

Transformations of runoff chemistry in the Arctic tundra, Northwest Territories, Canada

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Abstract:

The transformation of snowmelt water chemical composition during melt, elution and runoff in an Arctic tundra basin is investigated. The chemistry of the water flowing along pathways from the surface of melting snow to the 95.5 ha basin outlet is related to relevant hydrological processes. In so doing, this paper offers physically based explanations for the transformation of major ion concentrations and loads of runoff water associated with snowmelt and rainfall along hydrological pathways to the stream outlet. Late-lying snowdrifts were found to influence the ion chemistry in adjacent reaches of the stream channel greatly. As the initial pulse of ion-rich melt water drained from the snowdrift and was conveyed through hillslope flowpaths, the concentrations of most ions increased, and the duration of the peak ionic pulse lengthened. Over the first 3 m of overland flow, the concentrations of all ions except for NO_3^- increased by one to two orders of magnitude, with the largest increase for K^+ , Ca^{2+} and Mg^{2+} . This was roughly equivalent to the concentration increase that resulted from percolation of relatively dilute water through 0.25 m of unsaturated soil. The Na^+ and Cl^- were the dominant ions in snowmelt water, whereas Ca^{2+} and Mg^{2+} dominated the hillslope runoff. On slopes below a large melting snowdrift, ion concentrations of melt water flowing in the saturated layer of the soil were very similar to the relatively dilute concentrations found in surface runoff. However, once the snowdrift ablated, ion concentrations of subsurface flow increased above parent melt-water concentrations. Three seasonally characteristic hydrochemical regimes were identified in a stream reach adjacent to late-lying snowdrifts. In the first two stages, the water chemistry in the stream channel strongly resembled the hillslope drainage water. In the third stage, in-stream geochemical processes, including the weathering/ion exchange of Ca^{2+} and Mg^{2+} , were the main control of streamwater chemistry. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS runoff chemistry; hydrology; flowpaths; stream flow; Arctic; tundra; permafrost; soil pipes

INTRODUCTION

Seasonal snowmelt releases 8 to 9 months of wet and dry chemical deposition and most of the annual precipitation within a relatively short period, and so can strongly influence the hydrochemical input to small to medium-sized Arctic catchments. The influence of chemical inputs such as inorganic nitrogen on carbon cycling and primary productivity is potentially profound (Schindler and Bayley, 1993) and the redistribution of chemical compounds during snowmelt runoff is potentially a very important part of weathering and geochemical cycling in tundra. Improving the understanding of the influence of tundra hydrological processes and pathways on the fate of chemicals deposited to snow and ground surfaces is an essential step toward predicting the response of runoff chemistry and terrestrial geochemical budgets to changes in water and energy availability in this environment.

During winter, wind redistributes snow and its chemical load across the tundra from areas of short vegetation and high wind exposure to sites sheltered from the wind or with taller, denser vegetation (Pomeroy *et al.*, 1993). The snow ion load in depositional areas (e.g. snowdrifts) can be 8 to 10 times greater than in the

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open tundra, with the effect magnified for sea salts and diminished for NO_3^- , which is not conserved in blowing snow particles (Pomeroy *et al.*, 1991, 1995). Although these snowdrifts govern the length of the melt season and contribute significantly to the late melt runoff in medium-sized Arctic catchments (Marsh and Pomeroy, 1996; Quinton and Marsh, 1999), the chemical implications of snowdrift melt chemistry for the stream and interactions with the soil have not been assessed. Several studies examining the timing of the ion mass flux from deep, late-lying snow have found that the chemical concentration of initial melt water is enhanced to varying degrees, whereas later melt water is relatively dilute (Jones *et al.*, 2001). Much of the enhanced concentrations in early melt are due to diffusion of solute-rich water into melt water (Marsh and Pomeroy, 1999). Jones (1991) demonstrated that, within a snowpack, microbial consumption and release of inorganic nitrogen could substantially alter the snow nitrogen budget during melt, with large reductions in NO_3^- concentrations often observed. Other studies describe the opposite fate of NO_3^- in the snowpack, with nitrification often reported (Sueker *et al.*, 2001).

The chemistry of snowmelt water is not easily related to the chemical composition of small Arctic streams during the snowmelt freshet. In a study of the chemistry of headwater streams in Arctic tundra, Teare (1998) found that, during the snowmelt runoff period, all streams contained high levels of organic acids and relatively high concentrations of K^+ . A $\text{Ca}^{2+} - \text{SO}_4^{2-}$ signal predominated during the declining limb of the snowmelt runoff hydrograph, and a $\text{Ca}^{2+} - \text{HCO}_3^-$ signal characterized the low stream-flow conditions of summer. The $\text{Ca}^{2+} - \text{SO}_4^{2-}$ signal was attributed to interaction with lake sediments and mixing with sediment pore water, and the $\text{Ca}^{2+} - \text{HCO}_3^-$ signal was attributed to interaction with the Quaternary sediments underlying the stream channels (Teare, 1998). The ion composition of the streams contrasted strongly with the early melt peak in the primary chemical fluxes of Na^+ , Cl^- , SO_4^{2-} , and NO_3^- and the very low levels of K^+ and organic acids observed by Marsh and Pomeroy (1999) in nearby snowpacks. This suggests that the composition of the melt water that flowed through the soil to the stream changed markedly by mixing with soil water and interacting with the soils. Jones and Pomeroy (2001), working in a boreal catchment in Quebec, found that the degree to which the snow chemical composition was preserved in the hillslope runoff depended upon the extent of impermeable (concrete) frost in the soil. The substantial interannual variability in the extent of concrete frost, and in the ionic composition of the hillslope runoff, suggested complex and variable flow pathways that could not be elucidated.

Overland flow on tundra, permafrost hillslopes is generally limited to areas downslope of melting, late-lying snowdrifts. Melt water also percolates through the porous organic soils and moves rapidly downslope as interflow (Quinton and Marsh, 1999), even while the ground is still snow covered (Quinton and Marsh, 1998). Because the hydraulic conductivity of organic soils in this environment decreases exponentially with depth (Quinton *et al.*, 2000), the residence time of subsurface drainage water increases as the soil thaws and the zone of saturation descends through the wetted profile. As a result, the time available for chemical interaction between the water of the active and inactive soil pores is expected to increase as thaw progresses. The surface area for contact between pore water and soil also increases with increasing soil thaw due to a decrease in mean pore diameter with depth (Quinton *et al.*, 2000).

As the active layer thaws during and after melt and the water table perched above the frozen soil descends, the thickness of the unsaturated zone above it increases. Drying of the unsaturated layer concentrates the remaining solute in shrinking water films on soil particle surfaces. A water table rise due to rainfall or subsequent seasonal snowmelt could mix with these enriched films, altering the chemical composition of interflow from that of the original rainfall or snowmelt effluent. In Arctic Alaska for example, the concentration of some ionic species in hillslope runoff has been observed to increase following rain events (Hinzman *et al.*, 1998).

There is evidence that hydrochemical processes during tundra runoff alter the chemistry of waters derived from snowmelt and rainfall. In particular, the high chemical loads of sea salt, SO_4^{2-} and NO_3^- observed in snowdrifts may be altered before reaching the stream. The objectives of this paper are to characterize in detail the chemical transport and transformations of water draining along an Arctic tundra pathway from

