SPECIATION OF ALUMINUM IN DIFFERENT COMPARTMENTS OF A DRAINAGE BASIN DURING SNOWMELT

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ABSTRACT

It is hypothesized that streamwater chemistry during snowmelt is a function of the flowpath of water through the soils. Measurements made at St-Hippolyte, Québec, show the variation in aluminum speciation and concentration in the snowpack, incoming precipitation, shallow groundwater and the stream itself. The incoming precipitation contains very low concentrations of uncomplexed monomeric, complexed monomeric and polymeric aluminum; the concentrations found in the stream are therefore a result of the passage of the meltwater through the soils or of old water displaced by inflowing meltwater.

INTRODUCTION

In southern Québec there are two periods each year when maximum streamflow occurs. In the spring the melting snow, combined occasionally with heavy rainfall, can be expected to result in the maximum peak discharge for a normal year. During the fall the region receives relatively heavy rain and again stream discharge is quite high, although still 8 to 10 times less than that in the springtime. In summer and winter discharge is very low: during the former the precipitation is light and in the latter the precipitation is stored in the watershed as snow (Courchesne, 1984).

In terms of stream water chemistry the spring and fall seasons are viewed as the two critical periods during which the highest concentration of H^+ and soluble aluminum will be flushed into the streams. In addition, the effects of acid deposition are most severe at the end of any period of low outflow. Hence during spring snowmelt the pollutants that have accumulated in the snow are released in a very short period of time during the first major melt event. This problem is aggravated by the recrystallization of the ice and the segregation of the pollutants into a brine that is displaced with the first water flowing through the snowpack (Overrein et al., 1980). The first heavy rainfall after a very dry summer can produce a similar effect by washing the accumulated pollutants from the vegetation and forest floor.

Although the accumulated pollutants from atmospheric deposition flushed from the system early in the spring and fall, it is important to keep in mind the contribution of natural weathering products. During the winter and summer the soluble material resulting from the breakdown of inorganic (mineral) and organic material in the soils will remain in place. One of the most striking examples of this is the abundance of soluble organic material that is released by leaves as they fall in the autumn. Since much of this soluble material is not leached out during the winter it provides a rich flush of material early in the snowmelt period.

The spring snowmelt period is widely recognized as being critical to the aquatic environment. The flush of pollutants from the terrestrial to the aquatic ecosystems can cause a sharp drop in the pH of lake or stream waters and a rise in the amount of dissolved reactive aluminum (Schofield and Trojnar, 1980; Charette et al. 1984; LaZerte, 1984; Seip et al., 1984). These chemical changes are believed to be related to sudden fishkills in lakes, even where the water chemistry during the rest of the year poses no threat to fish (Grahn, 1980; Overrein et al. 1980). The spring melt is also responsible for the recharge of surface and ground waters in many catchment basins; hence the chemistry of meltwaters is of prime importance to the long-term degradation of fish habitats.

The objective of this paper is to show the variation in chemistry in different waters found in a small Laurentian watershed during snowmelt. Although data were collected between the end of February and May, 1984, only a part of that period will be discussed: Phase II (April 2-11) and Phase III (April 12-30) represent the first major flush of meltwater and the period of maximum continuous discharge, respectively. This one-month period encompasses the major flush into the stream of water and dissolved material that was stored in the snowpack or the soils. Phases I and IV are of relatively less interest since they represent pre- and post-melt periods of much lower discharge.

STUDY SITE

The Lac Pin Blanc watershed is located in the "Station de Biologie de l'Université de Montréal" near St-Hippolyte Québec (46°N, 74°W), about 80 km north of Montréal. The catchment has a surface area of 0.56 km^2. The drainage system consists of a first-order stream that flows for most of the year although it may become intermittent during the summer months. A depression in the bedrock formed by glacial action is now occupied by a small pond (Lac Pin Blanc), about 0.01 km^2, that is gradually being filled with organic matter. The area receives about 1100 mm of precipitation annually of which 30 % falls as snow (Wilson, 1971).

The bedrock of this area is precambrian anorthosite of the Morin series. Except for outcrops along many of the divides between watersheds the bedrock is covered by till with a mineralogical composition similar to that of the anorthosite. In most parts of the watershed the till is thin with an average depth of about 1 m; here the soils are Orthic Humo-Ferric or Ferro-Humic Podzols. In the depression near the pond organic soils have become established, either Humisols or Mesisols depending on the degree of decomposition of the material. A more detailed description of the soils can be found in Hendershot et al. (1984) and Dufresne (1984).

