Biogeochemistry **13**: 177—197, 1991

Stream chemistry and hydrologic pathways during snowmelt in a small watershed adjacent Lake Superior

R. STOTTLEMYER[1] & D. TOCZYDLOWSKI

Department of Biological Sciences, Michigan Technological University, Houghton, MI 49931, USA ([1] present address: Water Resources Division, National Park Service, 240 W. Prospect, Fort Collins, CO 80526, USA)

Received 1 March 1990; accepted 6 May 1991

Key words: Lake Superior, nutrient budgets, snow chemistry, snowmelt, stream chemistry, watershed

Abstract. In regions with airborne contaminants and large snowpacks, there is concern over the impact that snowmelt chemical "pulses" — periods of sharp increase in meltwater solute concentration — could have on aquatic resources during spring runoff. A major variable in determining such an effect is the flow path of snowmelt solutes to the stream or lake. From December 1988, to late April 1989, the quality and quantity of precipitation, snowmelt, soil solution and streamwater were measured in a 176-ha gauged watershed on the south shore of Lake Superior. The main objectives were to (1) examine the change in flow path meltwaters take to the stream during distinct winter and spring hydrologic periods, (2) quantify ecosystem-level ion budgets prior to, during, and following snowmelt, and (3) examine if streamwater chemistry might be a sensitive indicator of change in ecosystem flow paths. Prior to peak snowmelt, groundwater made up 80% of stream discharge. During peak snowmelt, the groundwater level rose to the soil surface resulting in lateral water movement through near-surface macropores and as overland flow. Near the end of snowmelt, meltwaters exerted a piston action on deeper soil solution again increasing its relative contribution to streamwater discharge. Net groundwater drawdown during the study resulted in streamwater discharge about equal to precipitation inputs. Unfrozen soils and brief mid-winter thaws resulted in steady snowmelt throughout early and mid-winter. The snowpack lost > 50% of most ions prior to the period of major snowmelt and high stream discharge in late March and early April. Snowmelt and streamwater NO_3^- and NH_4^+ pulses occurred before the period of overland flow and peak streamwater discharge (April 4—24). During overland flow, stream discharge of total N, P, DOC, and AI peaked. Nutrient budgets computed for distinct hydrologic periods were much more helpful in explaining ecosystem pathways and processes than were changes in solute concentration. For the study period, watershed base cation (C_B) discharge was 23 times input and SO_4^{2-} discharge exceeded input by 42%. H^+ was the most strongly conserved ion with output < 0.2% of input. Also conserved were NH_4^+ with only 1.4% of input leaving the ecosystem and NO_3^- with output equal to 9.4% of input.

Introduction

Moderate to high inputs of acidic deposition have been found throughout the Upper Midwest (Glass & Loucks 1985). Superimposed on this chronic acidification is episodic acidification of surface waters following rain or snowmelt. In the last decade, interest in snowmelt came about from the general lack of information on the amount and quality of snowpack in the region, the high degree of variation in snowpack amount due to proximity of the Great Lakes, the large snowpacks and solute loads which occur in some areas, little knowledge of the processes whereby snowmelt solutes get to lakes and streams, and most recently concern over snowmelt solutes resulting in chemical "pulses" to surface waters (Abrahams et al. 1989; LaZerte & Dillon 1984). A snowmelt or surface water chemical pulse is defined as when the increase in solute concentration exceeds the increase in meltwater or streamwater discharge. Seasonal inputs of strong acids to lakes and streams from snowmelt have been documented in portions of the region with shallow soils and resistant bedrock (Jeffries et al. 1979; Kelso et al. 1986).

In the Northwestern U.S., the impact of surface water chemical pulses, primarily on recruitment and elevated mortality in fish, has been associated with increased surface water concentration of H^+, NO_3^-, SO_4^{2-}, Al, and Cd released from the snowpack or surface mineral soils. In very sensitive portions of the Great Lakes region, surface water acidification has been associated primarily with SO_4^{2-} (LaZerte & Dillion 1984).

Except for east of Lake Superior (Nicolson 1988), little study in this region has been undertaken where large snowpacks occur. Lake Superior rarely, if ever, freezes over, and large snow accumulations occur along its south shore. Winter precipitation also significantly increases with minor gain (150 m) in elevation (NOAA 1986; Stottlemyer 1982, 1987; Stottlemyer & Toczydlowski 1990). This results in a significant increase in snowpack solute load in the upper, more sensitive portions of a watershed (Likens et al. 1977; Slottlemyer & Rutkowski 1990). Winter precipitation averages about 40% of annual precipitation inputs. However, peak snowpack water equivalent (SWE) can approach 50% of annual precipitation input (Slottlemyer 1987). About 50% of annual stream runoff occurs during April and May (Miller et al. 1984; Stottlemyer & Toczydlowski 1990). Under these conditions, the potential for snowmelt chemical pulses to surface waters is high.

But a number of factors may mitigate the potential effects of large snowpack solute loads on aquatic ecosystems. These include soil chemical composition, the rate of input neutralization, groundwater residence time, and the flow path of inputs (Driscoll & Newton 1985; Reuss & Johnson

1986; Wels et al. 1990). Significant portions of the Lake Superior basin have elevated soil buffering capacity due to the widespread presence of carbonates in the glacial till brought south with the glaciers. The large snowpack insulates the soils and they remain unfrozen throughout winter which increases the opportunity for meltwater solutes to be retained or exchanged before reaching the stream or lake (Stottlemyer 1987; Stottlemyer & Rutkowski 1990). Thawed soils appear to be the major factor responsible for the small but steady snowpack moisture loss throughout winter. Periodic midwinter thaws also can raise the temperature of the snowpack sufficiently for major solute movement and release to the forest floor prior to rapid snowmelt and surface runoff (Peters 1984; Stottlemyer 1987; Stottlemyer & Toczydlowski 1990).

In view of the complexity of the mechanisms possibly regulating the passage of snowmelt pulses to aquatic systems and the potential for impact imposed by large snowpack H^+, NO_3^- and SO_4^{2-} loads, a better understanding of the processes involved in solute transport from snowmelt to lakes and streams is necessary. The primary objectives of this paper are to

- examine the change in flow paths meltwaters take to the stream during distinct winter and spring hydrologic periods,
- quantify change in ecosystem-level ion budgets prior to, during, and following snowmelt, and
- assess how responsive streamwater chemistry is to a change in meltwater pathway.

Materials and methods

The study area is a small (176 ha) first-order watershed vegetated by 55—65 yr old sugar maple (*Acer saccharum*) and white birch (*Betula papyrifera*) near Calumet in Michigan's Upper Peninsula. Unlike most catchments in the region, wetlands are not a major component (Wels et al. 1990). The watershed has a northwest aspect and uniform slope varying in elevation from about 190 to 375 m above mean sea level (Fig. 1). The bedrock is Precambrian metamorphic Portage Lake Volcanics (andesite and basalt). The soils (typic haplorthods) are alkaline glacial till and old beach deposits with a varying depth of 2—5 m with an almost impervious soil layer (ortstein) at 1.0—1.3 m depth.