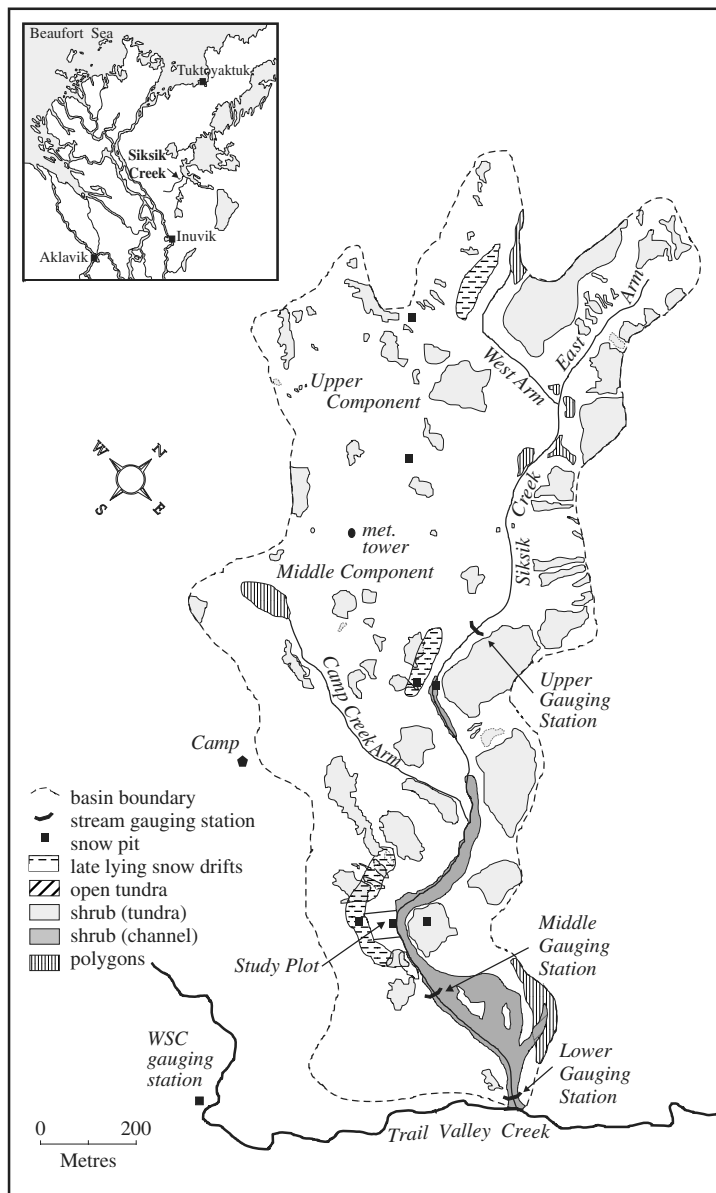


Figure 1. The Siksik Creek basin, showing the major biophysical terrain types, the three stream gauging stations, the snow pits, and the hillslope study plot

snowdrift to stream, and to relate the chemical mass balance of the surrounding small headwater catchment to hydrochemical processes.

STUDY SITE

The study was conducted at Siksik Creek ($68^{\circ}44'N$, $133^{\circ}28'W$) located approximately 55 km north-northeast of Inuvik, and 80 km south of Tuktoyaktuk on the Arctic Ocean (Figure 1). The watershed is located at the

northern fringe of the forest–tundra transition zone (Bliss and Matveyeva, 1992), and is within continuous permafrost (Heginbottom and Radburn, 1992). Siksik Creek drains a 95.5 ha area with elevations ranging between approximately 60 and 100 m a.s.l.

The climate at Siksik Creek, as inferred from the climate normals for Inuvik and Tuktoyaktuk (AES, 1982a,b), is characterized by short, cool summers and long cold winters, with 8 months of snow cover. The mean daily temperature rises above 0 °C in early June and falls below 0 °C in early October, with a mean annual air temperature of –9.8 °C at Inuvik and –10.9 °C at Tuktoyaktuk. The mean annual precipitation totals at Inuvik (266 mm) and Tuktoyaktuk (138 mm) are comprised of 66% and 47% snowfall respectively. Monthly precipitation is greatest in August, September and October, with most precipitation falling as rain in August and September, and as snow in October.

Mineral earth hummocks (Figure 2a) occur throughout the study basin, covering between 30% and 70% of hillslope surfaces. Their diameters range between 0.4 and 1 m, with their crests rising 0.1 to 0.4 m above the surrounding interhummock surface. The hummock surfaces are bare or support a thin layer of lichen (*Alectoria* and *Cladina* spp.). The interhummock vegetation consists of sedges (*Eriophorum* and *Carex* spp.) and small vascular plants (*Empetrum*, *Vaccinium*, *Ledum* and *Rubus* spp.) rooted in a continuous cover of moss (*Sphagnum* spp.). The peat in the interhummock area is ~0.3 to 0.4 m thick. The upper ~0.1 to 0.2 m is composed of living vegetation and lightly decomposed peat. Below this, the peat is moderately to strongly decomposed (Quinton and Marsh, 1999).

Water moves preferentially through the interhummock area, since the hummocks are raised, and the hydraulic conductivity of the organic soil is three to six orders of magnitude higher than that of the clay-rich hummocks (Quinton and Marsh, 1998). In the interhummock area, soil pipes, with diameters of 0.05 to 0.10 m are common on hillslopes with gradients \gtrsim 0.08, but were not observed on gradients of \lesssim 0.04. The soil pipes occur predominantly in the lower peat layer, with the upper layer forming an organic ‘roof’. By late summer, the average frost table depth was ~0.3 m in the interhummock area, compared with 0.6 m in the hummocks (Quinton and Marsh, 1998). Fine-grained, frost-susceptible soils underlie the organic cover throughout the basin.

At the onset of snowmelt runoff in the spring, the soil profile in the interhummock area is usually saturated or nearly saturated with ice, creating a relatively impermeable boundary close to the ground surface. Previous hydrological studies on this hillslope (Quinton and Marsh, 1998; Quinton *et al.*, 2000) demonstrated that, during soil thawing, the upper surface of the frozen, saturated soil coincides closely with the elevation of the 0 °C isotherm, i.e. the frost table. The frost table, therefore, approximates the lower boundary of the thawed, saturated layer through which subsurface water drains from the hillslope. The saturated, horizontal hydraulic conductivity k_s decreases from 10^{-3} m s⁻¹ to 10^{-6} m s⁻¹ between 0.1 and 0.3 m depth increments in the interhummock area (Quinton *et al.*, 2000). Given the depth dependency of k_s and the impermeable nature of the frost table in this environment, the frost table elevation is a major factor controlling the timing and magnitude of hillslope subsurface drainage.

METHODOLOGY

Field studies

Most field measurements were conducted between April and September 1992, with selected follow-up sampling and measurement during the same period of 1993. In late winter, 845 snow depths and 169 densities were measured along transects to estimate the snow water equivalent for each of the major biophysical cover types: open tundra, shrub tundra, channel shrub, open channel, and steep slopes where late-lying snowdrifts form, following the methodology of Pomeroy and Gray (1995). On 6 May, snow pits were dug with Teflon-coated shovels within each biophysical site type. In each pit, initial snow chemistry was measured by a mass weighted mean of samples extracted from the various physical layers. Snow samples were extracted using a