The vegetation on the well drained sites is a dominantly hardwood forest of Sugar maple (Acer saccharum), White birch (Betula papyrifera), Balsam fir (Abies balsamea) and Trembling aspen (Populus tremuloides). The poorly drained, organic soils have a vegetation cover of White cedar (Thuya occidentalis) and Speckled alder (Alnus rugosa). The pond is edged with a mat of moss (Sphagnum sp.).

MATERIALS AND METHODS

Field Study

Since 1983, the field site at Lac Pin Blanc has been used for studies on the effect of acid precipitation on a forested watershed. At the beginning of the 1984 snowmelt season (March 6-8) a snow survey was undertaken to quantify the amount and chemistry of the snow in the basin. Snow cores were collected using 5 cm diameter ABS plastic pipe sharpened at one end; depth measurements were taken from a scale on the outside of the corer. Six relatively homogeneous areas were identified within the basin on the basis of vegetation and slope. Each zone was sampled randomly, the number of samples collected being determined by the relative proportion of the surface area occupied by each. Finally the samples were bulked after thawing and a 1 L sample from each zone was saved for analysis.

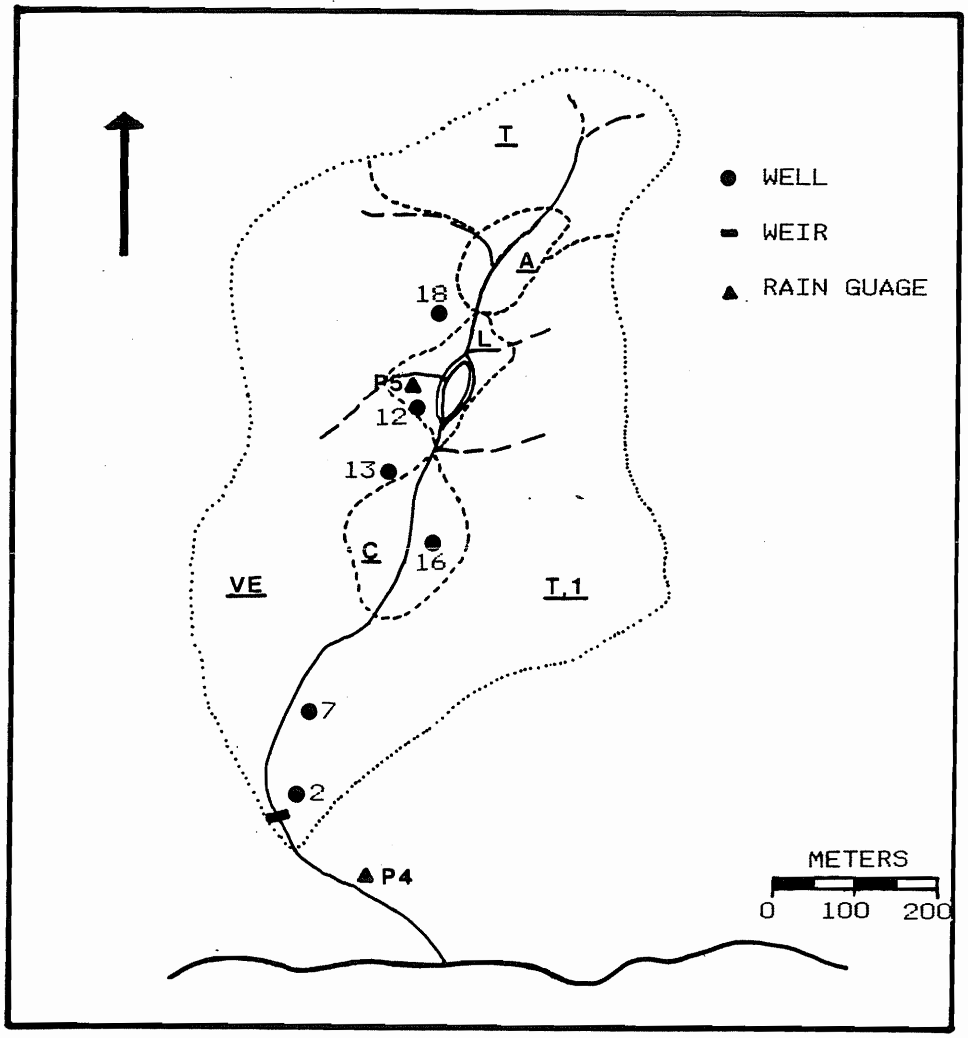

Figure 1. Map of the Lac Pin Blanc watershed showing location of the weir, the shallow groundwater wells and the six zones sampled during the snow survey.