The peak SWE in 1988—89 was 26 cm in March 14. This was below the 1980—87 average of 30.1 ± 8.5 cm (range 19—47 cm) (Stottlemyer, unpublished data). There was a significant ($P < 0.05$, two-way ANOVA, Student-Newman-Keuls) increase in snowfall and SWE with gain in

watershed elevation (cumulative precipitation increased from 25.5 cm to 33.5 cm). This has been observed in past study on this site (Stottlemyer and Rutkowski 1990).

Stream discharge was measured using a 30 cm wide Parshall flume equipped with Stevens F recorder, and stream temperature was continuously monitored by datalogger (LiCor model 1000). Four monitoring stations were located at intervals of increasing elevation in the watershed [C4 (190 m) near the mean elevation of Lake Superior, C3 (240 m), C2 (295 m) and C1 (350 m)] (Fig. 1). Each station was equipped with a bulk collector (36 cm diameter) to measure both precipitation quality and quantity. The collectors were not shielded.

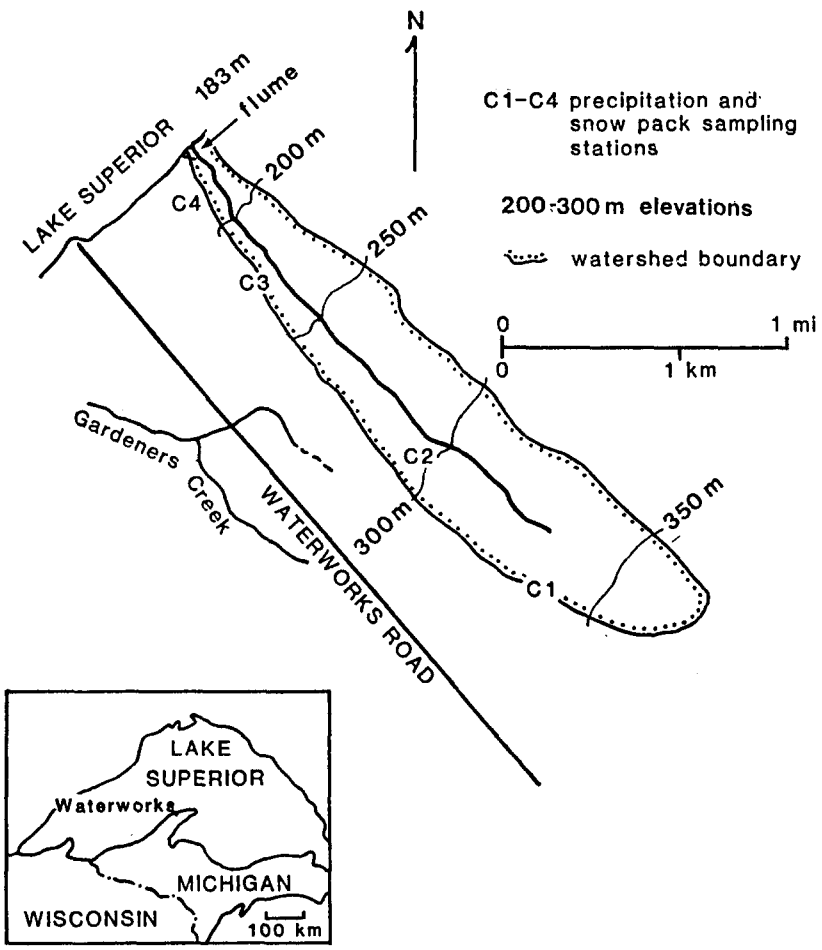


Fig. 1. Calumet Experimental Watershed (stippled boundary), Keweenaw Peninsula of Michigan, a 176 ha watershed draining into Lake Superior.

A transect (five sampling points) was established at each station where SWE and depth were determined using a Mount Rose sampler. Samples for chemical analyses were collected in a 10-cm diameter PVC tube. The snowpack sampling stations were located in openings to minimize canopy debris in the collectors. We have measured throughfall in the watershed for two winters and found no significant alteration of precipitation chemistry by the forest canopy (highest possible alteration was for NO_3^-, $P < 0.65$) (Stottlemyer 1987).

A fifth SWE transect and sampling station (C5) was established in the lower portion of the watershed between stations C3 and C4 about 20 m from the stream. Triplicate snow and soil lysimeter plots were located here. Each snowpack lysimeter consisted of a 2 × 3 m external cedar frame 15 cm in height and 2 cm thick. A 0.15 mm polyethylene sheet was placed directly on the forest floor following leaf fall and attached to the frame. Melt waters were directed by PVC tubing to a central 1.5 m deep pit with insulated cover. Within the pit, tipping bucket raingages recorded snowmelt rates and volume from each snow lysimeter. Pit temperature and the rate and timing of snowmelt were recorded on a Licor 1000 datalogger.

To sample forest floor leachate, triplicate zero-tension lysimeter plots were established each in proximity to one of the snow lysimeters. Each plot consisted of three lysimeters made of PVC tubing cut in half (area 310 cm^2) and carefully inserted beneath the forest litter layer. Each lysimeter was connected by 1.5 cm diameter PVC tubing to Nalgene linear polythylene bottles in small covered pits. Mineral soil solution was sampled from triplicate soil tension lysimeter plots each located in close proximity to one of the snow lysimeters. Each plot consisted of 3 lysimeters (ceramic cups, PVC tube, Soil Moisture Corp.) at both 15 (A & E) and 30 cm (Bhs) soil depths. Additional plot instrumentation included a datalogger to record mean daily snowpack temperature at 10 and 40 cm above the forest floor, soil temperature at 5 cm depth, daily mean and maximum/minimum air temperature; solar radiation; and a groundwater well equipped with a Stevens F float gauge for monitoring change in water table height. Wind data were obtained from the nearby (8 km) NOAA station at the Houghton County Airport which has an elevation similar to station C1.

An additional instrument and stream sampling station (C21) was established in the upper watershed at an elevation of approximately 320 m or between the elevations of stations C2 and C1. Its purpose was to monitor the relationship between snowpack melt, groundwater table and stream discharge near the head of the watershed. Instrumentation consisted of a datalogger to record mean daily air and snowpack temperatures

as outlined for station C5, stream temperature, and a groundwater well equipped with a Stevens F float gauge.

During snowmelt, grab samples for chemical analyses were collected in linear polyethylene amber bottles from each snow lysimeter during the middle (4—5 p.m.) of the daily melt period. When meltwater release rates became more variable sampling frequency was increased. Beginning in late January, soil lysimeters were sampled about every ten days until peak snowmelt at which time they were sampled about every three days. The zero tension lysimeters did not start to flow sufficiently until March when they were sampled on a schedule similar to the soil solution lysimeters.