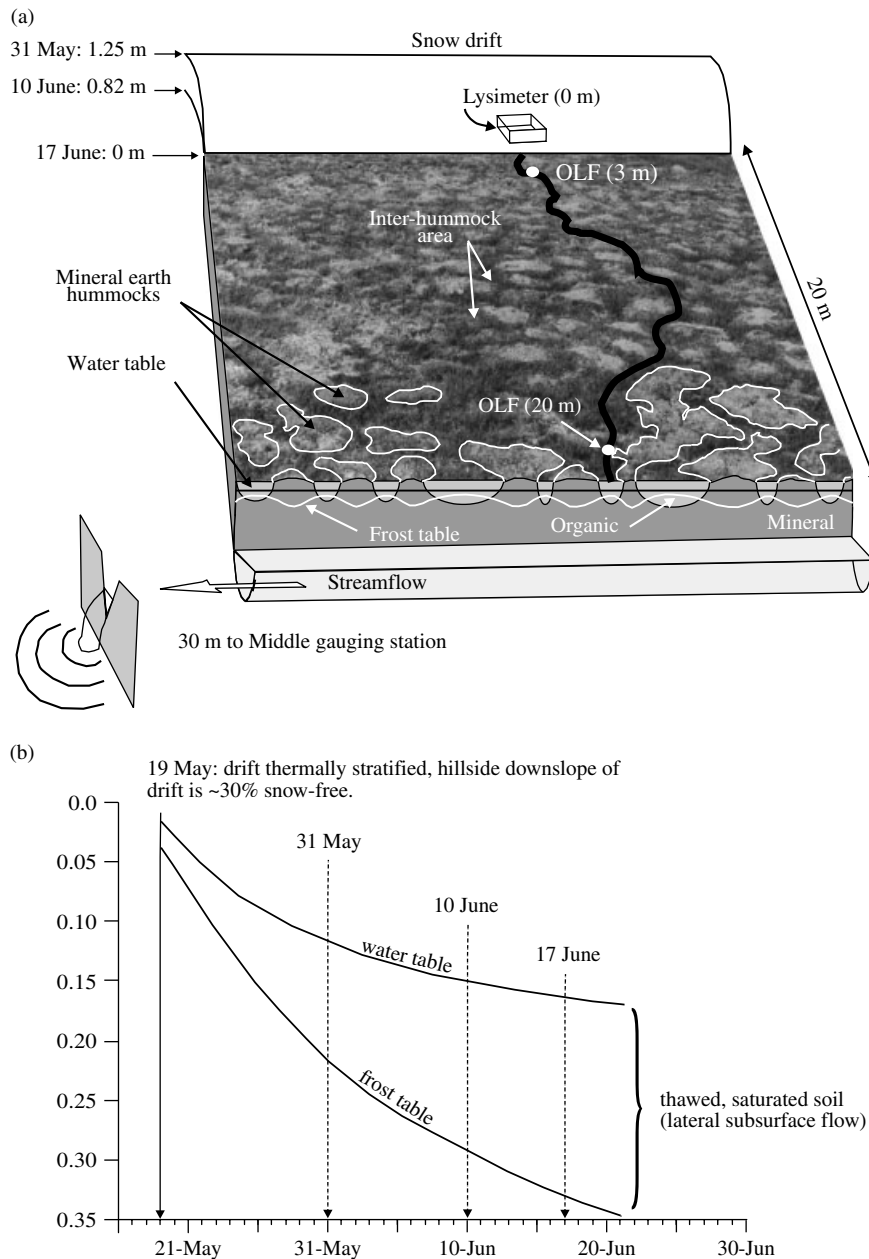


Figure 2. (a) A schematic of the hillslope study plot; (b) variation in the average depth of the frost table measured along the measurement transect and water table measured at the observation well 15 m downslope of the snowdrift at the study plot in 1992

200 cm³ polyethylene scoop that had been soaked and rinsed with deionized water. The snow samples were stored in clean polyethylene resealable bags, and allowed to melt at 20 °C.

By 21 May, the snowdrift had become isothermal at 0 °C. On that date, a 0.25 m² polyethylene lysimeter that had been soaked and rinsed with deionized water was installed at the base of the snowpack, following the methodology of Marsh and Woo (1985). Installing the lysimeter prior to the isothermal condition was

attempted, but it resulted in refreezing and ice blockage in the lysimeter. Each day, melt water was collected from the lysimeter in high-density polyethylene (HDPE) bottles that had been washed in nitric acid and then rinsed several times with deionized water.

Six rain-chemistry collectors, each consisting of a 0.15 m diameter polyethylene funnel attached to a 500 ml HDPE bottle, were located near the base camp (Figure 1). The gauges were positioned at a height of 1.5 m above the ground surface so as to minimize splash or entry of vegetation debris. Each gauge was checked and rinsed with deionized water daily, and following each rain event, at which time all accumulated rainwater was recovered, and a single composite sample was stored in a pre-washed HDPE bottle. A shielded Misco 0.2 m diameter tipping-bucket rain gauge was deployed at the same location in order to obtain a continuous rainfall for both years. This gauge was attached to a Campbell datalogger, which recorded total rainfall every 30 min.

On a northeast-facing hillslope (Figure 1), an intensive study plot was established so that water samples and discharge measurements could be taken along segments of a hillslope runoff pathway (Figure 2a). Upslope of the plot was a late-lying snowdrift that remained for 3 to 4 weeks after the melt of the surrounding snow. Following snowmelt, a graduated steel rod was used to measure the depth of the impermeable frost table below the ground surface. These measurements were made every second day at 0.5 m intervals along a 20 m transect that extended between the stream bank and the snowdrift. The transect included approximately an equal number of points in hummocks and in the interhummock organic-rich surface (Quinton and Marsh, 1998, 1999; Quinton *et al.*, 2000). The depth of the water table below the ground surface was measured daily at a stilling well, located 15 m downslope of the snowdrift, that was installed in the interhummock area during the fall of 1991. This well was also used to obtain water samples from the saturated layer, representing the subsurface drainage pathway. Overland flow from the study plot was measured using a flume box equipped with a 90° V-notch weir and stage recorder, located at the terminus of an ~20 m long ephemeral rill that conveyed the melt water from the snowdrift to the stream bank. Overland flow samples were collected daily at the flume box and 3 m downslope of the snowdrift along the same rill. Water draining from the outlet of natural soil pipes at the stream bank was also sampled.

Zero-tension, polyethylene lysimeters with a surface area of 0.1 m² and a depth of 0.05 m were used to collect water percolating through the unsaturated zone. Each lysimeter was covered with a perforated polyethylene sheet to prevent the overlying soil from collapsing into the 0.05 m thickness air space below. Four soil pits were excavated to the frost table, and a lysimeter was installed in each, so that its upper, perforated surface was 0.25 m below the ground surface. The intact organic soil block was then carefully positioned on top of the lysimeter.

The lysimeters were installed on 26 June 1992 and were sampled on 23 July. Following the initial sampling, each lysimeter was rinsed with deionized water, reinstalled in the ground, and covered with the soil block. Deionized water (1.5 l) was then applied to the surface of each soil block, which is equivalent to a rainfall depth of 15 mm. The deionized-water application took approximately 10 min for each lysimeter. The lysimeters were sampled 1 week later, on 29 July. No rain occurred during this period, so the accumulated water was assumed to have come only from the deionized water and any antecedent water in the unsaturated soil layer above the lysimeters.

Stream discharge was measured at the basin outlet (lower gauging station, drainage area 95.5 ha) using a reinforced plywood weir with a metal-plated 90° V-notch and a stilling well with a stage recorder. Discharge was also measured at two additional gauging stations located 275 m (middle gauging station, drainage area 83.4 ha) and 1175 m (upper gauging station, drainage area 43.9 ha) upstream of the outlet (Figure 1). Since these stations were under construction during the 1992 study season, discharge was not measured continuously until July of that year. Prior to that time, discharge was measured instantaneously using a Price AA current meter at the site of each station, twice daily during the snowmelt runoff period, and once daily thereafter. Water samples were collected manually at all the stations in both years in 250 ml HDPE bottles.

Analytical procedure

All water samples, including melted snow, percolate collected from the snow and soil lysimeters, hillslope drainage water and rainfall, were filtered through 0.4 μm Nuclepore filters. The pH was measured prior to filtering with a Ross combination electrode. All samples were then stored in washed HDPE bottles at cool temperatures and shipped to the National Hydrology Research Institute in Saskatoon for analysis. Anion analyses (Cl^- , NO_3^- , SO_4^{2-}) were conducted on a Dionex 2010i ion chromatograph with a 100 μl injection loop, 0.75 M NaHCO_3 –1.5 M Na_2CO_3 eluent, and suppressed conductivity detection. Samples were introduced by a Technicon sampler into the loop after mixing nine parts of sample to one part of concentrated eluent (10 \times the working eluent concentration). Cation analyses (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were performed using flame atomic absorption spectrophotometry on Perkin Elmer AAS models 460, 2380 and 5000.

The annual water balance was computed for the Siksik Creek drainage basin from

$$(\text{SWE} + P) - R = \Delta S \quad (1)$$

where SWE is the areally weighted mean pre-melt snow water equivalent of the five major biophysical terrain units computed from the results of the late-winter snow depth and density surveys, P is cumulative annual rainfall measured between snowmelt and freeze-up, R is the cumulative annual discharge measured at the lower gauging station (Figure 1), and ΔS is the change in storage. All units are in millimetres.

For each ion species under study, the annual mass balance was computed from

$$[(V_{\text{SWE}}C_{\text{SWE}}) + (V_{\text{P}}C_{\text{SP}})] - (V_{\text{R}}C_{\text{SR}}) = \Delta S_{\text{M}} \quad (2)$$

where V_{SWE} (m^3) is the snow water equivalent volume (computed as the product of the areally weighted SWE depth defined in Equation (1) and the basin area), C_{SWE} is the areally weighted ion concentration (computed from the snow pit data), V_{P} (m^3) is the cumulative rainfall volume (equal to the product of the cumulative rainfall depth and the basin area), C_{SP} is the average measured ion concentration of all rain events for which water samples were collected, V_{R} is the cumulative runoff volume (equal to the product of the cumulative runoff depth and the drainage area), and C_{SR} is the ion concentration measured in the stream channel. Because the variation in ion concentration over time is relatively large in the stream channel, $V_{\text{R}}C_{\text{SR}}$ was computed over daily periods with the assumption that ion concentrations measured in each daily water sample were representative of the volume of water that discharged from the stream channel over the daily interval since the last water sample was collected. The daily values of $V_{\text{R}}C_{\text{SR}}$ were then summed to arrive at a seasonal estimate. ΔS_{M} is the change in the ion mass (kilograms) stored in the basin.