Following the snow survey, each precipitation event was sampled at two open sites within the basin, one near the pond and the other at the outlet of the basin. For snow 20 L plastic buckets were used, while for rain 16 cm diameter funnels connected to 2 L polyethylene bottles with looped tygon tubing (to prevent evaporation) were used (Likens et al., 1967). The precipitation collectors were serviced daily when there was any precipitation; otherwise they were left open to the atmosphere between events. Whenever there was sufficient sample (500 mL minimum) each collector was analysed separately; if not, the water from the two sites located in the basin (P4 and P5 on Figure 1) were bulked. On some occasions several days' precipitation was bulked to provide enough sample to analyse.

Shallow groundwater wells located near the stream and pond were monitored during the snowmelt period (Figure 1). The wells are 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 height was measured daily and the water sampled about every five days. In this report the water chemistry from five of the wells is presented.

Stream discharge is taken from the water level in a small basin above a natural v-notch weir. This was measured continuously with a Belford water level recorder. The weir was calibrated using the dye dilution method of Adams (1966). Stream water samples were collected eight times a day using a Manning automatic water sampler; pairs of samples were then bulked to give four samples per day.

Laboratory Analyses

All samples were collected and stored in 1 L polyethylene bottles (Nalgene) that were previously washed with 50 % HCl and then rinsed three times with distilled water and twice with distilled-deionized water. Immediately on arrival in the field laboratory, the pH of the samples was measured using a Radiometer PHM 83 digital pH meter and a combination electrode. The samples were then filtered through S & S 595 filter paper to remove large impurities and stored at 4°C in the dark. All subsequent laboratory analyses were undertaken with a minimum of delay.

Electrical conductivity (EC) was measured with a Radiometer CDM 83 digital meter. Aluminum speciation was determined using the 8-hydroxyquinoline (oxine) method as developed by Lalande (1984). This method employs the reactivity of different forms of aluminum with oxine at two pH values to separate aluminum species: Measurement 1 is a 15 s extraction at pH 5.0; Measurement 2 is a 15 s extraction at pH 8.3; and Measurement 3 is a 60 min extraction at pH 8.3. Research has shown that the first measurement (Al_1) includes mainly monomeric uncomplexed aluminum such as Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$ and perhaps the dimer $Al_2(OH)_4^{2+}$. The second (Al_2) contains the same forms as Al_1 plus monomeric aluminum bound to fluoride or organic ligands. The third (Al_3) also includes polymeric forms of reactive aluminum that may be in either organic or inorganic form.

RESULTS AND DISCUSSION

Stream Hydrology

The stream hydrograph is presented in Figure 2. The hydrograph can be divided into four periods based on flow rate and stream chemistry. Phase I (March 21 - April 2) is characterized by a relatively low flow rate (about 10 L/s). This period follows an important thaw in February at which time the soils were free of ice and saturated to within about 20 cm of the surface in lowlying areas. Although this is a period of relatively low flow it does not correspond to the conditions of mid-winter when true base flow is observed and the soils are much drier or frozen.