Precipitation, snowpack and stream samples were collected weekly on Tuesday afternoons. During snowmelt, stream samples were collected more frequently based on a schedule developed from frequent sampling in earlier years (Stottlemyer 1987; Slottlemyer & Toczydlowski 1990). For the present study we sampled the stream daily at both the low and high discharge rates, and more frequently when the stream discharge pattern became yet more variable.

Stream water samples were collected just above the flume and at station C21 using amber linear polyethylene 500 ml bottles. For the analysis of DOC, additional samples were collected in glass bottles with Teflon-lined stoppers. Additional subsamples were collected for the analyses of total N, P and Al. Only the samples retained for total N and P analyses were frozen.

Samples were immediately brought into the laboratory. Snow samples were melted at room temperature in pre-rinsed, covered polyethylene containers. PH, specific conductance, and alkalinity (titration with 0.02N H_2SO_4 to pH 4.5) were determined as soon as samples reached room temperature. Filtered (pre-rinsed 0.45-μ m) subsamples were refrigerated (2 °C) and chemical analyses for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Cl^{-}, NO_3^{-}, PO_4^{-}, and SO_4^{2-} were conducted using ion chromatography (Dionex Model 2020). DOC was analyzed on a Dohrmann DC-180, total N and P on Technicon Auto Analyzer using the persulfate oxidation and Cd reduction method, and total Al was determined by AA (Perkin Elmer Model 5000).

Results

Hydrologic pathways

To better describe change in flow paths, we quantified hydrologic budgets for distinct periods: December 20—March 20, a period of falling groundwater table and stream discharge; March 21—April 3, a period of rapidly

increasing snowmelt, groundwater height, and stream discharge; April 4—24, the period of peak snowmelt and overland flow; and April 25—May 15, a period of declining groundwater height and streamwater discharge following snowpack loss (Table 1).

Table 1. Water flux during four time periods: *1.* declining groundwater and stream hydrographs (December 20—March 20), *2.* rising hydrographs (March 21 to April 3), *3.* overland flow (April 4—24), and *4.* declining hydrograph following snowpack loss (April 25—May 15).

Time period	Type[1]	Amount (cm)
12/20—03/21	PR	28.0
	SP	25.5
	SM	1.8
	SR	10.8
3/21—04/04	PR	2.4
	SP	19.8
	SM	8.6
	SR	4.8
04/04—04/24	PR	2.0
	SP	1.6
	SM	17.0
	SR	10.3
04/25—05/15	PR	0
	SP	0
	SM	0.8
	SR	5.3

[1] PR = precipitation, SP = snowpack as SWE, SM = snowmelt, and SR = streamwater discharge.

A permanent snowpack formed the third week of December (Fig. 2). Most precipitation input remained in the snowpack for the first six weeks. Maximum daily air temperatures remained below freezing up to January 24—29. However, during much of January there was a warming trend which resulted in snowpack temperatures at the 40 cm depth increasing to $> -3\,^{\circ}C$ and to near $0\,^{\circ}C$ at the 10 cm depth. In the snow lysimeters, snowmelt began January 7, and continued to February 2, during which the snowpack lost 0.8 cm of water. From February 21, to March 21, the daily maximum air temperature was often above freezing, the snowpack gradually became isothermal, and snowmelt, while small, was steady. The groundwater wells indicated most of this meltwater moved vertically through the forest soil.

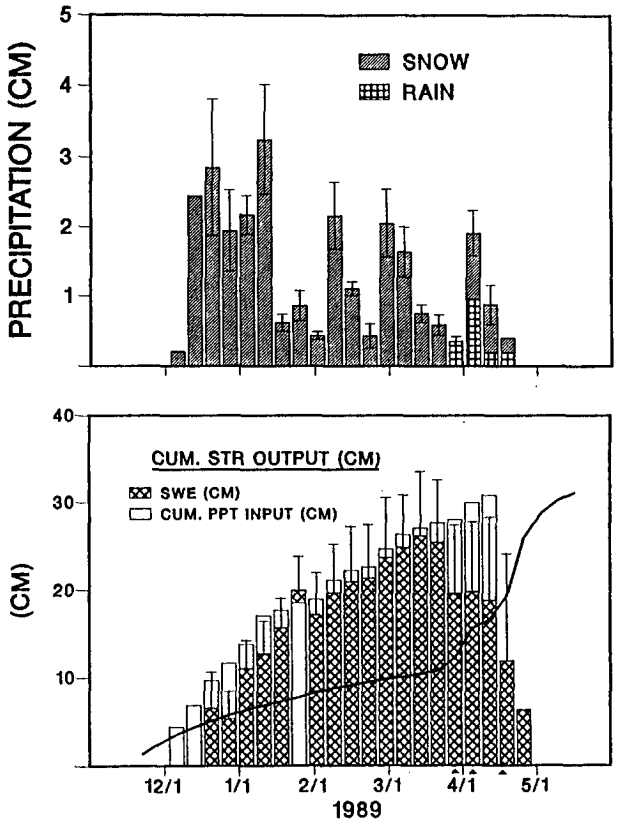


Fig. 2. Weekly average SWE, cumulative precipitation inputs, cumulative stream discharge, and weekly precipitation input as rain or snow for winter 1988—89. SWE brackets indicate one standard deviation. Arrows on x-axis (lower graph) indicate rain.

The period December 21, to March 21, had the highest mean weekly precipitation input, least snowmelt, baseflow streamwater discharge, and peak SWE. Sublimation during this period, as estimated from the difference between inputs to and from the snowpack at the lysimeter plots, was $< 3\%$. During this period, the groundwater table fell from a depth of 130 cm to > 200 cm.

From March 22, to April 4, there was a rapid increase in snowmelt and highly variable streamwater discharge. Sublimation was minimal. Mean groundwater height rose to < 75 cm, and daily streamwater discharge was 3x (0.36 cm d^{-1}) that of the previous period. The increase in groundwater height reflects not only local snowmelt, but likely some lateral sub-surface soil water movement from higher elevations (Roberge & Plamondon 1987).

In lower portions of the watershed, the groundwater table reached the soil surface on April 3—4, and again April 16—24. Streamwater discharge sharply increased during these thaws. When the groundwater table in the lower watershed began to decline by April 22, it reached the soil surface in the upper watershed. Extensive near-surface and overland flow occurred in the watershed April 4—7 and April 16—26. The latter was the period of greatest diurnal variation in streamwater discharge. Peak streamwater discharge occurred April 25.