RESULTS

Hillslope hydrology

The rate that water drained from the hillslope and through the stream channel varied with the degree of snowmelt and soil thaw. This is demonstrated by comparing the flow conditions of four specific dates (19 May, 31 May, 10 June and 17 June) representing different stages of the snowmelt runoff period. On 19 May, the snowdrift was thermally stratified; and the 20 m section between the snowdrift and the stream channel, which was entirely snow covered a few days earlier, was now about 30% snow free. The stream channel was filled with wet snow, and flooded in several areas, and did not yet conduct open channel flow. Instead, water in the channel moved slowly toward the basin outlet as seepage through the saturated channel snowpack. At this time, melt water percolated through the snowdrift at a rate of 1.33×10^{-6} to 1.99×10^{-6} m s^{-1} , as computed from the method of Marsh (1991), indicating that the melt water contribution of the snowdrift to the stream channel was negligible.

By 31 May, the snowdrift had been isothermal for about 10 days, and the rate of percolation through this 1.25 m deep pathway had increased to 6.02×10^{-5} m s^{-1} (Marsh, 1991), indicating that 24% of the overall

travel time from the surface of the melting snowdrift to the basin outlet was spent in percolation through the snowdrift. Overland flow began approximately 2 days before 31 May, and the entire hillslope downslope of the snowdrift was now snow free. The hillslope tracer tests at this time (Quinton *et al.*, 2000) indicated a mean pore velocity through the saturated soil layer (Figure 2b) of $\sim 8.10 \times 10^{-4} \text{ m s}^{-1}$. For the 20 m long hillslope, this represents approximately 53% of the overall travel time to the basin outlet. Less than 2% of this travel time was spent in the 275 m stream section between the study plot and the outlet, where open channel flow was now occurring, and the mean velocity was 0.34 m s^{-1} .

On 10 June, the depth of the snowdrift was 0.82 m, and the average percolation rate (Marsh, 1991) was $6.02 \times 10^{-5} \text{ m s}^{-1}$, representing $\sim 20\%$ of the overall travel time to the outlet. Overland flow, which peaked on the previous day (9 June), remained high. The pore velocity in the unsaturated layer had decreased to $3.70 \times 10^{-4} \text{ m s}^{-1}$, resulting from the lower position of the thawed saturated zone (Figure 2b). By this time, the subsurface hillslope flowpath was at 78% of the overall travel time to the outlet. Approximately 2.5% of the travel time was spent in the stream channel, where the average flow velocity was 0.16 m s^{-1} .

The snowdrift had melted at the snowmelt lysimeter by 17 June (Figure 3a), although it persisted until 19 June further upslope. Within a day of the snowdrift's disappearance, overland flow and flow from most soil pipes ceased, thereby leaving subsurface flow through the peat matrix as the only pathway to the stream channel. Continued soil thaw reduced the average pore velocity in this segment to $6.13 \times 10^{-5} \text{ m s}^{-1}$ (Quinton *et al.*, 2000), increasing the time spent in this 20 m pathway to over 98% of the overall travel time. The remaining $\sim 2\%$ of the travel time was spent in the stream channel with an average velocity of 0.12 m s^{-1} .

Major flowpaths

Snowmelt percolation. At all snow pits, the concentration factor (CF), the ratio of the ion concentration in the melt water to that in the parent snow, was largest for Ca^{2+} , with high values also occurring for Na^+ , Cl^- and Mg^{2+} . At the snowdrift, where the snow cover persisted for 3 to 4 weeks following the melt of the surrounding snow (Figure 3a), the CF values indicate an initial pulse of acidic, ion-rich melt water, followed by the drainage of relatively dilute water with a more neutral pH. The ion concentrations in the melt water from the snowdrift and CF values (Figure 3b) peaked on 27 May, after only 18% of the cumulative water equivalent was released (Figure 3c). By 2 June, when 35% of the SWE had melted and after the initial pulse of highly concentrated melt water, the cumulative mass flux of all ions (except K^+) exceeded 90%. The ion concentrations were low in the remaining 65% of the melt water from the drift.

Overland flow. An ephemeral rill, such as that depicted in Figure 2a, conveyed melt water across the 20 m snow-free valley bottom from the snowdrift to the stream bank. From 31 May to 3 June, while ions were preferentially eluted in melt waters from the snowdrift (Figure 3b), the difference in the ion concentrations of water sampled from the upslope (snowmelt lysimeter) and downslope of the 20 m rill were one to two orders of magnitude larger than the differences in ion concentrations from parent snow to melt water (Table I). As with the melt water, the enrichment in Ca^{2+} concentration was the largest in overland flow, followed by K^+ . The behaviour of NO_3^- concentration did not change appreciably during melting, and then decreased below the analytical detection limits during overland flow to the stream bank. Although the concentrations of NO_3^- and SO_4^{2-} in the melt water were similar to those of Ca^{2+} and Mg^{2+} for the 40-daily water samples taken along the rill, NO_3^- was detectable in only one overland flow sample (19 June) after travelling 3 m downslope and was not detected in any of the samples at the stream bank. Whereas NO_3^- concentrations decreased with flow distance, the average concentration of SO_4^{2-} was consistently higher in the overland flow than in the melt water (Table I), and often increased with overland flow distance.

Prior to the peak of overland flow (9 June), the concentration of each ion species in the melt water percolation and overland flow (20 m) decreased following the peak concentration on 27 May (Figure 3b). After 9 June, the snowdrift melt water did not strongly affect the ion concentrations of overland flow. For example, during the second half of June, the concentrations of Ca^{2+} and Mg^{2+} increased in overland flow, while they were

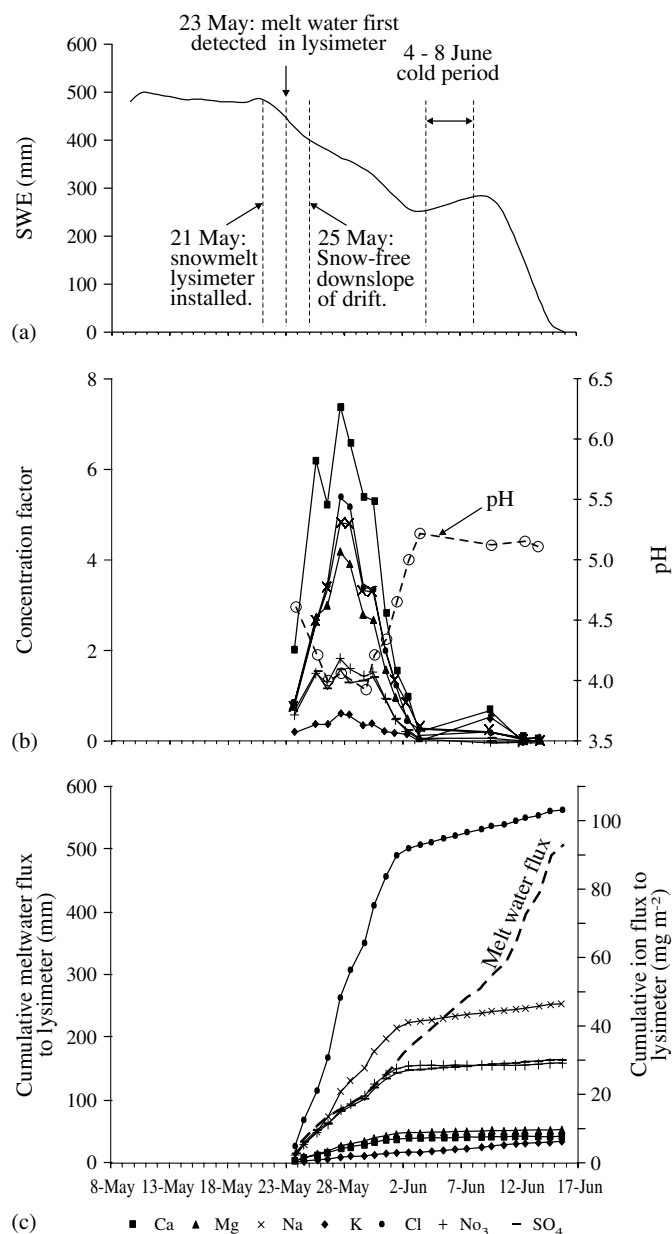


Figure 3. (a) The ablation of the late-lying snowdrift at the study plot in 1992; (b) the temporal variation in concentration factor and pH of the melt water collected from the base of the snowpack; and (c) the cumulative flux of ions and water from the snowdrift to the snowmelt lysimeter

decreasing in the melt water (Figure 4). During 9–13 June, the largest increase in concentrations occurred over the first 3 m of overland flow. The average concentration of all ions, except for NO_3^- , increased by one to two orders of magnitude in the 3 m flow distance, with the largest increase occurring for Ca^{2+} (178-fold), followed by Mg^{2+} (38-fold), and then K^+ (29-fold). The change in ion concentrations over the next flow increment (3 m to 20 m) was considerably lower, as the average concentration at 20 m during this period