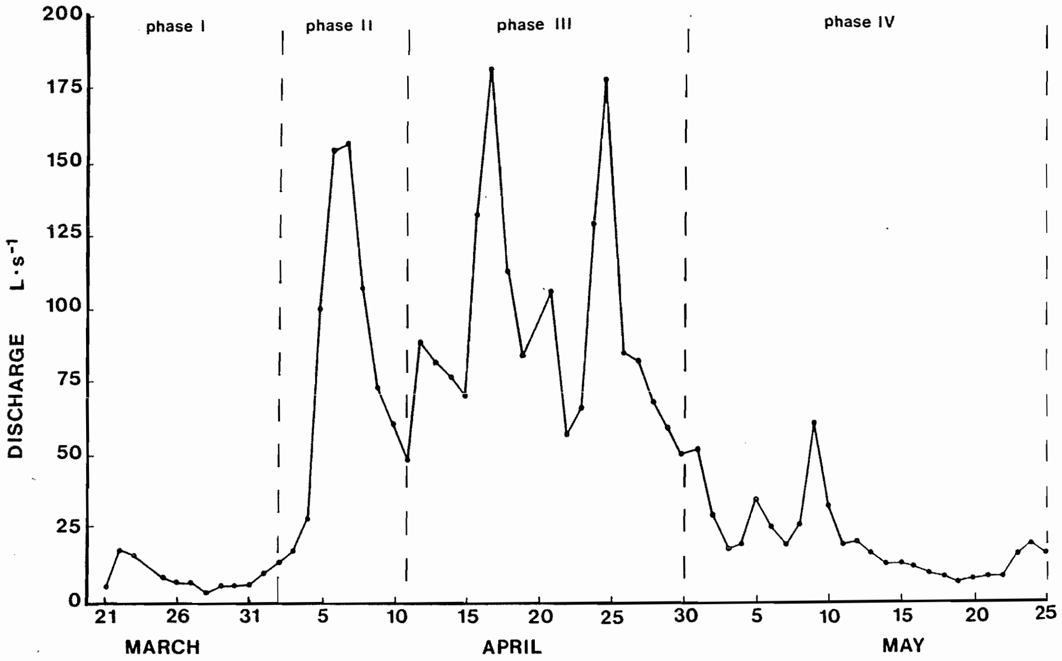

Figure 2. Stream hydrograph of the Lac Pin Blanc stream, spring 1984

Phase II (April 2-11) began with a sudden increase in temperature and two days of heavy rain. The rapid rise in discharge to 157 L/s corresponds to the first major leaching of the snowpack. This phase represents a transition between the low flows of Phase I, when the water was reaching the stream mainly through the B and C horizons, and Phase III when flow rates stayed high and the chemistry of the stream was quite different.

Phase III (April 12-30) was the period during which the maximum of the melt took place. Although the average discharge was 95 L/s there were three major peaks of 182, 106 and 178 L/s. The watertable remained at or near the surface in lowlying areas and saturation overland flow was common near the stream channel.

Phase IV (May 1-25) begins with the drop in discharge rate to values between 10 and 40 L/s with a single peak discharge of 70 L/s. Stream water chemistry and discharge varied markedly as a result of diurnal temperature and snowmelt rate. Towards the end of this period there was snow in only a very small percentage of the basin where it was protected from direct sunlight by coniferous vegetation or local relief.

Snowpack

Chemistry of the snowpack sampled and analysed before the start of the snowmelt is presented in Table 1 along with the physical characteristics of the snow. The largest units are VE, T, and T.1 that together occupy over 87% of the watershed; they have a hardwood forest vegetation dominated by Sugar maples. Unit C, covering 5.7% of the area, has organic soils and a vegetation of mainly White cedar. The two smallest units are also the most open; unit L, the lake, has 3.4% and unit A, covered by speckled alder, has 3.1% of the surface area.

Table 1. Snow survey of Lac Pin Blanc watershed performed on March 6-8, 1984.

Site	Depth cm	Density g/cm^3	Water equiv. cm	Fraction of water in snow-pack %	pH	EC uS/cm	Al_1 mg/L	Al_2 mg/L	Al_3 mg/L
WILLOWS A	124.8	0.282	35.19	3.2	5.25	10.4	0.007	0.012	0.021
LAKE L	98.3	0.292	28.70	2.9	5.01	13.1	0.016	0.020	0.026
CEDARS C	113.0	0.314	35.48	6.0	5.01	11.1	0.023	0.032	0.043
WEST SLOPE VE	111.2	0.307	34.14	32.8	5.05	13.9	0.034	0.037	0.056
NORTH SLOPE T	110.3	0.307	33.86	16.7	5.03	11.4	0.022	0.024	0.039
EAST SLOPE T.1	109.2	0.309	33.74	38.2	4.91	12.4	0.020	0.031	0.050
Weighted average	110.3	0.307	33.79	-	5.00	12.6	0.024	0.031	0.048

The pH of the snow waters is remarkably consistent, with a range of 4.91 to 5.05 for all units except the willows where the pH was 5.25. In general, the aluminum chemistry of the snowpack is dominated by monomeric uncomplexed aluminum (Al_1), about 50%, and polymeric forms (Al_3 - Al_2), about 35%.

Some important differences between zones do exist. Monomeric uncomplexed aluminum (Al_1) is much higher in the forested parts of the watershed, with a range of 0.022 to 0.034 mg/L Al than in the more open zones A and L, that have 0.007 and 0.016 mg/L Al, respectively. Total monomeric aluminum (Al_2) follows the same pattern as Al_1. It is interesting to note that the amount of polymeric aluminum (Al_3 - Al_2) is closely related to vegetation, being highest in the hardwood forest and lowest on the lake and in the willows. These changes may be due to throughfall effects or to the accumulation of dust (micro-litterfall) from the trees.