From March 21, to April 16, the pattern of streamwater discharge apparently was dominated by snowmelt inputs from lower portions of the watershed. The correlation (Pearson) between groundwater height at station C5 and streamwater discharge at the flume (C4) was 0.70 ($p < 0.001$) ($R = 0.32$, $p < 0.02$ for groundwater height at C21). By middle April, both the shape of the stream hydrograph and a major portion of its discharge were influenced by snowmelt inputs from upper portions of the drainage. From March 21, to April 26, which included both the period of increasing streamwater discharge and overland flow, stream discharge at the flume still was best correlated to groundwater height at station C5 ($R = 0.71$, $p < 0.001$; $R = 0.61$, $p < 0.001$ at station C21). From April 16 to May 15, which included both the major period of overland flow and decline in streamwater and groundwater hydrographs, streamwater discharge at the flume was best correlated with groundwater height at station C21 ($R = 0.87$, $p < 0.001$; $R = 0.81$, $p < 0.001$ for station C5). Only during the declining hydrographs, or April 26—May 15, did the correlation between stream discharge and groundwater height increase concurrently at both stations.

Ground provided >80% (9 cm) of the streamwater discharge during the period December 20—March 21, a time when the groundwater table fell about 150 cm (Table 1). During the period of rising hydrographs, or March 21—April 4, snowmelt exceeded streamwater discharge by almost 4 cm, and the groundwater table in the wells rose an average of about 140 cm. About 50% of the snowmelt served to recharge the groundwater table. Streamwater C_B concentration (see below) declined 34% and suggests that, conservatively, streamwater discharge consisted of 1.8—2.0 cm snowmelt which agreed with the hydrologic budget estimates.

During the period of most rapid snowmelt and overland flow (April 4—24), snowmelt again exceeded streamwater discharge by about 6.5 cm. Snowmelt rates were about 0.8 cm d^{-1}, streamwater discharge increased most rapidly, and peak streamwater discharge (192 Ls^{-1}) occurred April 25. We estimate that 1.7 cm of snowmelt occurred as overland flow. During this time, streamwater C_B concentration declined another 30% suggesting that a minimum of 3 cm of its discharge was made up of

snowmelt. Despite the higher snowmelt, the percent lost as streamflow was similar to the previous period. The unaccounted for snowmelt served to further recharge the soils in which the groundwater table rose an average of about 80 cm to the surface.

Following the period of overland flow to May 15, a time of declining hydrographs, the groundwater table fell 125 cm and streamwater discharge decreased to about 12 L^{-1}. Precipitation and snowmelt inputs were minimal and all streamwater discharge came from groundwater.

Solute flux

Temporal variation in ion flux during these hydrologic periods further indicates changing flowpaths.

For the study period, 70% of the precipitation occurred during December 20—March 20 (Table 1, Fig. 2). However, total ion input was much less (24%) with mean daily inputs of 0.5 to 1.1 eq ha^{-1} for C_B, NH_4^+, H^+, NO_3^- and SO_4^{2-} (Fig. 3). From March 21, to April 3, mean daily precipitation ion input increased especially for H^+, NH_4^+, NO_3^- and SO_4^{2-} which were 8x the mean of the previous period. This increase was due to early spring rain (Fig. 2) which was much higher in solute concentration than snowfall. From April 4, to May 15, following gradual loss of the regional snowpack, C_B and HCO_3^- input sharply increased relative to precipitation amount resulting in the highest average daily input of the winter. This likely reflected increased atmospheric inputs from exposed soils following loss of snowpack (Glass & Loucks 1986). All other ions had mean daily inputs similar to those before March 20.

Solute input was significantly higher at station C1 ($P < 0.05$, two-way ANOVA, Student-Newman-Keuls). Inputs were lowest at station C3 or C4 depending upon the ion. This difference was the result of change in precipitation amount, not ion concentration. Such an input change with relatively minor gain in elevation has been observed most winters (Stottlemyer 1987; Stottlemyer & Rutkowski 1990). The dominant precipitation ions were H^+ and SO_4^{2-} (Figs 3 & 4).

From December 20, to March 20, 7% of the winter's snowmelt occurred at the snow lysimeters (4% throughout the watershed). But except for NO_3^- and total N, the percent solute loss was less. This pattern reversed during March 21—April 4, when 26% of the snowmelt occurred and 44% (356 eq ha^{-1}) of the snowpack solute load was lost. Snowpack total N increased slightly (to 0.4 kg ha^{-1}), total P remained below detection levels, and DOC showed its sharpest loss (0.7 kg ha^{-1}). The snowpack lost > 50% of its total cumulative solute content by early April, prior to the period of peak snowmelt. Peak snowmelt (64%) occurred April