Table I. The weighted average ion concentrations of the three major layers in the parent snow of the snowdrift; the average ion concentration of the meltwater percolate for the period over which melt water was sampled from the snow lysimeter (23 May–13 June 1992), and the average ion concentrations for the 31 May–3 June and 9–13 June periods measured at the snowmelt lysimeter, at 3 m and 20 m downslope of the edge of the snowdrift along the rill conducting overland flow (OLF) to the stream bank at the study plot in 1992

Period	Sample type	Ion concentration ($\mu\text{eq l}^{-1}$)						
		Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
6 May	Parent snow	0.50	1.99	4.25	1.28	6.05	2.42	3.04
23 May–13 June	Percolate	1.59	3.39	8.49	0.41	12.45	2.03	2.42
31 May–3 June	Percolate	0.71	1.62	4.81	0.22	6.11	1.10	1.4
	OLF (20 m)	84.0	68.5	35.3	20.7	54.9	—	4.0
9–13 June	Percolate	0.12	0.22	0.62	0.32	0.84	0.05	0.17
	OLF (3 m)	21.3	8.3	12.03	9.23	14.22	—	2.85
	OLF (20 m)	34.33	27.78	15.80	9.66	13.09	—	1.32

was between 0.46 and 3.35 times what it was at 3m (Table I). For 31 May to 3 June and 9 to 13 June, Ca²⁺ and Mg²⁺ had replaced Na⁺ and Cl⁻ as the dominant ions along the 20 m overland flowpath.

In 1992, too few overland flow samples were collected to determine whether the ion pulse, which entered the hillslope from the snowdrift (Figure 3b), was preserved through the 20 m overland flowpath. However, in 1993, a sufficient number of samples were collected to show clearly a breakthrough of acidic, ion-rich water entering the stream (Figure 5a). The arrival of the ion-rich water at the stream was relatively early in the runoff period (5 June), by which time only 30% of the cumulative overland flow had occurred (Figure 5b). The limited snowmelt lysimeter data during 1993 (five sample days) indicated that Cl⁻ and Na⁺ dominated the melt water percolating from the snowdrift, as during 1992 (Figure 3c). Figure 5a also indicates that, as in 1992, Ca²⁺ and Mg²⁺ were the dominant ions in the overland runoff water entering the stream.

Percolation through unsaturated soil. The 0.25 m vertical pathway represents unsaturated soil flow from the ground surface to the top of the soil lysimeters. The ion concentrations in the deionized water applied to the top of the soil (Table II) were similar to that of the relatively dilute snowmelt percolate (e.g. 9–13 June; Table I). Ion concentrations increased one to two orders of magnitude; and, as with overland flow, SO₄²⁻ concentration also increased in the soil percolate, whereas NO₃⁻ remained below the analytical detection limit. The increase in ion concentration of the deionized water over the 0.25 m of soil percolation pathway (Table II) is roughly equivalent to that which occurred over the first 3 m of overland flow (Table I). The same experiment conducted using rainfall rather than deionized water as the input yielded similar results, with the exception of the behaviour of NO₃⁻ and SO₄²⁻, whose concentrations were lower in the soil lysimeters than in the rainfall (Table II). However, this difference is governed by the high average concentrations of SO₄²⁻ (9.7 $\mu\text{eq l}^{-1}$) and NO₃⁻ (4.3 $\mu\text{eq l}^{-1}$) in the rainfall, where only Ca²⁺ had a higher average concentration. The SO₄²⁻ concentration in the rainfall was about twice that of the peak SO₄²⁻ level in the snowmelt percolate, and an order of magnitude higher than the concentrations in the relatively dilute melt water percolate of the 9–13 June period.

Subsurface drainage. Ion concentrations in the soil saturated zone (Figure 4) peaked within 3 days following the peak in the ion concentrations in the melt water (Figure 3b), and then slowly decreased, so that by 17 June, 2 days before the snowdrift disappeared, the concentrations had returned near to their initial values of 26 May. The ion concentration in the saturated layer varied with the seasonal evolution of the hillslope hydrology discussed above. For example, on 31 May, the ion concentrations measured in the saturated layer were very similar to those measured in the overland flow arriving at the stream bank (Table III). By 10 June, several

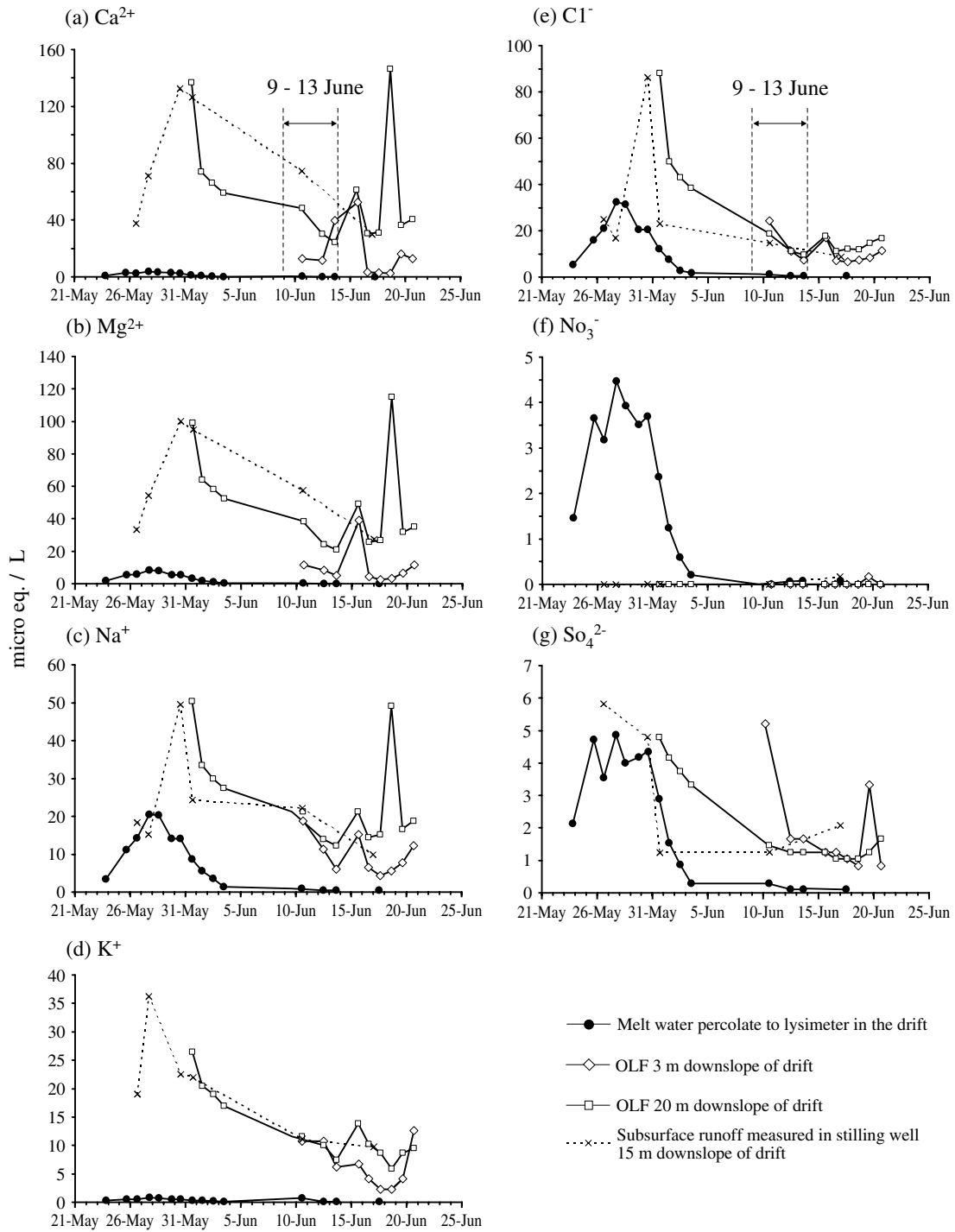


Figure 4. The ion concentration in the (i) melt water percolate from the snowdrift, (ii) overland flow (OLF) at 3 m downslope of the snowdrift, (iii) overland flow at 20 m downslope of the snowdrift, and (iv) subsurface runoff through the peat matrix sampled from the well 15 m downslope of the snowdrift. The period 9–13 June when samples were collected from the 0 m (lysimeter), 3 m and 20 m sampling points is identified for each ion

