to simplify the figure the individual points of the calculated Ali values were replaced with the best fit curve. It is clear that the patterns of the measured and calculated values for gibbsite and alunite do not appear to coincide. At high pH Ali is greater than would be found in equilibrium

with gibbsite or alunite while at low pH the measured values are too low. The calculated value of Ali based on jurbanite gives a much better fit to the measured values, although many of the solutions still appear over saturated at high pH and under saturated at low pH.

The relationships between measured Ali and those calculated with gibbsite, alunite and jurbanite were tested using regression analysis of the form:

$$\text{Ali (meas)} = C \text{ Ali (calc)}$$

where the constant  $C$  indicates the slope of the regression line; a slope of 1.0 would indicate that the measured values fell evenly about the line for the calculated values. For gibbsite, alunite and jurbanite the slopes were 15.4, 4.2 and 1.4 respectively and the standard errors of estimate were 35.7, 10.1 and 2.9 respectively. These results support the visual evaluation of the curves in Fig. 8 that the theoretical curve for jurbanite most closely follows the pattern of measured Ali versus pH.

Caution must be used in interpreting these data since only the median IAP for gibbsite (34.7) falls close to the theoretical solubility product ( $pK_{SO}$ ) of 34.2 at 2°C (May *et al.* 1979). The median IAP for alunite was calculated at 90.1 at 2°C, while published  $pK_{SO}$  values are near 88.5 when adjusted to 2°C, indicating that the solid phase controlling Al in the soil was less soluble than pure alunite (Adams and Rawajfih 1977). Similarly the median IAP for jurbanite was 20.3 at 2°C compared to values of  $pK_{SO}$  of 17 to 18 at 25°C for soils in which jurbanite was thought to be controlling Al solubility (Khanna *et al.* 1987; Freiesleben 1988). Data were not available to calculate the theoretical solubility of jurbanite at 2°C; these data are needed to verify whether this is a possible solid phase under snowmelt conditions at this site. Generally jurbanite is only considered to be a significant solid phase in controlling Al and  $SO_4$  in soils with pH below 4, however the effect of temperature on the mineral's stability needs to be taken into account (Drever 1988). Nonetheless, the slope of the pH-Ali curve for jurbanite fits the measured data much better than the curves of the other two minerals. The lower solubility in these soils could be due to the fact that the  $AlOHSO_4$  material is part of a surface complex rather than a separate mineral phase. The results suggest that modelling of Al solubility in these soils and stream waters might be better done using this (unknown) form of  $AlOHSO_4$  than gibbsite, as is commonly done (Reuss and Johnson 1986; Cosby *et al.* 1985; Hendershot and Courchesne 1991).

The apparent fit of the field data to the stoichiometry of an  $AlOHSO_4$  material can not be taken as proof that such a material is in fact controlling Al solubility. It should be noted that the solutions with the lowest pH are those from the surface soil horizons and hence have had the shortest contact time with the soil. That they are under saturated with respect to some mineral phase is therefore not unexpected. Similarly the solutions with the highest pH are those from the stream where mixing of water from soil and groundwater, combined with short contact times, could be responsible for the apparent over saturation.

## **Conclusion**

There can be little doubt that water trapped by the overland flow collectors has had enough contact with the soil to take on its chemical characteristics. Although we have observed water flowing along ice lenses in the snow-pack, we believe that this is a relatively small contribution to stream discharge compared to water that has chemistry similar to that of the soil solution. As discussed previously, water leaving the snow-pack early in the melt can be expected to contain very high concentrations of ions, such as  $\text{NO}_3$ . However, the small peaks observed in stream water chemistry can be more easily explained by water flowing through the soil than the snow pack.

Based on their behaviour during snowmelt, the ions can be divided into three groups. Concentrations of both  $\text{BC}$  and  $\text{SO}_4$  remained relatively constant throughout the melt period except for a small decrease at the start of the melt. It appears that the soil is able to buffer fluctuations in their concentrations by means of adsorption-desorption or precipitation-dissolution reactions. Concentrations of these ions were also constant with depth and hence tend to be poor indicators of water flow path.

Peaks in  $\text{NO}_3$  concentration in stream waters are an indication of significant contribution of flow through the upper soil horizons to stream discharge. The values of  $\text{NO}_3$  in soil and stream water also decrease as the melt period advances. The decrease may be due to the increased demand for N by plants and microorganisms as temperatures rise, or to denitrification as reducing conditions develop below the water table.

The concentration of Al and pH are fairly constant over time in the soils and show a gradual change with depth: as pH increases Al decreases, as would be expected. These measures appear to be the best indicators of the control exerted by water flow path on stream chemistry. Early in the melt when water reaches the stream mainly via the ground water Al was low and pH high. During the maximum melt, stream values of both pH and Al approach those in the upper metre of soil as water flows horizontally through this saturated zone.

The role of gibbsite in controlling Al solubility seems questionable in these soil and stream waters. More critical evaluation of the mechanisms of Al dissolution and precipitation is clearly warranted.

## **Acknowledgments**

This project was funded by grants from the Natural Sciences and Engineering Research Council of Canada, and Fonds pour la Formation de Chercheurs et l'Aide à la Recherche du Québec. We thank Claude Lapierre and Alain Dufresne for their assistance with field and laboratory work.

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First version received: 8 April, 1991

Revised version received: 23 September, 1991

Accepted: 15 October, 1991

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