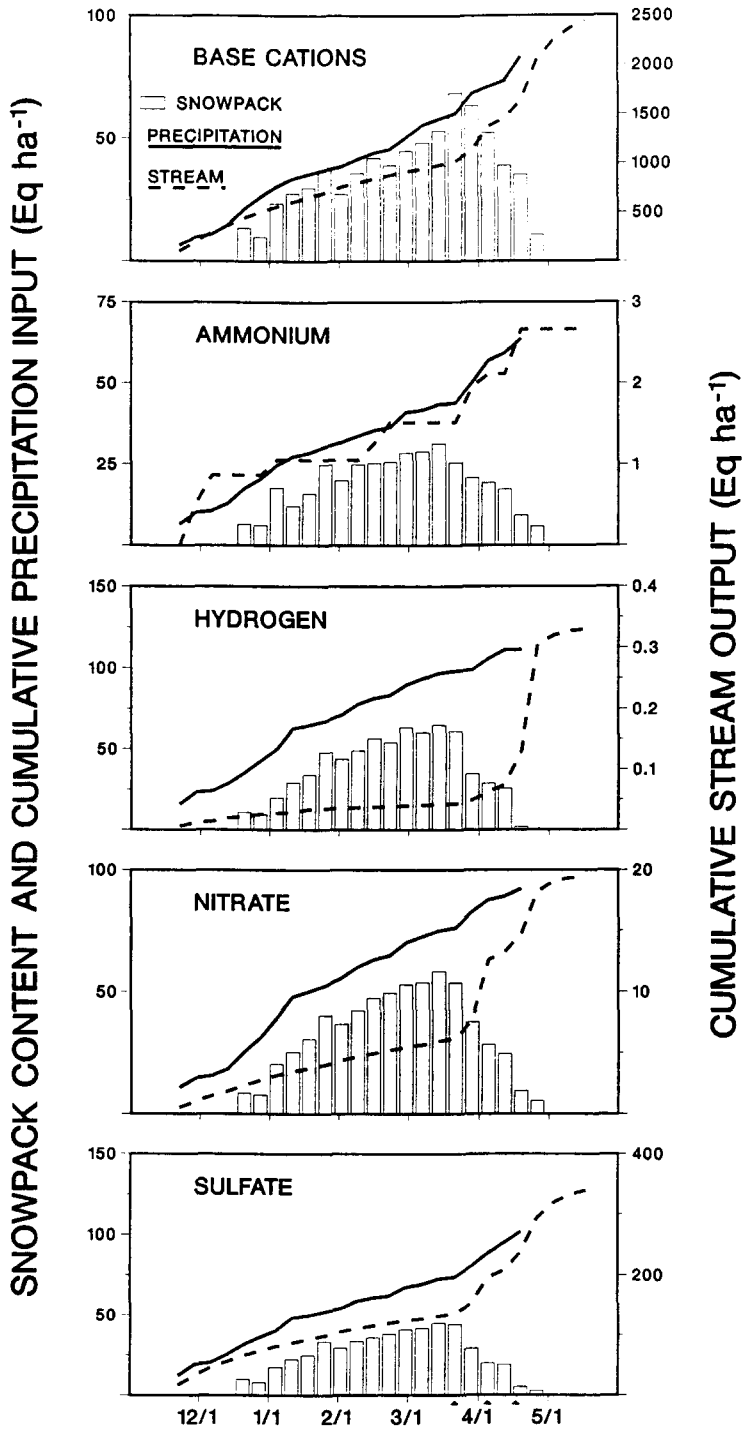


Fig. 3. Weekly average snowpack ion load, mean cumulative precipitation ion input, and cumulative stream ion output. Arrows on x-axis (lower graph) indicate rain.

4—24, but snowmelt ion loss was much less (21% or 173 eq ha^{-1}). The snowpack total N load gained slightly (0.6 kg ha^{-1}) from the previous period, total P was detectable but very small (10 g ha^{-1}), and DOC was further reduced by 0.4 kg ha^{-1}. The delay in loss of organic forms and their late gains in volume-weighted snowpack concentration suggests increased particulate material and canopy washoff entering the snowpack from the surrounding forest.

To estimate solute flux in forest floor leachate (FFL), we assumed that the snowmelt amount in the snow lysimeters also occurred at the nearby (10—15 m) FFL lysimeter plots. The FFL lysimeters did not collect much sample until middle March, and we stopped sampling them April 20, when most were inundated by overland flow. FFL flux estimates can then only be made for the period just prior to and during peak snowmelt (70% of total). Passage of snowmelt as FFL increased C_B flux (34 to 262 eq ha^{-1}), reduced H^+ (14 to 7 eq ha^{-1}), showed minor change in NH_4^+ and NO_3^-, and some gain in SO_4^{2-} (22 to 44 eq ha^{-1}). Al flux did not change (0.4 kg ha^{-1}) relative to snowmelt inputs, but total N flux increased 2.5x (to 1.5 kg ha^{-1}), total P increased (non-detectable to 98 g ha^{-1}), and DOC increased > 3x (to 10.9 kg ha^{-1}).

If we further assume meltwater reached the shallow mineral soil lysimeters (15 cm depth) and exclude the period April 4—24, when the lysimeters were usually immersed in groundwater, we see further significant change in ion flux. Marked increases occurred for those ions with snowpack concentrations less than in soil solution, i.e., C_B and SO_4^{2-}. During December 20—March 20, C_B flux in soil water increased relative to snowmelt (4.7 to 64 eq ha^{-1}) as did SO_4^{2-} (5.5 to 21 eq ha^{-1}). For ions with snowpack concentrations higher than in soil solution, the snowmelt flux was sharply reduced in surface mineral soils (H^+ 7.5 to 0.2, NH_4^+ 2.9 to 0.7, and NO_3^- 6.1 to 1.3 eq ha^{-1}). Total N remained unchanged with soil solution flux similar to snowpack losses. Change in mineral soil solution relative to snowmelt was most pronounced during the period of rising groundwater and streamwater discharge (March 21—April 3). Relative to meltwater inputs, C_B increased (118 to 315 eq ha^{-1}), SO_4^{2-} increased (65 to 100 eq ha^{-1}), as did total N (0.2 to 0.6 kg ha^{-1}), DOC (2.3 to about 13 kg ha^{-1}), and total Al (0.1 to 0.7 kg ha^{-1}).

Daily streamwater discharge of C_B, H^+, NH_4^+, NO_3^- and SO_4^{2-} was lowest (total of 7.2 eq ha^{-1}) from December 20, to March 20. It increased 5x during the March 21—April 3, period of rising groundwater. Streamwater discharge of NH_4^+ and NO_3^- peaked during this time. Daily discharge of Al and DOC increased 3x and total N 10x. Since soil solution concentrations and flux of nitrogen species is normally very low and only increases during the period of rising and peak groundwater hydrographs,

stream discharge likely reflected snowmelt inputs which also peaked at this time. However, streamwater discharge still only accounted for 6% of snowmelt inorganic nitrogen inputs. Total P was at detectable levels in streamwater, but its discharge for the period was small (4.3 g ha^{-1}). Peak streamwater discharge of C_B, H^+ and SO_4^{2-} occurred during April 4—24, when the groundwater table reached the soil surface. The stream became turbid and highly colored. The daily discharge of DOC (300 g ha^{-1}), N (36 g ha), P (0.8 g ha^{-1}), and Al (22 g ha^{-1}) also peaked at this time. Since snowmelt ion flux had dropped to 30—50% that of the March 21—April 3, period as did inputs of Al, DOC, and N, the elevated streamwater discharge of H^+, DOC, N and P suggests inputs from near-surface lateral moving water. The gain in H^+ discharge, while still very small (12 meq ha^{-1} d^{-1}), likely reflected increased organic contributions. The high C_B, SO_4^{2-} and total Al in stream discharge probably resulted from piston action exerting pressure on groundwater increasing its relative contribution to discharge.