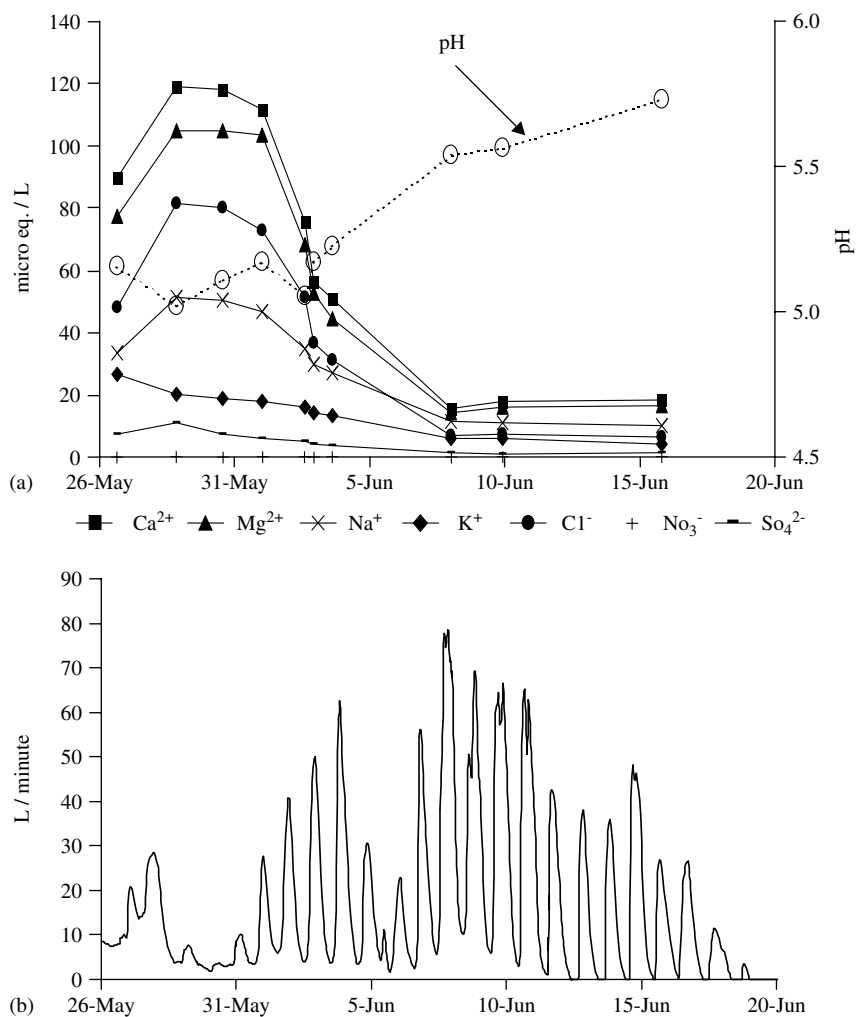


Figure 5. (a) The change in ion concentration and pH in the surface water draining from the study plot 20 m downslope of the snowdrift in 1993; (b) the overland flow rate continuously measured at the same location

Table II. The ion concentrations of the input and output water for the soil percolation experiments. The input concentrations are of (1) the deionized water applied to the ground surface during a rain-free period and (2) the average values for the four rainfall events that occurred between 4 June and 23 July 1992. The output concentrations are the average values of the water collected in the soil lysimeters

H ₂ O type		Ion concentration ($\mu\text{eq l}^{-1}$)						
		Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Deionized	Input	1.50	0.83	2.17	0.26	1.98	—	—
	Output	37.15	29.58	50.98	24.87	17.51	—	3.59
Rainfall	Input	10.75	4.17	2.17	3.14	2.54	4.26	9.74
	Output	18.0	19.17	31.74	27.69	31.92	0.00	2.92

Table III. Ion concentrations of the melt water percolate from the snowdrift, overland flow (OLF) at the stream bank (i.e. 20 m), subsurface flow (SSF) sampled from the observation well downslope of the snowdrift, and discharge from the outlet of the two main soil pipes at the stream bank on 31 May, 10 June and 17 June. For each date, the average depth of the frost table (FT) below the ground surface is given

Date	FT (m)	Sample	Ion concentration ($\mu\text{eq l}^{-1}$)						
			Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
31 May	0.22	Meltwater	1.43	3.17	8.66	0.31	12.20	2.37	2.89
		OLF	137.0	99.17	50.43	26.41	88.14	0.00	4.79
		SSF	126.5	95.0	24.35	22.05	23.16	0.00	1.25
10 June	0.29	Meltwater	0.36	0.46	1.00	0.73	0.30	0.00	0.28
		OLF	39.5	33.93	19.13	11.28	15.54	0.00	1.46
		SSF	74.5	57.5	22.17	11.03	14.69	0.00	1.25
		Pipe 6	16.0	15.0	13.48	8.21	12.43	0.00	2.29
		Pipe 9	22.50	18.33	13.04	11.28	10.17	0.00	1.25
17 June	0.33	Meltwater	0.00	0.07	0.45	0.14	0.61	0.08	0.12
		OLF	31.00	26.67	15.22	8.72	12.15	0.00	1.04
		SSF	30.00	27.50	10.00	9.74	8.76	0.16	2.08
		Pipe 6	8.00	8.33	7.83	6.15	9.04	0.00	1.46
		Pipe 9	10.00	8.33	8.70	6.15	9.60	0.00	1.88

soil pipes had begun discharging water from their stream bank outlets (Table III). This water was relatively dilute compared with the enriched water draining through the soil matrix and over the ground surface. By 17 June, when percolation to the snowmelt lysimeter had ceased, the concentration of all ions except for K⁺ in the water draining through the two main soil pipes increased at least by a factor of 2, and for Ca²⁺, Mg²⁺ and SO₄²⁻, by ~5 to 10 times.

Stream flow. At the middle gauging station, 30 m downstream of the study plot (Figure 1), three distinct hydrochemical regimes occurred that closely mirror the variations in ion chemistry observed in the hillslope flowpaths (Figure 6a). The early stage occurred from the onset of stream flow (30 May at 23:00; Figure 6b) until the highly concentrated initial pulse of ion-rich water passed the middle gauging station. During this stage, the streamwater was characterized by a relatively high concentration of Ca²⁺, Mg²⁺ and Cl⁻, and low pH values. The middle stage occurred in the period 3–12 June, and was characterized by relatively acidic water, although the concentrations of each ion were substantially lower, and Na⁺ replaced Cl⁻ as the dominant ion following Ca²⁺ and Mg²⁺. The late stage began by mid June, and was characterized by increasing concentrations of Ca²⁺, Mg²⁺, Na⁺ and SO₄²⁻ in the stream (Figure 6a). The pH of the streamwater also increased during this stage, from ~5.1 to over 6.0.

Mass balance

In both years, the annual runoff ratio ((SWE + P)/R) was ~0.5, and R was ~0.73 of the SWE (Table IV). The storage term provides a crude estimate of the evapotranspiration flux. The ion mass balance indicates that, at Siksik Creek, there is a net export of Ca²⁺, Mg²⁺, Na⁺, K⁺ and Cl⁻. In the case of Ca²⁺ and Mg²⁺, the mass export from the basin was an order of magnitude above that which was introduced by snowmelt and rainfall. Unlike for the other ions, there was a net import of NO₃⁻ and SO₄²⁻.