Precipitation

The chemistry and amount of precipitation during Phases II and III are presented in Table 2. In terms of the impact on the chemistry within the watershed, the snow meltwater is far more important than the precipitation, the former accounting for about 34 cm of water and the latter only 11. The pH of the rain is much more acidic than the snowpack (4.5 versus 5.0). Although the snowpack is the accumulation of precipitation during the winter, while the data on rain is from the spring period, previous research indicated that the rain chemistry presented here is typical of the initial snow chemistry. These differences show clearly the effect of ageing (accompanied by gaseous or leaching losses?) and the accumulation of dust on the snowpack water chemistry. These values are slightly higher than those of the annual precipitation as given by Bobée et al. (1982) as being pH

4.2. Surprisingly, the EC of the rain was very high during Phase III, reflecting a heavy loading of soluble material.

Table 2. Weighted average chemistry of precipitation in the Lac Pin Blanc watershed during Phases I and II of the spring snowmelt period 1984.

Phase	Water mm	pH	EC uS/cm	Al_1	Al_2	Al_3
				mg/L		
II	44.5	4.49	13.4	0.008	0.017	0.021
III	69.9	4.56	21.6	0.015	0.017	0.019
Analytical error		±0.02	±0.2	±0.005	±0.005	±0.005

The aluminum chemistry in the rain is somewhat different than that in the snowpack. The monomeric forms of aluminum (Al_2) account for between 80 to 90% of the total aluminum with the complexed (Al_2 - Al_3) being dominant (0.009 mg/L) during Phase II and the uncomplexed (0.015 mg/L) during Phase III. These values are admittedly at the limit of our analytical technique and thus the speciation calculated should not be given too much importance. However, the amount of aluminum in the precipitation compares well with the work of Johnson et al. (1981) at Hubbard Brook, New Hampshire. In contrast, Budd et al. (1981) have reported values as high as 0.10 mg/L in precipitation collected at McDonalds Branch, New Jersey.

Groundwater

Five shallow groundwater wells, three in mineral soils and two in organic soils, are discussed here. All of these wells are from either the concave part of the lower slopes or flat-lying areas near the stream channel. Other wells in higher topographic positions were dry most of the time and hence were not sampled regularly. Relative to the water moving into the soils, the pH of the groundwater is higher than that of the precipitation and similar to that in the snow.

In order to understand the behavior of the watershed it is necessary to consider Phase II and III separately. During Phase II, the first major flush of the snowmelt, the snowpack can be expected to lose much of the soluble impurities stored over the winter. The recrystallization of the ice into larger crystals causes the exclusion of soluble salts. This brine is then washed out of the snowpack early in the melt period. In part this may account for the relatively high EC in the groundwater during Phase II. Another contributing factor, particularly visible in the aluminum chemistry, is the abundance of soluble aluminum that comes from the accumulation of weathering products in the soils during the winter. The water in the wells has a very even distribution of forms of aluminum with about one-third in monomeric uncomplexed (Al_1), monomeric complexed (Al_2-Al_1) and polymeric forms (Al_3-Al_2). The values are three to four times those found in the snowpack.

During Phase III the EC and concentrations of all forms of aluminum dropped significantly: the aluminum values, on average, dropped to 50 to 60% and the EC to 80% of those measured in Phase II. This phenomenon of dropping concentrations during periods of high flow is exactly opposite to what was found in Phase II and in the studies of some other researchers (LaZerte, 1984; Campbell et al, 1984; Driscoll, 1980). These results are explained by the increasing purity of the meltwater as the melt proceeds and the washing out of accumulated soluble material from the soils themselves. Despite the significant drop in concentrations the speciation remains remarkably similar to that during Phase II.

Table 3. Average groundwater chemistry and water table height during Phases II and III of the 1984 snowmelt period.