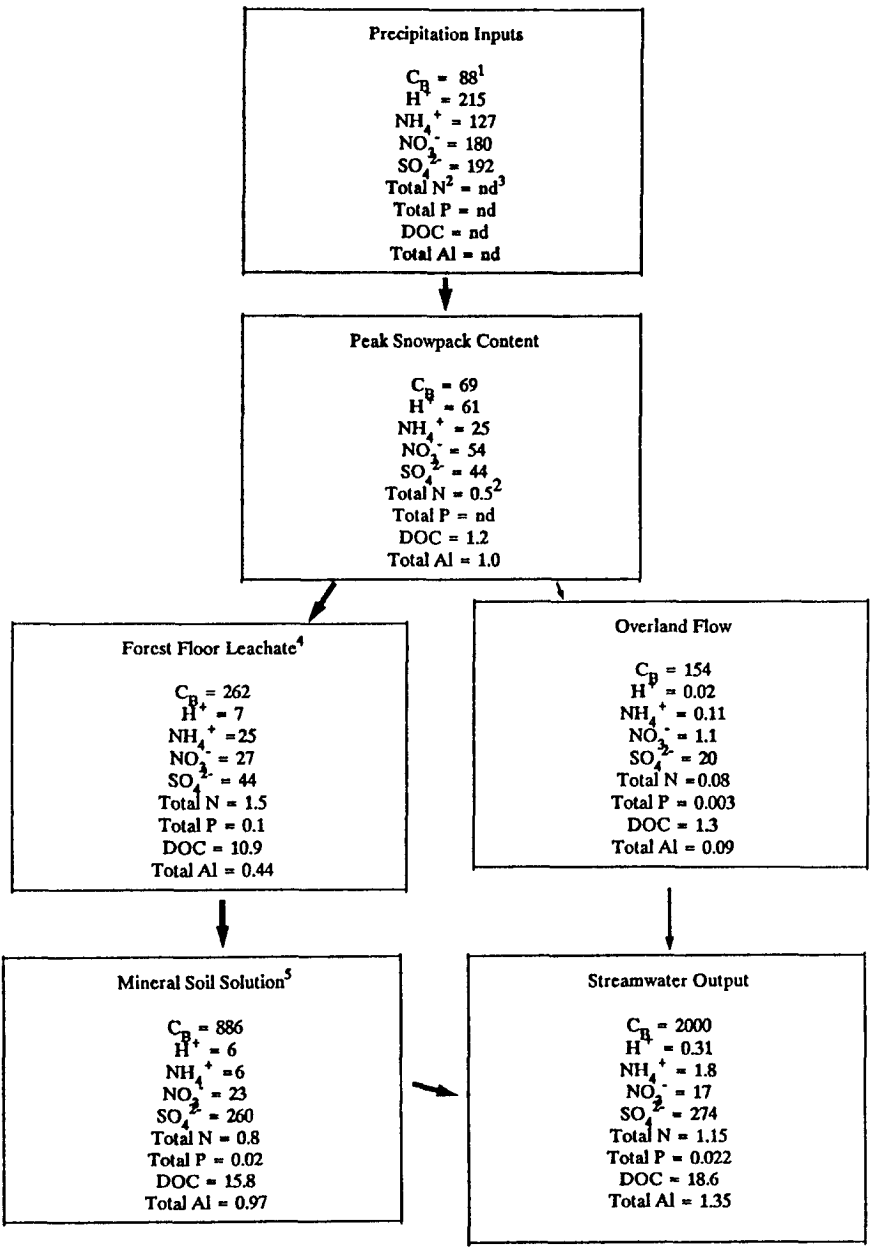
For the period of study, most alteration of solute inputs occurred by the time meltwaters had passed through the litter layer and into near-surface (15cm) mineral soils (Fig.4).

Change in surface water chemistry prior to and during spring thaw

Most streamwater ion pulses occurred during midwinter thaws. The first thaw began late the third week of December when there was a net SWE loss of 3.8 cm (Fig. 2). Stream discharge did not respond to this snowmelt, but the groundwater table rose 9 cm. Ca^{2+}, H^+, and Cl^- exhibited snowmelt pulses during this thaw. Ammonium loss from the snowpack was substantial (3.3 eq ha^{-1} or 36% of the snowpack load), and some apparently reached the stream (0.2 eq ha^{-1}) resulting in the only streamwater ion pulse.

A second thaw occurred January 4—10, with a SWE loss of 2.6 cm and stream and groundwater changes similar to the first thaw. Only NH_4^+ exhibited a snowmelt pulse during this thaw, but this loss was not observed in stream discharge. Another thaw occurred the week ending January 24, during which Ca^{2+}, K^+ and NH_4^+ exhibited snowmelt pulses. Only NH_4^+ exhibited a streamwater pulse with 0.2 eq ha^{-1} of the 6.2 eq ha^{-1} snowmelt loss apparently reaching the stream.

During the period January 7—March 14, stream discharge of C_B and HCO_3^-, expressed as a percentage of total winter discharge, consistently exceeded streamwater discharge by an average of about 20 and 40% respectively. C_B and HCO_3^- discharge further increased relative to streamwater discharge with the late January thaw, and the difference was even



[1] All ion amounts in eq ha^{-1}.
[2] Total N, P, DOC, and Al in kg ha^{-1}.
[3] nd = no data.
[4] For period mid March to April 20.
[5] Excludes period April 4 - 24.

Fig. 4. Box diagram of element budget for inputs, snowpack, litter leachate, overland flow, and streamwater discharge, December 20, 1988 to May 15, 1989, Calumet Experimental Watershed.

greater during the increased snowmelt beginning in middle March. Since groundwater concentrations of these two ions were highest relative to snowmelt concentration (Table 2), this shows a high proportion of groundwater contribution to surface runoff which increased during early snowmelt. This was further evidence of some piston action on groundwater increasing its relative contribution to surface runoff.

March 14—28, was a period of major net SWE loss (7.7 cm). Streamwater exhibited pulses for NH_4^+ and NO_3^- with discharge of 2.5% of the 17 eq ha^{-1} NH_4^+ and 6% of the 29 eq ha^{-1} NO_3^- in snowmelt. Beginning March 28, the period of peak daily snowmelt and just prior to sustained overland flow and peak streamwater discharge, the percentage of total winter discharge of C_B and HCO_3^- was 10—20% less than streamwater discharge. This condition prevailed until the end of snowmelt. As previously described for nitrogen species, it appears that near-surface macropore or pipe throughflow and surface lateral runoff now increased the relative proportion of dilute meltwaters to the stream (Roberge & Plamondon 1987). This led to the April maximum reduction in stream acid neutralization capacity (400 μ eq L^{-1}) of which about 90% was due to dilution.

The final snowmelt period commenced April 4, with the major SWE loss (13.4 cm) occurring during April 11—25 (Fig.2). Streamwater showed its sharpest H^+ pulse the week of April 18—25, but H^+ output was still only 0.7% of inputs. NO_3^- and SO_4^{2-} pulses also occurred that week. The NO_3^- output was 3.4 eq ha^{-1} or 19% of inputs while the SO_4^{2-} loss (56 eq ha^{-1}) exceeded the week's input. Despite the relatively large input of NH_4^+, its streamwater concentration was below detection. This was further evidence of the stronger conservation and/or transformation of NH_4^+ which occurs late in the snowmelt season (Stottlemyer & Toczydlowski 1990).

Using our estimates of overland flow, which we computed to be 1.7cm or 5.6% of total streamwater discharge, the relative solute load of organics and Al in this component exceeded the amount of water (Fig. 4). Expressed as a percentage of total streamwater solute discharge, overland flow contained 15% of the total P, and 7% of the total N, DOC, and Al.

For the study period, C_B output was 23 times input and SO_4^{2-} discharge exceeded input by 42% (Fig. 4). Correcting SO_4^{2-} input for estimates of dry deposition resulted in outputs exceeding inputs by only 20%. Inputs of total N, P, Al, and DOC were not determined. But output of these elements considerably exceeded peak snowpack content. H^+ was the most strongly conserved ion with output $<0.2\%$ of input. NH_4^+ was also strongly conserved with only 1.4% of input leaving the ecosystem as was NO_3^- with discharge 9.4% of input. Cl^-, a conservative ion occasionally used to check on input/output budget estimates, showed much higher

Table 2. Volume-weighted mean ion concentration (μ eq L^{-1}) and cation/anion ratio (C/A) from January 1, to April 28, 1989. Total Al, total N, and DOC are in μ mol L^{-1}.