DISCUSSION

Preferential elution (Davies *et al.*, 1987), dry deposition during snowmelt and possibly biological consumption of NO₃⁻ is indicated by the variation of CF values among the ion species eluted from the snowdrift (Figure 3b).

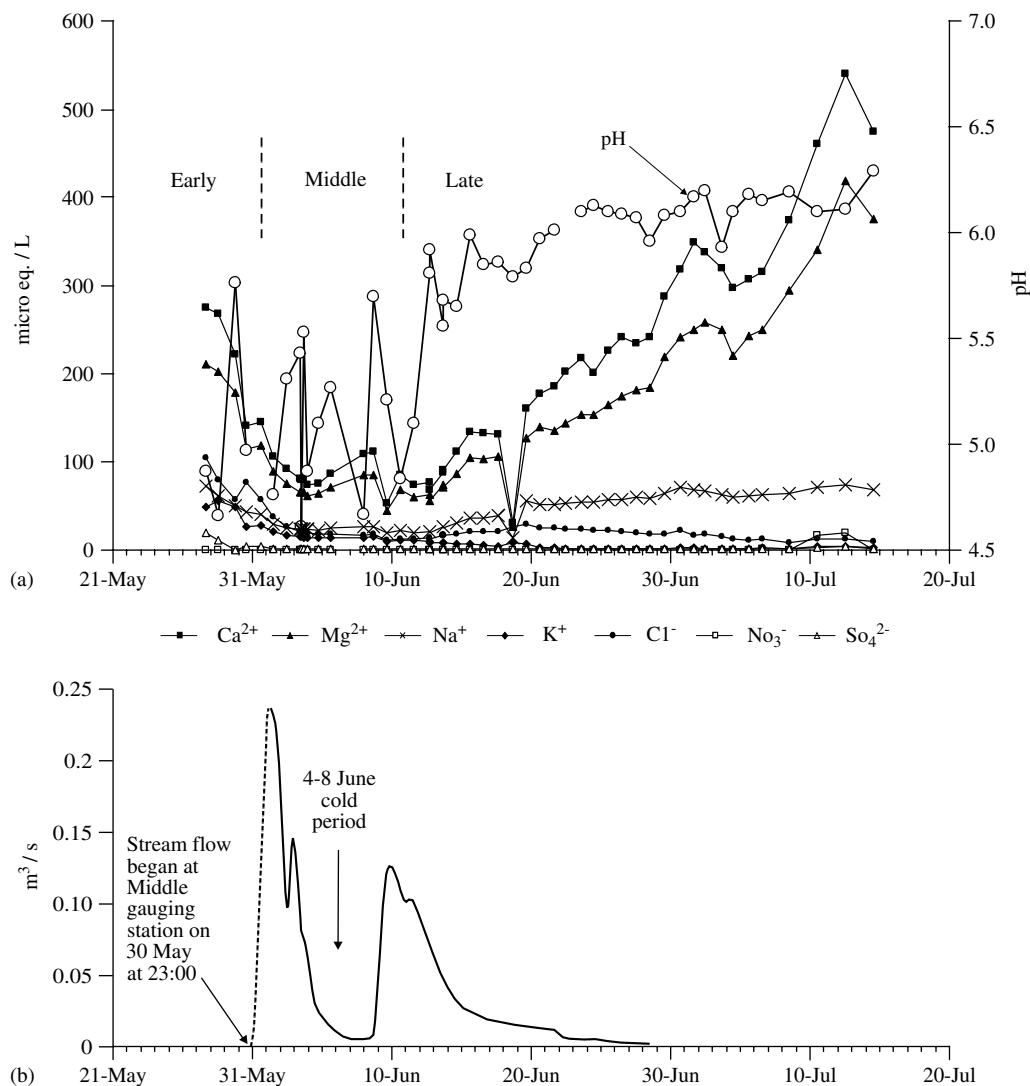


Figure 6. (a) The concentration of the major ions and the pH in the streamwater sampled from the middle gauging station on Siksik Creek, located 30 m downstream of the study plot; (b) discharge from Siksik Creek measured at the middle gauging station. The dashed line is used to connect the time between the initiation of open channel flow (30 May at 23:00) and the first discharge measurement

The high CF for Ca^{2+} , Na^+ , Cl^- and Mg^{2+} at each snow pit was likely the result of dry deposition, i.e. of local vegetation, mineral matter and sea salt aerosols, during snowmelt; while the relatively low CF values for NO_3^- and SO_4^{2-} reflect the low input of these ions over winter. Since no melt water accumulated in the snow lysimeter from installation on 21 May until 23 May (Figure 3a), it is unlikely that the NO_3^- and SO_4^{2-} eluted from the pack prior to the monitoring of snowpack chemistry. The possibility that these ions eluted from the pack through preferential pathways which by-passed the lysimeter also seems unlikely, since the cumulative depth of ~ 500 mm melt water collected in the lysimeter (Figure 3c) is similar to the pre-melt SWE above the lysimeter (Figure 3a).

The substantial increases in Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and K^+ along the overland flow pathway were almost certainly due to mixing of the melt water with the more highly concentrated soil solutions enriched by the

Table IV. Annual mass balances of water and the major ions for the Siksik Creek watershed for 1992 and 1993. The depth of water (mm) and the ionic mass (kg) is defined for each of the mass balance terms in Equation (1)

	Water	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
1992								
SWE	174.3	7.84	7.46	29.25	3.14	68.13	33.94	38.62
P	59.1	12.14	12.14	2.82	6.92	5.08	19.58	26.40
R	127.5	312.5	150.29	97.44	89.18	146.62	—	14.09
ΔS	105.9	-292.5	-140.0	-65.4	-79.1	-75.4	53.52	50.9
1993								
SWE	137.3	6.30	6.04	23.79	2.64	55.35	26.53	30.71
P	86.31	21.16	4.86	17.58	23.08	25.55	32.97	51.11
R	100.8	228.66	111.66	77.84	38.94	89.05	—	22.35
ΔS	122.7	-201.20	-100.75	-36.47	-13.22	-8.15	59.51	59.46

decomposing vegetation. The overland flow data show a solute concentration maximum at the time water began to move through and over the surface (Figure 5a), with maximum solute dilution coinciding with the peak in overland flow on 8 June 1993 (Figure 5b). The occurrence of the peak in subsurface ion concentrations 3 days following the peak in the melt water concentration (Figure 4) suggests that, as with the overland flow path, the initial pulse of melt water from the snowdrift propagated laterally through the soil. The uniform change in Ca²⁺, Mg²⁺, and K⁺ concentrations (Figure 4) suggests that the water in the saturated layer was relatively well mixed throughout the sampling period, whereas the rapid decrease in Cl⁻, SO₄²⁻, and Na⁺ concentrations suggests a marine influence. The NO₃⁻ concentration increases likely reflect an increase in soil NO₃⁻ concentration following freeze–thaw cycles with associated increased nitrogen mineralization over winter and decreased biological uptake during winter.

The snowmelt from the snowdrift was the primary hydrological input to each hillslope pathway. The overland flow rill and the subsurface pathway are physically distinct and did not interact, i.e. through return flow and reinfiltration. The ion chemistries of these two flowpaths, therefore, were compared to assess the influence of flowpath type on water chemistry. For example, on 31 May, the impermeable frost table was 0.22 m below the ground surface (Table III); consequently, the saturated layer was relatively close to the ground surface (Figure 2b). The hydraulic conductivity of the surface soil was sufficiently high to enable subsurface water to drain to the stream bank quickly, as through the overland flow pathway (Quinton and Marsh, 1999). By 10 June, the initial ion pulse had drained from the snowdrift; consequently, the ion concentrations in both overland flow and subsurface flowpaths decreased (Table III). Meanwhile, the relatively impermeable frost table had, on average, lowered 0.07 m into less-conductive peat, increasing the availability of Ca²⁺ and Mg²⁺, and a lengthening of the residence time for chemical interaction of the drainage water with soil solutions, including pore water in the mineral earth hummocks and substrate (Figure 2a). The Ca²⁺ and Mg²⁺ concentrations in the subsurface pathway decreased from 10 to 17 June despite a further 0.04 m of soil thaw (Table III). This suggests that the enriched melt-water pulse (Figure 3b), while still in the subsurface pathway on 10 June, had drained from the subsurface pathway by 17 June. Additionally, ion concentrations of the overland and subsurface pathways were similar again by 17 June.