Well no.	Water Table*	pH	EC uS/cm	Al_1	Al_2	Al_3
					mg/L	
Phase II						
2	20	5.11	17.6	0.038	0.070	0.130
7	10	4.97	17.2	0.072	0.142	0.198
12**	18	5.08	24.3	0.087	0.171	0.245
13	42	5.12	21.6	0.053	0.083	0.134
16**	0	5.16	24.4	0.073	0.174	0.230
Phase III						
2	10	5.08	15.0	0.025	0.049	0.073
7	12	5.02	14.9	0.038	0.077	0.120
12**	16	5.18	18.4	0.058	0.124	0.184
13	38	5.12	20.2	0.030	0.061	0.102
16**	0	5.06	16.0	0.022	0.061	0.087
Analytical error		±0.02	±0.2	±0.005	±0.005	±0.005

* Water table height measured from the surface of the soil in cm.
** Organic soil

The behavior of organic soils was similar to that of the mineral soils. Well 12 had a water table that remained below the surface and was much less leached-out than Well 16. During Phase II both of these organic soils had the highest EC and concentrations of aluminum. Well 12 had a water table at the surface (or above) during all of Phases II and III and its concentrations dropped markedly during the latter phase. Although large differences in the amounts of complexed and uncomplexed aluminum between mineral and organic soils were expected, no pattern could be discerned in the data.

Stream Water

The water flowing in the streams arrives by three pathways. During precipitation events some rain will fall directly into the watercourse; this makes up only a very small percentage of the discharge during snowmelt. A second pathway is by overland flow from the snowpack into the stream: this may be of some importance during the peaks in snowmelt or snowmelt/rainfall events. The most important pathway is certainly the groundwater: saturated subsurface flow links the snowpack to the stream and provides the major part of stream water.

The chemistry of the stream is controlled by the water flowing from the groundwater, although it is affected by overland flow. It should also be mentioned that the shallow groundwater wells that we used do not all extend to bedrock; hence there is a component of deeper groundwater flow that is not included in our sampling.

Table 4. Weighted average discharge and chemistry in the stream waters during Phases II and III.

Phase	Discharge L/s	pH	EC uS/cm	Al_1	Al_2 mg/L	Al_3
II	94	5.35	19.9	0.040	0.107	0.149
III	95	5.45	15.9	0.020	0.064	0.089
Analytical error		±0.02	±0.2	±0.005	±0.005	±0.005

During Phase II the pH of the stream was higher than that of the groundwater, while the EC was about the same. The higher pH reflects the contribution of deeper groundwater, in contact with higher pH soil material, on the overall stream chemistry. To a certain extent the same is true of the aluminum chemistry: the concentrations of Al_1, Al_2 and Al_3 are lower than the average concentration of the well waters. Although overland flow would also cause a dilution in the stream it does not account for the increase in pH. In terms of speciation there is a slight increase in the percentage of complexed monomeric aluminum (Al_2 - Al_1) relative to the groundwater. This reflects the higher pH of the stream and may be related to the movement of groundwater through the lower soil horizons where a pH increase causes the precipitation of some of the uncomplexed monomeric aluminum (Al_1).

During Phase III as in Phase II the same decrease in concentration is observed in the stream as is observed in the groundwater. Again the pH in the stream is higher than in the groundwater and the concentration of all three forms of aluminum decreases significantly. The washing-out of the pollutant load and the natural weathering products from the snow and the soils early in the snowmelt (Phase II) results in an improvement of water quality during the period of peak discharge (Phase III).

In the Lac Pin Blanc watershed, Phase II is the period of maximum pollutant transport into the streams. This period, which lasted nine days in 1984, would be responsible for the acid shock observed in many aquatic environments. Although the conditions in a larger watershed would probably result in a longer shock period, these results do point out the importance of sampling intensity in hydrological/environmental studies.

SUMMARY

1. The aluminum in the snowpack is mainly in monomeric uncomplexed forms with polymeric forms being the second most abundant. Total reactive aluminum averaged under 0.05 mg/L.

2. In the incident precipitation during the snowmelt period the aluminum was mainly in monomeric forms, the amounts of complexed and uncomplexed forms varying substantially. Only about 0.02 mg/L total reactive aluminum was measured.

3. In the groundwater the amount of total reactive aluminum is much higher, on the order of 0.10 to 0.20 mg/L. very evenly distributed between monomeric uncomplexed, monomeric complexed and polymeric forms.

4. The aluminum that reaches the stream has a slightly lower concentration than some of the wells, averaging between about 0.09 and 0.15 mg/L. The speciation is dominated by monomeric complexed aluminum with polymeric forms being secondary.

5. The pH of the water increases steadily as it moves through the watershed. The incoming precipitation has a pH of 4.5 or lower, the snowpack about 5.0, the wells from 5.0 to 5.2 and the stream an average of 5.4.

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