	C_B	Ca^{2+}	K^+	NH_4^+	H^+	NO_3^-	SO_4^{2-}	Cl^-	HCO_3^-	C/A	Al	N	DOC
Precipitation													
NADP @ MI99	13	8	1	13	27	19	22	1	—	1.29	—	—	—
Bulk @ MI99	31	19	2	20	25	23	27	3	—	1.35	—	—	—
Bulk @ Calumet	20	13	1	15	27	22	25	3	—	1.29	—	—	—
Snowpack													
C1—C4	21	14	1	11	21	19	15	2	—	1.59	—	—	—
C5	17	11	1	11	21	23	17	1	—	1.56	22	36	67
Snowmelt	56	41	4	22	20	36	33	3	—	1.58	18	50	175
Litter leachate	108	65	14	8	3	12	15	12	46	1.43	11	64	308
Soil solution (15 cm)	313	197	21	1	3	9	87	6	146	1.57	37	41	833
Soil solution (30 cm)	309	188	19	0.2	2	9	89	4	144	1.44	30	31	567
Upper stream (C2)	834	631	4	1	0.1	11	100	16	526	1.27	22	22	367
Lower stream (C4)	745	552	5	1	0.1	8	105	13	397	1.33	18	33	450

discharge than input even during this winter season. This, too, likely resulted from the relatively large surface and near-surface lateral flow of meltwaters (Mulholland et al. 1990). The peak snowpack total solute load was only 31% of the total winter input which was well below the long-term average (Stottlemyer & Rutkowski 1990).

Discussion and conclusions

The decline in groundwater height throughout winter until mid March indicated the increasingly important role of groundwater contributions to streamwater discharge up to the period of major snowmelt. During the study, watershed discharge about equalled inputs. However, after snowmelt the groundwater height was about 100 cm below that on December 1, 1988. This net loss of groundwater, which was about 19% of total streamwater discharge, increased outputs over what they likely would be through a longer season with higher evapotranspiration. Snowmelt is a major factor in replenishing groundwater in this region, and the drop in groundwater height could reflect the 1980's trend of major declines in precipitation input, groundwater recharge, and surface water runoff (Schindler et al. 1990).

Prior to peak snowmelt, most meltwater passed vertically into the soil. But some transfer to the stream likely occurred throughout winter aided by movement through near-surface soil macropores (Mulholland et al. 1990; Roberge & Plamondon 1987). The occurrence of midwinter streamwater NH_4^+ and NO_3^- pulses with concurrent small declines in streamwater concentrations of C_B, SO_4^{2-} and HCO_3^- during minor thaws suggest a small but consistent stream chemistry response. Instream metabolism could also account for some change especially for nitrogen species, but this was not examined. Near-surface lateral water movement was certainly in place by late March when streamwater C_B, SO_4^{2-} and HCO_3^- concentrations decreased 20—30% and inorganic N pulses were common. Thus even prior to peak snowmelt, change in streamwater chemistry appeared to be a good indicator of relatively subtle changes in meltwater pathways.

When the groundwater table reached the soil surface, the reduced time lag between peak diurnal groundwater and stream hydrograph height was evidence of a much greater percentage of snowmelt moving to the stream as surface runoff. During this time, the largest decline in streamwater C_B concentration (about 35%) occurred. This suggests that, conservatively, peak near-surface and overland runoff was a least one-third of total discharge at this time. Comparing streamwater discharge the week before

with that during overland flow showed an increase of 20%. In previous study, we estimated that overland flow may constitute up to 20% of total winter streamwater discharge (Stottlemyer & Toczydlowski 1990). Streamwater discharge increased most dramatically during the second period of overland flow or April 16—25. However, during this period C_B concentration only declined about 15% again pointing out the likely importance of increased piston action on soil solution. But it is also possible that the sustained near-surface runoff may have picked up considerable C_B from surface soils and litter. This indicates a limitation in using only solute concentration changes to explain pathways.

The prevalence of sandy to loamy-sand soils and rather slight topographic relief in our watershed, and in much of the region, do not appear conducive to overland flow. However, the combination of large snowpacks, an impervious cemented soil layer at one to two meters depth, and a pattern of snowmelt which permits meltwaters to occupy much of the soil water storage capacity prior to peak snowmelt results in very sharp rises in groundwater height and streamwater discharge. Therefore, the temporal pattern of snowmelt, more than SWE, may be a major source of variation in the extent of overland meltwater flow, and a major indirect source of year-to-year variation in ion and water budgets.

Compared to change in surface water solute concentrations, the budget approach gave a much more complete picture of the magnitude of effect overland flow and other hydrologic change had on stream chemistry. Streamwater solute concentration varied greatly during peak snowmelt due to major diurnal variation in the relative contributions of meltwater and groundwater. The peak discharge of DOC, organic N and P, and total Al, all elements with low snowpack concentrations, during overland flow points out the importance of near-surface flow paths in determining ecosystem exports. The ecosystem loss of total N and DOC during overland flow was a significant fraction of total winter output. Therefore, the magnitude of overland flow could be a major source of variation in annual ecosystem input/output budgets. While overland flow resulted in maximum dilution of those ions with high soil solution concentrations relative to snowmelt, the budget approach showed these ions to also have their highest streamwater discharges late in this period. But the process, piston action on soil solution, causing the increases was very different than that for N, P, and DOC. Except during overland flow, when total P discharge sharply increased, it does not appear this element is an effective indicator of flowpaths. We could find no significant relationship between its discharge or concentration to total N primarily because total P was often below or at detection limits.

Results from this study support earlier findings showing that a higher

percentage of midwinter snowpack solute release reaches the stream than does that associated with spring snowmelt (Stottlemyer 1987; Stottlemyer & Toczydlowski 1990). Many studies only focus on chemical pulses associated with peak snowmelt. Thus such midwinter pulses may be more pervasive than presently thought especially where soils remain thawed. However, placed in a budget context these midwinter pulses are minor contributors to the total ecosystem discharge of most elements.

The small but steady snowmelt collected in the snow lysimeters, beginning in early January, was further evidence of the consistent ion loss from the snowpack throughout most of winter. Comparisons of multi-year precipitation ion input with snowpack loads suggest that steady snowpack ion loss throughout winter is the rule for this site (Stottlemyer & Rutkowski 1990) and likely most other sites with thawed soils. Such steady snowmelt losses apparently are not the case where soils are frozen (Cadle et al. 1984), but this is not definite (Maule & Stein 1990).

These results confirm earlier investigation on this site which showed large snowmelt ionic losses prior to the occurrence of peak SWE losses. Early winter losses of this magnitude generally are not the rule in other portions of the region (Cadle et al. 1984; Semkin & Jeffries 1988). But, in many studies early winter snowpack chemistry is not monitored frequently enough to detect such losses.