The water equivalent of the snowdrift decreased by >50% of the peak value between 10 and 17 June (Figure 3a). The similar concentrations of Ca²⁺, Mg²⁺, and K⁺ in overland and subsurface flow on 17 June (Table III) demonstrated that the contribution of dilute melt water from rapid snowmelt during this period diluted the composition of the water in both the overland and the subsurface pathways. The water draining from the soil pipes was more dilute than the matrix water sampled from the stilling well, which suggests that chemical interactions and mixing in the soil pipes was relatively minor. The short travel time through the pipes (Quinton and Marsh, 1999) would have limited the time available for buffering of the melt water between the snowdrift and the stream bank. Also, soil pipes differ from the other hillslope drainage pathways

in that they contained very little stored water (Quinton, 1997). As a result, there would have been only limited mixing of the melt water with *in situ* water along this pathway. In contrast, water flowing through the soil matrix and over the ground surface would more readily interact and mix with water stored in the soil and vegetation, as well as in depressions.

The three hydrochemical stages observed for stream flow roughly coincided with the hydrological conditions of the adjacent hillslope study plot. The relatively high flow rates through each hillslope pathway early in the melt-runoff period resulted in connectivity of the hillslope with the stream, as indicated by the similarity between the ion concentrations of the hillslope flowpaths and the stream channel. For example, the initial peak in ion concentrations at the middle station (Figure 6a), located 30 m downstream of the study plot, occurred shortly after the peak in ion concentration in the melt water percolate from the snowdrift (Figure 3b); and the minimum pH of the stream channel (4.65) occurred within 1 day of the minimum pH of the melt water percolate (3.87) and of the overland runoff (4.51). The initial streamwater ion concentration peak occurred prior to the initiation of open channel flow (Figure 6b), indicating that substantial solute flux occurred through the channel while it was still filled with snow.

The middle geochemical stage (3–12 June) coincided with the period of high melt water input from the snowdrift, and extensive dilution of the overland flow and subsurface pathways on the hillslope. By the late geochemical stage in the stream, the hillslope input was provided by subsurface drainage. The relatively deep position of the frost table on the hillslopes at this time (Figure 2b) resulted in increased travel time to the stream bank, which increased the time for chemical exchange between mobile soil water and mineral sediments, and for water–vegetation interactions (e.g. microbial uptake of NO_3^- and SO_4^{2-}). However, in this stage, there appeared to be a decline in the influence of hillslope processes on the ion chemistry in the channel reach. The increase in the Ca^{2+} and Mg^{2+} concentrations in the channel with time (Figure 6a) could also reflect an increase in the importance of within-stream processes, as reported by Teare (1998), who showed that pH and the concentrations of Ca^{2+} and Mg^{2+} , increased through the summer period in Trail Valley Creek (Figure 1) due to increased exposure of streamwater to the calcareous stream sediments during low flows.

The annual solute budget indicates that the early high solute concentrations in streamwater came from initial melt waters mobilizing an accumulation of soil solutes (both from abiotic and biotic processes) that had accumulated over winter, not from the small solute inputs from snowmelt (Table IV). The much lower ion concentrations of pipe flow than matrix flow support this hypothesis, as it indicates that the snowdrift is important, not through its direct contribution of snow-derived ions, but rather as a medium of transport of eluted solutes from the soils. The large export of Ca^{2+} and Mg^{2+} from the basin was expected given the increasing concentration of these ions with flow distance along the hillslope and stream channel. The net export of the Na^+ and K^+ has also been reported for other Arctic basins (e.g. Hinzman *et al.*, 1998), and in this case is likely due to flushing of dry deposition of sea salts from the active layer. NO_3^- appears to be strongly retained in this environment once overland flow ceases and the slower, subsurface flowpaths prevail.

The concentrations of NO_3^- and SO_4^{2-} generally diminished with flow distance along all segments of the overall pathway leading to the basin outlet, indicating that biological assimilation and other processes removed these ions from solution. In the case of NO_3^- , net mineralization during the growing season is much lower than the vegetation demand; as a result, the aquatic export or consumption of inorganic nitrogen from basins with tundra or peat soils is often reported as negligible (e.g. Soulsby *et al.*, 1998; Brooks and Williams, 1999). The retention of SO_4^{2-} suggests that industrial pollution derived from Arctic aerosol (Jones, 1991) is retained in the terrestrial ecosystem, although Table IV indicates that the retention of SO_4^{2-} is only $\sim 0.5 \text{ kg ha}^{-1} \text{ year}^{-1}$, which is likely within budget errors.

Sources of error in the ion mass balance computations include errors in the field measurements of SWE, P and R (Table IV), and errors in the laboratory analyses of water samples. Measurements of SWE using snow tubes have been reported to overestimate the water equivalent by up to 10% (Goodison *et al.*, 1981). The value of P is likely a conservative estimate, because it does not include the numerous trace events common at high latitudes. The change in storage term ΔS provides a crude estimate of the annual basin evapotranspiration

for 1992 (106 mm) and 1993 (123 mm). These values are consistent with the findings of Marsh *et al.* (2004), who reported an average annual evapotranspiration of 110 mm for a 9 year study period at Trail Valley Creek (Figure 1).

During the laboratory analyses, numerous blank samples for bags, bottles, filters and analytical equipment were consistently below the limit of detection, indicating that no measurable contamination of samples occurred. The level of precision and limits of detection of the atomic absorption spectrophotometers and the ion chromatograph are normally at least an order of magnitude less than the levels measured in the relatively dilute melt water and snow samples. Every tenth sample was rerun in order to check the reproducibility of analytical results. For all ion species, concentrations for all duplicates were within 5% of the original analysis of the sample.

An ion charge balance (cations minus anions) was computed for each sample as a quality control index. The charge balance residuals for the snow and melt-water samples were typically less than 15% of total anions plus cations, suggesting that the concentrations of most of the major ions were determined. However, for hillslope runoff and stream-flow samples, a substantial charge imbalance (cation excess) developed as the thaw season progressed. This has also been reported for other Arctic streams (e.g. Everett *et al.*, 1989), and has been attributed to leaching of organic acids (Burse *et al.*, 1991). A review of the literature suggests that HCO_3^- is the dominant ion missing from the ion balance, followed by organic anions.

CONCLUSIONS

This paper traced the transformation of the snowmelt water chemical composition during melt, elution and runoff in an Arctic tundra basin. By relating the chemistry of the water flowing through the major flowpath types between the surface of melting snow and the basin outlet to the major hydrological processes operating within each flowpath type, this paper offers a physically based explanation for the transformation of major ion concentrations and loads of runoff water arising from snowmelt and rainfall in this environment. The mechanism for hydrochemical change of runoff water was mainly dilution by snowmelt with little or no chemical alteration by snowmelt solutes. The initial pulse of ion-rich melt water from the snowdrift flowed over and through the soil at a similar rate, owing to limited active layer development and the high hydraulic conductivity near the ground surface. Maximum dilution occurred with the peak flow rate in overland flow, and several days later in the subsurface pathway, owing to the lower flow rate through the peat matrix than over the ground surface. As this initial pulse was conveyed through hillslope flowpaths, the concentrations of most ions increased, the duration of the ion breakthrough lengthened, and Na^+ and Cl^- , the major ions in the snowmelt percolate arriving at the ground surface, were replaced with Ca^{2+} and Mg^{2+} .

The three hydrochemical stages observed for stream flow reflect the hydrological conditions of the adjacent hillslopes. The hydrochemistry of the stream channel and hillslopes was closely connected early in the snowmelt runoff period, due to the rapid lateral transit times through all hillslope pathways. Much of this hydrochemical stage preceded open channel flow in the stream. The main snowmelt runoff hydrograph peak in the stream occurred in the middle hydrochemical stage, which coincided with the period of high melt-water input from the snowdrift, and extensive dilution of the overland flow and subsurface pathways on the hillslope. The influence of the hillslope hydrology on stream hydrochemistry appeared to be lowest in the late stage, when all hillslope input was provided by subsurface drainage, and in-stream hydrochemical processes appeared to be increasingly important.

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