The primary factor responsible for loss of stream acid neutralization capacity during snowmelt runoff is dilution. As in earlier study on this site (Stottlemyer & Toczydlowski 1990), the strong acid anions NO_3^- and SO_4^{2-} may add to this reduction, but their combined contribution is small ($<10\%$). Their reduced contribution appears due, in part, to the large snowmelt loss of these ions well before the period of peak SWE loss, and the high ecosystem retention of NO_3^-.

H^+ retention was similar to that found in other moderately well buffered ecosystems, and considerably higher than found in ecosystems with more resistant bedrock (Likens et al. 1977; Nicolson 1988; Stottlemyer & Troendle 1987). The conservation of NH_4^+ was more in line with sensitive ecosystems, and the magnitude of NO_3^- conservation was more in line with moderately buffered western conifer ecosystems. Precipitation, soil solution, and streamwater concentrations of SO_4^{2-} did not differ greatly suggesting that the ecosystem is saturated. In this region, as in the Adirondacks, ecosystem assimilation and soil adsorption of SO_4^{2-} apparently are not significant in retaining inputs (Mollitor & Raynal 1982; Stottlemyer & Hanson 1989). C_B output was high relative to inputs, but this likely is a reflection of the large groundwater contributions to runoff during this season which may be enhanced due to the trend of regional drying. The outputs of N and Al appear in line with those of other studies

(Likens et al. 1977), however, DOC and P outputs were considerably larger. This again indicates that relatively high outputs of such elements concurrent with overland flow could constitute a major source of year-to-year variation in watershed element budgets.

Acknowledgements

This study was supported by the National Acid Precipitation Assessment Program and the National Park Service through funding to the Great Lakes Area Resource Studies Unit, Michigan Technological University. The authors thank P. Toczydlowski and R. Kepner for assistance in sample collection and analyses.

References

Abrahams PW, Tranter M, Davies TD & Blackwood IL (1989) Geochemical studies in a remote Scottish upland catchment: II. Streamwater chemistry during snow-melt. Water, Air, and Soil Pollut. 43: 231—248

Cadle SH, Dasch JM & Grossnickle NE (1984) Retention and release of chemical species by a northern Michigan snowpack. Water, Air, Soil Pollut. 22: 303—319

Driscoll CT & Newton RM (1985) Chemical characteristics of Adirondack lakes. Environ. Sci. Technol. 19: 1018—1024

Glass G & Loucks O (1986) Implications of a gradient in acid and ion deposition across the Northern Great Lakes States. Environ. Sci. & Technol. 20: 35—43

Jeffries DS, Cox CM & Dillon PJ (1979) Depression of pH in lakes and streams in Central Ontario during snowmelt. J. Fish. Res. Board Can. 26: 640—646

Kelso JRM, Minns CK, Lipsit JH & Jeffries DS (1986) Headwater lake chemistry during the spring freshet in North-Central Ontario. Water, Air, Soil Pollut. 29: 245—259

LaZerte BD & Dillon PJ (1984) Relative importance of anthropogenic versus natural sources of acidity in lakes and streams of Central Ontario. Can J. Fish. Aquat. Sci. 41: 1664—1677

Likens GE, Bormann FH, Pierce RS, Eaton, JS & Johnson NM (1977) Biogeochemistry of a Forested Ecosystem. Springer-Verlag, Inc., New York, 146 p.

Maule CP & Stein J (1990) Hydrologic flow path definition and partitioning of spring meltwater. Water Resour. Res. 26(12): 2959—2970

Miller JB, Oberg JL & Sieger T Jr (1984) Water resources data for Michigan: water year 1984. U.S. Geol. Surv. Water Data Rept. MI—84, 276 p.

Mollitor AV & Raynal DJ (1982) Acid precipitation and ionic movements in Adirondack forest soils. Soil Sci. Soc. Am. J. 46: 137—141

Mulholland PJ, Wilson GV & Jardine PM (1990) Hydrogeochemical response of a forested watershed to storms: Effects of preferential flow along shallow and deep pathways. Water Resour. Res. 26(12): 3021—3036

Nicolson JA (1988) Water and chemical budgets for terrestrial basins at the Turkey Lakes watershed. Can. J. Fish. Aquat. Sci. 45(Suppl. 1): 88—95

NOAA (1986) Climatological data of Michigan. National Oceanogr. Atmos. Admin., Vol. 100, Nos. 1—4

Peters NE (1984) Comparison of air and soil temperature as forested sites in the west-central Adirondack Mountains. Northeast. Environ. Sci. 3: 67—72

Reuss JO & Johnson DW (1986) Acid deposition and the acidification of soils and waters. Ecol. Studies # 59, Springer-Verlag, NY, 119 p.

Roberge J & Plamondon AP (1987) Snowmelt runoff pathways in a boreal forest hillslope, the role of pipe throughflow. J. Hydrol. 95: 39—54

Schindler DW, Beaty KG, Fee EJ, Cruikshank DR, DeBruyn ER, Findlay DL, Linsey GA, Shearer JA, Stainton MP & Turner MA (1990) Effects of climate warming on lakes of the central boreal forest. Science 250: 967—970

Semkin RG & Jeffries DS (1988) Chemistry of atmospheric deposition, the snowpack, and snowmelt in the Turkey Lakes watershed. Can. J. Fish. Aquat. Sci. 45(Suppl. 1): 38—46

Stottlemyer R (1982) Variation in ecosystem sensitivity and response to anthropogenic atmospheric inputs, Upper Great Lake region. In: Johnson AI & Clark RA (Eds) Int. Symp. Hydrometeorology (pp 79—83). American Water Resour. Assoc., Bethesda, MD

Stottlemyer R (1987) Snowpack ion accumulation and loss in a Lake Superior Basin watershed. Can. J. Fish. Aquat. Sci. 44(11): 1812—1819

Stottlemyer R & Hanson D Jr (1989) Atmospheric deposition and ionic concentrations in Forest Soils of Isle Royale National Park, Michigan. Soil Sci. Soc. Am. J. 52: 270—274

Stottlemyer R & Rutkowski D (1990) Multi-year trends in snowpack ion accumulation and loss, Northern Michigan. Water Resour. Res 26(4): 721—737

Stottlemyer R & Toczydlowski D (1990) Pattern of solute movement from snow into an Upper Michigan stream. Can. J. Fish. Aquat. Sci. 47(2): 290—300

Stottlemyer R & Troendle CA (1987) Trends in streamwater chemistry and input-output balances, Fraser Experimental Forest, Colorado. US Forest Service Rocky Mtn. For. Range Expt. Sta. Res. Pap. RM—275, 9 p.

Wels C, Cornett RJ & LeZerte BD (1990) Groundwater and wetland contributions to stream acidification: An isotopic analysis. Water Resour. Res. 26(12): 2993—3003